

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond.

Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with $\text{C}-\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{C}-\text{H}$ angles of 180° .

Exercise

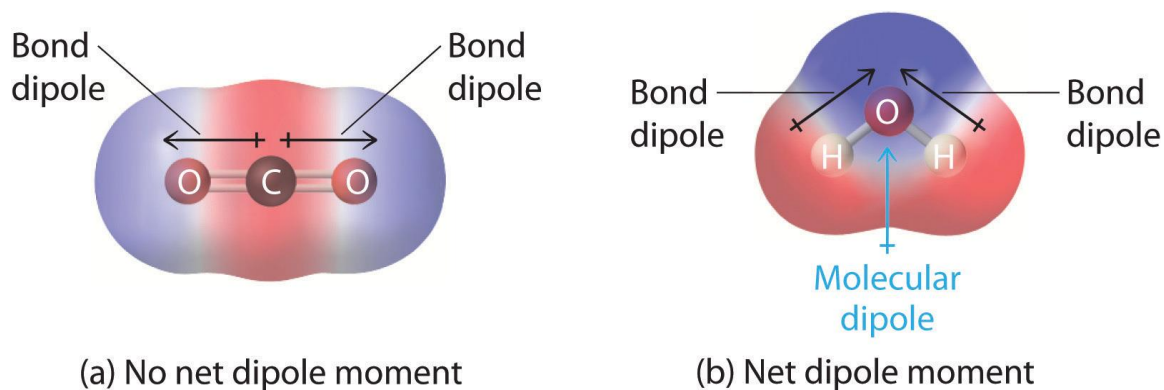
Predict the geometry of allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer: The terminal carbon atoms are trigonal planar, the central carbon is linear, and the $\text{C}-\text{C}-\text{C}$ angle is 180° .

Molecular Dipole Moments

In [Chapter 8 "Ionic versus Covalent Bonding"](#), you learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2 , a linear molecule (part (a) in [Figure 9.8 "How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures"](#)). Each $\text{C}-\text{O}$ bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two $\text{C}-\text{O}$ bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (part (b) in [Figure 9.8 "How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures"](#)); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules. (For more information on polar bonds, see [Chapter 4 "Reactions in Aqueous Solution"](#), [Section 4.1 "Aqueous Solutions"](#).)

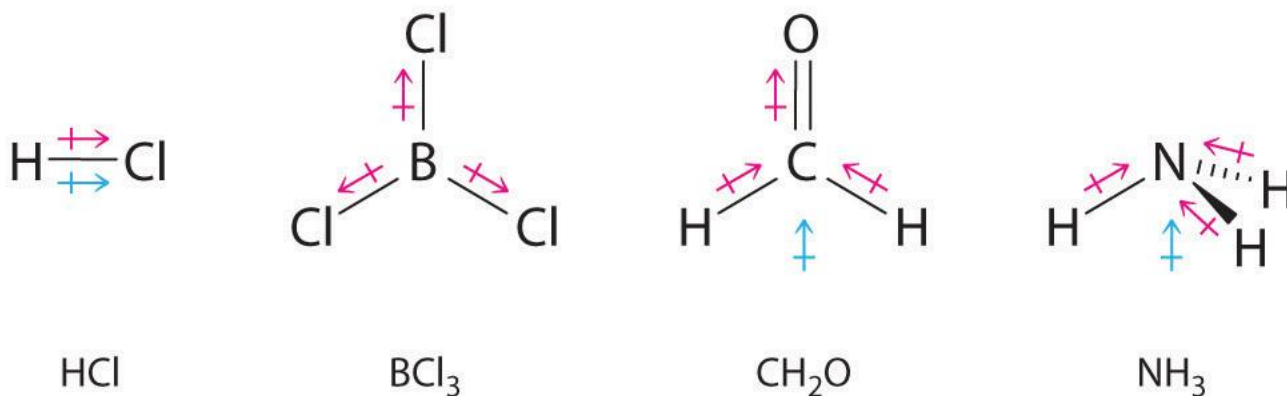
Figure 9.8 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures



(a) In CO_2 , the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O , the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure 9.9 "Molecules with Polar Bonds". In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like CHCl_3 is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

Figure 9.9 Molecules with Polar Bonds



Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl , CH_2O , NH_3 , and CHCl_3), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3 , CCl_4 , PF_5 , and SF_6).

Note the Pattern

Molecules with asymmetrical charge distributions have a net dipole moment.

Which molecule(s) has a net dipole moment?

1. H_2S
2. NHF_2
3. BF_3

Given: three chemical compounds

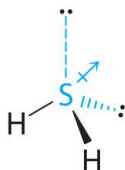
Asked for: net dipole moment

Strategy:

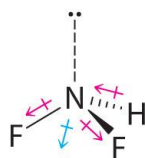
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 9.6 "Overview of Molecular Geometries"). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.

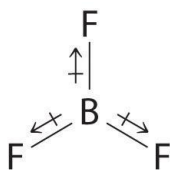


- 2.
3. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



- 5.
6. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment

of zero:



Exercise

Which molecule(s) has a net dipole moment?

1. CH_3Cl
2. SO_3
3. XeO_3

Answer: CH_3Cl ; XeO_3

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. A combination of VSEPR and a bonding model, such as Lewis electron structures, however, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

- The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no

information about bond lengths and the presence of multiple bonds.

1. What is the main difference between the VSEPR model and Lewis electron structures?
2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.
3. How does the VSEPR model deal with the presence of multiple bonds?
4. Three molecules have the following generic formulas: AX_2 , AX_2E , and AX_2E_2 . Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.
5. Which has the smaller angles around the central atom— H_2S or SiH_4 ? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?
6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?
7. When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.
8. How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?
9. Straight-chain alkanes do not have linear structures but are “kinked.” Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.
10. How is molecular geometry related to the presence or absence of a molecular dipole moment?
11. How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
12. What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is COF_2 likely to have a significant dipole moment? Explain your answer.
13. When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
14. Use the VSEPR model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.

- a. CH_3Cl
- b. PCl_3
- c. CO
- d. SF_6
- e. IF_5
- f. CH_3OCH_3
- g. CCl_3H
- h. H_3COH

15.

16. The idealized molecular geometry of BrF_5 is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF_5 ? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of BrF_5 ?

17. Which has the smallest bond angle around the central atom— H_2S , H_2Se , or H_2Te ? the largest? Justify your answers.

18. Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

1.

2.

3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.

4.

5.

6.

7.

8.

9.

- 10.
11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.
- 12.
13. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.
- 14.
- 15.
- 16.
- 17.

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule.

Classify the electron groups in each species as bonding pairs or lone pairs.

- a. BF_3
- b. PCl_3
- c. XeF_2
- d. AlCl_4^-
- e. CH_2Cl_2

2.

3. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.

- a. ICl_3
- b. CCl_3^+
- c. H_2Te
- d. XeF_4
- e. NH_4^+

4.

5. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the

lone pairs of electrons.

- a. HCl
- b. NF_3
- c. ICl_2^+
- d. N_3^-
- e. H_3O^+
- 6.

7. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

- a. SO_3
- b. NH_2^-
- c. NO_3^-
- d. I_3^-
- e. OF_2
- 8.

9. What is the molecular geometry of ClF_3 ? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

10. Predict the molecular geometry of each of the following.

- a. ICl_3
- b. AsF_5
- c. NO_2^-
- d. TeCl_4

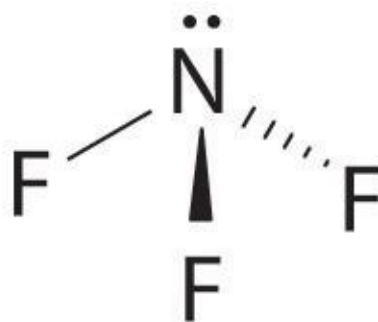
11.

12. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

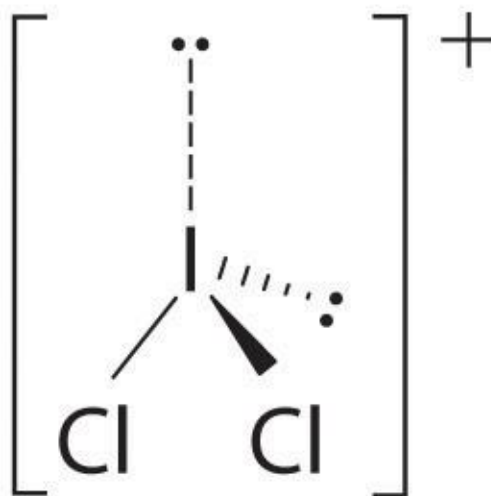
- a. NO
- b. HF
- c. PCl_3
- d. CO_2
- e. SO_2
- f. SF_4

- 13.
14. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.
- a. OF_2
 - b. BCl_3
 - c. CH_2Cl_2
 - d. TeF_4
 - e. CH_3OH
 - f. XeO_4
- 15.
16. Of the molecules $\text{Cl}_2\text{C}=\text{Cl}_2$, IF_3 , and SF_6 , which has a net dipole moment? Explain your reasoning.
17. Of the molecules SO_3 , XeF_4 , and $\text{H}_2\text{C}=\text{Cl}_2$, which has a net dipole moment? Explain your reasoning.

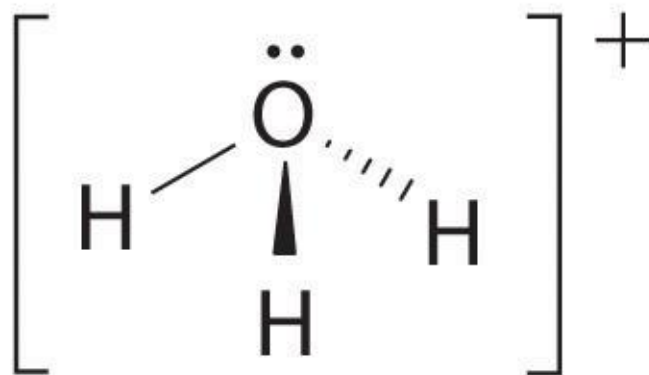
- 1.
- a. trigonal planar (all electron groups are bonding pairs)
 - b. tetrahedral (one lone pair on P)
 - c. trigonal bipyramidal (three lone pairs on Xe)
 - d. tetrahedral (all electron groups on Al are bonding pairs)
 - e. tetrahedral (all electron groups on C are bonding pairs)
- 2.
- 3.
- 4.
- a. four electron groups, linear molecular geometry
 - b. four electron groups, pyramidal molecular geometry



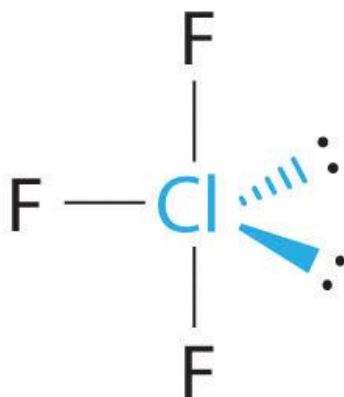
- c.
- d.
- e. four electron groups, bent molecular geometry?
- f.



- g.
- h. two electron groups, linear molecular geometry
- i. four electron groups, pyramidal molecular geometry
- j.



5.
6.



7.

8. The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

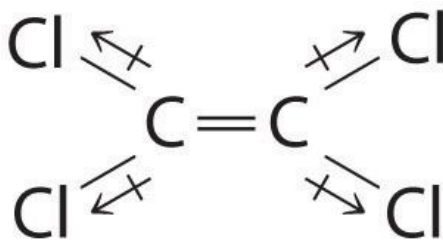
9.

10.

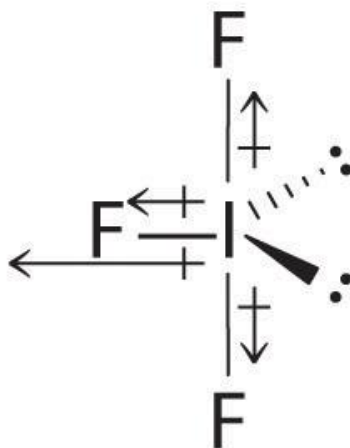
11.

12. $\text{Cl}_2\text{C}=\text{CCl}_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $\text{Cl}_2\text{C}=\text{CCl}_2$ does not have a net dipole moment

13. IF_3 : In this structure, the individual I–F bond dipoles cannot cancel one another, giving IF_3 a net dipole

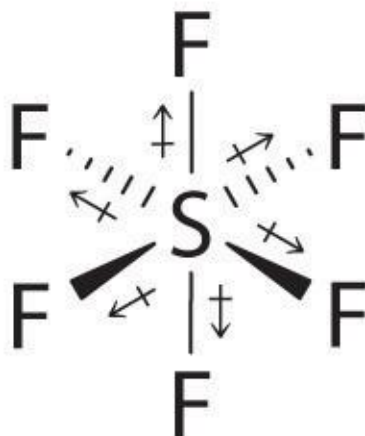


moment.



14. SF_6 : The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF_6 has no net dipole moment.

15.



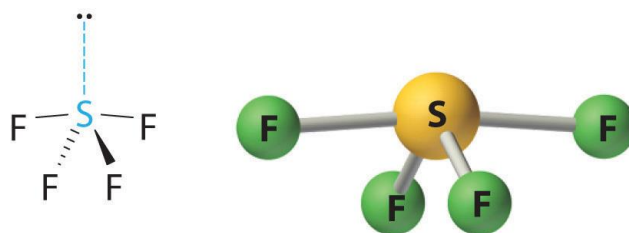
16.

17.

At 90° , the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

Answer

4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The $\text{F}_{\text{axial}}\text{--S--F}_{\text{axial}}$ angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

9.2 Localized Bonding and Hybrid Atomic Orbitals

LEARNING OBJECTIVE

1. To describe the bonding in simple compounds using valence bond theory.

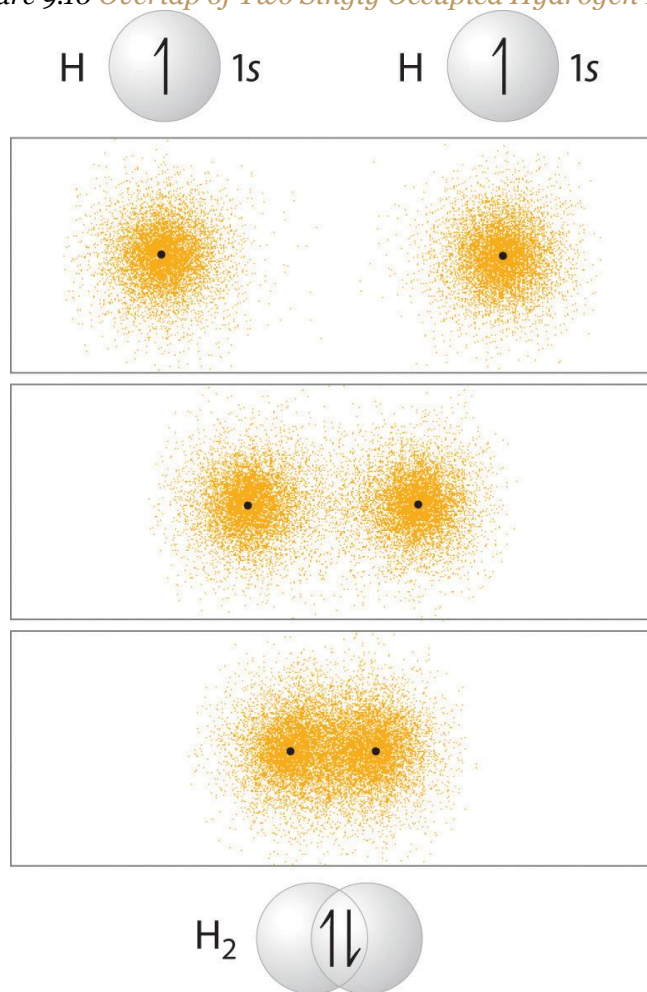
Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3 , respectively. In fact, structural studies have shown that the H-S-H and H-P-H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3 . More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X-M-X geometries. Instead, many of these species, including SrF_2 and BaF_2 , are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

Valence Bond Theory: A Localized Bonding Approach

In Chapter 8 "Ionic versus Covalent Bonding", you learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H-H distance of 74 pm (Figure 8.9 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms"). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a maximum of two electrons with opposite spin, in accordance with the Pauli principle. In this case, a bond

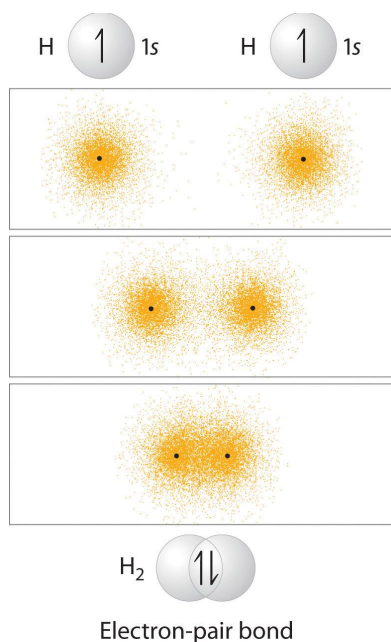
forms between the two hydrogen atoms when the singly occupied 1s atomic orbital of one hydrogen atom overlaps with the singly occupied 1s atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 9.10 "Overlap of Two Singly Occupied Hydrogen 1").

Figure 9.10 *Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond*



in H

Electron-pair bond



The formation of H_2 from two hydrogen atoms, each with a single electron in a $1s$ orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 9.11 "Three Different Ways to Form an Electron-Pair Bond" shows an electron-pair bond formed by the overlap of two ns atomic orbitals, two np atomic orbitals, and an ns and an np orbital where $n = 2$. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

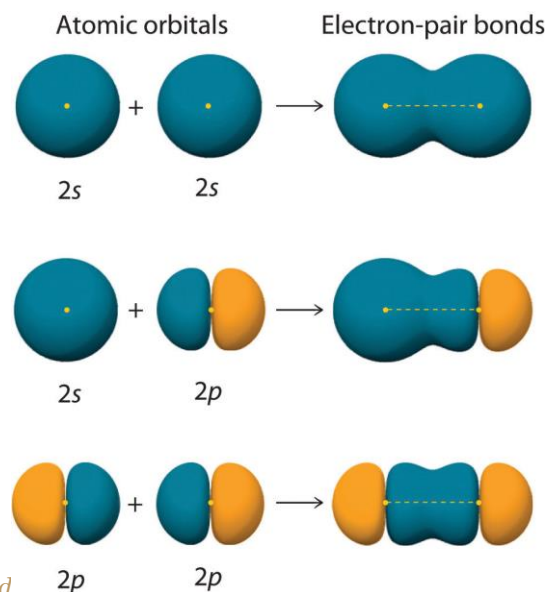


Figure 9.11 Three Different Ways to Form an Electron-Pair Bond

An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Let's examine the bonds in BeH_2 , for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled $2s$ subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied $1s$ orbitals on the H atoms. If a singly occupied $1s$ orbital on hydrogen were to overlap with a filled $2s$ orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its $2s$ electrons into an empty $2p$ orbital and reverse its spin, in a process called promotion:



In this excited state, the Be atom would have two singly occupied atomic orbitals (the $2s$ and one of the $2p$ orbitals), each of which could overlap with a singly occupied $1s$ orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2 , the two Be–H bonds would not be equivalent: the $1s$ orbital of one hydrogen atom would overlap with a Be $2s$ orbital, and the $1s$ orbital of the other

hydrogen atom would overlap with an orbital of a different energy, a Be $2p$ orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Hybridization of s and p Orbitals

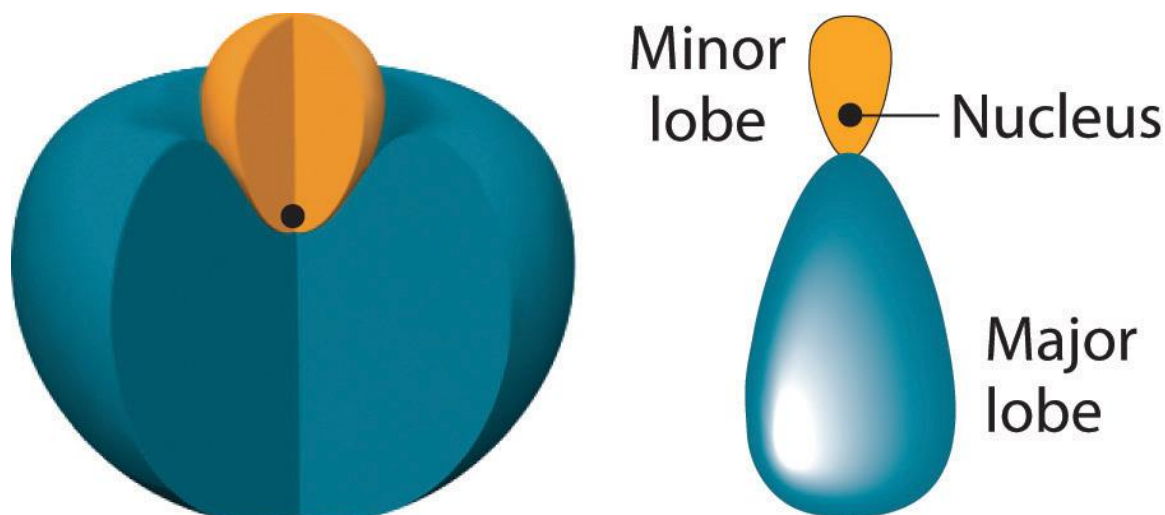
The localized bonding approach uses a process called hybridization, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

In BeH_2 , we can generate two equivalent orbitals by combining the $2s$ orbital of beryllium and any one of the three degenerate $2p$ orbitals. By taking the sum and the difference of Be $2s$ and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the z -axes, as shown in Figure 9.12 "The Formation of".^[1] This gives us Equation 9.1, where the value $1/\sqrt{2}$ is needed mathematically to indicate that the $2s$ and $2p$ orbitals contribute equally to each hybrid orbital.

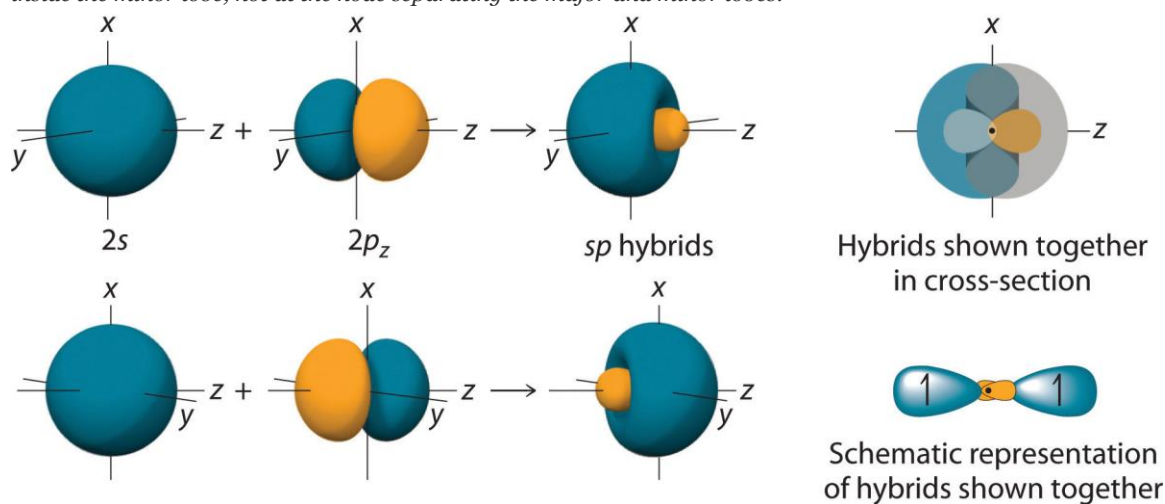
Equation 9.1

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \text{ and } sp = \frac{1}{\sqrt{2}}(2s - 2p_z)$$

Figure 9.12 The Formation of sp Hybrid Orbitals

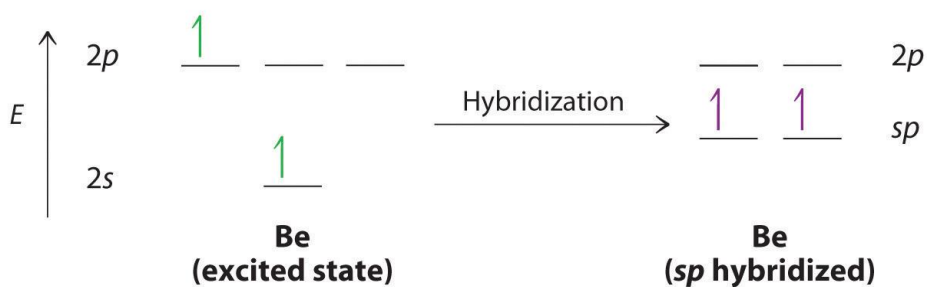


The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.



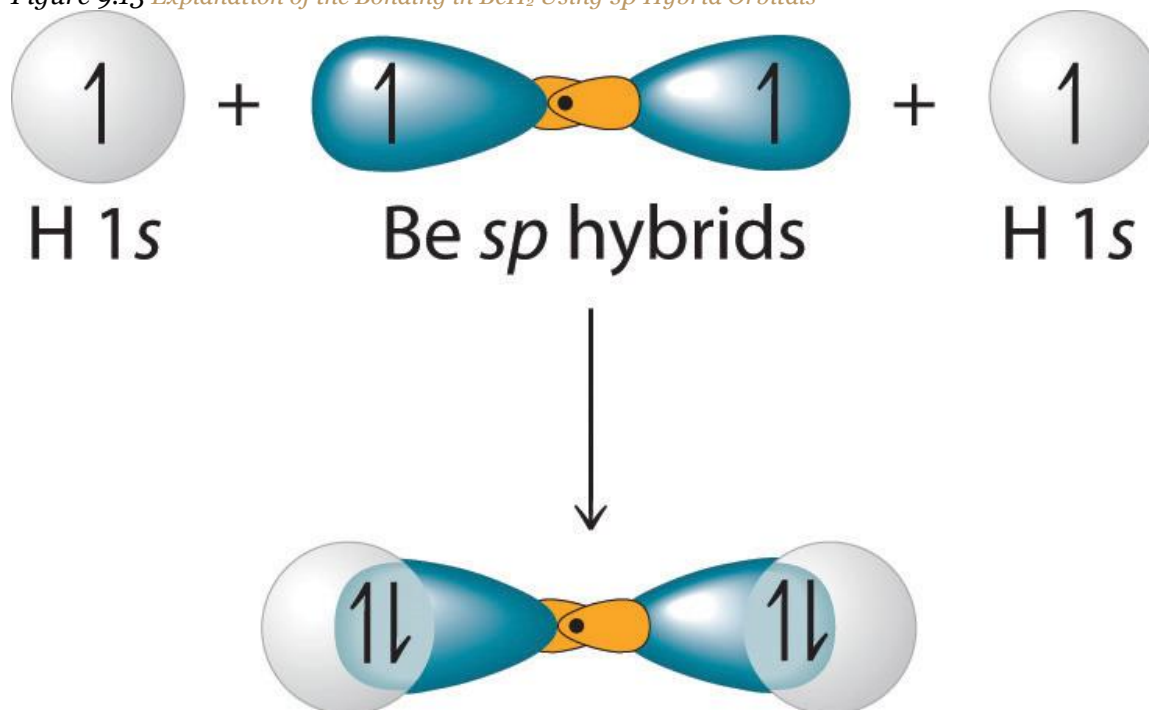
Taking the mathematical sum and difference of an ns and an np atomic orbital where $n = 2$ gives two equivalent sp hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called sp hybrids because they are formed from one s and one p orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure s and p orbitals, as illustrated in this diagram:



Each singly occupied *sp* hybrid orbital can now form an electron-pair bond with the singly occupied 1s atomic orbital of one of the H atoms. As shown in Figure 9.13 "Explanation of the Bonding in BeH", each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1s atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH₂ molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH₂ are equivalent in energy and why BeH₂ has a linear geometry.

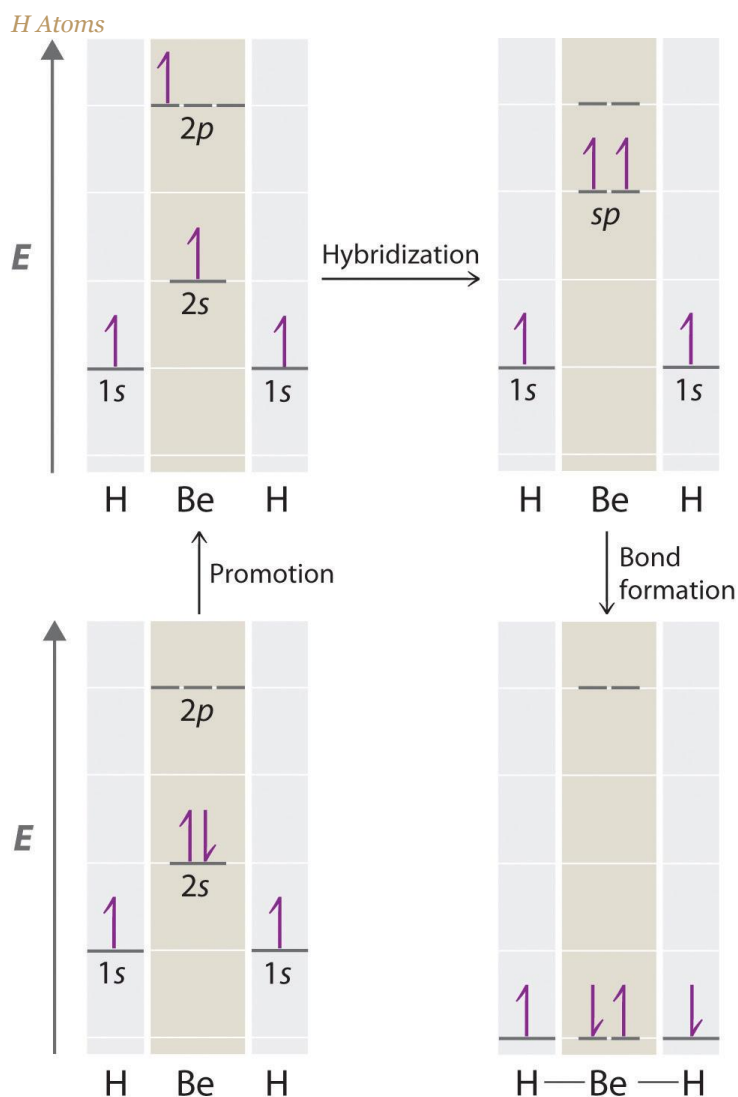
Figure 9.13 *Explanation of the Bonding in BeH₂ Using *sp* Hybrid Orbitals*



Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH₂ molecule is linear.

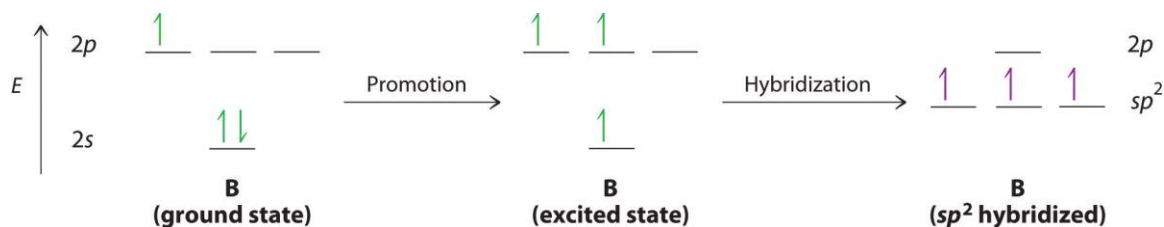
Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 9.14 "A Hypothetical Stepwise Process for the Formation of BeH"). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

Figure 9.14 A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous



The promotion of an electron from the $2s$ orbital of beryllium to one of the $2p$ orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable only if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3 , as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its $2s$ electrons to an unoccupied $2p$ orbital, however, followed by the hybridization of the three singly occupied orbitals (the $2s$ and two $2p$ orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

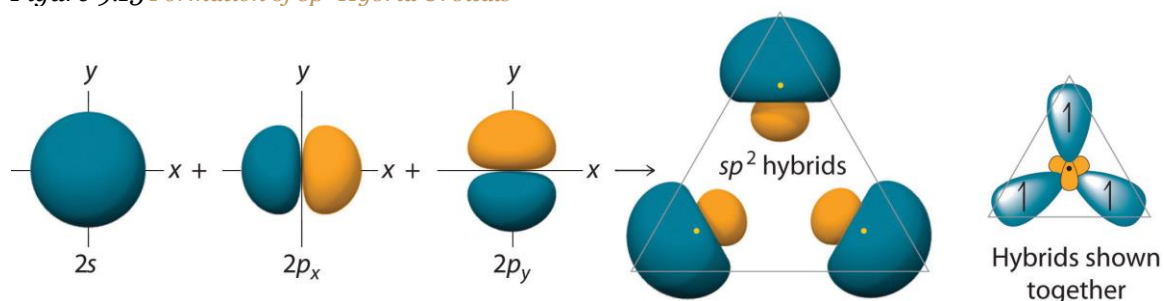


The hybrid orbitals are degenerate and are oriented at 120° angles to each other (Figure 9.15 "Formation of ").

Because the hybrid atomic orbitals are formed from one s and two p orbitals, boron is said to

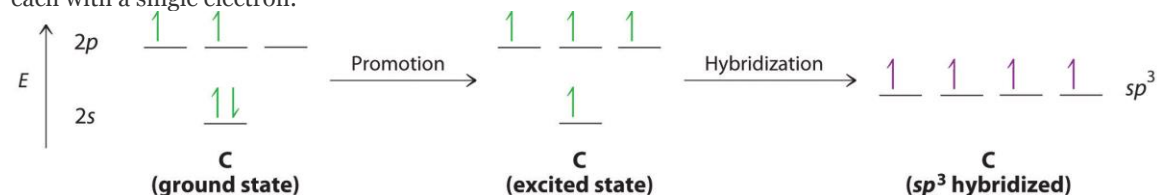
be sp^2 hybridized (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

Figure 9.15 Formation of sp^2 Hybrid Orbitals



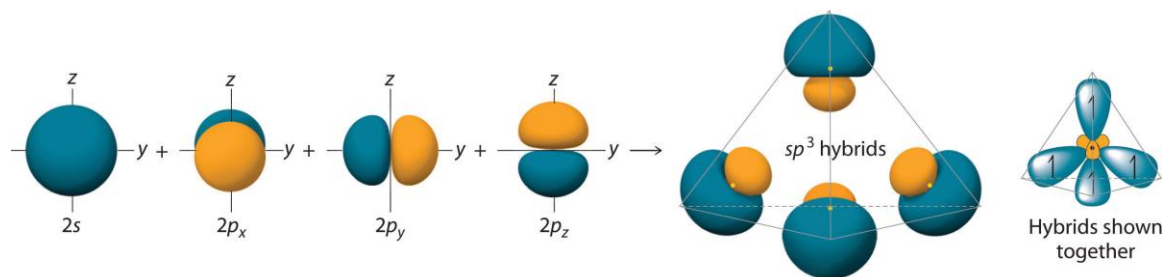
Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^2 2p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired $2p$ electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the $2s$ orbital and the three $2p$ orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 9.16 "Formation of "). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

Figure 9.16 Formation of sp^3 Hybrid Orbitals



Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Note the Pattern

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

The bonding in molecules such as NH_3 or H_2O , which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3 , for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its $2s$ and $2p$ orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O . Unfortunately, however, recent experimental evidence indicates that in CH_4 and NH_3 , the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

EXAMPLE 5

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

- a. H_2S
- b. CHCl_3

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A Using the approach from Example 1, determine the number of electron pairs and the molecular geometry of the molecule.

B From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

- a. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3s and 3p orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
- b. **A** The CHCl_3 molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2s and 2p orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their

3s and 3p valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

- the BF_4^- ion
- hydrazine ($\text{H}_2\text{N}-\text{NH}_2$)

Answer:

- B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.
- Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

Note the Pattern

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

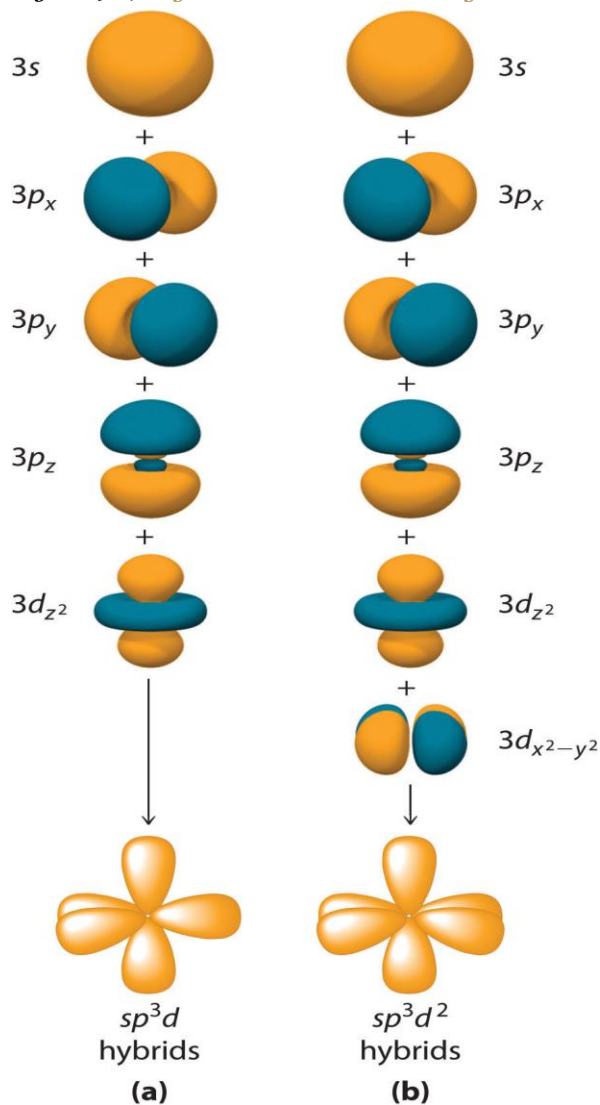
Hybridization Using d Orbitals

Hybridization is not restricted to the ns and np atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its ns and np orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the ns orbital, all three np orbitals, and one $(n - 1)d$ orbital gives a set of five sp^3d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure 9.17 "Hybrid Orbitals Involving "). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the ns orbital, all three np orbitals, and *two* nd orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 9.17 "Hybrid Orbitals Involving "). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal

and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

Figure 9.17 Hybrid Orbitals Involving d Orbitals



The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from ns , np , and nd atomic orbitals where $n = 4$.

EXAMPLE 6

What is the hybridization of the central atom in each species? Describe the bonding in each species.

- XeF_4
- SO_4^{2-}
- SF_4

Given: three chemical species

Asked for: hybridization of the central atom

Strategy:

A Determine the geometry of the molecule using the strategy in Example 1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.

B Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.

b. **A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.

c. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



a. To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl_4^+

b. BrF_3

c. SiF_6^{2-}

Answer:

- a. sp^3 with four P–Cl bonds
- b. sp^3d with three Br–F bonds and two lone pairs
- c. sp^3d^2 with six Si–F bonds

Hybridization using d orbitals allows chemists to explain the structures and properties of many molecules and ions.

Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-} . Because there are no $2d$ atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from $2s$, $2p$, and $3d$ atomic orbitals. The $3d$ orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.

EXAMPLE 7

What is the hybridization of the oxygen atom in OF_4 ? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A Predict the geometry of OF_4 using the VSEPR model.

B From the number of electron pairs around O in OF_4 , predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom

would have to be sp^3d hybridized. The only d orbital available for forming a set of sp^3d hybrid orbitals is a $3d$ orbital, which is *much* higher in energy than the $2s$ and $2p$ valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise

What is the hybridization of the boron atom in BF_6^{3-} ? Is this ion likely to exist?

Answer: sp^3d^2 hybridization; no

Summary

The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty np or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an ns and an np orbital gives rise to two equivalent **sp hybrids** oriented at 180° , whereas the combination of an ns and two or three np orbitals produces three equivalent **sp^2 hybrids** or four equivalent **sp^3 hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six **sp^3d^2 hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

KEY TAKEAWAY

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

CONCEPTUAL PROBLEMS

- Arrange sp , sp^3 , and sp^2 in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.
- What atomic orbitals are combined to form sp^3 , sp , sp^3d^2 , and sp^3d ? What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?

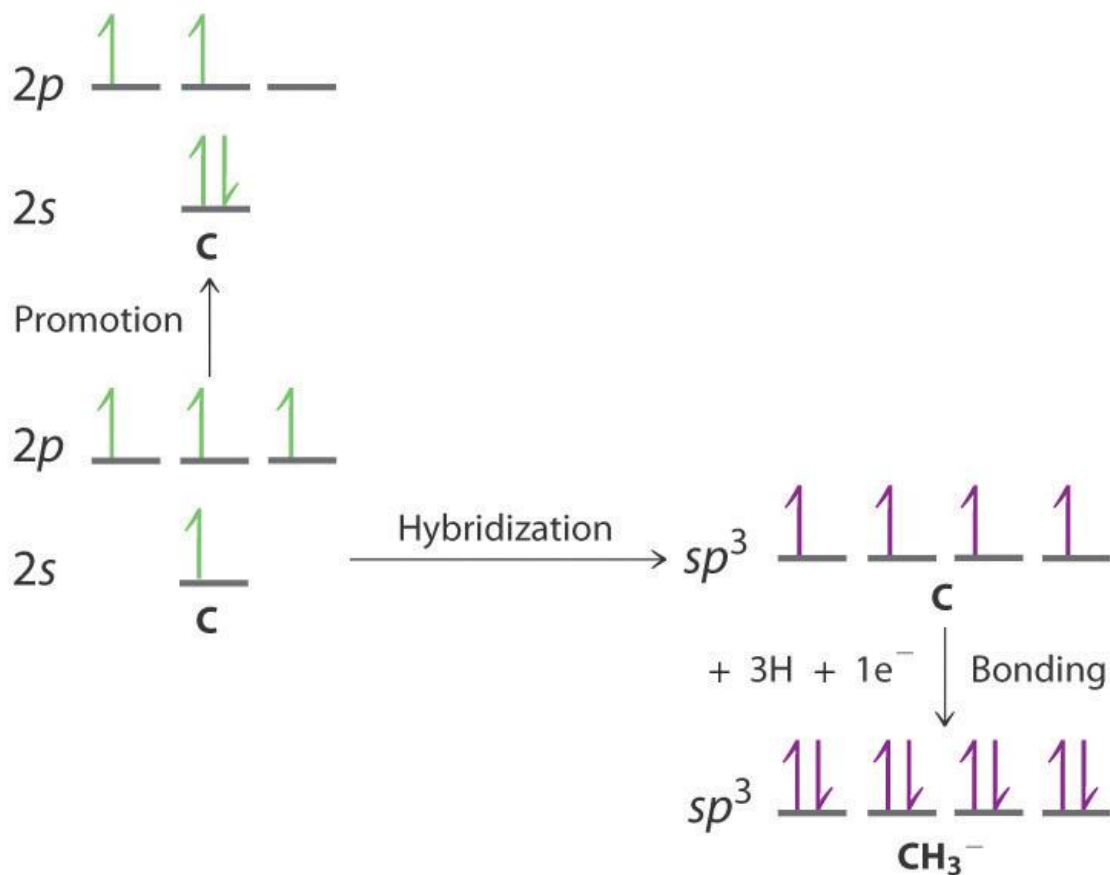
- Why is it incorrect to say that an atom with sp^2 hybridization will form only three bonds? The carbon atom in the carbonate anion is sp^2 hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?
- If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?
- How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?
- In the valence bond approach to bonding in BeF_2 , which step(s) require(s) an energy input, and which release(s) energy?
- The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?
- How are lone pairs on the central atom treated using hybrid orbitals?
- Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn't the nitrogen atom use sp^2 hybrid orbitals instead of sp^3 hybrids?
- Using arguments based on orbital hybridization, explain why the CCl_6^{2-} ion does not exist.
- Species such as NF_5^{2-} and OF_4^{2-} are unknown. If $3d$ atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?

NUMERICAL PROBLEMS

- Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^- . How does your diagram compare with that for methane? What is the molecular geometry?
- Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^+ . How does your diagram compare with that for methane? What is the molecular geometry?
- Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.
 - BBr_3
 - PCl_3
 - NO_3^-

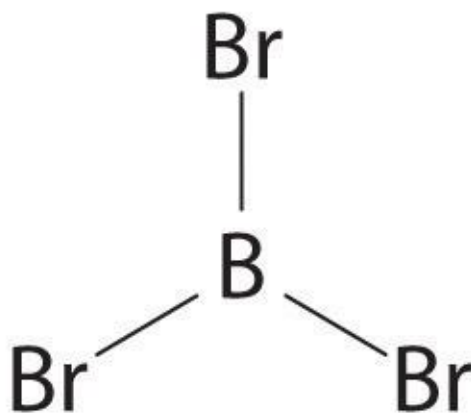
4. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.
- AsBr_3
 - CF_3^+
 - H_2O
5. What is the hybridization of the central atom in each of the following?
- CF_4
 - CCl_2^{2-}
 - IO_3^-
 - SiH_4
6. What is the hybridization of the central atom in each of the following?
- CCl_3^+
 - CBr_2O
 - CO_3^{2-}
 - IBr_2^-
7. What is the hybridization of the central atom in PF_6^- ? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?
8. What is the hybridization of the central atom in SF_5^- ? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

ANSWERS



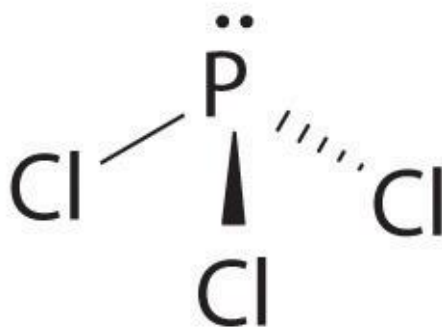
1.

The promotion and hybridization process is exactly the same as shown for CH_4 in the chapter. The only difference is that the C atom uses the four singly occupied sp^3 hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1-. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in NH_3 .

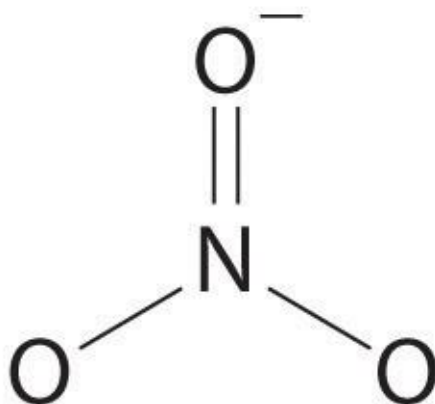


3.

a. sp^2 , trigonal planar



b. sp^3 , pyramidal



c. sp^2 , trigonal planar

5. The central atoms in CF_4 , CCl_2^{2-} , IO_3^- , and SiH_4 are all sp^3 hybridized.

7. The phosphorus atom in the PF_6^- ion is sp^3d^2 hybridized, and the ion is octahedral. The PF_6^- ion is isoelectronic with SF_6 and has essentially the same structure. It should therefore be a stable species.

[1] Because the difference $A - B$ can also be written as $A + (-B)$, in Figure 9.12 "The Formation of " and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by -1 and adding.

9.3 Delocalized Bonding and Molecular Orbitals

LEARNING OBJECTIVE

1. To use molecular orbital theory to predict bond order.

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. (For more information on semiconductors, see Chapter 12 "Solids", Section 12.6 "Bonding in Metals and

Semiconductors".) These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

In Chapter 6 "The Structure of Atoms", we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs)—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory, is a *delocalized* approach to bonding.

Note the Pattern

Molecular orbital theory is a delocalized bonding approach that explains the colors of compounds, their stability, and resonance.

Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2 , formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 6 "The Structure of Atoms", electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. (For more information on wave functions, see Chapter 6 "The Structure of Atoms", Section 6.5 "Atomic Orbitals and Their Energies".) The

1s atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1s wave functions, and the other produced by taking their *difference*:

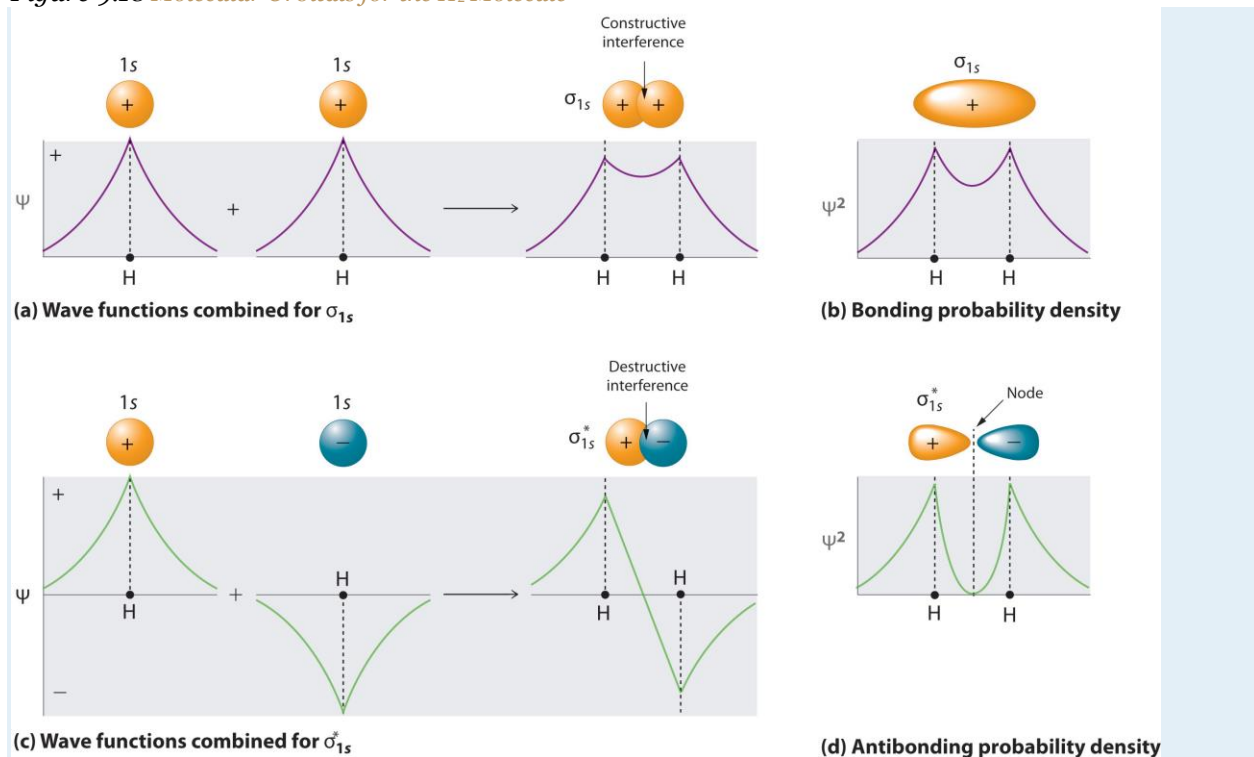
Equation 9.2

$$\sigma_{1s} = \frac{1}{\sqrt{2}}(\psi_{1s} + \psi_{1s}) \text{ and } \sigma_{1s}^* = \frac{1}{\sqrt{2}}(\psi_{1s} - \psi_{1s})$$

A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1s orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 9.18 “Molecular Orbitals for the H₂”). In a sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1s denotes the atomic orbitals from which the molecular orbital was derived.^[1]

Figure 9.18 Molecular Orbitals for the H₂ Molecule



(a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H₂ as the sum of the wave functions (ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall from Chapter 6 “The Structure of Atoms” that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an orbital for H₂ as the difference of the wave functions (ψ) of two H 1s atomic

orbitals. (d) This plot of the square of the wave function (Ψ^2) for the antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

Equation 9.3

$$\sigma_{1s} \approx 1s(A) + 1s(B)$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.18 "Molecular Orbitals for the H⁺"). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called ("sigma one ess star"). In a sigma star (σ^*) orbital, there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

Equation 9.4

$$\sigma^*_{1s} \approx 1s(A) - 1s(B)$$

Note the Pattern

A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. In contrast, electrons in the σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{1s} orbital is an antibonding molecular orbital.

Note the Pattern

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Energy-Level Diagrams

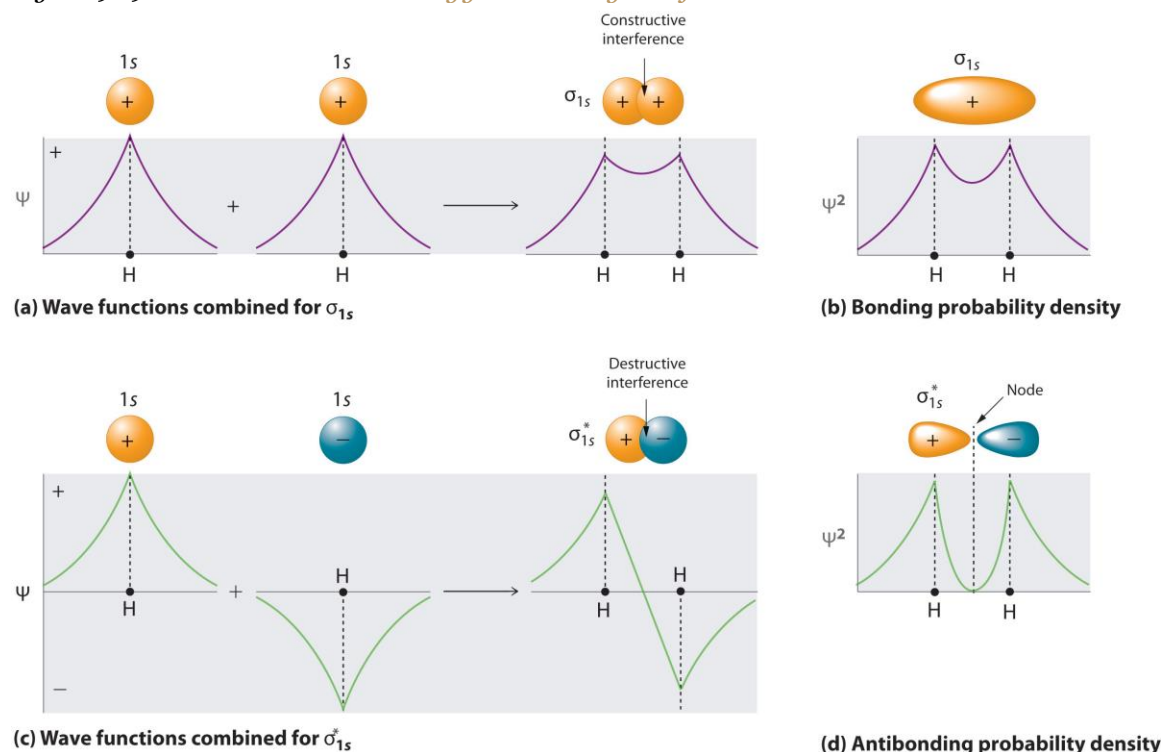
Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1s atomic orbitals. Conversely, electrons in the orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1s atomic orbitals. Consequently, the molecular orbital has a *higher* energy than either of the hydrogen 1s atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1s atomic orbitals, and the (antibonding) molecular orbital is *destabilized*. The relative energy levels of

these orbitals are shown in the energy-level diagram in Figure 9.19 "Molecular Orbital Energy-Level Diagram for H".

Note the Pattern

A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

Figure 9.19 *Molecular Orbital Energy-Level Diagram for H₂*



The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H₂ molecule is more stable (at a lower energy) than the two isolated H atoms.

To describe the bonding in a homonuclear diatomic molecule such as H₂, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 9.19 "Molecular Orbital Energy-Level Diagram for H"). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the

parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures described in Chapter 8 "Ionic versus Covalent Bonding", the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order is defined as one-half the *net* number of bonding electrons:

Equation 9.5

bond order

$$= \text{number of bonding electrons} - \text{number of antibonding electrons} / 2$$

To calculate the bond order of H_2 , we see from Figure 9.19 "Molecular Orbital Energy-Level Diagram for H_2 " that the σ_{1s} (bonding) molecular orbital contains two electrons, while the antibonding molecular orbital is empty. The bond order of H_2 is therefore

Equation 9.6

$$2 - 0 / 2 = 1$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure 9.19 "Molecular Orbital Energy-Level Diagram for H_2 " to describe the bonding in other pairs of atoms and ions where $n = 1$, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

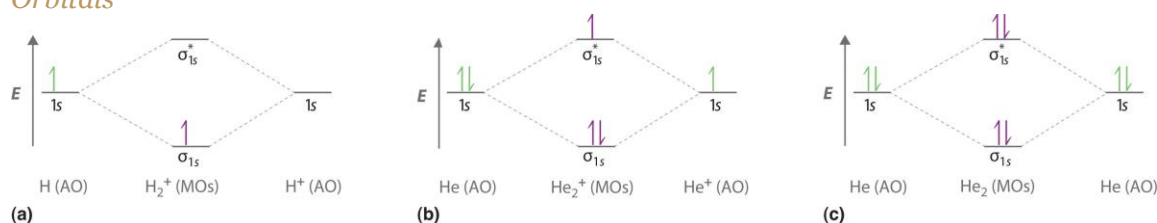
Part (a) in Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1" shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is $(1 - 0) / 2 = 0.5$. Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the

calculated bond order to predict the relative stability of species such as H_2^+ . With a bond order of only the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.1 "Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions", these predictions agree with the experimental data.

Part (b) in Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1" is the molecular orbital energy-level diagram for He_2^+ . This ion has a total of three valence electrons.

Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration. This electron configuration gives a bond order of $(2 - 1) / 2 = 1/2$. As with H_2^+ , the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2 . In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.1 "Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions").

Figure 9.20 Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals



(a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Table 9.1 Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$		106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1" is the molecular orbital energy-level diagram for He_2 . With a total of four valence electrons, both the σ_{1s} bonding and σ^*_{1s} antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^*_{1s})^2$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

Note the Pattern

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

EXAMPLE 8

Use a molecular orbital energy-level diagram, such as those in Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1", to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

A Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals.

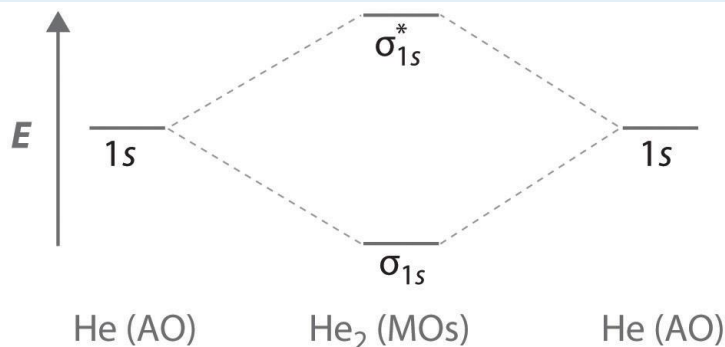
Draw the molecular orbital energy-level diagram for the system.

B Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

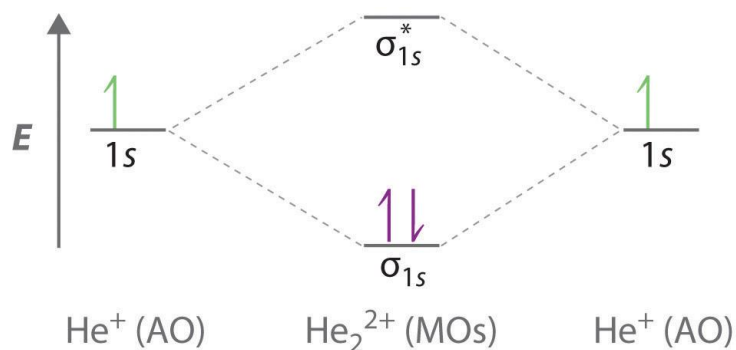
C Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1s atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1s atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

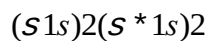
$$(2-0)/2=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer: H_2^{2-} has a valence electron configuration of

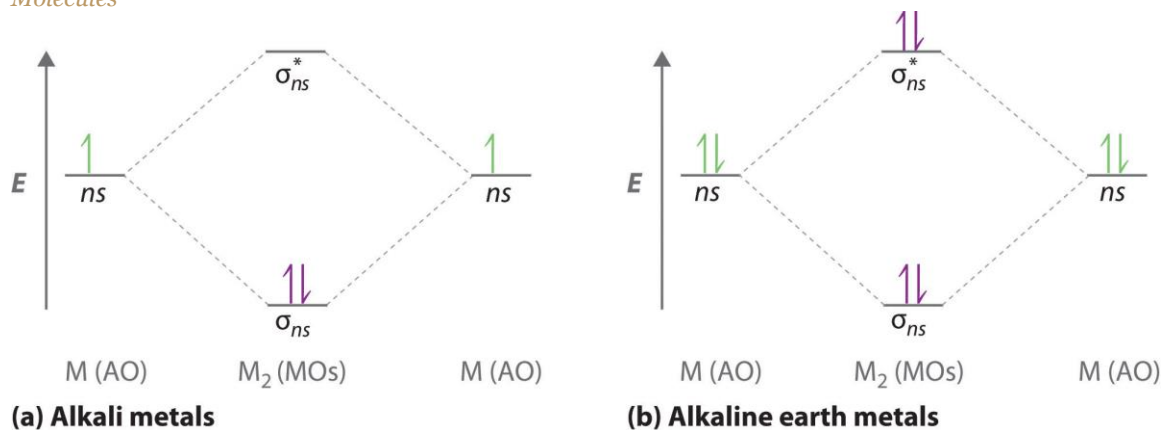


with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2 , for example) is shown in part (a) in Figure 9.21 "Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2)", where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ_{ns}^* antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2 , Na_2 , K_2 , Rb_2 , and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure 9.19 "Molecular Orbital Energy-Level Diagram for H_2 ". Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

Figure 9.21 Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules



(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1". As shown in part (b) in Figure 9.21 "Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M)", this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the antibonding orbital and give a bond order of 0. Thus Be_2 , Mg_2 , Ca_2 , Sr_2 , and Ba_2 are all expected to be unstable, in agreement with experimental data.^[2]

EXAMPLE 9

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

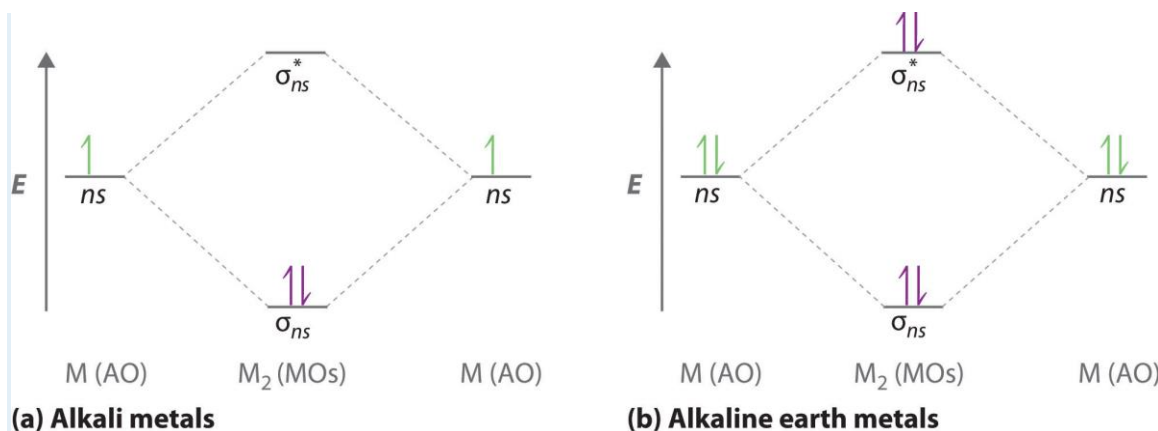
A Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

C Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a $[\text{Ne}]3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two $1s$ atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled molecular orbital, and an electron configuration.



(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be₂), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He₂ molecule in part (c) in Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1". As shown in part (b) in Figure 9.21 "Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M)", this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the antibonding orbital and give a bond order of 0. Thus Be₂, Mg₂, Ca₂, Sr₂, and Ba₂ are all expected to be unstable, in agreement with experimental data.^[2]

EXAMPLE 9

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na₂⁺ ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

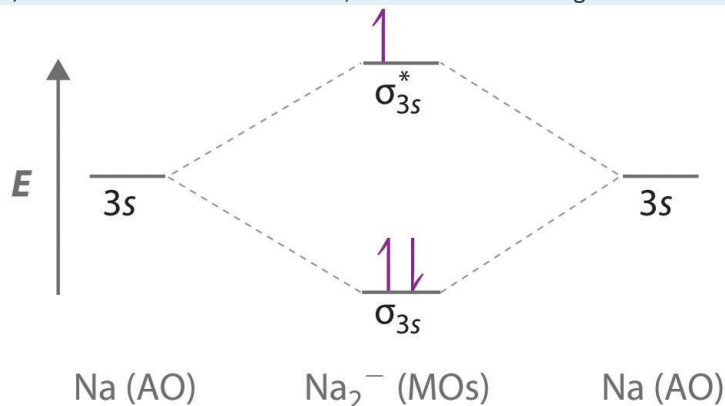
A Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B Determine the total number of valence electrons in the Na₂⁺ ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

C Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a $[\text{Ne}]3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1s atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s}^* molecular orbital, and a electron configuration.



C The bond order is $(2 - 1) / 2 = 0.5$. With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer: Ca_2^+ has a $(\sigma 4s)^2(\sigma^* 4s)^1$ electron configuration and a bond order of 1/2 should exist.

Molecular Orbitals Formed from ns and np Atomic Orbitals

Atomic orbitals other than ns orbitals can also interact to form molecular orbitals. Because individual p , d , and f orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall from Chapter 6 "The Structure of Atoms", Section 6.5 "Atomic Orbitals and Their Energies" that for each np subshell, for example, there are np_x , np_y , and np_z orbitals (Figure 6.25 "The Three Equivalent 2p"). All have the same energy and are therefore degenerate, but they have different spatial orientations.

Just as with ns orbitals, we can form molecular orbitals from np orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 9.22 "Formation of Molecular Orbitals from ",

it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the z -axis):

Equation 9.7

$$S_{npz} = npz(A) - npz(B)$$

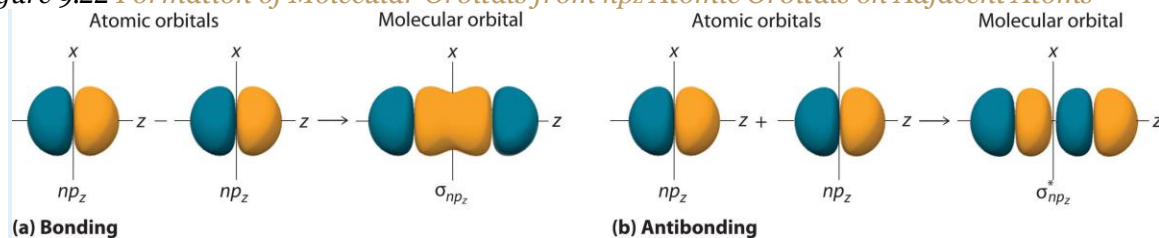
The other possible combination of the two npz orbitals is the mathematical sum:

Equation 9.8

$$S_{npz} = npz(A) + npz(B)$$

In this combination, shown in part (b) in Figure 9.22 "Formation of Molecular Orbitals from ", the positive lobe of one npz atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, it is called a antibonding molecular orbital. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

Figure 9.22 Formation of Molecular Orbitals from npz Atomic Orbitals on Adjacent Atoms



(a) By convention, in a linear molecule or ion, the z -axis always corresponds to the internuclear axis, with $+z$ to the right. As a result, the signs of the lobes of the npz atomic orbitals on the two atoms alternate $- + - +$, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical difference, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ^* (antibonding) molecular orbital corresponds to the mathematical sum, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

Note the Pattern

Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining p orbitals on each of the two atoms, np_x and np_y , do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 9.23 "Formation of π Molecular Orbitals from ", we see that we have two pairs of np orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital. The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π^*) orbital.

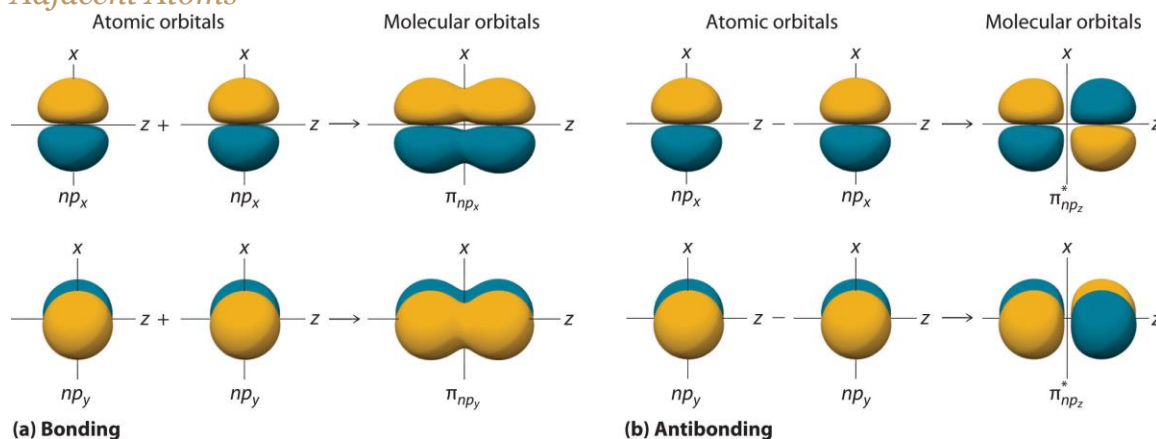
Equation 9.9

$$\rho_{np_x} = np_x(A) + np_x(B)$$

Equation 9.10

$$\rho_{np_x} = np_x(A) - np_x(B)$$

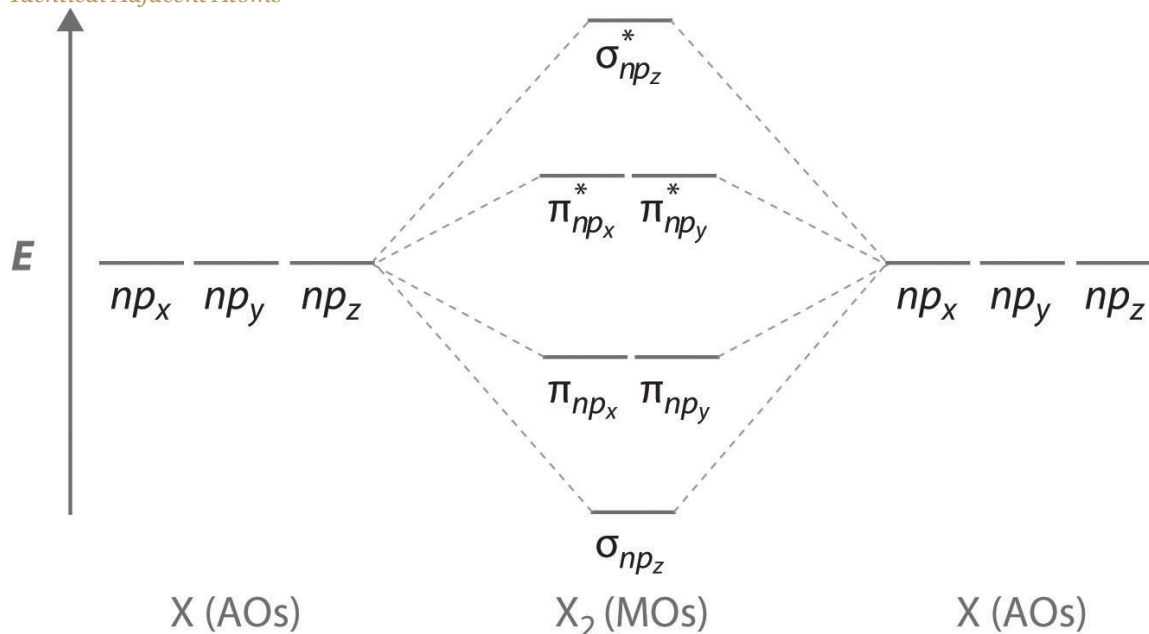
Figure 9.23 Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms



(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π^* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 9.24 "The Relative Energies of the σ and π Molecular Orbitals Derived from " is an energy-level diagram that can be applied to two identical interacting atoms that have three np atomic orbitals each. There are six degenerate p atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ^* molecular orbitals is significantly greater than the difference between the two π and π^* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

Figure 9.24 *The Relative Energies of the σ and π Molecular Orbitals Derived from np_x , np_y , and np_z Orbitals on Identical Adjacent Atoms*

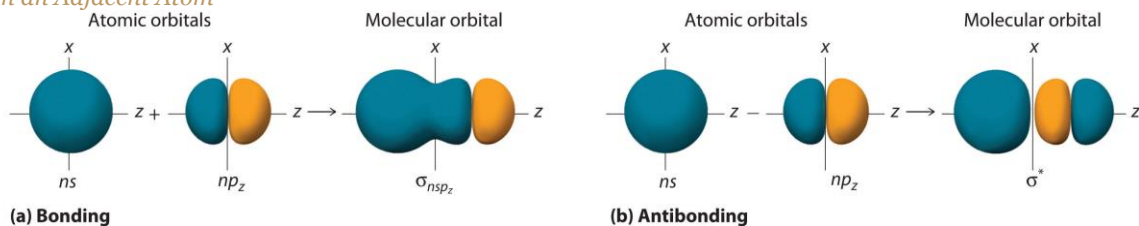


Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ^* molecular orbitals is greater than the energy difference between the π and π^* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an ns atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 9.25 "Formation of Molecular Orbitals from an ns and an np_z Atomic Orbital", the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ^* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 9.25 Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital

on an Adjacent Atom



(a) The

mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ^* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Molecular Orbital Diagrams for Period 2 Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2 , O_2 , and F_2 . When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Note the Pattern

The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2 . We use the diagram in part (a) in Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear

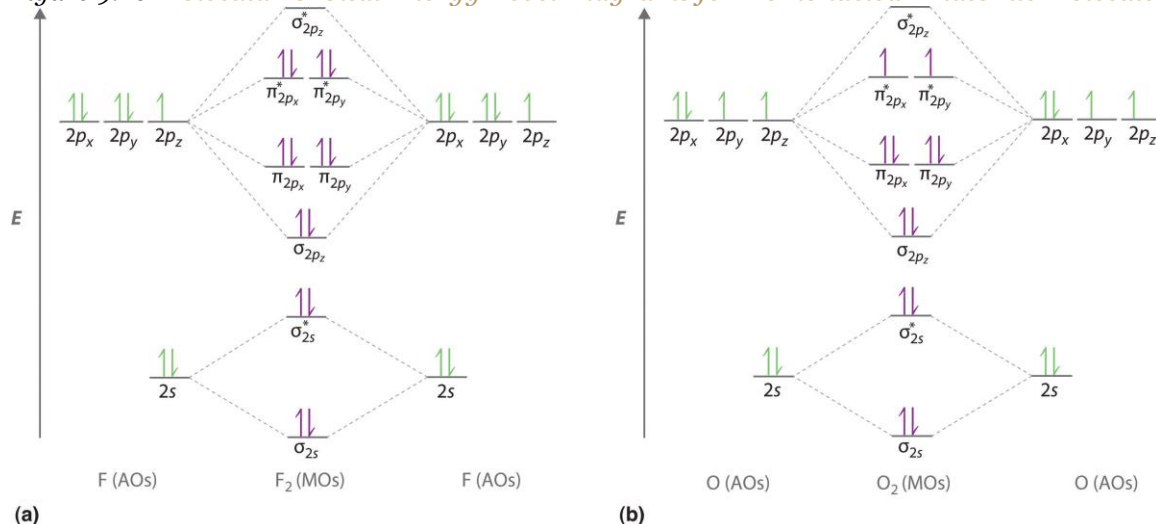
Diatomic Molecules"; the $n = 1$ orbitals (σ_{1s} and σ_{1s}^*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}^* molecular orbitals are much lower in energy than the molecular orbitals derived from the $2p$ atomic orbitals because of the large difference in energy between the $2s$ and $2p$ atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three $2p$ orbitals on each F is σ_{2pz} , and the next most stable are the two degenerate orbitals, π_{2px} and π_{2py} . For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the orbital is higher in energy than either of the degenerate orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}^* orbitals, 2 fill the σ_{2pz} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

We now turn to a molecular orbital description of the bonding in O_2 . It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2 , we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules". We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}^* orbitals, 2 more to fill the σ_{2pz} orbital, and 4 to fill the degenerate orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data (Table 8.5 "Bond Lengths and Bond Dissociation Energies for Bonds with Different

Bond Orders in Selected Gas-Phase Molecules at 298 K"): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

Figure 9.26 Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules



(a) For F_2 , with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^* 2p_z$, are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2 , with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $(\sigma^* 2p_x, \sigma^* 2p_y)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

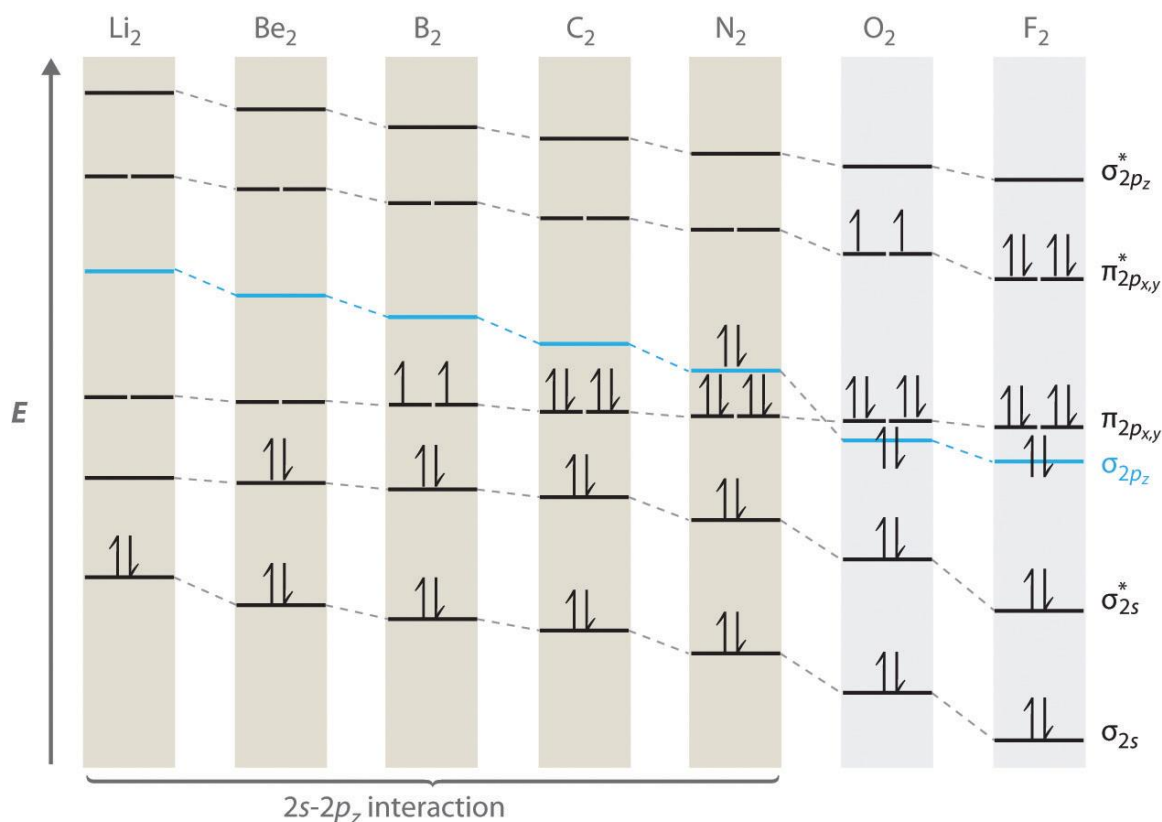
None of the other bonding models can predict the presence of two unpaired electrons in O_2 . Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 9.27 "Liquid O", it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O , CO_2 , and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen

atmosphere is that virtually all organic compounds, as well as H_2O , CO_2 , and N_2 , have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O , CO_2 , and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the $s\ 2p_z$ molecular orbital is slightly *higher* in energy than the degenerate orbitals. The difference in energy between the $2s$ and $2p$ atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the $2s$ electrons by electrons in the $2p$ subshell. The bonding interaction between the $2s$ orbital on one atom and the $2p_z$ orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the $s\ 2p_z$ orbital. Thus for Li_2 , Be_2 , B_2 , C_2 , and N_2 , the $s\ 2p_z$ orbital is higher in energy than the $s\ 3p_z$ orbitals, as shown in Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements". Experimentally, it is found that the energy gap between the ns and np atomic orbitals *increases* as the nuclear charge increases (Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"). Thus for example, the $s\ 2p_z$ molecular orbital is at a lower energy than the $p\ 2p_{x,y}$ pair.

Figure 9.28 Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements



Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li_2 through N_2 , the $s\ 2p_z$ orbital is higher in energy than the $p\ 2p_{x,y}$ orbitals. In contrast, the $s\ 2p_z$ orbital is lower in energy than the $p\ 2p_{x,y}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the $2s$ and $2p$ atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

EXAMPLE 10

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2 , a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

Strategy:

A Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2 . Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.

B Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2 .

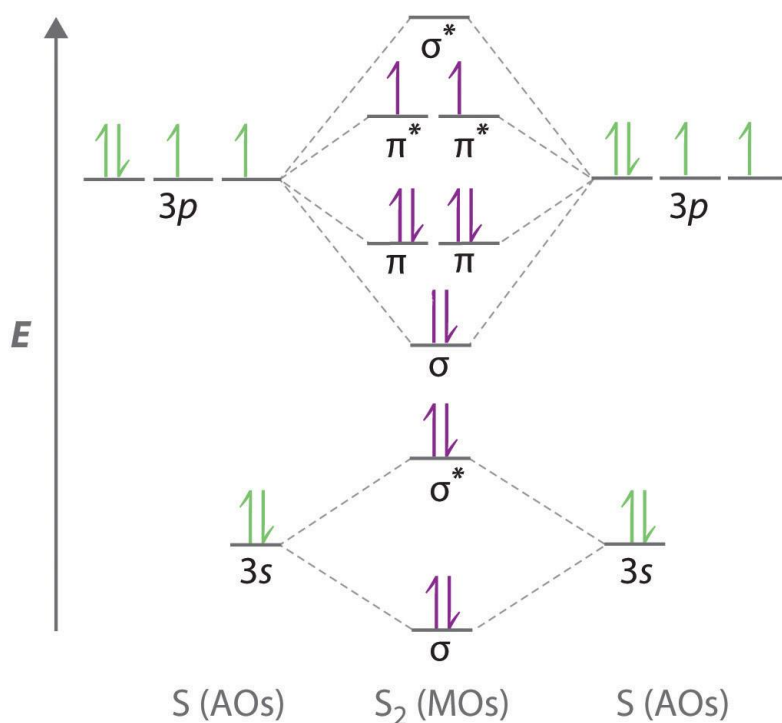
C Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.

D Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules" and Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements", we need to know how close in energy the $3s$ and $3p$ atomic orbitals are because their energy separation will determine whether the $p_{3px,y}$ or the s_{3pz} molecular orbital is higher in energy. Because the $ns-np$ energy gap *increases* as the nuclear charge increases (Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"), the molecular orbital will be lower in energy than the $p_{3px,y}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through p_{3px} and p_{3py} , leaving 2 electrons to occupy the degenerate p^*_{3px} and p^*_{3py} pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S₂ is $(s\ 3s)^2(s^* \ 3s)^2(s\ 3p_z)^2(p\ 3p_{x,y})^4(p^* \ 3p_{x,y})^2$ with 2 unpaired electrons. The bond order is $(8 - 4) \div 2 = 2$, so we predict an S=S double bond.

Exercise

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O₂²⁻).

Answer: $(s\ 2s)^2(s^* \ 2s)^2(s\ 2p_z)^2(p\ 2p_{x,y})^4(p^* \ 2p_{x,y})^4$; bond order of 1; no unpaired electrons

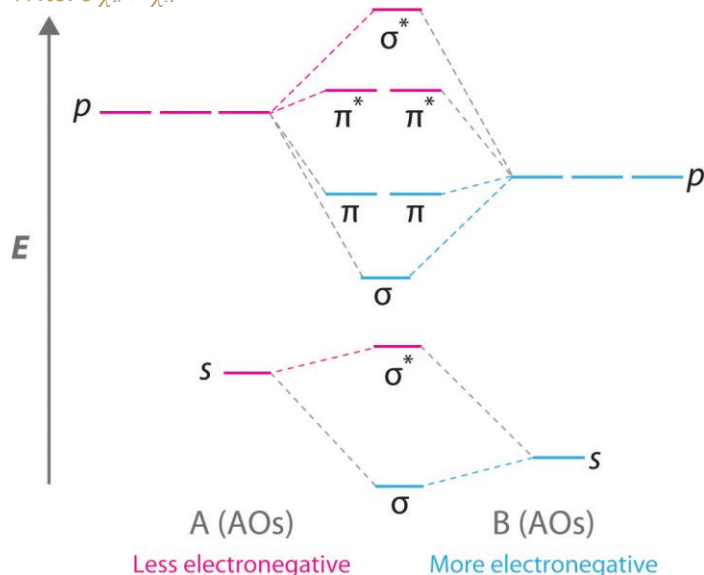
Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a

“skewed” molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 9.29 "Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$ ". The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

Figure 9.29 Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB,

Where $\chi_B > \chi_A$



The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom.

Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

Note the Pattern

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

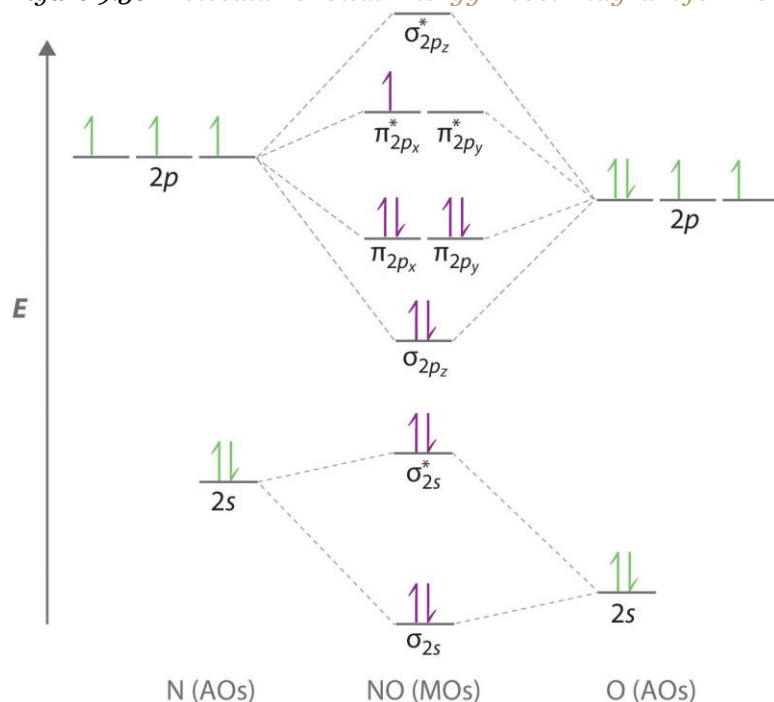
An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2 , which in turn is responsible for the brown color we associate with air pollution.

Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 9.30 "Molecular Orbital Energy-Level Diagram for NO") shows that the general pattern is similar to that for the O₂ molecule (see Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2p atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore $(8 - 3) / 2 = 2.5$. Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N₂ and O₂ molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

Figure 9.30 *Molecular Orbital Energy-Level Diagram for NO*



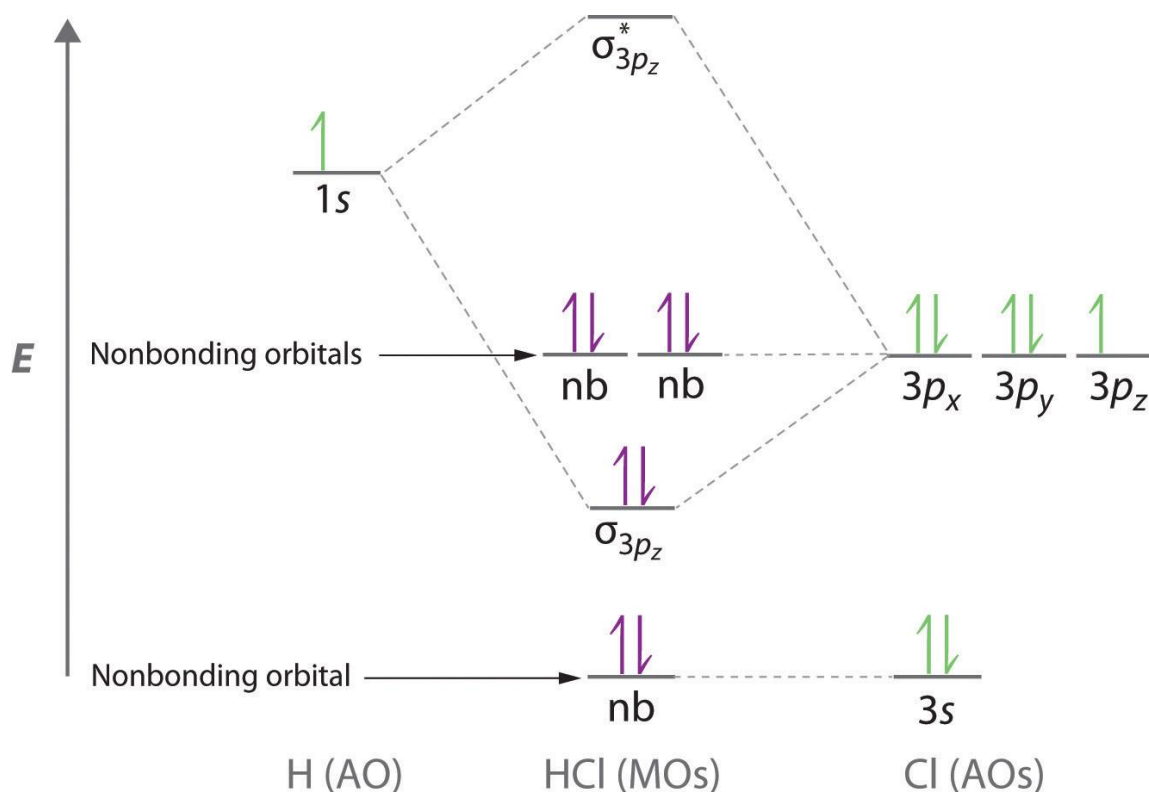
Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $(\sigma^* 2p_x, \sigma^* 2p_y)$ pair of orbitals.

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 9.30 "Molecular Orbital Energy-Level Diagram for NO", NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an $\text{N}\equiv\text{O}$ triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 9.31 "Molecular Orbital Energy-Level Diagram for HCl" that the 1s orbital of atomic hydrogen is closest in energy to the 3p orbitals of chlorine. Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3p orbitals. Of the three p orbitals, only one, designated as $3p_z$, can interact with the H 1s orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1s orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3s, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called nonbonding molecular orbitals. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is $(2 - 0) \div 2 = 1$. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1s atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $\text{H}\delta^+ - \text{Cl}\delta^-$ as described in Chapter 8 "Ionic versus Covalent Bonding".

Figure 9.31 *Molecular Orbital Energy-Level Diagram for HCl*



The hydrogen $1s$ atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Note the Pattern

Electrons in nonbonding molecular orbitals have no effect on bond order.

EXAMPLE 11

Use a “skewed” molecular orbital energy-level diagram like the one in Figure 9.29 “Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where χ ” to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

Asked for: “skewed” molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

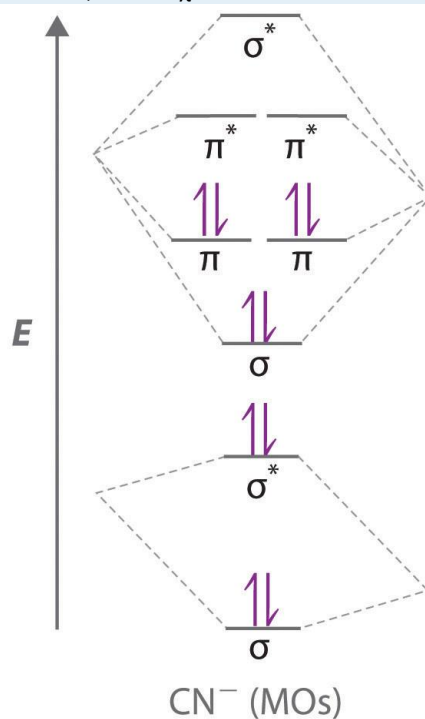
A Calculate the total number of valence electrons in CN^- . Then place these electrons in a molecular orbital energy-level diagram like Figure 9.29 “Molecular Orbital Energy-Level Diagram for a Heteronuclear

Diatomic Molecule AB, Where χ in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B Calculate the bond order and describe the bonding in CN^- .

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the -1 charge. Placing these electrons in an energy-level diagram like Figure 9.29 "Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where χ " fills the five lowest-energy orbitals, as shown here:



Because $\chi_{\text{N}} > \chi_{\text{C}}$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2 .

Exercise

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer: All molecular orbitals except the highest-energy σ^* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the

computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

Summary

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ^*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π^*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element.

Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

KEY TAKEAWAY

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

CONCEPTUAL PROBLEMS

1. What is the distinction between an atomic orbital and a molecular orbital? How many electrons can a molecular orbital accommodate?
2. Why is the molecular orbital approach to bonding called a *delocalized* approach?
3. How is the energy of an electron affected by interacting with more than one positively charged atomic nucleus at a time? Does the energy of the system increase, decrease, or remain unchanged? Why?
4. Constructive and destructive interference of waves can be used to understand how bonding and antibonding molecular orbitals are formed from atomic orbitals. Does constructive interference of waves result in increased or decreased electron probability density between the nuclei? Is the result of constructive interference best described as a bonding molecular orbital or an antibonding molecular orbital?
5. What is a "node" in molecular orbital theory? How is it similar to the nodes found in atomic orbitals?
6. What is the difference between an *s* orbital and a σ orbital? How are the two similar?
7. Why is a σ_{1s} molecular orbital lower in energy than the two *s* atomic orbitals from which it is derived? Why is a σ^*_{1s} molecular orbital higher in energy than the two *s* atomic orbitals from which it is derived?
8. What is meant by the term *bond order* in molecular orbital theory? How is the bond order determined from molecular orbital theory different from the bond order obtained using Lewis electron structures? How is it similar?
9. What is the effect of placing an electron in an antibonding orbital on the bond order, the stability of the molecule, and the reactivity of a molecule?
10. How can the molecular orbital approach to bonding be used to predict a molecule's stability? What advantages does this method have over the Lewis electron-pair approach to bonding?
11. What is the relationship between bond length and bond order? What effect do antibonding electrons have on bond length? on bond strength?

12. Draw a diagram that illustrates how atomic p orbitals can form both σ and π molecular orbitals. Which type of molecular orbital typically results in a stronger bond?
13. What is the minimum number of nodes in σ , π , σ^* , and π^* ? How are the nodes in bonding orbitals different from the nodes in antibonding orbitals?
14. It is possible to form both σ and π molecular orbitals with the overlap of a d orbital with a p orbital, yet it is possible to form only σ molecular orbitals between s and d orbitals. Illustrate why this is so with a diagram showing the three types of overlap between this set of orbitals. Include a fourth image that shows why s and d orbitals cannot combine to form a π molecular orbital.
15. Is it possible for an np_x orbital on one atom to interact with an np_y orbital on another atom to produce molecular orbitals? Why or why not? Can the same be said of np_y and np_z orbitals on adjacent atoms?
16. What is meant by *degenerate orbitals* in molecular orbital theory? Is it possible for σ molecular orbitals to form a degenerate pair? Explain your answer.
17. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals? Why are antibonding molecular orbitals higher in energy than the parent atomic orbitals?
18. What is meant by the *law of conservation of orbitals*?
19. Atomic orbitals on different atoms have different energies. When atomic orbitals from nonidentical atoms are combined to form molecular orbitals, what is the effect of this difference in energy on the resulting molecular orbitals?
20. If two atomic orbitals have different energies, how does this affect the orbital overlap and the molecular orbitals formed by combining the atomic orbitals?
21. Are the Al–Cl bonds in AlCl_3 stronger, the same strength, or weaker than the Al–Br bonds in AlBr_3 ? Why?
22. Are the Ga–Cl bonds in GaCl_3 stronger, the same strength, or weaker than the Sb–Cl bonds in SbCl_3 ? Why?
23. What is meant by a *nonbonding* molecular orbital, and how is it formed? How does the energy of a nonbonding orbital compare with the energy of bonding or antibonding molecular orbitals derived from the same atomic orbitals?
24. Many features of molecular orbital theory have analogs in Lewis electron structures. How do Lewis electron structures represent
 - a. nonbonding electrons?
 - b. electrons in bonding molecular orbitals?

25. How does electron screening affect the energy difference between the 2s and 2p atomic orbitals of the period 2 elements? How does the energy difference between the 2s and 2p atomic orbitals depend on the effective nuclear charge?
26. For σ versus π , π versus σ^* , and σ^* versus π^* , which of the resulting molecular orbitals is lower in energy?
27. The energy of a σ molecular orbital is usually lower than the energy of a π molecular orbital derived from the same set of atomic orbitals. Under specific conditions, however, the order can be reversed. What causes this reversal? In which portion of the periodic table is this kind of orbital energy reversal most likely to be observed?
28. Is the $s 2p_z$ molecular orbital stabilized or destabilized by interaction with the σ_{2s} molecular orbital in N_2 ? In O_2 ? In which molecule is this interaction most important?
29. Explain how the Lewis electron-pair approach and molecular orbital theory differ in their treatment of bonding in O_2 .
30. Why is it crucial to our existence that O_2 is paramagnetic?
31. Will NO or CO react more quickly with O_2 ? Explain your answer.
32. How is the energy-level diagram of a heteronuclear diatomic molecule, such as CO, different from that of a homonuclear diatomic molecule, such as N_2 ?
33. How does molecular orbital theory describe the existence of polar bonds? How is this apparent in the molecular orbital diagram of HCl?

ANSWERS

1. An atomic orbital is a region of space around an atom that has a non-zero probability for an electron with a particular energy. Analogously, a molecular orbital is a region of space in a molecule that has a non-zero probability for an electron with a particular energy. Both an atomic orbital and a molecular orbital can contain two electrons.
- 15 No. Because an np_x orbital on one atom is perpendicular to an np_y orbital on an adjacent atom, the net overlap between the two is zero. This is also true for np_y and np_z orbitals on adjacent atoms.

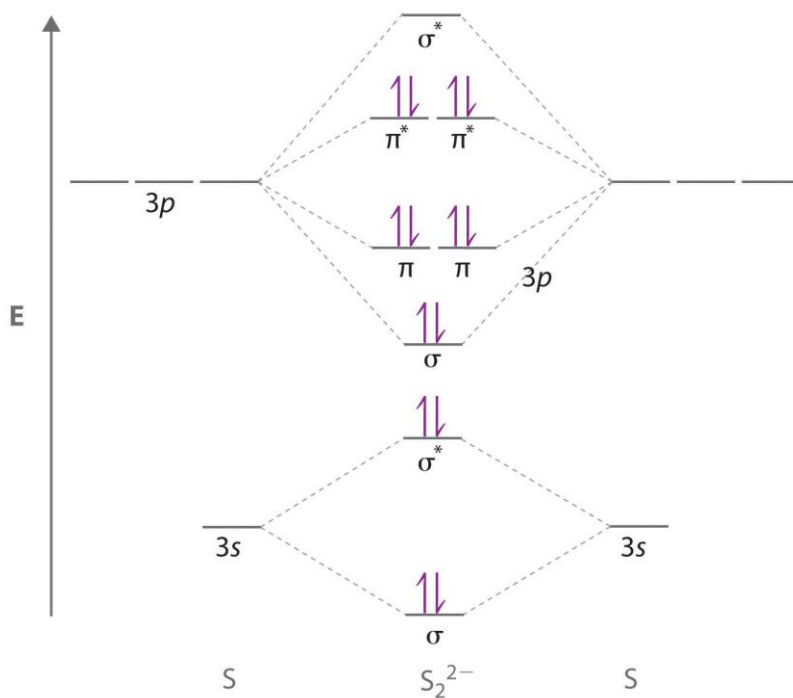
NUMERICAL PROBLEMS

1. Use a qualitative molecular orbital energy-level diagram to describe the bonding in S_2^{2-} . What is the bond order? How many unpaired electrons does it have?

2. Use a qualitative molecular orbital energy-level diagram to describe the bonding in F_2^{2+} . What is the bond order? How many unpaired electrons does it have?
3. If three atomic orbitals combine to form molecular orbitals, how many molecular orbitals are generated? How many molecular orbitals result from the combination of four atomic orbitals? From five?
4. If two atoms interact to form a bond, and each atom has four atomic orbitals, how many molecular orbitals will form?
5. Sketch the possible ways of combining two 1s orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.
6. Sketch the *four* possible ways of combining two 2p orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.
7. If a diatomic molecule has a bond order of 2 and six bonding electrons, how many antibonding electrons must it have? What would be the corresponding Lewis electron structure (disregarding lone pairs)? What would be the effect of a one-electron reduction on the bond distance?
8. What is the bond order of a diatomic molecule with six bonding electrons and no antibonding electrons? If an analogous diatomic molecule has six bonding electrons and four antibonding electrons, which has the stronger bond? the shorter bond distance? If the highest occupied molecular orbital in both molecules is bonding, how will a one-electron oxidation affect the bond length?
9. Qualitatively discuss how the bond distance in a diatomic molecule would be affected by adding an electron to
 - a. an antibonding orbital.
 - b. a bonding orbital.
10. Explain why the oxidation of O_2 decreases the bond distance, whereas the oxidation of N_2 *increases* the N–N distance. Could Lewis electron structures be employed to answer this problem?
11. Draw a molecular orbital energy-level diagram for Na_2^+ . What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will Na_2^+ , Na_2 , or Na_2^- be the most stable? Why?
12. Draw a molecular orbital energy-level diagram for Xe_2^+ , showing only the valence orbitals and electrons. What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an

- oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will Xe_2^{2+} , Xe_2^+ , or Xe_2 be most stable? Why?
13. Draw a molecular orbital energy-level diagram for O_2^{2-} and predict its valence electron configuration, bond order, and stability.
 14. Draw a molecular orbital energy-level diagram for C_2^{2-} and predict its valence electron configuration, bond order, and stability.
 15. If all the p orbitals in the valence shells of two atoms interact, how many molecular orbitals are formed? Why is it not possible to form three π orbitals (and the corresponding antibonding orbitals) from the set of six p orbitals?
 16. Draw a complete energy-level diagram for B_2 . Determine the bond order and whether the molecule is paramagnetic or diamagnetic. Explain your rationale for the order of the molecular orbitals.
 17. Sketch a molecular orbital energy-level diagram for each ion. Based on your diagram, what is the bond order of each species?
 - a. NO^+
 - b. NO^-
 18. The diatomic molecule BN has never been detected. Assume that its molecular orbital diagram would be similar to that shown for CN^- in Section 9.3 "Delocalized Bonding and Molecular Orbitals" but that the $s^2 p_z$ molecular orbital is higher in energy than the $p^2 p_z$ molecular orbitals.
 - a. Sketch a molecular orbital diagram for BN.
 - b. Based on your diagram, what would be the bond order of this molecule?
 - c. Would you expect BN to be stable? Why or why not?
 19. Of the species BN, CO, C_2 , and N_2 , which are isoelectronic?
 20. Of the species CN^- , NO^+ , B_2^{2-} , and O_2^+ , which are isoelectronic?

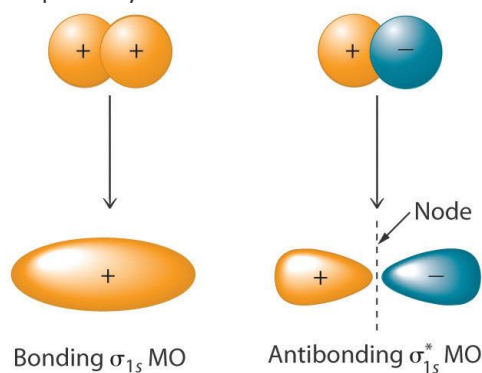
ANSWERS



Each S atom contributes 6 valence electrons
+ 2 e⁻ for charge = 14 e⁻

The bond order is 1, and the ion has no unpaired electrons.

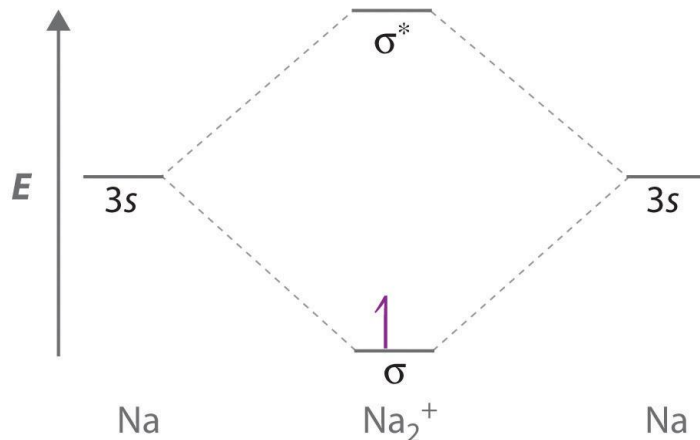
3. The number of molecular orbitals is always equal to the number of atomic orbitals you start with. Thus, combining three atomic orbitals gives three molecular orbitals, and combining four or five atomic orbitals will give four or five molecular orbitals, respectively.



7. Combining two atomic s orbitals gives two molecular orbitals, a σ (bonding) orbital with no nodal planes, and a σ^* (antibonding) orbital with a nodal plane perpendicular to the internuclear axis.

- Adding an electron to an antibonding molecular orbital will decrease the bond order, thereby increasing the bond distance.
- Adding an electron to a bonding molecular orbital will increase the bond order, thereby decreasing the bond distance.

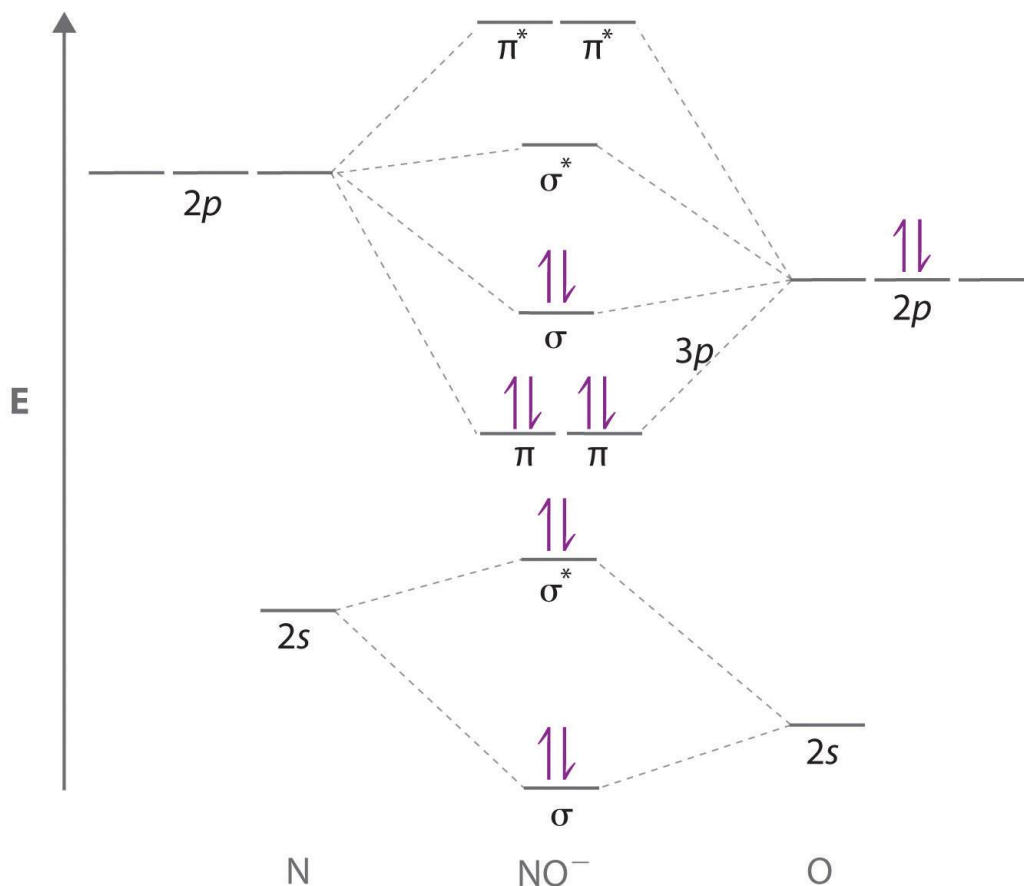
11. Sodium contains only a single valence electron in its $3s$ atomic orbital. Combining two $3s$ atomic orbitals gives two molecular orbitals; as shown in the diagram, these are a σ (bonding) orbital and a σ^* (antibonding) orbital.



1.

Although each sodium atom contributes one valence electron, the $+1$ charge indicates that one electron has been removed. Placing the single electron in the lowest energy molecular orbital gives a 1σ electronic configuration and a bond order of 0.5. Consequently, Na_2^+ should be a stable species. Oxidizing Na_2^+ by one electron to give Na_2^{2+} would remove the electron in the σ_{3s} molecular orbital, giving a bond order of 0.

Conversely, reducing Na_2^+ by one electron to give Na_2 would put an additional electron into the σ_{3s} molecular orbital, giving a bond order of 1. Thus, reduction to Na_2 would produce a more stable species than oxidation to Na_2^{2+} . The Na_2^- ion would have two electrons in the bonding σ_{3s} molecular orbital and one electron in the antibonding σ^*_{3s} molecular orbital, giving a bond order of 0.5. Thus, Na_2 is the most stable of the three species.



1. a.

a. The NO^+ ion has 10 valence electrons, which fill all the molecular orbitals up to and including the σ_{2p} . With eight electrons in bonding molecular orbitals and two electrons in antibonding orbitals, the bond order in NO^+ is $(8 - 2)/2 = 3$.

b. The NO^- ion contains two more electrons, which fill the σ^*_{2p} molecular orbital. The bond order in NO^- is $(8 - 4)/2 = 2$.

19. BN and C_2 are isoelectronic, with 12 valence electrons, while N_2 and CO are isoelectronic, with 14 valence electrons.

[1] The $\approx$ sign is used rather than an $=$ sign because we are ignoring certain constants that are not important to our argument.

9.4 Polyatomic Systems with Multiple Bonds

LEARNING OBJECTIVE

1. To explain resonance structures using molecular orbitals.

So far in our molecular orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using molecular orbitals formed by unhybridized np atomic orbitals.

Multiple Bonds

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the $\text{H}-\text{C}-\text{H}$ and $\text{H}-\text{C}-\text{C}$ angles in ethylene are approximately 120° . This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two $\text{C}-\text{H}$ ($sp^2 + s$) and one $\text{C}-\text{C}$ ($sp^2 + sp^2$) (part (a) in Figure 9.32 "Bonding in Ethylene").

The sp^2 hybridization can be represented as follows:

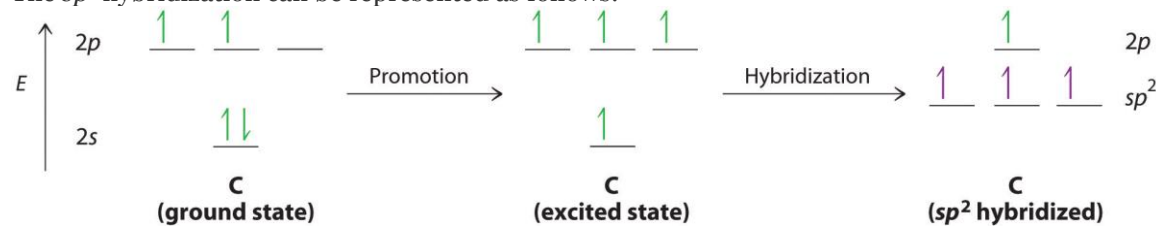
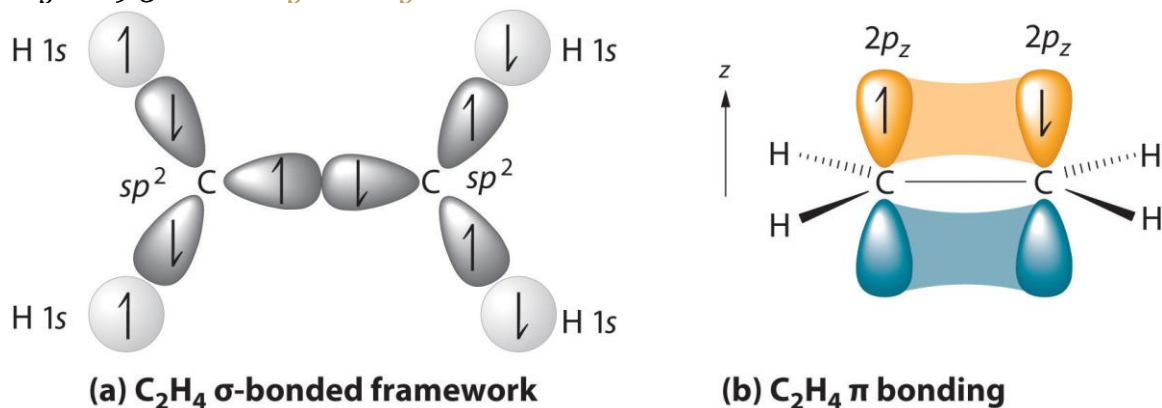


Figure 9.32 *Bonding in Ethylene*

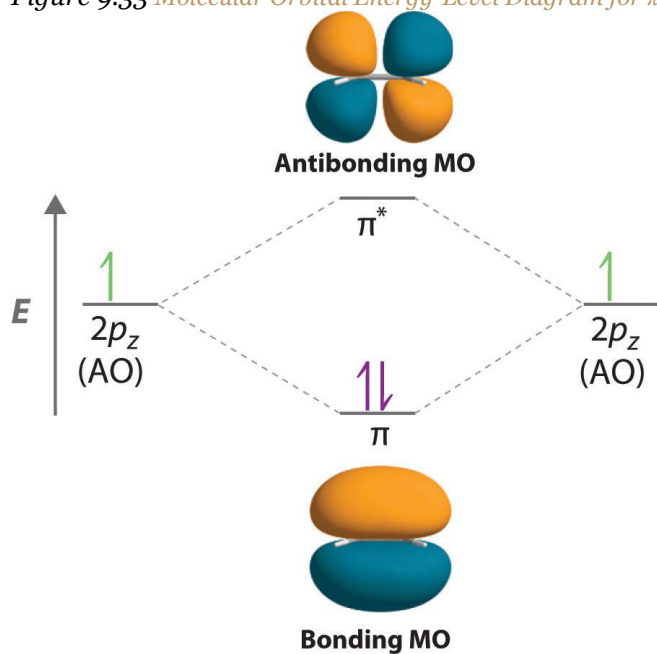


a) The σ -bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen $1s$ orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four $\text{C}-\text{H}$ bonds and one $\text{C}-\text{C}$ bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon-carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the z -axis.)

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 9.32 "Bonding in Ethylene"). The two singly occupied $2p_z$ orbitals

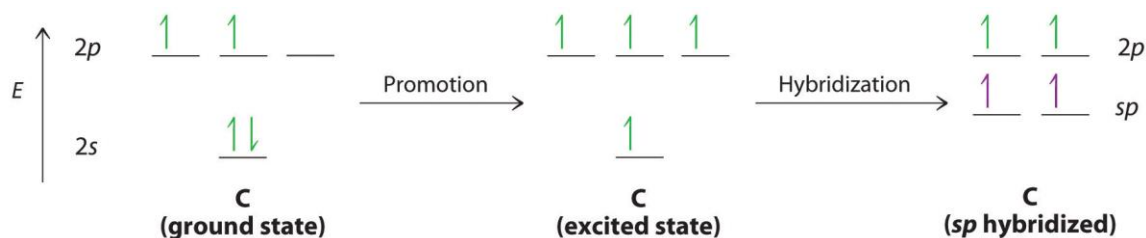
can overlap to form a π bonding orbital and a π^* antibonding orbital, which produces the energy-level diagram shown in Figure 9.33 "Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene". With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π^* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.

Figure 9.33 *Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene*



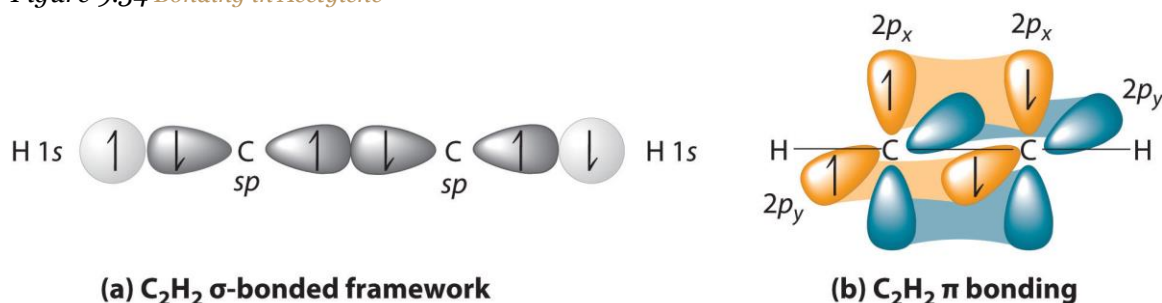
As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is sp hybridized. If one sp lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized $2p$ orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 9.34 "Bonding in Acetylene").



The two $2p$ orbitals on each carbon can align with the corresponding $2p$ orbitals on the adjacent carbon to simultaneously form a *pair* of π bonds (part (b) in Figure 9.34 "Bonding in Acetylene"). Because each of the unhybridized $2p$ orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

Figure 9.34 *Bonding in Acetylene*



(a) In the formation of the σ -bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen $1s$ orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

Note the Pattern

In complex molecules, hybrid orbitals and valence bond theory can be used to describe σ bonding, and unhybridized π orbitals and molecular orbital theory can be used to describe π bonding.

EXAMPLE 12

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

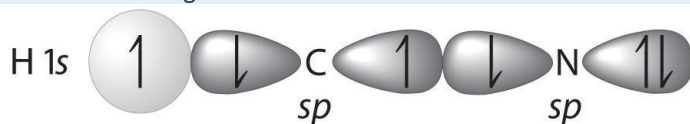
A From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ -bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.

B Determine the number of remaining valence electrons. Use any remaining unhybridized p orbitals to form π and π^* orbitals.

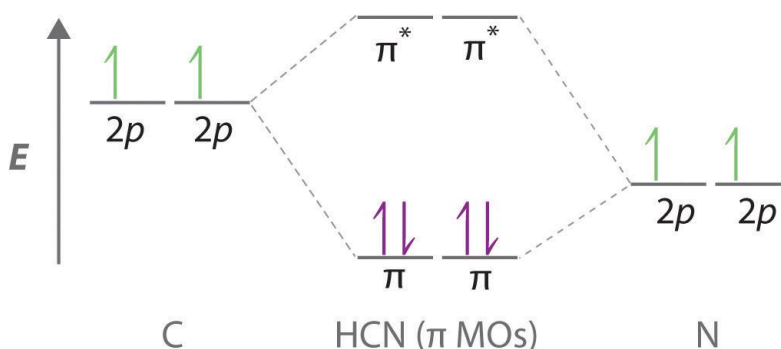
C Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of sp hybridization at carbon. Because the nitrogen atom can also be described as sp hybridized, we can use one sp hybrid on each atom to form a C–N σ bond. This leaves one sp hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized $2p$ atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four $2p$ atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π^* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



Exercise

Describe the bonding in formaldehyde ($\text{H}_2\text{C}=\text{O}$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

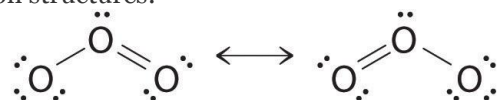
Answer:

σ -bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.

π bonding: Unhybridized, singly occupied $2p$ atomic orbitals on carbon and oxygen interact to form π (bonding) and π^* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

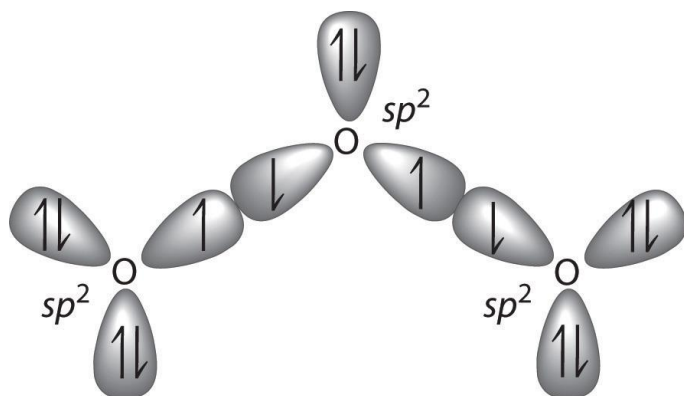
Molecular Orbitals and Resonance Structures

In Chapter 8 "Ionic versus Covalent Bonding", we used resonance structures to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). We showed that ozone can be represented by either of these Lewis electron structures:

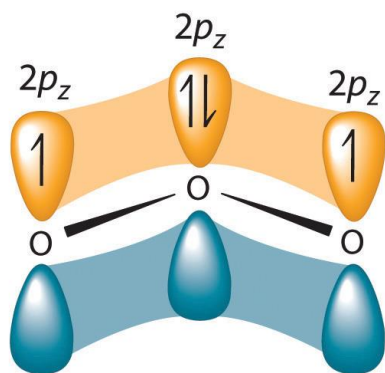


Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Figure 9.35 *Bonding in Ozone*



(a) O₃ σ -bond framework



(b) O₃ π bonding

(a) In the formation of the σ -bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O₃. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

Experimental evidence indicates that ozone has a bond angle of 117.5° . Because this angle is close to 120° , it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ -bonded framework shown in Figure 9.35 "Bonding in Ozone".

Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized $2p$ orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O₃ has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized $2p$ orbitals.

With a molecular orbital approach to describe the π bonding, three $2p$ atomic orbitals give us three molecular orbitals, as shown in Figure 9.36 "π Bonding in Ozone". One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π^* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; it is a nonbonding molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

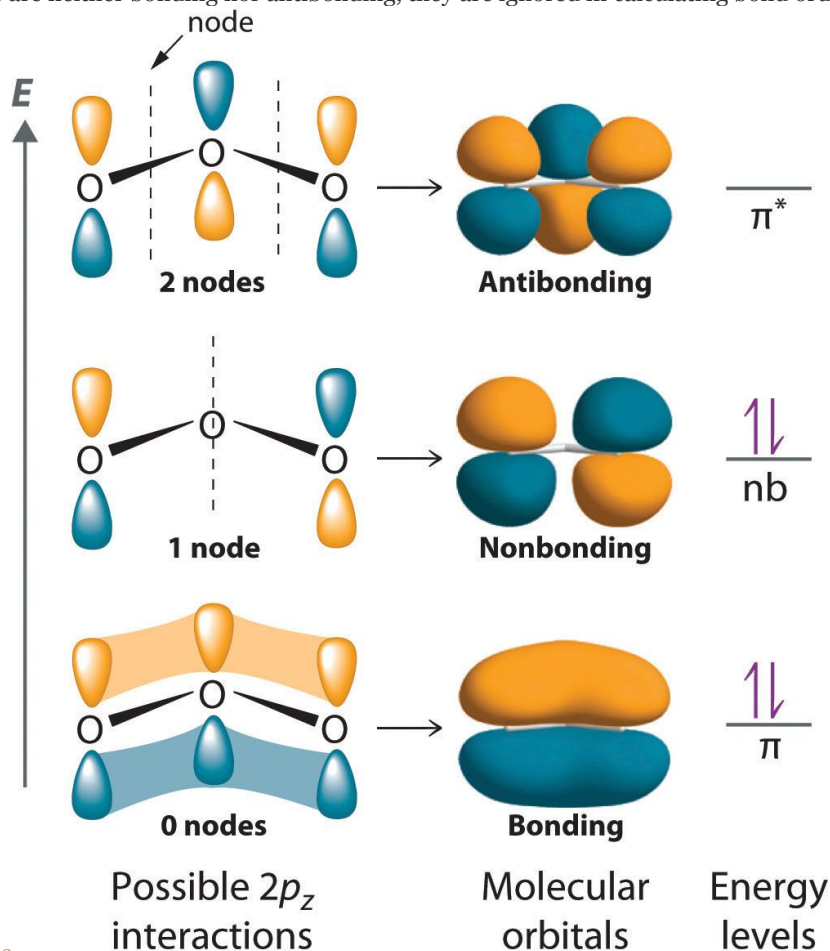


Figure 9.36 π Bonding in Ozone

The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π^* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is 12 per O–O bond. The combined σ/π bond order is thus 112 for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 9.36 "π Bonding in Ozone", thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding *three* oxygen atoms together, or $12p$ bond per O–O. We therefore predict the overall O–O bond order to be $1/2$ ($12p$ bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital approach, however, shows that the π nonbonding orbital is localized on the *terminal* O atoms, which suggests that they are more electron rich than the central O atom. The reactivity of ozone is consistent with the predicted charge localization.

Note the Pattern

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.

EXAMPLE 13

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A Calculate the number of valence electrons in NO_2^- . From the structure, predict the type of atomic orbital hybridization in the ion.

B Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.

C If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

Solution:

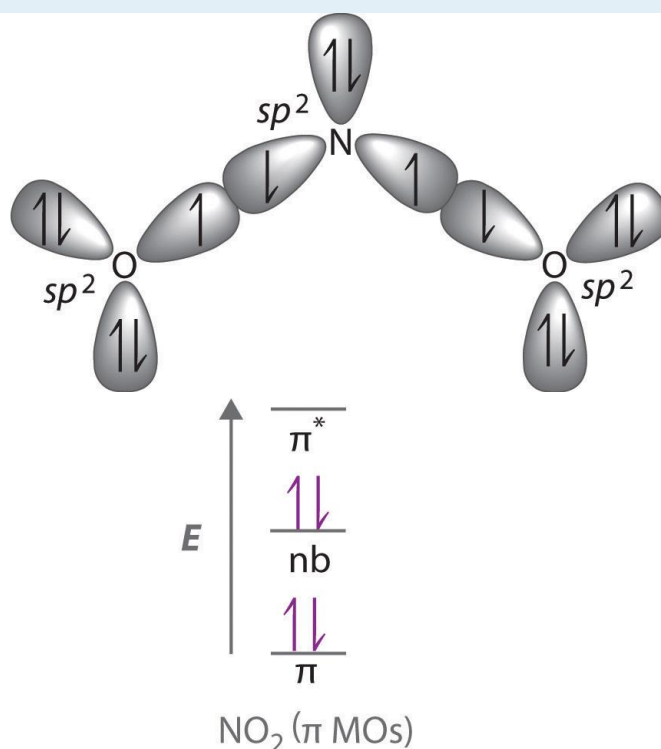
A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the -1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons.

Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen.

The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized $2p$ orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three $2p$ orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.

C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of $1/2$ per N–O bond. The overall N–O bond order is consistent with a resonance structure.



Exercise

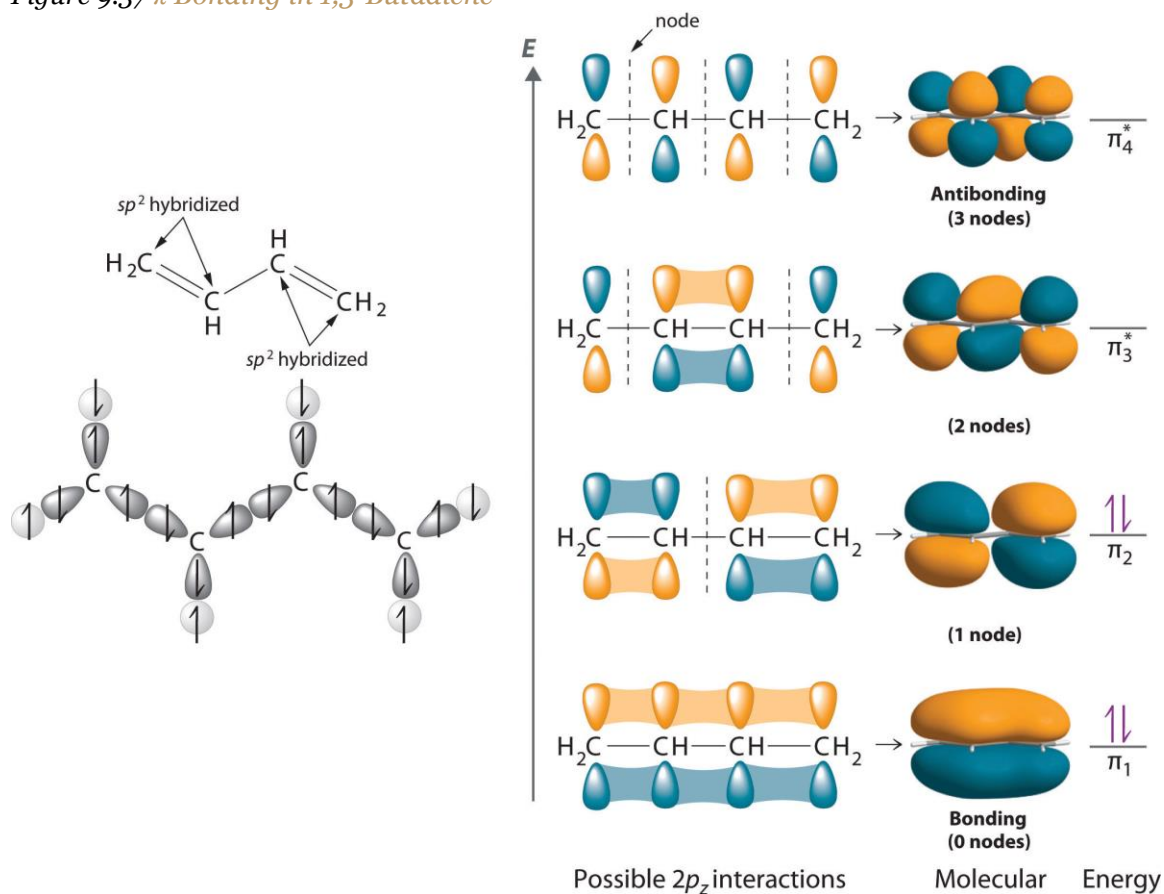
Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer: Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized $2p$ orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore 1.5.

The Chemistry of Vision

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in Figure 9.37 " π Bonding in 1,3-Butadiene". As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 9.38 "Molecular Orbital Energy-Level Diagrams for a Chain of "). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.

Figure 9.37 π Bonding in 1,3-Butadiene



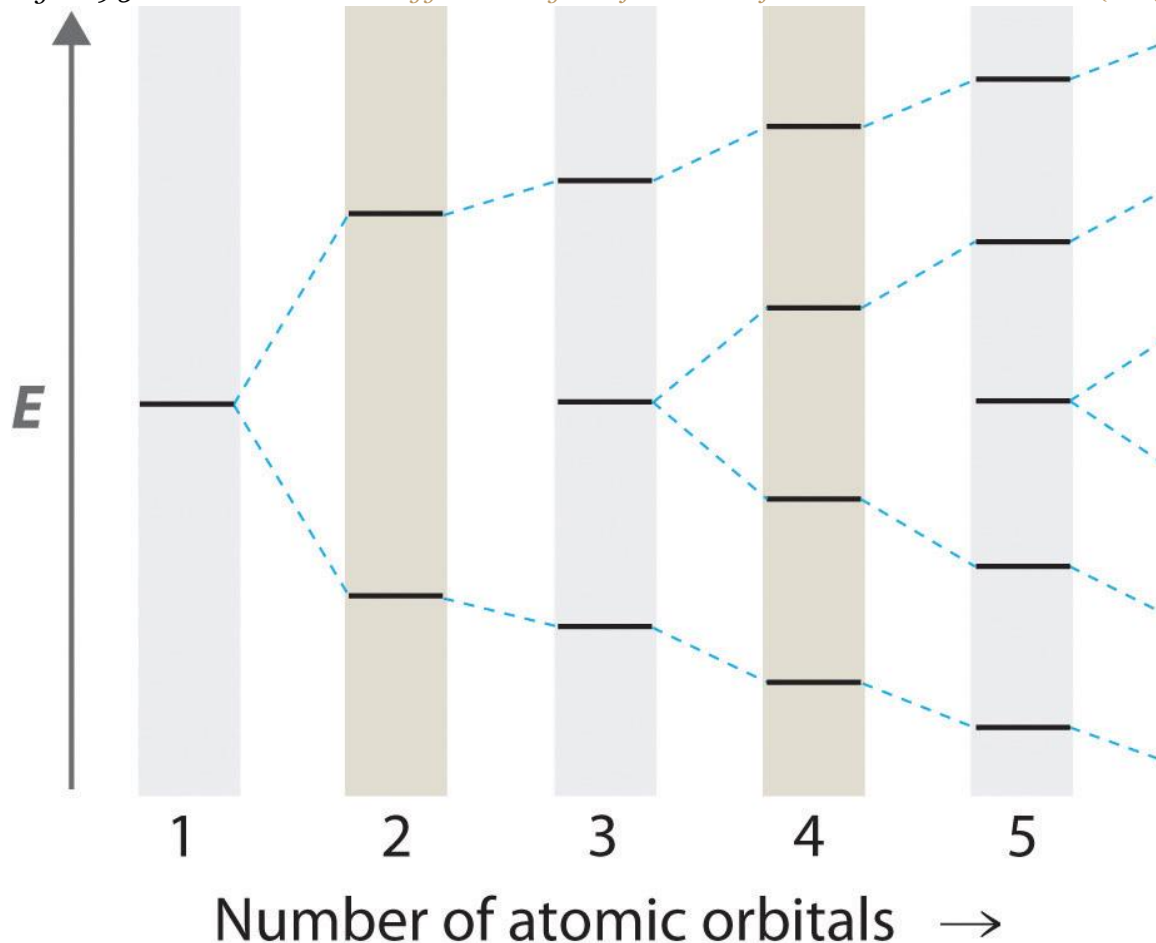
(a) 1,3-Butadiene σ -bonded framework

(b) 1,3-Butadiene π bonding

(a) If

each carbon atom is assumed to be sp^2 hybridized, we can construct a σ -bonded framework that accounts for the C–H and C–C single bonds, leaving four singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form four molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.

Figure 9.38 Molecular Orbital Energy-Level Diagrams for a Chain of n Like Orbitals That Interact ($n \leq 5$)



As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.

Note the Pattern

As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision.

in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

Summary

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized np orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2 . Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized np orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

KEY TAKEAWAY

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

CONCEPTUAL PROBLEMS

1. What information is obtained by using the molecular orbital approach to bonding in O_3 that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?
2. How is resonance explained using the molecular orbital approach?
3. Indicate what information can be obtained by each method:

	Lewis Electron Structures	VSEPR Model	Valence Bond Theory	Molecular Orbital Theory
Geometry				
Resonance				
Orbital Hybridization				
Reactivity				
Expanded Valences				

	Lewis Electron Structures	VSEPR Model	Valence Bond Theory	Molecular Orbital Theory
Bond Order				

NUMERICAL PROBLEMS

- Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in BCl_3 and CS_3^{2-} .
- Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in CO_2 and N_3^- .

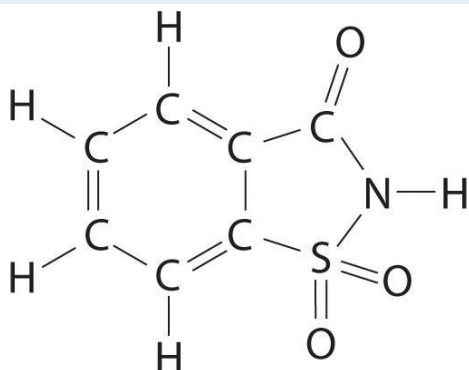
9.5 End-of-Chapter Material

APPLICATION PROBLEMS

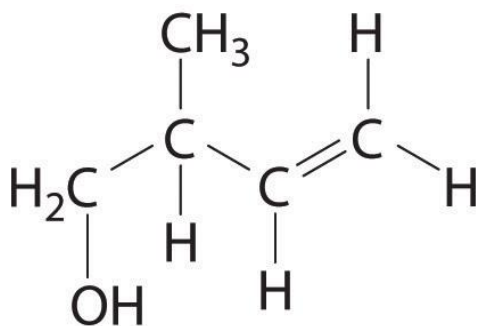
Problems marked with a ♦ involve multiple concepts.

- ♦ Sulfur hexafluoride (SF_6) is a very stable gas that is used in a wide range of applications because it is nontoxic, nonflammable, and noncorrosive. Unfortunately, it is also a very powerful “greenhouse gas” that is about 22,000 times more effective at causing global warming than the same mass of CO_2 .
 - Draw the Lewis electron structure of SF_6 and determine the number of electron groups around the central atom, the molecular geometry, and the hybridization of the central atom.
 - Suggest a reason for the extremely high stability of SF_6 .
 - Despite its rather high molecular mass (146.06 g/mol) and highly polar S–F bonds, SF_6 is a gas at room temperature (boiling point = -63°C). Why?
- ♦ The elevated concentrations of chlorine monoxide (ClO) that accompany ozone depletions in Earth’s atmosphere can be explained by a sequence of reactions. In the first step, chlorine gas is split into chlorine atoms by sunlight. Each chlorine atom then catalyzes the decomposition of ozone through a chlorine monoxide intermediate.
 - Write balanced chemical equations showing this sequence of reactions.
 - Sketch the molecular orbital energy-level diagram of ClO.
 - Does ClO contain any unpaired electrons?
 - Based on your molecular orbital diagram, is ClO likely to be a stable species? Explain your answer.

3. ♦ Saccharin is an artificial sweetener that was discovered in 1879. For several decades, it was used by people who had to limit their intake of sugar for medical reasons. Because it was implicated as a carcinogen in 1977, however, warning labels are now required on foods and beverages containing saccharin. The structure of this sweetener is as follows:

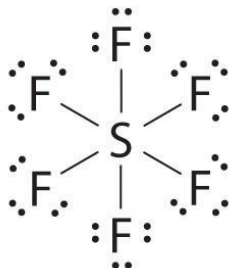


- Give the hybridization of all five atoms shown in bold in the structure. Note: all five atoms in the five-membered ring are coplanar.
 - The carbon–oxygen bond is drawn as a double bond. If the nitrogen and the carbon attached to the C=O group each contribute one electron to the bonding, use both a Lewis electron structure and a hybrid orbital approach to explain the presence of the double bond.
 - If sulfur and carbon each contribute one electron to nitrogen, how many lone pairs are present on the nitrogen?
 - What is the geometry of the sulfur atom?
 - The Lewis electron structure supports a single bond between the carbon and the nitrogen and a double bond between the carbon and the oxygen. In actuality, the C–O bond is longer than expected for a double bond, and the C–N bond is shorter. The nitrogen is also planar. Based on this information, what is the likely hybridization of the nitrogen? Using the concepts of molecular orbital theory, propose an explanation for this observation.
2. ♦ Pheromones are chemical signals used for communication between members of the same species. For example, the bark beetle uses an aggregation pheromone to signal other bark beetles to congregate at a particular site in a tree. Bark beetle infestations can cause severe damage because the beetles carry a fungal infection that spreads rapidly and can kill the tree. One of the components of this aggregation pheromone has the following structure:



1.
 - a. Give the hybridization of all atoms except hydrogen in this pheromone.
 - b. How many σ bonds are present in this molecule? How many π bonds are there?
 - c. Describe the bonding in this molecule using a combination of the localized and delocalized approaches.
2. Carbon monoxide is highly poisonous because it binds more strongly than O_2 to the iron in red blood cells, which transport oxygen in the blood. Consequently, a victim of CO poisoning suffocates from a lack of oxygen. Draw a molecular orbital energy-level diagram for CO. What is the highest occupied molecular orbital? Are any of the molecular orbitals degenerate? If so, which ones?

ANSWER



1.
 - a. There are six electron groups, the molecular geometry is octahedral, and the hybridization of S is sp^3d^2 .
 - b. With six fluorine atoms packed around the central sulfur atom, there is no room for another species to approach the sulfur to initiate a reaction. The polar S–F bonds are also expected to be quite strong, so breaking an S–F bond to initiate a reaction is unlikely under most conditions.
 - c. SF_6 is a gas at room temperature because it has no net dipole moment; the individual S–F bond dipoles cancel one another in this highly symmetrical structure. The absence of a dipole moment results in very weak interactions between SF_6 molecules, and as a result SF_6 is a gas rather than a liquid or a solid at room temperature.

Chapter 10

Gases

In Chapter 6 "The Structure of Atoms" through Chapter 9 "Molecular Geometry and Covalent Bonding Models" we focused on the *microscopic* properties of matter—the properties of individual atoms, ions, and molecules—and how the electronic structures of atoms and ions determine the stoichiometry and three-dimensional geometry of the compounds they form. We will now focus on *macroscopic* properties—the behavior of aggregates with large numbers of atoms, ions, or molecules. An understanding of macroscopic properties is central to an understanding of chemistry. Why, for example, are many substances gases under normal pressures and temperatures (1.0 atm, 25°C), whereas others are liquids or solids? We will examine each form of matter—gases, liquids, and solids—as well as the nature of the forces, such as hydrogen bonding and electrostatic interactions, that hold molecular and ionic compounds together in these three states.

In Chapter 10 "Gases", we explore the relationships among pressure, temperature, volume, and the amount of gases. You will learn how to use these relationships to describe the physical behavior of a sample of both a pure gaseous substance and mixtures of gases. By the end of this chapter, your understanding of the gas laws and the model used to explain the behavior of gases will allow you to explain how straws and hot-air balloons work, why hand pumps cannot be used in wells beyond a certain depth, why helium-filled balloons deflate so rapidly, and how a gas can be liquefied for use in preserving biological tissue.

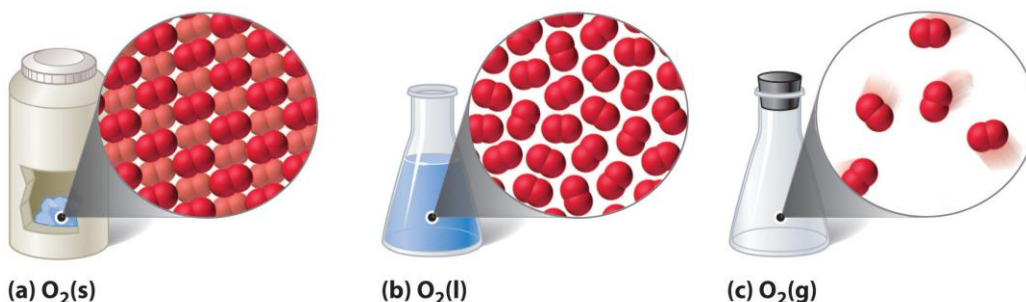
10.1 Gaseous Elements and Compounds

LEARNING OBJECTIVE

1. To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 10.1 "A Diatomic Substance (O)" compares the three states of matter and illustrates the differences at the molecular level.

Figure 10.1 A Diatomic Substance (O₂) in the Solid, Liquid, and Gaseous States



(a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vapor^[1] is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 10.1 "Properties of Water at 1.0 atm".

Table 10.1 Properties of Water at 1.0 atm

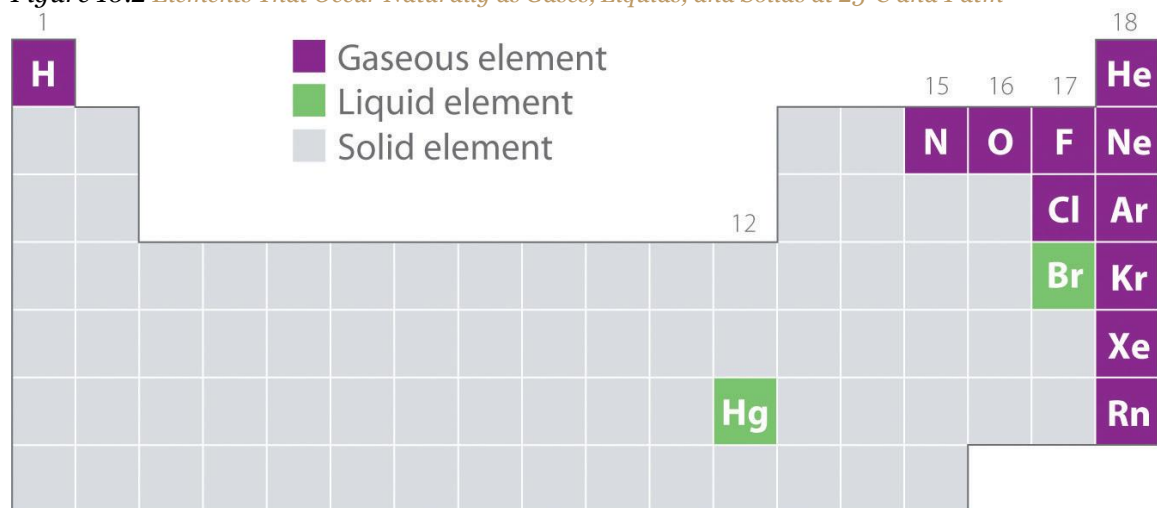
Temperature	State	Density (g/cm^3)
$\leq 0^\circ\text{C}$	solid (ice)	0.9167 (at 0.0°C)
0°C – 100°C	liquid (water)	0.9997 (at 4.0°C)
$\geq 100^\circ\text{C}$	vapor (steam)	0.005476 (at 127°C)

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure 10.2 "Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm" shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble

gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (H_2 , N_2 , O_2 , F_2 , and Cl_2). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (O_3), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as “room temperature and pressure”). Gallium (Ga), which melts at only 29.76°C , can be converted to a liquid simply by holding a container of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

Figure 10.2 Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm



The

noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

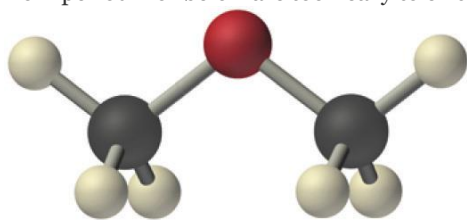
Many of the elements and compounds we have encountered so far are typically found as gases; some of the more common ones are listed in Table 10.2 "Some Common Substances That Are Gases at 25°C and 1.0 atm". Gaseous substances include many binary hydrides, such as the hydrogen halides (HX); hydrides of the chalcogens; hydrides of the group 15 elements N, P, and As; hydrides of the group 14 elements C, Si, and Ge; and diborane (B_2H_6). In addition, many of the simple covalent oxides of the nonmetals are gases, such as CO , CO_2 , NO , NO_2 , SO_2 , SO_3 , and ClO_2 . Many low-molecular-mass organic compounds are gases as well, including all the hydrocarbons with four or fewer carbon atoms and simple molecules such as dimethyl ether [$(\text{CH}_3)_2\text{O}$], methyl chloride (CH_3Cl), formaldehyde (CH_2O), and acetaldehyde (CH_3CHO). Finally, most of the commonly used refrigerants, such as the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs), which were discussed in Chapter 3 "Chemical Reactions", are gases.

Table 10.2 Some Common Substances That Are Gases at 25°C and 1.0 atm

Elements	Compounds	
He (helium)	HF (hydrogen fluoride)	C_2H_4 (ethylene)

Elements	Compounds	
Ne (neon)	HCl (hydrogen chloride)	C ₂ H ₂ (acetylene)
Ar (argon)	HBr (hydrogen bromide)	C ₃ H ₈ (propane)
Kr (krypton)	HI (hydrogen iodide)	C ₄ H ₁₀ (butane)
Xe (xenon)	HCN (hydrogen cyanide)*	CO (carbon monoxide)
Rn (radon)	H ₂ S (hydrogen sulfide)	CO ₂ (carbon dioxide)
H ₂ (hydrogen)	NH ₃ (ammonia)	NO (nitric oxide)
N ₂ (nitrogen)	PH ₃ (phosphine)	N ₂ O (nitrous oxide)
O ₂ (oxygen)	CH ₄ (methane)	NO ₂ (nitrogen dioxide)
O ₃ (ozone)	C ₂ H ₆ (ethane)	SO ₂ (sulfur dioxide)
F ₂ (fluorine)		
Cl ₂ (chlorine)		
*HCN boils at 26°C at 1 atm, so it is included in this table.		

All of the gaseous substances mentioned previously (other than the monatomic noble gases) contain covalent or polar covalent bonds and are nonpolar or polar molecules. In contrast, the strong electrostatic attractions in ionic compounds, such as NaBr (boiling point = 1390°C) or LiF (boiling point = 1673°C), prevent them from existing as gases at room temperature and pressure. In addition, the lightest members of any given family of compounds are most likely gases, and the boiling points of polar compounds are generally greater than those of nonpolar compounds of similar molecular mass. Therefore, in a given series of compounds, the lightest and least polar members are the ones most likely to be gases. With relatively few exceptions, however, compounds with more than about five atoms from period 2 or below are too heavy to exist as gases under normal conditions.



Dimethyl ether

Note the Pattern

Gaseous substances often contain covalent or polar covalent bonds, exist as nonpolar or slightly polar molecules, have relatively low molecular masses, and contain five or fewer atoms from periods 1 or 2.

While gases have a wide array of uses, a particularly grim use of a gaseous substance is believed to have been employed by the Persians on the Roman city of Dura in eastern Syria in the third century AD. The Persians dug a tunnel underneath the city wall to enter and conquer the city. Archeological evidence suggests that when the Romans responded with counter-tunnels to stop the siege, the Persians ignited bitumen and sulfur crystals to produce a dense, poisonous gas. It is likely that bellows or chimneys distributed the toxic fumes. The remains of about 20 Roman soldiers were discovered at the base of the city wall at the entrance to a tunnel that was less than 2 m high and 11 m long. Because it is highly unlikely that the Persians could have slaughtered so many Romans at the entrance to such a confined space, archeologists speculate that the ancient Persians used chemical warfare to successfully conquer the city.

EXAMPLE 1

Which compounds would you predict to be gases at room temperature and pressure?

- a. cyclohexene
- b. lithium carbonate
- c. cyclobutane
- d. vanadium(III) oxide
- e. benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$)

Given: compounds

Asked for: physical state

Strategy:

A Decide whether each compound is ionic or covalent. An ionic compound is most likely a solid at room temperature and pressure, whereas a covalent compound may be a solid, a liquid, or a gas.

B Among the covalent compounds, those that are relatively nonpolar and have low molecular masses are most likely gases at room temperature and pressure.

Solution:

A Lithium carbonate is Li_2CO_3 , containing Li^+ and CO_3^{2-} ions, and vanadium(III) oxide is V_2O_3 , containing V^{3+} and O^{2-} ions. Both are primarily ionic compounds that are expected to be solids. The remaining three compounds are all covalent.

B Benzoic acid has more than four carbon atoms and is polar, so it is not likely to be a gas. Both cyclohexene and cyclobutane are essentially nonpolar molecules, but cyclobutane (C_4H_8) has a significantly

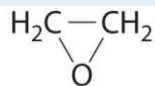
lower molecular mass than cyclohexene (C_6H_{10}), which again has more than four carbon atoms. We therefore predict that cyclobutane is most likely a gas at room temperature and pressure, while cyclohexene is a liquid. In fact, with a boiling point of only 12°C , compared to 83°C for cyclohexene, cyclobutane is indeed a gas at room temperature and pressure.

Exercise

Which compounds would you predict to be gases at room temperature and pressure?

- a. *n*-butanol
- b. ammonium fluoride (NH_4F)
- c. ClF

- d. ethylene oxide



- e. HClO_4

Answer: c; d

Summary

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2 , O_2). Many inorganic and organic compounds with four or fewer nonhydrogen atoms are also gases at room temperature and pressure. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

KEY TAKEAWAY

- The molecules in gaseous substances often contain covalent or polar covalent bonds, are nonpolar or slightly polar molecules, and have relatively low molecular masses.

CONCEPTUAL PROBLEMS

1. Explain the differences between the microscopic and the macroscopic properties of matter. Is the boiling point of a compound a microscopic or macroscopic property? molecular mass? Why?

2. Determine whether the melting point, the dipole moment, and electrical conductivity are macroscopic or microscopic properties of matter and explain your reasoning.
3. How do the microscopic properties of matter influence the macroscopic properties? Can you relate molecular mass to boiling point? Why or why not? Can polarity be related to boiling point?
4. For a substance that has gas, liquid, and solid phases, arrange these phases in order of increasing
 - a. density.
 - b. strength of intermolecular interactions.
 - c. compressibility.
 - d. molecular motion.
 - e. order in the arrangement of the molecules or atoms.
5. Explain what is wrong with this statement: "The state of matter largely determines the molecular properties of a substance."
6. Describe the most important factors that determine the state of a given compound. What external conditions influence whether a substance exists in any one of the three states of matter?
7. Which elements of the periodic table exist as gases at room temperature and pressure? Of these, which are diatomic molecules and which are monatomic? Which elements are liquids at room temperature and pressure? Which portion of the periodic table contains elements whose binary hydrides are most likely gases at room temperature?
8. Is the following observation correct? "Almost all nonmetal binary hydrides are gases at room temperature, but metal hydrides are all solids." Explain your reasoning.
9. Is the following observation correct? "All the hydrides of the chalcogens are gases at room temperature and pressure except the binary hydride of oxygen, which is a liquid." Explain your reasoning. Would you expect 1-chloropropane to be a gas? iodopropane? Why?
10. Explain why ionic compounds are not gases under normal conditions.

ANSWERS

- 1.
- 2.
- 3.
- 4.

5. The molecular properties of a substance control its state of matter under a given set of conditions, *not* the other way around. The presence of strong intermolecular forces favors a condensed state of matter (liquid or solid), while very weak intermolecular interaction favor the gaseous state. In addition, the shape of the molecules dictates whether a condensed phase is a liquid or a solid.
- 6.
7. Elements that exist as gases are mainly found in the upper right corner and on the right side of the periodic table. The following elements exist as gases: H, He, N, O, F, Ne, Cl, Ar, Kr, Xe, and Rn. Thus, half of the halogens, all of the noble gases, and the lightest chalcogens and picnogens are gases. Of these, all except the noble gases exist as diatomic molecules. Only two elements exist as liquids at a normal room temperature of 20°C–25°C: mercury and bromine. The upper right portion of the periodic table also includes most of the elements whose binary hydrides are gases. In addition, the binary hydrides of the elements of Groups 14–16 are gases.

[1] The distinction between a gas and a vapor is subtle: the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions (25°C, 1.0 atm). Nitrogen (N₂) and oxygen (O₂) are thus referred to as gases, but gaseous water in the atmosphere is called water vapor.

10.2 Gas Pressure

LEARNING OBJECTIVE

1. To describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities: *temperature* (expressed in kelvins), *volume* (expressed in liters), *amount* (expressed in moles), and *pressure* (in atmospheres). As we explain in this section and Section 10.3 "Relationships among Pressure, Temperature, Volume, and Amount", these variables are *not* independent. If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon

is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure (P) of the gas, the force (F) per unit area (A) of surface:

Equation 10.1

$$P = F/A$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 10.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. In the English system, the units of force are pounds and the units of area are square inches, so we often see pressure expressed in pounds per square inch (lb/in², or psi), particularly among engineers. For scientific measurements, however, the SI units for force are preferred. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m²), which is called the pascal (Pa), after the French mathematician Blaise Pascal (1623–1662):

Equation 10.2

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

To convert from pounds per square inch to pascals, multiply psi by 6894.757 [1 Pa = 1 psi (6894.757)].

Blaise Pascal (1623–1662)

In addition to his talents in mathematics (he invented modern probability theory), Pascal did research in physics and was an author and a religious philosopher as well. His accomplishments include invention of the first syringe and the first digital calculator and development of the principle of hydraulic pressure transmission now used in brake systems and hydraulic lifts.

EXAMPLE 2

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

- lying flat?
- standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

A Calculate the force exerted by the book and then compute the area that is in contact with a surface.

B Substitute these two values into Equation 10.1 to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall from Chapter 5 "Energy Changes in Chemical Reactions" that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$$F = ma = (2.00 \text{ kg})(9.8067 \text{ m/s}^2) = 19.6 \text{ (kg}\cdot\text{m)/s}^2 = 19.6 \text{ N}$$

a. **A** We calculated the force as 19.6 N. When the book is lying flat, the area is $(0.270 \text{ m})(0.210 \text{ m}) = 0.0567 \text{ m}^2$.

b. **B** The pressure exerted by the text lying flat is thus

$$P = 19.6 \text{ N} / 9.5 \times 10^{-3} \text{ m}^2 \\ = 2.1 \times 10^3 \text{ Pa}$$

c. **A** If the book is standing on its end, the force remains the same, but the area decreases:

$$(21.0 \text{ cm})(4.5 \text{ cm}) = (0.210 \text{ m})(0.045 \text{ m}) = 9.5 \times 10^{-3} \text{ m}^2$$

$$P = 19.6 \text{ N} / 9.5 \times 10^{-3} \text{ m}^2$$

B The pressure exerted by the book in this position is thus $= 2.1 \times 10^3 \text{ Pa}$

Thus the *pressure* exerted by the book varies by a factor of about six depending on its orientation, although the *force* exerted by the book does not vary.

Exercise

What pressure does a 60.0 kg student exert on the floor

- when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
- as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answers:

- a. $3.27 \times 10^4 \text{ Pa}$ (4.74 lb/in.^2)
- b. $5.9 \times 10^6 \text{ Pa}$ ($8.5 \times 10^2 \text{ lb/in.}^2$)

Atmospheric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface, and half of it is within the first 5.5 km (Figure 10.3 "Atmospheric Pressure"). Every point on Earth's surface experiences a net pressure called *atmospheric pressure*. The pressure exerted by the atmosphere is considerable: a 1.0 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 100 kPa:

Equation 10.3

$$\begin{aligned} \text{pressure} &= \\ (1.0 \times 10^4 \text{ kg})(9.807 \text{ m/s}^2) / \\ 1.0 \text{ m}^2 &= 0.98 \times 10^5 \text{ Pa} = 98 \text{ kPa} \end{aligned}$$

Figure 10.3 Atmospheric Pressure

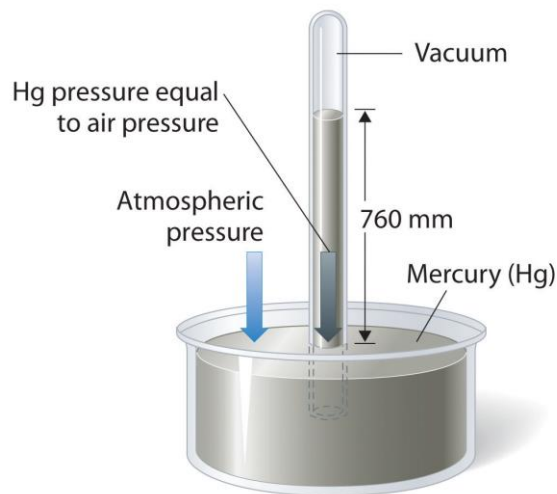
Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface, resulting in a pressure at the surface of $1.01 \times 10^5 \text{ N/m}^2$. This corresponds to a pressure of $101 \text{ kPa} = 760 \text{ mmHg} = 1 \text{ atm}$.

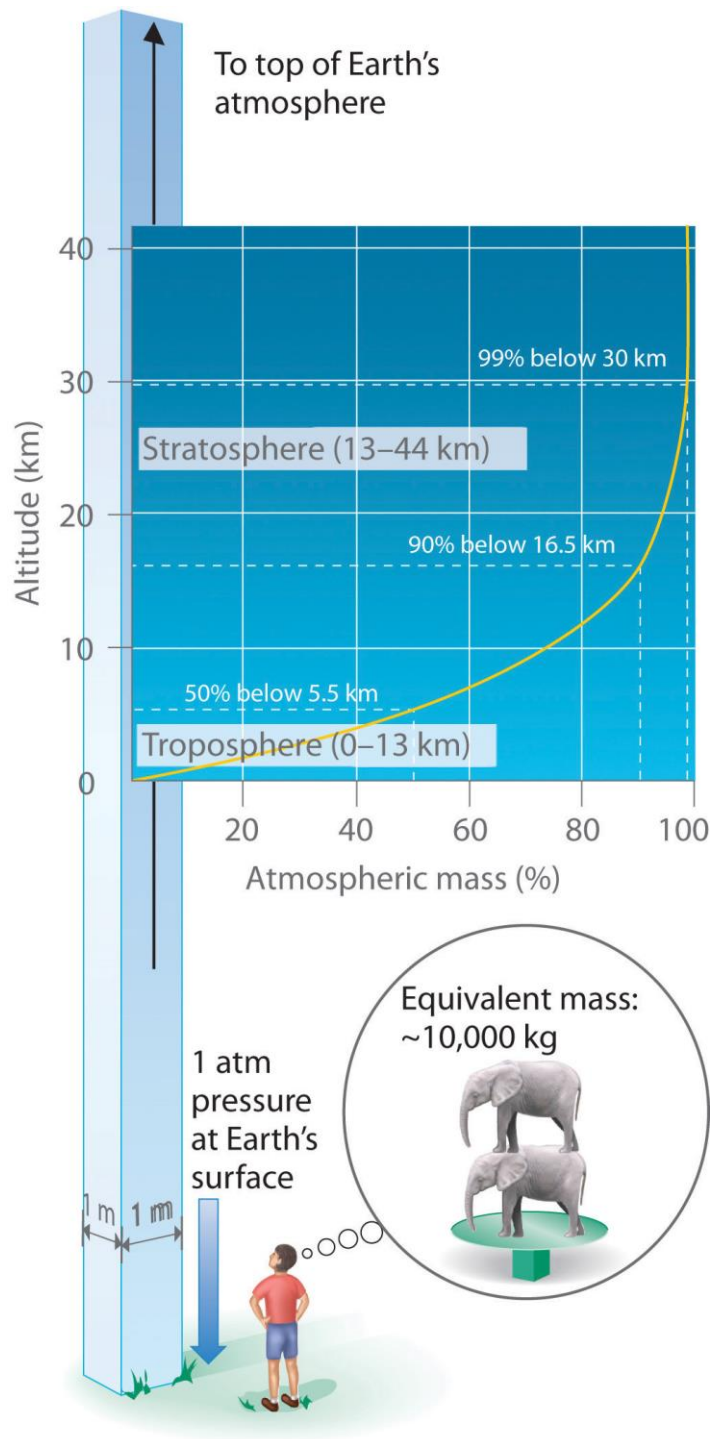
In English units, this is about 14 lb/in.^2 , but we are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of atmospheric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The atmospheric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

Atmospheric pressure can be measured using a barometer, a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 10.4 "A Mercury Barometer"). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in

the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a *vacuum*), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 10.4 "A Mercury Barometer". This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

Figure 10.4 A Mercury Barometer



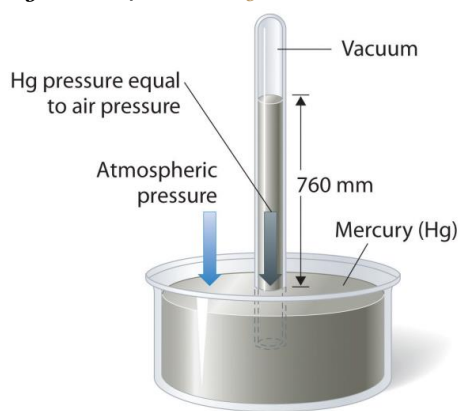


Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface, resulting in a pressure at the surface of $1.01 \times 10^5 \text{ N/m}^2$. This corresponds to a pressure of $101 \text{ kPa} = 760 \text{ mmHg} = 1 \text{ atm}$.

In English units, this is about 14 lb/in.², but we are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of atmospheric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The atmospheric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

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Figure 10.4 A Mercury Barometer



The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure atmospheric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard atmospheric pressure is the atmospheric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

Equation 10.4

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa}$$

Thus a pressure of 1 atm equals 760 mmHg exactly and is approximately equal to 100 kPa.

EXAMPLE 3

One of the authors visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14,000 ft). He noticed that even slight exertion was very difficult at this altitude, where the atmospheric pressure is only 454 mmHg. Convert this pressure to

- a. atmospheres.
- b. kilopascals.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and kilopascals

Strategy:

Use the conversion factors in Equation 10.4 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 10.4, we have $1 \text{ atm} = 760 \text{ mmHg} = 101.325 \text{ kPa}$. The pressure at 14,000 ft in atm is thus

$$P = (454 \text{ mmHg}) \left(\frac{1 \text{ atm}}{760 \text{ mmHg}} \right) = 0.597 \text{ atm}$$

The pressure in kPa is given by

$$\begin{aligned} P &= (0.597 \text{ atm}) \left(\frac{101.325 \text{ kPa}}{1 \text{ atm}} \right) \\ &= 60.5 \text{ kPa} \end{aligned}$$

Exercise

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal atmospheric pressure at this altitude is about 0.308 atm. Convert this pressure to

a. millimeters of mercury.

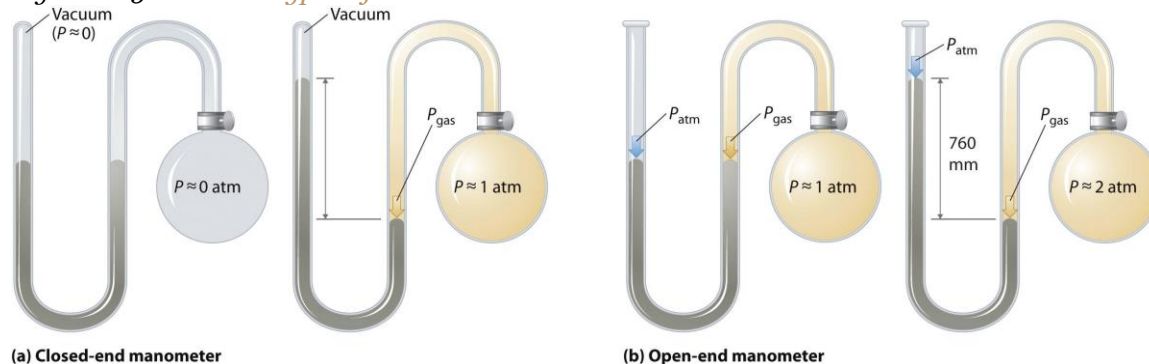
b. kilopascals.

Answer: a. 234 mmHg; b. 31.2 kPa

Manometers

Barometers measure atmospheric pressure, but manometers measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure 10.5 "The Two Types of Manometer". When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

Figure 10.5 *The Two Types of Manometer*



(a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1 \text{ atm}$), and the difference in the heights of the two columns gives the difference between atmospheric pressure and the pressure of the gas in the bulb.

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure 10.5 "The Two Types of Manometer", then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the atmospheric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the atmospheric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the atmospheric pressure minus the difference in the heights of the two columns.

EXAMPLE 4

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (At 25°C, the density of water is 0.9970 g/cm³; the density of mercury is 13.53 g/cm³.)

Given: pressure range and densities of water and mercury

Asked for: column height

Strategy:

A Calculate the height of a column of mercury corresponding to 0.200 atm in millimeters of mercury. This is the height needed for a mercury-filled column.

B From the given densities, use a proportion to compute the height needed for a water-filled column.

Solution:

A In millimeters of mercury, a gas pressure of 0.200 atm is

$$P = (0.200 \text{ atm})(760 \text{ mmHg} / 1 \text{ atm}) = 152 \text{ mmHg}$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

B Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury (d_{Hg}) to the density of water:

$$\begin{aligned}
 (\text{height}_{H_2O})(\rho_{H_2O}) &= (\text{height}_{Hg})(\rho_{Hg}) \\
 \text{height}_{H_2O} &= (\text{height}_{Hg})(\rho_{Hg}/\rho_{H_2O}) \\
 &= (152 \text{ mm})(13.53 \text{ g/cm}^3/1.00 \text{ g/cm}^3) \\
 &= 2.06 \times 10^3 \text{ mm } H_2O = 2.06 \text{ m } H_2O
 \end{aligned}$$

This answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise

Suppose you want to design a barometer to measure atmospheric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C; the density of liquid gallium at 25°C is 6.114 g/cm³. How tall a column of gallium do you need if $P = 1.00 \text{ atm}$?

Answer: 1.68 m

The answer to Example 4 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. If a column of water 2.06 m high corresponds to 0.200 atm, then 1.00 atm corresponds to a column height of $h/2.06\text{m} = 1/2$, $h=10.3\text{m}$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on atmospheric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for atmospheric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

Summary

Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m²). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *atmospheric pressure*, is about 101 kPa or 14.7 lb/in.² at sea level. Atmospheric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to atmospheric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard atmospheric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet

another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.

KEY TAKEAWAY

- Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer.

KEY EQUATION

Definition of pressure

$$P = F/A$$

CONCEPTUAL PROBLEMS

1. What four quantities must be known to completely describe a sample of a gas? What units are commonly used for each quantity?
2. If the applied force is constant, how does the pressure exerted by an object change as the area on which the force is exerted decreases? In the real world, how does this relationship apply to the ease of driving a small nail versus a large nail?
3. As the force on a fixed area increases, does the pressure increase or decrease? With this in mind, would you expect a heavy person to need smaller or larger snowshoes than a lighter person? Explain.
4. What do we mean by *atmospheric pressure*? Is the atmospheric pressure at the summit of Mt. Rainier greater than or less than the pressure in Miami, Florida? Why?
5. Which has the highest atmospheric pressure—a cave in the Himalayas, a mine in South Africa, or a beach house in Florida? Which has the lowest?
6. Mars has an average atmospheric pressure of 0.007 atm. Would it be easier or harder to drink liquid from a straw on Mars than on Earth? Explain your answer.
7. Is the pressure exerted by a 1.0 kg mass on a 2.0 m² area greater than or less than the pressure exerted by a 1.0 kg mass on a 1.0 m² area? What is the difference, if any, between the pressure of the atmosphere exerted on a 1.0 m² piston and a 2.0 m² piston?
8. If you used water in a barometer instead of mercury, what would be the major difference in the instrument?

ANSWER

3. Because pressure is defined as the force per unit area ($P = F/A$), increasing the force on a given area increases the pressure. A heavy person requires larger snowshoes than a lighter person. Spreading the force exerted on the heavier person by gravity (that is, their weight) over a larger area decreases the pressure exerted per unit of area, such as a square inch, and makes them less likely to sink into the snow.

NUMERICAL PROBLEMS

1. Calculate the pressure in atmospheres and kilopascals exerted by a fish tank that is 2.0 ft long, 1.0 ft wide, and 2.5 ft high and contains 25.0 gal of water in a room that is at 20°C; the tank itself weighs 15 lb ($d_{H_2O} = 1.00 \text{ g/cm}^3$ at 20°C). If the tank were 1 ft long, 1 ft wide, and 5 ft high, would it exert the same pressure? Explain your answer.
2. Calculate the pressure in pascals and in atmospheres exerted by a carton of milk that weighs 1.5 kg and has a base of 7.0 cm $\times$ 7.0 cm. If the carton were lying on its side (height = 25 cm), would it exert more or less pressure? Explain your reasoning.
3. If atmospheric pressure at sea level is $1.0 \times 10^5 \text{ Pa}$, what is the mass of air in kilograms above a 1.0 cm^2 area of your skin as you lie on the beach? If atmospheric pressure is $8.2 \times 10^4 \text{ Pa}$ on a mountaintop, what is the mass of air in kilograms above a 4.0 cm^2 patch of skin?
4. Complete the following table:

atm	kPa	mmHg	torr
1.40			
		723	
	43.2		

5. The SI unit of pressure is the pascal, which is equal to 1 N/m^2 . Show how the product of the mass of an object and the acceleration due to gravity result in a force that, when exerted on a given area, leads to a pressure in the correct SI units. What mass in kilograms applied to a 1.0 cm^2 area is required to produce a pressure of
 - a. 1.0 atm?
 - b. 1.0 torr?
 - c. 1 mmHg?
 - d. 1 kPa?

6. If you constructed a manometer to measure gas pressures over the range 0.60–1.40 atm using the liquids given in the following table, how tall a column would you need for each liquid? The density of mercury is 13.5 g/cm³. Based on your results, explain why mercury is still used in barometers, despite its toxicity.

	Liquid Density (20°C)	Column Height (m)
isopropanol	0.785	
coconut oil	0.924	
glycerine	1.259	

ANSWER

1. 5.4 kPa or 5.3×10^{-2} atm; 11 kPa, 1.1×10^{-3} atm; the same force acting on a smaller area results in a greater pressure.

10.3 Relationships among Pressure, Temperature, Volume, and Amount

LEARNING OBJECTIVE

1. To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (P) and its temperature (T), volume (V), and amount (n) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method as presented in Chapter 1 "Introduction to Chemistry".

The Relationship between Pressure and Volume

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

Robert Boyle (1627–1691)

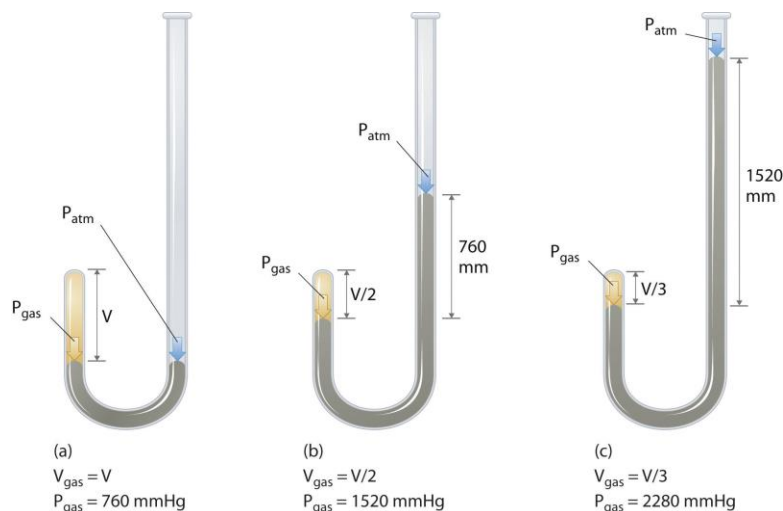
Boyle, the youngest (and 14th!) child of the Earl of Cork, was an important early figure in chemistry whose views were often at odds with accepted wisdom. Boyle's studies of gases are reported to have utilized a very tall J-tube that he set up in the entryway of his house, which was several stories tall. He is known for the gas law that bears his name and for his book, *The Sceptical Chymist*, which was published in 1661 and influenced chemists for many years after his death. In addition, one of Boyle's early essays on morals is said to have inspired Jonathan Swift to write *Gulliver's Travels*.

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure 10.6 "Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume". In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure *plus* the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure 10.7 "Plots of Boyle's Data"). A simple plot of V versus P gives a curve called a *hyperbola* and reveals an *inverse* relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

Equation 10.5

$$PV = \text{constant}$$

Figure 10.6 Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume



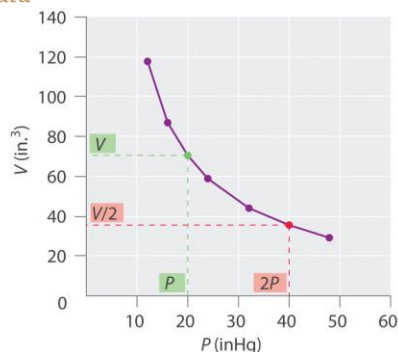
(a) Initially the gas is at a pressure of 1

atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V . (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is $V/2$. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to $V/3$.

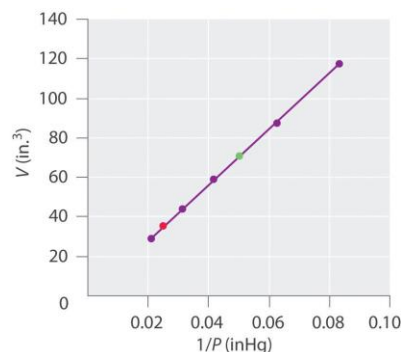
Figure 10.7 Plots of Boyle's Data

P (inHg)	V (in. ³)	PV
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400

(a) Data from Boyle's experiment



(b) Volume vs. pressure



(c) Volume vs. 1/pressure

(a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.³ rather than cm³) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus $1/\text{pressure}$ for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation $V = \text{constant}/P$.

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V :

Equation 10.6

$$V = \text{constant}P = \text{constant}(1/P) \text{ or } V \propto 1/P$$

where the $\propto$ symbol is read “is proportional to.” A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equation 10.5 and Equation 10.6. Dividing both sides of Equation 10.5 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle’s law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.*

The Relationship between Temperature and Volume

Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are heated. Because the same amount of substance now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density—in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles’s initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to -273.15°C (Figure 10.8 "The Relationship between Volume and Temperature").^[1] Note from part (a) in Figure 10.8 "The Relationship between Volume and Temperature" that the *slope* of the plot of V versus T varies for the same gas at different pressures but that the *intercept* remains constant at -273.15°C . Similarly, as shown in part (b) in Figure

10.8 "The Relationship between Volume and Temperature", plots of V versus T for different amounts of varied gases are straight lines with different slopes but the *same* intercept on the T axis.

Jacques Alexandre César Charles (1746–1823) and Joseph-Louis Gay-Lussac (1778–1850)

In 1783, Charles filled a balloon ("aerostatic globe") with hydrogen (generated by the reaction of iron with more than 200 kg of acid over several days) and flew successfully for almost an hour. When the balloon descended in a nearby village, however, the terrified townspeople destroyed it. In 1804, Gay-Lussac managed to ascend to 23,000 ft (more than 7000 m) to collect samples of the atmosphere to analyze its composition as a function of altitude. In the process, he had trouble breathing and nearly froze to death, but he set an altitude record that endured for decades. (To put Gay-Lussac's achievement in perspective, recall that modern jetliners cruise at only 35,000 ft!)

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that -273.15°C was the *lowest possible temperature* that could theoretically be achieved, for which he coined the term absolute zero (0 K).

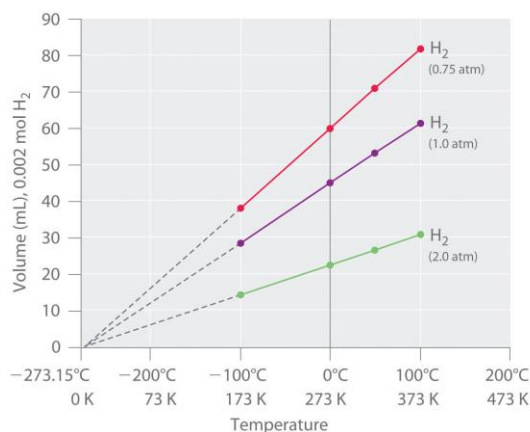
We can state Charles's and Gay-Lussac's findings in simple terms: *At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins).* This relationship, illustrated in part (b) in Figure 10.8 "The Relationship between Volume and Temperature", is often referred to as Charles's law and is stated mathematically as

Equation 10.7

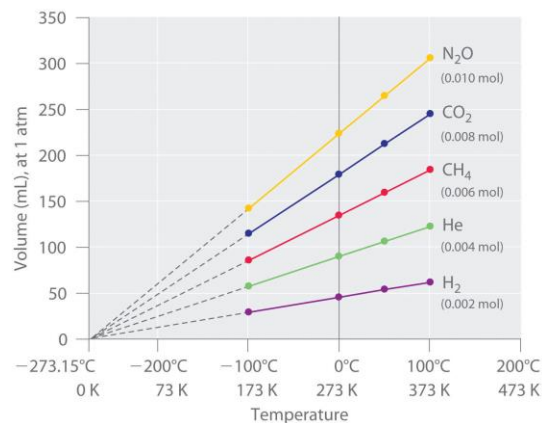
$$V = (\text{constant})[T(\text{in K})] \text{ or } V \propto T(\text{in K, at constant } P)$$

Charles's law is valid for virtually all gases at temperatures well above their boiling points. *Note that the temperature must be expressed in kelvins, not in degrees Celsius.*

Figure 10.8 The Relationship between Volume and Temperature



(a)



(b)

(a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to -100°C , and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ ($-273.15^\circ\text{C} = 0\text{ K}$). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of $V = 0$ at -273.15°C , regardless of the identity or the amount of the gas.

The Relationship between Amount and Volume

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure 10.9 "Avogadro's Hypothesis"). (This is the historic "Avogadro's hypothesis" introduced in Chapter 1 "Introduction to Chemistry".) A logical corollary, sometimes called Avogadro's law, describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

Equation 10.8

$$V = (\text{constant})(n) \text{ or } V \propto n \text{ (constant } T \text{ and } P)$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

Note the Pattern

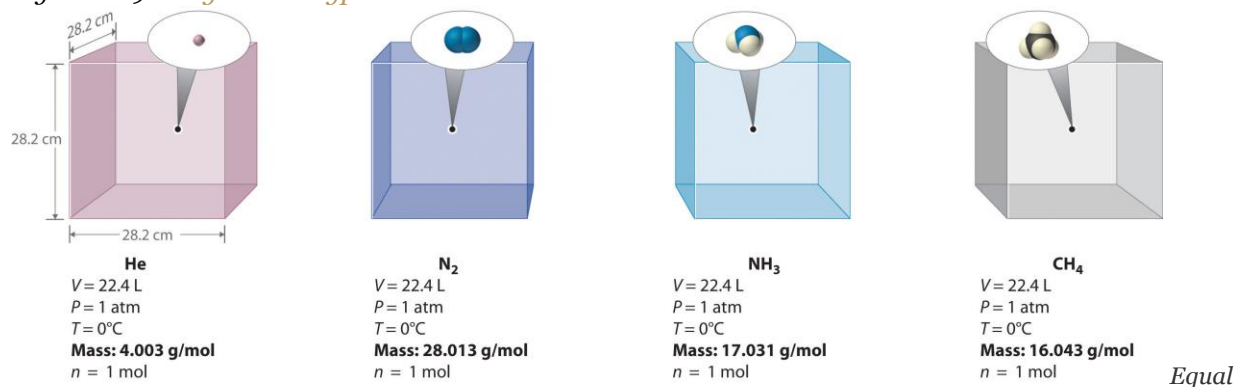
For a sample of gas,

V increases as P decreases (and vice versa)

V increases as T increases (and vice versa)

V increases as n increases (and vice versa)

Figure 10.9 *Avogadro's Hypothesis*

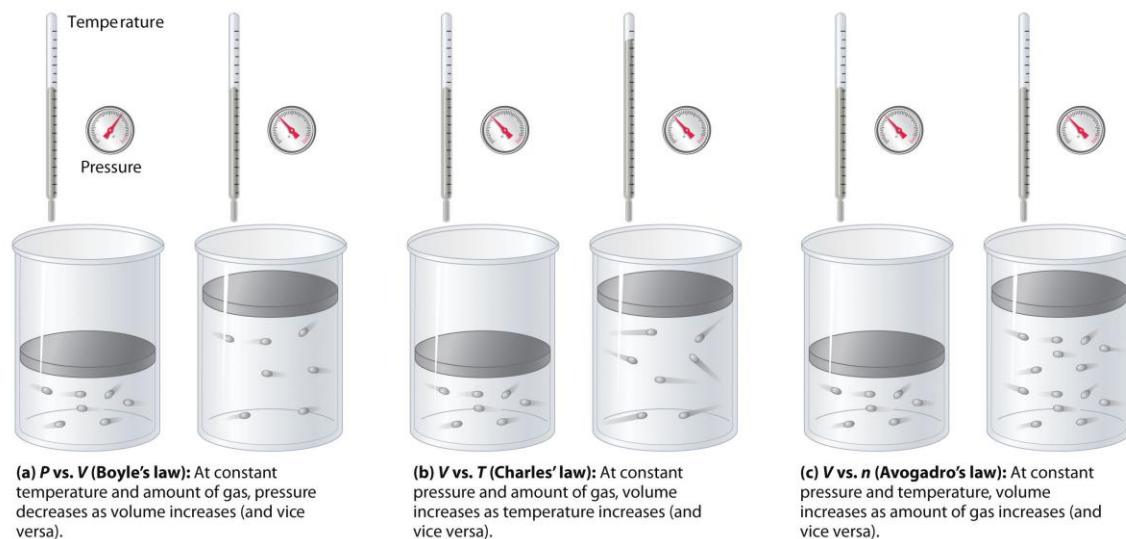


volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the mass of each gas sample is different even though all contain 1 mol of gas.

The relationships among the volume of a gas and its pressure, temperature, and amount are summarized in Figure 10.10 "The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas".

Volume *increases* with increasing temperature or amount but *decreases* with increasing pressure.

Figure 10.10 *The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas*



The

thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts.

Summary

Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**). Plots of the volume of gases versus temperature extrapolate to zero volume at -273.15°C , which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

KEY TAKEAWAY

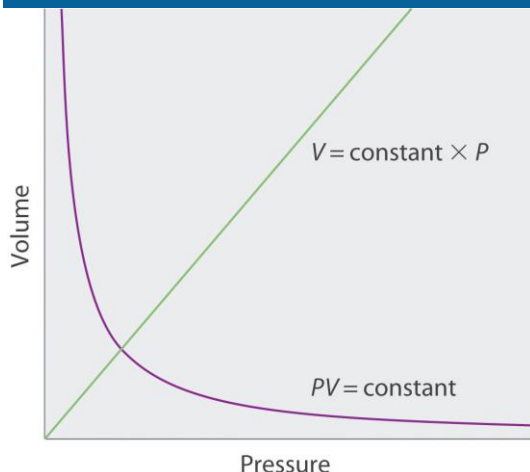
- The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas.

CONCEPTUAL PROBLEMS

- Sketch a graph of the volume of a gas versus the pressure on the gas. What would the graph of V versus P look like if volume was directly proportional to pressure?
- What properties of a gas are described by Boyle's law, Charles's law, and Avogadro's law? In each law, what quantities are held constant? Why does the constant in Boyle's law depend on the amount of gas used and the temperature at which the experiments are carried out?
- Use Charles's law to explain why cooler air sinks.

4. Use Boyle's law to explain why it is dangerous to heat even a small quantity of water in a sealed container.

ANSWER



NUMERICAL PROBLEMS

1. A 1.00 mol sample of gas at 25°C and 1.0 atm has an initial volume of 22.4 L. Calculate the results of each change, assuming all the other conditions remain constant.
 - a. The pressure is changed to 85.7 mmHg. How many milliliters does the gas occupy?
 - b. The volume is reduced to 275 mL. What is the pressure in millimeters of mercury?
 - c. The pressure is increased to 25.3 atm. What is the temperature in degrees Celsius?
 - d. The sample is heated to 30°C. What is the volume in liters?
 - e. The sample is compressed to 1255 mL, and the pressure is increased to 2555 torr. What is the temperature of the gas in kelvins?
2. A 1.00 mol sample of gas is at 300 K and 4.11 atm. What is the volume of the gas under these conditions? The sample is compressed to 6.0 atm at constant temperature, giving a volume of 3.99 L. Is this result consistent with Boyle's law?

ANSWER

1.
 - a. 1.99×10^5 mL
 - b. 6.19×10^4 mmHg
 - c. 7270°C
 - d. 22.8 L
 - e. 51.4 K

[1] A sample of gas cannot *really* have a volume of zero because any sample of matter must have *some* volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above -273.15°C .

10.4 The Ideal Gas Law

LEARNING OBJECTIVE

1. To use the ideal gas law to describe the behavior of a gas.

In Section 10.3 "Relationships among Pressure, Temperature, Volume, and Amount", you learned how the volume of a gas changes when its pressure, temperature, or amount is changed, as long as the other two variables are held constant. In this section, we describe how these relationships can be combined to give a general expression that describes the behavior of a gas.

Deriving the Ideal Gas Law

Any set of relationships between a single quantity (such as V) and several other variables (P , T , and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions derived in Section 10.3 "Relationships among Pressure, Temperature, Volume, and Amount" are as follows:

Boyle's law

$$V \propto 1/P (\text{at constant } n, T)$$

Charles's law

$$V \propto T (\text{at constant } n, P)$$

Avogadro's law

$$V \propto n (\text{at constant } T, P)$$

Combining these three expressions gives

Equation 10.9

$$V \propto nTP$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

Equation 10.10

$$V = (\text{constant})(nTP)$$

By convention, the proportionality constant in Equation 10.10 is called the gas constant, which is represented by the letter R . Inserting R into Equation 10.10 gives

Equation 10.11

$$V = RnTP = nRTP$$

Clearing the fractions by multiplying both sides of Equation 10.11 by P gives

Equation 10.12

$$PV = nRT$$

This equation is known as the ideal gas law.

An ideal gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the ideal gas law. In reality, there is no such thing as an ideal gas, but an ideal gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of an ideal gas. The ideal gas law can therefore be used to predict the behavior of real gases under most conditions. As you will learn in Section 10.8 "The Behavior of Real Gases", the ideal gas law does not work well at very low temperatures or very high pressures, where deviations from ideal behavior are most commonly observed.

Note the Pattern

Significant deviations from ideal gas behavior commonly occur at low temperatures and very high pressures.

Before we can use the ideal gas law, however, we need to know the value of the gas constant R . Its form depends on the units used for the other quantities in the expression. If V is expressed in liters (L), P in atmospheres (atm), T in kelvins (K), and n in moles (mol), then

Equation 10.13

$$R = 0.082057 \text{ (L}\cdot\text{atm)/(K}\cdot\text{mol)}$$

Because the product PV has the units of energy, as described in Chapter 5 "Energy Changes in Chemical Reactions", Section 5.1 "Energy and Work" and Essential Skills 4 (Chapter 5 "Energy Changes in Chemical Reactions", Section 5.6 "Essential Skills 4"), R can also have units of J/(K·mol) or cal/(K·mol):

Equation 10.14

$$R = 8.3145 \text{ J/(K}\cdot\text{mol)} = 1.9872 \text{ cal/(K}\cdot\text{mol)}$$

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and 1 atm pressure, referred to as standard temperature and pressure (STP). We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 10.11:

Equation 10.15

$$V = nRT/P = (1.000 \text{ mol})[(0.082057 \text{ L} \cdot \text{atm}) / (\text{K} \cdot \text{mol})] \\ (273.15 \text{ K})1.000 \text{ atm} = 22.41 \text{ L}$$

Thus the volume of 1 mol of an ideal gas at 0°C and 1 atm pressure is 22.41 L, approximately equivalent to the volume of three basketballs. The quantity 22.41 L is called the standard molar volume of an ideal gas. The molar volumes of several real gases at STP are given in Table 10.3 "Molar Volumes of Selected Gases at Standard Temperature (0°C) and Pressure (1 atm)", which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at STP. The relationships described in Section 10.3 "Relationships among Pressure, Temperature, Volume, and Amount" as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P , V , T , and n) are held fixed.

Table 10.3 Molar Volumes of Selected Gases at Standard Temperature (0°C) and Pressure (1 atm)

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H ₂	22.433
N ₂	22.402
O ₂	22.397
CO ₂	22.260
NH ₃	22.079

If n , R , and T are all constant in Equation 10.11, the equation reduces to

Equation 10.16

$$V = (\text{constant})(1/P) \text{ or } V \propto 1/P$$

which is exactly the same as Boyle's law in Equation 10.6.

Similarly, Charles's law states that the volume of a fixed quantity of gas is directly proportional to its temperature at constant pressure. If n and P in Equation 10.11 are fixed, then

Equation 10.17

$$V = nRT/P = (\text{constant})(T)$$

or $V \propto T$

which is exactly the same as Equation 10.7.

Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (P , V , T , and n). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (P , V , T , and n) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

EXAMPLE 5

The balloon that Charles used for his initial flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft³), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A Solve the ideal gas law for the unknown quantity, in this case n .

B Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for P , T , and V and asked to calculate n . If we solve the ideal gas law (Equation 10.12) for n , we obtain

$$n = PV/RT$$

B P and T are given in units that are not compatible with the units of the gas constant [$R = 0.082057$

(L·atm)/(K·mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$P = (745 \text{ mmHg}) \frac{1 \text{ atm}}{760 \text{ mmHg}}$$

$$P = 0.980 \text{ atm}$$

$$V = 31,150 \text{ L (given)}$$

$$T = 30 + 273 = 303 \text{ K}$$

Substituting these values into the expression we derived for n , we obtain

$$n = \frac{PV}{RT}$$

$$= \frac{(0.980 \text{ atm})(31,150 \text{ L})}{(0.082057 \text{ L} \cdot \text{atm}) / (\text{K} \cdot \text{mol})(303 \text{ K})}$$

$$= 1.23 \times 10^3 \text{ mol H}_2$$

Exercise

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2 . What is the pressure of the gas at 25°C ?

Answer: 1.5 atm

In Example 5, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 6.

EXAMPLE 6

Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was -10°C (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example 5?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A Use the results from Example 5 for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 86°F to 14°F . Begin by constructing a table showing the initial and final conditions.

B Rearrange the ideal gas law to isolate those quantities that differ between the initial and final states on one side of the equation, in this case V and T .

C Equate the ratios of those terms that change for the two sets of conditions. Making sure to use the appropriate units, insert the quantities and solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

	August (initial)	January (final)
T	$30^{\circ}\text{C} = 303\text{ K}$	$-10^{\circ}\text{C} = 263\text{ K}$
P	0.980 atm	0.980 atm
n	$1.23 \times 10^3\text{ mol H}_2$	$1.23 \times 10^3\text{ mol H}_2$
V	$31,150\text{ L}$	?

Thus we are asked to calculate the effect of a change in temperature on the volume of a fixed amount of gas at constant pressure.

B Recall that we can rearrange the ideal gas law to give

$$V = (nRP)(T)$$

Both n and P are the same in both cases, which means that nR/P is a constant. Dividing both sides by T gives

$$VT = nRP = \text{constant}$$

This is the relationship first noted by Charles.

C We see from this expression that under conditions where the amount (n) of gas and the pressure (P) do not change, the ratio V/T also does not change. If we have two sets of conditions for the same amount of gas at the same pressure, we can therefore write

$$V_1T_1 = V_2T_2$$

where the subscripts 1 and 2 refer to the initial and final conditions, respectively. Solving for V_2 and

inserting the given quantities in the appropriate units, we obtain

$$V_2 = V_1T_2T_1$$

$$= (31,150\text{ L})(263\text{ K})/303\text{ K}$$

$$= 2.70 \times 10^4\text{ L}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases.

Because we know that gas volume decreases with decreasing temperature, the final volume *must* be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

Exercise

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen ($T = -196^\circ\text{C}$). What is the final volume of the gas in the balloon?

Answer: 0.52 L

Example 6 illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle ($PV = \text{constant}$) and the relationship between volume and amount observed by Avogadro ($V/n = \text{constant}$). We will not do so, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example 6 can be applied in *any* such case, as we demonstrate in Example 7 (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

EXAMPLE 7

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise 5 (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

Given: initial volume, amount, temperature, and pressure; final temperature

Asked for: final pressure

Strategy:

Follow the strategy outlined in Example 6.

Solution:

Prepare a table to determine which parameters change and which are held constant:

	Initial	Final

	Initial	Final
V	0.406 L	0.406 L
n	0.025 mol	0.025 mol
T	25°C = 298 K	750°C = 1023 K
P	1.5 atm	?

Once again, two parameters are constant while one is varied, and we are asked to calculate the fourth. As before, we begin with the ideal gas law and rearrange it as necessary to get all the constant quantities on one side. In this case, because V and n are constant, we rearrange to obtain

$$P = (nRV)(T) = (\text{constant})(T)$$

Dividing both sides by T , we obtain an equation analogous to the one in Example 6, $P/T = nR/V = \text{constant}$.

Thus the ratio of P to T does not change if the amount and volume of a gas are held constant. We can thus write the relationship between any two sets of values of P and T for the same sample of gas at the same volume as

$$P_1 T_1 = P_2 T_2$$

In this example, $P_1 = 1.5 \text{ atm}$, $T_1 = 298 \text{ K}$, and $T_2 = 1023 \text{ K}$, and we are asked to find P_2 . Solving for P_2 and substituting the appropriate values, we obtain

$$\begin{aligned} P_2 &= P_1 T_2 / T_1 \\ &= (1.5 \text{ atm})(1023 \text{ K}) / 298 \text{ K} \\ &= 5.1 \text{ atm} \end{aligned}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

Exercise

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer: 23.4 atm

In Example 10.6 and Example 10.7, two of the four parameters (P , V , T , and n) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables P , V , and T are allowed to vary for a given sample of gas (hence n is constant), and we are interested in the change in the value of the third under the new conditions. If we

rearrange the ideal gas law so that P , V , and T , the quantities that change, are on one side and the constant terms (R and n for a given sample of gas) are on the other, we obtain

Equation 10.18

$$PVT = nR = \text{constant}$$

the quantity PV/T is constant if the total amount of gas is

Equation 10.19

$$P_1V_1/T_1 = P_2V_2/T_2$$

This equation can be solved for any of the quantities P_2 , V_2 , or T_2 if the initial conditions are known, as shown in Example 8.

EXAMPLE 8

We saw in Example 5 that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23×10^3 mol of H_2 gas initially at 30°C and 745 mmHg. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 mmHg and -30°C , respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

Given: initial pressure, temperature, amount, and volume; final pressure and temperature

Asked for: final volume

Strategy:

Follow the strategy outlined in Example 6.

Solution:

Begin by setting up a table of the two sets of conditions:

	Initial	Final
P	745 mmHg = 0.980 atm	312 mmHg = 0.411 atm
T	$30^\circ\text{C} = 303 \text{ K}$	$-30^\circ\text{C} = 243 \text{ K}$
n	$1.23 \times 10^3 \text{ mol } H_2$	$1.23 \times 10^3 \text{ mol } H_2$
V	31,150 L	?

Thus all the quantities except V_2 are known. Solving Equation 10.19 for V_2 and substituting the appropriate values give

$$V_2 = V_1(P_1T_2P_2T_1)$$

$$= (31,150 \text{ L})(0.980 \text{ atm})(243 \text{ K})(0.411 \text{ atm})(303 \text{ K})$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both T and $1/P$, the variable that changes the most will have the greatest effect on V . In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for V and then substituting the relevant parameters for an altitude of 23,000 ft:

$$V = nRTP$$

$$= (1.23 \times 10^3 \text{ mol})[0.082057$$

$$(L \cdot \text{atm}) / (K \cdot \text{mol})](243 \text{ K})0.411 \text{ atm}$$

$$= 5.97 \times 10^4 \text{ L}$$

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

Exercise

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer: 4.07×10^3

Using the Ideal Gas Law to Calculate Gas Densities and Molar Masses

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

Equation 10.20

$$nV = PRT$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (m , in grams) divided by its molar mass (M , in grams per mole):

Equation 10.21

$$n = m/M$$

Substituting this expression for n into Equation 10.20 gives

Equation 10.22

$$mMV = PRT$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

Equation 10.23

$$d = PM/RT$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).

EXAMPLE 9

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.

B Substitute these values into Equation 10.23 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$(4)(12.011) + (10)(1.0079) = 58.123 \text{ g/mol}$$

Using 0.082057 (L·atm)/(K·mol) for R means that we need to convert the temperature from degrees

Celsius to kelvins ($T = 25 + 273 = 298 \text{ K}$) and the pressure from millimeters of mercury to atmospheres:

$$(750 \text{ mmHg}) \left(\frac{1 \text{ atm}}{760 \text{ mmHg}} \right)$$

$$= 0.987 \text{ atm}$$

B Substituting these values into Equation 10.23 gives

$$M = dRTP$$

Exercise

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer: radon, 9.23 g/L; N₂, 1.17 g/L

A common use of Equation 10.23 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and reweighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 10.

EXAMPLE 10

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A Solve Equation 10.23 for the molar mass of the gas and then calculate the density of the gas from the information given.

B Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

C Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 10.23 for the molar mass gives

$$M = dRTP$$

Density is the mass of the gas divided by its volume:

$$d = m/V$$

$$= 0.289 \text{ g} / 0.157 \text{ L}$$

$$= 1.84 \text{ g} / \text{L}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291 \text{ K}$$

$$= (727 \text{ mmHg}) / (760 \text{ mmHg} / 1 \text{ atm})$$

$$= 0.957 \text{ atm}$$

The molar mass of the unknown gas is thus

$$M = dRTP$$

$$= (1.84 \text{ g} / \text{L}) [0.082057 (\text{L} \cdot \text{atm}) / (\text{K} \cdot \text{mol})] (291 \text{ K}) (0.957 \text{ atm})$$

$$= 45.9 \text{ g} / \text{mol}$$

C The atomic masses of N and O

are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$NO = 14 + 16 = 30 \text{ g} / \text{mol}$$

$$N_2O = (2)(14) + 16 = 44 \text{ g} / \text{mol}$$

$$NO_2 = 14 + (2)(16) = 46 \text{ g} / \text{mol}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

Exercise

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C;

density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer: 44 g/mol; CO₂

Summary

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, $PV = nRT$. The proportionality constant, R , is called the **gas constant** and has the value 0.08206 (L·atm)/(K·mol), 8.3145 J/(K·mol), or 1.9872 cal/(K·mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (P , V , T , or n) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of P , V , T , and n) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

KEY TAKEAWAY

- The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

KEY EQUATIONS

Ideal gas law

Equation 10.12: $PV = nRT$

Relationship between initial and final conditions

Equation 10.19: $P_1V_1T_1 = P_2V_2T_2$ n is constant

Density of a gas

Equation 10.23: $d = \frac{PM}{RT}$

CONCEPTUAL PROBLEMS

- For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?
- What is meant by STP? If a gas is at STP, what further information is required to completely describe the state of the gas?
- For a given amount of a gas, the volume, temperature, and pressure under any one set of conditions are related to the volume, the temperature, and the pressure under any other set of conditions by *the equation* $P_1V_1T_1 = P_2V_2T_2$.
Derive this equation from the ideal gas law., this equation reduces to one of the laws discussed
At constant temperature
inSection 10.3 "Relationships among Pressure, Temperature, Volume, and Amount"; which one? At constant pressure, this equation reduces to one of the laws discussed in Section 10.3 "Relationships among Pressure, Temperature, Volume, and Amount"; which one?
- Predict the effect of each change on one variable if the other variables are held constant.
 - If the number of moles of gas increases, what is the effect on the temperature of the gas?
 - If the temperature of a gas decreases, what is the effect on the pressure of the gas?
 - If the volume of a gas increases, what is the effect on the temperature of the gas?
 - If the pressure of a gas increases, what is the effect on the number of moles of the gas?
- What would the ideal gas law be if the following were true?
 - volume were proportional to pressure
 - temperature were proportional to amount
 - pressure were inversely proportional to temperature
 - volume were inversely proportional to temperature
 - both pressure and volume were inversely proportional to temperature
- Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

Given	Solve for
V_1, T_1, T_2, n_1	n_2
P_1, P_2, T_2, n_2	n_1
T_1, T_2	V_2
P_1, n_1	P_2

7. Given the following information and using the ideal gas law, what equation would you use to solve the problem?

Given	Solve for
P_1, P_2, T_1	T_2
V_1, n_1, n_2	V_2
T_1, T_2, V_1, V_2, n_2	n_1

8. Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?
9. Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.
- amount and volume
 - pressure and amount
 - temperature and volume
 - temperature and amount
 - pressure and temperature
10. Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

ANSWER

-
-
-
-
-
-
-
-
-

- a. $P/T = \text{constant}$
 - b. $V/T = \text{constant}$ (Charles' law)
 - c. $P/n = \text{constant}$
 - d. $PV = \text{constant}$ (Boyle's law)
 - e. $V/n = \text{constant}$ (Avogadro's law)
- 10.

NUMERICAL PROBLEMS

1. Calculate the number of moles in each sample at STP.
 - a. 1580 mL of NO_2
 - b. 847 cm^3 of HCl
 - c. 4.792 L of H_2
 - d. a $15.0 \text{ cm} \times 6.7 \text{ cm} \times 7.5 \text{ cm}$ container of ethane
2. Calculate the number of moles in each sample at STP.
 - a. 2200 cm^3 of CO_2
 - b. 1200 cm^3 of N_2
 - c. 3800 mL of SO_2
 - d. 13.75 L of NH_3
3. Calculate the mass of each sample at STP.
 - a. 36 mL of HI
 - b. 550 L of H_2S
 - c. 1380 cm^3 of CH_4
4. Calculate the mass of each sample at STP.
 - a. 3.2 L of N_2O
 - b. 65 cm^3 of Cl_2
 - c. 3600 mL of HBr
5. Calculate the volume in liters of each sample at STP.
 - a. 1.68 g of Kr
 - b. 2.97 kg of propane (C_3H_8)
 - c. 0.643 mg of $(\text{CH}_3)_2\text{O}$

6. Calculate the volume in liters of each sample at STP.
 - a. 3.2 g of Xe
 - b. 465 mg of CS₂
 - c. 5.34 kg of acetylene (C₂H₂)
7. Calculate the volume of each gas at STP.
 - a. 1.7 L at 28°C and 96.4 kPa
 - b. 38.0 mL at 17°C and 103.4 torr
 - c. 650 mL at -15°C and 723 mmHg
8. Calculate the volume of each gas at STP.
 - a. 2.30 L at 23°C and 740 mmHg
 - b. 320 mL at 13°C and 97.2 kPa
 - c. 100.5 mL at 35°C and 1.4 atm
9. A 8.60 L tank of nitrogen gas at a pressure of 455 mmHg is connected to an empty tank with a volume of 5.35 L. What is the final pressure in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.
10. At constant temperature, what pressure in atmospheres is needed to compress 14.2 L of gas initially at 25.2 atm to a volume of 12.4 L? What pressure is needed to compress 27.8 L of gas to 20.6 L under similar conditions?
11. One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is AlCl₃. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?
12. An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:
$$2 \text{C}_2\text{H}_2(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$$

At STP, what volume of CO₂(g) is produced?
13. Calculate the density of ethylene (C₂H₄) under each set of conditions.
 - a. 7.8 g at 0.89 atm and 26°C
 - b. 6.3 mol at 102.6 kPa and 38°C
 - c. 9.8 g at 3.1 atm and -45°C

14. Determine the density of O_2 under each set of conditions.
- 42 g at 1.1 atm and $25^\circ C$
 - 0.87 mol at 820 mmHg and $45^\circ C$
 - 16.7 g at 2.4 atm and $67^\circ C$
15. At $140^\circ C$, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?
16. What volume must a balloon have to hold 6.20 kg of H_2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is $-37^\circ C$ and the pressure is 369 mmHg?
17. What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is $10.0^\circ C$ and the pressure is 635.4 mmHg?
18. A typical automobile tire is inflated to a pressure of 28.0 lb/in.² Assume that the tire is inflated when the air temperature is $20^\circ C$; the car is then driven at high speeds, which increases the temperature of the tire to $43^\circ C$. What is the pressure in the tire? If the volume of the tire had increased by 8% at the higher temperature, what would the pressure be?
19. The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at $20^\circ C$ and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3 , what is the average molecular mass of air?
20. Kerosene has a self-ignition temperature of $255^\circ C$. It is a common accelerant used by arsonists, but its presence is easily detected in fire debris by a variety of methods. If a 1.0 L glass bottle containing a mixture of air and kerosene vapor at an initial pressure of 1 atm and an initial temperature of $23^\circ C$ is pressurized, at what pressure would the kerosene vapor ignite?

ANSWERS

- 1.
- $7.05 \times 10^{-2} \text{ mol}$
 - $3.78 \times 10^{-2} \text{ mol}$
 - 0.2138 mol
 - $3.4 \times 10^{-2} \text{ mol}$
- 2.
- 3.

- a. 0.21 g HI;
- b. 840 g H₂S;
- c. 0.988 g CH₄
- 4.
- 5.
- a. 0.449 L Kr
- b. 1510 L C₃H₈
- c. 3.13×10^{-4} L (CH₃)₂O
- 6.
- 7.
- a. 1.5 L
- b. 4.87 mL
- c. 650 mL
- 8.
- 9. 281 mmHg
- 10.
- 11. 20.9 kg Al, 5.20×10^4 L HCl
- 12.
- 13.
- a. 1.0 g/L
- b. 1.1 g/L
- c. 4.6 g/L
- 14.
- 15.
- 16.
- 17. 2174 L

10.5 Mixtures of Gases

LEARNING OBJECTIVE

1. To determine the contribution of each component gas to the total pressure of a mixture of gases.

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

Equation 10.24

$$P = n(RTV) = n(\text{constant})$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, *the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases*. This law was first discovered by John Dalton, the father of the atomic theory of matter.

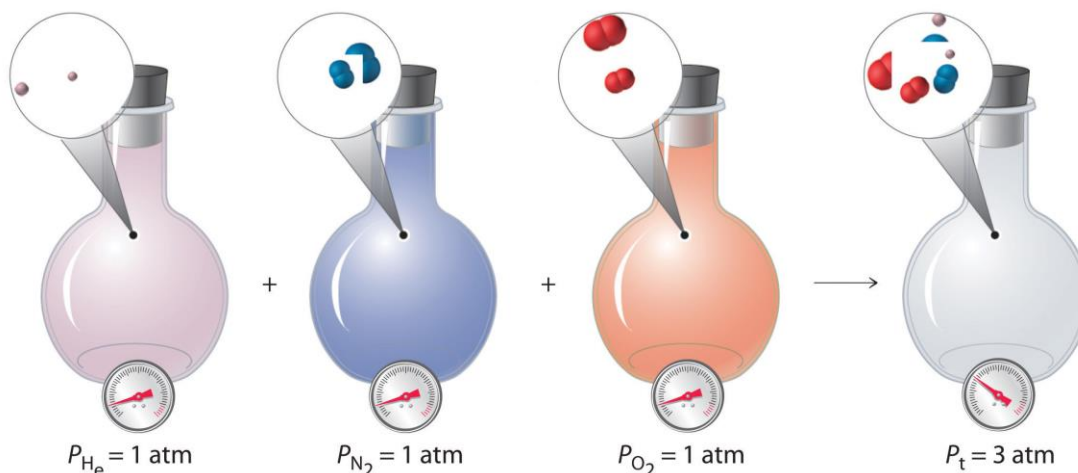
It is now known as Dalton's law of partial pressures. We can write it mathematically as

Equation 10.25

$$P_t = P_1 + P_2 + P_3 + \dots + P_i$$

where P_t is the total pressure and the other terms are the partial pressures of the individual gases (P_i).

Figure 10.11 Dalton's Law



The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

Equation 10.26

$$P_t = P_A + P_B = n_A(RTV) + n_B(RTV) = (n_A + n_B)(RTV)$$

More generally, for a mixture of i components, the total pressure is given by

Equation 10.27

$$P_t = (n_1 + n_2 + n_3 + \dots + n_i)(RTV)$$

restates in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on *only* the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 11.

EXAMPLE 11

For reasons that we will examine in , deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called “the bends.” At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such

depths contains 51.2 g of O₂ and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A Calculate the number of moles of He and O₂ present.

B Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$\begin{aligned} & (326.4 \text{ g}) \left(\frac{1.000 \text{ mol}}{4.0026 \text{ g}} \right) \\ & = 81.55 \text{ mol} \end{aligned}$$

The number of moles of O₂ is

$$(51.2 \text{ g}) \left(\frac{1.000 \text{ mol}}{32.00 \text{ g}} \right) = 1.60 \text{ mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$\begin{aligned} P_{O_2} &= n_{O_2} (RT/V) = (1.60 \text{ mol}) [0.082057 \text{ (L} \cdot \text{atm)} / (\text{K} \cdot \text{mol})] \\ & \quad (293.15 \text{ K}) (10.0 \text{ L}) = 3.85 \text{ atm} \\ P_{He} &= n_{He} (RT/V) \\ & \quad - (81.55 \text{ mol}) [0.082057 \text{ (L} \cdot \text{atm)}] \\ & \quad / (\text{K} \cdot \text{mol}) (293.15 \text{ K}) (10.0 \text{ L}) = 196 \text{ atm} \end{aligned}$$

The total pressure is the sum of the two partial pressures:

$$P_t = P_{O_2} + P_{He} = 3.85 \text{ atm} + 196 \text{ atm} = 200 \text{ atm}$$

Exercise

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

$$P_{CH_4} = 137 \text{ atm};$$

$$P_{C_2H_6} = 13.4 \text{ atm};$$

Answer: $P_t = 151 \text{ atm}$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present.

The mole fraction (X) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_t):

Equation 10.28

mole fraction of A = X_A

= moles A / total moles = n_A / n_t

The mole fraction is a dimensionless quantity between 0 and 1. If $X_A = 1.0$, then the sample is pure A, not a mixture. If $X_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT / V$ and $P_t = n_t RT / V$. The ratio of the two is thus

Equation 10.29

$P_A / P_t = n_A RT / V / n_t RT / V = n_A / n_t = X_A$

Rearranging this equation gives

Equation 10.30

$P_A = X_A P_t$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. Recall from () that by volume, Earth's atmosphere is about 78% N_2 , 21% O_2 , and 0.9% Ar, with trace amounts of gases such as CO_2 , H_2O , and others. This means that 78% of the particles present in the atmosphere are N_2 ; hence the mole fraction of N_2 is $78\% / 100\% = 0.78$. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using , we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

EXAMPLE 12

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

	Inhaled Air (mmHg)	Exhaled Air (mmHg)
P_{N_2}	597	568
P_{O_2}	158	116
P_{CO_2}	0.3	28
P_{H_2O}	5	48
P_{Ar}	8	8
P_t	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using .

Solution:

The mole fraction of any gas A is given by

$$X_A = P_A / P_t$$

where P_A is the partial pressure of A and P_t is the total pressure. In this case,

$$P_t = (767 \text{ mmHg})(1 \text{ atm} / 760 \text{ mmHg}) = 1.01 \text{ atm}$$

The following table gives the values of P_A and X_A for exhaled air.

	P_A	X_A
P_{N_2}	(568 mmHg) $(1 \text{ atm} / 760 \text{ mmHg})$ $= 0.747 \text{ atm}$	$0.747 \text{ atm} / 1.01 \text{ atm}$ $= 0.740$
P_{O_2}	(116 mmHg) $(1 \text{ atm} / 760 \text{ mmHg})$ $= 0.153 \text{ atm}$	$0.153 \text{ atm} / 1.01 \text{ atm}$ $= 0.151$

	P_A	X_A
PCO_2	(28 mmHg) $(1 \text{ atm} / 760 \text{ mmHg}) = 0.037 \text{ atm}$	$0.031 \text{ atm} / 1.01 \text{ atm}$ $= 0.037$
PH_2O	(48 mmHg) $(1 \text{ atm} / 760 \text{ mmHg}) = 0.063 \text{ atm}$	$= 0.063 \text{ atm}$ $0.063 \text{ atm} / 1.01 \text{ atm} = 0.062$

Exercise

We saw in Example 10 that Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2 , with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2 .

Answer : $PCO_2 = 86 \text{ atm}$; $PN_2 = 3 \text{ atm}$

Summary

The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

KEY TAKEAWAY

- The partial pressure of each gas in a mixture is proportional to its mole fraction.

KEY EQUATIONS

Mole fraction

$$X_A = \frac{\text{moles } A}{\text{total moles}} = \frac{n_A}{n_{\text{total}}}$$

Relationship between partial pressure and mole fraction

$$P_A = X_A P_{\text{total}}$$

CONCEPTUAL PROBLEMS

- Dalton's law of partial pressures makes one key assumption about the nature of the intermolecular interactions in a mixture of gases. What is it?
- What is the relationship between the partial pressure of a gas and its mole fraction in a mixture?

NUMERICAL PROBLEMS

- What is the partial pressure of each gas if the following amounts of substances are placed in a 25.0 L container at 25°C? What is the total pressure of each mixture?
 - 1.570 mol of CH_4 and 0.870 mol of CO_2
 - 2.63 g of CO and 1.24 g of NO_2
 - 1.78 kg of CH_3Cl and 0.92 kg of SO_2
- What is the partial pressure of each gas in the following 3.0 L mixtures at 37°C as well as the total pressure?
 - 0.128 mol of SO_2 and 0.098 mol of methane (CH_4)
 - 3.40 g of acetylene (C_2H_2) and 1.54 g of He
 - 0.267 g of NO, 4.3 g of Ar, and 0.872 g of SO_2
- In a mixture of helium, oxygen, and methane in a 2.00 L container, the partial pressures of He and O_2 are 13.6 kPa and 29.2 kPa, respectively, and the total pressure inside the container is 95.4 kPa. What is the partial pressure of methane? If the methane is ignited to initiate its combustion with oxygen and the system is then cooled to the original temperature of 30°C, what is the final pressure inside the container (in kilopascals)?
- A 2.00 L flask originally contains 1.00 g of ethane (C_2H_6) and 32.0 g of oxygen at 21°C. During ignition, the ethane reacts completely with oxygen to produce CO_2 and water vapor, and the temperature of the flask increases to 200°C. Determine the total pressure and the partial pressure of each gas before and after the reaction.
- If a 20.0 L cylinder at 19°C is charged with 5.0 g each of sulfur dioxide and oxygen, what is the partial pressure of each gas? The sulfur dioxide is ignited in the oxygen to produce sulfur trioxide gas, and the mixture is allowed to cool to 19°C at constant pressure. What is the final volume of the cylinder? What is the partial pressure of each gas in the piston?
- The highest point on the continent of Europe is Mt. Elbrus in Russia, with an elevation of 18,476 ft. The highest point on the continent of South America is Mt. Aconcagua in Argentina, with an elevation of 22,841 ft.
 - The following table shows the variation of atmospheric pressure with elevation. Use the data in the table to construct a plot of pressure versus elevation.

Elevation (km)	Pressure in Summer (mmHg)	Pressure in Winter (mmHg)
0.0	760.0	760.0
1.0	674.8	670.6

Elevation (km)	Pressure in Summer (mmHg)	Pressure in Winter (mmHg)
1.5	635.4	629.6
2.0	598.0	590.8
3.0	528.9	519.7
5.0	410.6	398.7
7.0	314.9	301.6
9.0	237.8	224.1

- b. Use your graph to estimate the pressures in millimeters of mercury during the summer and the winter at the top of both mountains in both atmospheres and kilopascals.
- c. Given that air is 20.95% O₂ by volume, what is the partial pressure of oxygen in atmospheres during the summer at each location?

ANSWERS

1. a. $P_{CH_4} = 1.54 \text{ atm}$, $P_{CO_2} = 0.851 \text{ atm}$, $P_T = 2.39 \text{ atm}$
- b. $P_{CO} = 0.0918 \text{ atm}$, $P_{NO_2} = 0.0264 \text{ atm}$, $P_T = 0.1182 \text{ atm}$, $P_T = 2.39 \text{ atm}$
- c. a. $P_{CH_3Cl} = 34.5 \text{ atm}$, $P_{SO_2} = 14 \text{ atm}$, $P_T = 49 \text{ atm}$
3. 52.6 kPa, 66.2 kPa

10.6 Gas Volumes and Stoichiometry

LEARNING OBJECTIVE

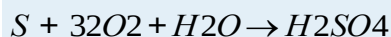
1. To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.

With the ideal gas law, we can use the relationship between the amounts of gases (in moles) and their volumes (in liters) to calculate the stoichiometry of reactions involving gases, if the pressure and temperature are known. This is important for several reasons. Many reactions that are carried out in the laboratory involve the formation or reaction

of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons. Gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing. As a chemical engineer said to one of the authors, "Gases always go where you want them to, liquids sometimes do, but solids almost never do."

EXAMPLE 13

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give SO_2 , followed by the reaction of SO_2 with O_2 in the presence of a catalyst to give SO_3 , which reacts with water to give H_2SO_4 . The overall chemical equation is as follows:



What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton of H_2SO_4 ?

Given: reaction, temperature, pressure, and mass of one product

Asked for: volume of gaseous reactant

Strategy:

A Calculate the number of moles of H_2SO_4 in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of O_2 required.

B Use the ideal gas law to determine the volume of O_2 required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

Solution:

$3\text{H}_2\text{SO}_4$. This is a standard stoichiometry problem of the type presented in Chapter 3 "Chemical Reactions", except this problem asks for the volume of one of the reactants (O_2) rather than its mass. We proceed exactly as in Chapter 3 "Chemical Reactions", using the strategy
mass of $\text{H}_2\text{SO}_4 \rightarrow$ moles $\text{H}_2\text{SO}_4 \rightarrow$ moles $\text{O}_2 \rightarrow$ liters O_2

A We begin by calculating the number of moles of H_2SO_4 in 1.00 tn:

$$\text{moles } \text{H}_2\text{SO}_4 = (1.00 \text{ tn } \text{H}_2\text{SO}_4)$$

$$((2000 \text{ lb } 1 \text{ tn}))((453.6 \text{ g } 1 \text{ lb}))$$

$$(1 \text{ mol } \text{H}_2\text{SO}_4 98.08 \text{ g}) = 9250 \text{ mol } \text{H}_2\text{SO}_4$$

We next calculate the number of moles of O_2 required:

$$\begin{aligned} \text{moles } O_2 &= (9250 \text{ mol } H_2SO_4) \\ (1.5 \text{ mol } O_2 / 1 \text{ mol } H_2SO_4) \\ &= 1.39 \times 10^4 \text{ mol } O_2 \end{aligned}$$

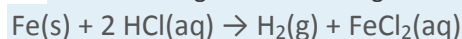
B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2 :

$$\begin{aligned} T &= 273 + 22 = 295 \text{ K} \quad P = (745 \text{ mmHg}) \\ (1 \text{ atm} / 760 \text{ mmHg}) &= 0.980 \text{ atm} \\ \text{Volume of } O_2 &= nRT/P = (1.39 \times 10^4 \text{ mol } O_2) \\ &[0.08206 \text{ (L} \cdot \text{atm)} / (\text{K} \cdot \text{mol})(295 \text{ K}) / 0.980 \text{ atm}] \\ &= 3.43 \times 10^5 \text{ L } O_2 \end{aligned}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 tn of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

Exercise

In Example 5, we saw that Charles used a balloon containing approximately 31,150 L of H_2 for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:



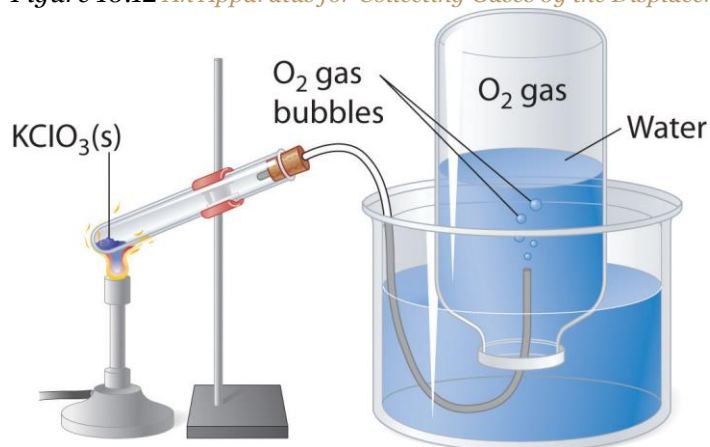
How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature was 30°C and the atmospheric pressure was 745 mmHg?

Answer: 68.6 kg of Fe (approximately 150 lb)

Many of the advances made in chemistry during the 18th and 19th centuries were the result of careful experiments done to determine the identity and quantity of gases produced in chemical reactions. For example, in 1774, Joseph Priestley was able to isolate oxygen gas by the thermal decomposition of mercuric oxide (HgO). In the 1780s, Antoine Lavoisier conducted experiments that showed that combustion reactions, which require oxygen, produce what we now know to be carbon dioxide. Both sets of experiments required the scientists to collect and manipulate gases produced in chemical reactions, and both used a simple technique that is still used in chemical laboratories today: collecting a gas by the displacement of water. As shown in Figure 10.12 "An Apparatus for Collecting Gases by the Displacement of Water", the gas produced in a reaction can be channeled through a tube into inverted bottles filled with water. Because the gas is less dense than liquid water, it bubbles to the top of the bottle, displacing the water.

Eventually, all the water is forced out and the bottle contains only gas. If a calibrated bottle is used (i.e., one with markings to indicate the volume of the gas) and the bottle is raised or lowered until the level of the water is the same both inside and outside, then the pressure within the bottle will exactly equal the atmospheric pressure measured separately with a barometer.

Figure 10.12 *An Apparatus for Collecting Gases by the Displacement of Water*



When $KClO_3(s)$ is heated, O_2 is produced according to the equation $KClO_3(s) \rightarrow KCl(s) + 3/2 O_2(g)$. The oxygen gas travels through the tube, bubbles up through the water, and is collected in a bottle as shown.

The only gases that cannot be collected using this technique are those that readily dissolve in water (e.g., NH_3 , H_2S , and CO_2) and those that react rapidly with water (such as F_2 and NO_2). Remember, however, when calculating the amount of gas formed in the reaction, the gas collected inside the bottle is *not* pure. Instead, it is a mixture of the product gas and water vapor. As we will discuss in Chapter 11 "Liquids", all liquids (including water) have a measurable amount of vapor in equilibrium with the liquid because molecules of the liquid are continuously escaping from the liquid's surface, while other molecules from the vapor phase collide with the surface and return to the liquid. The vapor thus exerts a pressure above the liquid, which is called the liquid's *vapor pressure*. In the case shown in Figure 10.12 "An Apparatus for Collecting Gases by the Displacement of Water", the bottle is therefore actually filled with a mixture of O_2 and water vapor, and the total pressure is, by Dalton's law of partial pressures, the sum of the pressures of the two components:

$$P_t = P_{O_2} + P_{H_2O}$$

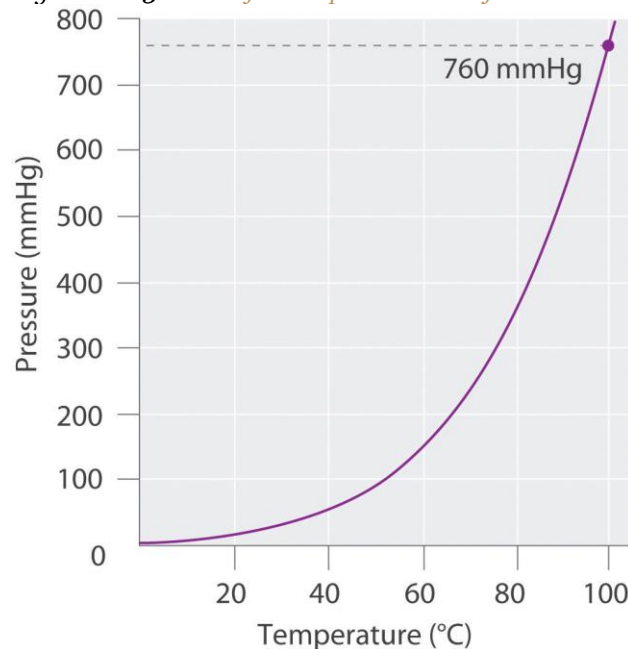
If we want to know the pressure of the gas generated in the reaction to calculate the amount of gas formed, we must first subtract the pressure due to water vapor from the total pressure. This is done by referring to tabulated values of the vapor pressure of water as a function of temperature (Table 10.4 "Vapor Pressure of Water at Various

Temperatures"). As shown in Figure 10.13 "A Plot of the Vapor Pressure of Water versus Temperature", the vapor pressure of water increases rapidly with increasing temperature, and at the normal boiling point (100°C), the vapor pressure is exactly 1 atm. The methodology is illustrated in Example 14.

Table 10.4 Vapor Pressure of Water at Various Temperatures

<i>T</i> (°C)	<i>P</i> (in mmHg)	<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>	<i>T</i>	<i>P</i>
0	4.58	21	18.66	35	42.2	92	567.2
5	6.54	22	19.84	40	55.4	94	611.0
10	9.21	23	21.08	45	71.9	96	657.7
12	10.52	24	22.39	50	92.6	98	707.3
14	11.99	25	23.77	55	118.1	100	760.0
16	13.64	26	25.22	60	149.5	102	815.8
17	14.54	27	26.75	65	187.7	104	875.1
18	15.48	28	28.37	70	233.8	106	937.8
19	16.48	29	30.06	80	355.3	108	1004.2
20	17.54	30	31.84	90	525.9	110	1074.4

Figure 10.13 A Plot of the Vapor Pressure of Water versus Temperature



The vapor pressure is very low (but not zero) at 0°C and reaches 1 atm = 760 mmHg at the normal boiling point, 100°C.

EXAMPLE 14

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:



This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the N_2 gas that results from the decomposition of a 5.00 g sample of NaN_3 could be collected by displacing water from an inverted flask, as in Figure 10.12 "An Apparatus for Collecting Gases by the Displacement of Water", what volume of gas would be produced at 22°C and 762 mmHg?

Given: reaction, mass of compound, temperature, and pressure

Asked for: volume of nitrogen gas produced

Strategy:

A Calculate the number of moles of N_2 gas produced. From the data in Table 10.4 "Vapor Pressure of Water at Various Temperatures", determine the partial pressure of N_2 gas in the flask.

B Use the ideal gas law to find the volume of N_2 gas produced.

Solution:

A Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of N_2 gas produced:

$$\begin{aligned} \text{moles } \text{N}_2 &= (5.00 \text{ g } \text{NaN}_3) \left(\frac{1 \text{ mol } \text{NaN}_3}{65.01 \text{ g } \text{NaN}_3} \right) \\ &\left(\frac{3 \text{ mol } \text{N}_2}{2 \text{ mol } \text{NaN}_3} \right) = 0.115 \text{ mol } \text{N}_2 \end{aligned}$$

The pressure given (762 mmHg) is the *total* pressure in the flask, which is the sum of the pressures due to the N_2 gas and the water vapor present. Table 10.4 "Vapor Pressure of Water at Various Temperatures" tells us that the vapor pressure of water is 19.84 mmHg at 22°C (295 K), so the partial pressure of the N_2 gas in the flask is only $762 - 19.84 = 742 \text{ mmHg} = 0.976 \text{ atm}$.

B Solving the ideal gas law for V and substituting the other quantities (in the appropriate units), we get

$$\begin{aligned} V &= nRT/P = (0.115 \text{ mol } \text{N}_2) \\ &[0.08206 \text{ (L}\cdot\text{atm)/(K}\cdot\text{mol)}](295 \text{ K})/0.976 \text{ atm} = 2.85 \text{ L} \end{aligned}$$

Exercise

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce H_2 gas according to the equation $\text{Zn(s)} + 2 \text{HCl(aq)} \rightarrow \text{H}_2\text{(g)} + \text{ZnCl}_2\text{(aq)}$. The resulting H_2 gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

Answer: 0.397 L

Summary

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.

KEY TAKEAWAY

- The ideal gas equation and the stoichiometry of a reaction can be used to calculate the volume of gas produced or consumed in a reaction.

CONCEPTUAL PROBLEMS

1. Why are so many industrially important reactions carried out in the gas phase?
2. The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?
3. Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

NUMERICAL PROBLEMS

1. Balance each chemical equation and then determine the volume of the indicated reactant at STP that is required for complete reaction. Assuming complete reaction, what is the volume of the products?
 - a. $\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$ given 2.4 mol of O_2
 - b. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$ given 0.78 g of H_2
 - c. $\text{C}_2\text{H}_6(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ given 1.91 mol of O_2
2. During the smelting of iron, carbon reacts with oxygen to produce carbon monoxide, which then reacts with iron(III) oxide to produce iron metal and carbon dioxide. If 1.82 L of CO_2 at STP is produced,
 - a. what mass of CO is consumed?
 - b. what volume of CO at STP is consumed?
 - c. how much O_2 (in liters) at STP is used?
 - d. what mass of carbon is consumed?
 - e. how much iron metal (in grams) is produced?
3. Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.
 - a. What is the mass of KClO_3 in the original sample?
 - b. What mass of oxygen is produced?
 - c. What is the volume of oxygen produced at STP?
4. The combustion of a 100.0 mg sample of an herbicide in excess oxygen produced 83.16 mL of CO_2 and 72.9 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 16.44 mg of chlorine. If the sample is known to contain only C, H, Cl, and N, determine the percent composition and the empirical formula of the herbicide.
5. The combustion of a 300.0 mg sample of an antidepressant in excess oxygen produced 326 mL of CO_2 and 164 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 23.28% oxygen. If the sample is known to contain only C, H, O, and N, determine the percent composition and the empirical formula of the antidepressant.

ANSWERS

3.
 - a. 2.20 g KClO_3
 - a. 0.863 g O_2

b. 604 mL O₂

5. Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: C₁₀H₁₀O₃N₂

10.7 The Kinetic Molecular Theory of Gases

LEARNING OBJECTIVE

1. To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.

5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In, we explain how this theory must be modified to account for the behavior of real gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a force exerted by the gas on the walls, just as a bowling ball exerts a force on the pins it strikes. Anything that increases the frequency with which the molecules strike the walls or increases the momentum of the gas molecules (i.e., how hard they hit the walls) increases the pressure; anything that decreases that frequency or the momentum of the molecules decreases the pressure.

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Recall from that the kinetic energy of an object is given by $KE = \frac{1}{2}mv^2$, where m is the mass of the object and v is its velocity, or speed. Postulate 5 refers to the *average* kinetic energy of the molecules of a gas, which can be represented as $\overline{KE}$. and states that at a given temperature, all gases have the same value of $\overline{KE}$.

The average kinetic energy of the molecules of a gas is therefore

Equation 10.31

$$\overline{KE} = \frac{1}{2}m\overline{v^2}$$

where $\overline{v^2}$

is the average of the squares of the speeds of the particles. For n particles,

Equation 10.32

$$\overline{v^2} = \frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}$$

The square root of v^2_{rms} is the root mean square (rms) speed (v_{rms}):

Equation 10.33

$$v_{\text{rms}} = \sqrt{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}$$

Compare this with the formula used to calculate the average speed:

Equation 10.34

$$\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, *not* the same average speed. In contrast, the most probable speed (v_p) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and v_p increases.

Note the Pattern

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

EXAMPLE 15

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed ($\bar{v}$), root mean square speed (v_{rms}), and most probable speed (v_p).

Given: particle speeds

Asked for: average speed ($\bar{v}$), root mean square speed (v_{rms}), and most probable speed (v_p)

Strategy:

Use to calculate the average speed and to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

$$= \frac{1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0}{8} = 5.6 \text{ m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$$

$$= \sqrt{\frac{1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2}{8}} = 6.3 \text{ m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_p = 6.0 \text{ m/s}$. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Exercise

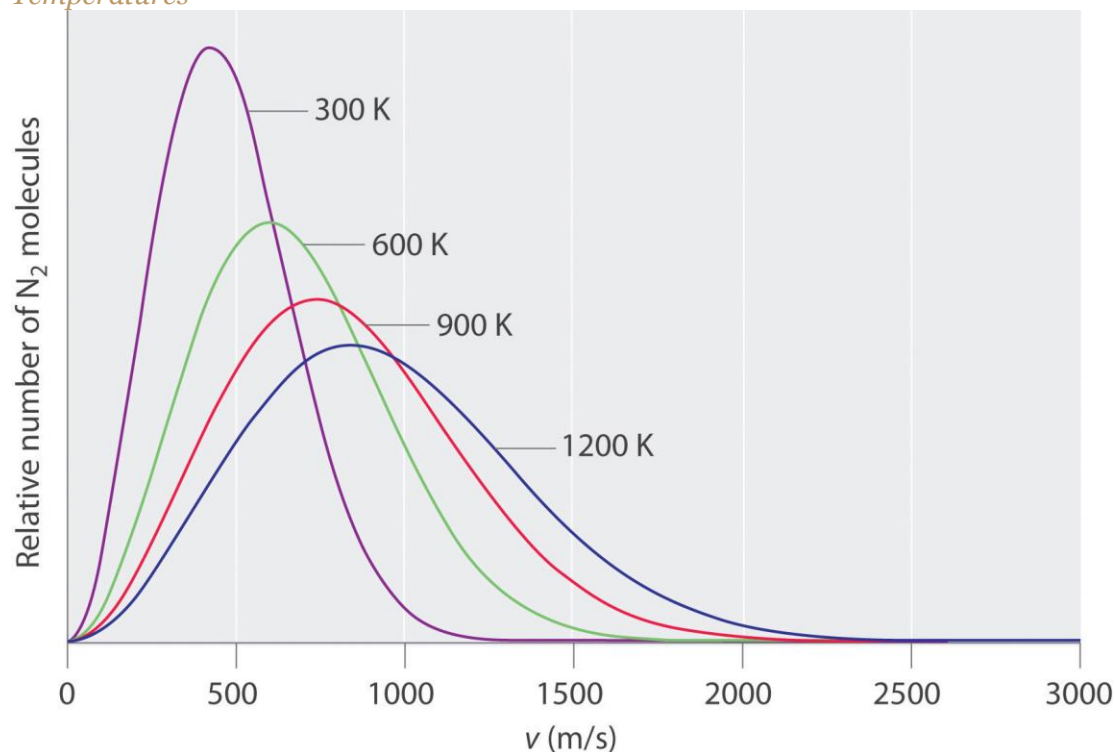
Ten particles were found to have speeds of 0.1, 1.0, 2.0, 3.0, 3.0, 3.0, 4.0, 4.0, 5.0, and 6.0 m/s. Calculate their average speed ($\bar{v}$), root mean square speed (v_{rms}), and most probable speed (v_p).

Answer: $\bar{v} = 3.1 \text{ m/s}$; $v_{rms} = 3.5 \text{ m/s}$; $v_p = 3.0 \text{ m/s}$

Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction, as you will learn in . This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in . Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

Figure 10.14 *The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures*



Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

Pressure versus Volume

At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.

Volume versus Temperature

Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.

Pressure of Gas Mixtures

Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

EXAMPLE 16

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C . What is the qualitative effect of this change on the

- average kinetic energy of the N_2 molecules?
- rms speed of the N_2 molecules?
- average speed of the N_2 molecules?
- impact of each N_2 molecule on the wall of the container during a collision with the wall?
- total number of collisions per second of N_2 molecules with the walls of the entire container?
- number of collisions per second of N_2 molecules with each square centimeter of the container wall?
- pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

- a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
- b. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
- c. If the rms speed of the N_2 molecules increases, the average speed also increases.
- d. If, on average, the particles are moving faster, then they strike the container walls with more energy.
- e. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
- f. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
- g. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

Exercise

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

- a. average kinetic energy of the He atoms?
- b. rms speed of the He atoms?
- c. average speed of the He atoms?
- d. impact of each He atom on the wall of the container during a collision with the wall?
- e. total number of collisions per second of He atoms with the walls of the entire container?
- f. number of collisions per second of He atoms with each square centimeter of the container wall?
- g. pressure of the He gas?

Answer: a. no change; b. no change; c. no change; d. no change; e. decreases; f. decreases; g. decreases

Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment. shows white fumes of solid ammonium chloride (NH_4Cl) forming when containers of aqueous ammonia and HCl are placed near each other, even with no draft to stir the air. This phenomenon suggests that NH_3 and HCl molecules (as well as the more complex organic molecules responsible for the aromas of pizza and perfumes) move without assistance.

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. As we shall see in , , and , diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. We can describe the phenomenon shown in by saying that the molecules of HCl and NH_3 are able to diffuse away from their containers, and that NH_4Cl is formed where the two gases come into contact. Similarly, we say that a perfume or an aroma diffuses throughout a room or a house. The related process, effusion, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship, $\text{rate} \propto 1/\sqrt{M}$, is referred to as Graham's law, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses. If r is the effusion rate and M is the molar mass, then

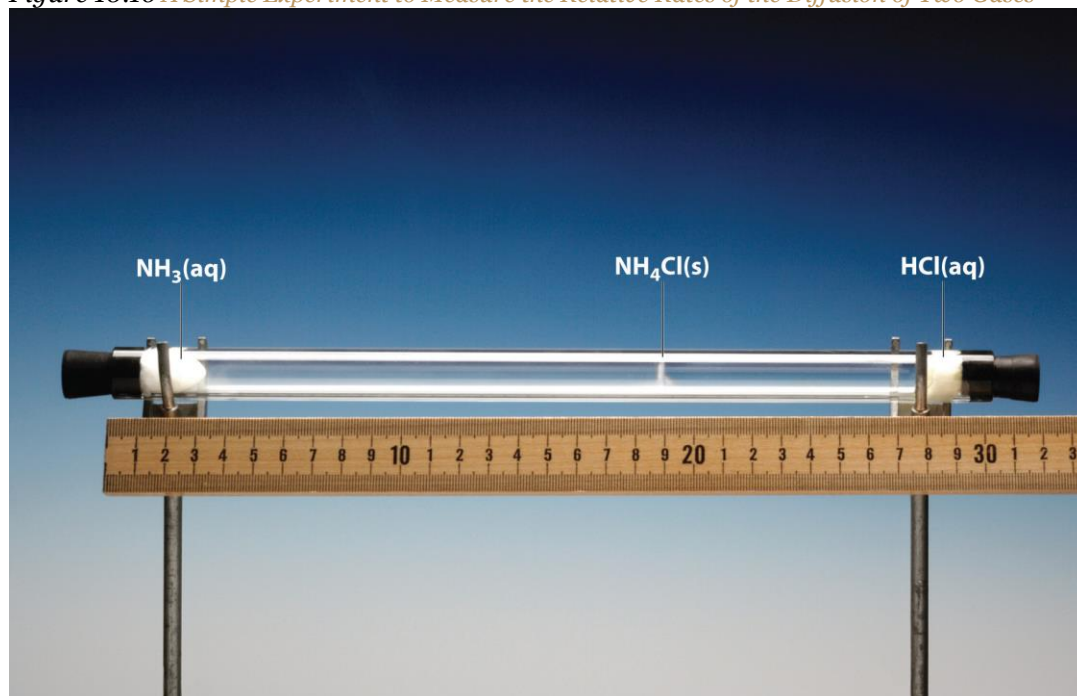
Equation 10.35

$$r_1/r_2 = \sqrt{M_2/M_1}$$

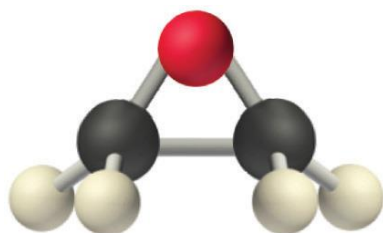
Although diffusion and effusion are different phenomena, the rate of diffusion is closely approximated using ; that is, if $M_1 < M_2$, then gas #1 will diffuse more rapidly than gas #2. This point is illustrated by the experiment shown in , which is a more quantitative version of the case shown in . The reaction is the same $[\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{g})]$,

but in this experiment, two cotton balls containing aqueous ammonia and HCl are placed along a meter stick in a draft-free environment, and the position at which the initial NH_4Cl fumes appear is noted. The white cloud forms much nearer the HCl-containing ball than the NH_3 -containing ball. Because ammonia ($M = 17.0 \text{ g/mol}$) diffuses much faster than HCl ($M = 36.5 \text{ g/mol}$), the NH_4Cl fumes form closer to HCl because the HCl molecules travel a shorter distance. The ratio of the distances traveled by NH_3 and HCl is about 1.7, in reasonable agreement with the ratio of 1.47 predicted by their molar masses $[(36.5/17.0)^{1/2} = 1.47]$.

Figure 10.16 *A Simple Experiment to Measure the Relative Rates of the Diffusion of Two Gases*



Cotton balls containing aqueous NH_3 (left) and HCl (right) are placed a measured distance apart in a draft-free environment, and the position at which white fumes of NH_4Cl first appear is noted. The puff of white NH_4Cl forms much closer to the HCl -containing ball than to the NH_3 -containing ball. The left edge of the white puff marks where the reaction was first observed. The position of the white puff ($18.8 - 3.3 = 15.5 \text{ cm}$ from the NH_3 , $28.0 - 18.8 = 9.2 \text{ cm}$ from the HCl , giving a ratio of distances of $15.5/9.2 = 1.7$) is approximately the location predicted by Graham's law based on the square root of the inverse ratio of the molar masses of the reactants (1.47).



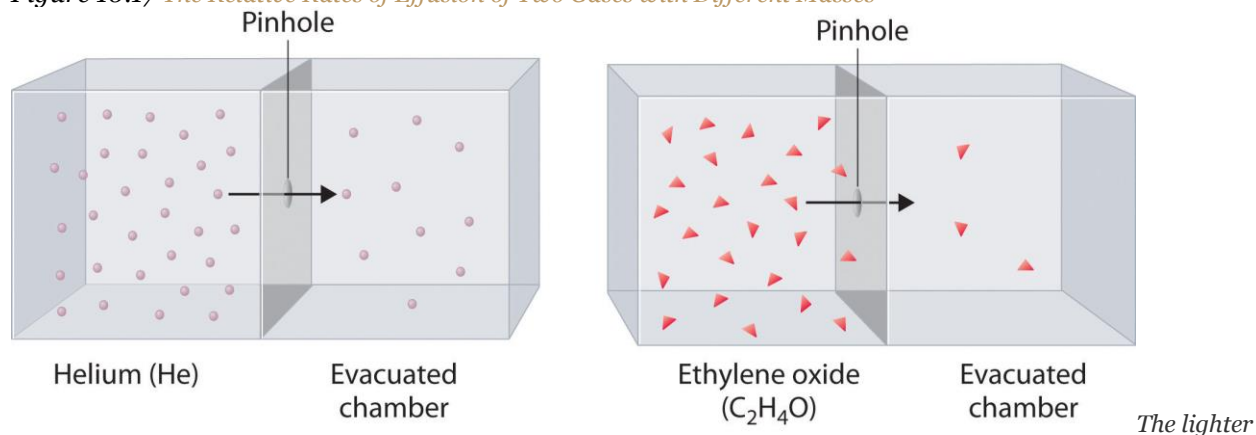
Ethylene oxide

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in for ethylene oxide and helium. Helium ($M = 4.00 \text{ g/mol}$) effuses much more rapidly than ethylene oxide ($M = 44.0 \text{ g/mol}$). Because helium is less dense than air, helium-filled balloons “float” at the end of a tethering string.

Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol , whereas air has an average molar mass of about 29 g/mol , pure helium effuses through the microscopic pores in the rubber balloon

times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Mylar balloons can retain their helium for days.

Figure 10.17 *The Relative Rates of Effusion of Two Gases with Different Masses*



He atoms ($M = 4.00 \text{ g/mol}$) effuse through the small hole more rapidly than the heavier ethylene oxide ($\text{C}_2\text{H}_4\text{O}$) molecules ($M = 44.0 \text{ g/mol}$), as predicted by Graham's law.

Note the Pattern

At a given temperature, heavier molecules move more slowly than lighter molecules.

EXAMPLE 17

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U . Naturally occurring uranium is only 0.720% ^{235}U , whereas most of the rest (99.275%) is ^{238}U , which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

- a. Calculate the ratio of the rates of effusion of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
- b. If n identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the n th power. How many effusion steps are needed to obtain 99.0% pure $^{235}\text{UF}_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}\text{UF}_6$

Strategy:

A Calculate the molar masses of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}\text{UF}_6$ after a single effusion step.

B Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

a. **A** The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U . Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}\text{UF}_6$ is

$$234.04 + (6)(18.998) = 349.03 \text{ g/mol}$$

The molar mass of $^{238}\text{UF}_6$ is

$$238.05 + (6)(18.998) = 352.04 \text{ g/mol}$$

The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using :

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6} = \sqrt{\frac{352.04}{349.03}} = 1.0043$$

Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is $(0.720\%)(1.0043) = 0.723\% \text{ }^{235}\text{UF}_6$.

B To obtain 99.0% pure $^{235}\text{UF}_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated:

$$\text{final purity} = (\text{initial purity})(\text{separation})^n$$

In this case, $0.990 = (0.00720)(1.0043)^n$, which can be rearranged to give

$$0.990/0.00720 = (1.0043)^n = 138$$

Taking the logarithm of both sides gives

$$\log 138 = n \log 1.0043 \quad n = \log 138 / \log 1.0043$$

$$= 1150 = 1.15 \times 10^3$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U . shows a small part of a system that is used to prepare enriched uranium on a large scale.

Exercise

Helium consists of two isotopes: ^3He (natural abundance = 0.000134%) and ^4He (natural abundance = 99.999866%). Their atomic masses are 3.01603 and 4.00260, respectively. Helium-3 has unique physical properties and is used in the study of ultralow temperatures. It is separated from the more abundant ^4He by a process of gaseous effusion.

- Calculate the ratio of the effusion rates of ^3He and ^4He and thus the enrichment possible in a single effusion step.
- How many effusion steps are necessary to yield 99.0% pure ^3He ?

Answer: a. ratio of effusion rates = 1.15200; one step gives 0.000154% ^3He ; b. 96 steps

Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

Equation 10.36

$$KE_{\text{avg}} = \frac{1}{2} M_1 v_{\text{rms}1}^2 = \frac{1}{2} M_2 v_{\text{rms}2}^2$$

Multiplying both sides by 2 and rearranging give

Equation 10.37

$$v_{\text{rms}2}^2 v_{\text{rms}1}^2 = M_1 M_2$$

Taking the square root of both sides gives

Equation 10.38

$$v_{\text{rms}2} v_{\text{rms}1} = \sqrt{M_1 M_2}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. This shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

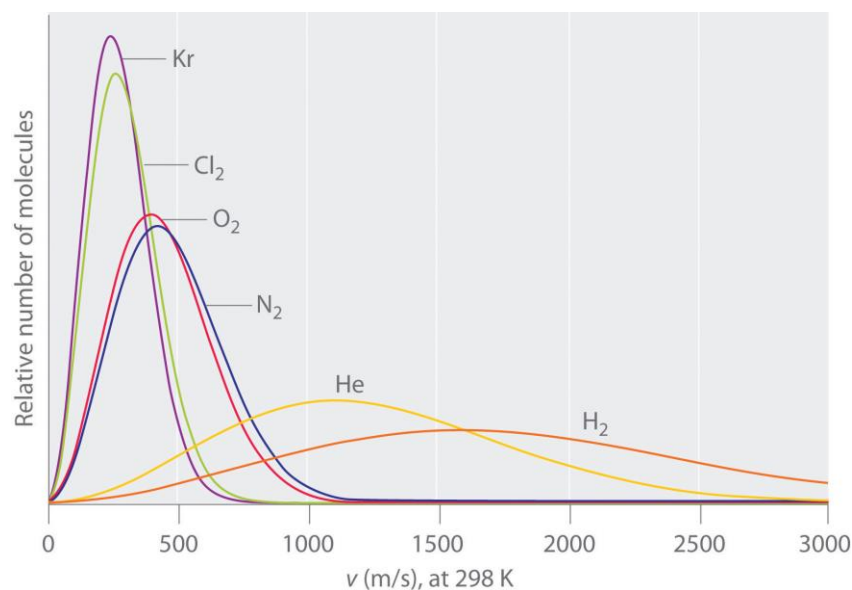
Typically, gaseous molecules have a speed of hundreds of meters per second (hundreds of miles per hour). The effect of molar mass on these speeds is dramatic, as illustrated in for some common gases. Because all gases have the same average kinetic energy, according to the Boltzmann distribution, molecules with lower masses, such as hydrogen and helium, have a wider distribution of speeds. The postulates of the kinetic molecular theory of gases lead to the following equation, which directly relates molar mass, temperature, and rms speed:

Equation 10.39

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

In this equation, v_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K·mol).

Figure 10.19 The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses



The lightest gases have a wider

distribution of speeds and the highest average speeds.

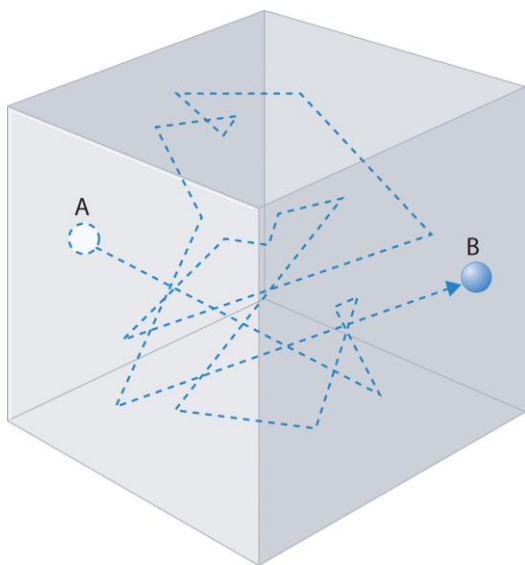
Note the Pattern

Molecules with lower masses have a wider distribution of speeds and a higher average speed.

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules.

Because gas molecules collide as often as 10^{10} times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line, as illustrated schematically in . The average distance traveled by a molecule between collisions is the mean free path. The denser the gas, the shorter the mean free path; conversely, as density decreases, the mean free path becomes longer because collisions occur less frequently. At 1 atm pressure and 25°C , for example, an oxygen or nitrogen molecule in the atmosphere travels only about 6.0×10^{-8} m (60 nm) between collisions. In the upper atmosphere at about 100 km altitude, where gas density is much lower, the mean free path is about 10 cm; in space between galaxies, it can be as long as 1×10^{10} m (about 6 million miles).

Figure 10.20 *The Path of a Single Particle in a Gas Sample*



The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

Note the Pattern

The denser the gas, the shorter the mean free path.

EXAMPLE 18

Calculate the rms speed of a sample of *cis*-2-butene (C_4H_8) at $20^\circ C$.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of *cis*-2-butene. Be certain that all quantities are expressed in the appropriate units and then use to calculate the rms speed of the gas.

Solution:

To use , we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is C_4H_8 , so its molar mass is 56.11 g/mol. Thus

$$\begin{aligned}
 M &= 56.11 \text{ g/mol} \\
 &= 56.11 \times 10^{-3} \text{ kg/mol} \\
 &= 20 + 273 = 293 \text{ K} \\
 R &= 8.3145 \text{ J/(K mol)} = 8.3145 \text{ (kg m}^2\text{)/(s}^2\text{K mol)} \\
 v_{rms} &= \sqrt{3RT/M} \\
 &= \sqrt{(3)(8.3145 \text{ (kg m}^2\text{)/(s}^2\text{K mol)})(293 \text{ K}) / (56.11 \times 10^{-3} \text{ kg/mol})} \\
 &= 3.61 \times 10^2 \text{ m/s}
 \end{aligned}$$

or approximately 810 mi/h.

Exercise

Calculate the rms speed of a sample of radon gas at 23°C.

Answer: 1.82×10^2 m/s (about 410 mi/h)

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not “ideal,” although their behavior usually approximates that of an ideal gas. In , we explore how the behavior of real gases differs from that of ideal gases.

Summary

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed (v_{rms})**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average. **Diffusion** is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, **effusion** is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (**Graham’s law**), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases. The **mean free path** of a molecule is the average distance it travels between collisions.

KEY TAKEAWAY

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.

KEY EQUATIONS

Average kinetic energy

$$: \overline{KE} = \frac{1}{2} m \overline{v^2}$$

Root mean square speed

$$v_{rms} = \sqrt{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2} \quad \text{--- } \checkmark$$

Graham's law for diffusion and effusion

$$r_1 r_2 = \sqrt{M_2 M_1} \quad \text{--- } \checkmark$$

Kinetic molecular theory of gases

$$v_{rms} = \sqrt{3RT/M} \quad \text{--- } \checkmark$$

CONCEPTUAL PROBLEMS

- Which of the following processes represents effusion, and which represents diffusion?
 - helium escaping from a hole in a balloon
 - vapor escaping from the surface of a liquid
 - gas escaping through a membrane
- Which postulate of the kinetic molecular theory of gases most readily explains the observation that a helium-filled balloon is round?
- Why is it relatively easy to compress a gas? How does the compressibility of a gas compare with that of a liquid? A solid? Why? Which of the postulates of the kinetic molecular theory of gases most readily explains these observations?
- What happens to the average kinetic energy of a gas if the rms speed of its particles increases by a factor of 2? How is the rms speed different from the average speed?
- Which gas—radon or helium—has a higher average kinetic energy at 100°C? Which has a higher average speed? Why? Which postulate of the kinetic molecular theory of gases most readily supports your answer?
- What is the relationship between the average speed of a gas particle and the temperature of the gas? What happens to the distribution of molecular speeds if the temperature of a gas is increased? Decreased?
- Qualitatively explain the relationship between the number of collisions of gas particles with the walls of a container and the pressure of a gas. How does increasing the temperature affect the number of collisions?
- What happens to the average kinetic energy of a gas at constant temperature if the
 - volume of the gas is increased?
 - pressure of the gas is increased?

9. What happens to the density of a gas at constant temperature if the
 - a. volume of the gas is increased?
 - b. pressure of the gas is increased?
10. Use the kinetic molecular theory of gases to describe how a decrease in volume produces an increase in pressure at constant temperature. Similarly, explain how a decrease in temperature leads to a decrease in volume at constant pressure.
11. Graham's law is valid only if the two gases are at the same temperature. Why?
12. If we lived in a helium atmosphere rather than in air, would we detect odors more or less rapidly than we do now? Explain your reasoning. Would we detect odors more or less rapidly at sea level or at high altitude? Why?

NUMERICAL PROBLEMS

1. At a given temperature, what is the ratio of the rms speed of the atoms of Ar gas to the rms speed of molecules of H_2 gas?
2. At a given temperature, what is the ratio of the rms speed of molecules of CO gas to the rms speed of molecules of H_2S gas?
3. What is the ratio of the rms speeds of argon and oxygen at any temperature? Which diffuses more rapidly?
4. What is the ratio of the rms speeds of Kr and NO at any temperature? Which diffuses more rapidly?
5. Deuterium (D) and tritium (T) are heavy isotopes of hydrogen. Tritium has an atomic mass of 3.016 amu and has a natural abundance of 0.000138%. The effusion of hydrogen gas (containing a mixture of H_2 , HD, and HT molecules) through a porous membrane can be used to obtain samples of hydrogen that are enriched in tritium. How many membrane passes are necessary to give a sample of hydrogen gas in which 1% of the hydrogen molecules are HT?
6. Samples of HBr gas and NH_3 gas are placed at opposite ends of a 1 m tube. If the two gases are allowed to diffuse through the tube toward one another, at what distance from each end of the tube will the gases meet and form solid NH_4Br ?

ANSWER

1. At any temperature, the rms speed of hydrogen is 4.45 times that of argon.

10.8 The Behavior of Real Gases

LEARNING OBJECTIVE

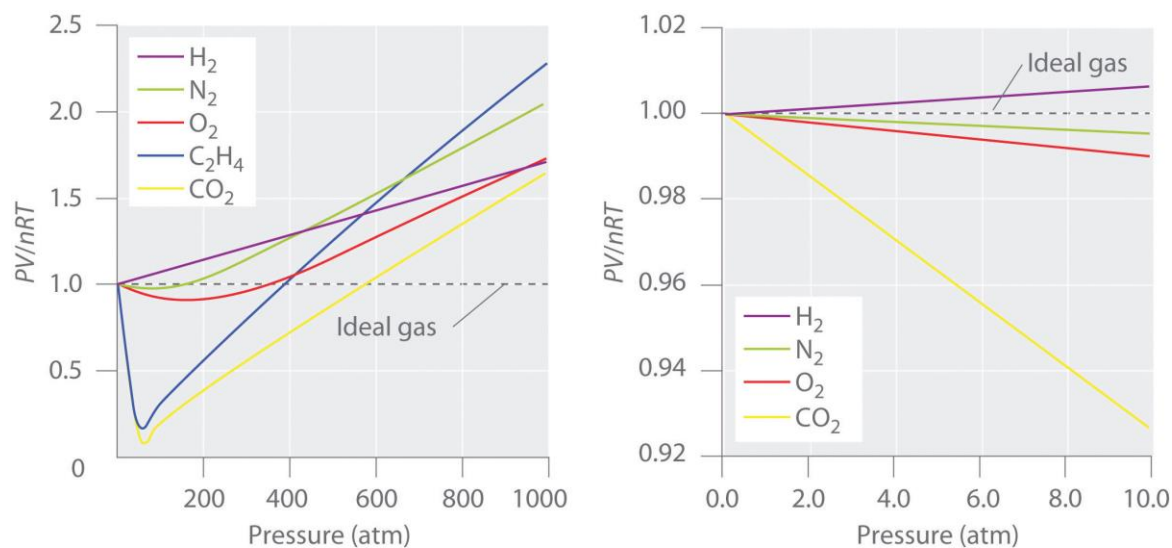
1. To recognize the differences between the behavior of an ideal gas and a real gas.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (part (a) in Figure 10.21 "Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures"). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (part (b) in Figure 10.21 "Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures"). Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure 10.22 "The Effect of Temperature on the Behavior of Real Gases" for N_2 . Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

Figure 10.21 Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures



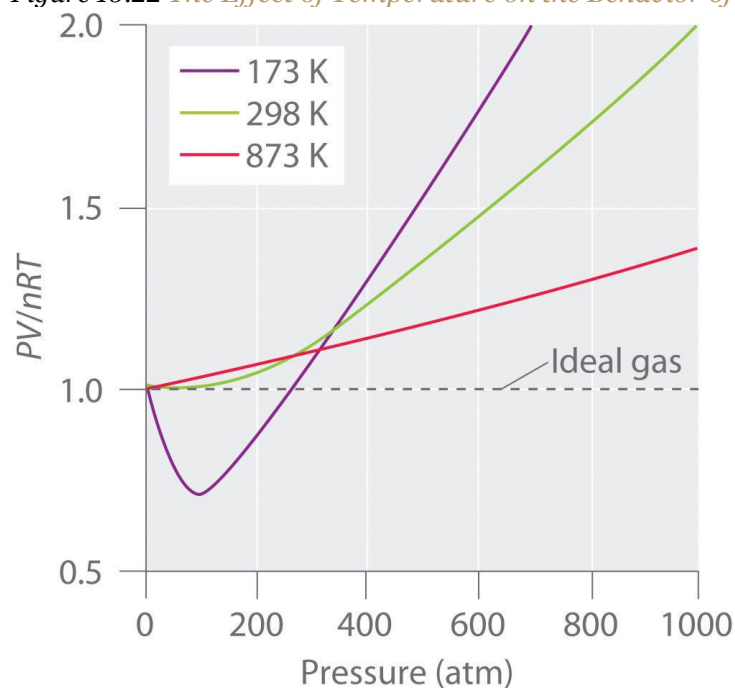
(a) PV/nRT at high pressures

(b) PV/nRT at low pressures

(a) In

these plots of PV/nRT versus P at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

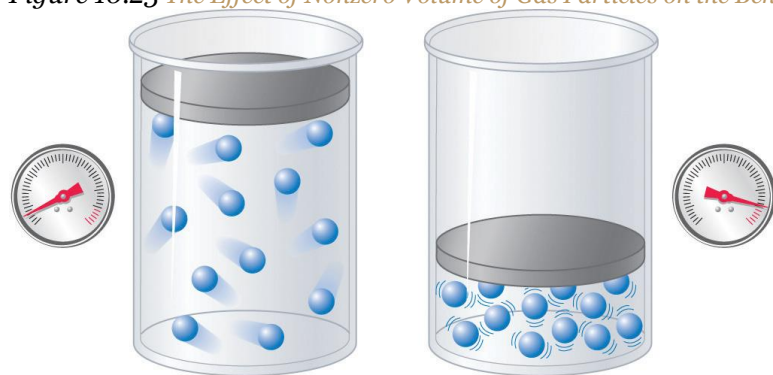
Figure 10.22 The Effect of Temperature on the Behavior of Real Gases



A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 10.23 "The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures"). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of PV/nRT is greater than the value predicted by the ideal gas law.

Figure 10.23 *The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures*



(a) Low pressure

(b) High pressure

(a) At low pressures, the volume occupied by

the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure 10.24 "The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls"). Thus as shown in Figure 10.22 "The Effect of Temperature on the Behavior of Real Gases", at low temperatures, the ratio of PV/nRT is

lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

Note the Pattern

Nonzero molecular volume makes the actual volume *greater* than predicted at high pressures; intermolecular attractions make the pressure *less* than predicted.

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called van der Waals equation,

Equation 10.40

$$(P + an^2/V^2)(V - nb) = nRT$$

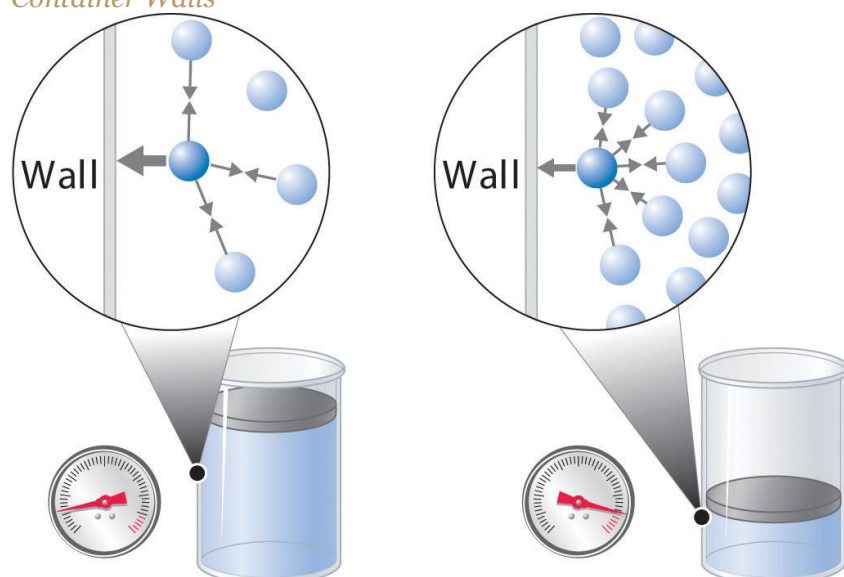
a and b are empirical constants that are different for each gas. The values of a and b are listed in Table 10.5 "van der Waals Constants for Some Common Gases" for several common gases. The pressure term— $P + (an^2/V^2)$ —corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure 10.24 "The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls". The volume term— $V - nb$ —corrects for the volume occupied by the gaseous molecules.

Table 10.5 van der Waals Constants for Some Common Gases

Gas	a (L ² ·atm)/mol ²	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167

Gas	a (L ² •atm)/mol ²	b (L/mol)
Ar	1.337	0.032
H ₂	0.2420	0.0265
N ₂	1.352	0.0387
O ₂	1.364	0.0319
Cl ₂	6.260	0.0542
NH ₃	4.170	0.0371
CH ₄	2.273	0.0430
CO ₂	3.610	0.0429

Figure 10.24 *The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls*



(a) Low pressure

(b) High pressure

(a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P , respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain

the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

EXAMPLE 19

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.0 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain a and b values for Cl_2 from Table 10.5 "van der Waals Constants for Some Common Gases". Use the van der Waals equation to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$(500 \text{ g})(1 \text{ mol} / 70.906 \text{ g}) = 7.05 \text{ mol Cl}_2$$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = nRT/V = (7.05 \text{ mol})[(0.08206 \text{ L} \cdot \text{atm}) / (\text{K} \cdot \text{mol})](298 \text{ K}) / 4.0 \text{ L} = 43 \text{ atm}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the a and b values for Cl_2 from Table 10.5 "van der Waals Constants for Some Common Gases". Solving for P gives

$$\begin{aligned}
 P &= nRT/V - nb - a n^2/V^2 \\
 &= (7.05 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol})(298 \text{ K})/4.0 \text{ L} \\
 &\quad - (7.05 \text{ mol})(0.0542 \text{ L} / \text{mol}) - (6.2602 \text{ L}^2 \cdot \text{atm} / \text{mol}^2)(7.05 \text{ mol})^2/(4.0 \text{ L})^2 = 47.7 \text{ atm} \\
 &\quad - 19.4 \text{ atm} = 28 \text{ atm (to two significant figures)}
 \end{aligned}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

- ideal gas law.
- van der Waals equation.

Answer: a. 77 atm; b. 67 atm

Liquefaction of Gases

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals a coefficients are relatively easy to liquefy because large a coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small a coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2 , N_2 , Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is

warmed, and the gases are separated according to their boiling points. In Chapter 11 "Liquids", we will consider in more detail the nature of the intermolecular forces that allow gases to liquefy.

Note the Pattern

A large value of a indicates the presence of relatively strong intermolecular attractive interactions.

The ultracold liquids formed from the liquefaction of gases are called *cryogenic liquids*, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 10.25 "A Liquid Natural Gas Transport Ship"). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about -162°C . It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of PV/nRT versus P at a given temperature; for an ideal gas, PV/nRT versus $P = 1$ under all conditions. At high pressures, most real gases exhibit larger PV/nRT values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit PV/nRT values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual

volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

KEY TAKEAWAY

- Molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

KEY EQUATION

van der Waals equation

$$\text{Equation 10.40: } (P + an^2/V^2)(V - nb) = nRT$$

CONCEPTUAL PROBLEMS

1. What factors cause deviations from ideal gas behavior? Use a sketch to explain your answer based on interactions at the molecular level.
2. Explain the effect of nonzero atomic volume on the ideal gas law at high pressure. Draw a typical graph of volume versus $1/P$ for an ideal gas and a real gas.
3. For an ideal gas, the product of pressure and volume should be constant, regardless of the pressure. Experimental data for methane, however, show that the value of PV decreases significantly over the pressure range 0 to 120 atm at 0°C . The decrease in PV over the same pressure range is much smaller at 100°C . Explain why PV decreases with increasing temperature. Why is the decrease less significant at higher temperatures.
4. What is the effect of intermolecular forces on the liquefaction of a gas? At constant pressure and volume, does it become easier or harder to liquefy a gas as its temperature increases? Explain your reasoning. What is the effect of increasing the pressure on the liquefaction temperature?
5. Describe qualitatively what a and b , the two empirical constants in the van der Waals equation, represent.
6. In the van der Waals equation, why is the term that corrects for volume negative and the term that corrects for pressure positive? Why is n/V squared?
7. Liquefaction of a gas depends strongly on two factors. What are they? As temperature is decreased, which gas will liquefy first—ammonia, methane, or carbon monoxide? Why?
8. What is a cryogenic liquid? Describe three uses of cryogenic liquids.

9. Air consists primarily of O₂, N₂, Ar, Ne, Kr, and Xe. Use the concepts discussed in this chapter to propose two methods by which air can be separated into its components. Which component of air will be isolated first?
10. How can gas liquefaction facilitate the storage and transport of fossil fuels? What are potential drawbacks to these methods?

NUMERICAL PROBLEMS

1. The van der Waals constants for xenon are $a = 4.19 \text{ (L}^2\cdot\text{atm)/mol}^2$ and $b = 0.0510 \text{ L/mol}$. If a 0.250 mol sample of xenon in a container with a volume of 3.65 L is cooled to -90°C , what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?
2. The van der Waals constants for water vapor are $a = 5.46 \text{ (L}^2\cdot\text{atm)/mol}^2$ and $b = 0.0305 \text{ L/mol}$. If a 20.0 g sample of water in a container with a volume of 5.0 L is heated to 120°C , what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

10.9 Essential Skills 5

TOPICS

- Preparing a Graph
- Interpreting a Graph

Previous Essential Skills sections presented the fundamental mathematical operations you need to know to solve problems by manipulating chemical equations. This section describes how to prepare and interpret graphs, two additional skills that chemistry students must have to understand concepts and solve problems.

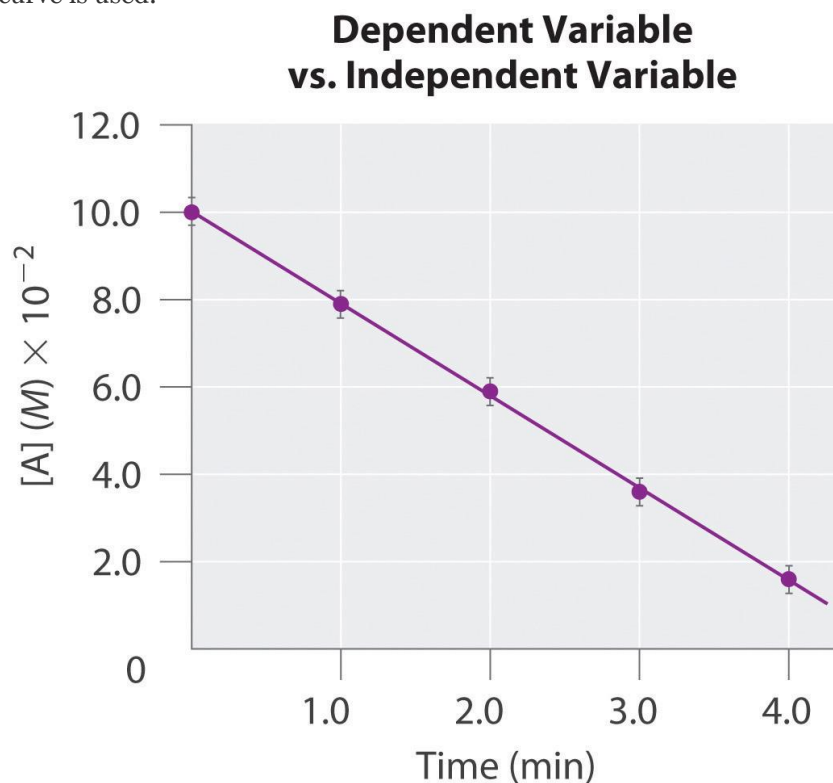
Preparing a Graph

A *graph* is a pictorial representation of a mathematical relationship. It is an extremely effective tool for understanding and communicating the relationship between two or more variables. Each axis is labeled with the name of the variable to which it corresponds, along with the unit in which the variable is measured, and each axis is divided by tic marks or grid lines into segments that represent those units (or multiples). The scale of the divisions should be chosen so that the plotted points are distributed across the entire graph. Whenever possible, data points should be combined with a bar that intersects the data point and indicates the range of error of the measurement, although for simplicity the bars are frequently omitted in undergraduate textbooks. Lines or curves that represent theoretical or computational results

are drawn using a “best-fit” approach; that is, data points are not connected as a series of straight-line segments; rather, a smooth line or curve is drawn that provides the best fit to the plotted data.

The independent variable is usually assigned to the horizontal, or x , axis (also called the *abscissa*), and the dependent variable to the vertical, or y , axis (called the *ordinate*). Let’s examine, for example, an experiment in which we are interested in plotting the change in the concentration of compound A with time. Because time does not depend on the concentration of A but the concentration of A does depend on the amount of time that has passed during the reaction, time is the independent variable and concentration is the dependent variable. In this case, the time is assigned to the horizontal axis and the concentration of A to the vertical axis.

We may plot more than one dependent variable on a graph, but the lines or curves corresponding to each set of data must be clearly identified with labels, different types of lines (a dashed line, for example), or different symbols for the respective data points (e.g., a triangle versus a circle). When words are used to label a line or curve, either a key identifying the different sets of data or a label placed next to each line or curve is used.



Interpreting a Graph

Two types of graphs are frequently encountered in beginning chemistry courses: linear and log-linear.

Here we describe each type.

Linear Graphs

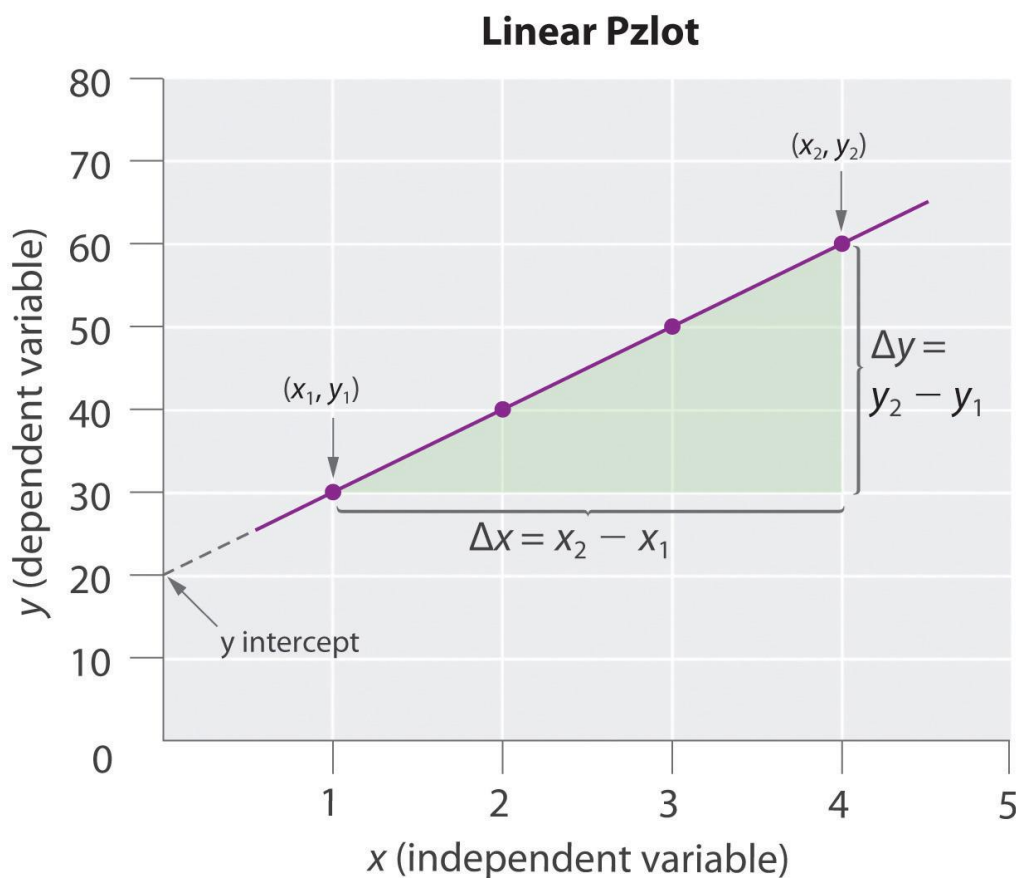
In a *linear graph*, the plot of the relationship between the variables is a straight line and thus can be expressed by the equation for a straight line:

$$y = mx + b$$

where m is the slope of the line and b is the point where the line intersects the vertical axis (where $x = 0$), called the *y-intercept*. The slope is calculated using the following formula:

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta y}{\Delta x} = \text{rise/run}$$

For accuracy, two widely separated points should be selected for use in the formula to minimize the effects of any reporting or measurement errors that may have occurred in any given region of the graph. For example, when concentrations are measured, limitations in the sensitivity of an instrument as well as human error may result in measurements being less accurate for samples with low concentrations than for those that are more concentrated. The graph of the change in the concentration of A with time is an example of a linear graph. The key features of a linear plot are shown on the generic example.



It is important to remember that when a graphical procedure is used to calculate a slope, the scale on each axis must be of the same order (they must have the same exponent). For example, although acceleration is a change in velocity over time ($\Delta v / \Delta t$), the slope of a linear plot of velocity versus time only gives the correct value for acceleration (m/s^2) if the average acceleration over the interval and the instantaneous acceleration are identical; that is, the acceleration must be constant over the same interval.

Log-Linear Graphs

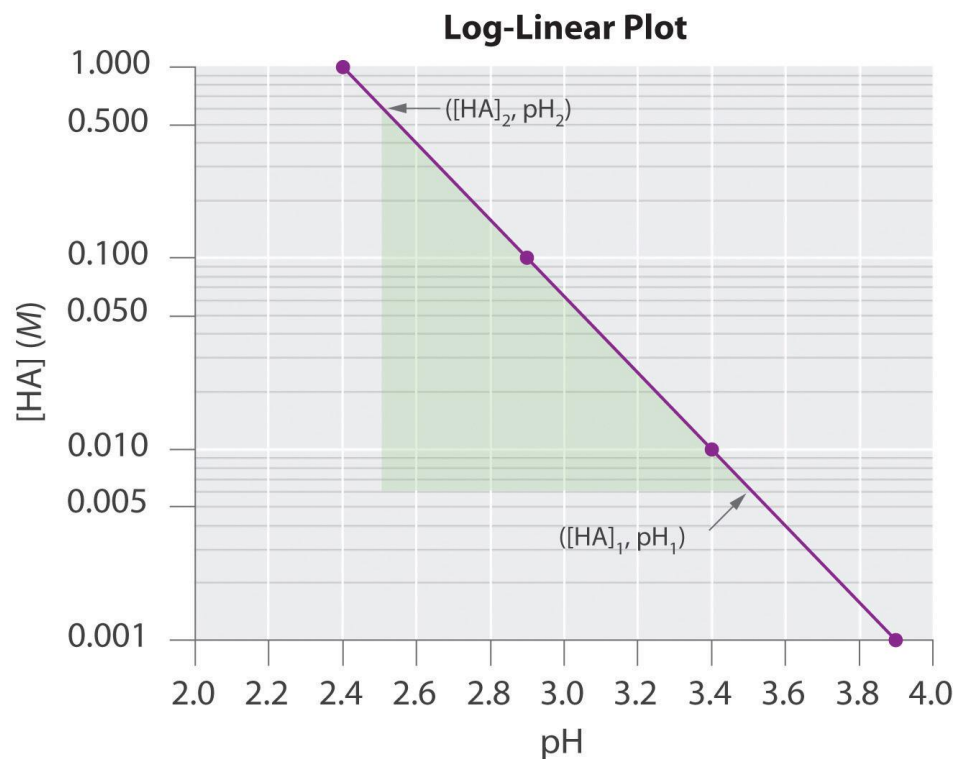
A log-linear plot is a representation of the following general mathematical relationship:

$$y = Acmx$$

Here, y is equal to some value Ac when $x = 0$. As described in Essential Skills 3 in Chapter 4 "Reactions in Aqueous Solution", Section 4.10 "Essential Skills 3", taking the logarithm of both sides produces

$$\log y = \log A + mx \log c = (m \log c)x + \log A$$

When expressed in this form, the equation is that of a straight line ($y = mx + b$), where the plot of y is on a logarithmic axis and $(m \log c)x$ is on a linear axis. This type of graph is known as a *log-linear plot*. Log-linear plots are particularly useful for graphing changes in pH versus changes in the concentration of another substance. One example of a log-linear plot, where $y = [\text{HA}]$ and $x = \text{pH}$, is shown here:



From the linear equation, a

log-linear plot has a y -intercept of $\log A$, so the value of A may be obtained directly from the plot *if the x axis begins at 0* (in this case it does not, as is often the case in pH plots). Using our example, however, we can calculate $[HA]$ at the y -intercept first by calculating the slope of the line using any two points and the

equation $\log[HA]_2 - \log[HA]_1 = pH_2 - pH_1$:

$$\log[HA]_2 - \log[HA]_1 = pH_2 - pH_1$$

$$\log[HA]_2 = \log[HA]_1 + pH_2 - pH_1$$

$$\log[HA]_2 = \log[HA]_1 + pH_2 - pH_1$$

Using any point along the line (e.g., $[HA] = 0.100$, $pH = 2.9$), we can then calculate the y -intercept

($pH = 0$):

$$\log[HA] = -2.0 \text{ } pH + b \quad -1.00 = [(-2.0)(2.9)] + b \quad 4.8 = b$$

Thus at a pH of 0.0, $\log[HA] = 4.8$ and $[HA] = 6.31 \times 10^4$ M. The exercises provide practice in drawing and interpreting graphs.

SKILL BUILDER ES1

a. The absorbance of light by various aqueous solutions of phosphate was measured and tabulated as follows:

Absorbance (400 nm)	PO_4^{3-} (mol/L)

Absorbance (400 nm)	PO ₄ ³⁻ (mol/L)
0.16	3.2×10^{-5}
0.38	8.4×10^{-5}
0.62	13.8×10^{-5}
0.88	19.4×10^{-5}

b. Graph the data with the dependent variable on the y axis and the independent variable on the x axis and then calculate the slope. If a sample has an absorbance of 0.45, what is the phosphate concentration in the sample?

c. The following table lists the conductivity of three aqueous solutions with varying concentrations. Create a plot from these data and then predict the conductivity of each sample at a concentration of 15.0×10^3 ppm.

	0 ppm	5.00×10^3 ppm	10.00×10^3 ppm
K ₂ CO ₃	0.0	7.0	14.0
Seawater	0.0	8.0	15.5
Na ₂ SO ₄	0.0	6.0	11.8

Solution:

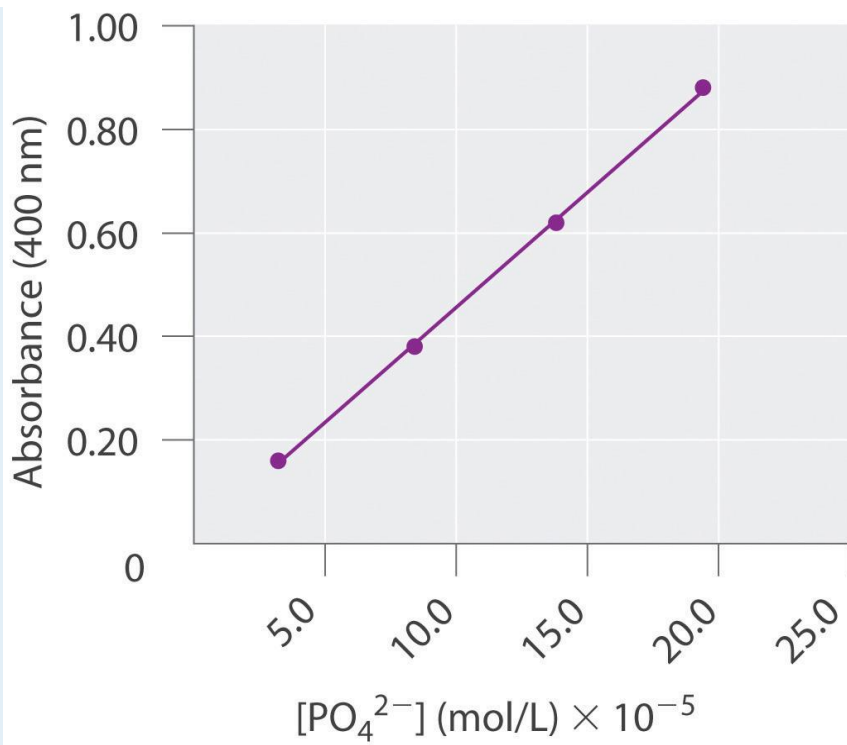
a. Absorbance is the dependent variable, and concentration is the independent variable. We calculate the slope using two widely separated data points:

$$m = \frac{\Delta y}{\Delta x} = \frac{0.62 - 0.16}{13.8 \times 10^{-5} - 3.2 \times 10^{-5}} = 4.3 \times 10^3$$

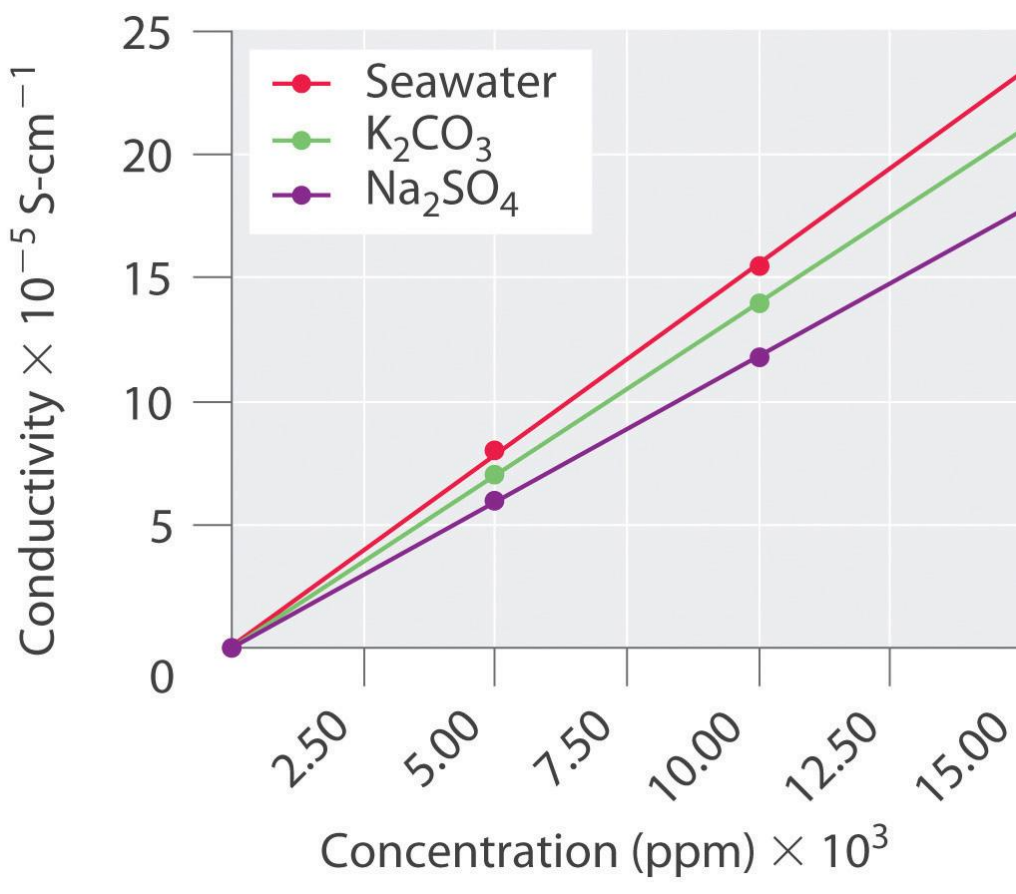
According to our graph, the y-intercept, b , is 0.00. Thus when $y = 0.45$,

$$0.45 = (4.3 \times 10^3)(x) + 0.00x = 10 \times 10^{-5}$$

This is in good agreement with a graphical determination of the phosphate concentration at an absorbance of 0.45, which gives a value of 10.2×10^{-5} mol/L.



Conductivity is the dependent variable, and concentration is the independent variable. From our graph, at 15.0×10^3 ppm, the conductivity of K_2CO_3 is predicted to be 21; that of seawater, 24; and that of Na_2SO_4 , 18.

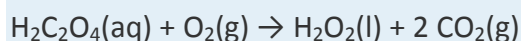


10.10 End-of-Chapter Material

APPLICATION PROBLEMS

Be sure you are familiar with the material in Essential Skills 5 (Section 10.9 "Essential Skills 5") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. ♦ Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) is a metabolic product of many molds. Although oxalic acid is toxic to humans if ingested, many plants and vegetables contain significant amounts of oxalic acid or oxalate salts. In solution, oxalic acid can be oxidized by air via the following chemical equation:

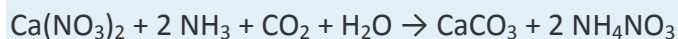


If a plant metabolized enough oxalic acid to produce 3.2 L of CO_2 on a day when the temperature was 29°C and the pressure was 752 mmHg, how many grams of oxalic acid were converted to CO_2 ? Given that air is 21% oxygen, what volume of air was needed for the oxidation?

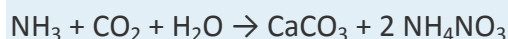
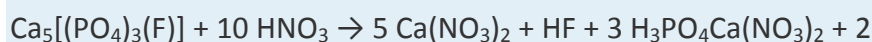
2. ♦ The decomposition of iron oxide is used to produce gas during the manufacture of porous, expanded materials. These materials have very low densities due to the swelling that occurs during the initial rapid heating. Consequently, they are used as additives to provide insulation in concrete, road building, and other construction materials. Iron oxide decomposes at 1150°C according to the following chemical equation:



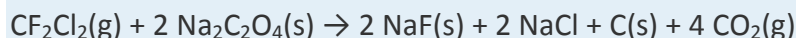
- Explain how this reaction could cause materials containing Fe_2O_3 to swell on heating.
 - If you begin with 15.4 g of Fe_2O_3 , what volume of O_2 gas at STP is produced?
 - What is the volume of the same amount of O_2 gas at 1200°C, assuming a constant pressure of 1.0 atm?
 - If 6.3 L of gas were produced at 1200°C and 1 atm, how many kilograms of Fe_2O_3 were initially used in the reaction? How many kilograms of Fe_3O_4 are produced?
3. ♦ A 70 kg man expends 480 kcal of energy per hour shoveling snow. The oxidation of organic nutrients such as glucose during metabolism liberates approximately 3.36 kcal of energy per gram of oxygen consumed. If air is 21% oxygen, what volume of air at STP is needed to produce enough energy for the man to clear snow from a walkway that requires 35 minutes of shoveling?
4. ♦ Calcium carbonate is an important filler in the processing industry. Its many uses include a reinforcing agent for rubber and improving the whiteness and hiding power of paints. When calcium nitrate is used as a starting material in the manufacture of fertilizers, calcium carbonate is produced according to the following chemical reaction:



- What volume of CO_2 at STP is needed to react completely with 28.0 g of calcium nitrate?
 - What volume of ammonia at STP is needed to react with the amount of calcium nitrate?
 - If this reaction were carried out in Denver, Colorado (pressure = 630 mmHg), what volumes of CO_2 and NH_3 at room temperature (20°C) would be needed?
5. ♦ Calcium nitrate used in the process described in Problem 4 is produced by the reaction of fluoroapatite— $\text{Ca}_5[(\text{PO}_4)_3(\text{F})]$ —with nitric acid:



- a. Your lab is in Denver, Colorado, and you have a cylinder with 8.40 L of CO_2 at room temperature (20°C) and 4.75 atm pressure. What would be the volume of the CO_2 gas at 630 mmHg? How many grams of fluoroapatite could be converted to CaCO_3 using the two reactions and this amount of CO_2 ?
 - b. If 3.50 L of a 0.753 M HF solution was produced during the conversion of fluoroapatite to calcium nitrate, how many grams of calcium carbonate could you produce, assuming 100% efficiency?
 - c. How many liters of ammonia gas at this higher altitude and 20°C are required to convert the calcium nitrate to calcium carbonate *and* to neutralize all of the HF solution?
 - d. If the reaction of fluoroapatite with nitric acid takes place at 330 atm and 80°C , what volumes of NH_3 and CO_2 are needed to convert 20.5 kg of fluoroapatite to calcium carbonate?
6. Mars has an average temperature of -47°C ; a surface pressure of 500 Pa; and an atmosphere that is 95% carbon dioxide, 3% nitrogen, and 2% argon by mass, with traces of other gases. What is the partial pressure (in atmospheres) of each gas in this atmosphere? A 5.0 L sample is returned to Earth and stored in a laboratory at 19°C and 1 atm. What is the volume of this sample?
7. ♦ Chlorofluorocarbons (CFCs) are inert substances that were long used as refrigerants. Because CFCs are inert, when they are released into the atmosphere they are not rapidly destroyed in the lower atmosphere. Instead, they are carried into the stratosphere, where they cause ozone depletion. A method for destroying CFC stockpiles passes the CFC through packed sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) powder at 270°C . The reaction for Freon-12 (CF_2Cl_2) is as follows:



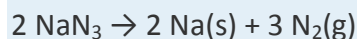
- a. If this reaction produced 11.4 L of CO_2 gas at 21°C and 752 mmHg, what mass of sodium oxalate was consumed in the reaction?
- b. If you had to design a reactor to carry out the reaction at a maximum safe pressure of 10.0 atm while destroying 1.0 kg of Freon-12, what volume reactor would you need?
- c. A 2.50 L reaction vessel is charged with 20.0 atm of Freon-12 and excess sodium oxalate at 20°C . The temperature is increased to 270°C , and the pressure is monitored as the reaction

progresses. What is the initial pressure at 270°C? What is the final pressure when the reaction has gone to completion?

8. ♦ The exhaust from a typical six-cylinder car contains the following average compositions of CO and CO₂ under different conditions (data reported as percent by volume; rpm = rotations per minute):

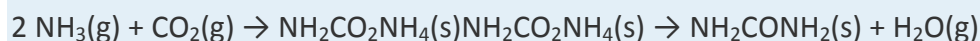
Species	Idling (1000 rpm)	Accelerating (4000 rpm)	Decelerating (800 rpm)
CO	1.0	1.2	0.60
CO ₂	0.80	0.40	0.40

- a. What are the mole fractions of CO and CO₂ under each set of conditions?
- b. If the engine takes in 4.70 L of air at STP mixed with fine droplets of gasoline (C₈H₁₈) with each rotation, how many grams of gasoline are burned per minute?
9. Automobile airbags inflate by the decomposition of sodium azide (NaN₃), which produces sodium metal and nitrogen gas according to the following chemical equation:



How many grams of sodium azide are needed to inflate a 15.0 L airbag at 20°C and 760 mmHg? The density of NaN₃ is 1.847 g/cm³. What is the volume of the gas produced compared to the solid reactant? Suggest a plausible reason to explain why skin burns can result from the inflation of an airbag during an automobile accident.

10. Under basic conditions, the reaction of hydrogen peroxide (H₂O₂) and potassium permanganate (KMnO₄) produces oxygen and manganese dioxide. During a laboratory exercise, you carefully weighed out your sample of KMnO₄. Unfortunately, however, you lost your data just before mixing the KMnO₄ with an H₂O₂ solution of unknown concentration. Devise a method to determine the mass of your sample of KMnO₄ using excess H₂O₂.
11. Carbonated beverages are pressurized with CO₂. In an attempt to produce another bubbly soda beverage, an intrepid chemist attempted to use three other gases: He, N₂, and Xe. Rank the four beverages in order of how fast the drink would go “flat” and explain your reasoning. Which beverage would have the shortest shelf life (i.e., how long will an *unopened* bottle still be good)? Explain your answer.
12. ♦ Urea is synthesized industrially by the reaction of ammonia and carbon dioxide to produce ammonium carbamate, followed by dehydration of ammonium carbamate to give urea and water. This process is shown in the following set of chemical equations:



- a. A 50.0 L reaction vessel is charged with 2.5 atm of ammonia and 2.5 atm of CO_2 at 50°C , and the vessel is then heated to 150°C . What is the pressure in the vessel when the reaction has gone to completion? If the vessel is then cooled to 20°C , what is the pressure?
- b. An aqueous solution of urea and water is drained from the reaction vessel. What is the molarity of the urea solution? Industrially, this reaction is actually carried out at pressures ranging from 130 to 260 atm and temperatures of approximately 180°C . Give a plausible reason for using these extreme conditions.
13. Explain what happens to the temperature, the volume, or the pressure of a gas during each operation and give the direction of heat flow, if any.
- a. The gas is allowed to expand from V_1 to V_2 ; a heat transfer occurs to maintain a constant gas temperature.
- b. The gas is allowed to expand from V_2 to V_3 with no concomitant heat transfer.
- c. The gas is compressed from V_3 to V_4 ; a heat transfer occurs to maintain a constant gas temperature.
- d. The gas is compressed from V_4 to V_1 ; no heat transfer occurs.

These four processes constitute the cycle used in refrigeration, in which a gas such as Freon is alternately compressed and allowed to expand in the piston of a compressor. Which step eventually causes the food in a refrigerator to cool? Where does the thermal energy go that was removed in the cooling process?

ANSWERS

1. 5.9 g oxalic acid, 7.8 L
- 2.
3. 278 L

Chapter 11

Liquids

In Chapter 10 "Gases", you learned that attractive intermolecular forces cause most gases to condense to liquids at high pressure, low temperature, or both. Substances that normally are liquids are held together by exactly the same forces that are responsible for the liquefaction of gases. One such substance is water, the solvent in which all biochemical reactions take place. Because of its thermal properties, water also modulates Earth's temperature, maintaining a temperature range suitable for life. Other liquids are used to manufacture objects that we use every day—for example, a solid material is converted to a liquid, the liquid is injected into a mold, and it is then solidified into complex shapes under conditions that are carefully controlled. To understand such processes, our study of the macroscopic properties of matter must include an understanding of the properties of liquids and the interconversion of the three states of matter: gases, liquids, and solids.

In this chapter, we look more closely at the intermolecular forces that are responsible for the properties of liquids, describe some of the unique properties of liquids compared with the other states of matter, and then consider changes in state between liquids and gases or solids. By the end of the chapter, you will understand what is happening at the molecular level when you dry yourself with a towel, why you feel cold when you come out of the water, why ice is slippery, and how it is possible to decaffeinate coffee without removing important flavor components. You will also learn how liquid crystal display (LCD) devices in electronic devices function, and how adhesive strips used to measure body temperature change color to indicate a fever.

11.1 The Kinetic Molecular Description of Liquids

LEARNING OBJECTIVE

1. To be familiar with the kinetic molecular description of liquids.

The kinetic molecular theory of gases described in Chapter 10 "Gases" gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

Density

The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance.

Densities of liquids are therefore more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.

Molecular Order

Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids discussed in Chapter 8 "Ionic versus Covalent Bonding", Section 8.2 "Ionic Bonding", the molecules in liquids are not arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.

Compressibility

Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.

Thermal Expansion

The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table 11.1 "The Density of Water at Various Temperatures" that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

Table 11.1 The Density of Water at Various Temperatures

T ($^\circ\text{C}$)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

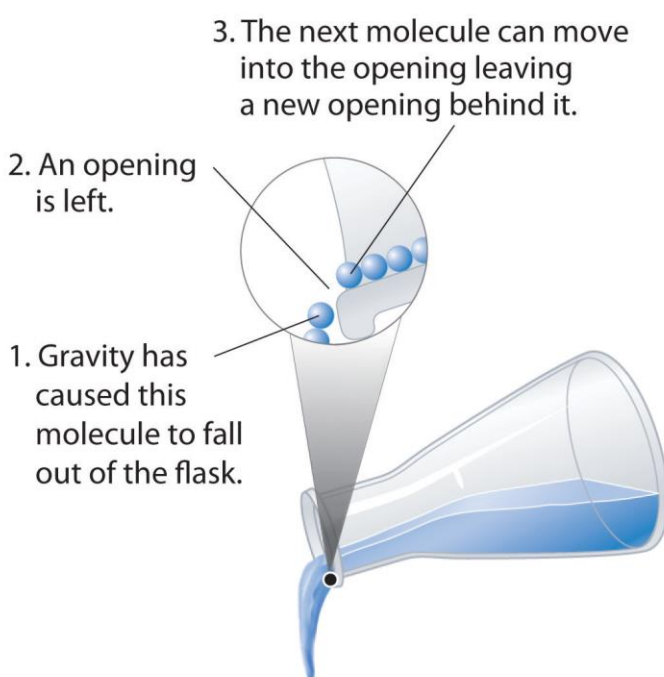
Diffusion

Molecules in liquids diffuse because they are in constant motion (Figure 11.1 "Molecular Diffusion in a Liquid"). A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.

Fluidity

Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 11.2 "Why Liquids Flow").

Figure 11.2 Why Liquids Flow



Molecules in a liquid are in constant motion.

Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container.

Summary

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described in Chapter 10 "Gases". This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers.

KEY TAKEAWAY

- The kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

CONCEPTUAL PROBLEMS

1. A liquid, unlike a gas, is virtually *incompressible*. Explain what this means using macroscopic and microscopic descriptions. What general physical properties do liquids share with solids? What properties do liquids share with gases?
2. Using a kinetic molecular approach, discuss the differences and similarities between liquids and gases with regard to
 - a. thermal expansion.
 - b. fluidity.
 - c. diffusion.
3. How must the ideal gas law be altered to apply the kinetic molecular theory of gases to liquids? Explain.
4. Why are the root mean square speeds of molecules in liquids less than the root mean square speeds of molecules in gases?

11.2 Intermolecular Forces

LEARNING OBJECTIVE

1. To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids but are more similar to solids. In contrast to *intramolecular* forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *intermolecular* forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

Note the Pattern

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law, see Chapter 10 "Gases", Section 10.8 "The Behavior of Real Gases".)

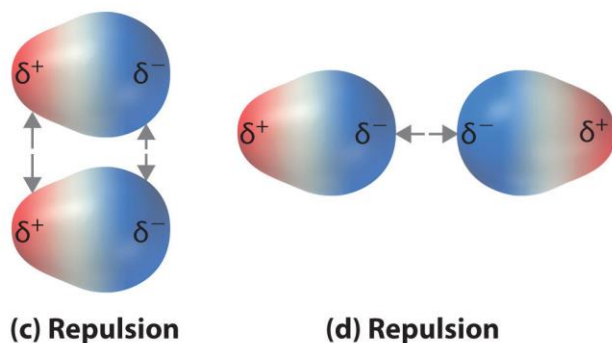
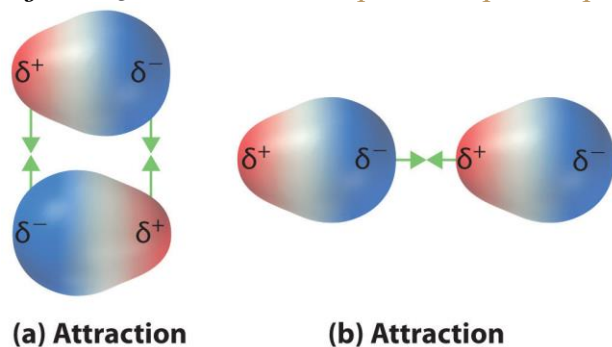
In this section, we explicitly consider three kinds of intermolecular interactions:^[1] *dipole–dipole interactions*, *London dispersion forces*, and *hydrogen bonds*. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Recall from Chapter 9 "Molecular Geometry and Covalent Bonding Models" that polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 11.3 "Attractive and Repulsive Dipole–Dipole Interactions". These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 11.3 "Attractive and Repulsive Dipole–Dipole Interactions"). Hence dipole–dipole interactions, such as those in part (b) in Figure 11.3 "Attractive and Repulsive Dipole–Dipole Interactions", are *attractive intermolecular interactions*, whereas those in part (d) in Figure 11.3 "Attractive and Repulsive Dipole–Dipole Interactions" are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 11.4 "Both Attractive and

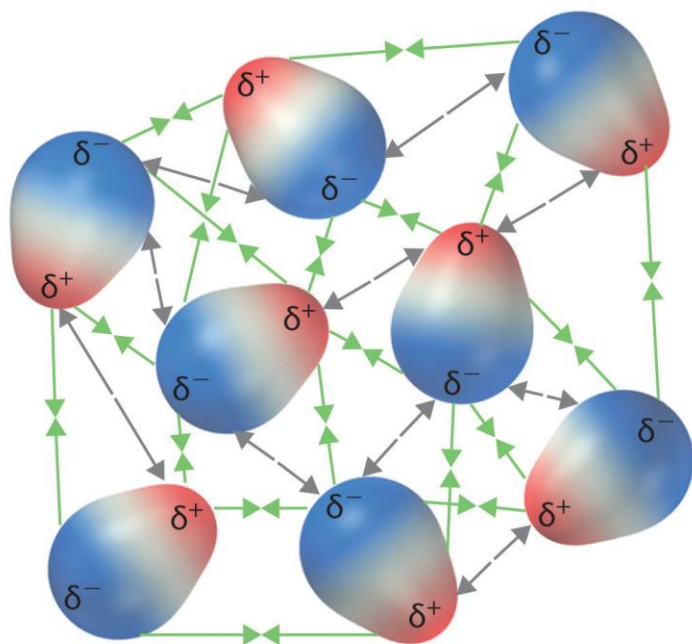
Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules". On average, however, the attractive interactions dominate.

Figure 11.3 *Attractive and Repulsive Dipole–Dipole Interactions*



(a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

Figure 11.4 *Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules*



Attraction 
 Repulsion 

Because each end of a dipole possesses only a

fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ± 1 , or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions we considered in **Chapter 8 "Ionic versus Covalent Bonding"**. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6 , or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in **Table 11.2 "Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass"**. Using what we learned in **Chapter 9 "Molecular Geometry and Covalent Bonding Models"** about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

Table 11.2 Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

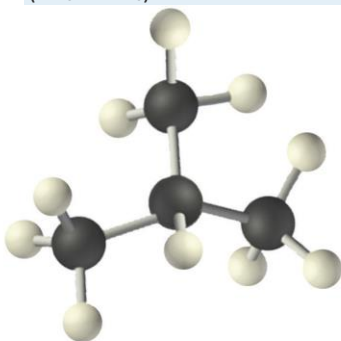
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C ₃ H ₆ (cyclopropane)	42	0	240
CH ₃ OCH ₃ (dimethyl ether)	46	1.30	248
CH ₃ CN (acetonitrile)	41	3.9	355

Note the Pattern

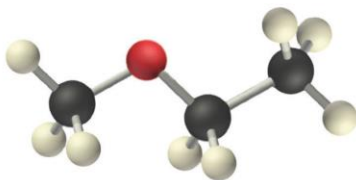
The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

EXAMPLE 1

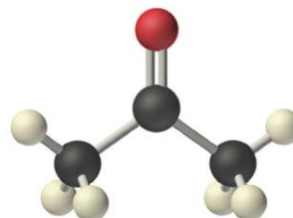
Arrange ethyl methyl ether (CH₃OCH₂CH₃), 2-methylpropane [isobutane, (CH₃)₂CHCH₃], and acetone (CH₃COCH₃) in order of increasing boiling points. Their structures are as follows:



2-Methylpropane



Ethyl methyl ether



Acetone

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but

nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O ; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = -11.7°C , and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($\text{CH}_3\text{SC}_2\text{H}_5$), dimethyl sulfoxide [$(\text{CH}_3)_2\text{S}=\text{O}$], and 2-methylbutane [isopentane, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$] in order of decreasing boiling points.

Answer: dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = -128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 11.3 "Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds").

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

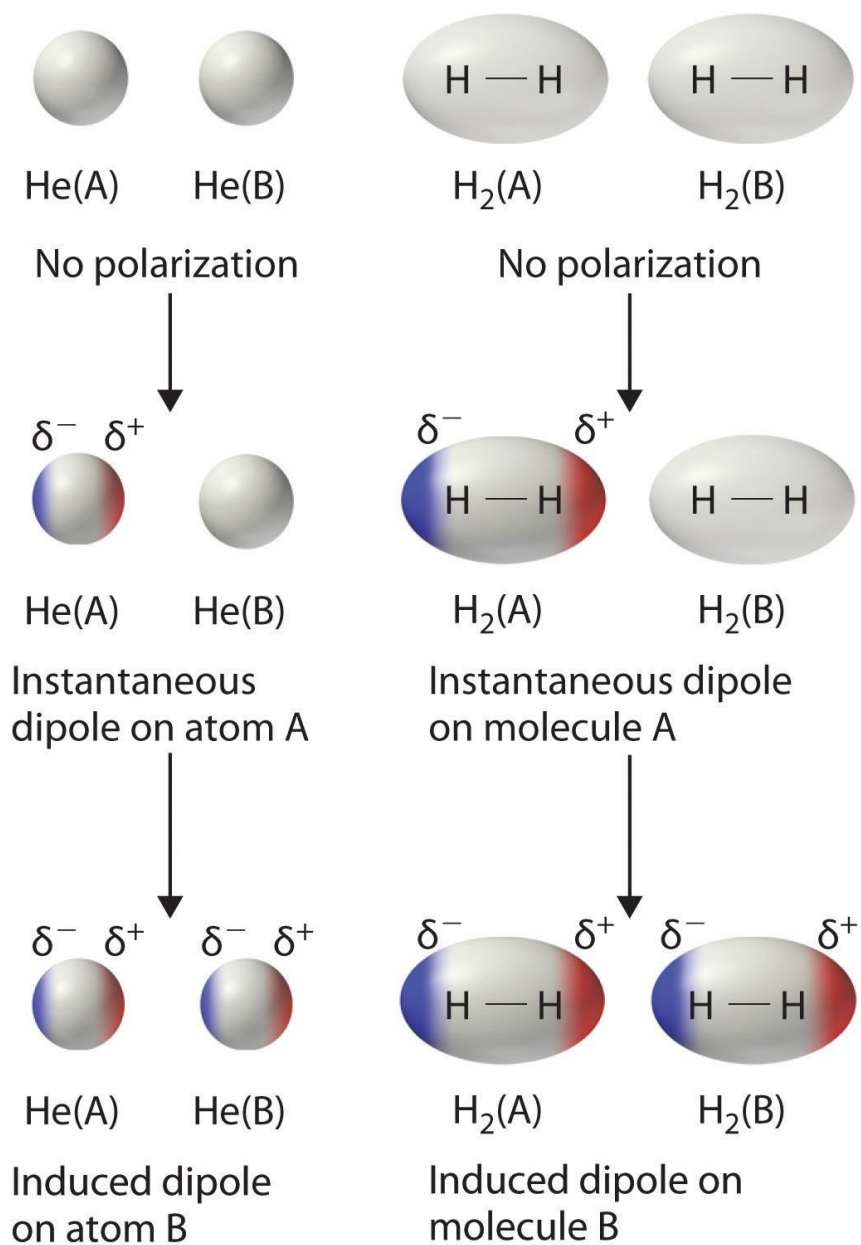
Table 11.3 Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point ($^\circ\text{C}$)	Boiling Point ($^\circ\text{C}$)
Ar	40	-189.4	-185.9

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Xe	131	-111.8	-108.1
N ₂	28	-210	-195.8
O ₂	32	-218.8	-183.0
F ₂	38	-219.7	-188.1
I ₂	254	113.7	184.4
CH ₄	16	-182.5	-161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 11.5 "Instantaneous Dipole Moments", the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6 , or 64-fold.

Figure 11.5 *Instantaneous Dipole Moments*



(a)

(b)

The formation of an instantaneous

dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 11.5 "Instantaneous Dipole Moments", tends to become more pronounced as atomic and molecular masses increase (Table 11.3 "Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds"). For example, Xe boils at -108.1°C ,

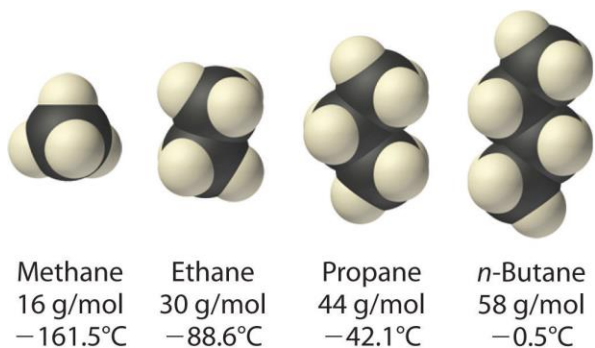
whereas He boils at -269°C . The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1s electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. (For more information on shielding, see Chapter 7 "The Periodic Table and Periodic Trends", Section 7.2 "Sizes of Atoms and Ions".) As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

Note the Pattern

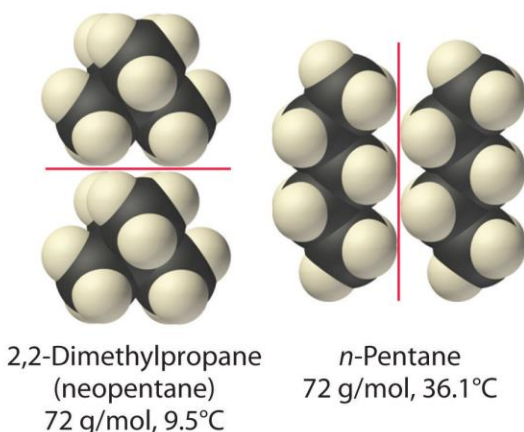
For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles, as we shall see when we discuss solutions in Chapter 13 "Solutions". Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 11.6 "Mass and Surface Area Affect the Strength of London Dispersion Forces"). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 11.6 "Mass and Surface Area Affect the Strength of London Dispersion Forces" shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12} . Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

Figure 11.6 *Mass and Surface Area Affect the Strength of London Dispersion Forces*



(a) Increasing mass and boiling point



(b) Increasing surface area and boiling point

(a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

EXAMPLE 2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(\text{CH}_3)_2\text{CHCH}_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (-42.1°C) < 2-methylpropane (-11.7°C) < *n*-butane (-0.5°C) < *n*-pentane (36.1°C).

Exercise

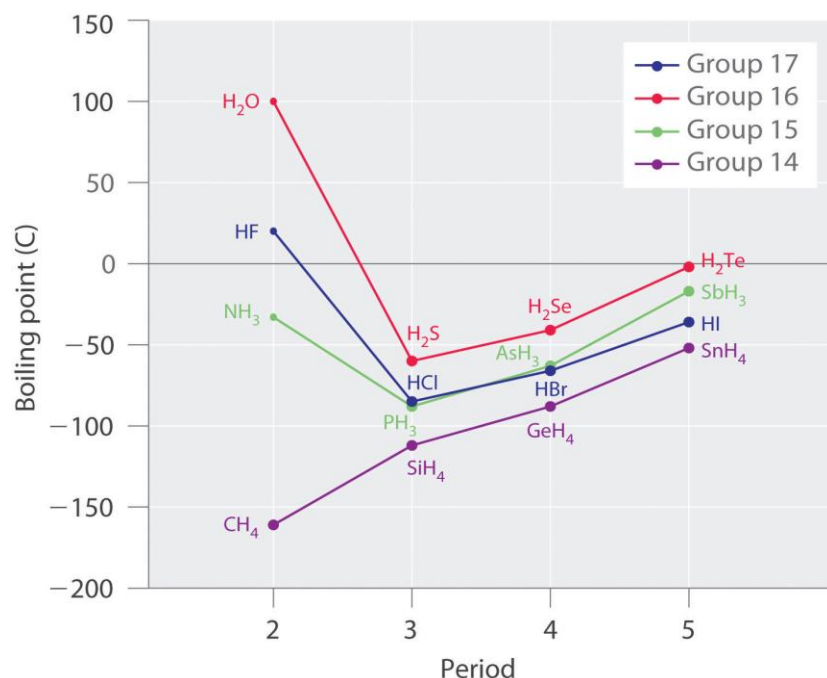
Arrange GeH_4 , SiCl_4 , SiH_4 , CH_4 , and GeCl_4 in order of decreasing boiling points.

Answer: GeCl_4 (87°C) > SiCl_4 (57.6°C) > GeH_4 (-88.5°C) > SiH_4 (-111.8°C) > CH_4 (-161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 11.7 "The Effects of Hydrogen Bonding on Boiling Points". Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of -130°C for water! Imagine the implications for life on Earth if water boiled at -130°C rather than 100°C .

Figure 11.7 *The Effects of Hydrogen Bonding on Boiling Points*

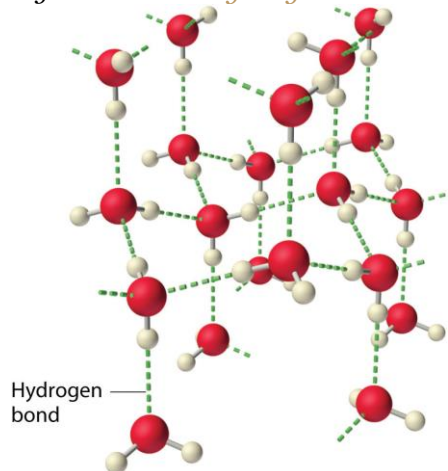


These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH₃, and H₂O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 11.8 "The Hydrogen-Bonded Structure of Ice". A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from

the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two $O \cdots H$ hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

Figure 11.8 The Hydrogen-Bonded Structure of Ice



Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Note the Pattern

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” (we will discuss how antifreeze works in Chapter 13 “Solutions”) and why unprotected pipes in houses break if they are allowed to freeze.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound.

Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3 . Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

EXAMPLE 3

Considering CH_3OH , C_2H_6 , Xe , and $(\text{CH}_3)_3\text{N}$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

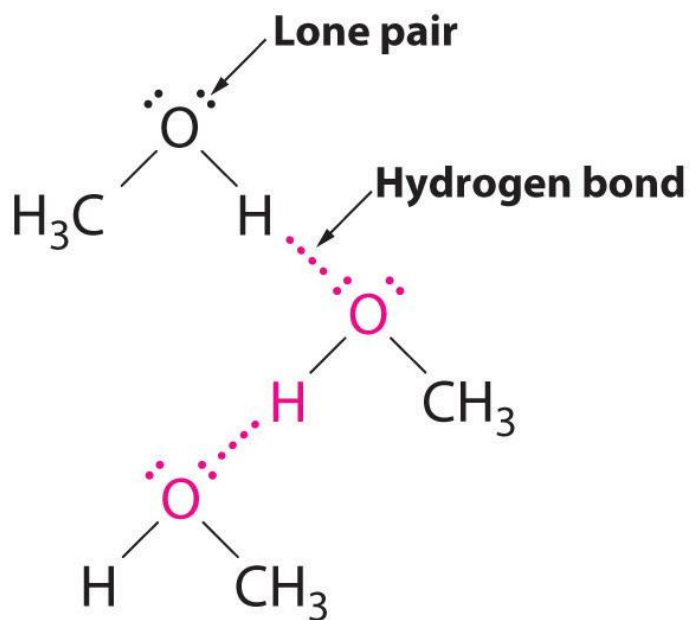
A Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(\text{CH}_3)_3\text{N}$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:

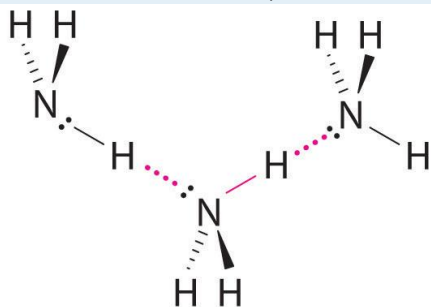


Hydrogen bonding in methanol

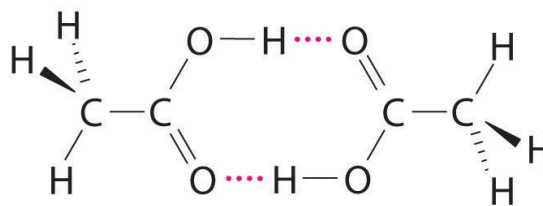
Exercise

Considering $\text{CH}_3\text{CO}_2\text{H}$, $(\text{CH}_3)_3\text{N}$, NH_3 , and CH_3F , which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer: $\text{CH}_3\text{CO}_2\text{H}$ and NH_3 ;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

EXAMPLE 4

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl , He , Ar , and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N₂O have very similar molar masses (40 and 44 g/mol, respectively), but N₂O is polar while Ar is not. Consequently, N₂O should have a higher boiling point. A C₆₀ molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N₂O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C₆₀ should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (–269°C) < Ar (–185.7°C) < N₂O (–88.5°C) < C₆₀ (>280°C) < NaCl (1465°C).

Exercise

Arrange 2,4-dimethylheptane, Ne, CS₂, Cl₂, and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS₂ (46.6°C) > Cl₂ (–34.6°C) > Ne (–246°C)

Summary

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions.

Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be

more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong $O \cdots H$ hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

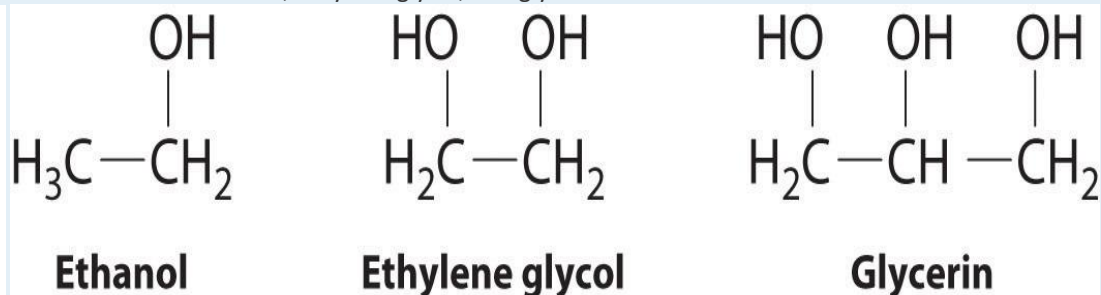
KEY TAKEAWAY

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

CONCEPTUAL PROBLEMS

1. What is the main difference between intramolecular interactions and intermolecular interactions? Which is typically stronger? How are changes of state affected by these different kinds of interactions?
2. Describe the three major kinds of intermolecular interactions discussed in this chapter and their major features. The hydrogen bond is actually an example of one of the other two types of interaction. Identify the kind of interaction that includes hydrogen bonds and explain why hydrogen bonds fall into this category.
3. Which are stronger—dipole–dipole interactions or London dispersion forces? Which are likely to be more important in a molecule with heavy atoms? Explain your answers.
4. Explain why hydrogen bonds are unusually strong compared to other dipole–dipole interactions. How does the strength of hydrogen bonds compare with the strength of covalent bonds?
5. Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?
6. Describe the effect of polarity, molecular mass, and hydrogen bonding on the melting point and boiling point of a substance.
7. Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?
8. Using acetic acid as an example, illustrate both attractive and repulsive intermolecular interactions. How does the boiling point of a substance depend on the magnitude of the repulsive intermolecular interactions?

9. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
10. The boiling points of the anhydrous hydrogen halides are as follows: HF, 19°C; HCl, -85°C; HBr, -67°C; and HI, -34°C. Explain any trends in the data, as well as any deviations from that trend.
11. Identify the most important intermolecular interaction in each of the following.
- SO₂
 - HF
 - CO₂
 - CCl₄
 - CH₂Cl₂
12. Identify the most important intermolecular interaction in each of the following.
- LiF
 - I₂
 - ICl
 - NH₃
 - NH₂Cl
13. Would you expect London dispersion forces to be more important for Xe or Ne? Why? (The atomic radius of Ne is 38 pm, whereas that of Xe is 108 pm.)
14. Arrange Kr, Cl₂, H₂, N₂, Ne, and O₂ in order of increasing polarizability. Explain your reasoning.
15. Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.
16. The structures of ethanol, ethylene glycol, and glycerin are as follows:



Arrange these compounds in order of increasing boiling point. Explain your rationale.

17. Do you expect the boiling point of H_2S to be higher or lower than that of H_2O ? Justify your answer.
18. Ammonia (NH_3), methylamine (CH_3NH_2), and ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) are gases at room temperature, while propylamine ($\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$) is a liquid at room temperature. Explain these observations.
19. Why is it not advisable to freeze a sealed glass bottle that is completely filled with water? Use both macroscopic and microscopic models to explain your answer. Is a similar consideration required for a bottle containing pure ethanol? Why or why not?
20. Which compound in the following pairs will have the higher boiling point? Explain your reasoning.
 - a. NH_3 or PH_3
 - b. ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) or ethanol
 - c. 2,2-dimethylpropanol [$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$] or *n*-butanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)
21. Some recipes call for vigorous boiling, while others call for gentle simmering. What is the difference in the temperature of the cooking liquid between boiling and simmering? What is the difference in energy input?
22. Use the melting of a metal such as lead to explain the process of melting in terms of what is happening at the molecular level. As a piece of lead melts, the temperature of the metal remains constant, even though energy is being added continuously. Why?
23. How does the O–H distance in a hydrogen bond in liquid water compare with the O–H distance in the covalent O–H bond in the H_2O molecule? What effect does this have on the structure and density of ice?
24.
 - a. Explain why the hydrogen bonds in liquid HF are stronger than the corresponding intermolecular $\text{H} \cdots \text{I}$ interactions in liquid HI.
 - b. In which substance are the individual hydrogen bonds stronger: HF or H_2O ? Explain your reasoning.
 - c. For which substance will hydrogen bonding have the greater effect on the boiling point: HF or H_2O ? Explain your reasoning.

ANSWERS

- 1.
- 2.
- 3.
- 4.

5. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.
- 6.
- 7.
- 8.
9. As the atomic mass of the halogens increases, so does the number of electrons and the average distance of those electrons from the nucleus. Larger atoms with more electrons are more easily polarized than smaller atoms, and the increase in polarizability with atomic number increases the strength of London dispersion forces. These intermolecular interactions are strong enough to favor the condensed states for bromine and iodine under normal conditions of temperature and pressure.
- 10.
- 11.
- a. The V-shaped SO_2 molecule has a large dipole moment due to the polar $\text{S}=\text{O}$ bonds, so dipole–dipole interactions will be most important.
- b. The $\text{H}-\text{F}$ bond is highly polar, and the fluorine atom has three lone pairs of electrons to act as hydrogen bond acceptors; hydrogen bonding will be most important.
- c. Although the $\text{C}=\text{O}$ bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.
- d. This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.
- e. This molecule has a small dipole moment, as well as polarizable Cl atoms. In such a case, dipole–dipole interactions and London dispersion forces are often comparable in magnitude.
- 12.
- 13.
- 14.
15. Water has two polar $\text{O}-\text{H}$ bonds with H atoms that can act as hydrogen bond donors, plus two lone pairs of electrons that can act as hydrogen bond acceptors, giving a net of *four* hydrogen bonds per H_2O molecule. Although methanol also has two lone pairs of electrons on oxygen that can act as hydrogen bond acceptors,

it only has one O–H bond with an H atom that can act as a hydrogen bond donor. Consequently, methanol can only form *two* hydrogen bonds per molecule on average, versus four for water. Hydrogen bonding therefore has a much greater effect on the boiling point of water.

16.

17.

18.

19.

20.

21. Vigorous boiling causes more water molecule to escape into the vapor phase, but does not affect the temperature of the liquid. Vigorous boiling requires a higher energy input than does gentle simmering.

[1] There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. (For more information on ionic bonding, see Chapter 8 "Ionic versus Covalent Bonding". For more information on the dissolution of ionic substances, see Chapter 4 "Reactions in Aqueous Solution" and Chapter 5 "Energy Changes in Chemical Reactions".)

11.3 Unique Properties of Liquids

LEARNING OBJECTIVE

1. To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions: surface tension, capillary action, and viscosity.

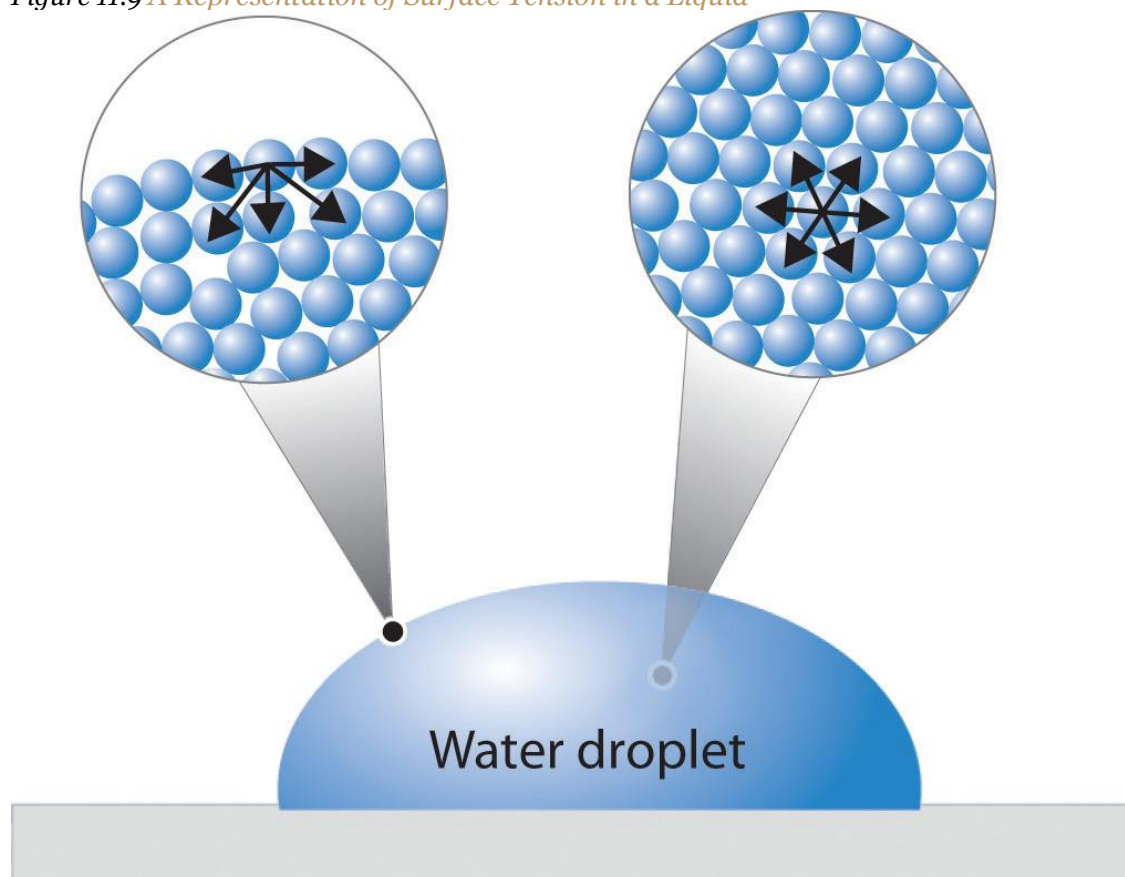
Surface Tension

We stated in Section 11.1 "The Kinetic Molecular Description of Liquids" that liquids tend to adopt the shapes of their containers. Why, then, do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces.

Figure 11.9 "A Representation of Surface Tension in a Liquid" presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert

attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads (see the chapter opener photo). A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

Figure 11.9 A Representation of Surface Tension in a Liquid



Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water (part (a) in Figure 11.10 "The Effects of the High Surface Tension of Liquid Water"). Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where $1 \text{ dyn} = 1 \times 10^{-5} \text{ N}$. The values of the surface tension of some representative liquids are listed in Table 11.4 "Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids". Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding, which we will discuss in more detail in Chapter 12 "Solids".

Table 11.4 Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3} \text{ J/m}^2$)	Viscosity ($\text{mPa}\cdot\text{s}$)	Vapor Pressure (mmHg)	Normal Boiling Point ($^{\circ}\text{C}$)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
<i>n</i> -hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				

Substance	Surface Tension ($\times 10^{-3} \text{ J/m}^2$)	Viscosity (mPa·s)	Vapor Pressure (mmHg)	Normal Boiling Point ($^{\circ}\text{C}$)
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0 $^{\circ}\text{C}$	75.6	1.79	4.6	—
20 $^{\circ}\text{C}$	72.8	1.00	17.5	—
60 $^{\circ}\text{C}$	66.2	0.47	149	—
100 $^{\circ}\text{C}$	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (*acapillary*), as shown in Figure 11.11 "The Phenomenon of Capillary Action". When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

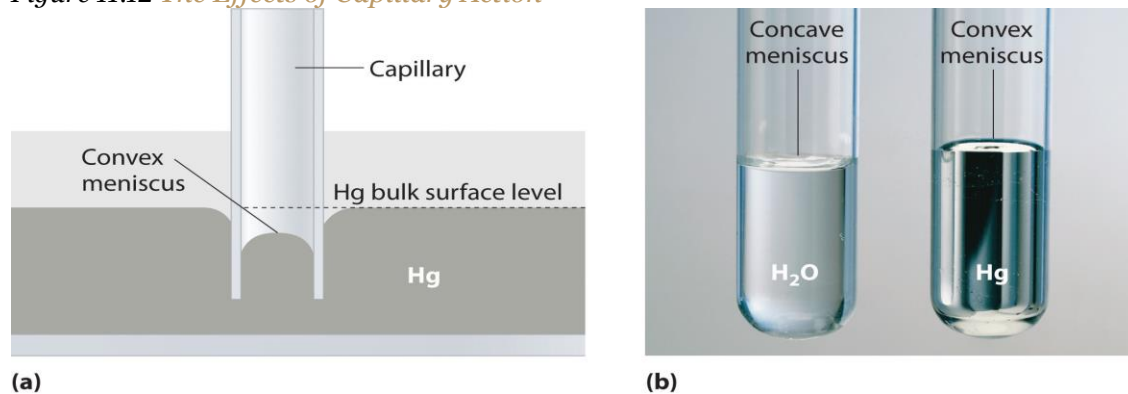
Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case

for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure 11.12 "The Effects of Capillary Action"). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (part (b) in Figure 11.12 "The Effects of Capillary Action").

Note the Pattern

Polar substances are drawn up a glass capillary and generally have a concave meniscus.

Figure 11.12 The Effects of Capillary Action

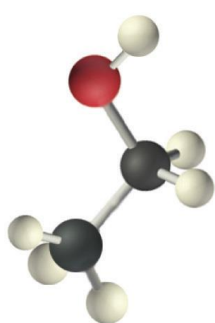


(a) This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is lower than the level of the liquid outside the tube. (b) Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus.

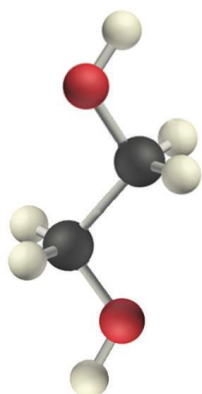
Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action.

Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity



Ethanol



Ethylene glycol

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as

gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa·s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.4 "Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids" and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

Note the Pattern

Viscosity increases as intermolecular interactions or molecular size increases.

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures. The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity. So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

EXAMPLE 5

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A Identify the cohesive forces in the motor oil.

B Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution:

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains. **B** Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer: Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

Surface tension is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

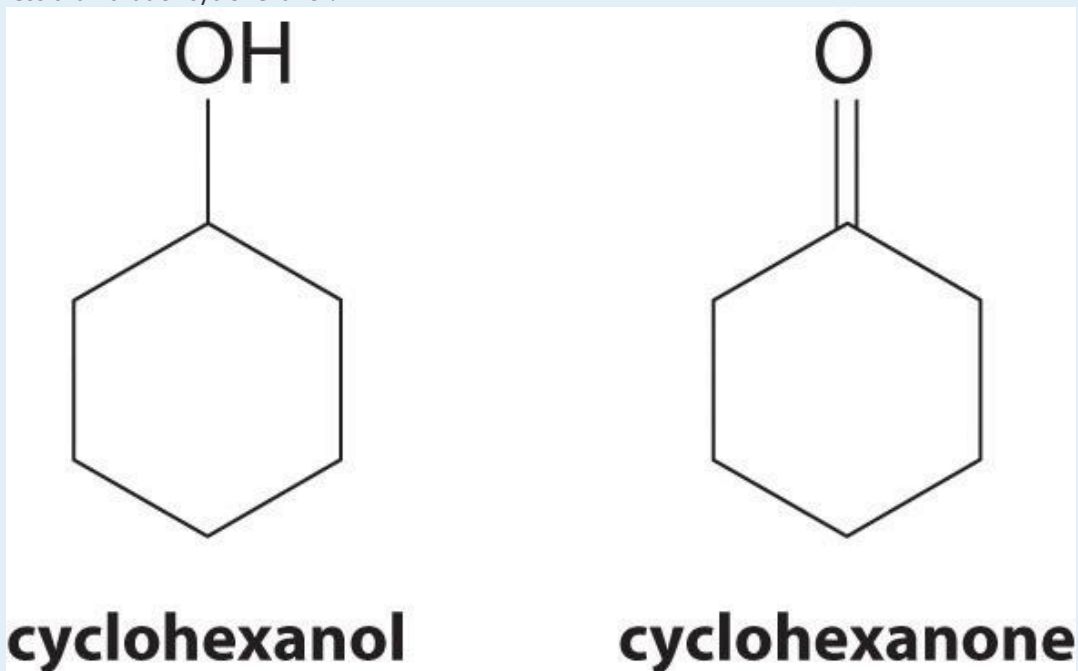
KEY TAKEAWAY

- Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions.

CONCEPTUAL PROBLEMS

1. Why is a water droplet round?

2. How is the environment of molecules on the surface of a liquid droplet different from that of molecules in the interior of the droplet? How is this difference related to the concept of surface tension?
3. Explain the role of intermolecular and intramolecular forces in surface tension.
4. A mosquito is able to walk across water without sinking, but if a few drops of detergent are added to the water, the insect will sink. Why?
5. Explain how soaps or surfactants decrease the surface tension of a liquid. How does the meniscus of an aqueous solution in a capillary change if a surfactant is added? Illustrate your answer with a diagram.
6. Of CH_2Cl_2 , hexane, and ethanol, which has the lowest viscosity? Which has the highest surface tension? Explain your reasoning in each case.
7. At 25°C , cyclohexanol has a surface tension of 32.92 mN/m^2 , whereas the surface tension of cyclohexanone, which is very similar chemically, is only 25.45 mN/m^2 . Why is the surface tension of cyclohexanone so much less than that of cyclohexanol?



8. What is

the relationship between

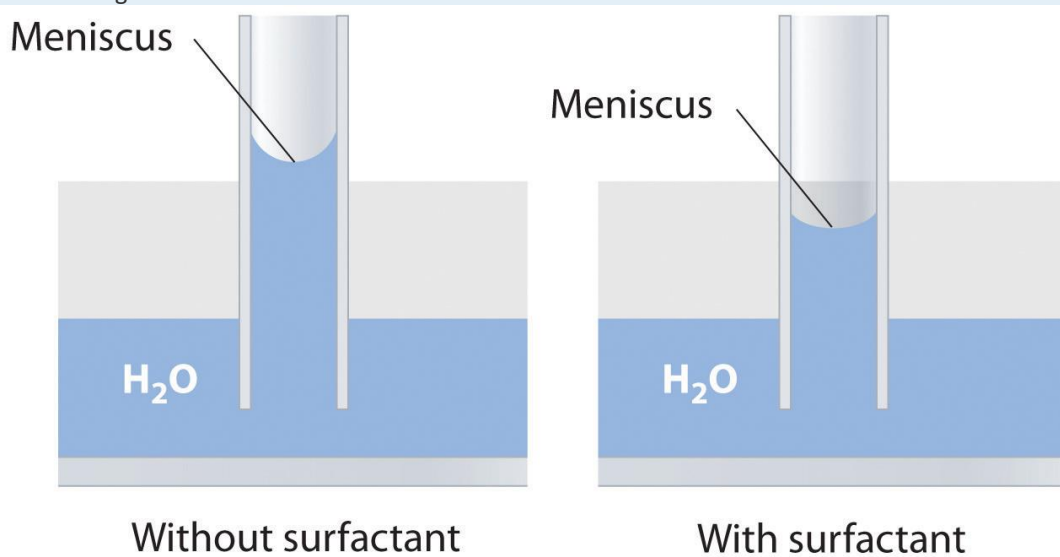
- a. surface tension and temperature?
- b. viscosity and temperature?

Explain your answers in terms of a microscopic picture.

8. What two opposing forces are responsible for capillary action? How do these forces determine the shape of the meniscus?
9. Which of the following liquids will have a concave meniscus in a glass capillary? Explain your reasoning.
- pentane
 - diethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$)
 - carbon tetrachloride
10. How does viscosity depend on molecular shape? What molecular features make liquids highly viscous?

ANSWERS

5. Adding a soap or a surfactant to water disrupts the attractive intermolecular interactions between water molecules, thereby decreasing the surface tension. Because water is a polar molecule, one would expect that a soap or a surfactant would also disrupt the attractive interactions responsible for adhesion of water to the surface of a glass capillary. As shown in the sketch, this would decrease the height of the water column inside the capillary, as well as making the meniscus less concave.



7. As the structures indicate, cyclohexanol is a polar substance that can engage in hydrogen bonding, much like methanol or ethanol; consequently, it is expected to have a higher surface tension due to stronger intermolecular interactions.

8. Cohesive forces are the intermolecular forces that hold the molecules of the liquid together, while adhesive forces are the attractive forces between the molecules of the liquid and the walls of the capillary. If the adhesive forces are stronger than the cohesive forces, the liquid is pulled up into the capillary and the meniscus is concave. Conversely, if the cohesive forces are stronger than the adhesive forces, the level of the liquid inside the capillary will be lower than the level outside the capillary, and the meniscus will be convex.

9. Viscous substances often consist of molecules that are much longer than they are wide and whose structures are often rather flexible. As a result, the molecules tend to become tangled with one another (much like overcooked spaghetti), which decreases the rate at which they can move through the liquid.

NUMERICAL PROBLEMS

1. The viscosities of five liquids at 25°C are given in the following table. Explain the observed trends in viscosity.

Compound	Molecular Formula	Viscosity (mPa·s)
benzene	C ₆ H ₆	0.604
aniline	C ₆ H ₅ NH ₂	3.847
1,2-dichloroethane	C ₂ H ₄ Cl ₂	0.779
heptane	C ₇ H ₁₆	0.357
1-heptanol	C ₇ H ₁₅ OH	5.810

2. The following table gives values for the viscosity, boiling point, and surface tension of four substances.

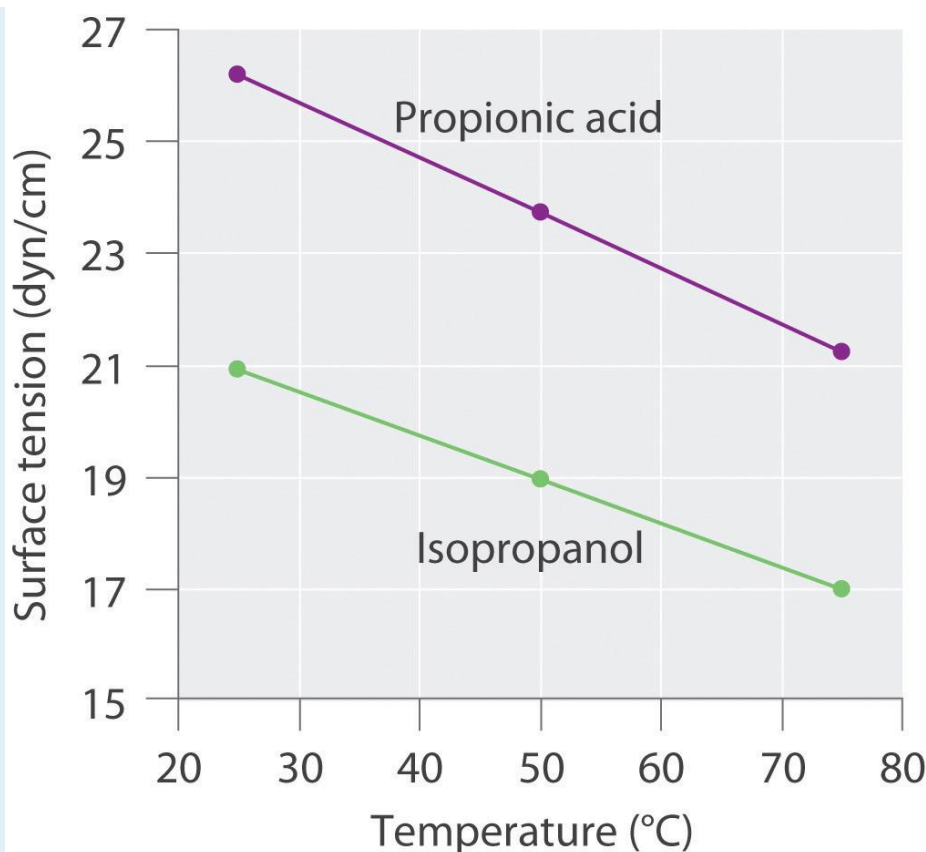
Examine these data carefully to see whether the data for each compound are internally consistent and point out any obvious errors or inconsistencies. Explain your reasoning.

Compound	Viscosity (mPa·s at 20°C)	Boiling Point (°C)	Surface Tension (dyn/cm at 25°C)
A	0.41	61	27.16
B	0.55	65	22.55
C	0.92	105	36.76
D	0.59	110	28.53

3. Surface tension data (in dyn/cm) for propanoic acid (C₃H₆O₂), and 2-propanol (C₃H₈O), as a function of temperature, are given in the following table. Plot the data for each compound and explain the differences between the two graphs. Based on these data, which molecule is more polar?

Compound	25°C	50°C	75°C
propanoic acid	26.20	23.72	21.23
2-propanol	20.93	18.96	16.98

ANSWER



3.

The plots of surface

tension versus temperature for propionic acid and isopropanol have essentially the same slope, but at all temperatures the surface tension of propionic acid is about 30% greater than for isopropanol. Because surface tension is a measure of the cohesive forces in a liquid, these data suggest that the cohesive forces for propionic acid are significantly greater than for isopropanol. Both substances consist of polar molecules with similar molecular masses, and the most important intermolecular interactions are likely to be dipole–dipole interactions. Consequently, these data suggest that propionic acid is more polar than isopropanol.

11.4 Vapor Pressure

LEARNING OBJECTIVE

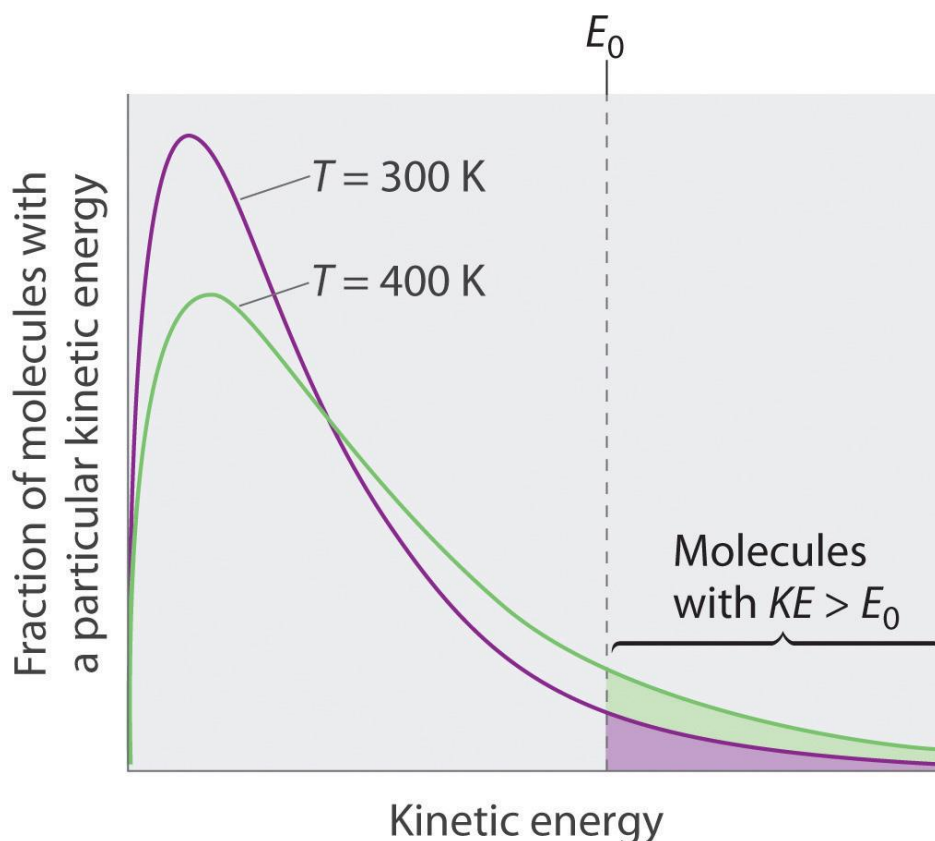
1. To know how and why the vapor pressure of a liquid varies with temperature.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (KE) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure 11.13 "The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures"), just as we did for a gas (Figure 10.19 "The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses"). As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0 . The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

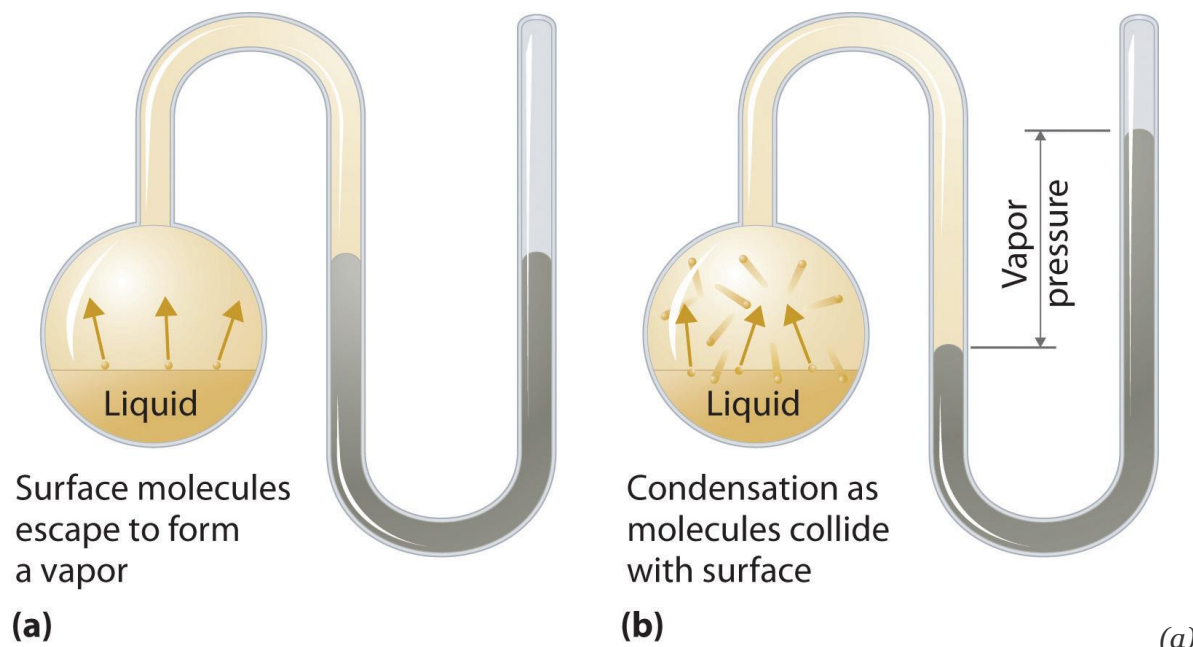
Figure 11.13 The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures



Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 11.14 "Vapor Pressure". When a liquid is introduced into an evacuated chamber (part (a) in Figure 11.14 "Vapor Pressure"), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

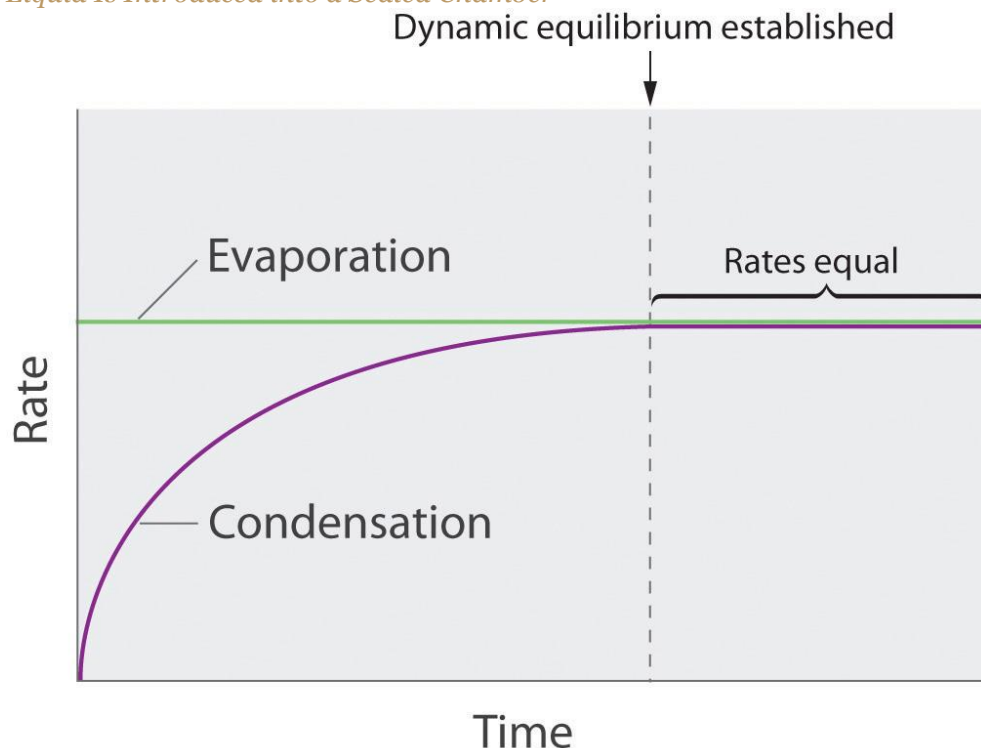
Figure 11.14 Vapor Pressure



When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant.

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 11.14 "Vapor Pressure"). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 11.15 "The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber".

Figure 11.15 *The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber*



The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation.

Equilibrium Vapor Pressure

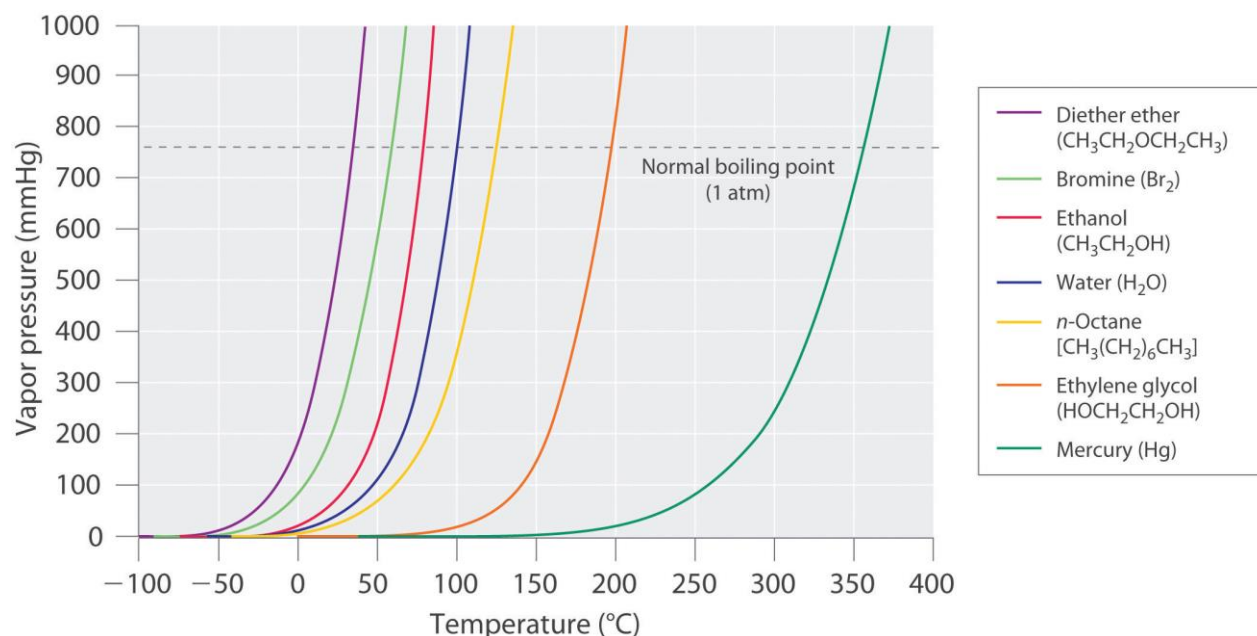
Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and

evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Table 11.4 "Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids") are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point (Table 11.4 "Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids"). It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 11.16 "The Vapor Pressures of Several Liquids as a Function of Temperature". Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

Figure 11.16 The Vapor Pressures of Several Liquids as a Function of Temperature



The point at which the vapor pressure curve crosses the $P = 1 \text{ atm}$ line (dashed) is the normal boiling point of the liquid.

Note the Pattern

Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.

The exponential rise in vapor pressure with increasing temperature in Figure 11.16 "The Vapor Pressures of Several Liquids as a Function of Temperature" allows us to use natural logarithms to express the nonlinear relationship as a linear one.^[1]

Equation 11.1

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + C$$

where $\ln P$ is the natural logarithm of the vapor pressure, ΔH_{vap} is the **enthalpy of vaporization**, R is the universal gas constant [$8.314 \text{ J}/(\text{mol}\cdot\text{K})$], T is the temperature in kelvins, and C is the y -intercept, which is a constant for any given line. A plot of $\ln P$ versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{\text{vap}}/R$. Equation 11.1, called the Clausius–Clapeyron equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at two temperatures and insert the values of P and T for these points into Equation 11.2, which is derived from the Clausius–Clapeyron equation:

Equation 11.2

$$\ln(P_2/P_1) = -\Delta H_{\text{vap}}/R(1/T_2 - 1/T_1)$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1 , we can use Equation 11.2 to calculate the vapor pressure P_2 at any other temperature T_2 , as shown in Example 6.

EXAMPLE 6

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

$T (^{\circ}\text{C})$	80.0	100	120	140
$P (\text{torr})$	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A Use Equation 11.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.

B Substitute the calculated value of ΔH_{vap} into Equation 11.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 11.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 11.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvins because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 11.2 gives

$$\ln(0.7457 \text{ torr} / 0.0888 \text{ torr}) = - \Delta H_{\text{vap}} / (8.314 \text{ J} / (\text{mol} \cdot \text{K}) [1/(120 + 273) \text{ K} - 1/(80.0 + 273) \text{ K}])$$

$$\ln(8.398) = - \Delta H_{\text{vap}} / (8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - 1/(2.88 \times 10^{-4} \text{ K}^{-1}))$$

$$2.13 = - \Delta H_{\text{vap}} (- 0.346 \times 10^{-4}) \text{ J} \cdot \text{mol}^{-1} / \Delta H_{\text{vap}}$$

$$= 61,400 \text{ J} / \text{mol} = 61.4 \text{ kJ} / \text{mol}$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln(P_2 / 0.0888 \text{ torr}) = - 61,400 \text{ J} \cdot \text{mol}^{-1} / (8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - 1/(160 + 273) \text{ K} - 1/(80.0 + 273) \text{ K}) = 3.86$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln(P_2 / 0.0888 \text{ torr}) = 3.86$$

$$P_2 / 0.0888 \text{ torr} = e^{3.86} = 47.5$$

$$P_2 = 4.21 \text{ torr}$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

Exercise

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer: 1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 11.16 "The Vapor Pressures of Several Liquids as a Function of Temperature" are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water

boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C .

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C , respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 11.5 "The Boiling Points of Water at Various Locations on Earth" lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

Note the Pattern

As pressure increases, the boiling point of a liquid increases and vice versa.

Table 11.5 The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water ($^{\circ}\text{C}$)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	-1312	799	101.4

EXAMPLE 7

Use Figure 11.16 "The Vapor Pressures of Several Liquids as a Function of Temperature" to estimate the following.

- a. the boiling point of water in a pressure cooker operating at 1000 mmHg
- b. the pressure required for mercury to boil at 250°C

Given: data in Figure 11.16 "The Vapor Pressures of Several Liquids as a Function of Temperature", pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A To estimate the boiling point of water at 1000 mmHg, refer to Figure 11.16 "The Vapor Pressures of Several Liquids as a Function of Temperature" and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

- a. **A** The vapor pressure curve of water intersects the $P = 1000$ mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
- b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

Exercise

Use the data in Figure 11.16 "The Vapor Pressures of Several Liquids as a Function of Temperature" to estimate the following.

- a. the normal boiling point of ethylene glycol
- b. the pressure required for diethyl ether to boil at 20°C.

Answer:

- a. 200°C
- b. 450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor**

pressure above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

KEY TAKEAWAYS

- The equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- The relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius–Clapeyron equation.

KEY EQUATIONS

Clausius–Clapeyron equation

Equation 11.1: $\ln P = - \frac{\Delta H_{\text{vap}}}{R(1T)} + C$

Using vapor pressure at two temperatures to calculate ΔH_{vap}

Equation 11.2: $\ln (P_2/P_1) = - \frac{\Delta H_{\text{vap}}}{R(1/T_2 - 1/T_1)}$

CONCEPTUAL PROBLEMS

1. What is the relationship between the boiling point, vapor pressure, and temperature of a substance and atmospheric pressure?
2. What is the difference between a volatile liquid and a nonvolatile liquid? Suppose that two liquid substances have the same molecular mass, but one is volatile and the other is nonvolatile. What differences in the molecular structures of the two substances could account for the differences in volatility?

3. An “old wives’ tale” states that applying ethanol to the wrists of a child with a very high fever will help to reduce the fever because blood vessels in the wrists are close to the skin. Is there a scientific basis for this recommendation? Would water be as effective as ethanol?
4. Why is the air over a strip of grass significantly cooler than the air over a sandy beach only a few feet away?
5. If gasoline is allowed to sit in an open container, it often feels much colder than the surrounding air. Explain this observation. Describe the flow of heat into or out of the system, as well as any transfer of mass that occurs. Would the temperature of a sealed can of gasoline be higher, lower, or the same as that of the open can? Explain your answer.
6. What is the relationship between the vapor pressure of a liquid and
 - a. its temperature?
 - b. the surface area of the liquid?
 - c. the pressure of other gases on the liquid?
 - d. its viscosity?
7. At 25°C, benzene has a vapor pressure of 12.5 kPa, whereas the vapor pressure of acetic acid is 2.1 kPa. Which is more volatile? Based on the intermolecular interactions in the two liquids, explain why acetic acid has the lower vapor pressure.

NUMERICAL PROBLEMS

1. Acetylene (C_2H_2), which is used for industrial welding, is transported in pressurized cylinders. Its vapor pressure at various temperatures is given in the following table. Plot the data and use your graph to estimate the vapor pressure of acetylene at 293 K. Then use your graph to determine the value of ΔH_{vap} for acetylene. How much energy is required to vaporize 2.00 g of acetylene at 250 K?

T (K)	145	155	175	200	225	250	300
P (mmHg)	1.3	7.8	32.2	190	579	1370	5093

2. The following table gives the vapor pressure of water at various temperatures. Plot the data and use your graph to estimate the vapor pressure of water at 25°C and at 75°C. What is the vapor pressure of water at 110°C? Use these data to determine the value of ΔH_{vap} for water.

T (°C)	0	10	30	50	60	80	100
P (mmHg)	4.6	9.2	31.8	92.6	150	355	760

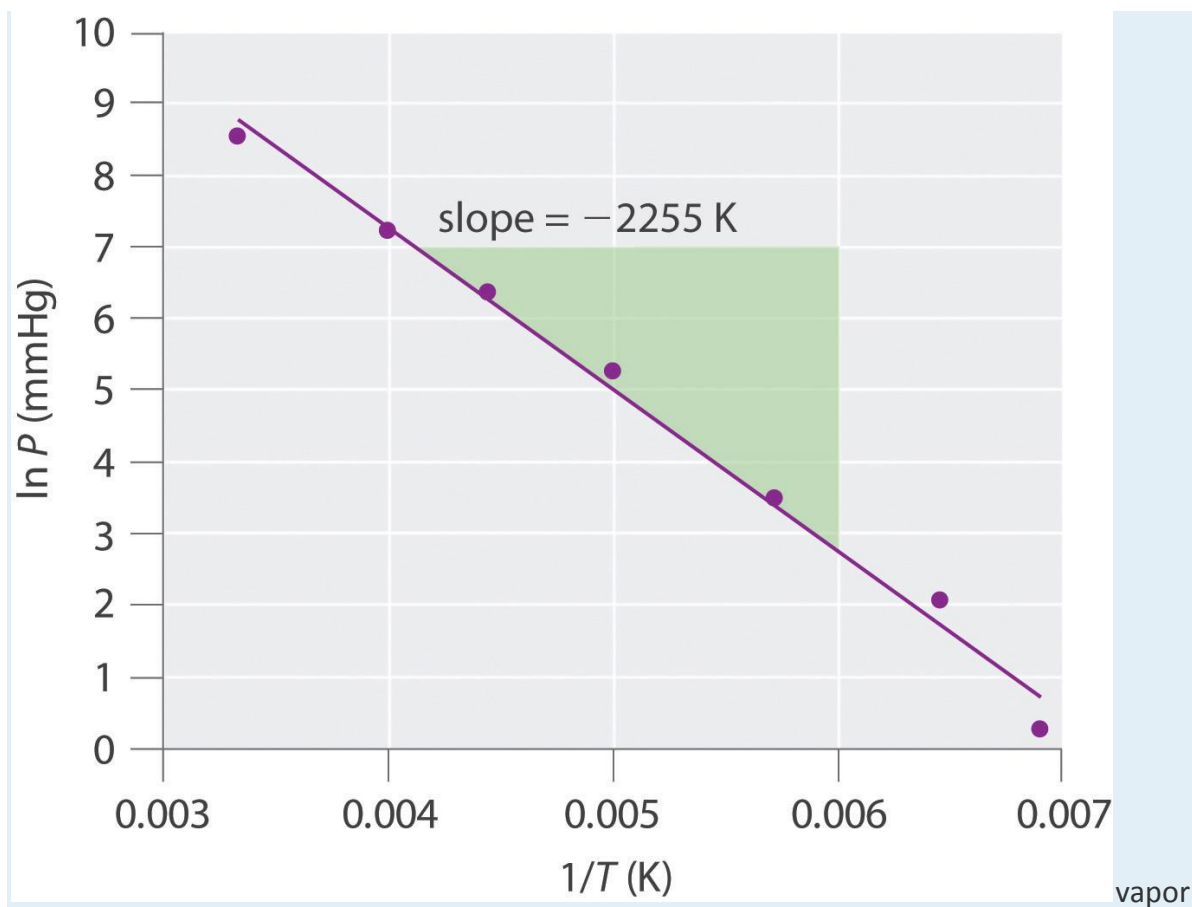
3. The ΔH_{vap} of carbon tetrachloride is 29.8 kJ/mol, and its normal boiling point is 76.8°C. What is its boiling point at 0.100 atm?
4. The normal boiling point of sodium is 883°C. If ΔH_{vap} is 97.4 kJ/mol, what is the vapor pressure (in millimeters of mercury) of liquid sodium at 300°C?
5. An unknown liquid has a vapor pressure of 0.860 atm at 63.7°C and a vapor pressure of 0.330 atm at 35.1°C. Use the data in Table 11.6 "Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances" in Section 11.5 "Changes of State" to identify the liquid.
6. An unknown liquid has a boiling point of 75.8°C at 0.910 atm and a boiling point of 57.2°C at 0.430 atm. Use the data in Table 11.6 "Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances" in Section 11.5 "Changes of State" to identify the liquid.
7. If the vapor pressure of a liquid is 0.850 atm at 20°C and 0.897 atm at 25°C, what is the normal boiling point of the liquid?
8. If the vapor pressure of a liquid is 0.799 atm at 99.0°C and 0.842 atm at 111°C, what is the normal boiling point of the liquid?
9. The vapor pressure of liquid SO₂ is 33.4 torr at -63.4°C and 100.0 torr at -47.7 K.
 - a. What is the ΔH_{vap} of SO₂?
 - b. What is its vapor pressure at -24.5 K?
 - c. At what temperature is the vapor pressure equal to 220 torr?
10. The vapor pressure of CO₂ at various temperatures is given in the following table:

T (°C)	-120	-110	-100	-90
P (torr)	9.81	34.63	104.81	279.5

- a. What is ΔH_{vap} over this temperature range?
- b. What is the vapor pressure of CO₂ at -70°C?
- c. At what temperature does CO₂ have a vapor pressure of 310 torr?

ANSWERS

1.



pressure at 273 K is 3050 mmHg; $\Delta H_{\text{vap}} = 18.7 \text{ kJ/mol}$, 1.44 kJ

- 2.
3. 12.5°C
- 4.
5. $\Delta H_{\text{vap}} = 28.9 \text{ kJ/mol}$, *n*-hexane
- 6.
7. $\Delta H_{\text{vap}} = 7.81 \text{ kJ/mol}$, 36°C

[1] For a review of natural logarithms, refer to Essential Skills 6 in Section 11.9 "Essential Skills 6".

11.5 Changes of State

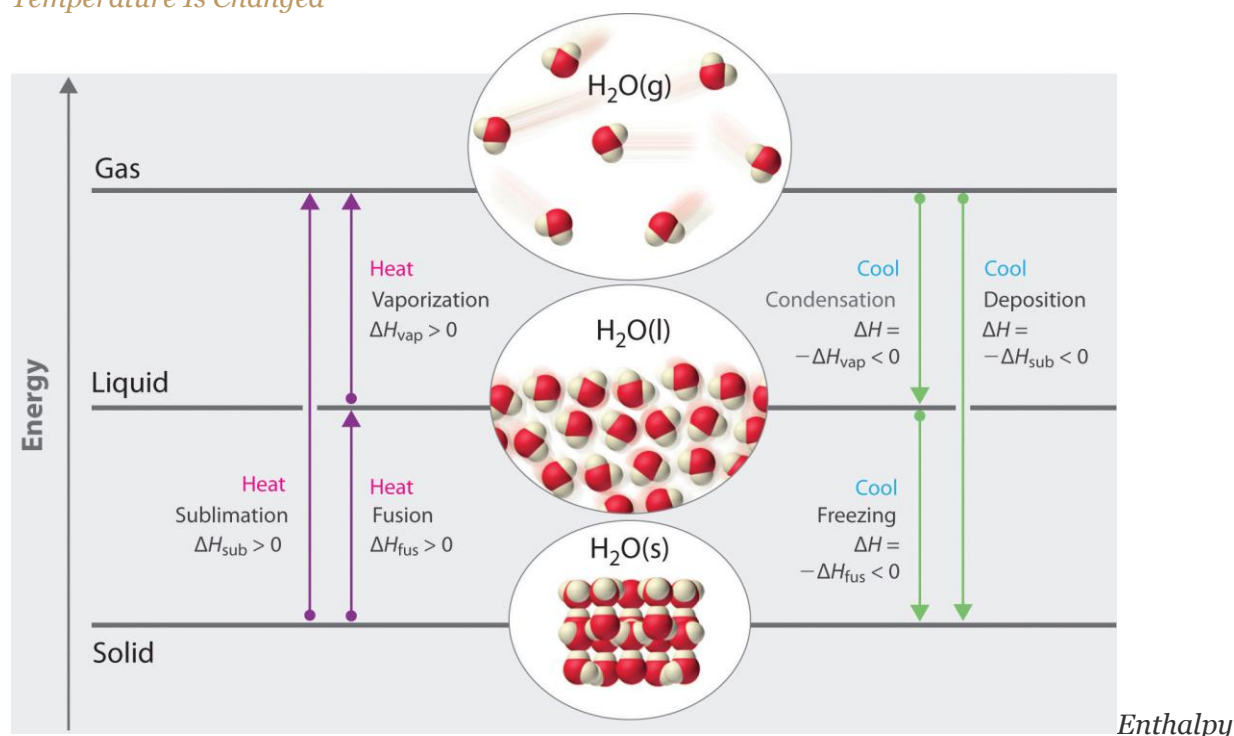
LEARNING OBJECTIVE

1. To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid).

and vice versa). We use dry ice, which is solid CO_2 , as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure 11.17 "The Three Phases of Matter and the Processes That Interconvert Them When the Temperature Is Changed".

Figure 11.17 The Three Phases of Matter and the Processes That Interconvert Them When the Temperature Is Changed



changes that accompany phase transitions are indicated by purple and green arrows.

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid,

gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure 11.17 "The Three Phases of Matter and the Processes That Interconvert Them When the Temperature Is Changed".

In Chapter 5 "Energy Changes in Chemical Reactions", we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table 11.6 "Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances". The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

Table 11.6 Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N ₂	-210.0	0.71	-195.8	5.6
HCl	-114.2	2.00	-85.1	16.2
Br ₂	-7.2	10.6	58.8	30.0
CCl ₄	-22.6	2.56	76.8	29.8
CH ₃ CH ₂ OH (ethanol)	-114.1	4.93	78.3	38.6
CH ₃ (CH ₂) ₄ CH ₃ (<i>n</i> -hexane)	-95.4	13.1	68.7	28.9
H ₂ O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

Note the Pattern

ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO₂ (dry ice); iodine (Figure 11.18 "The Sublimation of Solid Iodine"); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure 11.17 "The Three Phases of Matter and the Processes That Interconvert Them When the Temperature Is Changed", the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same T ; this is an application of Hess's law. (For more information about Hess's law, see Chapter 5 "Energy Changes in Chemical Reactions", Section 5.2 "Enthalpy").

Equation 11.3

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

The Sublimation of Solid Iodine

When solid iodine is heated at ordinary atmospheric pressure, it sublimates. When the I₂ vapor comes in contact with a cold surface, it deposits I₂ crystals.

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs) discussed in Chapter 3 "Chemical Reactions" in connection with the ozone layer. The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C, as demonstrated later in Example 8.

Temperature Curves

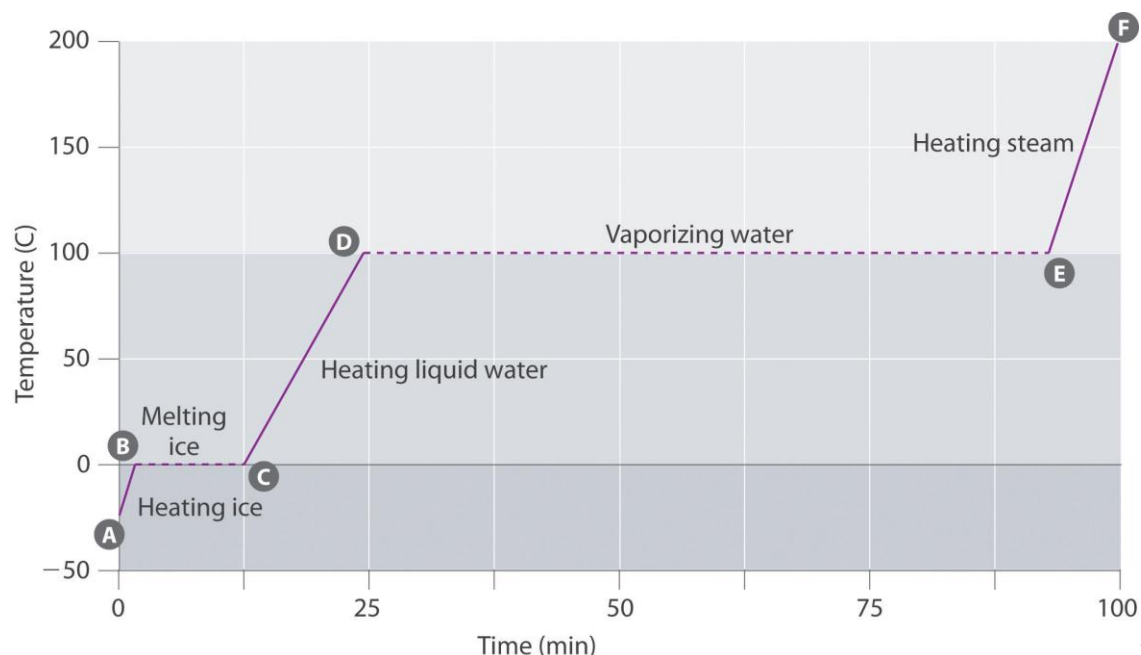
The processes on the right side of Figure 11.17 "The Three Phases of Matter and the Processes That Interconvert Them When the Temperature Is Changed"—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use

refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure 11.19 "A Heating Curve for Water" shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and -23°C ; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C . As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C , the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

Figure 11.19 *A Heating Curve for Water*



This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and -23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

Note the Pattern

The temperature of a sample does not change during a phase change.

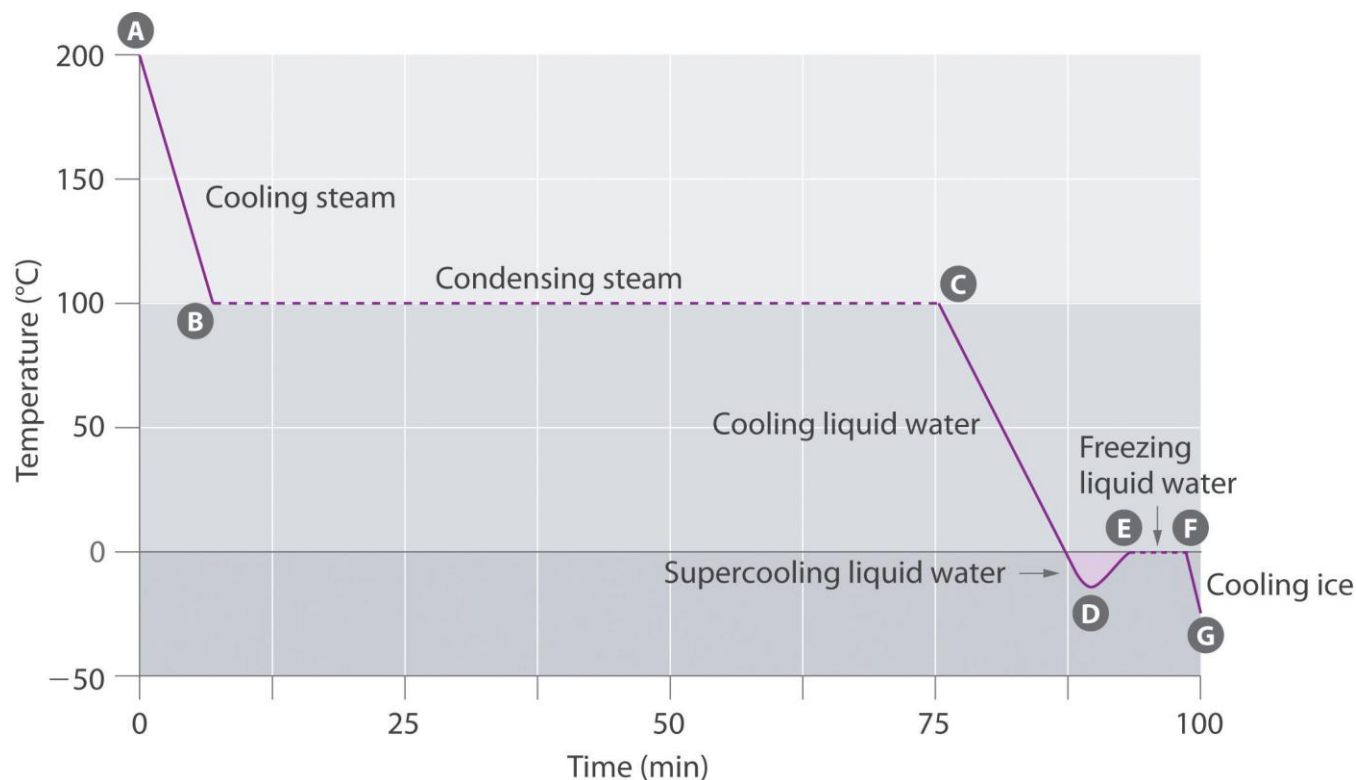
If heat is added at a constant rate, as in Figure 11.19 "A Heating Curve for Water", then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 11.19 "A Heating Curve for Water", the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 11.20 "A Cooling Curve for Water" plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 11.19 "A Heating Curve for Water", the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

Figure 11.20 A Cooling Curve for Water



This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about -10°C , rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimates directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimates, it absorbs heat from the cloud, often with the desired results.

EXAMPLE 8

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g·°C) and 2.062 J/(g·°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy:

Substitute the values given into the general equation relating heat gained to heat lost (Equation 5.39) to obtain the final temperature of the mixture.

Solution:

Recall from Chapter 5 "Energy Changes in Chemical Reactions" that when two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C:

$$q_{\text{lost}}(\text{iced tea})[C_s(\text{H}_2\text{O})](\Delta T_{\text{iced tea}})(500 \text{ g})[4.184 \text{ J/(g}\cdot^\circ\text{C)}](T_f - 20.0^\circ\text{C}) \\ (2090 \text{ J/}^\circ\text{C)}(T_f) - 4.18 \times 10^4 \text{ J} 2.53 \times 10^4 \text{ J} 11.0^\circ\text{C} = -$$

$$q_{\text{gained}} = - \{ (m_{\text{ice}})[C_s(\text{H}_2\text{O})](\Delta T_{\text{ice}}) + (m_{\text{ice}})\Delta H_{\text{fus}}(\text{ice}) \} \\ = - [(50.0 \text{ g})[4.184 \text{ J/(g}\cdot^\circ\text{C)}](T_f - 0.0^\circ\text{C})] + ((50.0 \text{ g})18.0 \text{ g/mol} \\ (6.01 \times 10^3 \text{ J/mol}) = - [(209 \text{ J/}^\circ\text{C)}(T_f) + 1.67 \times 10^4 \text{ J}] \\ = (2310 \text{ J/}^\circ\text{C)}T_f = T_f$$

Exercise

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at -5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you can't remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at -5.0°C to your body's internal temperature of 37°C . Use the data in

Example 8

Answer: 200 kJ (4.1 kJ to bring the ice from -5.0°C to 0.0°C , 133.6 kJ to melt the ice at 0.0°C , and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Summary

Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation** (ΔH_{sub}) and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

KEY TAKEAWAY

- Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes.

CONCEPTUAL PROBLEMS

1. In extremely cold climates, snow can disappear with no evidence of its melting. How can this happen? What change(s) in state are taking place? Would you expect this phenomenon to be more common at high or low altitudes? Explain your answer.
2. Why do car manufacturers recommend that an automobile should not be left standing in subzero temperatures if its radiator contains only water? Car manufacturers also warn car owners that they should check the fluid level in a radiator only when the engine is cool. What is the basis for this warning? What is likely to happen if it is ignored?
3. Use Hess's law and a thermochemical cycle to show that, for any solid, the enthalpy of sublimation is equal to the sum of the enthalpy of fusion of the solid and the enthalpy of vaporization of the resulting liquid.
4. Three distinct processes occur when an ice cube at -10°C is used to cool a glass of water at 20°C . What are they? Which causes the greatest temperature change in the water?
5. When frost forms on a piece of glass, crystals of ice are deposited from water vapor in the air. How is this process related to sublimation? Describe the energy changes that take place as the water vapor is converted to frost.
6. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?
 - a. ice melting
 - b. distillation
 - c. condensation forming on a window
 - d. the use of dry ice to create a cloud for a theatrical production
7. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?
 - a. evaporation of methanol
 - b. crystallization
 - c. liquefaction of natural gas
 - d. the use of naphthalene crystals to repel moths

8. Why do substances with high enthalpies of fusion tend to have high melting points?
9. Why is the enthalpy of vaporization of a compound invariably much larger than its enthalpy of fusion?
10. What is the opposite of fusion, sublimation, and condensation? Describe the phase change in each pair of opposing processes and state whether each phase change is exothermic or endothermic.
11. Draw a typical heating curve (temperature versus amount of heat added at a constant rate) for conversion of a solid to a liquid and then to a gas. What causes some regions of the plot to have a positive slope? What is happening in the regions of the plot where the curve is horizontal, meaning that the temperature does not change even though heat is being added?
12. If you know the mass of a sample of a substance, how could you use a heating curve to calculate the specific heat of the substance, as well as the change in enthalpy associated with a phase change?
13. Draw the heating curve for a liquid that has been superheated. How does this differ from a normal heating curve for a liquid? Draw the cooling curve for a liquid that has been supercooled. How does this differ from a normal cooling curve for a liquid?

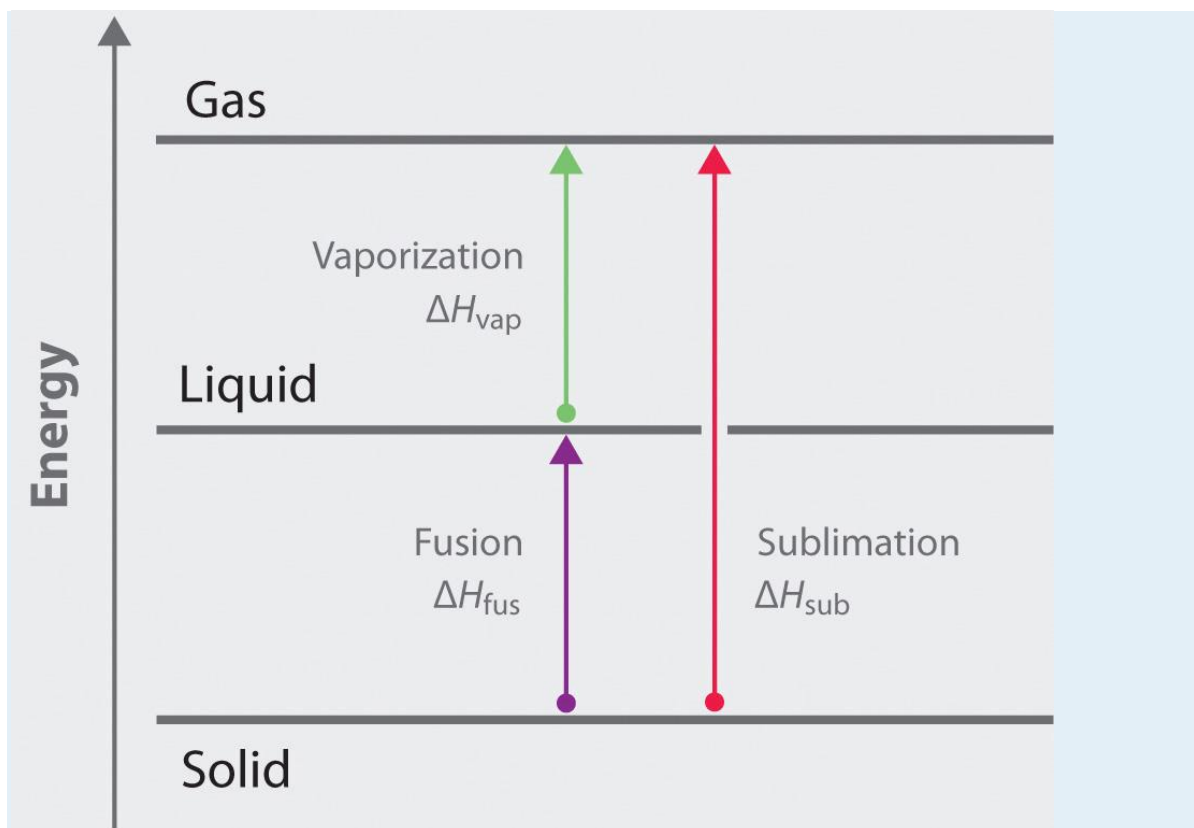
ANSWERS

1. When snow disappears without melting, it must be subliming directly from the solid state to the vapor state. The rate at which this will occur depends solely on the partial pressure of water, not on the total pressure due to other gases. Consequently, altitude (and changes in atmospheric pressure) will not affect the rate of sublimation directly.
- 2.
3. The general equations and enthalpy changes for the changes of state involved in converting a solid to a gas

are:

$$\begin{aligned}
 &\text{solid} \rightarrow \text{liquid} \rightarrow \text{gas} \\
 &\Delta H_{\text{fus}} \quad \Delta H_{\text{vap}} \quad \Delta H_{\text{sub}} \\
 &\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}
 \end{aligned}$$

The relationship between these enthalpy changes is shown schematically in the thermochemical cycle below:

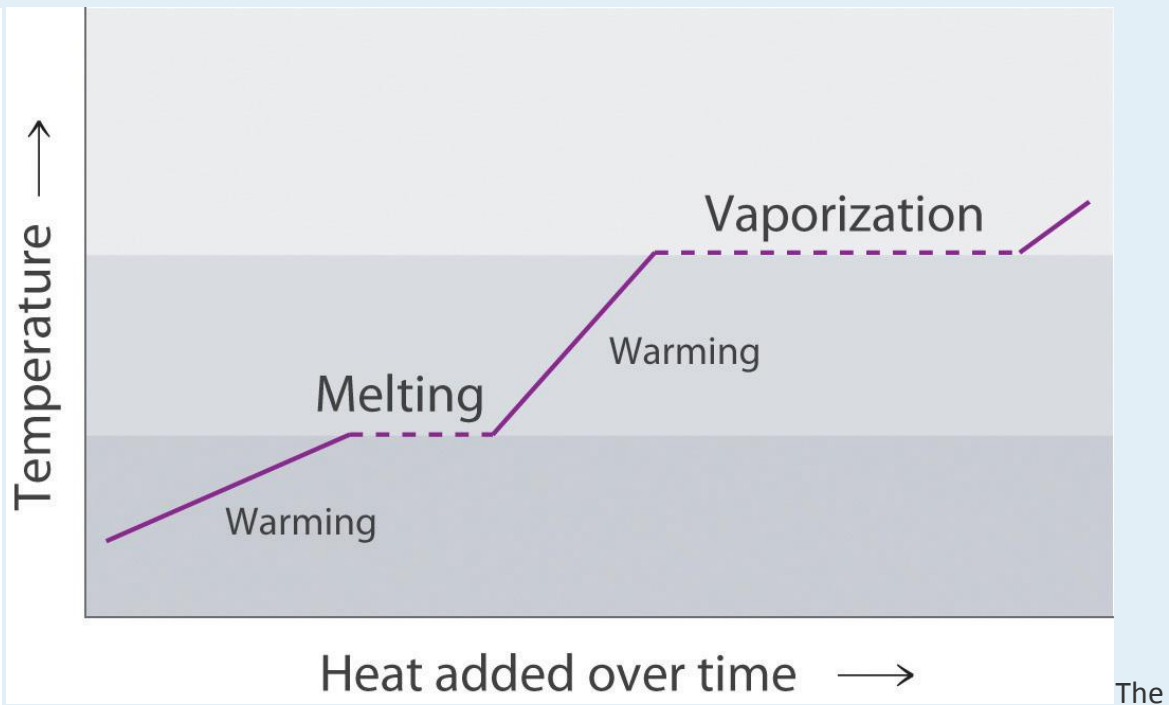


4. The formation of frost on a surface is an example of deposition, which is the reverse of sublimation. The change in enthalpy for deposition is equal in magnitude, but opposite in sign, to ΔH_{sub} , which is a positive number: $\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$.
- 5.
6.
 - a. liquid + heat $\rightarrow$ vapor: endothermic
 - b. liquid $\rightarrow$ solid + heat: exothermic
 - c. gas $\rightarrow$ liquid + heat: exothermic
 - d. solid + heat $\rightarrow$ vapor: endothermic
- 7.
8. The enthalpy of vaporization is larger than the enthalpy of fusion because vaporization requires the addition of enough energy to disrupt all intermolecular interactions and create a gas in which the molecules move essentially independently. In contrast, fusion requires much less energy, because the intermolecular interactions in a liquid and a solid are similar in magnitude in all condensed phases. Fusion requires only

enough energy to overcome the intermolecular interactions that lock molecules in place in a lattice, thereby allowing them to move more freely.

9.

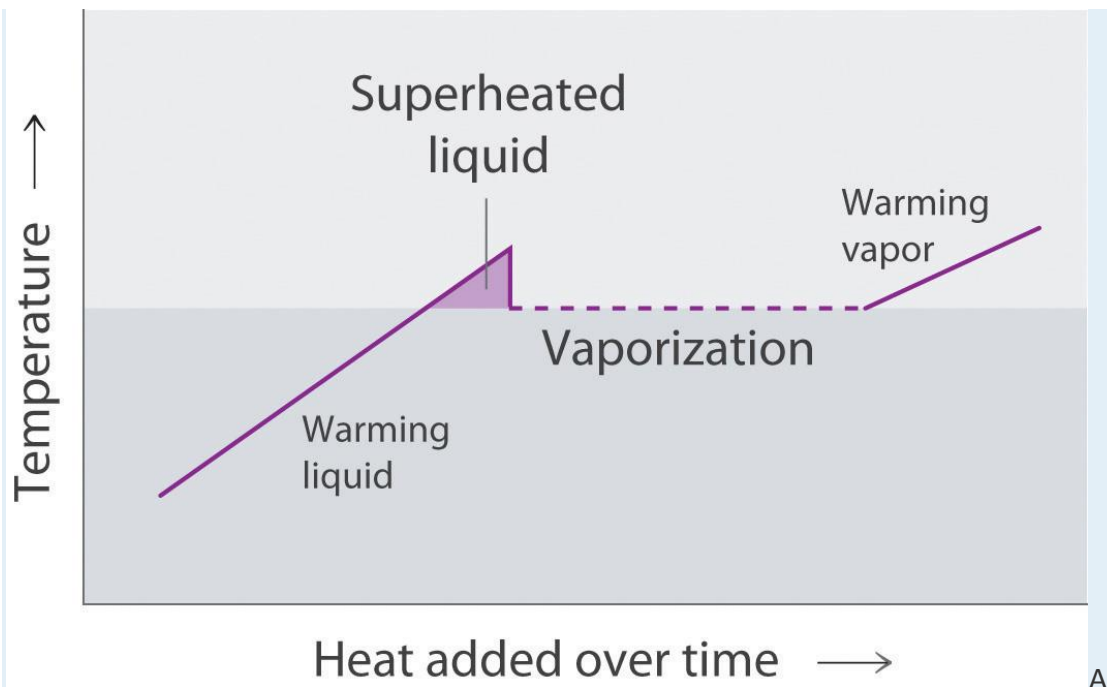
10.



The portions of the curve with a positive slope correspond to heating a single phase, while the horizontal portions of the curve correspond to phase changes. During a phase change, the temperature of the system does not change, because the added heat is melting the solid at its melting point or evaporating the liquid at its boiling point.

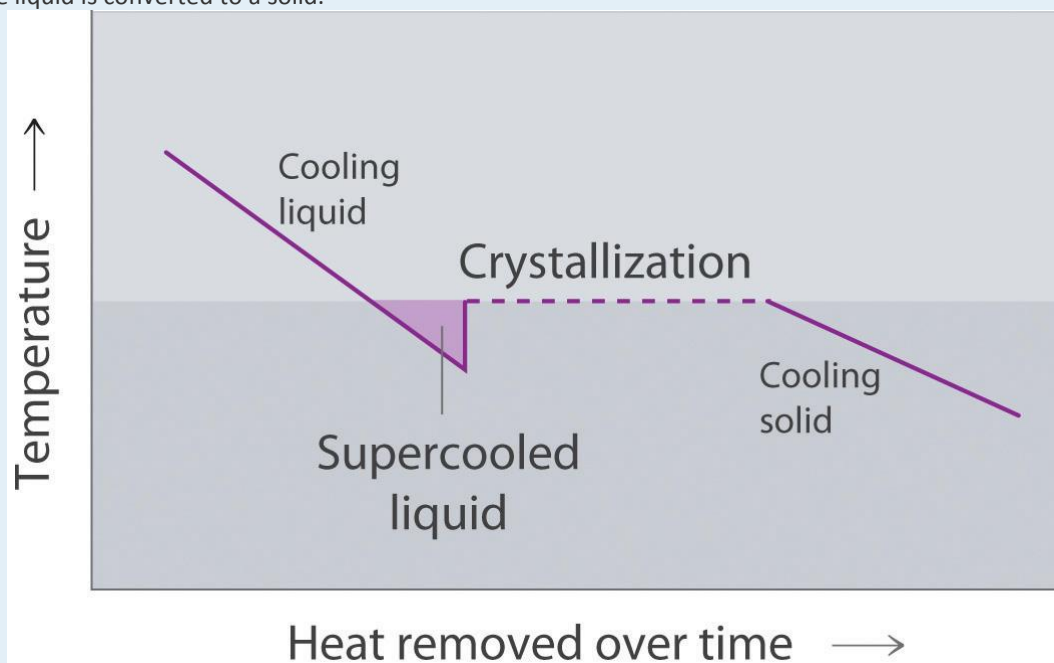
11.

12.



A superheated liquid exists temporarily as liquid with a temperature above the normal boiling point of the liquid. When a supercooled liquid boils, the temperature drops as the liquid is converted to vapor.

Conversely, a supercooled liquid exists temporarily as a liquid with a temperature lower than the normal melting point of the solid. As shown below, when a supercooled liquid crystallizes, the temperature increases as the liquid is converted to a solid.



NUMERICAL PROBLEMS

1. The density of oxygen at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of oxygen.

T (K)	60	70	80	90	100	120	140
d (mol/L)	40.1	38.6	37.2	35.6	0.123	0.102	0.087

2. The density of propane at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of propane.

T (K)	100	125	150	175	200	225	250	275
d (mol/L)	16.3	15.7	15.0	14.4	13.8	13.2	0.049	0.044

3. Draw the cooling curve for a sample of the vapor of a compound that has a melting point of 34°C and a boiling point of 77°C as it is cooled from 100°C to 0°C .
4. Propionic acid has a melting point of -20.8°C and a boiling point of 141°C . Draw a heating curve showing the temperature versus time as heat is added at a constant rate to show the behavior of a sample of propionic acid as it is heated from -50°C to its boiling point. What happens above 141°C ?
5. A 0.542 g sample of I_2 requires 96.1 J of energy to be converted to vapor. What is the enthalpy of sublimation of I_2 ?
6. A 2.0 L sample of gas at 210°C and 0.762 atm condenses to give 1.20 mL of liquid, and 476 J of heat is released during the process. What is the enthalpy of vaporization of the compound?
7. One fuel used for jet engines and rockets is aluminum borohydride $[\text{Al}(\text{BH}_4)_3]$, a liquid that readily reacts with water to produce hydrogen. The liquid has a boiling point of 44.5°C . How much energy is needed to vaporize 1.0 kg of aluminum borohydride at 20°C , given a ΔH_{vap} of 30 kJ/mol and a molar heat capacity (C_p) of $194.6 \text{ J}/(\text{mol}\cdot\text{K})$?
8. How much energy is released when freezing 100.0 g of dimethyl disulfide ($\text{C}_2\text{H}_6\text{S}_2$) initially at 20°C ? Use the following information: melting point = -84.7°C , $\Delta H_{\text{fus}} = 9.19 \text{ kJ/mol}$, $C_p = 118.1 \text{ J}/(\text{mol}\cdot\text{K})$.

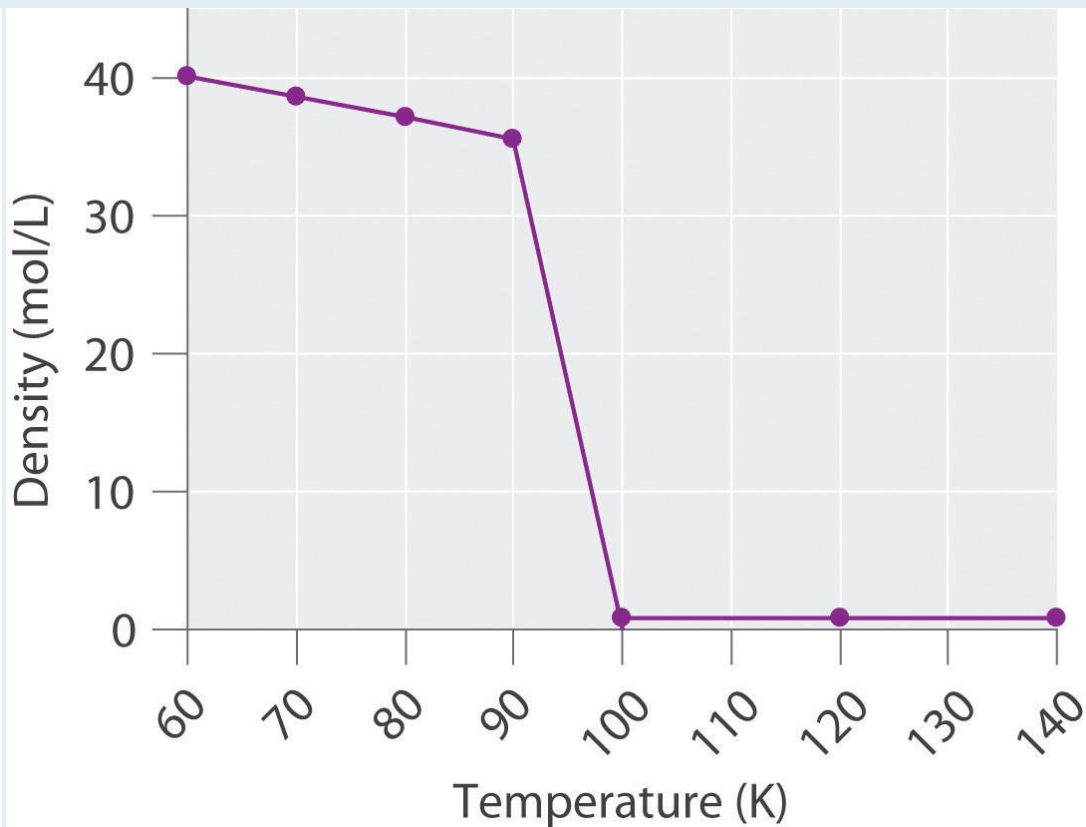
The following four problems use the following information (the subscript p indicates measurements taken at constant pressure): $\Delta H_{\text{fus}}(\text{H}_2\text{O}) = 6.01 \text{ kJ/mol}$, $\Delta H_{\text{vap}}(\text{H}_2\text{O}) = 40.66 \text{ kJ/mol}$, $C_{p(s)}(\text{crystalline H}_2\text{O}) = 38.02 \text{ J}/(\text{mol}\cdot\text{K})$, $C_{p(l)}(\text{liquid H}_2\text{O}) = 75.35 \text{ J}/(\text{mol}\cdot\text{K})$, and $C_{p(g)}(\text{H}_2\text{O gas}) = 33.60 \text{ J}/(\text{mol}\cdot\text{K})$.

9. How much heat is released in the conversion of 1.00 L of steam at 21.9 atm and 200°C to ice at -6.0°C and 1 atm?

10. How much heat must be applied to convert a 1.00 g piece of ice at -10°C to steam at 120°C ?
11. How many grams of boiling water must be added to a glass with 25.0 g of ice at -3°C to obtain a liquid with a temperature of 45°C ?
12. How many grams of ice at -5.0°C must be added to 150.0 g of water at 22°C to give a final temperature of 15°C ?

ANSWERS

1.

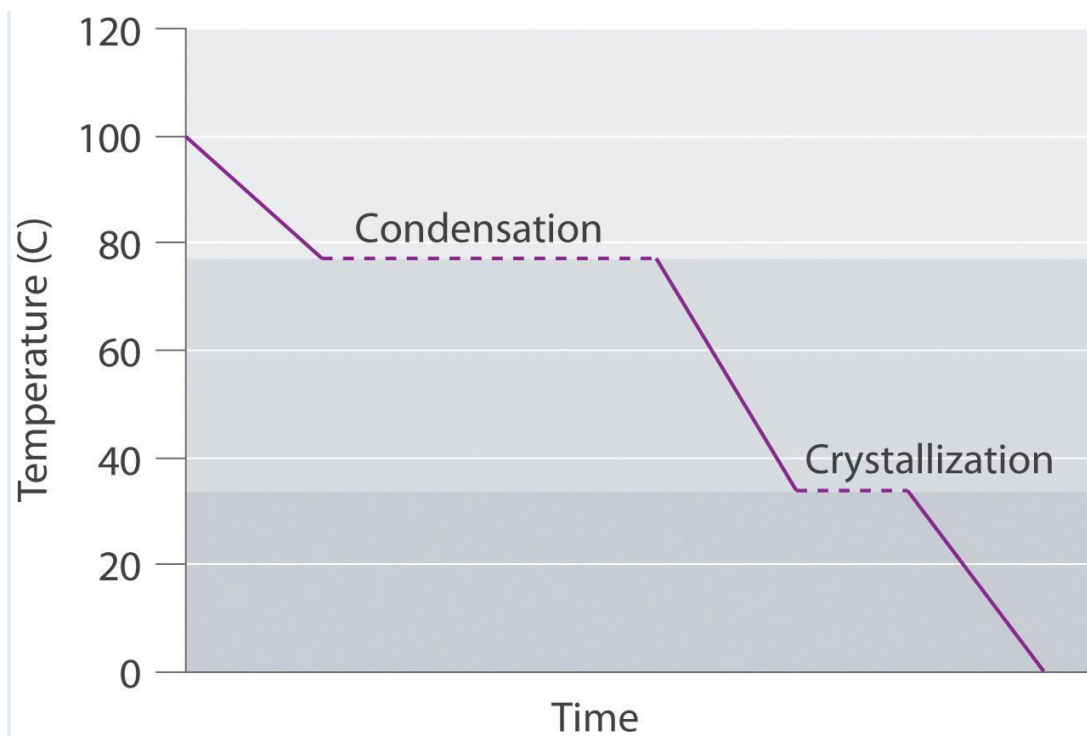


The

transition from a liquid to a gaseous phase is accompanied by a drastic decrease in density. According to the data in the table and the plot, the boiling point of liquid oxygen is between 90 and 100 K (actually 90.2 K).

2.

3.



5. 45.0 kJ/mol

7. 488 kJ

9. 32.6 kJ

10. 57 g

11.6 Critical Temperature and Pressure

LEARNING OBJECTIVE

1. To know what is meant by the critical temperature and pressure of a liquid.

In Chapter 10 "Gases", Section 10.8 "The Behavior of Real Gases", we saw that a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a

substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point of a substance. The critical temperatures and pressures of several common substances are listed in Table 11.7 "Critical Temperatures and Pressures of Some Simple Substances".

Note the Pattern

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Table 11.7 Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c ($^{\circ}\text{C}$)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
$\text{CH}_3\text{CH}_2\text{OH}$ (ethanol)	240.9	61.4
He	-267.96	2.27
Hg	1477	1587
CH_4	-82.6	46.0
N_2	-146.9	33.9
H_2O	374.0	217.7

Supercritical Fluids

To understand what happens at the critical point, consider the effects of temperature and pressure on the densities of liquids and gases, respectively. As the temperature of a liquid increases, its density decreases. As the pressure of a gas increases, its density increases. At the critical point, the liquid and gas phases have exactly the same density, and only a single phase exists. This single phase is called a supercritical fluid, which exhibits many of the properties of a gas but has a density more typical of a liquid. For example, the density of water at its critical point ($T = 374^{\circ}\text{C}$, $P = 217.7$ atm) is 0.32 g/mL, about one-third that of liquid water at room temperature but much greater than that of water vapor under most conditions. The transition between a liquid/gas mixture and a supercritical phase is demonstrated

for a sample of benzene in Figure 11.21 "Supercritical Benzene". At the critical temperature, the meniscus separating the liquid and gas phases disappears.

Benzene

Below the critical temperature of benzene ($T_c = 289^\circ\text{C}$), the meniscus between the liquid and gas phases is apparent. At the critical temperature, the meniscus disappears because the density of the vapor is equal to the density of the liquid. Above T_c , a dense homogeneous fluid fills the tube.

In the last few years, supercritical fluids have evolved from laboratory curiosities to substances with important commercial applications. For example, carbon dioxide has a low critical temperature (31°C), a comparatively low critical pressure (73 atm), and low toxicity, making it easy to contain and relatively safe to manipulate. Because many substances are quite soluble in supercritical CO_2 , commercial processes that use it as a solvent are now well established in the oil industry, the food industry, and others. Supercritical CO_2 is pumped into oil wells that are no longer producing much oil to dissolve the residual oil in the underground reservoirs. The less-viscous solution is then pumped to the surface, where the oil can be recovered by evaporation (and recycling) of the CO_2 . In the food, flavor, and fragrance industry, supercritical CO_2 is used to extract components from natural substances for use in perfumes, remove objectionable organic acids from hops prior to making beer, and selectively extract caffeine from whole coffee beans without removing important flavor components. The latter process was patented in 1974, and now virtually all decaffeinated coffee is produced this way. The earlier method used volatile organic solvents such as methylene chloride (dichloromethane [CH_2Cl_2], boiling point = 40°C), which is difficult to remove completely from the beans and is known to cause cancer in laboratory animals at high doses.

EXAMPLE 9

Arrange methanol, *n*-butane, *n*-pentane, and N_2O in order of increasing critical temperatures.

Given: compounds

Asked for: order of increasing critical temperatures

Strategy:

A Identify the intermolecular forces in each molecule and then assess the strengths of those forces.

B Arrange the compounds in order of increasing critical temperatures.

Solution:

A The critical temperature depends on the strength of the intermolecular interactions that hold a substance together as a liquid. In N_2O , a slightly polar substance, weak dipole–dipole interactions and

London dispersion forces are important. Butane (C_4H_{10}) and pentane (C_5H_{12}) are larger, nonpolar molecules that exhibit only London dispersion forces. Methanol, in contrast, should have substantial intermolecular hydrogen bonding interactions. Because hydrogen bonds are stronger than the other intermolecular forces, methanol will have the highest T_c . London forces are more important for pentane than for butane because of its larger size, so *n*-pentane will have a higher T_c than *n*-butane. The only remaining question is whether N_2O is polar enough to have stronger intermolecular interactions than pentane or butane. Because the electronegativities of O and N are quite similar, the answer is probably no, so N_2O should have the lowest T_c . **B** We therefore predict the order of increasing critical temperatures as $\text{N}_2\text{O} < n\text{-butane} < n\text{-pentane} < \text{methanol}$. The actual values are N_2O (36.9°C) $< n\text{-butane}$ (152.0°C) $< n\text{-pentane}$ (196.9°C) $< \text{methanol}$ (239.9°C). This is the same order as their normal boiling points— N_2O (-88.7°C) $< n\text{-butane}$ (-0.2°C) $< n\text{-pentane}$ (36.0°C) $< \text{methanol}$ (65°C)—because both critical temperature and boiling point depend on the relative strengths of the intermolecular interactions.

Exercise

Arrange ethanol, methanethiol (CH_3SH), ethane, and *n*-hexanol in order of increasing critical temperatures.

Answer: ethane (32.3°C) $< \text{methanethiol}$ (196.9°C) $< \text{ethanol}$ (240.9°C) $< n\text{-hexanol}$ (336.9°C)

Molten Salts and Ionic Liquids

Heating a salt to its melting point produces a molten salt. If we heated a sample of solid NaCl to its melting point of 801°C , for example, it would melt to give a stable liquid that conducts electricity. The characteristics of molten salts other than electrical conductivity are their high heat capacity, ability to attain very high temperatures (over 700°C) as a liquid, and utility as solvents because of their relatively low toxicity.

Molten salts have many uses in industry and the laboratory. For example, in solar power towers in the desert of California, mirrors collect and focus sunlight to melt a mixture of sodium nitrite and sodium nitrate. The heat stored in the molten salt is used to produce steam that drives a steam turbine and a generator, thereby producing electricity from the sun for southern California.

Due to their low toxicity and high thermal efficiency, molten salts have also been used in nuclear reactors to enable operation at temperatures greater than 750°C . One prototype reactor tested in the 1950s used a fuel and a coolant consisting of molten fluoride salts, including NaF , ZrF_4 , and UF_4 . Molten salts are also

useful in catalytic processes such as coal gasification, in which carbon and water react at high temperatures to form CO and H₂.

Note the Pattern

Molten salts are good electrical conductors, have a high heat capacity, can maintain a high temperature as a liquid, and are relatively nontoxic.

Although molten salts have proven highly useful, more recently chemists have been studying the characteristics of ionic liquids, ionic substances that are *liquid* at room temperature and pressure. These substances consist of small, symmetrical anions, such as PF₆⁻ and BF₄⁻, combined with larger, asymmetrical organic cations that prevent the formation of a highly organized structure, resulting in a low melting point. By varying the cation and the anion, chemists can tailor the liquid to specific needs, such as using a solvent in a given reaction or extracting specific molecules from a solution. For example, an ionic liquid consisting of a bulky cation and anions that bind metal contaminants such as mercury and cadmium ions can remove those toxic metals from the environment. A similar approach has been applied to removing uranium and americium from water contaminated by nuclear waste.

Note the Pattern

Ionic liquids consist of small, symmetrical anions combined with larger asymmetrical cations, which produce a highly polar substance that is a liquid at room temperature and pressure.

The initial interest in ionic liquids centered on their use as a low-temperature alternative to molten salts in batteries for missiles, nuclear warheads, and space probes. Further research revealed that ionic liquids had other useful properties—for example, some could dissolve the black rubber of discarded tires, allowing it to be recovered for recycling. Others could be used to produce commercially important organic compounds with high molecular mass, such as Styrofoam and Plexiglas, at rates 10 times faster than traditional methods.

Summary

A substance cannot form a liquid above its **critical temperature**, regardless of the applied pressure. Above the critical temperature, the molecules have enough kinetic energy to overcome the intermolecular attractive forces. The minimum pressure needed to liquefy a substance at its critical temperature is its **critical pressure**. The combination of the critical temperature and critical pressure of a substance is its **critical point**. Above the critical temperature and pressure, a substance exists as a dense fluid called a **supercritical fluid**, which resembles a gas in that it completely fills its container but has a density

comparable to that of a liquid. A **molten salt** is a salt heated to its melting point, giving a stable liquid that conducts electricity. **Ionic liquids** are ionic substances that are liquids at room temperature. Their disorganized structure results in a low melting point.

KEY TAKEAWAY

- The critical temperature and critical pressure of a substance define its critical point, beyond which the substance forms a supercritical fluid.

CONCEPTUAL PROBLEMS

1. Describe the changes that take place when a liquid is heated above its critical temperature. How does this affect the physical properties?
2. What is meant by the term *critical pressure*? What is the effect of increasing the pressure on a gas to above its critical pressure? Would it make any difference if the temperature of the gas was greater than its critical temperature?
3. Do you expect the physical properties of a supercritical fluid to be more like those of the gas or the liquid phase? Explain. Can an ideal gas form a supercritical fluid? Why or why not?
4. What are the limitations in using supercritical fluids to extract organic materials? What are the advantages?
5. Describe the differences between a molten salt and an ionic liquid. Under what circumstances would an ionic liquid be preferred over a molten salt?

11.7 Phase Diagrams

LEARNING OBJECTIVE

1. To understand the general features of a phase diagram.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample.

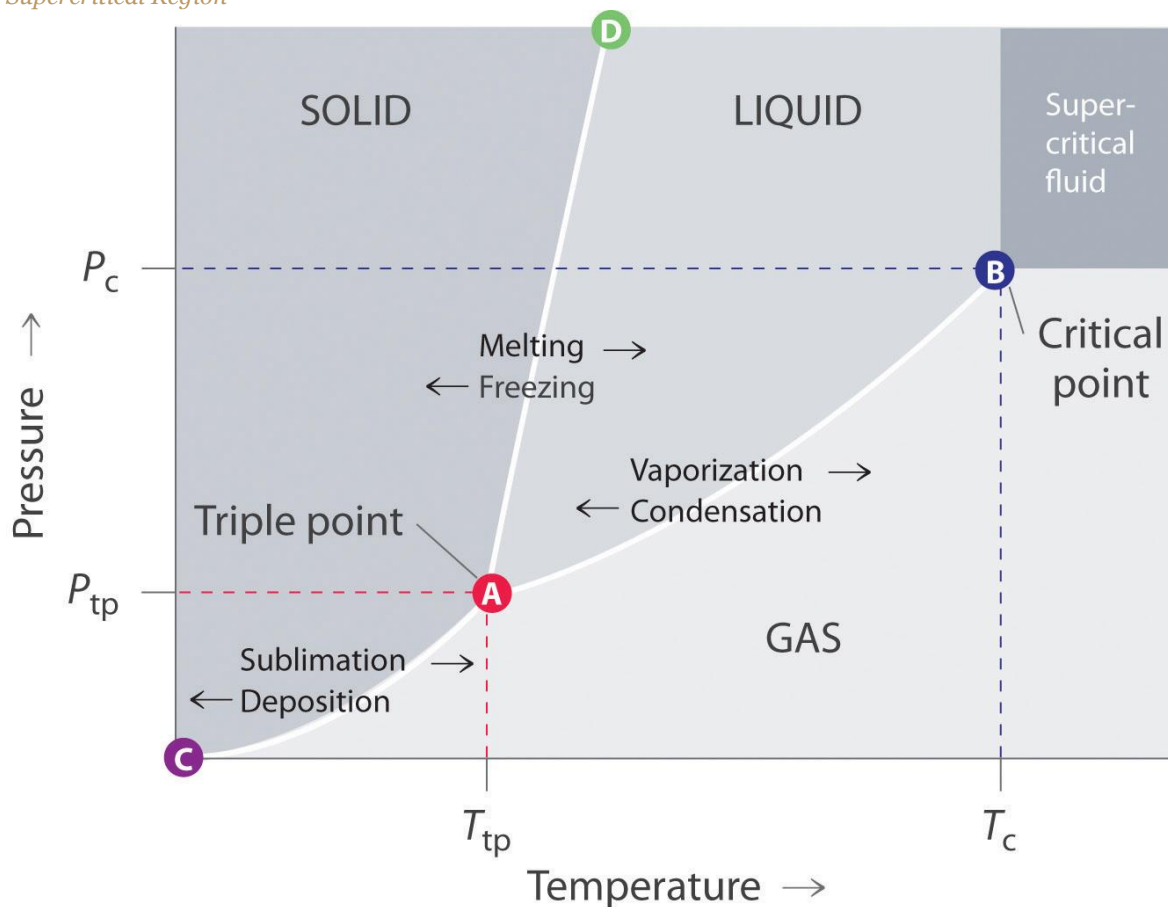
A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 11.22 "A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region"). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 11.22 "A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region")

corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right).

The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

Figure 11.22 A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region



Note the Pattern

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

General Features of a Phase Diagram

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 11.22 "A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region", the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.4 "Vapor Pressure". It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of

the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

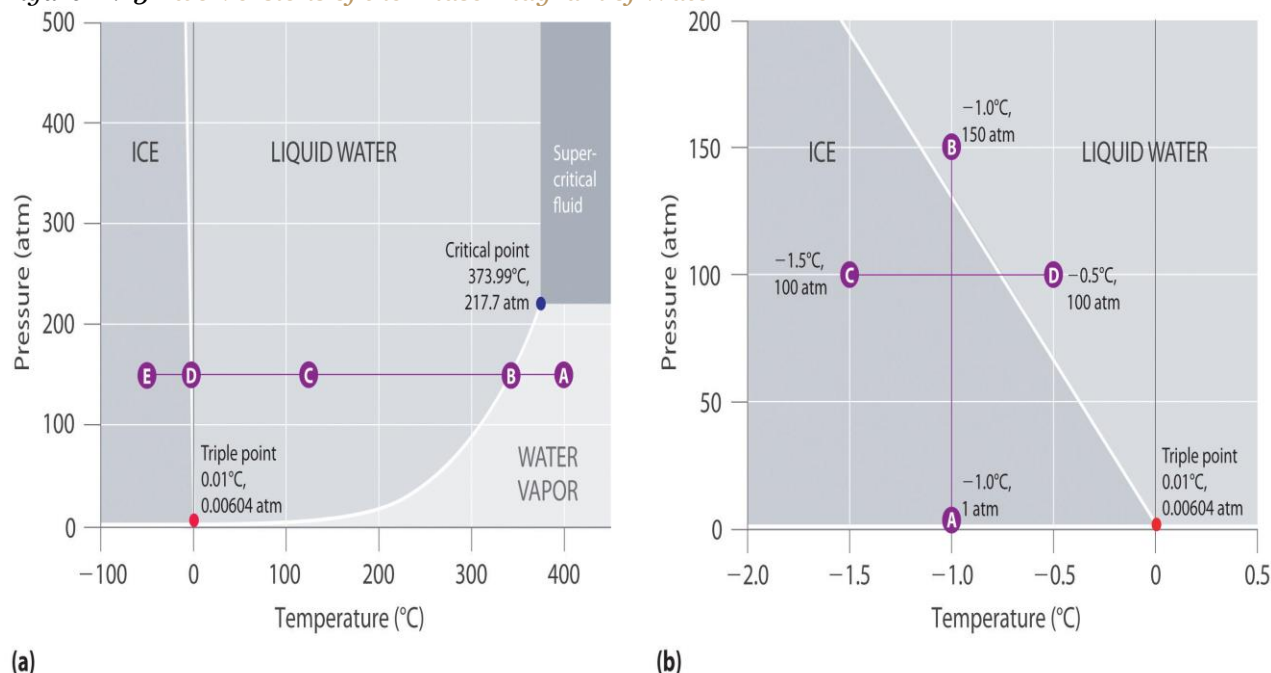
Remember that a phase diagram, such as the one in Figure 11.22 "A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region", is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 11.23 "Two Versions of the Phase Diagram of Water" shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm , therefore, ice does not melt to a liquid as the temperature increases; the solid sublimates directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm . Then, as the temperature is increased, the water sublimates, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee). The phase diagram for water illustrated in part (b) in Figure 11.23 "Two Versions of the Phase Diagram of Water" shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 11.22 "A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region"; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at -9°C . Water behaves this way because it is one of the few known substances for which the crystalline solid is *less*

dense than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

Figure 11.23 *Two Versions of the Phase Diagram of Water*



(a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 10.)

In part (b) in Figure 11.23 "Two Versions of the Phase Diagram of Water", point A is located at $P = 1$ atm and $T = -1.0^{\circ}\text{C}$, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at -1.0°C . We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively

satisfying, it is incorrect, as we can show by a simple calculation. Recall from Chapter 10 "Gases" that pressure (P) is the force (F) applied per unit area (A):

Equation 11.4

$$P = FA$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

Equation 11.5

$$F = mg$$

where m is the mass and g is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

Equation 11.6

$$F = (75.0 \text{ kg})(9.81 \text{ m/s}^2) = 736 \text{ (kg}\cdot\text{m)/s}^2 = 736 \text{ N}$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

Equation 11.7

$$A = (2.0 \times 10^{-3} \text{ m})(25 \times 10^{-2} \text{ m}) = 5.0 \times 10^{-4} \text{ m}^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

Equation 11.8

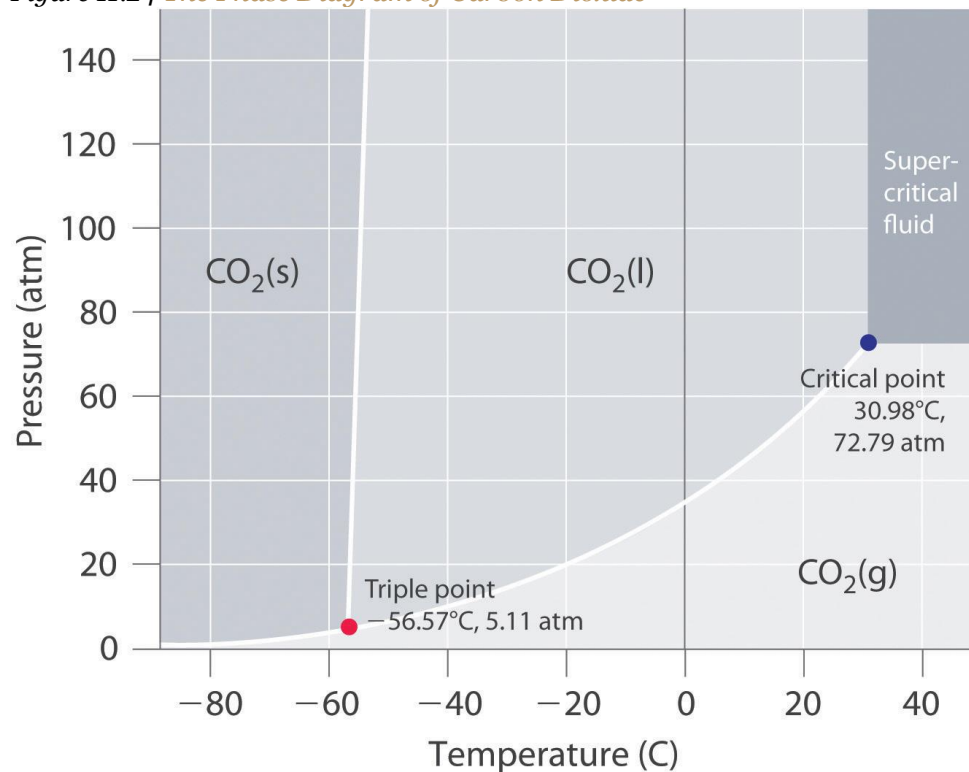
$$\begin{aligned} P &= 736 \text{ N} / 5.0 \times 10^{-4} \text{ m}^2 \\ &= 1.5 \times 10^6 \text{ N/m}^2 = 1.5 \times 10^6 \text{ Pa} = 15 \text{ atm} \end{aligned}$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C , and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about -7°C , when the number of lubricating surface water layers decreases.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO₂ (Figure 11.24 "The Phase Diagram of Carbon Dioxide") has a more typical melting curve, sloping up and to the right. The triple point is -56.6°C and 5.11 atm, which means that liquid CO₂ cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO₂ sublimates directly to the vapor while maintaining a temperature of -78.5°C , the normal sublimation temperature. Solid CO₂ is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed. Also notice the critical point at 30.98°C and 72.79 atm. In addition to the uses discussed in Section 11.6 "Critical Temperature and Pressure", supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

Figure 11.24 *The Phase Diagram of Carbon Dioxide*



Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

EXAMPLE 10

Referring to the phase diagram of water in Figure 11.23 "Two Versions of the Phase Diagram of Water",

- predict the physical form of a sample of water at 400°C and 150 atm.
- describe the changes that occur as the sample in part (a) is slowly allowed to cool to -50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.

B Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

A Locate the starting point on the phase diagram in part (a) in Figure 11.23 "Two Versions of the Phase Diagram of Water". The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at $T = 400^{\circ}\text{C}$ and $P = 150\text{ atm}$ is a gas.

B Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 11.23 "Two Versions of the Phase Diagram of Water". At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to -50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At $P = 150\text{ atm}$ and $T = -50^{\circ}\text{C}$, therefore, the sample is solid ice.

Exercise

Referring to the phase diagram of water in Figure 11.23 "Two Versions of the Phase Diagram of Water", predict the physical form of a sample of water at -0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer: The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

Summary

The states of matter exhibited by a substance under different temperatures and pressures can be summarized graphically in a **phase diagram**, which is a plot of pressure versus temperature. Phase diagrams contain discrete regions corresponding to the solid, liquid, and gas phases. The solid and liquid regions are separated by the melting curve of the substance, and the liquid and gas regions are separated by its vapor pressure curve, which ends at the critical point. Within a given region, only a single phase is stable, but along the lines that separate the regions, two phases are in equilibrium at a given temperature and pressure. The lines separating the three phases intersect at a single point, the **triple point**, which is the only combination of temperature and pressure at which all three phases can coexist in equilibrium. Water has an unusual phase diagram: its melting point decreases with increasing pressure because ice is less dense than liquid water. The phase diagram of carbon dioxide shows that liquid carbon dioxide cannot exist at atmospheric pressure. Consequently, solid carbon dioxide sublimates directly to a gas.

KEY TAKEAWAY

- A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system. It shows the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical region.

CONCEPTUAL PROBLEMS

1. A phase diagram is a graphic representation of the stable phase of a substance at any combination of temperature and pressure. What do the lines separating different regions in a phase diagram indicate? What information does the slope of a line in a phase diagram convey about the physical properties of the phases it separates? Can a phase diagram have more than one point where three lines intersect?
2. If the slope of the line corresponding to the solid/liquid boundary in the phase diagram of water were positive rather than negative, what would be the effect on aquatic life during periods of subzero temperatures? Explain your answer.

ANSWER

1. The lines in a phase diagram represent boundaries between different phases; at any combination of temperature and pressure that lies on a line, two phases are in equilibrium. It is physically impossible for more than three phases to coexist at any combination of temperature and pressure, but in principle there can be more than one triple point in a phase diagram. The slope of the line separating two phases depends

upon their relative densities. For example, if the solid–liquid line slopes up and to the *right*, the liquid is less dense than the solid, while if it slopes up and to the *left*, the liquid is denser than the solid.

2.

NUMERICAL PROBLEMS

1. Naphthalene ($C_{10}H_8$) is the key ingredient in mothballs. It has normal melting and boiling points of 81°C and 218°C , respectively. The triple point of naphthalene is 80°C at 1000 Pa. Use these data to construct a phase diagram for naphthalene and label all the regions of your diagram.
2. Argon is an inert gas used in welding. It has normal boiling and freezing points of 87.3 K and 83.8 K, respectively. The triple point of argon is 83.8 K at 0.68 atm. Use these data to construct a phase diagram for argon and label all the regions of your diagram.

11.8 Liquid Crystals

LEARNING OBJECTIVE

1. To describe the properties of liquid crystals.

When cooled, most liquids undergo a simple phase transition to an ordered crystalline solid, a relatively rigid substance that has a fixed shape and volume. (For more information on the characteristics of matter, see Chapter 1 "Introduction to Chemistry", Section 1.3 "A Description of Matter".) In the phase diagrams for these liquids, there are no regions between the liquid and solid phases. Thousands of substances are known, however, that exhibit one or more phases intermediate between the liquid state, in which the molecules are free to tumble and move past one another, and the solid state, in which the molecules or ions are rigidly locked into place. In these intermediate phases, the molecules have an ordered arrangement and yet can still flow like a liquid. Hence they are called liquid crystals, and their unusual properties have found a wide range of commercial applications. They are used, for example, in the liquid crystal displays (LCDs) in digital watches, calculators, and computer and video displays.

The first documented example of a liquid crystal was reported by the Austrian Frederick Reinitzer in 1888. Reinitzer was studying the properties of a cholesterol derivative, cholesteryl benzoate, and noticed that it behaved strangely as it melted. The white solid first formed a cloudy white liquid phase at 145°C , which reproducibly transformed into a clear liquid at 179°C (Figure 11.25 "Cholesteryl Benzoate"). The

transitions were completely reversible: cooling molten cholesteryl benzoate below 179°C caused the clear liquid to revert to a milky one, which then crystallized at the melting point of 145°C.

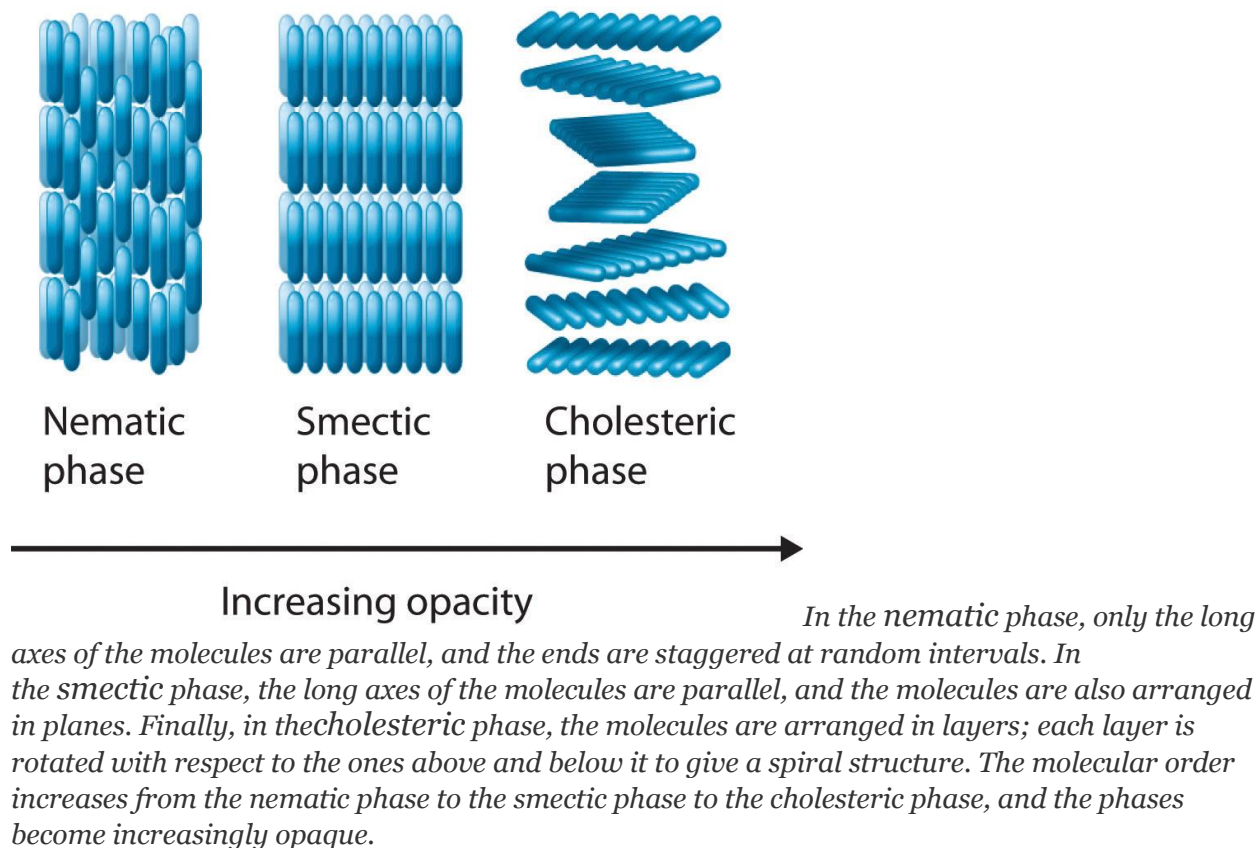
Cholesteryl Benzoate

(a) When the temperature is greater than 179°C, the substance is an isotropic liquid through which images can be seen. (b) When the temperature is between 145°C and 179°C, the substance is in the cholesteric liquid crystalline phase and is an opaque, milky liquid.

In a normal liquid, the molecules possess enough thermal energy to overcome the intermolecular attractive forces and tumble freely. This arrangement of the molecules is described as isotropic, which means that it is equally disordered in all directions. Liquid crystals, in contrast, are anisotropic: their properties depend on the direction in which they are viewed. Hence liquid crystals are not as disordered as a liquid because the molecules have some degree of alignment.

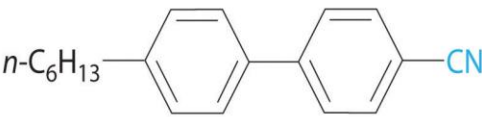
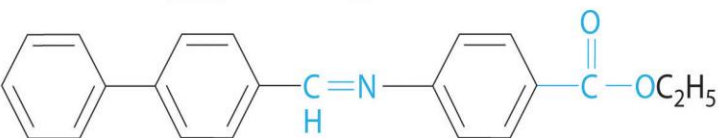
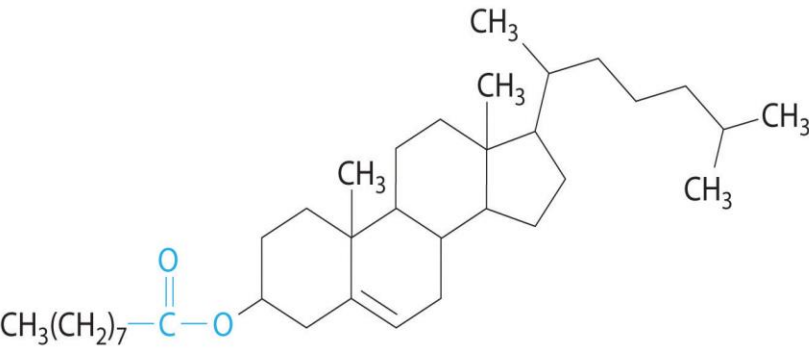
Most substances that exhibit the properties of liquid crystals consist of long, rigid rod- or disk-shaped molecules that are easily polarizable and can orient themselves in one of three different ways, as shown in Figure 11.26 "The Arrangement of Molecules in the Nematic, Smectic, and Cholesteric Liquid Crystal Phases". In the nematic phase, the molecules are not layered but are pointed in the same direction. As a result, the molecules are free to rotate or slide past one another. In the smectic phase, the molecules maintain the general order of the nematic phase but are also aligned in layers. Several variants of the smectic phase are known, depending on the angle formed between the molecular axes and the planes of molecules. The simplest such structure is the so-called smectic A phase, in which the molecules can rotate about their long axes within a given plane, but they cannot readily slide past one another. In the cholesteric phase, the molecules are directionally oriented and stacked in a helical pattern, with each layer rotated at a slight angle to the ones above and below it. As the degree of molecular ordering increases from the nematic phase to the cholesteric phase, the liquid becomes more opaque, although direct comparisons are somewhat difficult because most compounds form only one of these liquid crystal phases when the solid is melted or the liquid is cooled.

Figure 11.26 The Arrangement of Molecules in the Nematic, Smectic, and Cholesteric Liquid Crystal Phases



Molecules that form liquid crystals tend to be rigid molecules with polar groups that exhibit relatively strong dipole–dipole or dipole–induced dipole interactions, hydrogen bonds, or some combination of both. Some examples of substances that form liquid crystals are listed in Figure 11.27 "Structures of Typical Molecules That Form Liquid Crystals*" along with their characteristic phase transition temperature ranges. In most cases, the intermolecular interactions are due to the presence of polar or polarizable groups. Aromatic rings and multiple bonds between carbon and nitrogen or oxygen are especially common. Moreover, many liquid crystals are composed of molecules with two similar halves connected by a unit having a multiple bond.

*Figure 11.27 Structures of Typical Molecules That Form Liquid Crystals**

Structure	Liquid Crystal Phase	Liquid Crystalline Temperature Range (°C)
	Nematic	14–28
	Smectic	121–131
	Cholesteric	78–90

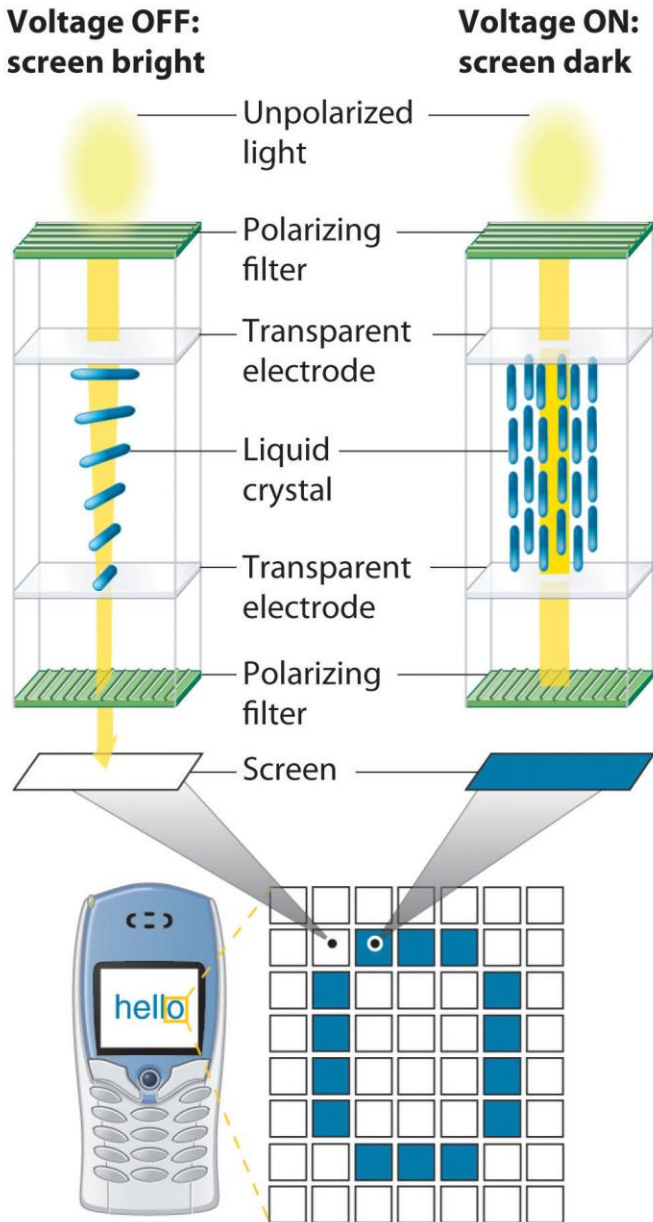
**Polar or polarizable groups are indicated in blue.*

Because of their anisotropic structures, liquid crystals exhibit unusual optical and electrical properties. The intermolecular forces are rather weak and can be perturbed by an applied electric field. Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly. Nematic liquid crystals, for example, tend to be relatively translucent, but many of them become opaque when an electric field is applied and the molecular orientation changes. This behavior is ideal for producing dark images on a light or an opalescent background, and it is used in the LCDs in digital watches; handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation. Although each application differs in the details of its construction and operation, the basic principles are similar, as illustrated in Figure 11.28 "Schematic Drawing of an LCD Device, Showing the Various Layers".

Note the Pattern

Liquid crystals tend to form from long, rigid molecules with polar groups.

Figure 11.28 Schematic Drawing of an LCD Device, Showing the Various Layers

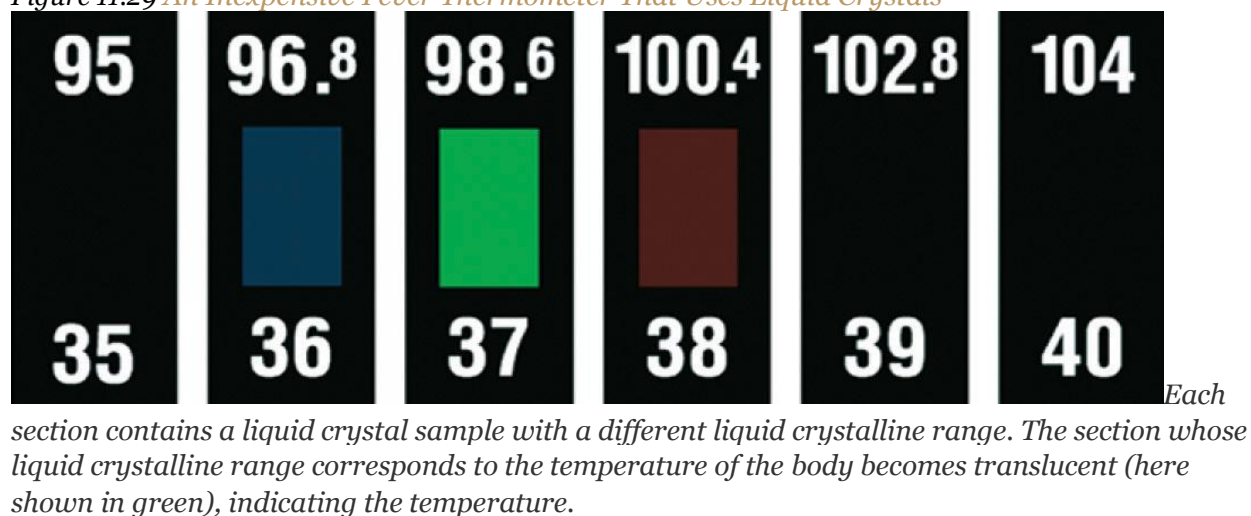


Applying a voltage to selected segments of the device will produce any of the numbers. The device is a sandwich that contains several very thin layers, consisting of (from top to bottom) a sheet of polarizer to produce polarized light, a transparent electrode, a thin layer of a liquid crystalline substance, a second transparent electrode, a second polarizer, and a screen. Applying an electrical voltage to the liquid crystal changes its orientation slightly, which rotates the plane of the polarized light and makes the area appear dark.

Changes in molecular orientation that are dependent on temperature result in an alteration of the wavelength of reflected light. Changes in reflected light produce a change in color, which can be customized by using either a single type of liquid crystalline material or mixtures. It is therefore possible to build a liquid crystal thermometer that indicates temperature by color (Figure 11.29 "An Inexpensive

Fever Thermometer That Uses Liquid Crystals") and to use liquid crystals in heat-sensitive films to detect flaws in electronic board connections where overheating can occur.

Figure 11.29 An Inexpensive Fever Thermometer That Uses Liquid Crystals



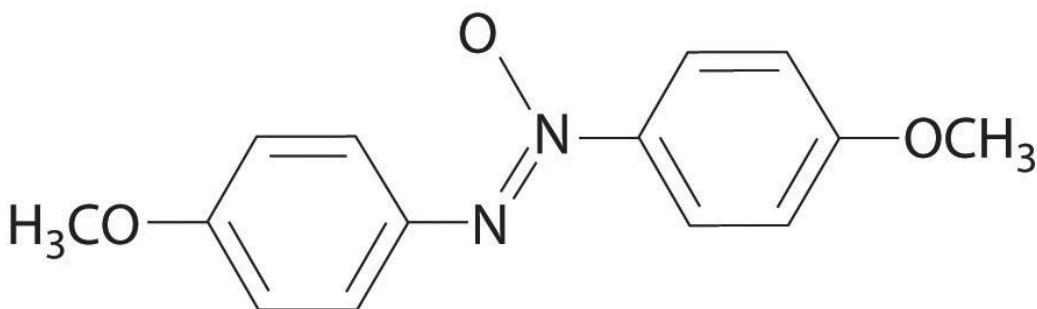
We also see the effect of liquid crystals in nature. Iridescent green beetles, known as jewel beetles, change color because of the light-reflecting properties of the cells that make up their external skeletons, not because of light absorption from their pigment. The cells form helices with a structure like those found in cholesteric liquid crystals. When the pitch of the helix is close to the wavelength of visible light, the cells reflect light with wavelengths that lead to brilliant metallic colors. Because a color change occurs depending on a person's angle of view, researchers in New Zealand are studying the beetles to develop a thin material that can be used as a currency security measure. The automobile industry is also interested in exploring such materials for use in paints that would change color at different viewing angles.

With only molecular structure as a guide, one cannot precisely predict which of the various liquid crystalline phases a given compound will actually form. One can, however, identify molecules containing the kinds of structural features that tend to result in liquid crystalline behavior, as demonstrated in Example 11.

EXAMPLE 11

Which molecule is most likely to form a liquid crystalline phase as the isotropic liquid is cooled?

- isooctane (2,2,4-trimethylpentane)
- ammonium thiocyanate [$\text{NH}_4(\text{SCN})$]
- p*-azoxyanisole



***p*-Azoxyanisole**

d.

sodium decanoate $\{\text{Na}[\text{CH}_3(\text{CH}_2)_8\text{CO}_2]\}$

Given: compounds

Asked for: liquid crystalline behavior

Strategy:

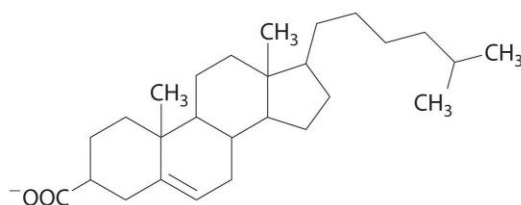
Determine which compounds have a rigid structure and contain polar groups. Those that do are likely to exhibit liquid crystal behavior.

Solution:

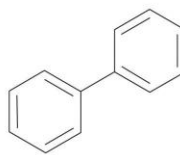
- a. Isooctane is not long and rigid and contains no polar groups, so it is unlikely to exhibit liquid crystal behavior.
- b. Ammonium thiocyanate is ionic, and ionic compounds tend to have high melting points, so it should not form a liquid crystalline phase. In fact, ionic compounds that form liquid crystals are very rare indeed.
- b. *p*-Azoxyanisole combines two planar phenyl rings linked through a multiply bonded unit, and it contains polar groups. The combination of a long, rigid shape and polar groups makes it a reasonable candidate for a liquid crystal.
- c. Sodium decanoate is the sodium salt of a straight-chain carboxylic acid. The *n*-alkyl chain is long, but it is flexible rather than rigid, so the compound is probably not a liquid crystal.

Exercise

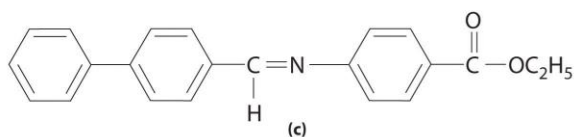
Which compound is least likely to form a liquid crystal phase?



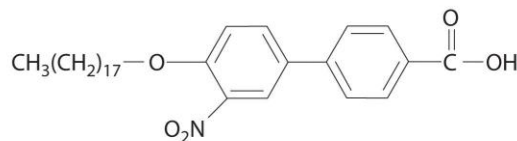
(a) Cholesterol acetate



(b) Biphenyl



(c)



(d)

Answer: (b) Biphenyl; although it is rather long and rigid, it lacks any polar substituents.

Summary

Many substances exhibit phases that have properties intermediate between those of a crystalline solid and a normal liquid. These substances, which possess long-range molecular order but still flow like liquids, are called **liquid crystals**. Liquid crystals are typically long, rigid molecules that can interact strongly with one another; they do not have **isotropic** structures, which are completely disordered, but rather have **anisotropic** structures, which exhibit different properties when viewed from different directions. In the **nematic phase**, only the long axes of the molecules are aligned, whereas in the **smectic phase**, the long axes of the molecules are parallel and the molecules are arranged in planes. In the **cholesteric phase**, the molecules are arranged in planes, but each layer is rotated by a certain amount with respect to those above and below it, giving a helical structure.

KEY TAKEAWAY

- Liquid crystals tend to consist of rigid molecules with polar groups, and their anisotropic structures exhibit unusual optical and electrical properties.

CONCEPTUAL PROBLEMS

- Describe the common structural features of molecules that form liquid crystals. What kind of intermolecular interactions are most likely to result in a long-chain molecule that exhibits liquid crystalline behavior? Does an electrical field affect these interactions?
- What is the difference between an *isotropic* liquid and an *anisotropic* liquid? Which is more anisotropic—a cholesteric liquid crystal or a nematic liquid crystal?

11.9 Essential Skills 6

TOPICS

- Natural Logarithms
- Calculations Using Natural Logarithms

Essential Skills 3 in Chapter 4 "Reactions in Aqueous Solution", Section 4.10 "Essential Skills 3", introduced the common, or base-10, logarithms and showed how to use the properties of exponents to perform logarithmic calculations. In this section, we describe natural logarithms, their relationship to common logarithms, and how to do calculations with them using the same properties of exponents.

Natural Logarithms

Many natural phenomena exhibit an exponential rate of increase or decrease. Population growth is an example of an exponential rate of increase, whereas a runner's performance may show an exponential decline if initial improvements are substantially greater than those that occur at later stages of training. Exponential changes are represented logarithmically by ex , where e is an irrational number whose value is approximately 2.7183. The *natural logarithm*, abbreviated as $\ln$, is the power x to which e must be raised to obtain a particular number. The natural logarithm of e is 1 ($\ln e = 1$).

Some important relationships between base-10 logarithms and natural logarithms are as follows:

$$10^1 = 10 = e^{2.303} \ln ex = x \ln 10 = \ln(e^{2.303}) = 2.303 \log 10 = \ln e = 1$$

According to these relationships, $\ln 10 = 2.303$ and $\log 10 = 1$. Because multiplying by 1 does not change an equality,

$$\ln 10 = 2.303 \log 10$$

Substituting any value y for 10 gives

$$\ln y = 2.303 \log y$$

Other important relationships are as follows:

$$\log Ax = x \log A \ln ex = x \ln e = x = e^{\ln x}$$

Entering a value x , such as 3.86, into your calculator and pressing the "ln" key gives the value of $\ln x$, which is 1.35 for $x = 3.86$. Conversely, entering the value 1.35 and pressing "ex" key gives an answer of

$$3.86. \quad \text{Hence} \quad e^{\ln 3.86} = e^{1.35} = 3.86 \ln(e^{3.86}) = 3.86$$

SKILL BUILDER ES1

Calculate the natural logarithm of each number and express each as a power of the base e .

a. 0.523

b. 1.63

Solution:

a. $\ln(0.523) = -0.648; e^{-0.648} = 0.523$

b. $\ln(1.63) = 0.489; e^{0.489} = 1.63$

SKILL BUILDER ES2

What number is each value the natural logarithm of?

a. 2.87

b. 0.030

c. -1.39

Solution:

a. $\ln x = 2.87; x = e^{2.87} = 17.6 = 18$ to two significant figures

b. $\ln x = 0.030; x = e^{0.030} = 1.03 = 1.0$ to two significant figures

c. $\ln x = -1.39; x = e^{-1.39} = 0.249 = 0.25$

Calculations with Natural Logarithms

Like common logarithms, natural logarithms use the properties of exponents. We can expand Table 4.5

"Relationships in Base-10 Logarithms" in Essential Skills 3 to include natural logarithms:

Operation	Exponential Form	Logarithm
Multiplication	$(10^a)(10^b) = 10^{a+b}$	$\log(ab) = \log a + \log b$
	$(e^x)(e^y) = e^{x+y}$	$\ln(exey) = \ln(ex) + \ln(ey) = x + y$
Division	$\frac{10^a}{10^b} = 10^{a-b}$	$\log\left(\frac{a}{b}\right) = \log a - \log b$ $\ln\left(\frac{xy}{z}\right) = \ln(xy) - \ln(z)$ $\ln(exey) = \ln(ex) - \ln(ey) = x - y$
	$\frac{e^x}{e^y} = e^{x-y}$	$\ln\left(\frac{xy}{z}\right) = \ln(xy) - \ln(z)$ $\ln(exey) = \ln(ex) - \ln(ey) = x - y$
Inverse		$\log(1a) = -\log a$ $\ln(1x) = -\ln x$

The number of significant figures in a number is the same as the number of digits after the decimal point in its logarithm. For example, the natural logarithm of 18.45 is 2.9151, which means that $e^{2.9151}$ is equal to 18.45.

SKILL BUILDER ES3

Calculate the natural logarithm of each number.

a. 22×18.6

0.512.67 c. 0.079×1.485

20.50.026

Solution:

a. $\ln(22 \times 18.6) = \ln(22) + \ln(18.6) = 3.09 + 2.923 = 6.01$. Alternatively, $22 \times 18.6 = 410$;

$\ln(410) = 6.02$.

$\ln(0.512.67) = \ln(0.51) - \ln(2.67)$

b. $= -0.67 - 0.982 = -1.65$. $(0.19) = -1.66$.

Alternatively, $0.512.67 = 0.19$; $\ln$

c. $\ln(0.079 \times 1.485) = \ln(0.079) + \ln(1.485) = -2.54 + 0.395 = -2.15$. Alternatively,

$0.079 \times 1.485 = 0.12$; $\ln(0.12) = -2.12$.

$\ln(20.50.026) = \ln(20.5) - \ln(0.026)$

d. $= 3.0204 - (-3.65) = 6.67$. $(790) = 6.67$.

Alternatively, $20.50.026 = 790$; $\ln$

The answers obtained using the two methods may differ slightly due to rounding errors.

SKILL BUILDER ES4

Calculate the natural logarithm of each number.

a. 34×16.5

b. a. $2.100.052$ 0.402×3.930

a. $0.16410.7$

Solution:

a. 6.33

b. 3.70

c. 0.457

d. -4.178

[1] On some calculators, pressing [INV] and then [$\ln x$] is equivalent to pressing [$\ln$].

11.10 End-of-Chapter Material

APPLICATION PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 6 (Section 11.9 "Essential Skills 6") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. During cold periods, workers in the citrus industry often spray water on orange trees to prevent them from being damaged, even though ice forms on the fruit.
 - a. Explain the scientific basis for this practice.
 - b. To illustrate why the production of ice prevents damage to the fruit during cold weather, calculate the heat released by formation of ice from 1000 L of water at 10°C.
2. ♦ Relative humidity is the ratio of the actual partial pressure of water in the air to the vapor pressure of water at that temperature (i.e., if the air was completely saturated with water vapor), multiplied by 100 to give a percentage. On a summer day in the Chesapeake, when the temperature was recorded as 35°C, the partial pressure of water was reported to be 33.9 mmHg.
 - a. The following table gives the vapor pressure of water at various temperatures. Calculate the relative humidity.

<i>T</i> (°C)	0	10	30	50	60	80	100
<i>P</i> (mmHg)	4.6	9.2	31.8	92.6	150	355	760

- b. Why does it seem “drier” in the winter, even though the relative humidity may be the same as in the summer?
3. ♦ Liquids are frequently classified according to their physical properties, such as surface tension, vapor pressure, and boiling point. Such classifications are useful when substitutes are needed for a liquid that might not be available.
 - a. Draw the structure of methanol, benzene, pentane, toluene, cyclohexane, 1-butanol, trichloroethylene, acetic acid, acetone, and chloroform.
 - b. Identify the most important kind of intermolecular interaction in each.
 - c. Sort the compounds into three groups with similar characteristics.
 - d. If you needed a substitute for trimethylpentane, from which group would you make your selection?
4. ♦ In the process of freeze drying, which is used as a preservation method and to aid in the shipping or storage of fruit and biological samples, a sample is cooled and then placed in a compartment in which a very low pressure is maintained, ≈ 0.01 atm.
 - a. Explain how this process removes water and “dries” the sample.
 - b. Identify the phase change that occurs during this process.

- c. Using the Clausius–Clapeyron equation, show why it is possible to remove water and still maintain a low temperature at this pressure.
5. ♦ Many industrial processes for preparing compounds use “continuous-flow reactors,” which are chemical reaction vessels in which the reactants are mixed and allowed to react as they flow along a tube. The products are removed at a certain distance from the starting point, when the reaction is nearly complete. The key operating parameters in a continuous-flow reactor are temperature, reactor volume, and reactant flow rate. As an industrial chemist, you think you have successfully modified a particular process to produce a higher product yield by substituting one reactant for another. The viscosity of the new reactant is, however, greater than that of the initial reactant.
- a. Which of the operating parameters will be most greatly affected by this change?
- b. What other parameter could be changed to compensate for the substitution?
- c. Predict the possible effects on your reactor and your process if you do not compensate for the substitution.

Chapter 12

Solids

In this chapter, we turn our attention to the structures and properties of solids. The solid state is distinguished from the gas and liquid states by a rigid structure in which the component atoms, ions, or molecules are usually locked into place. In many solids, the components are arranged in extended three-dimensional patterns, producing a wide range of properties that can often be tailored to specific functions. Thus diamond, an allotrope of elemental carbon, is one of the hardest materials known, yet graphite, another allotrope of carbon, is a soft, slippery material used in pencil lead and as a lubricant. Metallic sodium is soft enough to be cut with a dull knife, but crystalline sodium chloride turns into a fine powder when struck with a hammer.

Solids, also called *materials*, are so important in today’s technology that the subdisciplines of solid-state chemistry and materials science are among the most active and exciting areas of modern chemical research. After presenting a basic survey of the structures of solids, we will examine how the properties of solids are determined by their composition and structure. We will also explore the principles underlying the electrical properties of metals, insulators, semiconductors (which are at the heart of the modern electronics industry), and superconductors. By the end of the chapter, you will know why some metals “remember” their shape after being bent and why ceramics are used in jet engines. You will also understand why carbon- or boron-fiber materials are used in high-performance golf

clubs and tennis rackets, why nylon is used to make parachutes, and how solid electrolytes improve the performance of high-capacity batteries.

12.1 Crystalline and Amorphous Solids

LEARNING OBJECTIVE

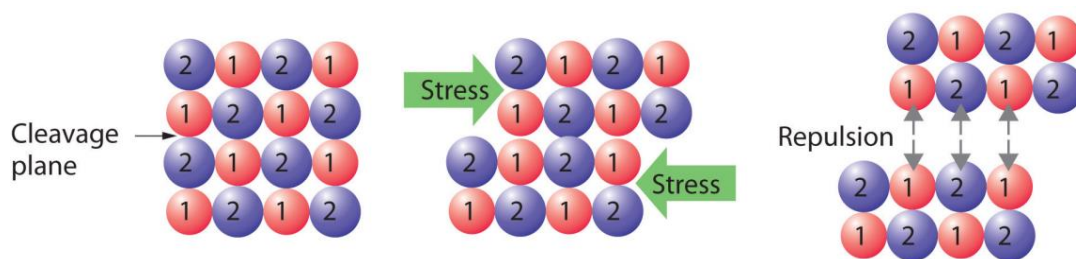
1. To know the characteristic properties of crystalline and amorphous solids.

With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the *positions* of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal lattice, thus producing a crystalline solid, or they can aggregate with no particular order, in which case they form an amorphous solid (from the Greek *ámorphos*, meaning “shapeless”).

Crystalline solids, or *crystals*, have distinctive internal structures that in turn lead to distinctive flat surfaces, or *faces*. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material (see **Section 12.3 "Structures of Simple Binary Compounds"**). The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (**Figure 12.1 "Cleaving a Crystal of an Ionic Compound along a Plane of Ions"**), for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.

Crystalline faces. *The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS₂), or at other angles, as in quartz.*

Figure 12.1 Cleaving a Crystal of an Ionic Compound along a Plane of Ions



Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glass. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO_2 and both consist of linked SiO_4 tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO_2 is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of $4 \times 10^{13} \text{ K/s}$, which prevents the atoms from arranging themselves into a regular array.

12.1 Crystalline and Amorphous Solids

LEARNING OBJECTIVE

1. To know the characteristic properties of crystalline and amorphous solids.

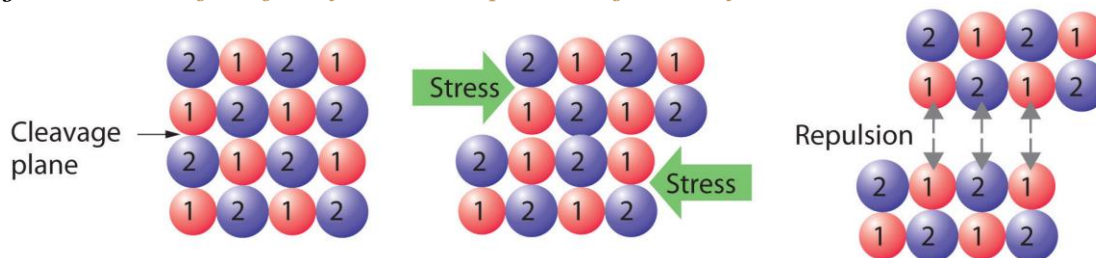
With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider

the *positions* of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal lattice, thus producing a crystalline solid, or they can aggregate with no particular order, in which case they form an amorphous solid (from the Greek *ámorphos*, meaning “shapeless”).

Crystalline solids, or *crystals*, have distinctive internal structures that in turn lead to distinctive flat surfaces, or *faces*. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material (see Section 12.3 “Structures of Simple Binary Compounds”). The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (Figure 12.1 “Cleaving a Crystal of an Ionic Compound along a Plane of Ions”), for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.

Crystalline faces. *The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS₂), or at other angles, as in quartz.*

Figure 12.1 *Cleaving a Crystal of an Ionic Compound along a Plane of Ions*

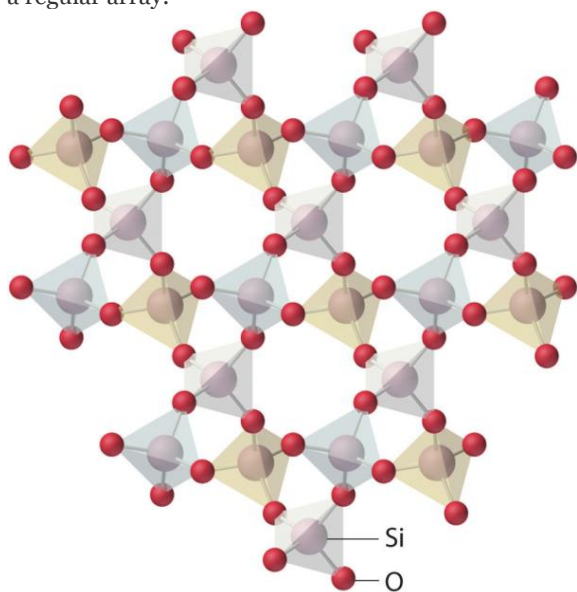


Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glass. Almost any substance can solidify

in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO_2 and both consist of linked SiO_4 tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO_2 is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of 4×10^{13} K/s, which prevents the atoms from arranging themselves into a regular array.



he lattice of crystalline quartz (SiO_2). The atoms form a regular arrangement in a structure that consists of linked tetrahedra.

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

Note the Pattern

Crystals have sharp, well-defined melting points; amorphous solids do not.

Summary

Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a **crystal lattice**), which results in a **crystalline solid**, or more or less randomly to produce an **amorphous solid**. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

KEY TAKEAWAY

- Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays.

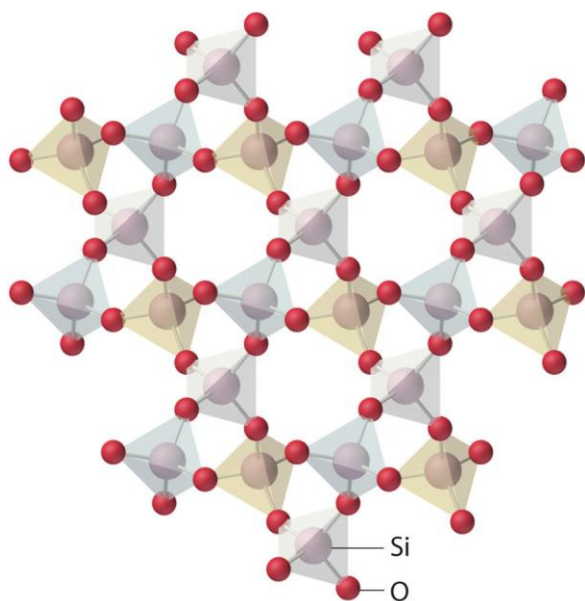
CONCEPTUAL PROBLEMS

1. Compare the solid and liquid states in terms of
 - a. rigidity of structure.
 - b. long-range order.
 - c. short-range order.
2. How do amorphous solids differ from crystalline solids in each characteristic? Which of the two types of solid is most similar to a liquid?
 - a. rigidity of structure
 - b. long-range order
 - c. short-range order
3. Why is the arrangement of the constituent atoms or molecules more important in determining the properties of a solid than a liquid or a gas?
4. Why are the structures of solids usually described in terms of the positions of the constituent atoms rather than their motion?
5. What physical characteristics distinguish a crystalline solid from an amorphous solid? Describe at least two ways to determine experimentally whether a material is crystalline or amorphous.
6. Explain why each characteristic would or would not favor the formation of an amorphous solid.
 - a. slow cooling of pure molten material

- b. impurities in the liquid from which the solid is formed
 - c. weak intermolecular attractive forces
7. A student obtained a solid product in a laboratory synthesis. To verify the identity of the solid, she measured its melting point and found that the material melted over a 12°C range. After it had cooled, she measured the melting point of the same sample again and found that this time the solid had a sharp melting point at the temperature that is characteristic of the desired product. Why were the two melting points different? What was responsible for the change in the melting point?

ANSWERS

- 1.
- 2.
- 3. The arrangement of the atoms or molecules is more important in determining the properties of a solid because of the greater persistent long-range order of solids. Gases and liquids cannot readily be described by the spatial arrangement of their components because rapid molecular motion and rearrangement defines many of the properties of liquids and gases.
- 4.
- 5.
- 6.
- 7. The initial solid contained the desired compound in an amorphous state, as indicated by the wide temperature range over which melting occurred. Slow cooling of the liquid caused it to crystallize, as evidenced by the sharp second melting point observed at the expected temperature.



The lattice of crystalline quartz (SiO_2). The atoms form a regular arrangement in a structure that consists of linked tetrahedra.

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

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12.2 The Arrangement of Atoms in Crystalline Solids

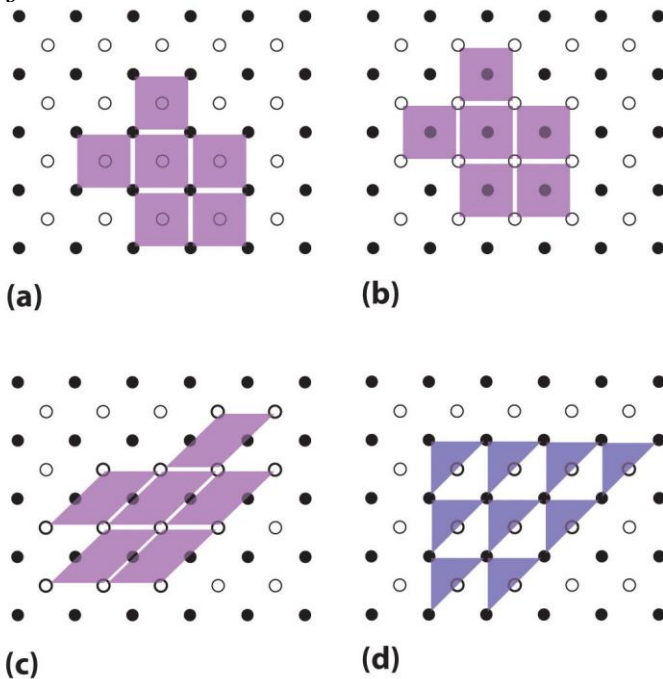
LEARNING OBJECTIVES

1. To recognize the unit cell of a crystalline solid.
2. To calculate the density of a solid given its unit cell.

Because a crystalline solid consists of repeating patterns of its components in three dimensions (a **crystal lattice**), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a **unit cell**. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.

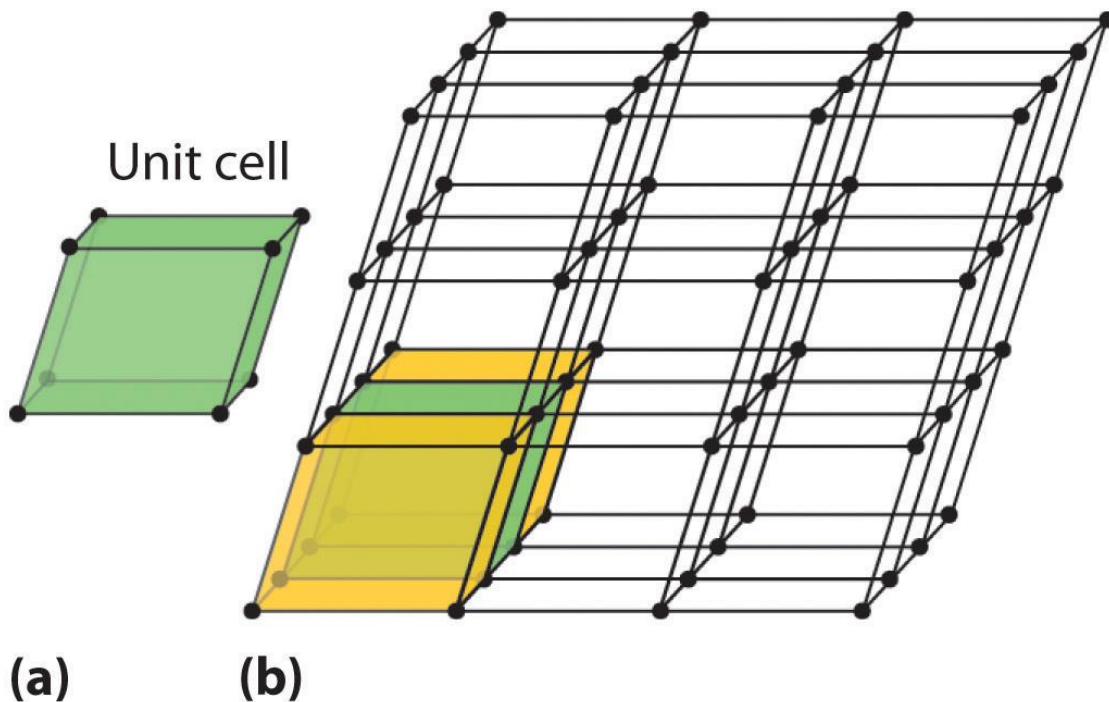
Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in **Figure 12.2 "Unit Cells in Two Dimensions"**. Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in part (d) in **Figure 12.2 "Unit Cells in Two Dimensions"** is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in **Figure 12.3 "Unit Cells in Three Dimensions"**.

Figure 12.2 Unit Cells in Two Dimensions



(a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern.

Figure 12.3 Unit Cells in Three Dimensions

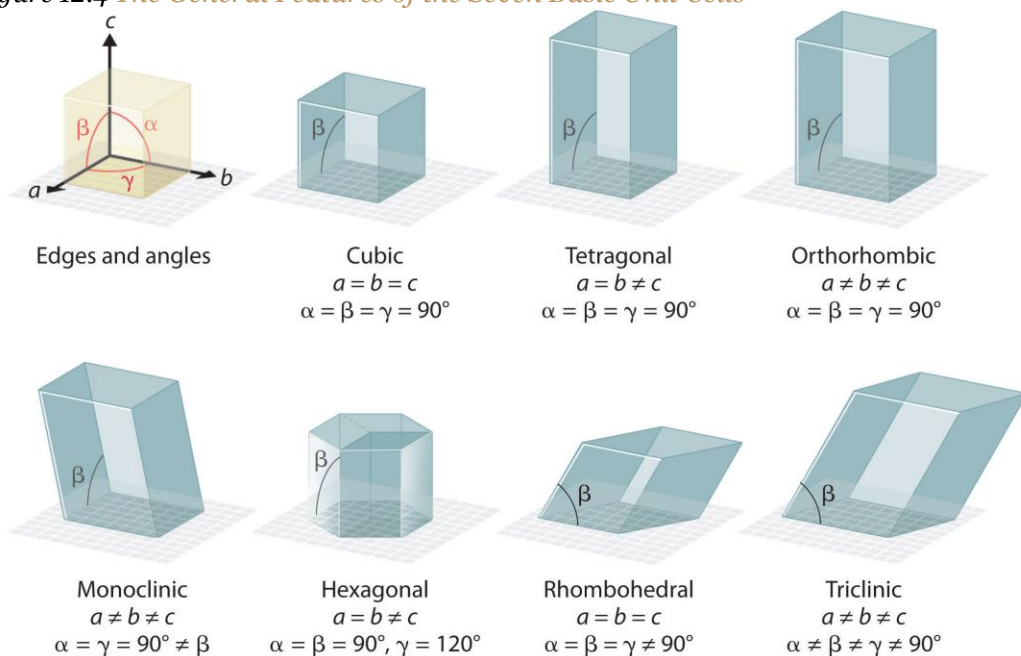


These images show (a) a three-dimensional unit cell and (b) the resulting regular three-dimensional lattice.

The Unit Cell

There are seven fundamentally different kinds of unit cells, which differ in the relative lengths of the edges and the angles between them (Figure 12.4 "The General Features of the Seven Basic Unit Cells"). Each unit cell has six sides, and each side is a parallelogram. We focus primarily on the cubic unit cells, in which all sides have the same length and all angles are 90° , but the concepts that we introduce also apply to substances whose unit cells are not cubic.

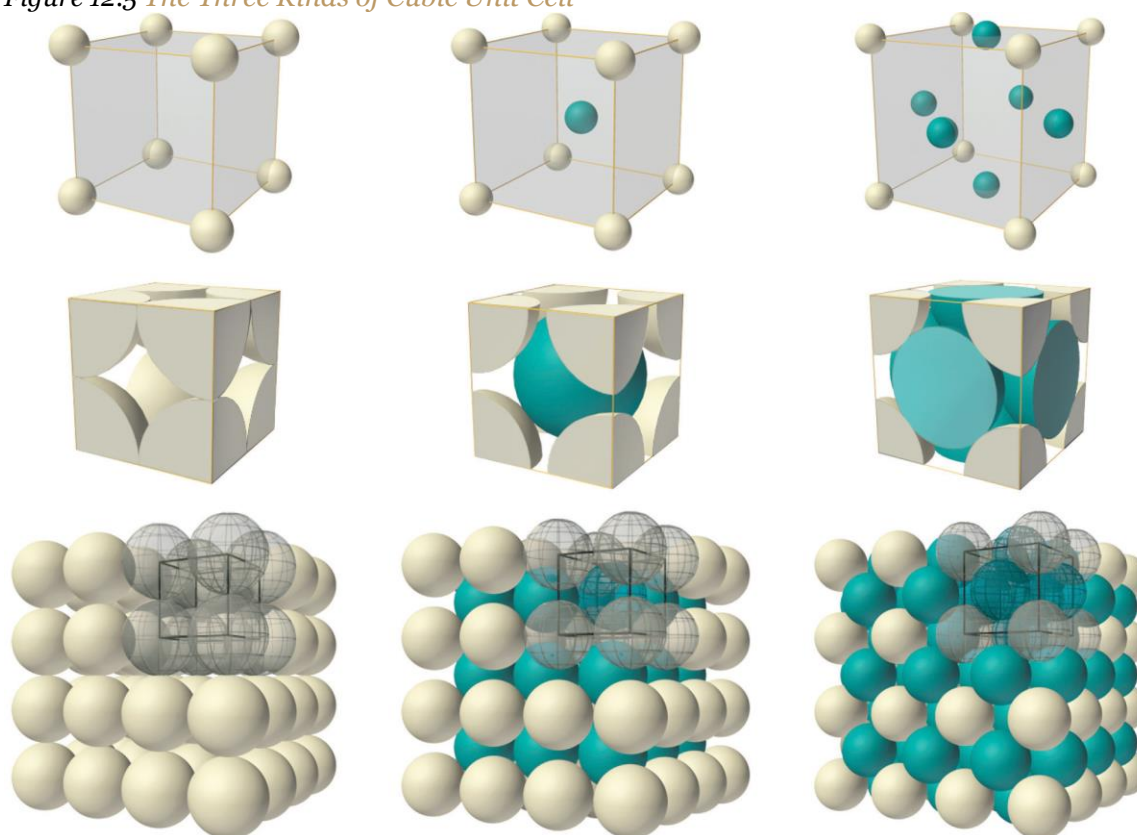
Figure 12.4 The General Features of the Seven Basic Unit Cells



The lengths of the edges of the unit cells are indicated by a , b , and c , and the angles are defined as follows: α , the angle between b and c ; β , the angle between a and c ; and γ , the angle between a and b .

If the cubic unit cell consists of eight component atoms, molecules, or ions located at the corners of the cube, then it is called simple cubic (part (a) in Figure 12.5 "The Three Kinds of Cubic Unit Cell"). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc) (part (b) in Figure 12.5 "The Three Kinds of Cubic Unit Cell"). If there are components in the center of each face in addition to those at the corners of the cube, then the unit cell is face-centered cubic (fcc) (part (c) in Figure 12.5 "The Three Kinds of Cubic Unit Cell").

Figure 12.5 *The Three Kinds of Cubic Unit Cell*



(a) Simple cubic

(b) Body-centered cubic

(c) Face-centered cubic

For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells.

As indicated in Figure 12.5 "The Three Kinds of Cubic Unit Cell", a solid consists of a large number of unit cells arrayed in three dimensions. Any intensive property of the bulk material, such as its density, must therefore also be related to its unit cell. Because **density** is the mass of substance per unit volume, we can calculate the density of the bulk material from the density of a single unit cell. To do this, we need to know the size of the unit cell (to obtain its volume), the molar mass of its components, and the number of components per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 12.5 "The Three Kinds of Cubic Unit Cell". For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore counted as 1/2 atom per unit cell. Similarly, an atom that lies on the edge of a unit cell is shared by four adjacent unit cells, so it contributes 1/4 atom to each. An atom at a corner of a unit cell is shared by all eight adjacent unit cells and therefore contributes 1/8 atom to each.^[1] In contrast, atoms that lie

entirely within a unit cell, such as the atom in the center of a body-centered cubic unit cell, belong to only that one unit cell.

Note the Pattern

For all unit cells except hexagonal, atoms on the faces contribute $\frac{1}{2}$ atom to each unit cell, atoms on the edges contribute $\frac{1}{4}$ atom to each unit cell, and atoms on the corners contribute $\frac{1}{8}$ atom to each unit cell.

EXAMPLE 1

Metallic gold has a face-centered cubic unit cell (part (c) in Figure 12.5 "The Three Kinds of Cubic Unit Cell"). How many Au atoms are in each unit cell?

Given: unit cell

Asked for: number of atoms per unit cell

Strategy:

Using Figure 12.5 "The Three Kinds of Cubic Unit Cell", identify the positions of the Au atoms in a face-centered cubic unit cell and then determine how much each Au atom contributes to the unit cell. Add the contributions of all the Au atoms to obtain the total number of Au atoms in a unit cell.

Solution:

As shown in Figure 12.5 "The Three Kinds of Cubic Unit Cell", a face-centered cubic unit cell has eight atoms at the corners of the cube and six atoms on the faces. Because atoms on a face are shared by two unit cells, each counts as $\frac{1}{2}$ atom per unit cell, giving $6 \times \frac{1}{2} = 3$ Au atoms per unit cell. Atoms on a corner are shared by eight unit cells and hence contribute only $\frac{1}{8}$ atom per unit cell, giving $8 \times \frac{1}{8} = 1$ Au atom per unit cell. The total number of Au atoms in each unit cell is thus $3 + 1 = 4$.

Exercise

Metallic iron has a body-centered cubic unit cell (part (b) in Figure 12.5 "The Three Kinds of Cubic Unit Cell"). How many Fe atoms are in each unit cell?

Answer: two

Now that we know how to count atoms in unit cells, we can use unit cells to calculate the densities of simple compounds. Note, however, that we are assuming a solid consists of a perfect regular array of unit cells, whereas real substances contain impurities and defects that affect many of their bulk properties, including density. Consequently, the results of our calculations will be close but not necessarily identical to the experimentally obtained values.

EXAMPLE 2

Calculate the density of metallic iron, which has a body-centered cubic unit cell (part (b) in Figure 12.5 "The Three Kinds of Cubic Unit Cell") with an edge length of 286.6 pm.

Given: unit cell and edge length

Asked for: density

Strategy:

A Determine the number of iron atoms per unit cell.

B Calculate the mass of iron atoms in the unit cell from the molar mass and Avogadro's number. Then divide the mass by the volume of the cell.

Solution:

A We know from Example 1 that each unit cell of metallic iron contains two Fe atoms.

B The molar mass of iron is 55.85 g/mol. Because density is mass per unit volume, we need to calculate the mass of the iron atoms in the unit cell from the molar mass and Avogadro's number and then divide the mass by the volume of the cell (making sure to use suitable units to get density in g/cm³):

$$\begin{aligned} \text{mass of Fe} &= (2 \text{ atoms Fe}) / (1 \text{ mol} / 6.022 \times 10^{23} \text{ atoms}) \times (55.85 \text{ g/mol}) \\ &= 1.855 \times 10^{-22} \text{ g} \\ \text{volume} &= [(286.6 \text{ pm})(10^{-12} \text{ m/pm}) \\ &\quad (10.2 \text{ cm})]^3 = 2.354 \times 10^{-23} \text{ cm}^3 \\ \text{density} &= 1.855 \times 10^{-22} \text{ g} / 2.354 \times 10^{-23} \text{ cm}^3 = 7.880 \text{ g/cm}^3 \end{aligned}$$

This result compares well with the tabulated experimental value of 7.874 g/cm³.

Exercise

Calculate the density of gold, which has a face-centered cubic unit cell (part (c) in Figure 12.5 "The Three Kinds of Cubic Unit Cell") with an edge length of 407.8 pm.

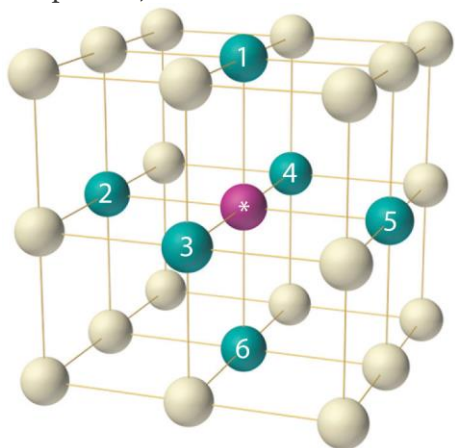
Answer: 19.29 g/cm³

Packing of Spheres

Our discussion of the three-dimensional structures of solids has considered only substances in which all the components are identical. As we shall see, such substances can be viewed as consisting of identical spheres packed together in space; the way the components are packed together produces the different unit cells. Most of the substances with structures of this type are metals.

Simple Cubic Structure

The arrangement of the atoms in a solid that has a simple cubic unit cell was shown in part (a) in Figure 12.5 "The Three Kinds of Cubic Unit Cell". Each atom in the lattice has only six nearest neighbors in an octahedral arrangement. Consequently, the simple cubic lattice is an inefficient way to pack atoms together in space: only 52% of the total space is filled by the atoms. The only element that crystallizes in a simple cubic unit cell is polonium. Simple cubic unit cells are, however, common among binary ionic compounds, where each cation is surrounded by six anions and vice versa.



The arrangement of atoms in a simple cubic unit cell. Each atom in the lattice has six nearest neighbors in an octahedral arrangement.

Body-Centered Cubic Structure

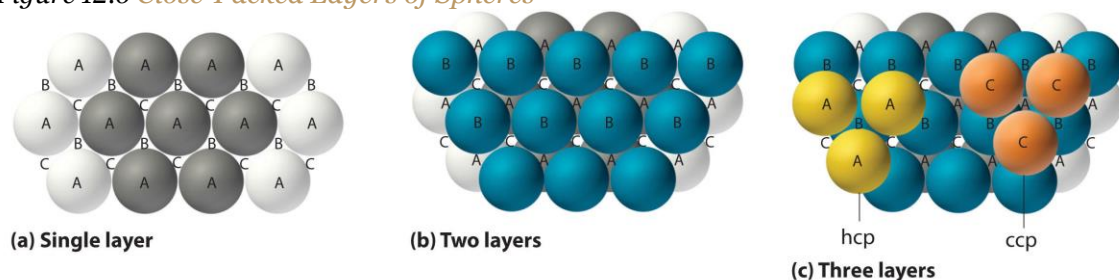
The body-centered cubic unit cell is a more efficient way to pack spheres together and is much more common among pure elements. Each atom has eight nearest neighbors in the unit cell, and 68% of the volume is occupied by the atoms. As shown in part (b) in Figure 12.5 "The Three Kinds of Cubic Unit Cell", the body-centered cubic structure consists of a single layer of spheres in contact with each other and aligned so that their centers are at the corners of a square; a second layer of spheres occupies the square-shaped "holes" above the spheres in the first layer. The third layer of spheres occupies the square holes formed by the second layer, so that each lies directly above a sphere in the first layer, and so forth. All the alkali metals, barium, radium, and several of the transition metals have body-centered cubic structures.

Hexagonal Close-Packed and Cubic Close-Packed Structures

The most efficient way to pack spheres is the close-packed arrangement, which has two variants. A single layer of close-packed spheres is shown in part (a) in Figure 12.6 "Close-Packed Layers of Spheres". Each sphere is surrounded by six others in the same plane to produce a hexagonal arrangement. Above any set of seven spheres are six depressions arranged in a hexagon. In principle, all six sites are the same, and any one of them could be occupied by an atom in the next layer. Actually, however, these six sites can be

divided into two sets, labeled B and C in part (a) in Figure 12.6 "Close-Packed Layers of Spheres". Sites B and C differ because as soon as we place a sphere at a B position, we can no longer place a sphere in any of the three C positions adjacent to A and vice versa.

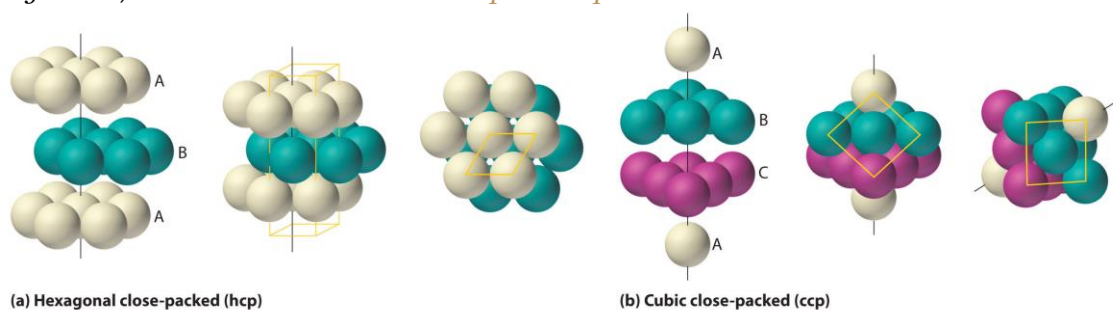
Figure 12.6 Close-Packed Layers of Spheres



(a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second layer occupying the B positions. (c) Placing the atoms in the third layer over the atoms at A positions in the first layer gives the hexagonal close-packed structure. Placing the third-layer atoms over the C positions gives the cubic close-packed structure.

If we place the second layer of spheres at the B positions in part (a) in Figure 12.6 "Close-Packed Layers of Spheres", we obtain the two-layered structure shown in part (b) in Figure 12.6 "Close-Packed Layers of Spheres". There are now two alternatives for placing the first atom of the third layer: we can place it directly over one of the atoms in the first layer (an A position) or at one of the C positions, corresponding to the positions that we did *not* use for the atoms in the first or second layers (part (c) in Figure 12.6 "Close-Packed Layers of Spheres"). If we choose the first arrangement and repeat the pattern in succeeding layers, the positions of the atoms alternate from layer to layer in the pattern ABABAB..., resulting in a hexagonal close-packed (hcp) structure (part (a) in Figure 12.7 "Close-Packed Structures: hcp and ccp"). If we choose the second arrangement and repeat the pattern indefinitely, the positions of the atoms alternate as ABCABC..., giving a cubic close-packed (ccp) structure (part (b) in Figure 12.7 "Close-Packed Structures: hcp and ccp"). Because the ccp structure contains hexagonally packed layers, it does not look particularly cubic. As shown in part (b) in Figure 12.7 "Close-Packed Structures: hcp and ccp", however, simply rotating the structure reveals its cubic nature, which is identical to a fcc structure. The hcp and ccp structures differ only in the way their layers are stacked. Both structures have an overall packing efficiency of 74%, and in both each atom has 12 nearest neighbors (6 in the same plane plus 3 in each of the planes immediately above and below).

Figure 12.7 Close-Packed Structures: hcp and ccp



The illustrations in (a) show an exploded view, a side view, and a top view of the hcp structure. The simple hexagonal unit cell is outlined in the side and top views. Note the similarity to the hexagonal unit cell shown in Figure 12.4 "The General Features of the Seven Basic Unit Cells". The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube.

Table 12.1 "Properties of the Common Structures of Metals" compares the packing efficiency and the number of nearest neighbors for the different cubic and close-packed structures; the number of nearest neighbors is called the coordination number. Most metals have hcp, ccp, or bcc structures, although several metals exhibit both hcp and ccp structures, depending on temperature and pressure.

Table 12.1 Properties of the Common Structures of Metals

Structure	Percentage of Space Occupied by Atoms	Coordination Number
simple cubic	52	6
body-centered cubic	68	8
hexagonal close packed	74	12
cubic close packed (identical to face-centered cubic)	74	12

Summary

The smallest repeating unit of a crystal lattice is the **unit cell**. The **simple cubic** unit cell contains only eight atoms, molecules, or ions at the corners of a cube. A **body-centered cubic (bcc)** unit cell contains one additional component in the center of the cube. A **face-centered cubic (fcc)** unit cell contains a component in the center of each face in addition to those at the corners of the cube. Simple cubic and bcc arrangements fill only 52% and 68% of the available space with atoms, respectively. The **hexagonal close-packed (hcp) structure** has an ABABAB... repeating arrangement, and the **cubic close-packed (ccp) structure** has an ABCABC... repeating pattern; the latter is identical to an fcc lattice. The

hcp and ccp arrangements fill 74% of the available space and have a **coordination number** of 12 for each atom in the lattice, the number of nearest neighbors. The simple cubic and bcc lattices have coordination numbers of 6 and 8, respectively.

KEY TAKEAWAY

- A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure.

CONCEPTUAL PROBLEMS

1. Why is it valid to represent the structure of a crystalline solid by the structure of its unit cell? What are the most important constraints in selecting a unit cell?
2. All unit cell structures have six sides. Can crystals of a solid have more than six sides? Explain your answer.
3. Explain how the intensive properties of a material are reflected in the unit cell. Are all the properties of a bulk material the same as those of its unit cell? Explain your answer.
4. The experimentally measured density of a bulk material is slightly *higher* than expected based on the structure of the pure material. Propose two explanations for this observation.
5. The experimentally determined density of a material is *lower* than expected based on the arrangement of the atoms in the unit cell, the formula mass, and the size of the atoms. What conclusion(s) can you draw about the material?
6. Only one element (polonium) crystallizes with a simple cubic unit cell. Why is polonium the only example of an element with this structure?
7. What is meant by the term *coordination number* in the structure of a solid? How does the coordination number depend on the structure of the metal?
8. Arrange the three types of cubic unit cells in order of increasing packing efficiency. What is the difference in packing efficiency between the hcp structure and the ccp structure?
9. The structures of many metals depend on pressure and temperature. Which structure—bcc or hcp—would be more likely in a given metal at very high pressures? Explain your reasoning.
10. A metal has two crystalline phases. The *transition temperature*, the temperature at which one phase is converted to the other, is 95°C at 1 atm and 135°C at 1000 atm. Sketch a phase diagram for this substance. The metal is known to have either a ccp structure or a simple cubic structure. Label the regions in your diagram appropriately and justify your selection for the structure of each phase.

NUMERICAL PROBLEMS

1. Metallic rhodium has an fcc unit cell. How many atoms of rhodium does each unit cell contain?
2. Chromium has a structure with two atoms per unit cell. Is the structure of this metal simple cubic, bcc, fcc, or hcp?
3. The density of nickel is 8.908 g/cm^3 . If the metallic radius of nickel is 125 pm, what is the structure of metallic nickel?
4. The density of tungsten is 19.3 g/cm^3 . If the metallic radius of tungsten is 139 pm, what is the structure of metallic tungsten?
5. An element has a density of 10.25 g/cm^3 and a metallic radius of 136.3 pm. The metal crystallizes in a bcc lattice. Identify the element.
6. A 21.64 g sample of a nonreactive metal is placed in a flask containing 12.00 mL of water; the final volume is 13.81 mL. If the length of the edge of the unit cell is 387 pm and the metallic radius is 137 pm, determine the packing arrangement and identify the element.
7. A sample of an alkali metal that has a bcc unit cell is found to have a mass of 1.000 g and a volume of 1.0298 cm^3 . When the metal reacts with excess water, the reaction produces 539.29 mL of hydrogen gas at 0.980 atm and 23°C . Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
8. A sample of an alkaline earth metal that has a bcc unit cell is found to have a mass 5.000 g and a volume of 1.392 cm^3 . Complete reaction with chlorine gas requires 848.3 mL of chlorine gas at 1.050 atm and 25°C . Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
9. Lithium crystallizes in a bcc structure with an edge length of 3.509 Å. Calculate its density. What is the approximate metallic radius of lithium in picometers?
10. Vanadium is used in the manufacture of rust-resistant vanadium steel. It forms bcc crystals with a density of 6.11 g/cm^3 at 18.7°C . What is the length of the edge of the unit cell? What is the approximate metallic radius of the vanadium in picometers?
11. A simple cubic cell contains one metal atom with a metallic radius of 100 pm.
 - a. Determine the volume of the atom(s) contained in one unit cell [the volume of a sphere = $(4/3)\pi r^3$].

- b. What is the length of one edge of the unit cell? (Hint: there is no empty space between atoms.)
- c. Calculate the volume of the unit cell.
- d. Determine the packing efficiency for this structure.
- e. Use the steps in Problem 11 to calculate the packing efficiency for a bcc unit cell with a metallic radius of 1.00 Å.

ANSWERS

1. four
- 2.
3. fcc
- 4.
5. molybdenum
- 6.
7. sodium, unit cell edge = 428 pm, $r = 185$ pm
- 8.
9. $d = 0.5335$ g/cm³, $r = 151.9$ pm

12.3 Structures of Simple Binary Compounds

LEARNING OBJECTIVES

1. To use the cation:anion radius ratio to predict the structures of simple binary compounds.
2. To understand how x-rays are diffracted by crystalline solids.

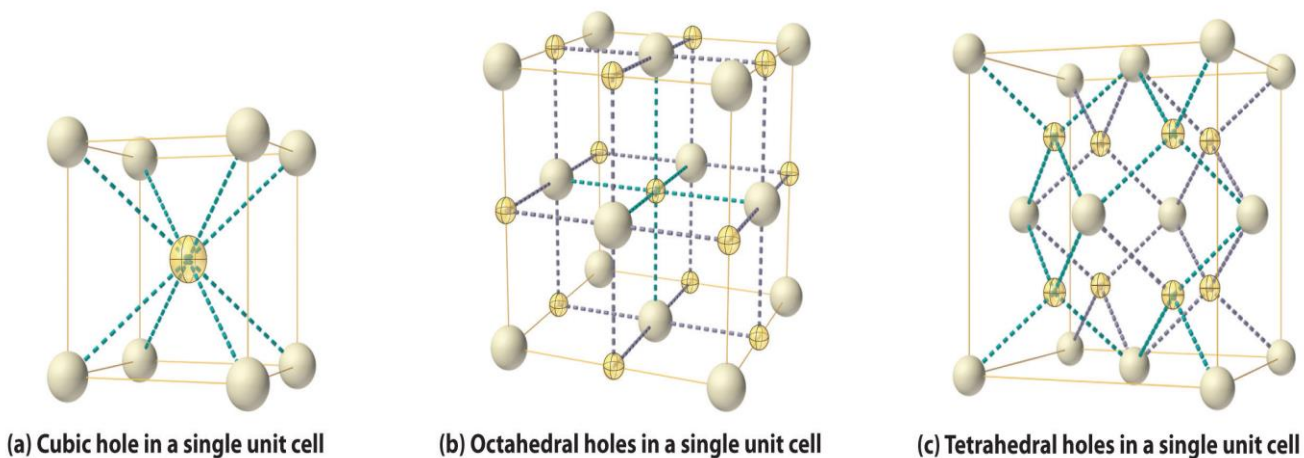
The structures of most binary compounds can be described using the packing schemes we have just discussed for metals. To do so, we generally focus on the arrangement in space of the largest species present. In ionic solids, this generally means the anions, which are usually arranged in a simple cubic, bcc, fcc, or hcp lattice. (For more information about anions, see Chapter 7 "The Periodic Table and Periodic Trends", Section 7.2 "Sizes of Atoms and Ions".) Often, however, the anion lattices are not truly "close packed"; because the cations are large enough to prop them apart somewhat, the anions are not actually in contact with one another. In ionic compounds, the cations usually occupy the "holes" between the anions, thus balancing the negative charge. The ratio of cations to anions

within a unit cell is required to achieve electrical neutrality and corresponds to the bulk stoichiometry of the compound.

Common Structures of Binary Compounds

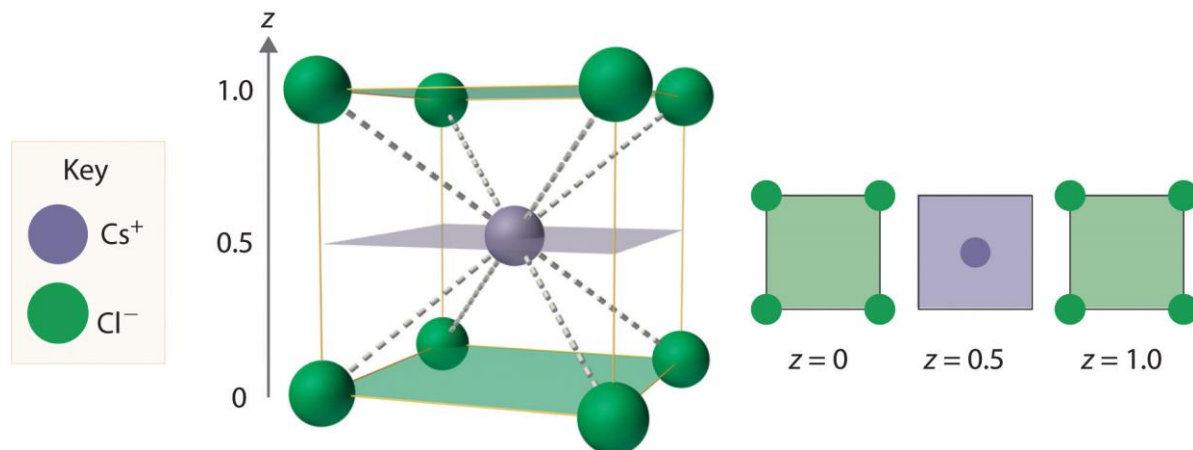
As shown in part (a) in Figure 12.8 "Holes in Cubic Lattices", a simple cubic lattice of anions contains only one kind of hole, located in the center of the unit cell. Because this hole is equidistant from all eight atoms at the corners of the unit cell, it is called a cubic hole. An atom or ion in a cubic hole therefore has a coordination number of 8. Many ionic compounds with relatively large cations and a 1:1 cation:anion ratio have this structure, which is called the cesium chloride structure (Figure 12.9 "The Cesium Chloride Structure") because CsCl is a common example.^[1] Notice in Figure 12.9 "The Cesium Chloride Structure" that the $z = 0$ and the $z = 1.0$ planes are always the same. This is because the $z = 1.0$ plane of one unit cell becomes the $z = 0$ plane of the succeeding one. The unit cell in CsCl contains a single Cs^+ ion as well as $8 \times \frac{1}{8} \text{Cl}^- = 1 \text{Cl}^-$ ion, for an overall stoichiometry of CsCl. The cesium chloride structure is most common for ionic substances with relatively large cations, in which the ratio of the radius of the cation to the radius of the anion is in the range shown in Table 12.2 "Relationship between the Cation:Anion Radius Ratio and the Site Occupied by the Cations".

Figure 12.8 Holes in Cubic Lattices



The three illustrations show (a) the cubic hole that is in the center of a simple cubic lattice of anions, (b) the locations of the octahedral holes in a face-centered cubic lattice of anions, and (c) the locations of the tetrahedral holes in a face-centered cubic lattice of anions.

Figure 12.9 The Cesium Chloride Structure



The

Cs^+ ion occupies the cubic hole in the center of a cube of Cl^- ions. The drawings at the right are horizontal cross-sections through the unit cell at the bottom ($z = 0$) and halfway between the bottom and top ($z = 0.5$). A top cross-section ($z = 1$) is identical to $z = 0$. Such cross-sections often help us visualize the arrangement of atoms or ions in the unit cell more easily.

Table 12.2 Relationship between the Cation:Anion Radius Ratio and the Site Occupied by the Cations

Approximate Range of Cation:Anion Radius Ratio	Hole Occupied by Cation	Cation Coordination Number
0.225–0.414	tetrahedral	4
0.414–0.732	octahedral	6
0.732–1.000	cubic	8

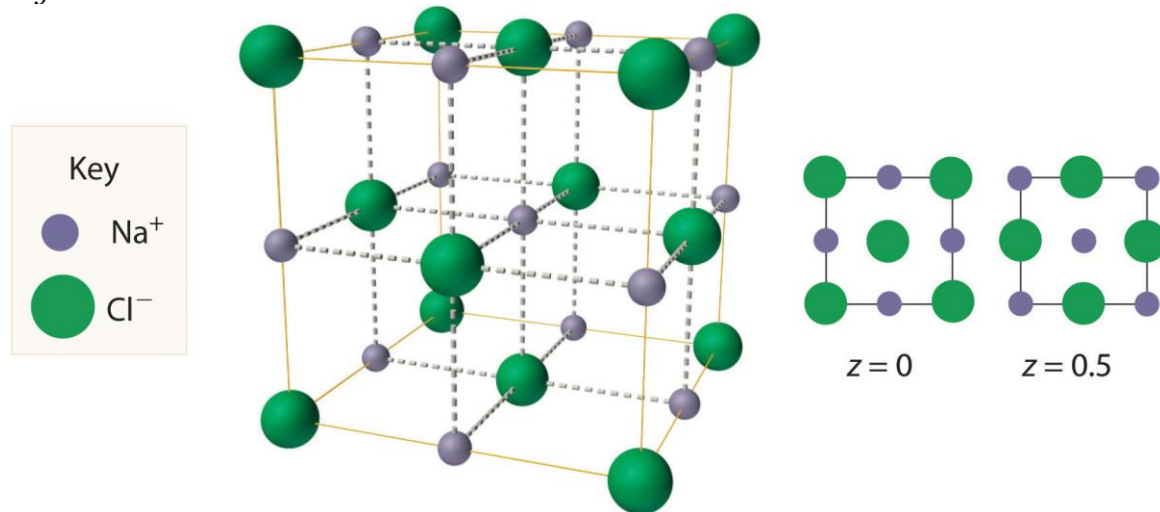
Note the Pattern

Very large cations occupy cubic holes, cations of intermediate size occupy octahedral holes, and small cations occupy tetrahedral holes in the anion lattice.

In contrast, a face-centered cubic (fcc) array of atoms or anions contains two types of holes: octahedral holes, one in the center of the unit cell plus a shared one in the middle of each edge (part (b) in Figure 12.8 "Holes in Cubic Lattices"), and tetrahedral holes, located between an atom at a corner and the three atoms at the centers of the adjacent faces (part (c) in Figure 12.8 "Holes in Cubic Lattices"). As shown in Table 12.2 "Relationship between the Cation:Anion Radius Ratio and the Site Occupied by the Cations", the ratio of the radius of the cation to the radius of the anion is the most important determinant of whether cations occupy the cubic holes in a cubic anion lattice or the octahedral or tetrahedral holes in an fcc lattice of anions. Very large cations occupy cubic holes in a cubic anion lattice, cations of intermediate size tend to occupy the octahedral holes in an fcc anion lattice, and relatively small cations tend to occupy the tetrahedral holes in an fcc anion lattice. In general, larger cations have higher coordination numbers than small cations.

The most common structure based on a fcc lattice is the sodium chloride structure (Figure 12.10 "The Sodium Chloride Structure"), which contains an fcc array of Cl^- ions with Na^+ ions in all the octahedral holes. We can understand the sodium chloride structure by recognizing that filling all the octahedral holes in an fcc lattice of Cl^- ions with Na^+ ions gives a total of 4 Cl^- ions (one on each face gives $6 \times \frac{1}{2} = 3$ plus one on each corner gives $8 \times \frac{1}{8} = 1$, for a total of 4) and 4 Na^+ ions (one on each edge gives $12 \times \frac{1}{4} = 3$ plus one in the middle, for a total of 4). The result is an electrically neutral unit cell and a stoichiometry of NaCl. As shown in Figure 12.10 "The Sodium Chloride Structure", the Na^+ ions in the sodium chloride structure also form an fcc lattice. The sodium chloride structure is favored for substances with two atoms or ions in a 1:1 ratio and in which the ratio of the radius of the cation to the radius of the anion is between 0.414 and 0.732. It is observed in many compounds, including MgO and TiC.

Figure 12.10 The Sodium Chloride Structure

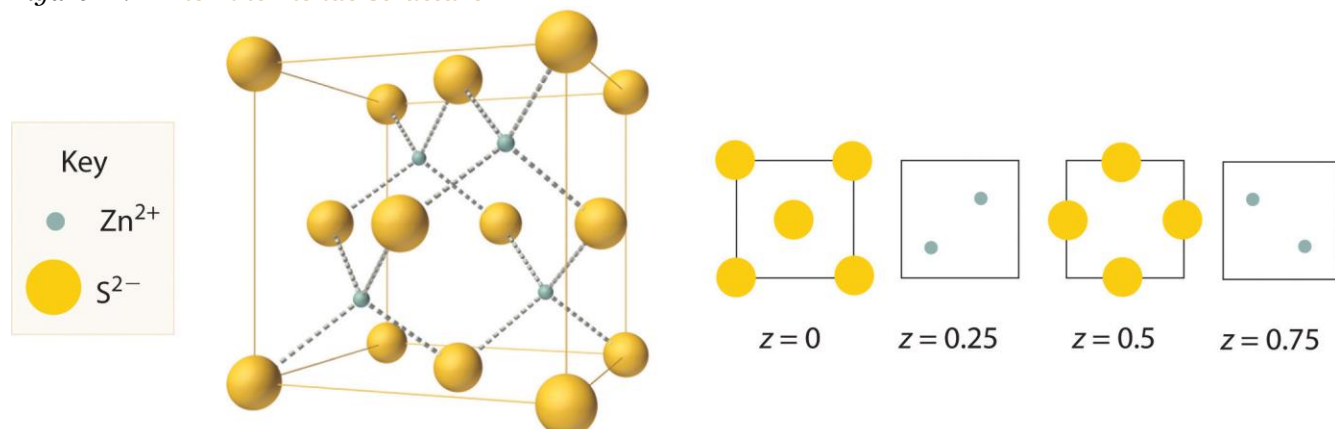


In NaCl, the Na^+ ions occupy the octahedral holes in an fcc lattice of Cl^- ions, resulting in an fcc array of Na^+ ions as well.

The structure shown in Figure 12.11 "The Zinc Blende Structure" is called the zinc blende structure, from the common name of the mineral ZnS. It results when the cation in a substance with a 1:1 cation:anion ratio is much smaller than the anion (if the cation:anion radius ratio is less than about 0.414). For example, ZnS contains an fcc lattice of S^{2-} ions, and the cation:anion radius ratio is only about 0.40, so we predict that the cation would occupy either a tetrahedral hole or an octahedral hole. In fact, the relatively small Zn^{2+} cations occupy the tetrahedral holes in the lattice. If all 8 tetrahedral holes in the unit cell were occupied by Zn^{2+} ions, however, the unit cell would contain 4 S^{2-} and 8 Zn^{2+} ions, giving a formula of Zn_2S and a net charge of +4 per unit cell. Consequently, the Zn^{2+} ions occupy *every other* tetrahedral hole, as

shown in Figure 12.11 "The Zinc Blende Structure", giving a total of 4 Zn^{2+} and 4 S^{2-} ions per unit cell and a formula of ZnS . The zinc blende structure results in a coordination number of 4 for each Zn^{2+} ion and a tetrahedral arrangement of the four S^{2-} ions around each Zn^{2+} ion.

Figure 12.11 The Zinc Blende Structure



Zn^{2+} ions occupy every other tetrahedral hole in the fcc array of S^{2-} ions. Each Zn^{2+} ion is surrounded by four S^{2-} ions in a tetrahedral arrangement.

EXAMPLE 3

- If all the tetrahedral holes in an fcc lattice of anions are occupied by cations, what is the stoichiometry of the resulting compound?
- Use the ionic radii given in Figure 7.9 "Ionic Radii (in Picometers) of the Most Common Oxidation States of the " to identify a plausible oxygen-containing compound with this stoichiometry and structure.

Given: lattice, occupancy of tetrahedral holes, and ionic radii

Asked for: stoichiometry and identity

Strategy:

A Use Figure 12.8 "Holes in Cubic Lattices" to determine the number and location of the tetrahedral holes in an fcc unit cell of anions and place a cation in each.

B Determine the total number of cations and anions in the unit cell; their ratio is the stoichiometry of the compound.

C From the stoichiometry, suggest reasonable charges for the cation and the anion. Use the data in Figure 7.9 "Ionic Radii (in Picometers) of the Most Common Oxidation States of the " to identify a cation–anion combination that has a cation:anion radius ratio within a reasonable range.

Solution:

- A** Figure 12.8 "Holes in Cubic Lattices" shows that the tetrahedral holes in an fcc unit cell of anions are located entirely within the unit cell, for a total of eight (one near

each corner). **B** Because the tetrahedral holes are located entirely within the unit cell, there are eight cations per unit cell. We calculated previously that an fcc unit cell of anions contains a total of four anions per unit cell. The stoichiometry of the compound is therefore M_8Y_4 or, reduced to the smallest whole numbers, M_2Y .

- b. **C** The M_2Y stoichiometry is consistent with a lattice composed of M^+ ions and Y^{2-} ions. If the anion is O^{2-} (ionic radius 140 pm), we need a monocation with a radius no larger than about $140 \times 0.414 = 58$ pm to fit into the tetrahedral holes. According to Figure 7.9 "Ionic Radii (in Picometers) of the Most Common Oxidation States of the ", none of the monocations has such a small radius; therefore, the most likely possibility is Li^+ at 76 pm. Thus we expect Li_2O to have a structure that is an fcc array of O^{2-} anions with Li^+ cations in all the tetrahedral holes.

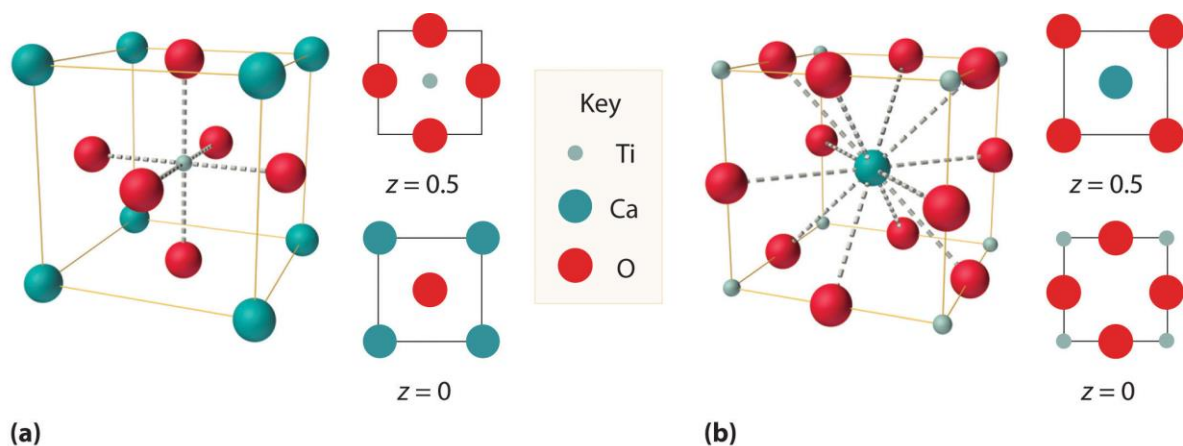
Exercise

If only half the octahedral holes in an fcc lattice of anions are filled by cations, what is the stoichiometry of the resulting compound?

Answer: MX_2 ; an example of such a compound is cadmium chloride ($CdCl_2$), in which the empty cation sites form planes running through the crystal.

We examine only one other structure of the many that are known, the perovskite structure. *Perovskite* is the generic name for oxides with two different kinds of metal and have the general formula $MM'O_3$, such as $CaTiO_3$. The structure is a body-centered cubic (bcc) array of two metal ions, with one M (Ca in this case) located at the corners of the cube, and the other M' (in this case Ti) in the centers of the cube. The oxides are in the centers of the square faces (part (a) in Figure 12.12 "The Perovskite Structure of $CaTiO$ "). The stoichiometry predicted from the unit cell shown in part (a) in Figure 12.12 "The Perovskite Structure of $CaTiO$ " agrees with the general formula; each unit cell contains $8 \times \frac{1}{8} = 1$ Ca, 1 Ti, and $6 \times \frac{1}{2} = 3$ O atoms. The Ti and Ca atoms have coordination numbers of 6 and 12, respectively. We will return to the perovskite structure when we discuss high-temperature superconductors in Section 12.7 "Superconductors".

Figure 12.12 The Perovskite Structure of $CaTiO_3$

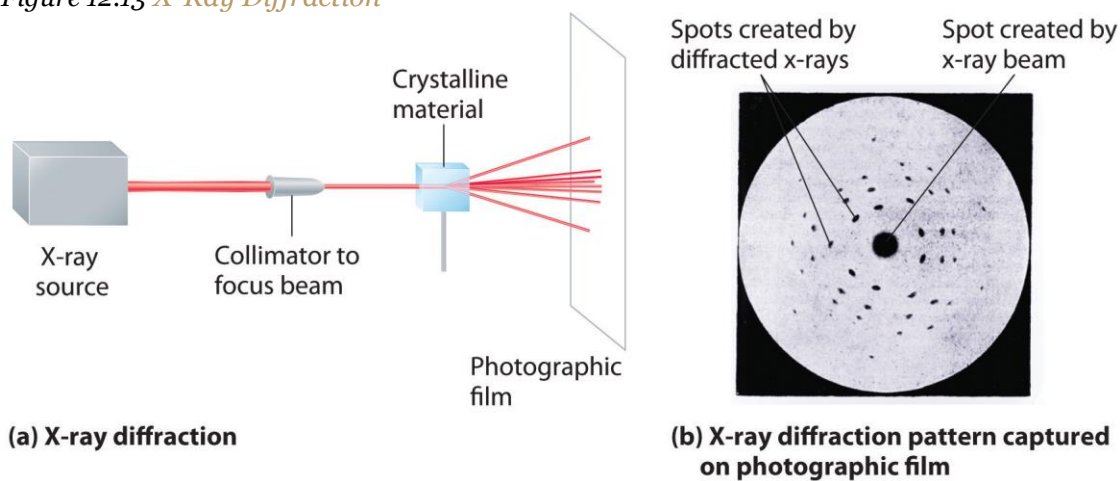


Two equivalent views are shown: (a) a view with the Ti atom at the center and (b) an alternative view with the Ca atom at the center.

X-Ray Diffraction

As you learned in Chapter 6 "The Structure of Atoms", the wavelengths of x-rays are approximately the same magnitude as the distances between atoms in molecules or ions. Consequently, x-rays are a useful tool for obtaining information about the structures of crystalline substances. In a technique called x-ray diffraction, a beam of x-rays is aimed at a sample of a crystalline material, and the x-rays are diffracted by layers of atoms in the crystalline lattice (part (a) in Figure 12.13 "X-Ray Diffraction"). When the beam strikes photographic film, it produces an x-ray diffraction pattern, which consists of dark spots on a light background (part (b) in Figure 12.13 "X-Ray Diffraction"). In 1912, the German physicist Max von Laue (1879–1960; Nobel Prize in Physics, 1914) predicted that x-rays should be diffracted by crystals, and his prediction was rapidly confirmed. Within a year, two British physicists, William Henry Bragg (1862–1942) and his son, William Lawrence Bragg (1890–1972), had worked out the mathematics that allows x-ray diffraction to be used to measure interatomic distances in crystals. The Braggs shared the Nobel Prize in Physics in 1915, when the son was only 25 years old. Virtually everything we know today about the detailed structures of solids and molecules in solids is due to the x-ray diffraction technique.

Figure 12.13 X-Ray Diffraction



These illustrations show (a) a schematic drawing of x-ray diffraction and (b) the x-ray diffraction pattern of a zinc blende crystalline solid captured on photographic film.

Recall from Chapter 6 "The Structure of Atoms" that two waves that are in phase interfere constructively, thus reinforcing each other and generating a wave with a greater amplitude. In contrast, two waves that are out of phase interfere destructively, effectively canceling each other. When x-rays interact with the components of a crystalline lattice, they are scattered by the electron clouds associated with each atom. As shown in Figure 12.5 "The Three Kinds of Cubic Unit Cell", Figure 12.7 "Close-Packed Structures: hcp and ccp", and Figure 12.8 "Holes in Cubic Lattices", the atoms in crystalline solids are typically arranged in planes. Figure 12.14 "The Reflection of X-Rays from Two Adjacent Planes of Atoms Can Result in Constructive Interference of the X-Rays" illustrates how two adjacent planes of atoms can scatter x-rays in a way that results in constructive interference. If two x-rays that are initially in phase are diffracted by two planes of atoms separated by a distance d , the lower beam travels the extra distance indicated by the lines BC and CD . The *angle of incidence*, designated as θ , is the angle between the x-ray beam and the planes in the crystal. Because $BC = CD = d \sin \theta$, the extra distance that the lower beam in Figure 12.14 "The Reflection of X-Rays from Two Adjacent Planes of Atoms Can Result in Constructive Interference of the X-Rays" must travel compared with the upper beam is $2d \sin \theta$. For these two x-rays to arrive at a detector in phase, the extra distance traveled must be an integral multiple n of the wavelength λ :

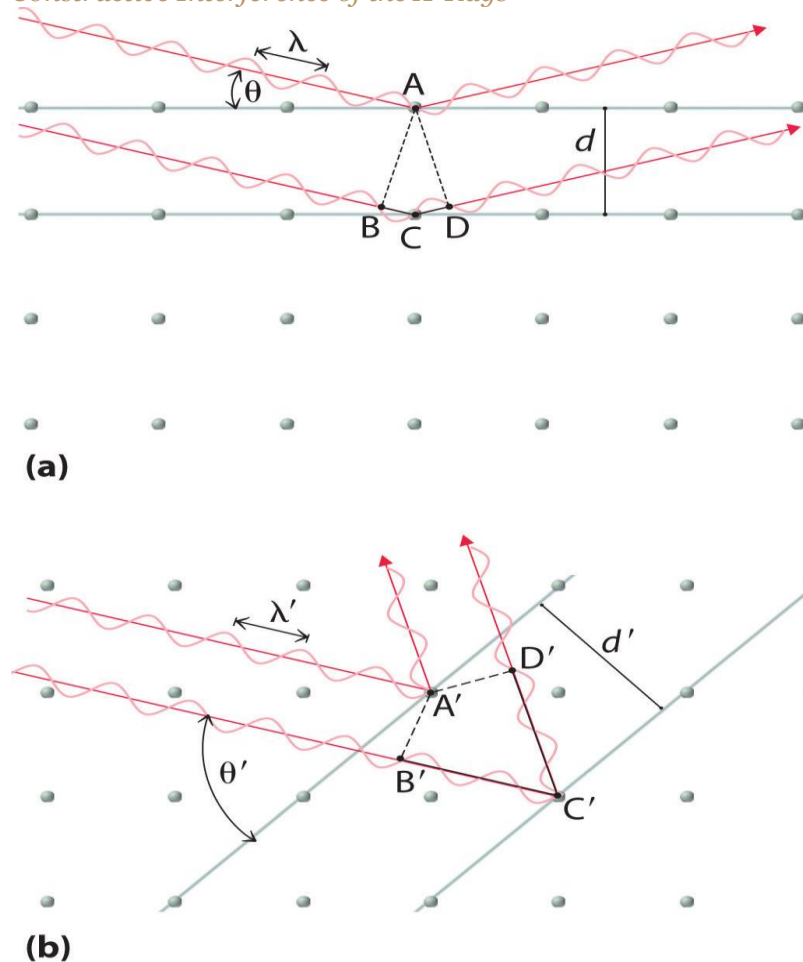
Equation 12.1

$$2d \sin \theta = n\lambda$$

Equation 12.1 is the Bragg equation. The structures of crystalline substances with both small molecules and ions or very large biological molecules, with molecular masses in excess of 100,000 amu, can now be

determined accurately and routinely using x-ray diffraction and the Bragg equation. Example 4 illustrates how to use the Bragg equation to calculate the distance between planes of atoms in crystals.

Figure 12.14 *The Reflection of X-Rays from Two Adjacent Planes of Atoms Can Result in Constructive Interference of the X-Rays*



(a) The x-ray diffracted by the lower layer of atoms must travel a distance that is longer by $2d \sin \theta$ than the distance traveled by the x-ray diffracted by the upper layer of atoms. Only if this distance (BC plus CD) equals an integral number of wavelengths of the x-rays (i.e., only if $\lambda = 2d \sin \theta$) will the x-rays arrive at the detector in phase. (b) In a solid, many different sets of planes of atoms can diffract x-rays. Each has a different interplanar distance and therefore diffracts the x-rays at a different angle θ , which produces a characteristic pattern of spots.

EXAMPLE 4

X-rays from a copper x-ray tube ($\lambda = 1.54062 \text{ \AA}$ or 154.062 pm)^[2] are diffracted at an angle of 10.89° from a sample of crystalline gold. Assuming that $n = 1$, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to four significant figures.

Given: wavelength, diffraction angle, and number of wavelengths

Asked for: distance between planes

Strategy:

Substitute the given values into the Bragg equation and solve to obtain the distance between planes.

Solution:

We are given n , θ , and λ and asked to solve for d , so this is a straightforward application of the Bragg equation. For an answer in angstroms, we do not even have to convert units. Solving the Bragg equation for d gives

$$d = n / 2 \sin \theta$$

and substituting values gives

$$\begin{aligned} d &= (1)(1.54062 \text{ \AA}) / 2 \sin 10.89^\circ \\ &= 4.077 \text{ \AA} = 407.7 \text{ pm} \end{aligned}$$

This value corresponds to the edge length of the fcc unit cell of elemental gold.

Exercise

X-rays from a molybdenum x-ray tube ($\lambda = 0.709300 \text{ \AA}$) are diffracted at an angle of 7.11° from a sample of metallic iron. Assuming that $n = 1$, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to three significant figures.

Answer: 2.87 Å or 287 pm (corresponding to the edge length of the bcc unit cell of elemental iron)

Summary

The structures of most binary compounds are dictated by the packing arrangement of the largest species present (the anions), with the smaller species (the cations) occupying appropriately sized holes in the anion lattice. A simple cubic lattice of anions contains a single **cubic hole** in the center of the unit cell. Placing a cation in the cubic hole results in the **cesium chloride structure**, with a 1:1 cation:anion ratio and a coordination number of 8 for both the cation and the anion. An fcc array of atoms or ions contains both **octahedral holes** and **tetrahedral holes**. If the octahedral holes in an fcc lattice of anions are filled with cations, the result is a **sodium chloride structure**. It also has a 1:1 cation:anion ratio, and each ion has a coordination number of 6. Occupation of half the tetrahedral holes by cations results in the **zinc blende structure**, with a 1:1 cation:anion ratio and a coordination number of 4 for the cations.

More complex structures are possible if there are more than two kinds of atoms in a solid. One example is the **perovskite structure**, in which the two metal ions form an alternating bcc array with the anions in the centers of the square faces. Because the wavelength of x-ray radiation is comparable to the interatomic distances in most solids, **x-ray diffraction** can be used to provide information about the structures of crystalline solids. X-rays diffracted from different planes of atoms in a solid reinforce one another if they are in phase, which occurs only if the extra distance they travel corresponds to an integral number of wavelengths. This relationship is described by the **Bragg equation**: $2d \sin \theta = n\lambda$.

KEY TAKEAWAY

- The ratio of cations to anions within a unit cell produces electrical neutrality and corresponds to the bulk stoichiometry of a compound, the structure of which can be determined using x-ray diffraction.

KEY EQUATION

Bragg equation

Equation 12.1: $2d \sin \theta = n\lambda$

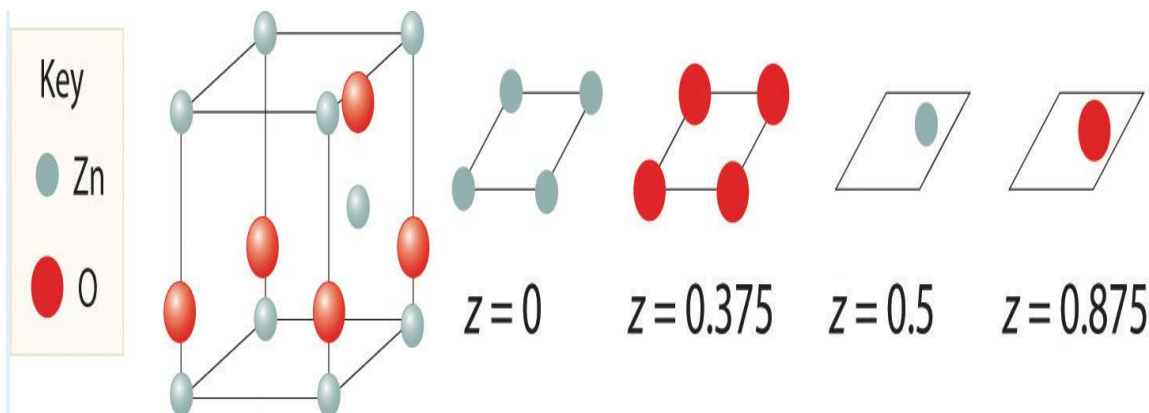
CONCEPTUAL PROBLEMS

1. Using circles or spheres, sketch a unit cell containing an octahedral hole. Which of the basic structural types possess octahedral holes? If an ion were placed in an octahedral hole, what would its coordination number be?
2. Using circles or spheres, sketch a unit cell containing a tetrahedral hole. Which of the basic structural types possess tetrahedral holes? If an ion were placed in a tetrahedral hole, what would its coordination number be?
3. How many octahedral holes are there in each unit cell of the sodium chloride structure? Potassium fluoride contains an fcc lattice of F^- ions that is identical to the arrangement of Cl^- ions in the sodium chloride structure. Do you expect K^+ ions to occupy the tetrahedral or octahedral holes in the fcc lattice of F^- ions?
4. The unit cell of cesium chloride consists of a cubic array of chloride ions with a cesium ion in the center. Why then is cesium chloride described as having a simple cubic structure rather than a bcc structure? The unit cell of iron also consists of a cubic array of iron atoms with an iron atom in the center of the cube. Is this a bcc or a simple cubic unit cell? Explain your answer.

5. Why are x-rays used to determine the structure of crystalline materials? Could gamma rays also be used to determine crystalline structures? Why or why not?
6. X-rays are higher in energy than most other forms of electromagnetic radiation, including visible light. Why can't you use visible light to determine the structure of a crystalline material?
7. When x-rays interact with the atoms in a crystal lattice, what relationship between the distances between planes of atoms in the crystal structure and the wavelength of the x-rays results in the scattered x-rays being exactly in phase with one another? What difference in structure between amorphous materials and crystalline materials makes it difficult to determine the structures of amorphous materials by x-ray diffraction?
8. It is possible to use different x-ray sources to generate x-rays with different wavelengths. Use the Bragg equation to predict how the diffraction angle would change if a molybdenum x-ray source (x-ray wavelength = 70.93 pm) were used instead of a copper source (x-ray wavelength = 154.1 pm).
9. Based on the Bragg equation, if crystal A has larger spacing in its diffraction pattern than crystal B, what conclusion can you draw about the spacing between layers of atoms in A compared with B?

NUMERICAL PROBLEMS

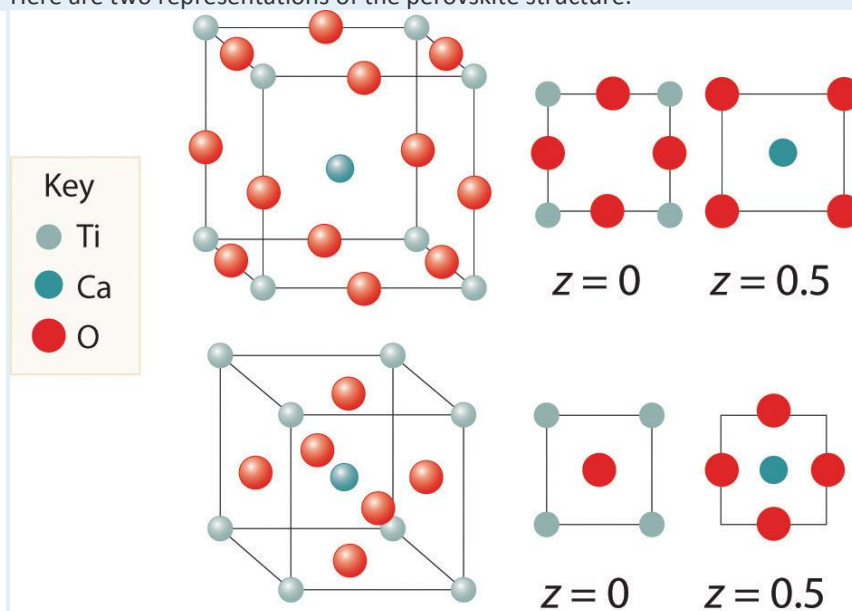
1. Thallium bromide crystallizes in the cesium chloride structure. This bcc structure contains a Tl^+ ion in the center of the cube with Br^- ions at the corners. Sketch an alternative unit cell for this compound.
2. Potassium fluoride has a lattice identical to that of sodium chloride. The potassium ions occupy octahedral holes in an fcc lattice of fluoride ions. Propose an alternative unit cell that can also represent the structure of KF.
3. Calcium fluoride is used to fluoridate drinking water to promote dental health. Crystalline CaF_2 ($d = 3.1805 \text{ g/cm}^3$) has a structure in which calcium ions are located at each corner and the middle of each edge of the unit cell, which contains eight fluoride ions per unit cell. The length of the edge of this unit cell is $5.463 \text{ \AA}$. Use this information to determine Avogadro's number.
4. Zinc and oxygen form a compound that is used as both a semiconductor and a paint pigment. This compound has the following structure:



What

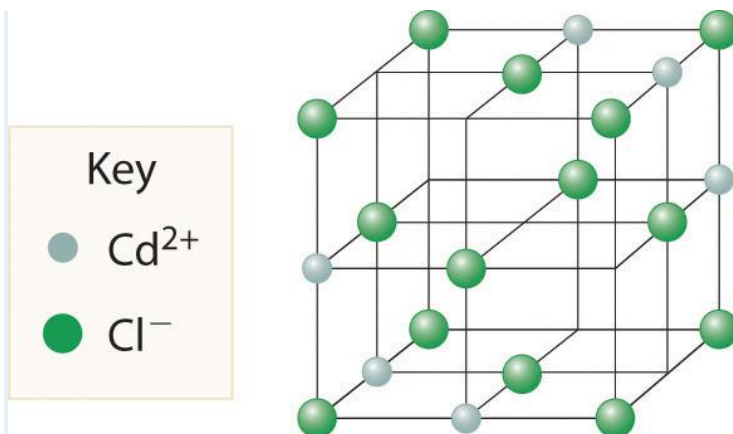
is the empirical formula of this compound?

5. Here are two representations of the perovskite structure:



Are they identical? What is the empirical formula corresponding to each representation?

- The salt MX_2 has a cubic close-packed (ccp) structure in which all the tetrahedral holes are filled by anions. What is the coordination number of M? of X?
- A compound has a structure based on simple cubic packing of the anions, and the cations occupy half of the cubic holes. What is the empirical formula of this compound? What is the coordination number of the cation?
- Barium and fluoride form a compound that crystallizes in the fluorite structure, in which the fluoride ions occupy all the tetrahedral holes in a ccp array of barium ions. This particular compound is used in embalming fluid. What is its empirical formula?
- Cadmium chloride is used in paints as a yellow pigment. Is the following structure consistent with an empirical formula of $CdCl_2$? If not, what is the empirical formula of the structure shown?



10. Use the information in the following table to decide whether the cation will occupy a tetrahedral hole, an octahedral hole, or a cubic hole in each case.

Cation Radius (pm)	Anion Radius (pm)
78.0	132
165	133
81	174

10. Calculate the angle of diffraction when x-rays from a copper tube ($\lambda = 154 \text{ pm}$) are diffracted by planes of atoms parallel to the faces of the cubic unit cell for Mg (260 pm), Zn (247 pm), and Ni (216 pm). The length on one edge of the unit cell is given in parentheses; assume first-order diffraction ($n = 1$).
11. If x-rays from a copper target ($\lambda = 154 \text{ pm}$) are scattered at an angle of 17.23° by a sample of Mg, what is the distance (in picometers) between the planes responsible for this diffraction? How does this distance compare with that in a sample of Ni for which $\theta = 20.88^\circ$?

ANSWERS

- 1.
- 2.
3. $d = 3.1805 \text{ g/cm}^3$; Avogadro's number = $6.023 \times 10^{23} \text{ mol}^{-1}$
- 4.
5. Both have same stoichiometry, CaTiO_3
- 6.
7. Stoichiometry is MX_2 ; coordination number of cations is 8
- 8.
9. No, the structure shown has an empirical formula of Cd_3Cl_8 .

10.

11. Mg: 17.2°, Zn: 18.2°, Ni: 20.9°

[1] Solid-state chemists tend to describe the structures of new compounds in terms of the structure of a well-known reference compound. Hence you will often read statements such as “Compound X possesses the cesium chloride (or sodium chloride, etc.) structure” to describe the structure of compound X.

[2] In x-ray diffraction, the angstrom (Å) is generally used as the unit of wavelength.

12.4 Defects in Crystals

LEARNING OBJECTIVE

1. To understand the origin and nature of defects in crystals.

The crystal lattices we have described represent an idealized, simplified system that can be used to understand many of the important principles governing the behavior of solids. In contrast, real crystals contain large numbers of defects (typically more than 10^4 per milligram), ranging from variable amounts of impurities to missing or misplaced atoms or ions. These defects occur for three main reasons:

1. It is impossible to obtain any substance in 100% pure form. Some impurities are always present.
2. Even if a substance were 100% pure, forming a perfect crystal would require cooling the liquid phase infinitely slowly to allow all atoms, ions, or molecules to find their proper positions. Cooling at more realistic rates usually results in one or more components being trapped in the “wrong” place in a lattice or in areas where two lattices that grew separately intersect.
3. Applying an external stress to a crystal, such as a hammer blow, can cause microscopic regions of the lattice to move with respect to the rest, thus resulting in imperfect alignment.

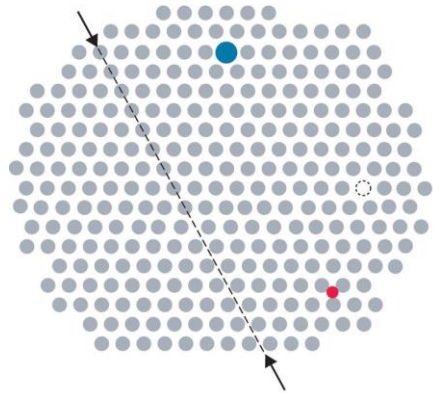
In this section, we discuss how defects determine some of the properties of solids. We begin with solids that consist of neutral atoms, specifically metals, and then turn to ionic compounds.

Defects in Metals

Metals can have various types of defects. A point defect is any defect that involves only a single particle (a lattice point) or sometimes a very small set of points. A line defect is restricted to a row of lattice points,

and a plane defect involves an entire plane of lattice points in a crystal. A vacancy occurs where an atom is missing from the normal crystalline array; it constitutes a tiny void in the middle of a solid (). We focus primarily on point and plane defects in our discussion because they are encountered most frequently.

Figure 12.15 Common Defects in Crystals



In this two-dimensional representation of a crystal lattice containing substitutional and interstitial impurities, vacancies, and line defects, a dashed line and arrows indicate the position of the line defect.

Impurities

Impurities can be classified as interstitial or substitutional. An interstitial impurity is usually a smaller atom (typically about 45% smaller than the host) that can fit into the octahedral or tetrahedral holes in the metal lattice (). Steels consist of iron with carbon atoms added as interstitial impurities (). The inclusion of one or more transition metals or semimetals can improve the corrosion resistance of steel.

Table 12.3 Compositions, Properties, and Uses of Some Types of Steel

Name of Steel	Typical Composition*	Properties	Applications
low-carbon	<0.15% C	soft and ductile	wire
mild carbon	0.15%–0.25% C	malleable and ductile	cables, chains, and nails
high-carbon	0.60%–1.5% C	hard and brittle	knives, cutting tools, drill bits, and springs
stainless	15%–20% Cr, 1%–5% Mn, 5%–10% Ni, 1%–3% Si, 1% C, 0.05% P	corrosion resistant	cutlery, instruments, and marine fittings
invar	36% Ni	low coefficient of thermal expansion	measuring tapes and meter sticks
manganese	10%–20% Mn	hard and wear resistant	armor plate, safes, and rails
high-speed	14%–20% W	retains hardness at high temperatures	high-speed cutting tools

Name of Steel	Typical Composition*	Properties	Applications
silicon	1%–5% Si	hard, strong, and highly magnetic	magnets in electric motors and transformers
*In addition to enough iron to bring the total percentage up to 100%, most steels contain small amounts of carbon (0.5%–1.5%) and manganese (<2%).			

In contrast, a substitutional impurity is a different atom of about the same size that simply replaces one of the atoms that compose the host lattice (). Substitutional impurities are usually chemically similar to the substance that constitutes the bulk of the sample, and they generally have atomic radii that are within about 15% of the radius of the host. For example, strontium and calcium are chemically similar and have similar radii, and as a result, strontium is a common impurity in crystalline calcium, with the Sr atoms randomly occupying sites normally occupied by Ca.

Note the Pattern

Interstitial impurities are smaller atoms than the host atom, whereas substitutional impurities are usually chemically similar and are similar in size to the host atom.

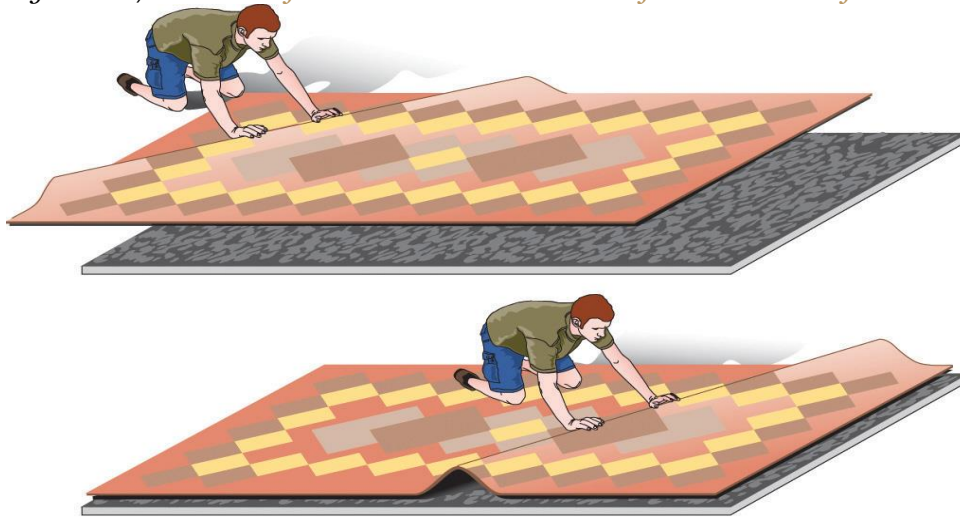
Dislocations, Deformations, and Work Hardening

Inserting an extra plane of atoms into a crystal lattice produces an edge dislocation. A familiar example of an edge dislocation occurs when an ear of corn contains an extra row of kernels between the other rows (). An edge dislocation in a crystal causes the planes of atoms in the lattice to deform where the extra plane of atoms begins (). The edge dislocation frequently determines whether the entire solid will deform and fail under stress.

Deformation occurs when a dislocation moves through a crystal. To illustrate the process, suppose you have a heavy rug that is lying a few inches off-center on a nonskid pad. To move the rug to its proper place, you could pick up one end and pull it. Because of the large area of contact between the rug and the pad, however, they will probably move as a unit. Alternatively, you could pick up the rug and try to set it back down exactly where you want it, but that requires a great deal of effort (and probably at least one extra person). An easier solution is to create a small wrinkle at one end of the rug (an edge dislocation) and gradually push the wrinkle across, resulting in a net movement of the rug as a whole (part (a) in). Moving the wrinkle requires only a small amount of energy because only a small part of the rug is actually moving at any one time. Similarly, in a solid, the contacts between layers are broken in only one place at a time, which facilitates the deformation process.



Figure 12.17 *The Role of Dislocation in the Motion of One Planar Object across Another*



(a) Dislocation



(b) Pinning

(a) Pushing a wrinkle across the rug results in a net movement of the rug with relatively little expenditure of energy because at any given time only a very small amount of the rug is not in contact with the floor. (b) A second intersecting wrinkle prevents movement of the first by “pinning” it.

If the rug we have just described has a *second* wrinkle at a different angle, however, it is very difficult to move the first one where the two wrinkles intersect (part (b) in); this process is called pinning. Similarly, intersecting dislocations in a solid prevent them from moving, thereby increasing the mechanical strength of the material. In fact, one of the major goals of materials science is to find ways to pin dislocations to strengthen or harden a material.

Pinning can also be achieved by introducing selected impurities in appropriate amounts. Substitutional impurities that are a mismatch in size to the host prevent dislocations from migrating smoothly along a plane. Generally, the higher the concentration of impurities, the more effectively they block migration, and the stronger the material. For example, bronze, which contains about 20% tin and 80% copper by

mass, produces a much harder and sharper weapon than does either pure tin or pure copper. Similarly, pure gold is too soft to make durable jewelry, so most gold jewelry contains 75% (18 carat) or 58% (14 carat) gold by mass, with the remainder consisting of copper, silver, or both.

If an interstitial impurity forms polar covalent bonds to the host atoms, the layers are prevented from sliding past one another, even when only a small amount of the impurity is present. For example, because iron forms polar covalent bonds to carbon, the strongest steels need to contain only about 1% carbon by mass to substantially increase their strength ().

Most materials are polycrystalline, which means they consist of many microscopic individual crystals called *grains* that are randomly oriented with respect to one another. The place where two grains intersect is called a grain boundary. The movement of a deformation through a solid tends to stop at a grain boundary. Consequently, controlling the grain size in solids is critical for obtaining desirable mechanical properties; fine-grained materials are usually much stronger than coarse-grained ones.



Grain boundaries. As a polycrystalline material solidifies, grains with irregular shapes form. The interfaces between grains constitute grain boundaries. (Squares represent unit cells within grains.)

Work hardening is the introduction of a dense network of dislocations throughout a solid, which makes it very tough and hard. If all the defects in a single 1 cm³ sample of a work-hardened material were laid end to end, their total length could be 10⁶ km! The legendary blades of the Japanese and Moorish swordsmiths owed much of their strength to repeated work hardening of the steel. As the density of defects increases, however, the metal becomes more brittle (less malleable). For example, bending a paper clip back and forth several times increases its brittleness from work hardening and causes the wire to break.

Memory Metal

The compound NiTi, popularly known as “memory metal” or nitinol (nickel–titanium Naval Ordnance Laboratory, after the site where it was first prepared), illustrates the importance of deformations. If a straight piece of NiTi wire is wound into a spiral, it will remain in the spiral shape indefinitely, *unless* it is warmed to 50°C–60°C, at which point it will spontaneously straighten out again. The chemistry behind the temperature-induced change in shape is moderately complex, but for our purposes it is sufficient to know that NiTi can exist in two different solid phases. The high-temperature phase has the cubic cesium chloride structure, in which a Ti atom is embedded in the center of a cube of Ni atoms (or vice versa). The low-temperature phase has a related but kinked structure, in which one of the angles of the unit cell is no longer 90°. Bending an object made of the low-temperature (kinked) phase creates defects that change the pattern of kinks within the structure. If the object is heated to a temperature greater than about 50°C, the material undergoes a transition to the cubic high-temperature phase, causing the object to return to its original shape. The shape of the object above 50°C is controlled by a complex set of defects and dislocations that can be relaxed or changed only by the thermal motion of the atoms.

Memory metal has many other practical applications, such as its use in temperature-sensitive springs that open and close valves in the automatic transmissions of cars. Because NiTi can also undergo pressure- or tension-induced phase transitions, it is used to make wires for straightening teeth in orthodontic braces and in surgical staples that change shape at body temperature to hold broken bones together.

Another flexible, fatigue-resistant alloy composed of titanium and nickel is Flexon. Originally discovered by metallurgists who were creating titanium-based alloys for use in missile heat shields, Flexon is now used as a durable, corrosion-resistant frame for glasses, among other uses.

EXAMPLE 5

Because steels with at least 4% chromium are much more corrosion resistant than iron, they are collectively sold as “stainless steel.” Referring to the composition of stainless steel in and, if needed, the atomic radii in , predict which type of impurity is represented by each element in stainless steel, excluding iron, that are present in at least 0.05% by mass.

Given: composition of stainless steel and atomic radii

Asked for: type of impurity

Strategy:

Using the data in and the atomic radii in , determine whether the impurities listed are similar in size to an iron atom. Then determine whether each impurity is chemically similar to Fe. If similar in both size and chemistry, the impurity is likely to be a substitutional impurity. If not, it is likely to be an interstitial impurity.

Solution:

According to , stainless steel typically contains about 1% carbon, 1%–5% manganese, 0.05% phosphorus, 1%–3% silicon, 5%–10% nickel, and 15%–20% chromium. The three transition elements (Mn, Ni, and Cr) lie near Fe in the periodic table, so they should be similar to Fe in chemical properties and atomic size (atomic radius = 125 pm). Hence they almost certainly will substitute for iron in the Fe lattice. Carbon is a second-period element that is nonmetallic and much smaller (atomic radius = 77 pm) than iron. Carbon will therefore tend to occupy interstitial sites in the iron lattice. Phosphorus and silicon are chemically quite different from iron (phosphorus is a nonmetal, and silicon is a semimetal), even though they are similar in size (atomic radii of 106 and 111 pm, respectively). Thus they are unlikely to be substitutional impurities in the iron lattice or fit into interstitial sites, but they could aggregate into layers that would constitute plane defects.

Exercise

Consider nitrogen, vanadium, zirconium, and uranium impurities in a sample of titanium metal. Which is most likely to form an interstitial impurity? a substitutional impurity?

Answer: nitrogen; vanadium

Defects in Ionic and Molecular Crystals

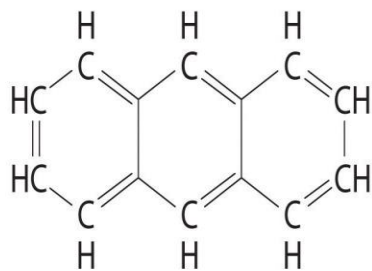
All the defects and impurities described for metals are seen in ionic and molecular compounds as well. Because ionic compounds contain both cations and anions rather than only neutral atoms, however, they exhibit additional types of defects that are not possible in metals.

The most straightforward variant is a substitutional impurity in which a cation or an anion is replaced by another of similar charge and size. For example, Br^- can substitute for Cl^- , so tiny amounts of Br^- are usually present in a chloride salt such as CaCl_2 or BaCl_2 . If the substitutional impurity and the host have *different* charges, however, the situation becomes more complicated. Suppose, for example, that

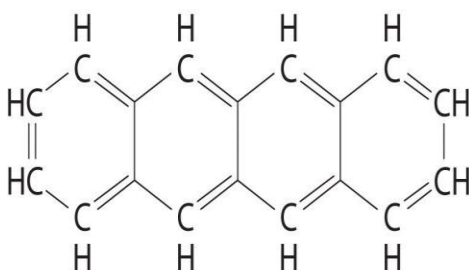
Sr^{2+} (ionic radius = 118 pm) substitutes for K^+ (ionic radius = 138 pm) in KCl. Because the ions are approximately the same size, Sr^{2+} should fit nicely into the face-centered cubic (fcc) lattice of KCl. The difference in charge, however, must somehow be compensated for so that electrical neutrality is preserved. The simplest way is for a second K^+ ion to be lost elsewhere in the crystal, producing a vacancy. Thus substitution of K^+ by Sr^{2+} in KCl results in the introduction of *two* defects: a site in which an Sr^{2+} ion occupies a K^+ -position and a vacant cation site. Substitutional impurities whose charges do not match the host's are often introduced intentionally to produce compounds with specific properties (see).

Virtually all the colored gems used in jewelry are due to substitutional impurities in simple oxide structures. For example, $\alpha\text{-Al}_2\text{O}_3$, a hard white solid called *corundum* that is used as an abrasive in fine sandpaper, is the primary component, or *matrix*, of a wide variety of gems. Because many trivalent transition metal ions have ionic radii only a little larger than the radius of Al^{3+} (ionic radius = 53.5 pm), they can replace Al^{3+} in the octahedral holes of the oxide lattice. Substituting small amounts of Cr^{3+} ions (ionic radius = 75 pm) for Al^{3+} gives the deep red color of ruby, and a mixture of impurities (Fe^{2+} , Fe^{3+} , and Ti^{4+}) gives the deep blue of sapphire. True amethyst contains small amounts of Fe^{3+} in an SiO_2 (quartz) matrix. The same metal ion substituted into different mineral lattices can produce very different colors. For example, Fe^{3+} ions are responsible for the yellow color of topaz and the violet color of amethyst. The distinct environments cause differences in *d* orbital energies, enabling the Fe^{3+} ions to absorb light of different frequencies, a topic we describe in more detail in .

Substitutional impurities are also observed in *molecular* crystals if the structure of the impurity is similar to the host, and they can have major effects on the properties of the crystal. Pure anthracene, for example, is an electrical conductor, but the transfer of electrons through the molecule is much slower if the anthracene crystal contains even very small amounts of tetracene despite their strong structural similarities.



Anthracene

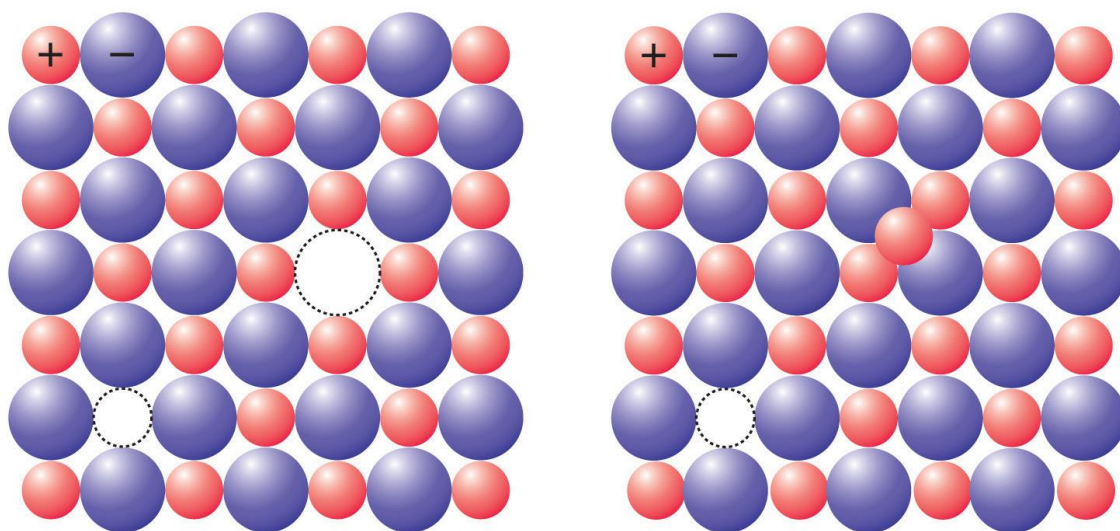


Tetracene

If a cation or an anion is simply

missing, leaving a vacant site in an ionic crystal, then for the crystal to be electrically neutral, there must be a corresponding vacancy of the ion with the opposite charge somewhere in the crystal. In compounds such as KCl, the charges are equal but opposite, so one anion vacancy is sufficient to compensate for each cation vacancy. In compounds such as CaCl_2 , however, *two* Cl^- anion sites must be vacant to compensate for each missing Ca^{2+} cation. These pairs (or sets) of vacancies are called Schottky defects and are particularly common in simple alkali metal halides such as KCl (part (a) in). Many microwave diodes, which are devices that allow a current to flow in a single direction, are composed of materials with Schottky defects.

Figure 12.18 *The Two Most Common Defects in Ionic Solids*



(a) Schottky defect

(b) Frenkel defect

(a) A

Schottky defect in KCl shows the missing cation/anion pair. (b) A Frenkel defect in AgI shows a misplaced Ag^+ cation.

Occasionally one of the ions in an ionic lattice is simply in the wrong position. An example of this phenomenon, called a Frenkel defect, is a cation that occupies a tetrahedral hole rather than an octahedral hole in the anion lattice (part (b) in). Frenkel defects are most common in salts that have a large anion and a relatively small cation. To preserve electrical neutrality, one of the normal cation sites, usually octahedral, must be vacant.

Frenkel defects are particularly common in the silver halides AgCl , AgBr , and AgI , which combine a rather small cation (Ag^+ , ionic radius = 115 pm) with large, polarizable anions. Certain more complex salts with a second cation in addition to Ag^+ and Br^- or I^- have so many Ag^+ ions in tetrahedral holes that they are good electrical conductors in the solid state; hence they are called solid electrolytes. (As you learned in , most ionic compounds do not conduct electricity in the solid state, although they do conduct electricity when molten or dissolved in a solvent that separates the ions, allowing them to migrate in response to an applied electric field.) In response to an applied voltage, the cations in solid electrolytes can diffuse rapidly through the lattice via octahedral holes, creating Frenkel defects as the cations migrate. Sodium–sulfur batteries use a solid Al_2O_3 electrolyte with small amounts of solid Na_2O . Because the electrolyte cannot leak, it cannot cause corrosion, which gives a battery that uses a solid electrolyte a significant advantage over one with a liquid electrolyte.

EXAMPLE 6

In a sample of NaCl, one of every 10,000 sites normally occupied by Na^+ is occupied instead by Ca^{2+} .

Assuming that all of the Cl^- sites are fully occupied, what is the stoichiometry of the sample?

Given: ionic solid and number and type of defect

Asked for: stoichiometry

Strategy:

A Identify the unit cell of the host compound. Compute the stoichiometry if 0.01% of the Na^+ sites are occupied by Ca^{2+} . If the overall charge is greater than 0, then the stoichiometry must be incorrect.

B If incorrect, adjust the stoichiometry of the Na^+ ion to compensate for the additional charge.

Solution:

A Pure NaCl has a 1:1 ratio of Na^+ and Cl^- ions arranged in an fcc lattice (the sodium chloride structure). If all the anion sites are occupied by Cl^- , the negative charge is -1.00 per formula unit. If 0.01% of the Na^+ sites are occupied by Ca^{2+} ions, the cation stoichiometry is $\text{Na}_{0.99}\text{Ca}_{0.01}$. This results in a positive charge of $(0.99)(+1) + (0.01)(+2) = +1.01$ per formula unit, for a net charge in the crystal of $+1.01 + (-1.00) = +0.01$ per formula unit. Because the overall charge is greater than 0, this stoichiometry must be incorrect.

B The most plausible way for the solid to adjust its composition to become electrically neutral is for some of the Na^+ sites to be vacant. If one Na^+ site is vacant for each site that has a Ca^{2+} cation, then the cation stoichiometry is $\text{Na}_{0.98}\text{Ca}_{0.01}$. This results in a positive charge of $(0.98)(+1) + (0.01)(+2) = +1.00$ per formula unit, which exactly neutralizes the negative charge. The stoichiometry of the solid is thus $\text{Na}_{0.98}\text{Ca}_{0.01}\text{Cl}_{1.00}$.

Exercise

In a sample of MgO that has the sodium chloride structure, 0.02% of the Mg^{2+} ions are replaced by Na^+ ions. Assuming that all of the cation sites are fully occupied, what is the stoichiometry of the sample?

Answer: If the formula of the compound is $\text{Mg}_{0.98}\text{Na}_{0.02}\text{O}_{1-x}$, then x must equal 0.01 to preserve electrical neutrality. The formula is thus $\text{Mg}_{0.98}\text{Na}_{0.02}\text{O}_{0.99}$.

Nonstoichiometric Compounds

The law of multiple proportions (see), states that chemical compounds contain fixed integral ratios of atoms. In fact, nonstoichiometric compounds contain large numbers of defects, usually vacancies, which give rise to stoichiometries that can depart significantly from simple integral ratios *without affecting the fundamental structure of the crystal*. Nonstoichiometric compounds frequently consist of transition

metals, lanthanides, and actinides, with polarizable anions such as oxide (O^{2-}) and sulfide (S^{2-}). Some common examples are listed in , along with their basic structure type. These compounds are nonstoichiometric because their constituent metals can exist in multiple oxidation states in the solid, which in combination preserve electrical neutrality.

Table 12.4 Some Nonstoichiometric Compounds

Compound	Observed Range of x
Oxides*	
Fe_xO	0.85–0.95
Ni_xO	0.97–1.00
TiO_x	0.75–1.45
VO_x	0.9–1.20
NbO_x	0.9–1.04
Sulfides	
Cu_xS	1.77–2.0
Fe_xS	0.80–0.99
ZrS_x	0.9–1.0
*All the oxides listed have the sodium chloride structure.	

One example is iron(II) oxide (ferrous oxide), which produces the black color in clays and is used as an abrasive. Its stoichiometry is *not* FeO because it always contains less than 1.00 Fe per O^{2-} (typically 0.90–0.95). This is possible because Fe can exist in both the +2 and +3 oxidation states. Thus the difference in charge created by a vacant Fe^{2+} site can be balanced by two Fe^{2+} sites that have Fe^{3+} ions instead [$+2$ vacancy = $(3 - 2) + (3 - 2)$]. The crystal lattice is able to accommodate this relatively high fraction of substitutions and vacancies with no significant change in structure.

Note the Pattern

Because a crystal must be electrically neutral, any defect that affects the number or charge of the cations *must be compensated* by a corresponding defect in the number or charge of the anions.

Summary

Real crystals contain large numbers of **defects**. Defects may affect only a single point in the lattice (a **point defect**), a row of lattice points (a **line defect**), or a plane of atoms (a **plane defect**). A point defect can be an atom missing from a site in the crystal (a **vacancy**) or an impurity atom that occupies

either a normal lattice site (a **substitutional impurity**) or a hole in the lattice between atoms (an **interstitial impurity**). In an **edge dislocation**, an extra plane of atoms is inserted into part of the crystal lattice. Multiple defects can be introduced into materials so that the presence of one defect prevents the motion of another, in a process called **pinning**. Because defect motion tends to stop at **grain boundaries**, controlling the size of the grains in a material controls its mechanical properties. In addition, a process called **work hardening** introduces defects to toughen metals. **Schottky defects** are a coupled pair of vacancies—one cation and one anion—that maintains electrical neutrality. A **Frenkel defect** is an ion that occupies an incorrect site in the lattice. Cations in such compounds are often able to move rapidly from one site in the crystal to another, resulting in high electrical conductivity in the solid material. Such compounds are called **solid electrolytes**. **Nonstoichiometric compounds** have variable stoichiometries over a given range with no dramatic change in crystal structure. This behavior is due to a large number of vacancies or substitutions of one ion by another ion with a different charge.

KEY TAKEAWAY

- Defects determine the behavior of solids, but because ionic compounds contain both cations and anions, they exhibit additional types of defects that are not found in metals.

CONCEPTUAL PROBLEMS

- How are defects and impurities in a solid related? Can a pure, crystalline compound be free of defects? How can a substitutional impurity produce a vacancy?
- Why does applying a mechanical stress to a covalent solid cause it to fracture? Use an atomic level description to explain why a metal is ductile under conditions that cause a covalent solid to fracture.
- How does work hardening increase the strength of a metal? How does work hardening affect the physical properties of a metal?
- Work-hardened metals and covalent solids such as diamonds are both susceptible to cracking when stressed. Explain how such different materials can both exhibit this property.
- Suppose you want to produce a ductile material with improved properties. Would impurity atoms of similar or dissimilar atomic size be better at maintaining the ductility of a metal? Why? How would introducing an impurity that forms polar covalent bonds with the metal atoms affect the ductility of the metal? Explain your reasoning.

6. Substitutional impurities are often used to tune the properties of material. Why are substitutional impurities generally more effective at high concentrations, whereas interstitial impurities are usually effective at low concentrations?
7. If an O^{2-} ion (ionic radius = 132 pm) is substituted for an F^- ion (ionic radius = 133 pm) in an ionic crystal, what structural changes in the ionic lattice will result?
8. How will the introduction of a metal ion with a different charge as an impurity induce the formation of oxygen vacancies in an ionic metal-oxide crystal?
9. Many nonstoichiometric compounds are transition metal compounds. How can such compounds exist, given that their nonintegral cation:anion ratios apparently contradict one of the basic tenets of Dalton's atomic theory of matter?
10. If you wanted to induce the formation of oxygen vacancies in an ionic crystal, which would you introduce as substitutional impurities—cations with a higher positive charge or a lower positive charge than the cations in the parent structure? Explain your reasoning.

ANSWERS

- 1.
- 2.
- 3.
- 4.
5. Impurity atoms of similar size and with similar chemical properties would be most likely to maintain the ductility of the metal, because they are unlikely to have a large effect on the ease with which one layer of atoms can move past another under mechanical stress. Larger impurity atoms are likely to form "bumps" or kinks that will make it harder for layers of atoms to move across one another. Interstitial atoms that form polar covalent bonds with the metal atoms tend to occupy spaces between the layers; they act as a "glue" that holds layers of metal atoms together, which greatly decreases the ductility.
- 6.
7. Since O^{2-} and F^- are both very similar in size, substitution is possible without disruption of the ionic packing. The difference in charge, however, requires the formation of a vacancy on another F^- site to maintain charge neutrality.
- 8.

9. Most transition metals form at least two cations that differ by only one electron. Consequently, nonstoichiometric compounds containing transition metals can maintain electrical neutrality by gaining electrons to compensate for the absence of anions or the presence of additional metal ions. Conversely, such compounds can lose electrons to compensate for the presence of additional anions or the absence of metal ions. In both cases, the positive charge on the transition metal is adjusted to maintain electrical neutrality.
- 10.

NUMERICAL PROBLEMS

1. The ionic radius of K^+ is 133 pm, whereas that of Na^+ is 98 pm. Do you expect K^+ to be a common substitutional impurity in compounds containing Na^+ ? Why or why not?
2. Given Cs (262 pm), Tl (171 pm), and B (88 pm) with their noted atomic radii, which atom is most likely to act as an interstitial impurity in an Sn lattice (Sn atomic radius = 141 pm)? Why?
3. After aluminum, iron is the second most abundant metal in Earth's crust. The silvery-white, ductile metal has a body-centered cubic (bcc) unit cell with an edge length of 286.65 pm.
 - a. Use this information to calculate the density of iron.
 - b. What would the density of iron be if 0.15% of the iron sites were vacant?
 - c. How does the mass of 1.00 cm^3 of iron without defects compare with the mass of 1.00 cm^3 of iron with 0.15% vacancies?
4. Certain ceramic materials are good electrical conductors due to high mobility of oxide ions resulting from the presence of oxygen vacancies. Zirconia (ZrO_2) can be doped with yttrium by adding Y_2O_3 . If 0.35 g of Y_2O_3 can be incorporated into 25.0 g of ZrO_2 while maintaining the zirconia structure, what is the percentage of oxygen vacancies in the structure?
5. Which of the following ions is most effective at inducing an O^{2-} vacancy in crystal of CaO? The ionic radii are O^{2-} , 132 pm; Ca^{2+} , 100 pm; Sr^{2+} , 127 pm; F^- , 133 pm; La^{3+} , 104 pm; and K^+ , 133 pm. Explain your reasoning.

ANSWERS

1. No. The potassium is much larger than the sodium ion.
- 2.
3.
 - a. 7.8744 g/cm^3
 - b. 7.86 g/cm^3

- c. Without defects, the mass is 0.15% greater.
- 4.
5. The lower charge of K^+ makes it the best candidate for inducing an oxide vacancy, even though its ionic radius is substantially larger than that of Ca^{2+} . Substituting two K^+ ions for two Ca^{2+} ions will decrease the total positive charge by two, and an oxide vacancy will maintain electrical neutrality. For example, if 10% of the Ca^{2+} ions are replaced by K^+ , we can represent the change as going from $Ca_{20}O_{20}$ to $K_2Ca_{18}O_{20}$, which has a net charge of +2. Loss of one oxide ion would give a composition of $K_2Ca_{18}O_{19}$, which is electrically neutral.

12.5 Correlation between Bonding and the Properties of Solids

LEARNING OBJECTIVE

1. To understand the correlation between bonding and the properties of solids.

Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as *ionic*, *molecular*, *covalent (network)*, or *metallic*. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Ionic Solids

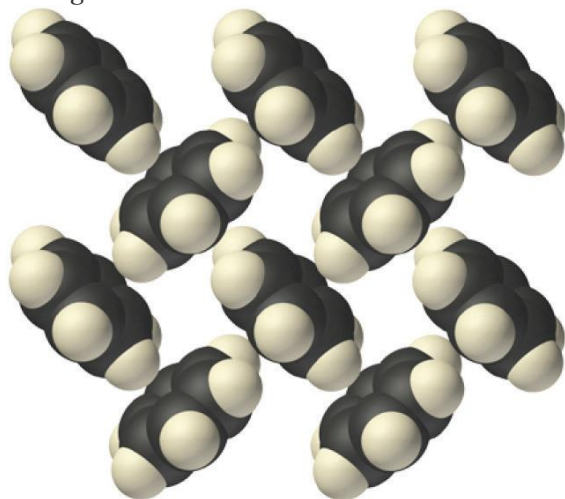
You learned in that an ionic solid consists of positively and negatively charged ions held together by electrostatic forces. (For more information about ionic solids, see , .) The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy**, the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase, is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and F^- (133 pm) versus O^{2-} (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases,

however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

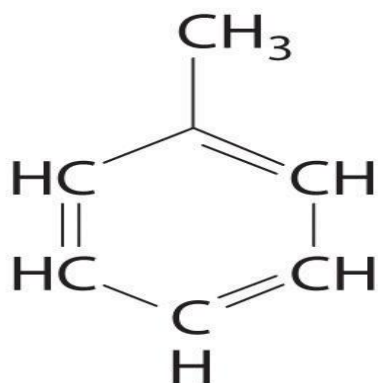
Molecular solids consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these, which were discussed in . The arrangement of the molecules in solid benzene is as follows:



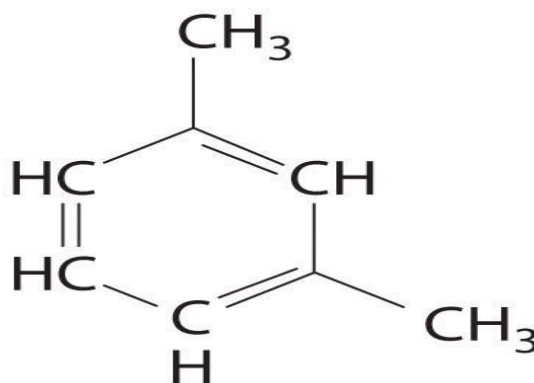
The structure of solid benzene. In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles.

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene (C_{10}H_8), and anthracene ($\text{C}_{14}\text{H}_{10}$), with one, two, and three fused aromatic rings, are 5.5°C , 80.2°C , and 215°C , respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($\text{C}_6\text{H}_5\text{CH}_3$) and *m*-xylene [*m*- $\text{C}_6\text{H}_4(\text{CH}_3)_2$] have melting points of -95°C and -48°C , respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



Toluene



m-Xylene

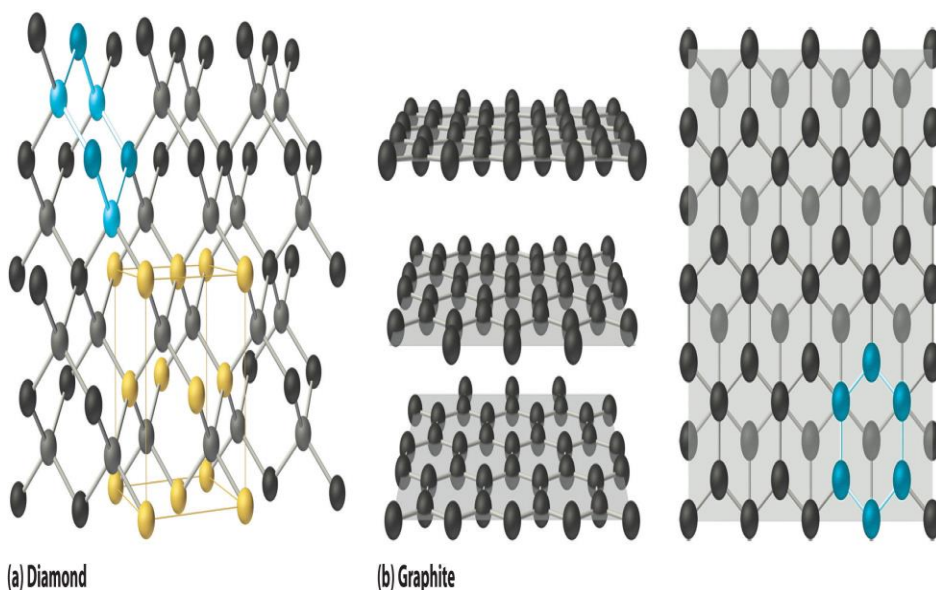
Toluene

and m-xylene. The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene.

Covalent Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in , consists of sp^3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.

Figure 12.19 The Structures of Diamond and Graphite



(a) Diamond consists of sp^3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer.

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in , except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in , can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because

strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in . It contains planar networks of six-membered rings of sp^2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized $2p_z$ orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in . In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimates at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons.

compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 12.5 A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
sulfur (s)	64.22	226
iodine (s)	62.42	149

Metallic Solids

Metals are characterized by their ability to reflect light, called luster, their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solids are dense, with each atom having as many as 12 nearest neighbors.

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

Note the Pattern

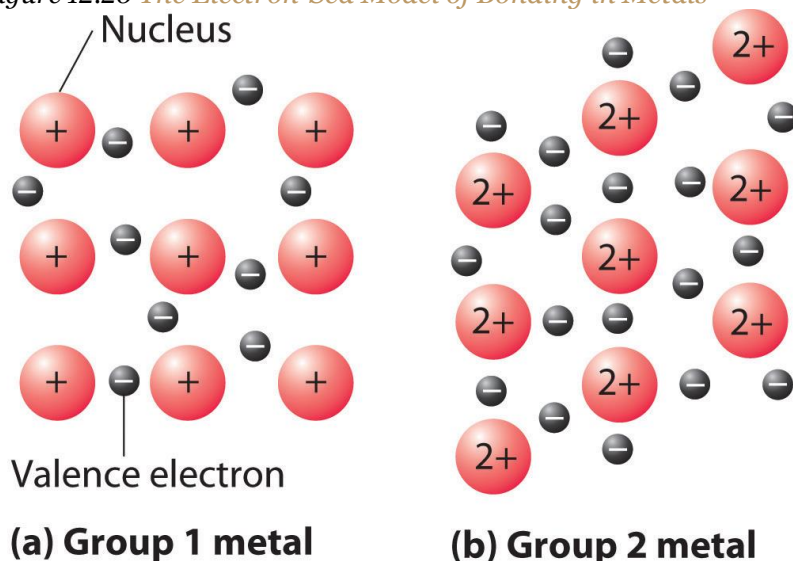
Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the *d* block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron sea (δ^-). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode,

thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. A more complete description of metallic bonding is presented in .

Figure 12.20 *The Electron-Sea Model of Bonding in Metals*



Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a “sea” of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.

Substitutional Alloys

An alloy is a mixture of metals with metallic properties that differ from those of its constituent elements. Brass (Cu and Zn in a 2:1 ratio) and bronze (Cu and Sn in a 4:1 ratio) are examples of substitutional alloys, which are metallic solids with large numbers of substitutional impurities. In contrast, small numbers of interstitial impurities, such as carbon in the iron lattice of steel, give an interstitial alloy. Because scientists can combine two or more metals in varying proportions to tailor the properties of a material for particular applications, most of the metallic substances we encounter are actually alloys. Examples include the low-melting-point alloys used in solder (Pb and Sn in a 2:1 ratio) and in fuses and fire sprinklers (Bi, Pb, Sn, and Cd in a 4:2:1:1 ratio).

The compositions of most alloys can vary over wide ranges. In contrast, intermetallic compounds consist of certain metals that combine in only specific proportions. Their compositions are largely determined by the relative sizes of their component atoms and the ratio of the total number of valence electrons to the number of atoms present (the *valence electron density*). The structures and physical properties of intermetallic compounds are frequently quite different from those of their constituent elements, but they may be similar to elements with a similar valence electron density. For example, Cr_3Pt is an intermetallic compound used to coat razor blades advertised as “platinum coated”; it is very hard and dramatically lengthens the useful life of the razor blade. With similar valence electron densities, Cu and PdZn have been found to be virtually identical in their catalytic properties.

Some general properties of the four major classes of solids are summarized in .

Table 12.6 Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous
*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.			

Note the Pattern

The general order of increasing strength of interactions in a solid is molecular solids < ionic solids $\approx$ metallic solids < covalent solids.

EXAMPLE 7

Classify Ge, RbI, $\text{C}_6(\text{CH}_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.

B Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the *p* block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound $\text{C}_6(\text{CH}_3)_6$ is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a *d*-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $\text{C}_6(\text{CH}_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $\text{C}_6(\text{CH}_3)_6 < \text{Zn} \sim \text{RbI} < \text{Ge}$. The actual melting points are $\text{C}_6(\text{CH}_3)_6$, 166°C ; Zn, 419°C ; RbI, 642°C ; and Ge, 938°C . This agrees with our prediction.

Exercise

Classify C_{60} , BaBr_2 , GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer: C_{60} (molecular) $<$ AgZn (metallic) $\sim$ BaBr_2 (ionic) $<$ GaAs (covalent). The actual melting points are C_{60} , about 300°C ; AgZn, about 700°C ; BaBr_2 , 856°C ; and GaAs, 1238°C .

Summary

The major types of solids are ionic, molecular, covalent, and metallic. **Ionic solids** consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. **Molecular solids** are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. **Covalent solids** consist of two- or three-dimensional networks of

atoms held together by covalent bonds; they tend to be very hard and have high melting points. **Metallic solids** have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An **alloy** is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (**substitutional alloys**), by inserting smaller atoms into holes in the metal lattice (**interstitial alloys**), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form **intermetallic compounds** with unique properties.

KEY TAKEAWAY

- Solids can be classified as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions is molecular < ionic $\approx$ metallic < covalent.

CONCEPTUAL PROBLEMS

- Four vials labeled A–D contain sucrose, zinc, quartz, and sodium chloride, although not necessarily in that order. The following table summarizes the results of the series of analyses you have performed on the contents:

	A	B	C	D
Melting Point	high	high	high	low
Thermal Conductivity	poor	poor	good	poor
Electrical Conductivity in Solid State	moderate	poor	high	poor
Electrical Conductivity in Liquid State	high	poor	high	poor
Hardness	hard	hard	soft	soft
Luster	none	none	high	none

- Match each vial with its contents.
- Do ionic solids generally have higher or lower melting points than molecular solids? Why? Do ionic solids generally have higher or lower melting points than covalent solids? Explain your reasoning.
- The strength of London dispersion forces in molecular solids tends to increase with molecular mass, causing a smooth increase in melting points. Some molecular solids, however, have significantly lower melting points than predicted by their molecular masses. Why?

5. Suppose you want to synthesize a solid that is both heat resistant and a good electrical conductor. What specific types of bonding and molecular interactions would you want in your starting materials?
6. Explain the differences between an interstitial alloy and a substitutional alloy. Given an alloy in which the identity of one metallic element is known, how could you determine whether it is a substitutional alloy or an interstitial alloy?
7. How are intermetallic compounds different from interstitial alloys or substitutional alloys?

ANSWERS

1.
 - a. NaCl, ionic solid
 - b. quartz, covalent solid
 - c. zinc, metal
 - d. sucrose, molecular solid
- 2.
- 3.
- 4.
5. In a substitutional alloy, the impurity atoms are similar in size and chemical properties to the atoms of the host lattice; consequently, they simply replace some of the metal atoms in the normal lattice and do not greatly perturb the structure and physical properties. In an interstitial alloy, the impurity atoms are generally much smaller, have very different chemical properties, and occupy holes between the larger metal atoms. Because interstitial impurities form covalent bonds to the metal atoms in the host lattice, they tend to have a large effect on the mechanical properties of the metal, making it harder, less ductile, and more brittle. Comparing the mechanical properties of an alloy with those of the parent metal could be used to decide whether the alloy were a substitutional or interstitial alloy.
- 6.

NUMERICAL PROBLEMS

1. Will the melting point of lanthanum(III) oxide be higher or lower than that of ferrous bromide? The relevant ionic radii are as follows: La^{3+} , 104 pm; O^{2-} , 132 pm; Fe^{2+} , 83 pm; and Br^{-} , 196 pm. Explain your reasoning.
2. Draw a graph showing the relationship between the electrical conductivity of metallic silver and temperature.
3. Which has the higher melting point? Explain your reasoning in each case.

- a. Os or Hf
- b. SnO_2 or ZrO_2
- c. Al_2O_3 or SiO_2
4. Draw a graph showing the relationship between the electrical conductivity of a typical semiconductor and temperature.

ANSWER

- 1.
- 2.
- 3.
- a. Osmium has a higher melting point, due to more valence electrons for metallic bonding.
- b. Zirconium oxide has a higher melting point, because it has greater ionic character.
- c. Aluminum oxide has a higher melting point, again because it has greater ionic character.

12.6 Bonding in Metals and Semiconductors

LEARNING OBJECTIVE

1. To describe the electrical properties of a solid using band theory.

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model described in . The molecular orbital theory we used in to explain the delocalized π bonding in polyatomic ions and molecules such as NO_2^- , ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

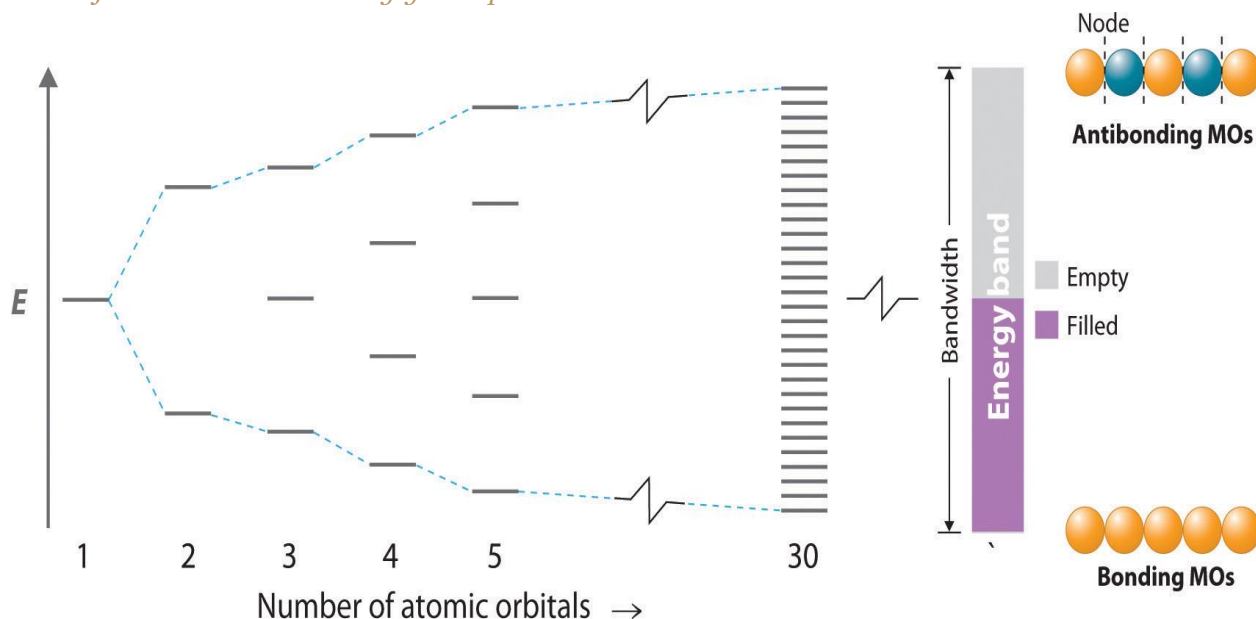
Band Theory

In a 1 mol sample of a metal, there can be more than 10^{24} orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of n metal atoms, each containing a single electron in an s orbital. We use this example to describe an approach to metallic bonding called band theory, which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of, which is the same as the molecular orbital diagram in , shows the pattern of molecular orbitals that results from the interaction of ns orbitals as n increases from 2 to 5.

Figure 12.21 *The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of n Atoms, Each of Which Contains a Singly Occupied s Orbital*



This is the same diagram as , with the addition of the far right-hand portion, corresponding to $n = 30$ and $n = \infty$. As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.

As we saw in , the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For $n = 30$, there are still discrete, well-resolved energy levels, but as n increases from 30 to a number close to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of

energy levels, as shown on the right in , each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations. The continuous set of allowed energy levels shown on the right in is called an energy band. The difference in energy between the highest and lowest energy levels is the bandwidth and is proportional to the strength of the interaction between orbitals on adjacent atoms: the stronger the interaction, the larger the bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the same as the number of interacting atomic orbitals, the band contains n energy levels corresponding to the combining of s orbitals from n metal atoms. Each of the original s orbitals could contain a maximum of two electrons, so the band can accommodate a total of $2n$ electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each s orbital, so there are only n electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the *bonding* molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

Multidimensional Systems

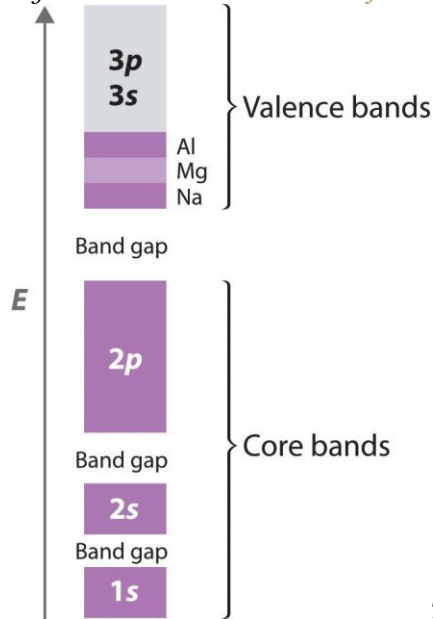
The previous example was a one-dimensional array of atoms that had only s orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in p and d orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in , with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

Band Gap

Because the $1s$, $2s$, and $2p$ orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (). These bands are completely filled (both the bonding and antibonding levels are

completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gap. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

Figure 12.22 The Band Structures of the Period 3 Metals Na, Mg, and Al



The 3s and 3p valence bands overlap in energy to form a continuous set of energy

levels that can hold a maximum of eight electrons per atom.

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3s and 3p in) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3s and 3p atomic orbitals are wider than the energy gap between them, so the result is overlapping bands. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3s and 3p bands is also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3s orbital and six electrons for each set of 3p orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in . The partially filled valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

Requirements for Metallic Behavior

For a solid to exhibit metallic behavior, it must have a set of delocalized orbitals forming a band of allowed energy levels, and the resulting band must be only partially filled (10%–90%) with electrons. Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

Note the Pattern

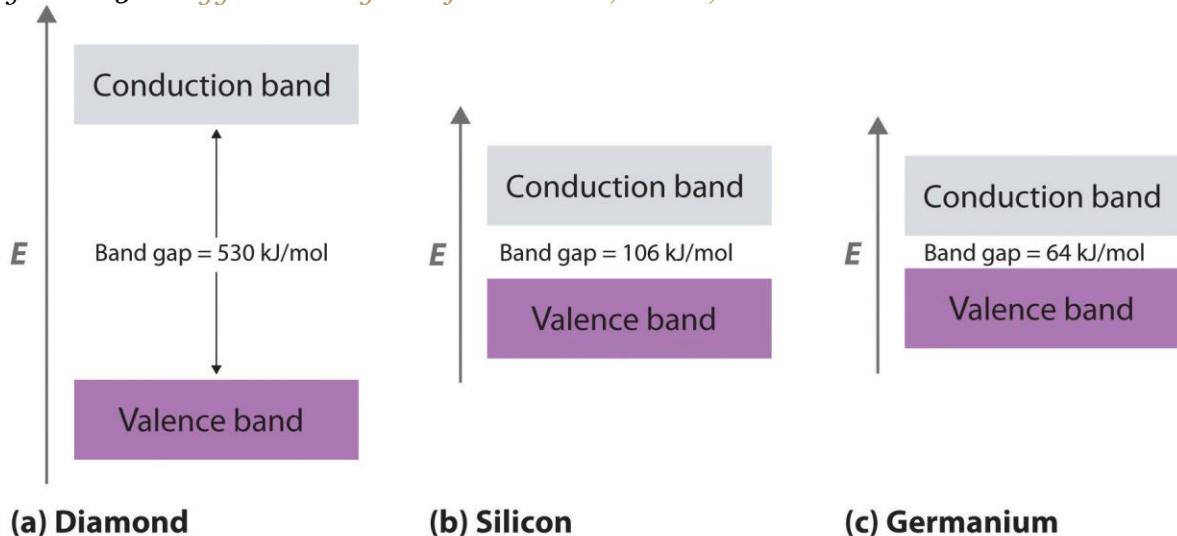
Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence ns , $(n - 1)d$, and np orbitals (with a total capacity of 18 electrons per metal atom) or their ns and $(n - 1)d$ orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators

In contrast to metals, electrical insulators are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in part (a) in . Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2s and 2p orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

Figure 12.23 *Energy-Band Diagrams for Diamond, Silicon, and Germanium*



The band gap gets smaller from C to Ge.

Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we

go down group 14 (part (b) and part (c) of). (For more information on bond strengths, see , .)

Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction band.

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a “hole” in the valence band that is equivalent to a *positive* charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a “bucket brigade” mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (). Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductors. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in .

Figure 12.24 A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

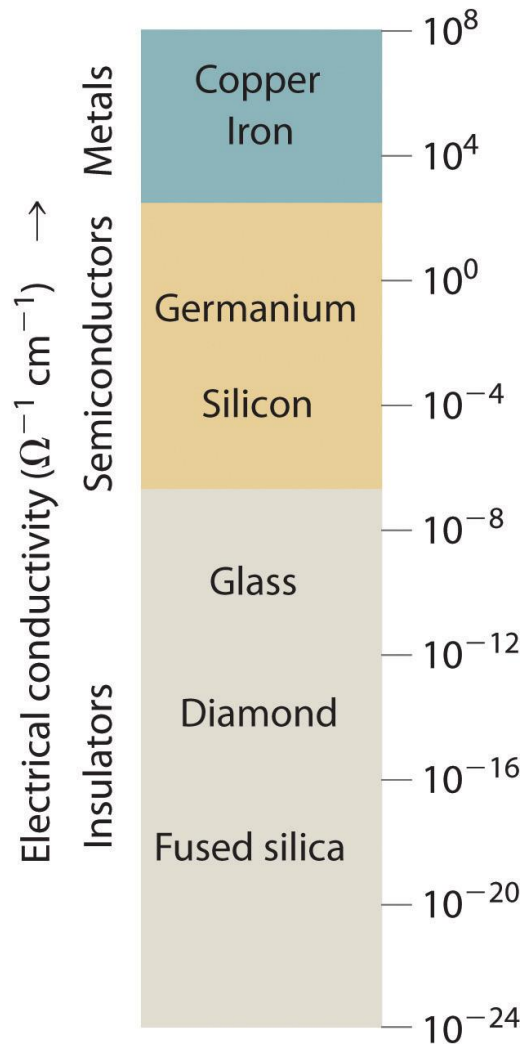
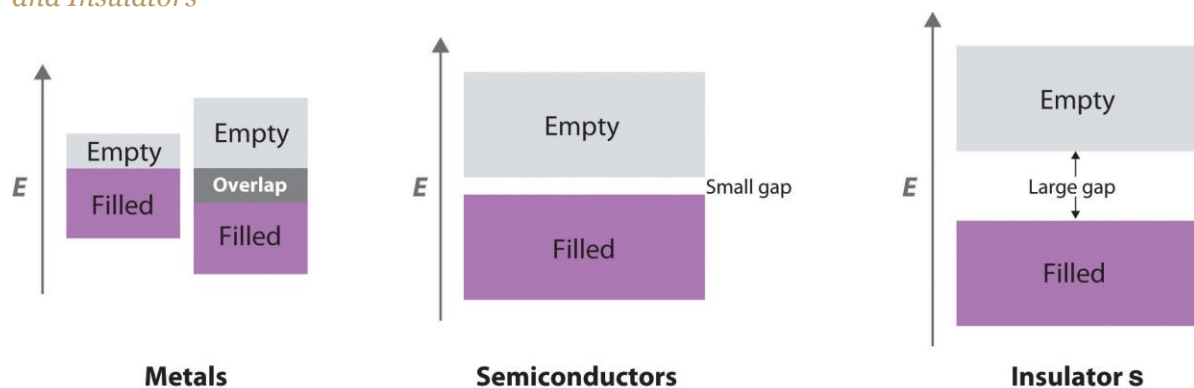


Figure 12.25 A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators

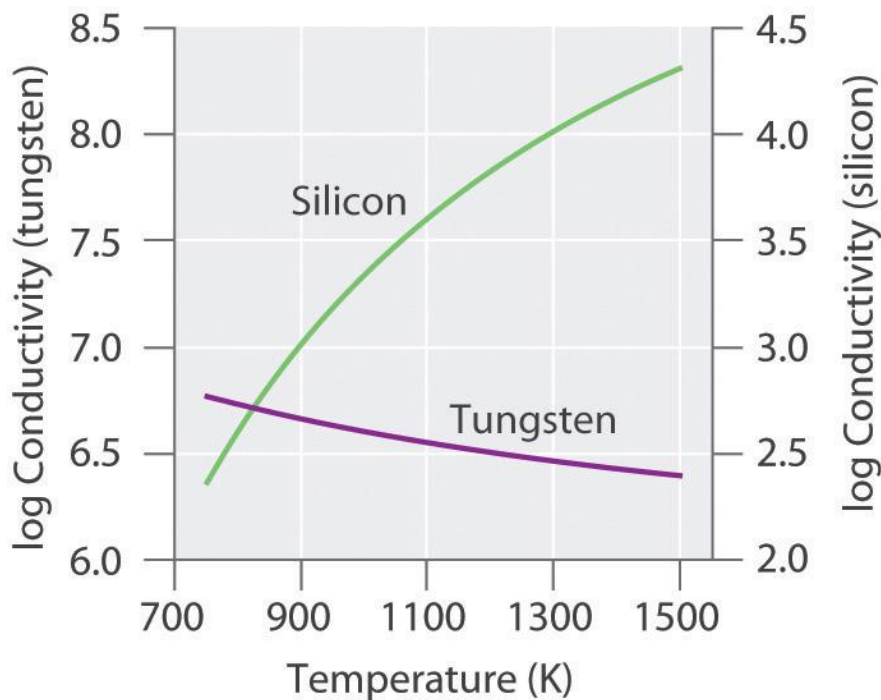


Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).

Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the *net* motion of the electron through the crystal, and the *lower* the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus *decreasing* the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in.

Figure 12.26 The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor



The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.

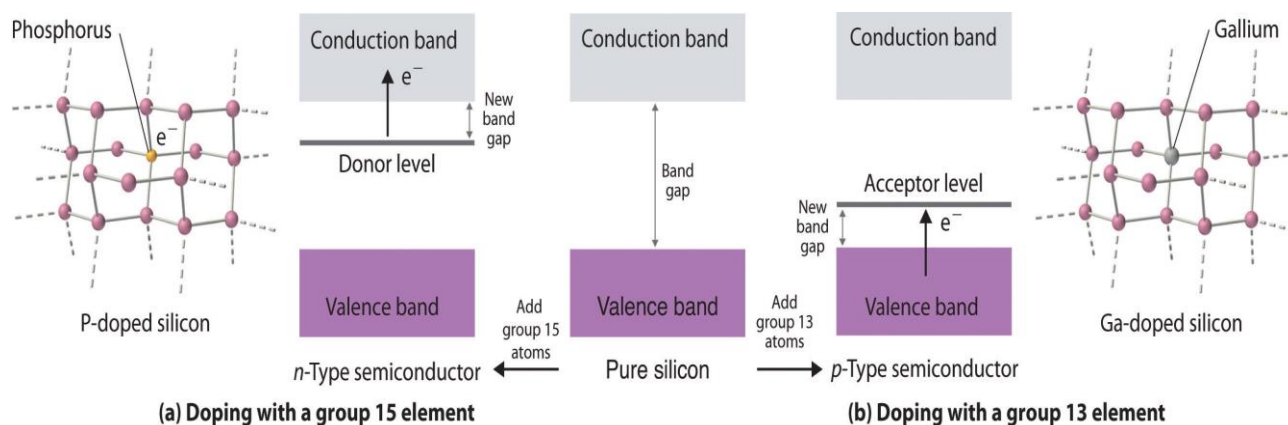
Note the Pattern

The electrical conductivity of a semiconductor *increases* with increasing temperature, whereas the electrical conductivity of a metal *decreases* with increasing temperature.

n- and *p*-Type Semiconductors

Doping is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains *more* valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in part (a) in , adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an *n-type semiconductor*, with the *n* indicating that the added charge carriers are negative (they are electrons).

Figure 12.27 Structures and Band Diagrams of n-Type and p-Type Semiconductors



(a) Doping silicon with a group 15 element results in a new *filled* level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new *empty* level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.

If the impurity atoms contain *fewer* valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in *increased* conductivity because the impurity atoms generate holes in the valence band. As shown in part (b) in , adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p-type semiconductor*, with the *p* standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

Note the Pattern

n-Type semiconductors are *negative* charge carriers; the impurity has *more* valence electrons than the host. *p*-Type semiconductors are *positive* charge carriers; the impurity has *fewer* valence electrons than the host.

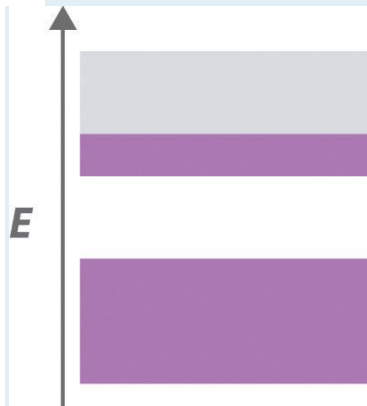
The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise

amounts of desired impurities and assembling silicon chips and other complex devices with junctions between n - and p -type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C , scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced p -type semiconductors, whereas doping them with boron and deuterium achieves n -type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

EXAMPLE 8

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.



- Predict the electrical properties of this solid.
- What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
- What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

Given: band structure

Asked for: variations in electrical properties with conditions

Strategy:

A Based on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.

B After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.

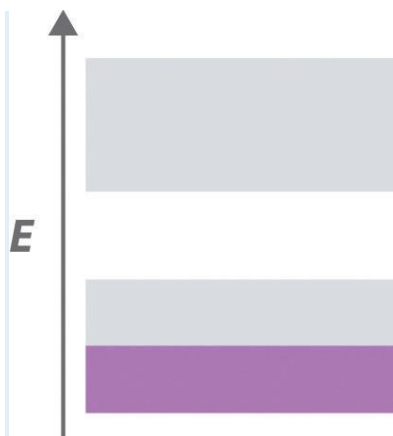
C Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

Solution:

- a. **A** The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
- b. **B** Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.
- c. **C** Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

Exercise

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.



- Predict the electrical properties of the solid.
- What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
- What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

Answer:

- The solid has a partially filled band, so it has the electrical properties of a conductor.
- Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.
- Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

Summary

Band theory assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an **energy band**. The difference in energy between the highest and lowest allowed levels within a given band is the **bandwidth**, and the difference in energy between the highest level of one band and the lowest level of the band above it is the **band gap**. If the width of adjacent bands is larger than the energy gap between them, **overlapping bands** result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy

levels. If a solid has a filled valence band with a relatively low-lying empty band above it (a **conduction band**), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then migrate through the crystal, resulting in electrical conductivity. **Electrical insulators** are poor conductors because their valence bands are full. **Semiconductors** have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by **doping**, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an ***n*-type semiconductor** with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a ***p*-type semiconductor** that also exhibits increased electrical conductivity.

KEY TAKEAWAY

- Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid.

CONCEPTUAL PROBLEMS

1. Can band theory be applied to metals with two electrons in their valence *s* orbitals? with no electrons in their valence *s* orbitals? Why or why not?
2. Given a sample of a metal with 10^{20} atoms, how does the width of the band arising from *p* orbital interactions compare with the width of the band arising from *s* orbital interactions? from *d* orbital interactions?
3. Diamond has one of the lowest electrical conductivities known. Based on this fact, do you expect diamond to be colored? Why? How do you account for the fact that some diamonds are colored (such as “pink” diamond or “green” diamond)?
4. Why do silver halides, used in the photographic industry, have band gaps typical of semiconducting materials, whereas alkali metal halides have very large band gaps?
5. As the ionic character of a compound increases, does its band gap increase or decrease? Why?
6. Why is silicon, rather than carbon or germanium, used in the semiconductor industry?

7. Carbon is an insulator, and silicon and germanium are semiconductors. Explain the relationship between the valence electron configuration of each element and their band structures. Which will have the higher electrical conductivity at room temperature—silicon or germanium?
8. How does doping affect the electrical conductivity of a semiconductor? Draw the effect of doping on the energy levels of the valence band and the conduction band for both an *n*-type and a *p*-type semiconductor.

ANSWERS

- 1.
- 2.
3. The low electrical conductivity of diamond implies a very large band gap, corresponding to the energy of a photon of ultraviolet light rather than visible light. Consequently, diamond should be colorless. Pink or green diamonds contain small amounts of highly colored impurities that are responsible for their color.
- 4.
5. As the ionic character of a compound increases, the band gap will also increase due to a decrease in orbital overlap. Remember that overlap is greatest for orbitals of the same energy, and that the difference in energy between orbitals on adjacent atoms increases as the difference in electronegativity between the atoms increases. Thus, large differences in electronegativity increase the ionic character, decrease the orbital overlap, and increase the band gap.
- 6.
- 7.
- 8.

NUMERICAL PROBLEMS

1. Of Ca, N, B, and Ge, which will convert pure silicon into a *p*-type semiconductor when doping? Explain your reasoning.
2. Of Ga, Si, Br, and P, which will convert pure germanium into an *n*-type semiconductor when doping? Explain your reasoning.

12.7 Superconductors

LEARNING OBJECTIVE

1. To become familiar with the properties of superconductors.

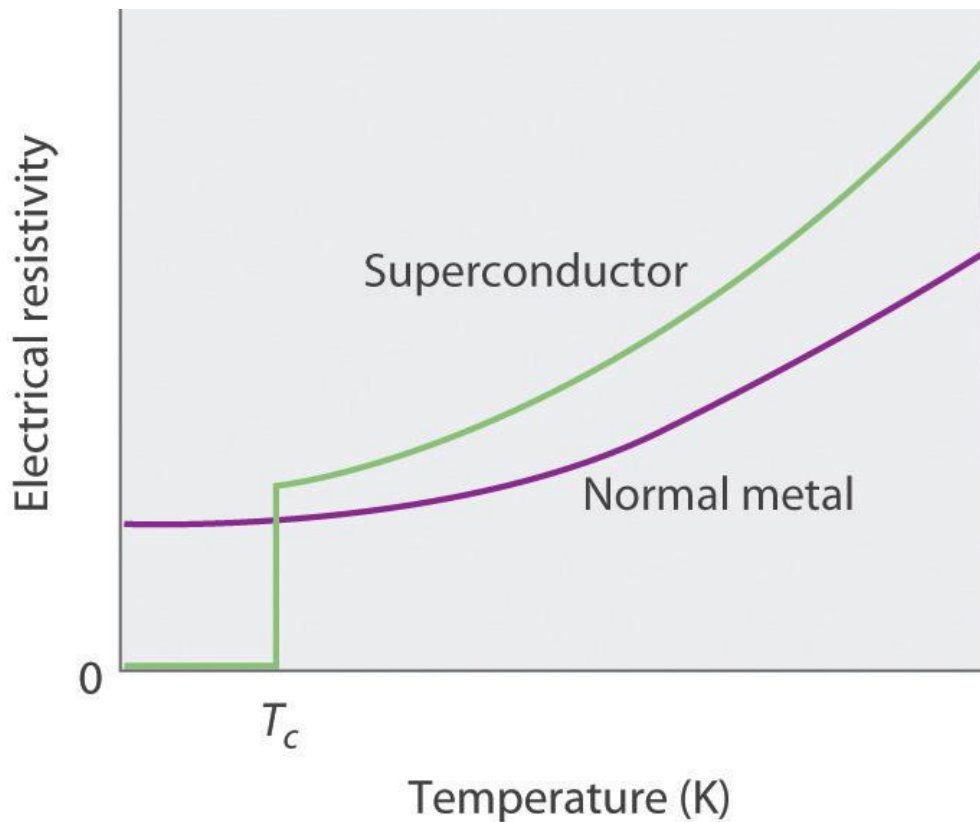
The phenomenon of superconductivity was discovered by the Danish physicist H. Kamerlingh Onnes (1853–1926; Nobel Prize in Physics, 1913), who found a way to liquefy helium, which boils at 4.2 K and 1 atm pressure. To exploit the very low temperatures made possible by this new cryogenic fluid, he began a systematic study of the properties of metals, especially their electrical properties. Because the electrical resistance of a sample is technically easier to measure than its conductivity, Onnes measured the *resistivity* of his samples. The resistivity and conductivity of a material are inversely proportional:

Equation 12.2

$$\text{conductivity} = 1/\text{resistivity}$$

In 1911, Onnes discovered that at about 4 K, the resistivity of metallic mercury (melting point = 234 K) decreased suddenly to essentially zero, rather than continuing to decrease only slowly with decreasing temperature as expected (). He called this phenomenon superconductivity because a resistivity of zero means that an electrical current can flow forever. Onnes soon discovered that many other metallic elements exhibit superconductivity at very low temperatures. Each of these superconductors has a characteristic superconducting transition temperature (T_c) at which its resistivity drops to zero. At temperatures less than their T_c , superconductors also completely expel a magnetic field from their interior (part (a) in). This phenomenon is called the Meissner effect after one of its discoverers, the German physicist Walther Meissner, who described the phenomenon in 1933. Due to the Meissner effect, a superconductor will actually “float” over a magnet, as shown in part (b) in .

Figure 12.28 The Temperature Dependence of the Electrical Resistivity of a Normal Metal and a Superconductor



The superconducting transition temperature (T_c) is the temperature at which the resistivity of a superconductor drops to zero.

(a) Below its T_c , a superconductor completely expels magnetic lines of force from its interior. (b) In magnetic levitation, a small magnet “floats” over a disk of a high-temperature superconducting material ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$) cooled in liquid nitrogen.

BCS Theory

For many years, the phenomenon of superconductivity could not be satisfactorily explained by the laws of conventional physics. In the early 1950s, however, American physicists John Bardeen, Leon Cooper, and John Schrieffer formulated a theory for superconductivity that earned them the Nobel Prize in Physics in 1972. According to the BCS theory (named for the initials of their last names), electrons are able to travel through a solid with zero resistance because of attractive interactions involving two electrons that are at some distance from each other. As one electron moves through the lattice, the surrounding nuclei are attracted to it. The motion of the nuclei can create a transient (short-lived) hole that pulls the second electron in the same direction as the first. The nuclei then return to their original positions to avoid colliding with the second electron as it approaches. The pairs of electrons, called Cooper pairs, migrate

through the crystal as a unit. The electrons in Cooper pairs change partners frequently, like dancers in a ballet.

According to the BCS theory, as the temperature of the solid increases, the vibrations of the atoms in the lattice increase continuously, until eventually the electrons cannot avoid colliding with them. The collisions result in the loss of superconductivity at higher temperatures.

The phenomenon of superconductivity suggested many exciting technological applications. For example, using superconducting wires in power cables would result in zero power losses, even over distances of hundreds of miles. Additionally, because superconductors expel magnetic fields, a combination of magnetic rails and superconducting wheels (or vice versa) could be used to produce *magnetic levitation* of, for example, a train over the track, resulting in friction-free transportation.

Unfortunately, for many years the only superconductors known had serious limitations, especially the need for very low temperatures, which required the use of expensive cryogenic fluids such as liquid He. In addition, the superconducting properties of many substances are destroyed by large electrical currents or even moderately large magnetic fields, making them useless for applications in power cables or high-field magnets. The ability of materials such as NbTi, NbSn, Nb₃Si, and Nb₃Ge to tolerate rather high magnetic fields, however, has led to a number of commercial applications of superconductors, including high-field magnets for nuclear magnetic resonance (NMR) spectrometers and magnetic resonance imaging (MRI) instruments in medicine, which, unlike x-rays, can detect small changes in soft tissues in the body.

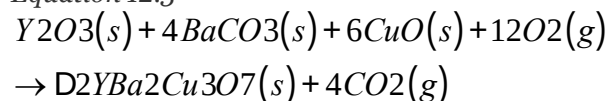
High-Temperature Superconductors

Because of these limitations, scientists continued to search for materials that exhibited superconductivity at temperatures greater than 77 K (the temperature of liquid nitrogen, the least expensive cryogenic fluid). In 1986, Johannes G. Bednorz and Karl A. Müller, working for IBM in Zurich, showed that certain mixed-metal oxides containing La, Ba, and Cu exhibited superconductivity above 30 K. These compounds had been prepared by French workers as potential solid catalysts some years earlier, but their electrical properties had never been examined at low temperatures. Although initially the scientific community was extremely skeptical, the compounds were so easy to prepare that the results were confirmed within a few weeks. These high-temperature superconductors earned Bednorz and Müller the Nobel Prize in Physics in 1987. Subsequent research has produced new compounds with related structures that are

superconducting at temperatures as high as 135 K. The best known of these was discovered by Paul Chu and Maw-Kuen Wu Jr. and is called the “Chu–Wu phase” or the 1-2-3 superconductor.

The formula for the 1-2-3 superconductor is $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, where x is about 0.1 for samples that superconduct at about 95 K. If $x \approx 1.0$, giving a formula of $\text{YBa}_2\text{Cu}_3\text{O}_6$, the material is an electrical insulator. The superconducting phase is thus a nonstoichiometric compound, with a fixed ratio of metal atoms but a variable oxygen content. The overall equation for the synthesis of this material is as follows:

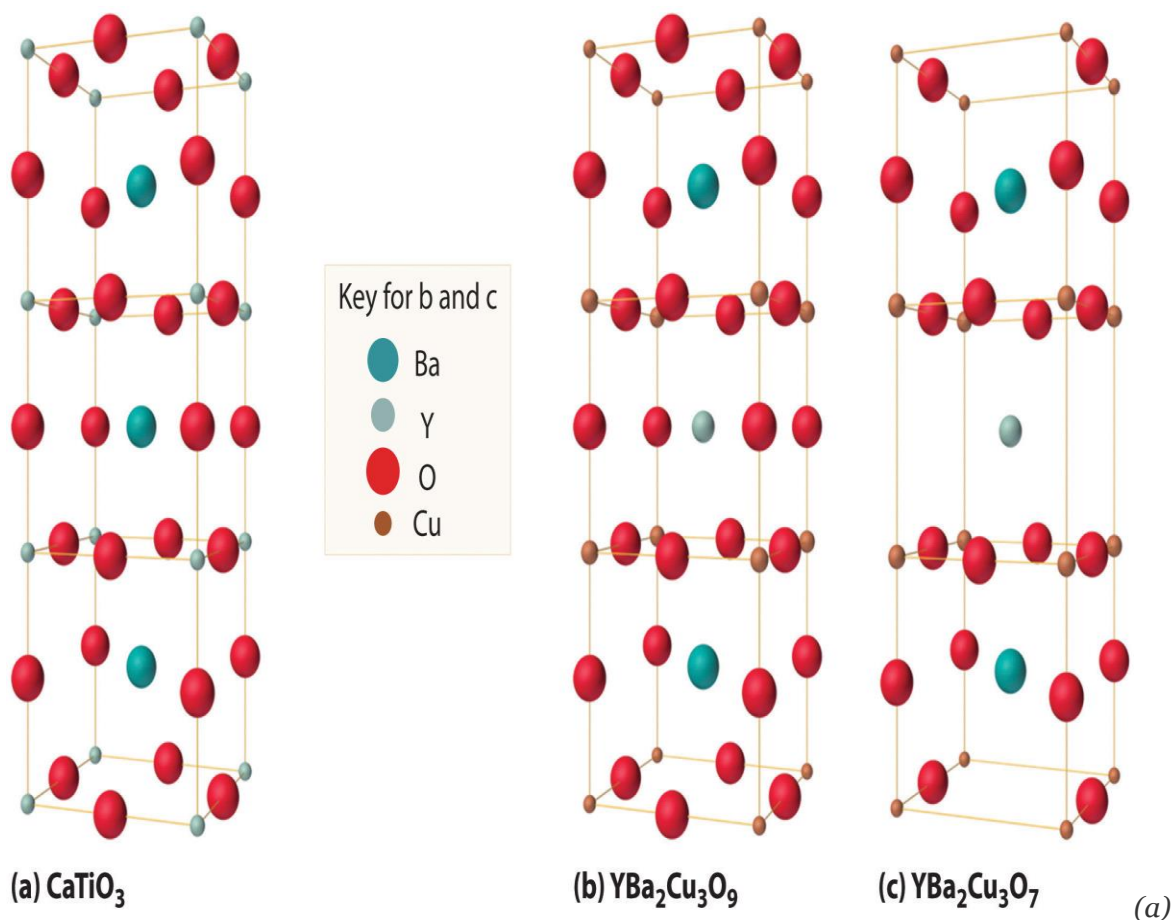
Equation 12.3



If we assume that the superconducting phase is really stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_7$, then the average oxidation states of O, Y, Ba, and Cu are -2 , $+3$, $+2$, and $+7/3$, *respectively*. The simplest way to view the average oxidation state of Cu is to assume that two Cu atoms per formula unit are present as Cu^{2+} and one is present as the rather unusual Cu^{3+} . In $\text{YBa}_2\text{Cu}_3\text{O}_6$, the insulating form, the oxidation state of Cu is $+5/3$, so there are two Cu^{2+} and one Cu^+ per formula unit.

As shown in , the unit cell of the 1-2-3 superconductor is related to the unit cell of the simple perovskite structure (part (b) in). The only difference between the superconducting and insulating forms of the compound is that an O atom has been removed from between the Cu^{3+} ions, which destroys the chains of Cu atoms and leaves the Cu in the center of the unit cell as Cu^+ . The chains of Cu atoms are crucial to the formation of the superconducting state.

Figure 12.30 The Relationship of the Structure of a Superconductor Consisting of Y-Ba-Cu-O to a Simple Perovskite Structure



Stacking three unit cells of the Ca-centered CaTiO_3 perovskite structure (part (b) in) together with (b) replacement of all Ti atoms by Cu, replacement of Ca in the top and bottom cubes by Ba, and replacement of Ca in the central cube by Y gives a $\text{YBa}_2\text{Cu}_3\text{O}_9$ stoichiometry. (c) The removal of two oxygen atoms per unit cell gives the nominal $\text{YBa}_2\text{Cu}_3\text{O}_7$ stoichiometry of the superconducting material.

lists the ideal compositions of some of the known high-temperature superconductors that have been discovered in recent years. Engineers have learned how to process the brittle polycrystalline 1-2-3 and related compounds into wires, tapes, and films that can carry enormous electrical currents. Commercial applications include their use in infrared sensors and in analog signal processing and microwave devices.

Table 12.7 The Composition of Various Superconductors

Compound	T_c (K)
$\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$	13.5
$(\text{La}_{2-x}\text{Sr}_x)\text{CuO}_4$	35

Compound	T_c (K)
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	95
$\text{Bi}_2(\text{Sr}_{2-x}\text{Ca}_x)\text{CuO}_6^*$	80
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}^*$	110
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}^*$	125
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8^*$	133
K_3C_{60}	18
Rb_3C_{60}	30
*Nominal compositions only. Oxygen deficiencies or excesses are common in these compounds.	

EXAMPLE 9

Calculate the average oxidation state of Cu in a sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with $x = 0.5$. How do you expect its structure to differ from those shown in for $\text{YBa}_2\text{Cu}_3\text{O}_9$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$?

Given: stoichiometry

Asked for: average oxidation state and structure

Strategy:

A Based on the oxidation states of the other component atoms, calculate the average oxidation state of Cu that would make an electrically neutral compound.

B Compare the stoichiometry of the structures shown in with the stoichiometry of the given compound to predict how the structures differ.

Solution:

A The net negative charge from oxygen is $(7.0 - 0.5)(-2) = -13$, and the sum of the charges on the Y and Ba atoms is $[1 \times (+3)] + [2 \times (+2)] = +7$. This leaves a net charge of -6 per unit cell, which must be compensated for by the three Cu atoms, for a net charge of $+6/3 = +2$ per Cu.

B The most likely structure would be one in which every other O atom between the Cu atoms in the Cu chains of $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been removed.

Exercise

Calculate the average oxidation state of Cu in a sample of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$. Assume that Hg is present as Hg^{2+} .

Answer: +2

Summary

Superconductors are solids that at low temperatures exhibit zero resistance to the flow of electrical current, a phenomenon known as **superconductivity**. The temperature at which the electrical resistance of a substance drops to zero is its **superconducting transition temperature (T_c)**. Superconductors also expel a magnetic field from their interior, a phenomenon known as the **Meissner effect**. Superconductivity can be explained by the **BCS theory**, which says that electrons are able to travel through a solid with no resistance because they couple to form pairs of electrons (Cooper pairs). **High-temperature superconductors** have T_c values greater than 30 K.

KEY TAKEAWAY

- Superconductivity can be described using the BCS theory, in which Cooper pairs of electrons migrate through the crystal as a unit.

CONCEPTUAL PROBLEMS

1. Why does the BCS theory predict that superconductivity is not possible at temperatures above approximately 30 K?
2. How does the formation of Cooper pairs lead to superconductivity?

ANSWER

1. According to BCS theory, the interactions that lead to formation of Cooper pairs of electrons are so weak that they should be disrupted by thermal vibrations of lattice atoms above about 30 K.

12.8 Polymeric Solids

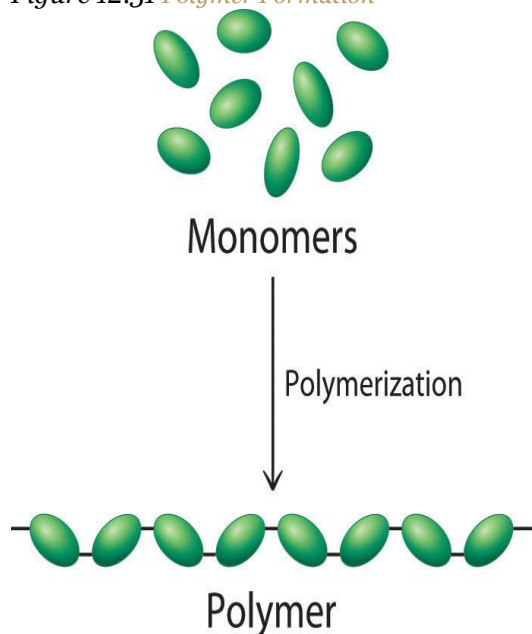
LEARNING OBJECTIVE

1. To understand the differences between synthetic and biological polymers.

Most of the solids discussed so far have been molecules or ions with low molecular masses, ranging from tens to hundreds of atomic mass units. Many of the molecular materials in consumer goods today, however, have very high molecular masses, ranging from thousands to millions of atomic mass units, and are formed from a carefully controlled series of reactions that produce giant molecules called **polymers** (from the Greek *poly* and *meros*, meaning “many parts”). Polymers are used in corrective eye lenses, plastic containers, clothing and textiles, and medical implant devices, among many other uses. They consist of basic structural units called **monomers**, which are repeated many times in each molecule. As shown schematically in **Figure 12.31** “Polymer

Formation", polymerization is the process by which monomers are connected into chains or networks by covalent bonds. Polymers can form via a *condensation reaction*, in which two monomer molecules are joined by a new covalent bond and a small molecule such as water is eliminated, or by an *addition reaction*, a variant of a condensation reaction in which the components of a species AB are added to adjacent atoms of a multiple bond. (For more information about condensation and addition reactions, see Chapter 3 "Chemical Reactions", Section 3.5 "Classifying Chemical Reactions".) Many people confuse the terms *plastics* and *polymers*. Plastic is the property of a material that allows it to be molded into almost any shape. Although many plastics are polymers, many polymers are not plastics. In this section, we introduce the reactions that produce naturally occurring and synthetic polymers.

Figure 12.31 Polymer Formation



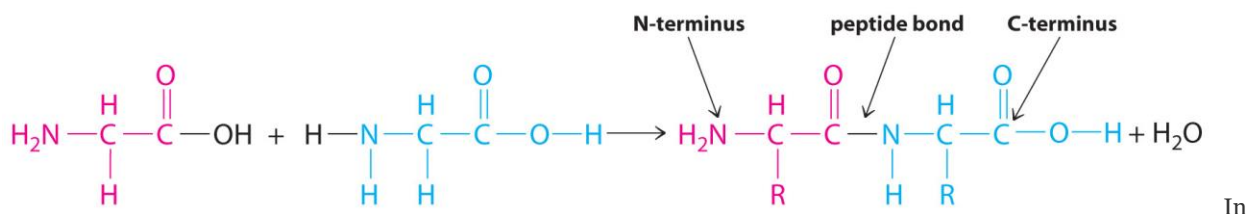
During a polymerization reaction, a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.

Note the Pattern

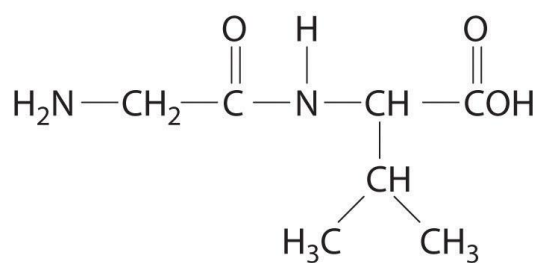
Polymers are formed via condensation or addition reactions.

Naturally Occurring Polymers: Peptides and Proteins

Polymers that occur naturally are crucial components of all organisms and form the fabric of our lives. Hair, silk, skin, feathers, muscle, and connective tissue are all primarily composed of proteins, the most familiar kind of naturally occurring, or biological, polymer. The monomers of many biological polymers are the amino acids introduced in Chapter 5 "Energy Changes in Chemical Reactions", Section 5.4 "Thermochemistry and Nutrition", each called an *amino acid residue*. The residues are linked together by amide bonds, also called peptide bonds, via a condensation reaction where H_2O is eliminated:



the above equation, R represents an alkyl or aryl group, or hydrogen, depending on the amino acid. We write the structural formula of the product with the free amino group on the left (the *N-terminus*) and the free carboxylate group on the right (the *C-terminus*). For example, the structural formula for the product formed from the amino acids glycine and valine (glycyl-valine) is as follows:



Glycyl-valine

The most

important difference between synthetic and naturally occurring polymers is that the former usually contain very few different monomers, whereas biological polymers can have as many as 20 different kinds of amino acid residues arranged in many different orders. Chains with less than about 50 amino acid residues are called peptides, whereas those with more than about 50 amino acid residues are called proteins. Many proteins are enzymes, which are catalysts that increase the rate of a biological reaction.

Note the Pattern

Synthetic polymers usually contain only a few different monomers, whereas biological polymers can have many kinds of monomers, such as amino acids arranged in different orders.

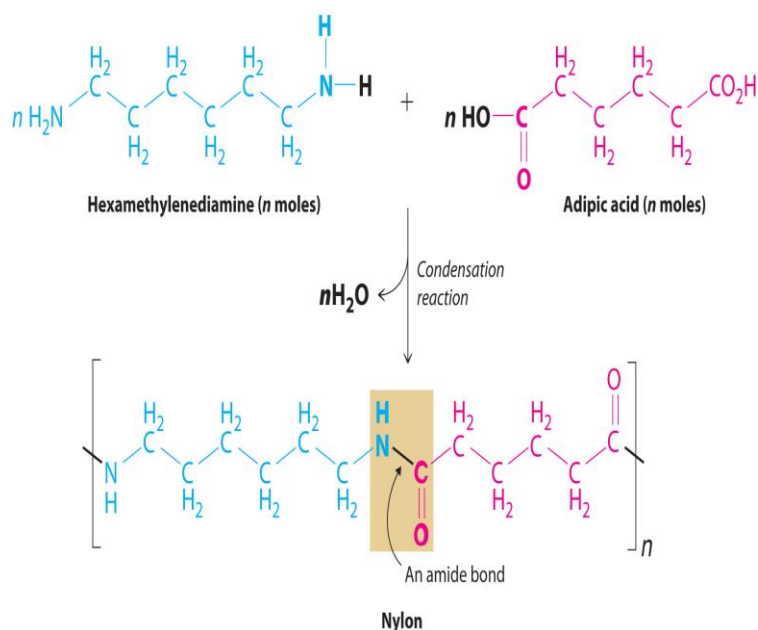
Many small peptides have potent physiological activities. The *endorphins*, for example, are powerful, naturally occurring painkillers found in the brain. Other important peptides are the hormones vasopressin and oxytocin. Although their structures and amino acid sequences are similar, vasopressin is a blood pressure regulator, whereas oxytocin induces labor in pregnant women and milk production in nursing mothers. Oxytocin was the first biologically active peptide to be prepared in the laboratory by Vincent du Vigneaud (1901–1978), who was awarded the Nobel Prize in Chemistry in 1955.

Synthetic Polymers

Many of the synthetic polymers we use, such as plastics and rubbers, have commercial advantages over naturally occurring polymers because they can be produced inexpensively. Moreover, many synthetic polymers are actually more desirable than their natural counterparts because scientists can select monomer units to tailor the physical properties of the resulting polymer for particular purposes. For example, in many applications, wood has been replaced by plastics that are more durable, lighter, and easier to shape and maintain. Polymers are also increasingly used in engineering applications where weight reduction and corrosion resistance are required. Steel rods used to support concrete structures, for example, are often coated with a polymeric material when the structures are near ocean environments where steel is vulnerable to corrosion (For more information on corrosion, see Chapter 19 "Electrochemistry", Section 19.6 "Corrosion".) In fact, the use of polymers in engineering applications is a very active area of research.

Probably the best-known example of a synthetic polymer is *nylon* (Figure 12.32 "The Synthesis of Nylon"). Its monomers are linked by amide bonds (which are called peptide bonds in biological polymers), so its physical properties are similar to those of some proteins because of their common structural unit—the amide group. Nylon is easily drawn into silky fibers that are more than a hundred times longer than they are wide and can be woven into fabrics. Nylon fibers are so light and strong that during World War II, all available nylon was commandeered for use in parachutes, ropes, and other military items. With polymer chains that are fully extended and run parallel to the fiber axis, nylon fibers resist stretching, just like naturally occurring silk fibers, although the structures of nylon and silk are otherwise different. Replacing the flexible $-\text{CH}_2-$ units in nylon by aromatic rings produces a stiffer and stronger polymer, such as the very strong polymer known as Kevlar. Kevlar fibers are so strong and rigid that they are used in lightweight army helmets, bulletproof vests, and even sailboat and canoe hulls, all of which contain multiple layers of Kevlar fabric.

Figure 12.32 The Synthesis of Nylon



Nylon is a synthetic condensation polymer created by the reaction of a dicarboxylic acid and a diamine to form amide bonds and water.

Not all synthetic polymers are linked by amide bonds—for example, *polyesters* contain monomers that are linked by ester bonds. Polyesters are sold under trade names such as Dacron, Kodel, and Fortrel, which are used in clothing, and Mylar, which is used in magnetic tape, helium-filled balloons, and high-tech sails for sailboats. Although the fibers are flexible, properly prepared Mylar films are almost as strong as steel. Polymers based on skeletons with only carbon are all synthetic. Most of these are formed from ethylene ($\text{CH}_2=\text{CH}_2$), a two-carbon building block, and its derivatives. The relative lengths of the chains and any branches control the properties of polyethylene. For example, higher numbers of branches produce a softer, more flexible, lower-melting-point polymer called low-density polyethylene (LDPE), whereas high-density polyethylene (HDPE) contains few branches. Substances such as glass that melt at relatively low temperatures can also be formed into fibers, producing *fiberglass*.

Because most synthetic fibers are neither soluble nor low melting, multistep processes are required to manufacture them and form them into objects. Graphite fibers are formed by heating a precursor polymer at high temperatures to decompose it, a process called pyrolysis. The usual precursor for graphite is polyacrylonitrile, better known by its trade name—Orlon. A similar approach is used to prepare fibers of silicon carbide using an organosilicon precursor such as polydimethylsilane $\{[-(\text{CH}_3)_2\text{Si}-]_n\}$. A new type of fiber consisting of carbon nanotubes, hollow cylinders of carbon just one atom thick, is lightweight,

strong, and impact resistant. Its performance has been compared to that of Kevlar, and it is being considered for use in body armor, flexible solar panels, and bombproof trash bins, among other uses. Because there are no good polymer precursors for elemental boron or boron nitride, these fibers have to be prepared by time-consuming and costly indirect methods. Even though boron fibers are about eight times stronger than metallic aluminum and 10% lighter, they are significantly more expensive. Consequently, unless an application requires boron's greater resistance to oxidation, these fibers cannot compete with less costly graphite fibers.

EXAMPLE 10

Polyethylene is used in a wide variety of products, including beach balls and the hard plastic bottles used to store solutions in a chemistry laboratory. Which of these products is formed from the more highly branched polyethylene?

Given: type of polymer

Asked for: application

Strategy:

Determine whether the polymer is LDPE, which is used in applications that require flexibility, or HDPE, which is used for its strength and rigidity.

Solution:

A highly branched polymer is less dense and less rigid than a relatively unbranched polymer. Thus hard, strong polyethylene objects such as bottles are made of HDPE with relatively few branches. In contrast, a beach ball must be flexible so it can be inflated. It is therefore made of highly branched LDPE.

Exercise

Which products are manufactured from LDPE and which from HDPE?

- a. lawn chair frames
- b. rope
- c. disposable syringes
- d. automobile protective covers

Answer:

- a. HDPE

- b. LDPE
- c. HDPE
- d. LDPE

Summary

Polymers are giant molecules that consist of long chains of units called **monomers** connected by covalent bonds. **Polymerization** is the process of linking monomers together to form a polymer. **Plastic** is the property of a material that allows it to be molded. Biological polymers formed from amino acid residues are called **peptides** or **proteins**, depending on their size. **Enzymes** are proteins that catalyze a biological reaction. A particle that is more than a hundred times longer than it is wide is a **fiber**, which can be formed by a high-temperature decomposition reaction called **pyrolysis**.

KEY TAKEAWAY

- Polymers are giant molecules formed from addition or condensation reactions and can be classified as either biological or synthetic polymers.

CONCEPTUAL PROBLEMS

1. How are amino acids and proteins related to monomers and polymers? Draw the general structure of an amide bond linking two amino acid residues.
2. Although proteins and synthetic polymers (such as nylon) both contain amide bonds, different terms are used to describe the two types of polymer. Compare and contrast the terminology used for the
 - a. smallest repeating unit.
 - b. covalent bond connecting the units.

12.9 Contemporary Materials

LEARNING OBJECTIVE

1. To become familiar with the properties of some contemporary materials.

In addition to polymers, other materials, such as ceramics, high-strength alloys, and composites, play a major role in almost every aspect of our lives. Until relatively recently, steel was used for any application that required an especially strong and durable material, such as bridges, automobiles, airplanes, golf clubs, and tennis rackets. In the last 15 to 20 years, however, graphite or boron fiber golf clubs and tennis rackets have made wood and steel obsolete for these items. Likewise, a modern jet engine now is largely composed of Ti and Ni by weight rather than steel (). The

percentage of iron in wings and fuselages is similarly low, which indicates the extent to which other materials have supplanted steel. The Chevrolet Corvette introduced in 1953 was considered unusual because its body was constructed of fiberglass, a composite material, rather than steel; by 1992, Jaguar fabricated an all-aluminum limited-edition vehicle. In fact, the current models of many automobiles have engines that are made mostly of aluminum rather than steel. In this section, we describe some of the chemistry behind three classes of contemporary materials: ceramics, superalloys, and composites.

Table 12.8 The Approximate Elemental Composition of a Modern Jet Engine

Element	Percentage by Mass
titanium	38
nickel	37
chromium	12
cobalt	6
aluminum	3
niobium	1
tantalum	0.025

Ceramics

A ceramic is any nonmetallic, inorganic solid that is strong enough for use in structural applications. Traditional ceramics, which are based on metal silicates or aluminosilicates, are the materials used to make pottery, china, bricks, and concrete. Modern ceramics contain a much wider range of components and can be classified as either *ceramic oxides*, which are based on metal oxides such as alumina (Al_2O_3), zirconia (ZrO_2), and beryllia (BeO), or *nonoxide ceramics*, which are based on metal carbides such as silicon carbide (carborundum, SiC) and tungsten carbide (WC), or nitrides like silicon nitride (Si_3N_4) and boron nitride (BN).

All modern ceramics are hard, lightweight, and stable at very high temperatures. Unfortunately, however, they are also rather brittle, tending to crack or break under stresses that would cause metals to bend or dent. Thus a major challenge for materials scientists is to take advantage of the desirable properties of ceramics, such as their thermal and oxidative stability, chemical inertness, and toughness, while finding ways to decrease their brittleness to use them in new applications. Few metals can be used in jet engines, for example, because most lose mechanical strength and react with oxygen at the very high operating

temperatures inside the engines (approximately 2000°C). In contrast, ceramic oxides such as Al_2O_3 cannot react with oxygen regardless of the temperature because aluminum is already in its highest possible oxidation state (Al^{3+}). Even nonoxide ceramics such as silicon and boron nitrides and silicon carbide are essentially unreactive in air up to about 1500°C. Producing a high-strength ceramic for service use involves a process called sintering, which fuses the grains into a dense and strong material ().

Effects of sintering magnesium oxide grains: (a) the microstructure before sintering; (b) the microstructure of the ceramic after sintering for two hours at 1250°C; and (c) the microstructure after sintering for two hours at 1450°C. During the sintering process, the grains fuse, forming a dense and strong material.

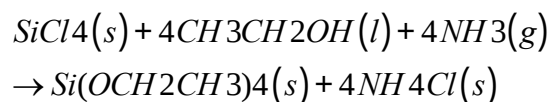
Note the Pattern

Ceramics are hard, lightweight, and able to withstand high temperatures, but they are also brittle.

One of the most widely used raw materials for making ceramics is clay. Clay minerals consist of hydrated alumina (Al_2O_3) and silica (SiO_2) that have a broad range of impurities, including barium, calcium, sodium, potassium, and iron. Although the structures of clay minerals are complicated, they all contain layers of metal atoms linked by oxygen atoms. Water molecules fit between the layers to form a thin film of water. When hydrated, clays can be easily molded, but during high-temperature heat treatment, called *firing*, a dense and strong ceramic is produced.

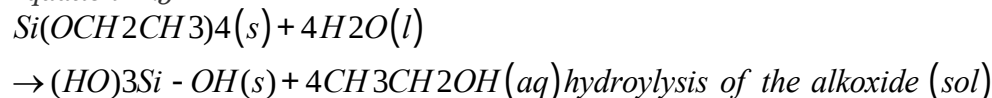
Because ceramics are so hard, they are easily contaminated by the material used to grind them. In fact, the ceramic often grinds the metal surface of the mill almost as fast as the mill grinds the ceramic! The sol-gel process was developed to address this problem. In this process, a water-soluble precursor species, usually a metal or semimetal alkoxide $[\text{M}(\text{OR})_n]$ undergoes a hydrolysis reaction to form a cloudy aqueous dispersion called a *sol*. The sol contains particles of the metal or semimetal hydroxide $[\text{M}(\text{OH})_n]$, which are typically 1–100 nm in diameter. As the reaction proceeds, molecules of water are eliminated from between the $\text{M}(\text{OH})_n$ units in a condensation reaction, and the particles fuse together, producing oxide bridges, $\text{M}-\text{O}-\text{M}$. Eventually, the particles become linked in a three-dimensional network that causes the solution to form a *gel*, similar to a gelatin dessert. Heating the gel to 200°C–500°C causes more water to be eliminated, thus forming small particles of metal oxide that can be amazingly uniform in size. This chemistry starts with highly pure SiCl_4 and proceeds via the following reactions:

Equation 12.4

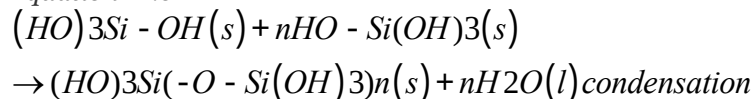


alkoxide formation

Equation 12.5



Equation 12.6



Nature uses the same process to create opal gemstones.

Superalloys

Superalloys are high-strength alloys, often with a complex composition, that are used in systems requiring mechanical strength, high surface stability (minimal flaking or pitting), and resistance to high temperatures. The aerospace industry, for example, requires materials that have high strength-to-weight ratios to improve the fuel efficiency of advanced propulsion systems, and these systems must operate safely at temperatures greater than 1000°C.

Note the Pattern

Superalloys are used in systems requiring mechanical strength, minimal flaking or pitting, and high-temperature resistance.

Although most superalloys are based on nickel, cobalt, or iron, other metals are used as well. Pure nickel or cobalt is relatively easily oxidized, but adding small amounts of other metals (Al, Co, Cr, Mo, Nb, Ti, and W) results in an alloy that has superior properties. Consequently, most of the internal parts of modern gas turbine jet engines are now made of superalloys based on either nickel (used in blades and disks) or cobalt (used in vanes, combustion chamber liners, and afterburners). The cobalt-based superalloys are not as strong as the nickel-based ones, but they have excellent corrosion resistance at high temperatures.

Other alloys, such as aluminum–lithium and alloys based on titanium, also have applications in the aerospace industry. Because aluminum–lithium alloys are lighter, stiffer, and more resistant to fatigue at high temperatures than aluminum itself, they are used in engine parts and in the metal “skins” that cover wings and bodies. Titanium’s high strength, corrosion resistance, and lightweight properties are equally

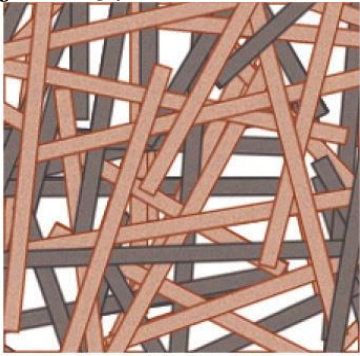
desirable for applications where minimizing weight is important (as in airplanes). Unfortunately, however, metallic titanium reacts rapidly with air at high temperatures to form TiN and TiO_2 . The welding of titanium or any similar processes must therefore be carried out in an argon or inert gas atmosphere, which adds significantly to the cost. Initially, titanium and its alloys were primarily used in military applications, but more recently, they have been used as components of the airframes of commercial planes, in ship structures, and in biological implants.

Composite Materials

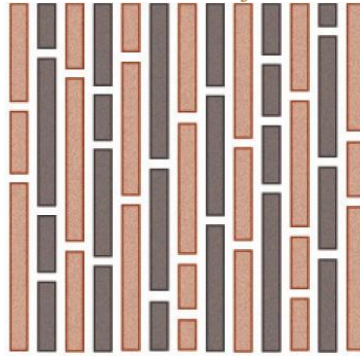
Composite materials have at least two distinct components: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix and limit the growth of cracks by pinning defects in the bulk material (). The resulting material is stronger, tougher, stiffer, and more resistant to corrosion than either component alone. Composites are thus the nanometer-scale equivalent of reinforced concrete, in which steel rods greatly increase the mechanical strength of the cement matrix, and are extensively used in the aircraft industry, among others. For example, the Boeing 777 is 9% composites by weight, whereas the newly developed Boeing 787 is 50% composites by weight. Not only does the use of composite materials reduce the weight of the aircraft, and therefore its fuel consumption, but it also allows new design concepts because composites can be molded. Moreover, by using composites in the Boeing 787 multiple functions can be integrated into a single system, such as acoustic damping, thermal regulation, and the electrical system.

Three distinct types of composite material are generally recognized, distinguished by the nature of the matrix. These are polymer-matrix composites, metal-matrix composites, and ceramic-matrix composites.

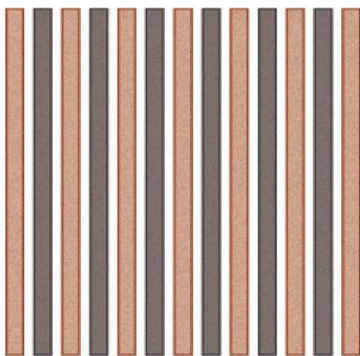
Figure 12.34 Some Possible Arrangements of Fibers in Fiber-Reinforced Composite Materials



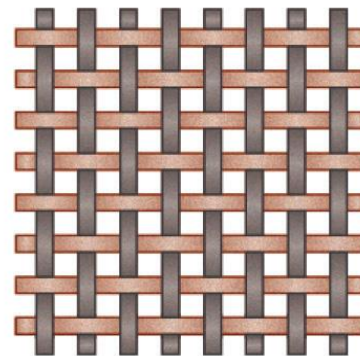
Discontinuous and randomly oriented



Discontinuous and aligned



Continuous and aligned



Fabric

The arrangements shown range from discontinuous and randomly oriented to continuous and aligned. The fibers limit the growth of cracks by pinning defects within the matrix.

Note the Pattern

Composites are stronger, tougher, stiffer, and more resistant to corrosion than their components alone.

Fiberglass is a polymer-matrix composite that consists of glass fibers embedded in a polymer, forming tapes that are then arranged in layers impregnated with epoxy. The result is a strong, stiff, lightweight material that is resistant to chemical degradation. It is not strong enough, however, to resist cracking or puncturing on impact. Stronger, stiffer polymer-matrix composites contain fibers of carbon (graphite), boron, or polyamides such as Kevlar. High-tech tennis rackets and golf clubs as well as the skins of modern military aircraft such as the “stealth” F-117A fighters and B-2 bombers are made from both

carbon fiber–epoxy and boron fiber–epoxy composites. Compared with metals, these materials are 25%–50% lighter and thus reduce operating costs. Similarly, the space shuttle payload bay doors and panels are made of a carbon fiber–epoxy composite. The structure of the Boeing 787 has been described as essentially one giant macromolecule, where everything is fastened through cross-linked chemical bonds reinforced with carbon fiber.

Metal-matrix composites consist of metals or metal alloys reinforced with fibers. They offer significant advantages for high-temperature applications but pose major manufacturing challenges. For example, obtaining a uniform distribution and alignment of the reinforcing fibers can be difficult, and because organic polymers cannot survive the high temperatures of molten metals, only fibers composed of boron, carbon, or ceramic (such as silicon carbide) can be used. Aluminum alloys reinforced with boron fibers are used in the aerospace industry, where their strength and lightweight properties make up for their relatively high cost. The skins of hypersonic aircraft and structural units in the space shuttle are made of metal-matrix composites.

Ceramic-matrix composites contain ceramic fibers in a ceramic matrix material. A typical example is alumina reinforced with silicon carbide fibers. Combining the two very high-melting-point materials results in a composite that has excellent thermal stability, great strength, and corrosion resistance, while the SiC fibers reduce brittleness and cracking. Consequently, these materials are used in very high-temperature applications, such as the leading edge of wings of hypersonic airplanes and jet engine parts. They are also used in the protective ceramic tiles on the space shuttle, which contain short fibers of pure SiO_2 mixed with fibers of an aluminum–boron–silicate ceramic. These tiles are excellent thermal insulators and extremely light (their density is only about 0.2 g/cm^3). Although their surface reaches a temperature of about 1250°C during reentry into Earth’s atmosphere, the temperature of the underlying aluminum alloy skin stays below 200°C .

EXAMPLE 11

An engineer is tasked with designing a jet ski hull. What material is most suited to this application? Why?

Given: design objective

Asked for: most suitable material

Strategy:

Determine under what conditions the design will be used. Then decide what type of material is most appropriate.

Solution:

A jet ski hull must be lightweight to maximize speed and fuel efficiency. Because of its use in a marine environment, it must also be resistant to impact and corrosion. A ceramic material provides rigidity but is brittle and therefore tends to break or crack under stress, such as when it impacts waves at high speeds. Superalloys provide strength and stability, but a superalloy is probably too heavy for this application. Depending on the selection of metals, it might not be resistant to corrosion in a marine environment either. Composite materials, however, provide strength, stiffness, and corrosion resistance; they are also lightweight materials. This is not a high-temperature application, so we do not need a metal-matrix composite or a ceramic-matrix composite. The best choice of material is a polymer-matrix composite with Kevlar fibers to increase the strength of the composite on impact.

Exercise

In designing a new generation of space shuttle, National Aeronautics and Space Administration (NASA) engineers are considering thermal-protection devices to protect the skin of the craft. Among the materials being considered are titanium- or nickel-based alloys and silicon-carbide ceramic reinforced with carbon fibers. Why are these materials suitable for this application?

Answer: Ti- or Ni-based alloys have a high strength-to-weight ratio, resist corrosion, and are safe at high temperatures. Reinforced ceramic is lightweight; has high thermal and oxidative stability; and is chemically inert, tough, and impact resistant.

Summary

Ceramics are nonmetallic, inorganic solids that are typically strong; they have high melting points but are brittle. The two major classes of modern ceramics are ceramic oxides and nonoxide ceramics, which are composed of nonmetal carbides or nitrides. The production of ceramics generally involves pressing a powder of the material into the desired shape and sintering at a temperature just below its melting point. The necessary fine powders of ceramic oxides with uniformly sized particles can be produced by the **sol-gel process**. **Superalloys** are new metal phases based on cobalt, nickel, or iron that exhibit unusually high temperature stability and resistance to oxidation. **Composite materials** consist of at least two

phases: a matrix that constitutes the bulk of the material and fibers or granules that act as a reinforcement. **Polymer-matrix composites** have reinforcing fibers embedded in a polymer matrix. **Metal-matrix composites** have a metal matrix and fibers of boron, graphite, or ceramic. **Ceramic-matrix composites** use reinforcing fibers, usually also ceramic, to make the matrix phase less brittle.

KEY TAKEAWAY

- Materials that have contemporary applications include ceramics, high-strength alloys, and composites, whose properties can be modified as needed.

CONCEPTUAL PROBLEMS

- Can a compound based on titanium oxide qualify as a ceramic material? Explain your answer.
- What features make ceramic materials attractive for use under extreme conditions? What are some potential drawbacks of ceramics?
- How do composite materials differ from the other classes of materials discussed in this chapter? What advantages do composites have versus other materials?
- How does the matrix control the properties of a composite material? What is the role of an additive in determining the properties of a composite material?

12.10 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

- ♦ Cadmium selenide (CdSe) is a semiconductor used in photoconductors and photoelectric cells that conduct electricity when illuminated. In a related process, a CdSe crystal can absorb enough energy to excite electrons from the valence band to the conduction band, and the excited electrons can return to the valence band by emitting light. The relative intensity and peak wavelength of the emitted light in one experiment are shown in the following table:

Relative Intensity (%)	Wavelength (nm)	Temperature (°C)
100	720	23
50	725	45
10	730	75

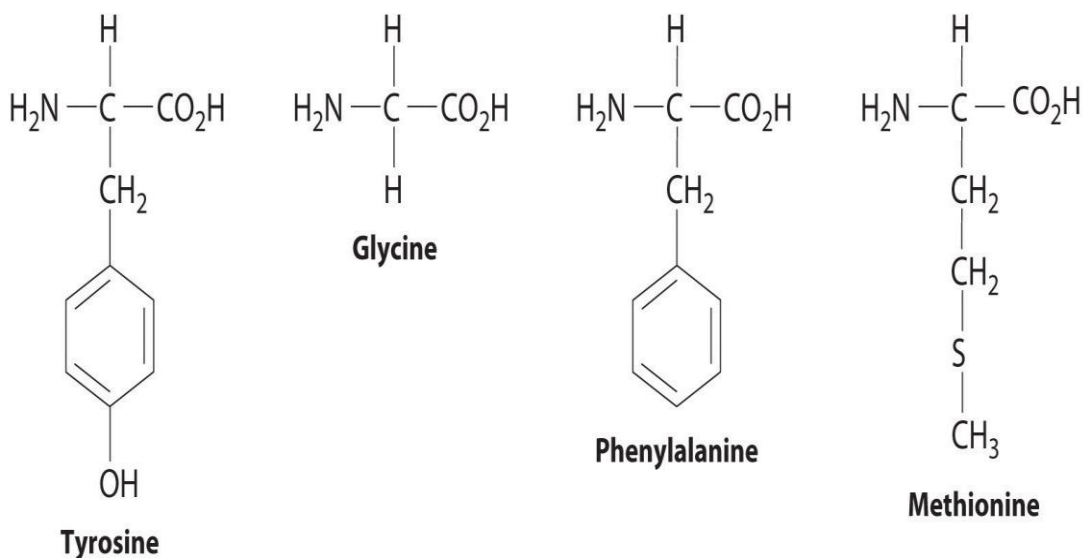
- a. Explain why the emitted light shifts to longer wavelength at higher temperatures. (Hint: consider the expansion of the crystal and the resulting changes in orbital interactions when heated.)
- b. Why does the relative intensity of the emitted light decrease as the temperature increases?
2. A large fraction of electrical energy is currently lost as heat during transmission due to the electrical resistance of transmission wires. How could superconducting technology improve the transmission of electrical power? What are some potential drawbacks of this technology?
3. Light-emitting diodes (LEDs) are semiconductor-based devices that are used in consumer electronics products ranging from digital clocks to fiber-optic telephone transmission lines. The color of the emitted light is determined in part by the band gap of the semiconductor. Electrons can be promoted to the conduction band and return to the valence band by emitting light or by increasing the magnitude of atomic vibrations in the crystal, which increases its temperature. If you wanted to increase the efficiency of an LED display, and thereby the intensity of the emitted light, would you increase or decrease the operating temperature of the LED? Explain your answer.
4. ♦ Strips of pure Au and Al are often used in close proximity to each other on circuit boards. As the boards become warm during use, however, the metals can diffuse, forming a purple alloy known as “the purple plague” between the strips. Because the alloy is electrically conductive, the board short-circuits. A structural analysis of the purple alloy showed that its structure contained a face-centered cubic (fcc) lattice of atoms of one element, with atoms of the other element occupying tetrahedral holes. What type of alloy is this? Which element is most likely to form the fcc lattice? Which element is most likely to occupy the tetrahedral holes? Explain your answers. What is the empirical formula of the “purple plague”?
5. ♦ Glasses are mixtures of oxides, the main component of which is silica (SiO_2). Silica is called the *glass former*, while additives are referred to as *glass modifiers*. The crystalline lattice of the glass former breaks down during heating, producing the random atomic arrangements typical of a liquid. Adding a modifier and cooling the melt rapidly produces a glass. How does the three-dimensional structure of the glass differ from that of the crystalline glass former? Would you expect the melting point of a glass to be higher or lower than that of pure SiO_2 ? Lead glass, a particular favorite of the Romans, was formed by adding lead oxide as the modifier.

Would you expect lead glass to be more or less dense than soda-lime glass formed by adding sodium and potassium salts as modifiers?

6. Many glasses eventually crystallize, rendering them brittle and opaque. Modifying agents such as TiO_2 are frequently added to molten glass to reduce their tendency to crystallize. Why does the addition of small amounts of TiO_2 stabilize the amorphous structure of glass?
7. ♦ The carbon–carbon bond distances in polyacetylene $(-\text{CH}=\text{CH}-)_n$ alternate between short and long, resulting in the following band structure:



- a. polyacetylene a metal, a semiconductor, or an insulator?
- b. Based on its band structure, how would treating polyacetylene with a potent oxidant affect its electrical conductivity? What would be the effect of treating polyacetylene with small amounts of a powerful reductant? Explain your answers.
- c. Enkephalins are pentapeptides, short biopolymers that are synthesized by humans to control pain. Enkephalins bind to certain receptors in brain cells, which are also known to bind morphine and heroin. One enkephalin has the structure tyrosine–glycine–glycine–phenylalanine–methionine. Draw its structure.



9. A

polymerization reaction is used to synthesize Saran, a flexible material used in packaging film and seat covers. The monomeric unit for Saran is 1,1-dichloroethylene ($\text{CH}_2=\text{CCl}_2$), also known as vinylidene chloride. Draw a reasonable structure for the polymer. Why do pieces of Saran “cling” to one another when they are brought in contact?

8. Polymers are often amorphous solids. Like other materials, polymers can also undergo phase changes. For example, many polymers are flexible above a certain temperature, called the *glass-transition temperature* (T_g). Below the glass transition temperature, the polymer becomes hard and brittle. Biomedical devices that replace or augment parts of the human body often contain a wide variety of materials whose properties must be carefully controlled.
 - a. Polydimethylsiloxane has a T_g of -123°C , whereas poly(methylmethacrylate) has a T_g of 105°C . Which of these polymers is likely to be used in dentures, and which is likely to be used for soft-tissue replacement?
 - b. If you were designing biomedical devices, which class of biomaterials (alloys, ceramics, or polymers) would you consider for finger joint replacements, eyeball replacements, windpipe replacements, shoulder joint replacements, and bridging bone fractures? Explain your answers.

Chapter 13

Solutions

We explored the general properties of gases, liquids, and solids in Chapter 10 "Gases", Chapter 11 "Liquids", and Chapter 12 "Solids", respectively. Most of the discussion focused on pure substances containing a single kind of atom, molecule, or cation–anion pair. The substances we encounter in our daily lives, however, are usually mixtures rather than pure substances. Some are *heterogeneous mixtures*, which consist of at least two phases that are not uniformly dispersed on a microscopic scale; others are *homogeneous mixtures*, consisting of a single phase in which the components are uniformly distributed. (For more information about homogeneous mixtures, see Chapter 1 "Introduction to Chemistry", Section 1.3 "A Description of Matter".) Homogeneous mixtures are also called solutions; they include the air we breathe, the gas we use to cook and heat our homes, the water we drink, the gasoline or diesel fuel that powers engines, and the gold and silver jewelry we wear.

Beads of oil in water. When a nonpolar liquid such as oil is dispersed in a polar solvent such as water, it does not dissolve, but forms spherical beads. Oil is insoluble in water because the intermolecular interactions ***within*** the solute (oil) and the solvent (water) are stronger than the intermolecular interactions ***between*** the solute and the solvent.

Many of the concepts that we will use in our discussion of solutions were introduced in earlier chapters. In Chapter 4 "Reactions in Aqueous Solution", for example, we described reactions that occur in aqueous solution and how to use *molarity* to describe concentrations. In Chapter 4 "Reactions in Aqueous Solution", Chapter 7 "The Periodic Table and Periodic Trends", and Chapter 11 "Liquids", we introduced the principles that govern ion–ion and molecule–molecule interactions in pure substances; similar interactions also occur in solutions. Now we use the principles developed in those chapters to understand the factors that determine how much of one substance can dissolve in another, and how the properties of a solution differ from those of its components.

The properties of mixtures of gases were described in Chapter 10 "Gases", and the properties of certain types of solid solutions, such as alloys and doped semiconductors, were discussed in Chapter 12 "Solids". This chapter focuses on liquid solutions, aqueous or otherwise. By the end of this chapter, your understanding of solutions will enable you to explain why the radiator in your car must contain ethylene glycol to avoid damage to the engine on cold winter nights, why salt is spread on icy roads in the winter (and why it isn't effective when the temperature is too low), why certain vitamins accumulate in your body at toxic levels while others are rapidly excreted, and how salt can be removed from seawater to provide drinking water.

13.1 Factors Affecting Solution Formation

LEARNING OBJECTIVE

1. To understand how enthalpy and entropy changes affect solution formation.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the *solvent*, and the substance or substances present in lesser amounts are the *solute(s)*. The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be *soluble* in the solvent. lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

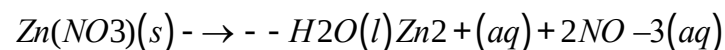
Table 13.1 Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO ₂ gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H ₂ in Pd (used for H ₂ storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

Equation 13.1



Because Zn(NO₃)₂ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc *appears* to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

Equation 13.2



Note the Pattern

Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is *soluble* in aqueous hydrochloric acid because it is chemically transformed when it dissolves. *The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

Substances that form a single homogeneous phase in all proportions are said to be completely miscible in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere (see) and natural gas (see).

The Role of Enthalpy in Solution Formation

As we saw in –, energy is required to overcome the intermolecular interactions in a solute. This energy can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation, or hydration when the solvent is water. Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use the same type of thermochemical cycle described in to analyze the energetics of solution formation. (For more information about state functions, see , .) The process occurs in three discrete steps, indicated by ΔH_1 , ΔH_2 , and ΔH_3 in . The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

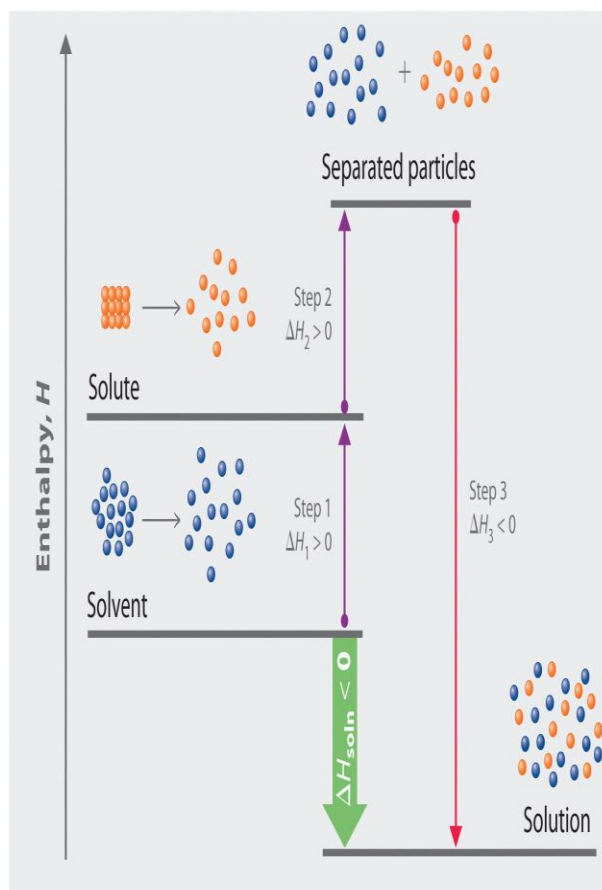
Equation 13.3

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

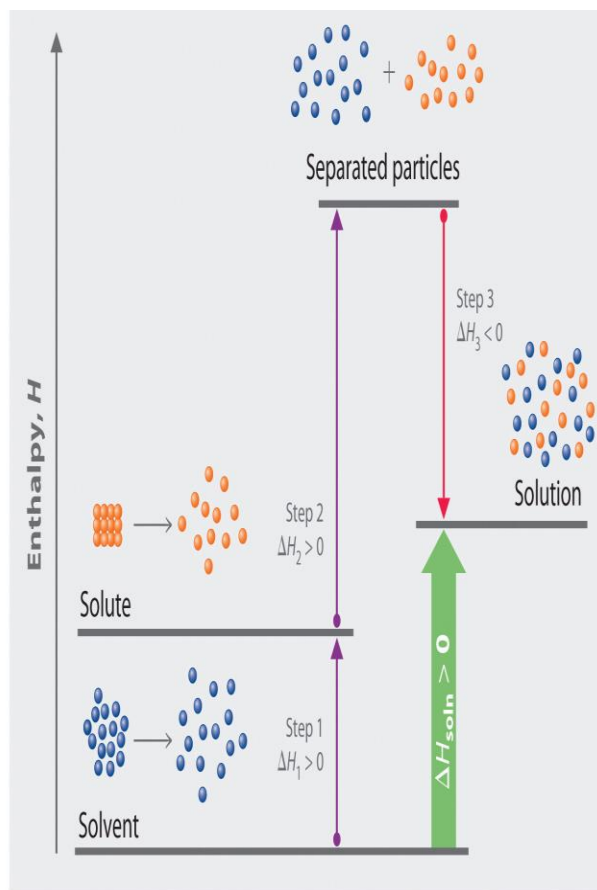
When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{\text{soln}} < 0$).

When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. As you learned in , the higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (–3791 kJ/mol), are generally insoluble in all solvents.

Figure 13.1 Enthalpy Changes That Accompany the Formation of a Solution



(a) Exothermic solution formation



(b) Endothermic solution formation

Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2 , the overall process is exothermic ($\Delta H_{\text{soln}} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2 , the overall process is endothermic ($\Delta H_{\text{soln}} > 0$).

As you will see in , a positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the *total* energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for

example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C ().

Cold Compresses: These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its *entropy*, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detail in , but for now we can state that entropy(*S*) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, is arbitrarily assigned an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and *n*-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the *n*-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. *All spontaneous processes with $\Delta H \geq 0$ are characterized by an increase in entropy.* In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

Note the Pattern

All spontaneous processes with $\Delta H \geq 0$ are characterized by an increase in entropy.

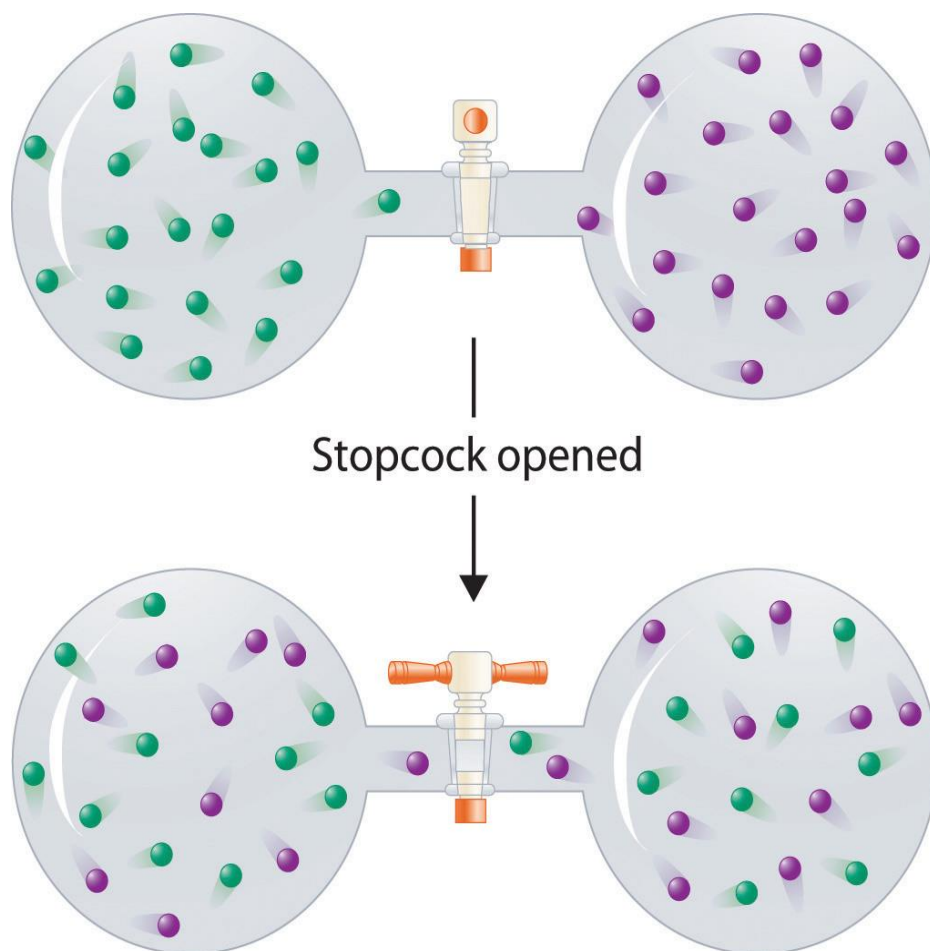
summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

Table 13.2 Relative Changes in Enthalpies for Different Solute–Solvent Combinations*

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	$\Delta H_{\text{soln}}(\Delta H_1 + \Delta H_2 + \Delta H_3)$	Result of Mixing Solute and Solvent†
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form
* ΔH_1 , ΔH_2 , and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in .				
†In all four cases, entropy increases.				

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{\text{soln}} \approx 0$), and the entropic factor due to the increase in disorder is dominant (). Consequently, all gases dissolve readily in one another in all proportions to form solutions. We will return to a discussion of enthalpy and entropy in, where we treat their relationship quantitatively.

Figure 13.3 Formation of a Solution of Two Gases



(top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

EXAMPLE 1

Considering LiCl, benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$), and naphthalene, which will be most soluble and which will be least soluble in water?

Given: three compounds

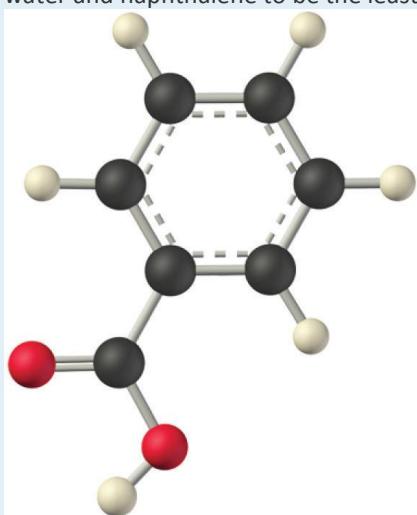
Asked for: relative solubilities in water

Strategy:

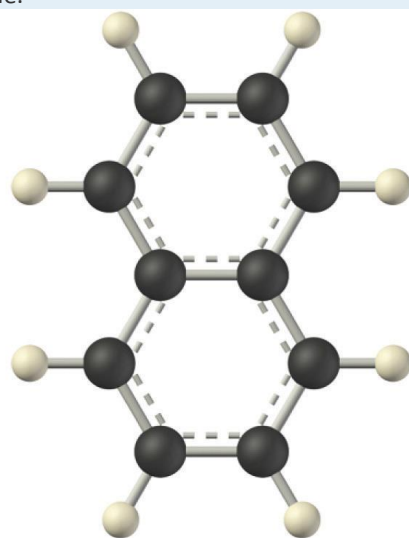
Assess the relative magnitude of the enthalpy change for each step in the process shown in . Then use to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

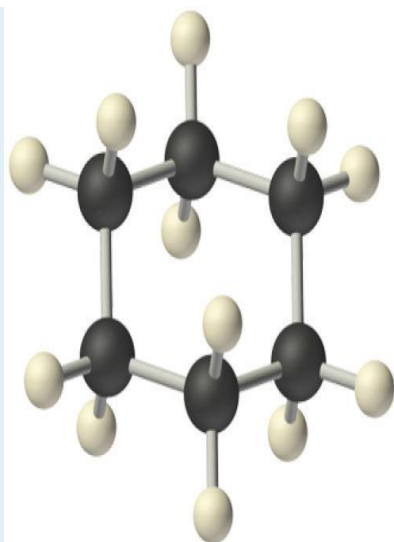
The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.



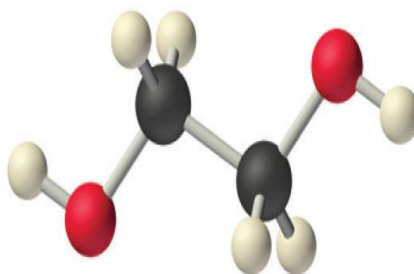
Benzoic acid



Naphthalene



Cyclohexane



Ethylene glycol

Exercise

Considering ammonium chloride, cyclohexane, and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), which will be most soluble and which will be least soluble in benzene?

Answer: The most soluble is cyclohexane; the least soluble is ammonium chloride.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the *solvent*, and the components present in lesser amounts are the *solute(s)*. The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are **miscible**, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are **immiscible**. **Solvation** is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called **hydration**. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln} , is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{\text{soln}} < 0$) processes favor solution formation. In addition, the change in **entropy**, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

KEY TAKEAWAY

- The magnitude of the changes in both enthalpy and entropy must be considered when predicting whether a given solute–solvent combination will spontaneously form a solution.

CONCEPTUAL PROBLEMS

1. Classify each of the following as a heterogeneous mixture or homogeneous mixture. Explain your rationale in each case.
 - a. aqueous ammonia
 - b. liquid decongestant
 - c. vinegar
 - d. seawater
 - e. gasoline
 - f. fog
2. Solutions and heterogeneous mixtures are at the extreme ends of the solubility scale. Name one type of mixture that is intermediate on this scale. How are the properties of the mixture you have chosen different from those of a solution or a heterogeneous mixture?
3. Classify each process as simple dissolution or a chemical reaction.
 - a. a naphthalene mothball dissolving in benzene
 - b. a sample of a common drain cleaner that has a mixture of NaOH crystals and Al chunks dissolving in water to give H₂ gas and an aqueous solution of Na⁺, OH[−], and Al³⁺ ions
 - c. an iron ship anchor slowly dissolving in seawater
 - d. sodium metal dissolving in liquid ammonia
4. Classify each process as simple dissolution or a chemical reaction.
 - a. a sugar cube dissolving in a cup of hot tea
 - b. SO₃ gas dissolving in water to produce sulfuric acid
 - c. calcium oxide dissolving in water to produce a basic solution
 - d. metallic gold dissolving in a small quantity of liquid mercury
5. You notice that a gas is evolved as you are dissolving a solid in a liquid. Will you be able to recover your original solid by evaporation? Why or why not?

6. Why is heat evolved when sodium hydroxide pellets are dissolved in water? Does this process correspond to simple dissolution or a chemical reaction? Justify your answer.
7. Which process(es) is the simple formation of a solution, and which process(es) involves a chemical reaction?
 - a. mixing an aqueous solution of NaOH with an aqueous solution of HCl
 - b. bubbling HCl gas through water
 - c. adding iodine crystals to CCl₄
 - d. adding sodium metal to ethanol to produce sodium ethoxide (C₂H₅O⁻Na⁺) and hydrogen gas
8. Using thermochemical arguments, explain why some substances that do not form a solution at room temperature will form a solution when heated. Explain why a solution can form even when ΔH_{soln} is positive.
9. If you wanted to formulate a new compound that could be used in an instant cold pack, would you select a compound with a positive or negative value of ΔH_{soln} in water? Justify your answer.
10. Why is entropy the dominant factor in the formation of solutions of two or more gases? Is it possible for two gases to be immiscible? Why or why not?

ANSWERS

1. Homogeneous mixtures: aqueous ammonia, liquid decongestant, vinegar, and gasoline. Heterogeneous mixtures: seawater and fog.
- 2.
- 3.
- 4.
- 5.
- 6.
7. All are chemical reactions except dissolving iodine crystals in CCl₄.

13.2 Solubility and Molecular Structure

LEARNING OBJECTIVE

1. To understand the relationship between solubility and molecular structure.

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (part (a) in). This is not, however, a unidirectional process. If

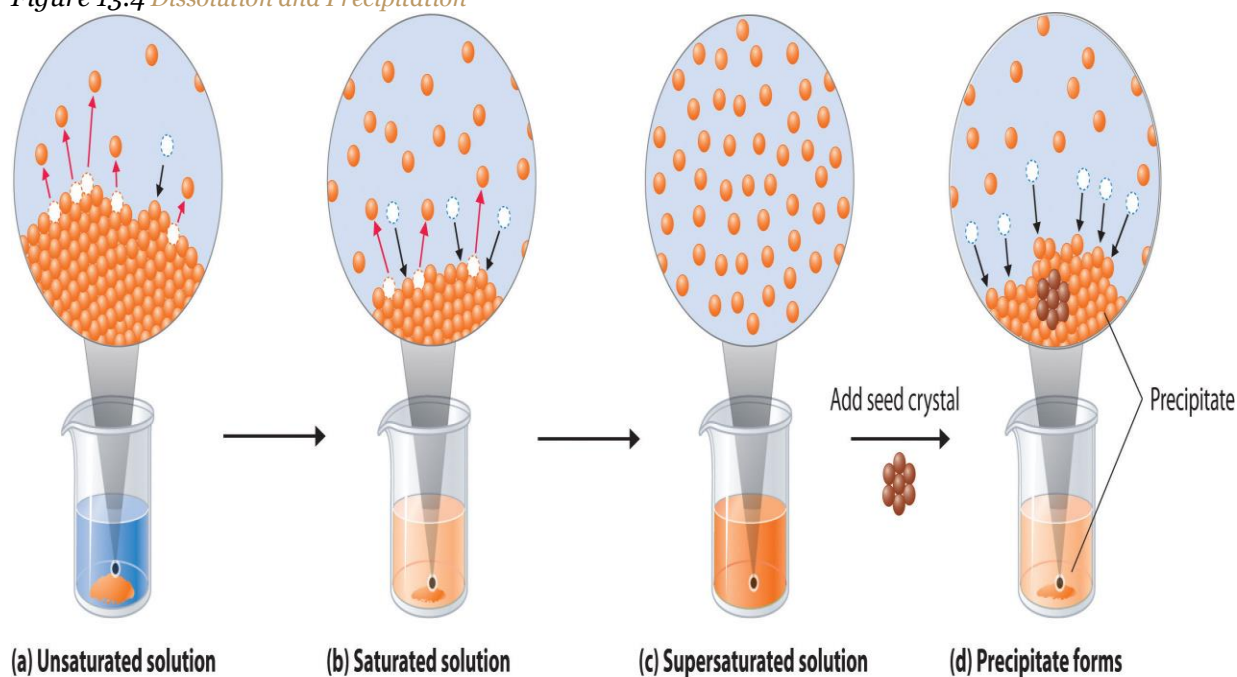
the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called *crystallization*. Dissolution and crystallization continue as long as excess solid is present, resulting in a *dynamic equilibrium* analogous to the equilibrium that maintains the vapor pressure of a liquid. (For more information about vapor pressure, see , .) We can represent these opposing processes as follows:

Equation 13.4



Although the terms *precipitation* and *crystallization* are both used to describe the separation of solid solute from a solution, *crystallization* refers to the formation of a solid with a well-defined crystalline structure, whereas *precipitation* refers to the formation of any solid phase, often one with very small particles.

Figure 13.4 *Dissolution and Precipitation*



(a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

Factors Affecting Solubility

The maximum amount of a solute that can dissolve in a solvent at a specified temperature and pressure is its solubility. Solubility is often expressed as the mass of solute per volume (g/L) or mass of solute per mass of solvent (g/g), or as the moles of solute per volume (mol/L). Even for very soluble substances, however, there is usually a limit to how much solute can dissolve in a given quantity of solvent. In general, the solubility of a substance depends on not only the energetic factors we have discussed but also the temperature and, for gases, the pressure. At 20°C, for example, 177 g of NaI, 91.2 g of NaBr, 35.9 g of NaCl, and only 4.1 g of NaF dissolve in 100 g of water. At 70°C, however, the solubilities increase to 295 g of NaI, 119 g of NaBr, 37.5 g of NaCl, and 4.8 g of NaF. As you learned in , the lattice energies of the

sodium halides increase from NaI to NaF. The fact that the solubilities decrease as the lattice energy increases suggests that the ΔH_2 term dominates for this series of compounds.

A solution with the maximum possible amount of solute is saturated. If a solution contains less than the maximum amount of solute, it is *unsaturated*. When a solution is saturated and excess solute is present, the rate of dissolution is exactly equal to the rate of crystallization (part (b) in). Using the value just stated, a saturated aqueous solution of NaCl, for example, contains 35.9 g of NaCl per 100 mL of water at 20°C. We can prepare a homogeneous saturated solution by adding excess solute (in this case, greater than 35.9 g of NaCl) to the solvent (water), stirring until the maximum possible amount of solute has dissolved, and then removing undissolved solute by filtration.

Note the Pattern

The solubility of most solids increases with increasing temperature.

Because the solubility of most solids increases with increasing temperature, a saturated solution that was prepared at a higher temperature usually contains more dissolved solute than it would contain at a lower temperature. When the solution is cooled, it can therefore become supersaturated (part (c) in). Like a supercooled or superheated liquid (see), a supersaturated solution is unstable. Consequently, adding a small particle of the solute, a seed crystal, will usually cause the excess solute to rapidly precipitate or crystallize, sometimes with spectacular results, as was shown in . The rate of crystallization in is greater than the rate of dissolution, so crystals or a precipitate form (part (d) in). In contrast, adding a seed crystal to a saturated solution reestablishes the dynamic equilibrium, and the *net* quantity of dissolved solute no longer changes.

Because crystallization is the reverse of dissolution, a substance that requires an input of heat to form a solution ($\Delta H_{\text{soln}} > 0$) releases that heat when it crystallizes from solution ($\Delta H_{\text{crys}} < 0$). The amount of heat released is proportional to the amount of solute that exceeds its solubility. Two substances that have a positive enthalpy of solution are sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$), both of which are used in commercial hot packs, small bags of supersaturated solutions used to warm hands (see).

Interactions in Liquid Solutions

The interactions that determine the solubility of a substance in a liquid depend largely on the chemical nature of the solute (such as whether it is ionic or molecular) rather than on its physical state (solid,

liquid, or gas). We will first describe the general case of forming a solution of a molecular species in a liquid solvent and then describe the formation of a solution of an ionic compound.

Solutions of Molecular Substances in Liquids

The London dispersion forces, dipole–dipole interactions, and hydrogen bonds that hold molecules to other molecules are generally weak. Even so, energy is required to disrupt these interactions. As we described in , unless some of that energy is recovered in the formation of new, favorable solute–solvent interactions, the increase in entropy on solution formation is not enough for a solution to form.

For solutions of gases in liquids, we can safely ignore the energy required to separate the solute molecules ($\Delta H_2 = 0$) because the molecules are already separated. Thus we need to consider only the energy required to separate the solvent molecules (ΔH_1) and the energy released by new solute–solvent interactions (ΔH_3).

Nonpolar gases such as N_2 , O_2 , and Ar have no dipole moment and cannot engage in dipole–dipole interactions or hydrogen bonding. Consequently, the only way they can interact with a solvent is by means of London dispersion forces, which may be weaker than the solvent–solvent interactions in a polar solvent. It is not surprising, then, that nonpolar gases are most soluble in nonpolar solvents. In this case, ΔH_1 and ΔH_3 are both small and of similar magnitude. In contrast, for a solution of a nonpolar gas in a polar solvent, ΔH_1 is far greater than ΔH_3 . As a result, nonpolar gases are less soluble in polar solvents than in nonpolar solvents. For example, the concentration of N_2 in a saturated solution of N_2 in water, a polar solvent, is only 7.07×10^{-4} M compared with 4.5×10^{-3} M for a saturated solution of N_2 in benzene, a nonpolar solvent.

The solubilities of nonpolar gases in water generally increase as the molecular mass of the gas increases, as shown in . This is precisely the trend expected: as the gas molecules become larger, the strength of the solvent–solute interactions due to London dispersion forces increases, approaching the strength of the solvent–solvent interactions.

Table 13.3 Solubilities of Selected Gases in Water at 20°C and 1 atm Pressure

Gas	Solubility (M) $\times 10^{-4}$
He	3.90
Ne	4.65
Ar	15.2
Kr	27.9

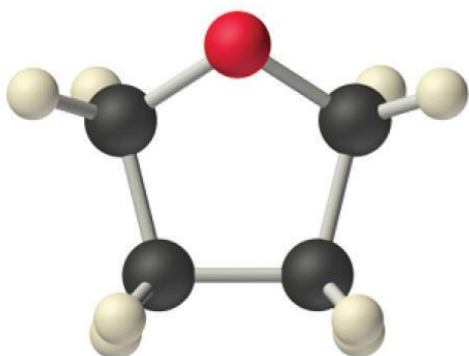
Gas	Solubility (M) $\times 10^{-4}$
Xe	50.2
H ₂	8.06
N ₂	7.07
CO	10.6
O ₂	13.9
N ₂ O	281
CH ₄	15.5

Virtually all common organic liquids, whether polar or not, are miscible. The strengths of the intermolecular attractions are comparable; thus the enthalpy of solution is expected to be small ($\Delta H_{\text{soln}} \approx 0$), and the increase in entropy drives the formation of a solution. If the predominant intermolecular interactions in two liquids are very different from one another, however, they may be immiscible. For example, organic liquids such as benzene, hexane, CCl₄, and CS₂ (S=C=S) are nonpolar and have no ability to act as hydrogen bond donors or acceptors with hydrogen-bonding solvents such as H₂O, HF, and NH₃; hence they are immiscible in these solvents. When shaken with water, they form separate phases or layers separated by an *interface* (), the region between the two layers. Just because two liquids are immiscible, however, does *not* mean that they are completely insoluble in each other. For example, 188 mg of benzene dissolves in 100 mL of water at 23.5°C. Adding more benzene results in the separation of an upper layer consisting of benzene with a small amount of dissolved water (the solubility of water in benzene is only 178 mg/100 mL of benzene).

Water is immiscible with both CCl₄ and hexane. When all three liquids are mixed, they separate into three distinct layers. Because water is less dense than CCl₄, the water layer floats on the CCl₄. In contrast, hexane is less dense than water, so the hexane floats on the water layer. Because I₂ is intensely purple and quite soluble in both CCl₄ and hexane, but insoluble in water, a small amount of I₂ has been added to help identify the hexane and CCl₄ layers.

The solubilities of simple alcohols in water are given in . Only the three lightest alcohols (methanol, ethanol, and *n*-propanol) are completely miscible with water. As the molecular mass of the alcohol increases, so does the proportion of hydrocarbon in the molecule. Correspondingly, the importance of

hydrogen bonding and dipole–dipole interactions in the pure alcohol decreases, while the importance of London dispersion forces increases, which leads to progressively fewer favorable electrostatic interactions with water. Organic liquids such as acetone, ethanol, and tetrahydrofuran are sufficiently polar to be completely miscible with water yet sufficiently nonpolar to be completely miscible with all organic solvents.

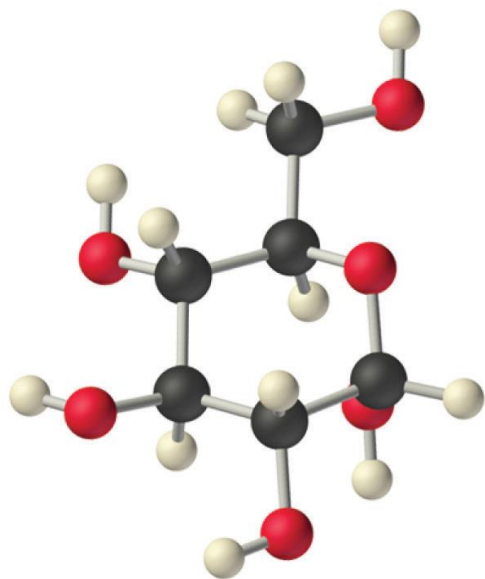


Tetrahydrofuran (THF)

Table 13.4 Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

Alcohol	Solubility (mol/100 g of H ₂ O)
methanol	completely miscible
ethanol	completely miscible
<i>n</i> -propanol	completely miscible
<i>n</i> -butanol	0.11
<i>n</i> -pentanol	0.030
<i>n</i> -hexanol	0.0058
<i>n</i> -heptanol	0.0008

The same principles govern the solubilities of molecular solids in liquids. For example, elemental sulfur is a solid consisting of cyclic S₈ molecules that have no dipole moment. Because the S₈ rings in solid sulfur are held to other rings by London dispersion forces, elemental sulfur is insoluble in water. It is, however, soluble in nonpolar solvents that have comparable London dispersion forces, such as CS₂ (23 g/100 mL). In contrast, glucose contains five –OH groups that can form hydrogen bonds. Consequently, glucose is very soluble in water (91 g/120 mL of water) but essentially insoluble in nonpolar solvents such as benzene. The structure of one isomer of glucose is shown here.



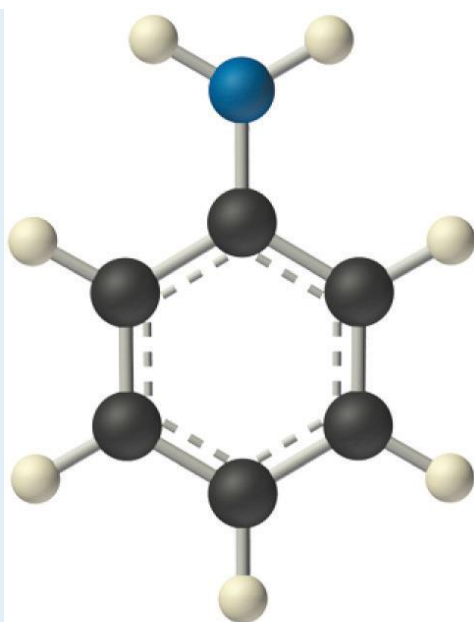
D-Glucose

Low-molecular-mass hydrocarbons with highly electronegative and polarizable halogen atoms, such as chloroform (CHCl_3) and methylene chloride (CH_2Cl_2), have both significant dipole moments and relatively strong London dispersion forces. These hydrocarbons are therefore powerful solvents for a wide range of polar and nonpolar compounds. Naphthalene, which is nonpolar, and phenol ($\text{C}_6\text{H}_5\text{OH}$), which is polar, are very soluble in chloroform. In contrast, the solubility of ionic compounds is largely determined not by the polarity of the solvent but rather by its *dielectric constant*, a measure of its ability to separate ions in solution, as you will soon see.

EXAMPLE 2

Identify the most important solute–solvent interactions in each solution.

- iodine in benzene
- aniline ($\text{C}_6\text{H}_5\text{NH}_2$) in dichloromethane (CH_2Cl_2)



Aniline

iodine in water

Given: components of solutions

Asked for: predominant solute–solvent interactions

Strategy:

Identify all possible intermolecular interactions for both the solute and the solvent: London dispersion forces, dipole–dipole interactions, or hydrogen bonding. Determine which is likely to be the most important factor in solution formation.

Solution:

- a. Benzene and I_2 are both nonpolar molecules. The only possible attractive forces are London dispersion forces.
- b. Aniline is a polar molecule with an $-NH_2$ group, which can act as a hydrogen bond donor. Dichloromethane is also polar, but it has no obvious hydrogen bond acceptor. Therefore, the most important interactions between aniline and CH_2Cl_2 are likely to be London interactions.
- c. Water is a highly polar molecule that engages in extensive hydrogen bonding, whereas I_2 is a nonpolar molecule that cannot act as a hydrogen bond donor or acceptor. The slight solubility of I_2 in water (1.3×10^{-3} mol/L at $25^\circ C$) is due to London dispersion forces.

Exercise

Identify the most important interactions in each solution:

- a. ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) in acetone
- b. acetonitrile ($\text{CH}_3\text{C}\equiv\text{N}$) in acetone
- c. *n*-hexane in benzene

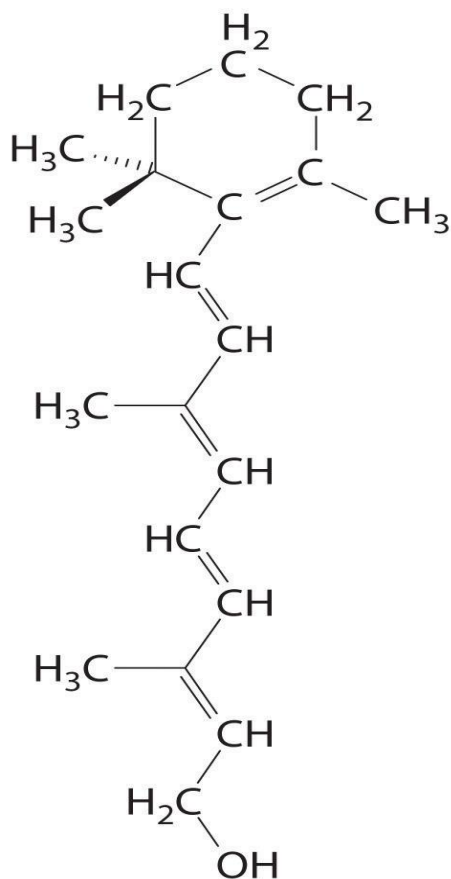
Answer:

- a. hydrogen bonding
- b. London interactions
- c. London dispersion forces

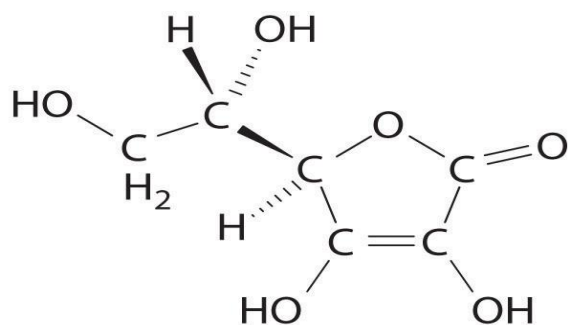
Hydrophilic and Hydrophobic Solutes

A solute can be classified as hydrophilic (literally, “water loving”), meaning that it has an electrostatic attraction to water, or hydrophobic (“water fearing”), meaning that it repels water. A hydrophilic substance is polar and often contains O–H or N–H groups that can form hydrogen bonds to water. For example, glucose with its five O–H groups is hydrophilic. In contrast, a hydrophobic substance may be polar but usually contains C–H bonds that do not interact favorably with water, as is the case with naphthalene and *n*-octane. Hydrophilic substances tend to be very soluble in water and other strongly polar solvents, whereas hydrophobic substances are essentially insoluble in water and soluble in nonpolar solvents such as benzene and cyclohexane.

The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either *fat soluble* or *water soluble*. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend to be absorbed into fatty tissues and stored there. In contrast, water-soluble vitamins, such as vitamin C, are polar, hydrophilic molecules that circulate in the blood and intracellular fluids, which are primarily aqueous. Water-soluble vitamins are therefore excreted much more rapidly from the body and must be replenished in our daily diet. A comparison of the chemical structures of vitamin A and vitamin C quickly reveals why one is hydrophobic and the other hydrophilic.



Vitamin A
(*trans*-Retinol)

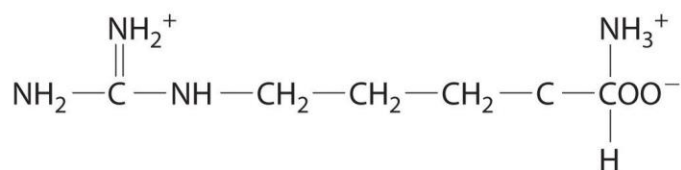


Vitamin C
(L-Ascorbic acid)

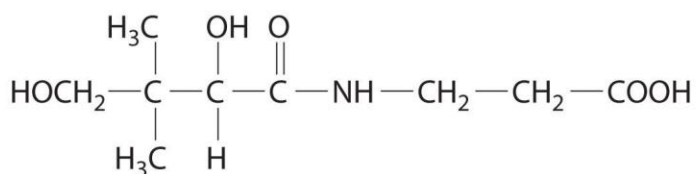
Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a significant health hazard when consumed in large amounts. For example, the livers of polar bears and other large animals that live in cold climates contain large amounts of vitamin A, which have occasionally proven fatal to humans who have eaten them.

EXAMPLE 3

The following substances are essential components of the human diet:



Arginine



Pantothenic acid



Oleic acid

Using what you know of hydrophilic and hydrophobic solutes, classify each as water soluble or fat soluble and predict which are likely to be required in the diet on a daily basis.

- arginine
- pantothenic acid
- oleic acid

Given: chemical structures

Asked for: classification as water soluble or fat soluble; dietary requirement

Strategy:

Based on the structure of each compound, decide whether it is hydrophilic or hydrophobic. If it is hydrophilic, it is likely to be required on a daily basis.

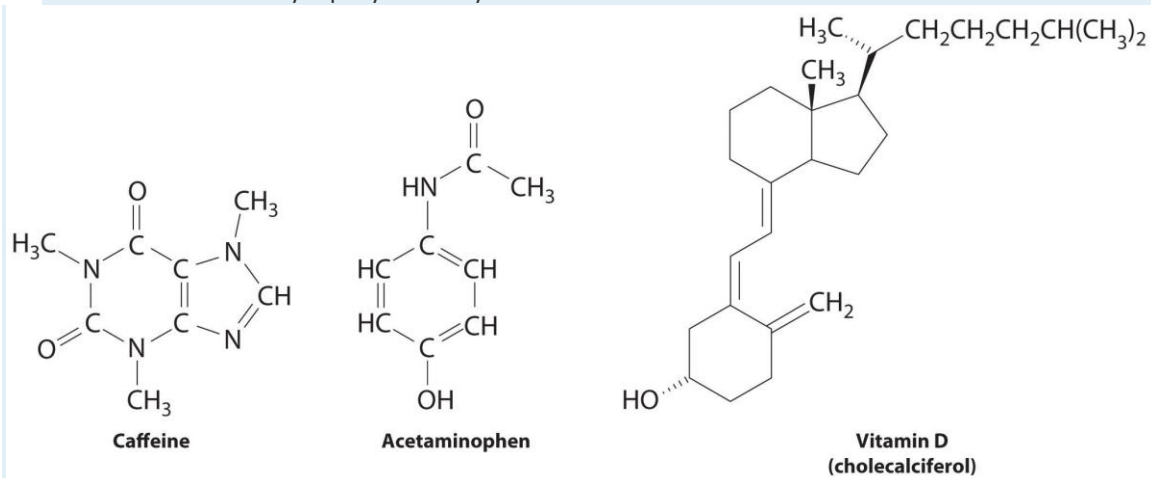
Solution:

- Arginine is a highly polar molecule with two positively charged groups and one negatively charged group, all of which can form hydrogen bonds with water. As a result, it is hydrophilic and required in our daily diet.
- Although pantothenic acid contains a hydrophobic hydrocarbon portion, it also contains several polar functional groups ($-\text{OH}$ and $-\text{CO}_2\text{H}$) that should interact strongly with water. It is therefore likely to be water soluble and required in the diet. (In fact, pantothenic acid is almost always a component of multiple-vitamin tablets.)

- c. Oleic acid is a hydrophobic molecule with a single polar group at one end. It should be fat soluble and not required daily.

Exercise

These compounds are consumed by humans: caffeine, acetaminophen, and vitamin D. Identify each as primarily hydrophilic (water soluble) or hydrophobic (fat soluble), and predict whether each is likely to be excreted from the body rapidly or slowly.



Answer: Caffeine and acetaminophen are water soluble and rapidly excreted, whereas vitamin D is fat soluble and slowly excreted.

Solid Solutions

Solutions are not limited to gases and liquids; solid solutions also exist. For example, amalgams, which are usually solids, are solutions of metals in liquid mercury. Because most metals are soluble in mercury, amalgams are used in gold mining, dentistry, and many other applications. A major difficulty when mining gold is separating very small particles of pure gold from tons of crushed rock. One way to accomplish this is to agitate a suspension of the crushed rock with liquid mercury, which dissolves the gold (as well as any metallic silver that might be present). The very dense liquid gold–mercury amalgam is then isolated and the mercury distilled away.

An alloy is a solid or liquid solution that consists of one or more elements in a metallic matrix. A solid alloy has a single homogeneous phase in which the crystal structure of the solvent remains unchanged by the presence of the solute. Thus the microstructure of the alloy is uniform throughout the sample.

Examples are substitutional and interstitial alloys such as brass or solder. (For more information about alloys, see ,) Liquid alloys include sodium/potassium and gold/mercury. In contrast, a *partial* alloy

solution has two or more phases that can be homogeneous in the distribution of the components, but the microstructures of the two phases are *not* the same. As a liquid solution of lead and tin is cooled, for example, different crystalline phases form at different cooling temperatures. As you learned in , alloys usually have properties that differ from those of the component elements.

Network solids such as diamond, graphite, and SiO_2 are insoluble in all solvents with which they do not react chemically. The covalent bonds that hold the network or lattice together are simply too strong to be broken under normal conditions. They are certainly much stronger than any conceivable combination of intermolecular interactions that might occur in solution. Most metals are insoluble in virtually all solvents for the same reason: the delocalized metallic bonding is much stronger than any favorable metal atom–solvent interactions. Many metals react with solutions such as aqueous acids or bases to produce a solution. However, as we saw in , in these instances the metal undergoes a chemical transformation that cannot be reversed by simply removing the solvent.

Note the Pattern

Solids with very strong intermolecular bonding tend to be insoluble.

Solubilities of Ionic Substances in Liquids

introduced you to guidelines for predicting the solubility of ionic compounds in water. Ionic substances are generally most soluble in polar solvents; the higher the lattice energy, the more polar the solvent must be to overcome the lattice energy and dissolve the substance. Because of its high polarity, water is the most common solvent for ionic compounds. Many ionic compounds are soluble in other polar solvents, however, such as liquid ammonia, liquid hydrogen fluoride, and methanol. Because all these solvents consist of molecules that have relatively large dipole moments, they can interact favorably with the dissolved ions.

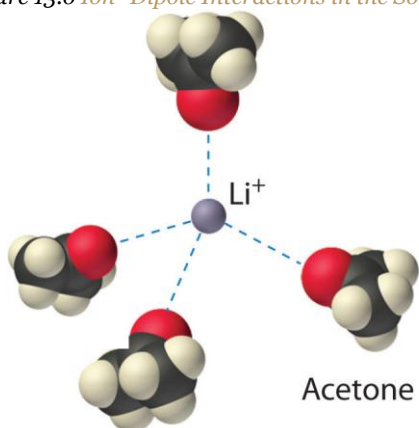
The interaction of water with Na^+ and Cl^- ions in an aqueous solution of NaCl was illustrated in . The ion–dipole interactions between Li^+ ions and acetone molecules in a solution of LiCl in acetone are shown in . The energetically favorable Li^+ –acetone interactions make ΔH_3 sufficiently negative to overcome the positive ΔH_1 and ΔH_2 . Because the dipole moment of acetone (2.88 D), and thus its polarity, is actually larger than that of water (1.85 D), one might even expect that LiCl would be more soluble in acetone than in water. In fact, the opposite is true: 83 g of LiCl dissolve in 100 mL of water at 20°C , but only about 4.1 g of LiCl dissolve in 100 mL of acetone. This apparent contradiction arises from the fact that the dipole

moment is a property of a single molecule in the gas phase. A more useful measure of the ability of a solvent to dissolve ionic compounds is its dielectric constant (ϵ), which is the ability of a bulk substance to decrease the electrostatic forces between two charged particles. By definition, the dielectric constant of a vacuum is 1. In essence, a solvent with a high dielectric constant causes the charged particles to behave as if they have been moved farther apart. At 25°C, the dielectric constant of water is 80.1, one of the highest known, and that of acetone is only 21.0. Hence water is better able to decrease the electrostatic attraction between Li^+ and Cl^- ions, so LiCl is more soluble in water than in acetone. This behavior is in contrast to that of molecular substances, for which polarity is the dominant factor governing solubility.

Note the Pattern

A solvent's dielectric constant is the most useful measure of its ability to dissolve ionic compounds. A solvent's polarity is the dominant factor in dissolving molecular substances.

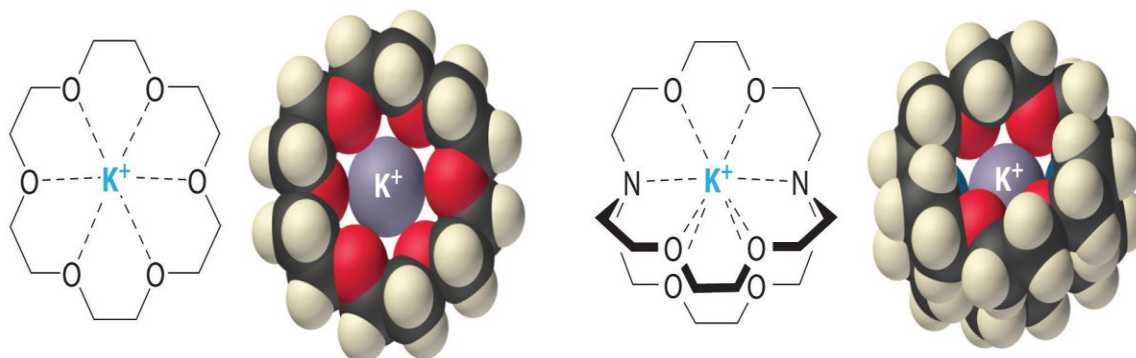
Figure 13.6 Ion–Dipole Interactions in the Solvation of Li^+ Ions by Acetone, a Polar Solvent



It is also possible to dissolve ionic compounds in organic solvents

using crown ethers, cyclic compounds with the general formula $(\text{OCH}_2\text{CH}_2)_n$. Crown ethers are named using both the total number of atoms in the ring and the number of oxygen atoms. Thus 18-crown-6 is an 18-membered ring with six oxygen atoms (part (a) in). The cavity in the center of the crown ether molecule is lined with oxygen atoms and is large enough to be occupied by a cation, such as K^+ . The cation is stabilized by interacting with lone pairs of electrons on the surrounding oxygen atoms. Thus crown ethers solvate cations inside a hydrophilic cavity, whereas the outer shell, consisting of C–H bonds, is hydrophobic. Crown ethers are useful for dissolving ionic substances such as KMnO_4 in organic solvents such as isopropanol $[(\text{CH}_3)_2\text{CHOH}]$ (). The availability of crown ethers with cavities of different sizes allows specific cations to be solvated with a high degree of selectivity.

Figure 13.7 Crown Ethers and Cryptands



(a) Crown ether

(b) Cryptand

(a) The potassium complex of the crown ether 18-crown-6. Note how the cation is nestled within the central cavity of the molecule and interacts with lone pairs of electrons on the oxygen atoms. (b) The potassium complex of 2,2,2-cryptand, showing how the cation is almost hidden by the cryptand. Cryptands solvate cations via lone pairs of electrons on both oxygen and nitrogen atoms.

(a) Normally KMnO_4 , which is intensely purple, is completely insoluble in isopropanol, which has a relatively low dielectric constant. (b) In the presence of a small amount of 18-crown-6, KMnO_4 dissolves in isopropanol, as shown by the reddish-purple color caused by permanganate ions in solution.

Cryptands (from the Greek *kryptós*, meaning “hidden”) are compounds that can completely surround a cation with lone pairs of electrons on oxygen and nitrogen atoms (part (b) in). The number in the name of the cryptand is the number of oxygen atoms in each strand of the molecule. Like crown ethers, cryptands can be used to prepare solutions of ionic compounds in solvents that are otherwise too nonpolar to dissolve them.

Summary

The **solubility** of a substance is the maximum amount of a solute that can dissolve in a given quantity of solvent; it depends on the chemical nature of both the solute and the solvent and on the temperature and pressure. When a solution contains the maximum amount of solute that can dissolve under a given set of conditions, it is a **saturated solution**. Otherwise, it is *unsaturated*. **Supersaturated solutions**, which contain more dissolved solute than allowed under particular conditions, are not stable; the addition of a **seed crystal**, a small particle of solute, will usually cause the excess solute to crystallize. A system in which crystallization and dissolution occur at the same rate is in *dynamic equilibrium*. The solubility of a substance in a liquid is determined by intermolecular interactions, which also determine whether two liquids are miscible. Solutes can be classified as **hydrophilic** (water loving) or **hydrophobic** (water fearing). Vitamins with hydrophilic structures are water soluble, whereas those with hydrophobic

structures are fat soluble. Many metals dissolve in liquid mercury to form **amalgams**. Covalent network solids and most metals are insoluble in nearly all solvents. The solubility of ionic compounds is largely determined by the **dielectric constant (ϵ)** of the solvent, a measure of its ability to decrease the electrostatic forces between charged particles. Solutions of many ionic compounds in organic solvents can be dissolved using **crown ethers**, cyclic polyethers large enough to accommodate a metal ion in the center, or **cryptands**, compounds that completely surround a cation.

KEY TAKEAWAY

- The strength of intramolecular bonding determines the solubility of a solute in a given solvent.

CONCEPTUAL PROBLEMS

- If a compound is only slightly soluble in a particular solvent, what are the relative strengths of the solvent–solvent and solute–solute interactions versus the solute–solvent interactions?
- Predict whether each of the following sets of conditions favors formation of a solution:

Intermolecular Attractive Forces (Solute)	Intermolecular Attractive Forces (Solvent)	ΔH_{soln}
London dispersion	hydrogen bonding	slightly positive
dipole–dipole	hydrogen bonding	very negative
ionic	dipole–dipole	slightly positive
ionic	London dispersion	positive

- Arrange the following liquids in order of increasing solubility in water: *t*-butanol [(CH₃)₃COH], benzene, ammonia, and heptane. Justify your answer.
- Which compound in each pair will be more soluble in water? Explain your reasoning in each case.
 - toluene (C₇H₈) or ethyl ether (C₂H₅OC₂H₅)
 - chloroform (CHCl₃) or acetone (CH₃COCH₃)
 - carbon tetrachloride (CCl₄) or tetrahydrofuran (C₄H₈O)
 - CaCl₂ or CH₂Cl₂
- Which compound in each pair will be more soluble in benzene? Explain your reasoning in each case.

- a. cyclohexane or methanol
 - b. I_2 or $MgCl_2$
 - c. methylene chloride (CH_2Cl_2) or acetic acid
6. Two water-insoluble compounds—*n*-decylamine [$CH_3(CH_2)_9NH_2$] and *n*-decane—can be separated by the following procedure: The compounds are dissolved in a solvent such as toluene that is immiscible with water. When adding an aqueous HCl solution to the mixture and stirring vigorously, the HCl reacts with one of the compounds to produce a salt. When the stirring is stopped and the mixture is allowed to stand, two layers are formed. At this point, each layer contains only one of the two original compounds. After the layers are separated, adding aqueous NaOH to the aqueous layer liberates one of the original compounds, which can then be removed by stirring with a second portion of toluene to extract it from the water.
- a. Identify the compound that is present in each layer following the addition of HCl. Explain your reasoning.
 - b. How can the original compounds be recovered from the toluene solution?
7. Bromine and iodine are both soluble in CCl_4 , but bromine is much more soluble. Why?
8. A solution is made by mixing 50.0 mL of liquid A with 75.0 mL of liquid B. Which is the solute, and which is the solvent? Is it valid to assume that the volume of the resulting solution will be 125 mL? Explain your answer.
9. The compounds NaI, NaBr, and NaCl are far more soluble in water than NaF, a substance that is used to fluoridate drinking water. In fact, at 25°C the solubility of NaI is 184 g/100 mL of water, versus only 4.2 g/100 mL of water for NaF. Why is sodium iodide so much more soluble in water? Do you expect KCl to be more soluble or less soluble in water than NaCl?
10. When water is mixed with a solvent with which it is immiscible, the two liquids usually form two separate layers. If the density of the nonaqueous solvent is 1.75 g/mL at room temperature, sketch the appearance of the heterogeneous mixture in a beaker and label which layer is which. If you were not sure of the density and the identity of the other liquid, how might you be able to identify which is the aqueous layer?
11. When two liquids are immiscible, the addition of a third liquid can occasionally be used to induce the formation of a homogeneous solution containing all three.
- a. Ethylene glycol ($HOCH_2CH_2OH$) and hexane are immiscible, but adding acetone [$(CH_3)_2CO$] produces a homogeneous solution. Why does adding a third solvent produce a homogeneous solution?

- b. Methanol and *n*-hexane are immiscible. Which of the following solvents would you add to create a homogeneous solution—water, *n*-butanol, or cyclohexane? Justify your choice.
12. Some proponents of vitamin therapy for combating illness encourage the consumption of large amounts of fat-soluble vitamins. Why can this be dangerous? Would it be as dangerous to consume large amounts of water-soluble vitamins? Why or why not?
13. Why are most metals insoluble in virtually all solvents?
14. Because sodium reacts violently with water, it is difficult to weigh out small quantities of sodium metal for a reaction due to its rapid reaction with small amounts of moisture in the air. Would a Na/Hg amalgam be as sensitive to moisture as metallic sodium? Why or why not? A Na/K alloy is a liquid at room temperature. Will it be more or less sensitive to moisture than solid Na or K?
15. Dental amalgams often contain high concentrations of Hg, which is highly toxic. Why isn't dental amalgam toxic?
16. Arrange 2,2,3-trimethylpentane, 1-propanol, toluene (C₇H₈), and dimethyl sulfoxide [(CH₃)₂S=O] in order of increasing dipole moment. Explain your reasoning.
17. Arrange acetone, chloroform, cyclohexane, and 2-butanol in order of increasing dielectric constant. Explain your reasoning.
18. Dissolving a white crystalline compound in ethanol gave a blue solution. Evaporating the ethanol from the solution gave a bluish-crystalline product, which slowly transformed into the original white solid on standing in the air for several days. Explain what happened. How does the mass of the initial bluish solid compare with the mass of the white solid finally recovered?
19. You have been asked to develop a new drug that could be used to bind Fe³⁺ ions in patients who suffer from iron toxicity, allowing the bound iron to be excreted in the urine. Would you consider a crown ether or a cryptand to be a reasonable candidate for such a drug? Explain your answer.
20. Describe two different situations in which fractional crystallization will not work as a separation technique when attempting to isolate a single compound from a mixture.
21. You have been given a mixture of two compounds—A and B—and have been told to isolate pure A. You know that pure A has a lower solubility than pure B and that the solubilities of both A and B increase with temperature. Outline a procedure to isolate pure A. If B had the lower solubility, could you use the same procedure to isolate pure A? Why or why not?

ANSWERS

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.
7. London dispersion forces increase with increasing atomic mass. Iodine is a solid while bromine is a liquid due to the greater intermolecular interactions between the heavier iodine atoms. Iodine is less soluble than bromine in virtually all solvents because it requires more energy to separate I_2 molecules than Br_2 molecules.
- 8.
- 9.
- 10.
11.
 - a. A third solvent with intermediate polarity and/or dielectric constant can effectively dissolve both of the immiscible solvents, creating a single liquid phase.
 - b. *n*-butanol—it is intermediate in polarity between methanol and *n*-hexane, while water is more polar than either and cyclohexane is comparable to *n*-hexane.
- 12.
- 13.
- 14.
15. In dental amalgam, the mercury atoms are locked in a solid phase that does not undergo corrosion under physiological conditions; hence, the mercury atoms cannot readily diffuse to the surface where they could vaporize or undergo chemical reaction.
- 16.
- 17.
- 18.
- 19.
- 20.

21. Dissolve the mixture of A and B in a solvent in which they are both soluble when hot and relatively insoluble when cold, filter off any undissolved B, and cool slowly. Pure A should crystallize, while B stays in solution. If B were less soluble, it would be impossible to obtain pure A by this method in a single step, because some of the less soluble compound (B) will always be present in the solid that crystallizes from solution.

13.3 Units of Concentration

LEARNING OBJECTIVE

1. To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.

There are several different ways to quantitatively describe the concentration of a solution. For example, molarity was introduced in as a useful way to describe solution concentrations for reactions that are carried out in solution. Mole fractions, introduced in , are used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example 4 reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

EXAMPLE 4

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

- a. What is its molarity?
- b. What is its mole fraction?

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

A Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.

B Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

Solution:

a. **A** The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass. The volume of the solution equals its mass divided by its density. The calculations follow:

$$\begin{aligned} \text{moles } CH_3CO_2H &= 3.78 \text{ g } CH_3CO_2H / 60.05 \text{ g/mol} = 0.0629 \text{ mol} \\ \text{volume} &= \text{mass} / \text{density} = 100.0 \text{ g solution} / 1.00 \text{ g/mL} = 100 \text{ mL} \\ \text{molarity of } CH_3CO_2H &= \text{moles } CH_3CO_2H / \text{liter solution} \\ &= 0.0629 \text{ mol } CH_3CO_2H / (100 \text{ mL}) (1 \text{ L} / 1000 \text{ mL}) = 0.629 \text{ M } CH_3CO_2H \end{aligned}$$

This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than 12 mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

b. **B** To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g – 3.78 g) = 96.2 g of water. We have

$$\text{moles } H_2O = 96.2 \text{ g } H_2O / 18.02 \text{ g/mol} = 5.34 \text{ mol } H_2O$$

The mole fraction X of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$\begin{aligned} X_{CH_3CO_2H} &= \text{moles } CH_3CO_2H / (\text{moles } CH_3CO_2H + \text{moles } H_2O) \\ &= 0.0629 \text{ mol} / (0.0629 \text{ mol} + 5.34 \text{ mol}) = 0.0116 = 1.16 \times 10^{-2} \end{aligned}$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

Exercise

A solution of HCl gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of HCl per 100.0 g of solution, and its density is 1.10 g/mL.

- What is its molarity?
- What is its mole fraction?

Answer:

a. 6.10 M HCl

b. $X_{\text{HCl}} = 0.111$

The concentration of a solution can also be described by its molality (m), the number of moles of solute per *kilogram* of solvent:

Equation 13.5

$$\text{molality}(m) = \frac{\text{moles solute}}{\text{kilogram solvent}}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of H₂O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 m solution.

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as mass percentage, parts per million (ppm), or parts per billion (ppb):

Equation 13.6

$$\text{mass percentage} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) (100)$$

Equation 13.7

$$\text{parts per million (ppm)} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) (10^6)$$

Equation 13.8

$$\text{parts per billion (ppb)} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) (10^9)$$

In the health sciences, the concentration of a solution is typically expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per 1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H₂SO₄ per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

EXAMPLE 5

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

- a. What is the molarity of the solution?
- b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A Use the concentration of the solute in parts per million to calculate the molarity.

B Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. **A** To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\text{molarity} = \frac{\text{moles}}{\text{liter solution}}$$

$$\begin{aligned} \text{b.} \quad &= (12.7 \text{ mg})(1 \text{ g}/1000 \text{ mg})(1 \text{ mol}/78.114 \text{ g})(1.00 \text{ L}) \\ &= 1.63 \times 10^{-4} \text{ M} \end{aligned}$$

c. **B** We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

mass of benzene

$$\begin{aligned} &= (12.7 \text{ mg benzene})(250 \text{ mL})/1000 \text{ mL} \\ &= 3.18 \text{ mg} = 3.18 \times 10^{-3} \text{ g benzene} \end{aligned}$$

Exercise

The maximum allowable concentration of lead in drinking water is 9.0 ppb. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution? Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer: $4.3 \times 10^{-8} \text{ M}$; $2 \times 10^{-6} \text{ g}$

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C , the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C . For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as we saw in . As you will learn in , mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 6.

Table 13.5 Different Units for Expressing the Concentrations of Solutions*

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (X)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
mass	[mass of solute (g)]/mass of	Useful when masses are known but molecular

Unit	Definition	Application
percentage (%)	$\text{solution (g)} \times 100$	masses are unknown.
parts per thousand (ppt)	$[\text{mass of solute/mass of solution}] \times 10^3$ (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	$[\text{mass of solute/mass of solution}] \times 10^6$ (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	$[\text{mass of solute/mass of solution}] \times 10^9$ (μg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.		

EXAMPLE 6

Vodka is essentially a solution of pure ethanol in water. Typical vodka is sold as “80 proof,” which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

- the mass percentage
- the mole fraction
- the molarity
- the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.

B Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.

C Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.

D Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. **A** Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$\text{mass of EtOH} = (40.0 \text{ mL})(0.789 \text{ g/mL}) = 31.6 \text{ g EtOH}$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

a. **B** The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\begin{aligned} \text{\%EtOH} &= (\text{mass of EtOH} / \text{mass of solution})(100) \\ \text{b.} \quad &= (31.6 \text{ g EtOH} / (31.6 \text{ g EtOH} + 60.0 \text{ g H}_2\text{O})) (100) = 34.5\% \end{aligned}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$\begin{aligned} \text{moles EtOH} &= (31.6 \text{ g EtOH}) \\ &/ (46.07 \text{ g EtOH/mol}) \\ &= 0.686 \text{ mol CH}_3\text{CH}_2\text{OH} \end{aligned}$$

Similarly, the number of moles of water is

$$\begin{aligned} \text{moles H}_2\text{O} &= (60.0 \text{ g H}_2\text{O}) \\ &/ (18.02 \text{ g H}_2\text{O/mol}) = 3.33 \text{ mol H}_2\text{O} \end{aligned}$$

The mole fraction of ethanol is thus

$$\text{c.} \quad X_{\text{EtOH}} = 0.686 \text{ mol} / (0.686 \text{ mol} + 3.33 \text{ mol}) = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

d. $M_{EtOH} = (0.686 \text{ mol} / 100 \text{ mL}) \times (1000 \text{ mL}) = 6.86 \text{ M}$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{EtOH} = (0.686 \text{ mol EtOH} / 60.0 \text{ g H}_2\text{O}) \times (1000 \text{ g/kg})$$

$$= 11.4 \text{ mol EtOH/kg H}_2\text{O} = 11.4 \text{ m}$$

Exercise

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

- mass percentage
- mole fraction
- molarity
- molality

Answer:

- mass percentage toluene = 24.8%
- $X_{\text{toluene}} = 0.219$
- 2.35 M toluene
- 3.59 m toluene

Summary

The **concentration** of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); *mole fraction*, the ratio of the number of moles of solute to the total number of moles of substances present; **mass percentage**, the ratio of the mass of the solute to the mass of the solution times 100; **parts per thousand (ppt)**, grams of solute per kilogram of solution; **parts per million (ppm)**, milligrams of solute per kilogram of solution; **parts per billion (ppb)**, micrograms of solute per kilogram of solution; and **molality (m)**, the number of moles of solute per kilogram of solvent.

KEY TAKEAWAY

- Different units are used to express the concentrations of a solution depending on the application.

KEY EQUATIONS

molality

: $\text{molality } (m) = \frac{\text{moles solute}}{\text{kilogram solvent}}$

mass percentage

$\text{ppm} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) (10^6)$

parts per million

$\text{ppb} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) (10^9)$

parts per billion

$\text{ppm} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) (10^6)$

CONCEPTUAL PROBLEMS

1. Does the molality have the same numerical value as the molarity for a highly concentrated aqueous solution of fructose ($\text{C}_6\text{H}_{12}\text{O}_6$) (approximately 3.2 M)? Why or why not?
2. Explain why the molality and molarity of an aqueous solution are not always numerically identical. Will the difference between the two be greater for a dilute or a concentrated solution? Explain your answer.
3. Under what conditions are molality and molarity likely to be equal? Is the difference between the two greater when water is the solvent or when the solvent is not water? Why?
4. What is the key difference between using mole fraction or molality versus molarity to describe the concentration of a solution? Which unit(s) of concentration is most appropriate for experiments that must be carried out at several different temperatures?
5. An experiment that relies on very strict control of the reaction stoichiometry calls for adding 50.0 mL of a 0.95 M solution of A to 225 mL of a 1.01 M solution of B, followed by heating for 1 h at 60°C. To save time, a student decided to heat solution B to 60°C before measuring out 225 mL of solution B, transferring it to the flask containing solution A, and proceeding normally. This change in procedure caused the yield of product to be less than usual. How could such an apparently minor change in procedure have resulted in a decrease in the yield?

NUMERICAL PROBLEMS

1. Complete the following table for aqueous solutions of the compounds given.

Compound	Molarity (M)	Solution Density (g/mL)	Mole Fraction (X)
H ₂ SO ₄	18.0	1.84	
CH ₃ COOH		1.00	7.21×10^{-3}
KOH	3.60	1.16	

2. Complete the following table for each compound given.

Compound	Mass (g)	Volume of Solution (mL)	Molarity (M)
Na ₂ SO ₄	7.80	225	
KNO ₃		125	1.27
NaO ₂ CCH ₃	18.64		0.95

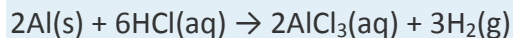
- How would you prepare 100.0 mL of an aqueous solution with 0.40 M KI? a solution with 0.65 M NaCN?
- Calculate the molality of a solution with 775 mg of NaCl in 500.0 g of water. Do you expect the molarity to be the same as the molality? Why or why not?
- What is the molarity of each solution?
 - 12.8 g of glucose (C₆H₁₂O₆) in water, total volume 150.0 mL
 - 9.2 g of Na₃PO₄ in water, total volume 200.0 mL
 - 843 mg of I₂ in EtOH, total volume 150.0 mL
- A medication used to treat abnormal heart rhythms is labeled "Procainamide 0.5 g/250 cc." Express this concentration in parts per thousand.
- Meperidine is a medication used for pain relief. A bottle of meperidine is labeled as 50 mg/mL. Express this concentration in parts per thousand.
- An aqueous solution that is 4.61% NaOH by mass has a density of 1.06 g/mL. Calculate the molarity of the solution, the mole fraction of NaOH, and the molality of the solution.
- A solution of concentrated phosphoric acid contains 85.0% H₃PO₄ by mass and has a density of 1.684 g/mL. Calculate the following.
 - the molarity of the solution
 - the mole fraction of H₃PO₄
 - the molality of the solution

10. A solution of commercial concentrated nitric acid is 16 M HNO_3 and has a density of 1.42 g/mL. What is the percentage of HNO_3 in the solution by mass? What is the molality?
11. A commercial aqueous ammonia solution contains 28.0% NH_3 by mass and has a density of 0.899 g/mL. Calculate the following.
 - a. the molarity
 - b. the mole fraction
12. Concentrated, or glacial, acetic acid is pure acetic acid and has a density of 1.053 g/mL. It is widely used in organic syntheses, in the manufacture of rayon and plastics, as a preservative in foods, and occasionally to treat warts. What volume of glacial acetic acid is required to prepare 5.00 L of a 1.75 M solution of acetic acid in ethanol?
13. Solutions of sodium carbonate decahydrate, also known as washing soda, are used as skin cleansers. The solubility of this compound in cold water is 21.52 g/100 mL. If a saturated solution has a density of 1.20 g/mL, what is its molarity? What is the mole fraction of sodium carbonate decahydrate in this solution?
14. Hydrogen peroxide (H_2O_2) is usually sold over the counter as an aqueous solution that is 3% by mass. Assuming a solution density of 1.01 g/mL, what is the molarity of hydrogen peroxide? What is the molar concentration of a solution that is 30% hydrogen peroxide by mass (density = 1.112 g/mL)? How would you prepare 100.0 mL of a 3% solution from the 30% solution?
15. Determine the concentration of a solution with 825 mg of Na_2HPO_4 dissolved in 450.0 mL of H_2O at 20°C in molarity, molality, mole fraction, and parts per million. Assume that the density of the solution is the same as that of water. Which unit of concentration is most convenient for calculating vapor pressure changes? Why?
16. How many moles of Cl^- are there in 25.0 mL of a 0.15 M CaCl_2 solution?
17. How many moles of Na^+ are there in 25.0 g of a $1.33 \times 10^{-3} \text{ M}$ Na_2HPO_4 solution? What is the sodium concentration of this solution in ppb?
18. How many grams of copper are there in 30.0 mL of a 0.100 M CuSO_4 solution?
19. How many grams of nitrate ion are there in 75.0 g of a $1.75 \times 10^{-4} \text{ M}$ $\text{Pb}(\text{NO}_3)_2$ solution? What is the nitrate concentration of the solution in ppb?
20. How many milliliters of a 0.750 M solution of K_2CrO_4 are required to deliver 250 mg of chromate ion?
21. How many milliliters of a $1.95 \times 10^{-6} \text{ M}$ solution of Ag_3PO_4 are required to deliver 14.0 mg of Ag^+ ?
22. Iron reacts with bromine according to the following equation:



How many milliliters of a 5.0×10^{-2} M solution of bromine in water are required to react completely with 750.0 mg of iron metal?

23. Aluminum reacts with HCl according to the following equation:



If 25.0 mL of a solution of HCl in water is required to react completely with 1.05 g of aluminum metal, what is the molarity of the HCl solution?

24. The precipitation of silver chloride is a diagnostic test for the presence of chloride ion. If 25.0 mL of 0.175 M AgNO_3 are required to completely precipitate the chloride ions from 10.0 mL of an NaCl solution, what was the original concentration of NaCl?

25. Barium sulfate is virtually insoluble. If a 10.0 mL solution of 0.333 M $\text{Ba(NO}_3)_2$ is stirred with 40.0 mL of a 0.100 M Na_2SO_4 , how many grams of barium sulfate will precipitate? Which reactant is present in excess? What is its final concentration?

ANSWERS

1.

Compound	Molarity (M)	Solution Density (g/mL)	Mole Fraction (X)
H_2SO_4	18.0	1.84	0.82
CH_3COOH	0.393	1.00	7.21×10^{-3}
KOH	3.60	1.16	6.33×10^{-2}

2.

3. 100.0 ml of 0.40 M KI: dissolve 6.64 g of KI in enough water to make 100.0 mL of solution; 100.0 ml of 0.65 M NaCN: dissolve 3.18 g of NaCN in enough water to make 100.0 mL of solution.

4.

5.

- a. 0.474 M glucose
- b. 0.28 M Na_3PO_4
- c. 0.0221 M I_2

6.

7.

- 8.
- 9.
- a. 14.6 M
- b. $X = 0.510$
- c. 57.7 m
- 10.
- 11.
- a. 14.8 M
- b. $X = 0.292$
- 12.
13. The molarity is 0.745 M, and the mole fraction is 0.0134.
- 14.
15. The molarity is 0.0129 M, the molality is 0.0129 m, the mole fraction is 2.33×10^{-4} , and the solution contains 1830 ppm Na_2HPO_4 . Mole fraction is most useful for calculating vapor pressure, because Raoult's law states that the vapor pressure of a solution containing a non-volatile solute is equal to the mole fraction of solvent times the vapor pressure of the pure solvent. The mole fraction of the solvent is just one minus the mole fraction of solute.
- 16.
17. 6.65×10^{-5} mol sodium; 6.14×10^4 ppb
- 18.
19. 1.63×10^{-3} g; 2.17×10^4 ppb
- 20.
21. 2.22×10^4 mL or 22.2 L
- 22.
23. 4.68 M HCl
- 24.
25. 0.777 g BaSO_4 ; Na_2SO_4 ; 0.0134 M Na_2SO_4

13.4 Effects of Temperature and Pressure on Solubility

LEARNING OBJECTIVE

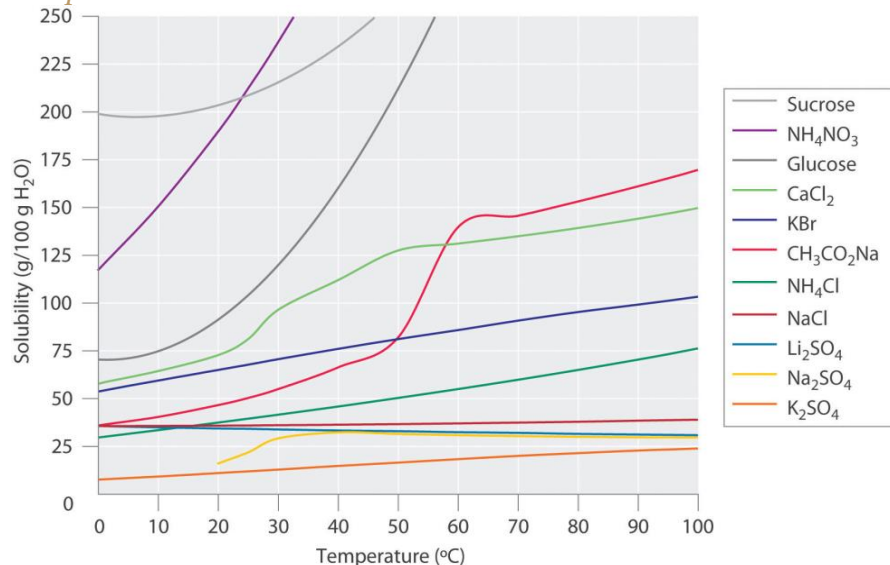
1. To understand the relationship among temperature, pressure, and solubility.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

Effect of Temperature on the Solubility of Solids

Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature" shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and $\text{CH}_3\text{CO}_2\text{Na}$) exhibit a dramatic increase in solubility with increasing temperature. Others (such as NaCl and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

Figure 13.9 Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature



Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.

Notice in particular the curves for NH_4NO_3 and CaCl_2 . The dissolution of ammonium nitrate in water is endothermic ($\Delta H_{\text{soln}} = +25.7 \text{ kJ/mol}$), whereas the dissolution of calcium chloride is exothermic ($\Delta H_{\text{soln}} = -68.2 \text{ kJ/mol}$), yet Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature" shows that the solubility of both compounds increases sharply with increasing

temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C . According to the temperature curves in Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature", both compounds dissolve in water at 80°C , and all 50 g of KBr remains in solution at 0°C . Only about 36 g of $\text{CH}_3\text{CO}_2\text{Na}$ are soluble in 100 g of water at 0°C , however, so approximately 114 g ($150\text{ g} - 36\text{ g}$) of $\text{CH}_3\text{CO}_2\text{Na}$ crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original $\text{CH}_3\text{CO}_2\text{Na}$ in essentially pure form in only one step.

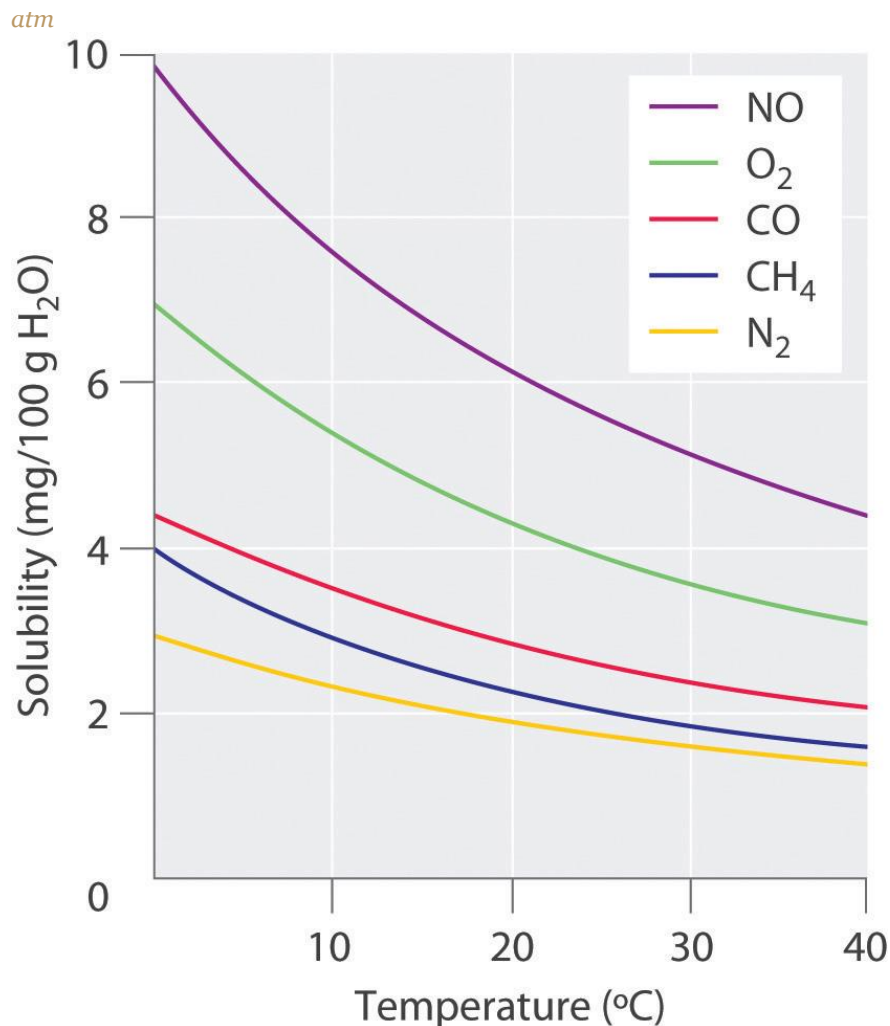
Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature" and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be *more* soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 13.10 "Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm". Attractive intermolecular interactions in the gas phase are essentially zero for most substances. When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic

process ($\Delta H_{\text{soln}} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas.^[1]

Figure 13.10 Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1

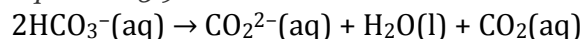


The solubilities of all gases decrease with increasing temperature.

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called “boiler scale,” a deposit that can seriously decrease the capacity of hot water pipes (Figure 13.11 "Boiler Scale in a Water Pipe"). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern

France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex and will be described in more detail in Chapter 17 "Solubility and Complexation Equilibriums", but the driving force is the loss of dissolved CO_2 from solution. Hard water contains dissolved Ca^{2+} and HCO_3^- (bicarbonate) ions. Calcium bicarbonate $[\text{Ca}(\text{HCO}_3)_2]$ is rather soluble in water, but calcium carbonate (CaCO_3) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

Equation 13.9



Heating the solution decreases the solubility of CO_2 , which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.

Calcium carbonate (CaCO_3) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved CO_2 is driven into the gas phase at high temperatures.

In *thermal pollution*, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of O_2 at higher temperatures (Figure 13.10 "Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm"), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.

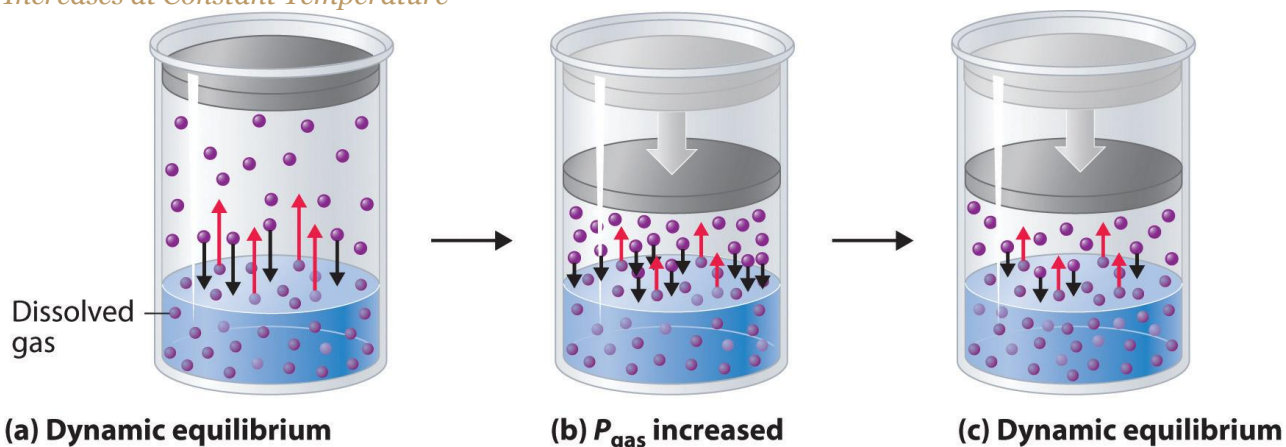
A similar effect is seen in the rising temperatures of bodies of water such as the Chesapeake Bay, the largest estuary in North America, where global warming has been implicated as the cause (For more information on global warming, see Chapter 5 "Energy Changes in Chemical Reactions", Section 5.5

"Energy Sources and the Environment".) For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eelgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 13.12 "A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature", which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

Figure 13.12 *A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature*



(a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (For more information on vapor pressure, see Chapter 11 "Liquids", Section 11.3 "Unique Properties of Liquids".) (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

Equation 13.10

$$C = kP$$

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature. Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore $\text{mol}/(\text{L}\cdot\text{atm}) = \text{M}/\text{atm}$. Values of

the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 13.6 "Henry's Law Constants for Selected Gases in Water at 20°C".

As the data in Table 13.6 "Henry's Law Constants for Selected Gases in Water at 20°C" demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O₂ is almost twice as soluble as N₂. Although London dispersion forces are too weak to explain such a large difference, O₂ is paramagnetic and hence more polarizable than N₂, which explains its high solubility.

Table 13.6 Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10 ⁻⁴
He	3.9
Ne	4.7
Ar	15
H ₂	8.1
N ₂	7.1
O ₂	14
CO ₂	392

Gases that react chemically with water, such as HCl and the other hydrogen halides, H₂S, and NH₃, do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give H⁺(aq) and Cl⁻(aq), *not* dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

Note the Pattern

Gases that react with water do not obey Henry's law.

Henry's law has important applications. For example, bubbles of CO₂ form as soon as a carbonated beverage is opened because the drink was bottled under CO₂ at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO₂ above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N₂ from the air dissolves in the diver's internal fluids. If the diver ascends too quickly,

the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as “the bends.” These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry’s law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at $37^\circ C$ (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these “blood substitutes” do not require refrigeration and have a long shelf life. Their very high Henry’s law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

EXAMPLE 7

The Henry’s law constant for O_2 in water at $25^\circ C$ is $1.27 \times 10^{-3} \text{ M/atm}$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at $25^\circ C$ at an atmospheric pressure of 1.00 atm.

Given: Henry’s law constant, mole fraction of O_2 , and pressure

Asked for: solubility

Strategy:

A Use Dalton’s law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton’s law of partial pressures, see Chapter 10 “Gases”, Section 10.5 “Mixtures of Gases”.)

B Use Henry’s law to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton’s law, the partial pressure of O_2 is proportional to the mole fraction of O_2 :

$$P_A = X_A P_t = (0.21)(1.00 \text{ atm}) = 0.21 \text{ atm}$$

B From Henry’s law, the concentration of dissolved oxygen under these conditions is

$$CO_2 = k_{PO_2} = (1.27 \times 10^{-3} \text{ M/atm})(0.21 \text{ atm}) = 2.7 \times 10^{-4} \text{ M}$$

Exercise

To understand why soft drinks “fizz” and then go “flat” after being opened, calculate the concentration of dissolved CO_2 in a soft drink

- bottled under a pressure of 5.0 atm of CO_2 .
- in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately 3×10^{-4} atm).

The Henry’s law constant for CO_2 in water at 25°C is 3.4×10^{-2} M/atm.

Answer:

- 0.17 M
- 1×10^{-5} M

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using **fractional crystallization**, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. **Henry’s law** describes the relationship between the pressure and the solubility of a gas.

KEY TAKEAWAY

- The solubility of a solid may increase or decrease with increasing temperature, whereas the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

CONCEPTUAL PROBLEMS

- Use the kinetic molecular theory of gases discussed in Chapter 10 "Gases" to explain why the solubility of virtually all gases in liquids decreases with increasing temperature.
- An industrial plant uses water from a nearby stream to cool its reactor and returns the water to the stream after use. Over a period of time, dead fish start to appear downstream from the plant, but there is no evidence for any leaks of potentially toxic chemicals into the stream. What other factor might be causing the fish to die?

3. One manufacturer's instructions for setting up an aquarium specify that if boiled water is used, the water must be cooled to room temperature and allowed to stand overnight before fish are added. Why is it necessary for the water to stand?
4. Using a carbonated beverage as an example, discuss the effect of temperature on the "fizz." How does the "foaminess" of a carbonated beverage differ between Los Angeles, California, and Denver, Colorado?
5. A common laboratory technique for degassing a solvent is to place it in a flask that is sealed to the atmosphere and then evacuate the flask to remove any gases above the liquid. Why is this procedure effective? Why does the temperature of the solvent usually decrease substantially during this process?

ANSWERS

- 1.
- 2.
3. When water is boiled, all of the dissolved oxygen and nitrogen are removed. When the water is cooled to room temperature, it initially contains very little dissolved oxygen. Allowing the water to stand overnight allows oxygen in the air to dissolve, so that the fish will not suffocate.
- 4.
5. Evacuating the flask to remove gases decreases the partial pressure of oxygen above the solution. According to Henry's law, the solubility of any gas decreases as its partial pressure above the solution decreases. Consequently, dissolved oxygen escapes from solution into the gas phase, where it is removed by the vacuum pump. Filling the flask with nitrogen gas and repeating this process several times effectively removes almost all of the dissolved oxygen. The temperature of the solvent decreases because some solvent evaporates as well during this process. The heat that is required to evaporate some of the liquid is initially removed from the rest of the solvent, decreasing its temperature.

NUMERICAL PROBLEMS

1. The solubility of CO_2 in water at 0°C and 1 atm is 0.335 g/100 g of H_2O . At 20°C and 1 atm, the solubility of CO_2 in water is 0.169 g/100 g of H_2O .
 - a. What volume of CO_2 would be released by warming 750 g of water saturated with CO_2 from 0°C to 20°C ?
 - b. What is the value of the Henry's law constant for CO_2 under each set of conditions?

2. The solubility of O₂ in 100 g of H₂O at varying temperatures and a pressure of 1 atm is given in the following table:

Solubility (g)	Temperature (°C)
0.0069	0
0.0054	10
0.0043	20

- What is the value of the Henry's law constant at each temperature?
- Does Henry's law constant increase or decrease with increasing temperature?
- At what partial pressure of O₂ would the concentration of O₂ in water at 0°C be the same as the concentration in water at 20°C at a partial pressure of 1 atm?
- Assuming that air is 20% O₂ by volume, at what atmospheric pressure would the O₂ concentration be the same at 20°C as it is at atmospheric pressure and 0°C?

ANSWER

- 0.678 L CO₂
 - $k_0^\circ\text{C} = 7.61 \times 10^{-2} \text{ M/atm}$, $k_{20}^\circ\text{C} = 3.84 \times 10^{-2} \text{ M/atm}$

[1] The phenomenon is similar to that involved in the increase in vapor pressure of a pure liquid with increasing temperature, as discussed in Chapter 11 "Liquids". In the case of vapor pressure, however, it is attractive forces between *solvent* molecules that are being overcome by the added thermal energy when the temperature is increased.

13.4 Effects of Temperature and Pressure on Solubility

LEARNING OBJECTIVE

- To understand the relationship among temperature, pressure, and solubility.

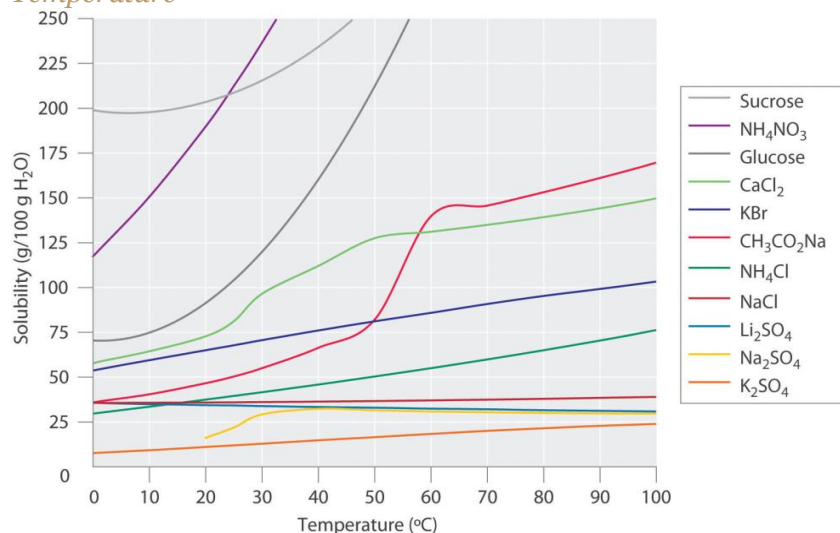
Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

Effect of Temperature on the Solubility of Solids

Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature" shows plots of the solubilities of several organic and inorganic compounds in water as a

function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and $\text{CH}_3\text{CO}_2\text{Na}$) exhibit a dramatic increase in solubility with increasing temperature. Others (such as NaCl and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

Figure 13.9 Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature



Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.

Notice in particular the curves for NH_4NO_3 and CaCl_2 . The dissolution of ammonium nitrate in water is endothermic ($\Delta H_{\text{soln}} = +25.7 \text{ kJ/mol}$), whereas the dissolution of calcium chloride is exothermic ($\Delta H_{\text{soln}} = -68.2 \text{ kJ/mol}$), yet Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature" shows that the solubility of both compounds increases sharply with increasing temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate

($\text{CH}_3\text{CO}_2\text{Na}$) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C . According to the temperature curves in Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature", both compounds dissolve in water at 80°C , and all 50 g of KBr remains in solution at 0°C . Only about 36 g of $\text{CH}_3\text{CO}_2\text{Na}$ are soluble in 100 g of water at 0°C , however, so approximately 114 g ($150\text{ g} - 36\text{ g}$) of $\text{CH}_3\text{CO}_2\text{Na}$ crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original $\text{CH}_3\text{CO}_2\text{Na}$ in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature" and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be *more* soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

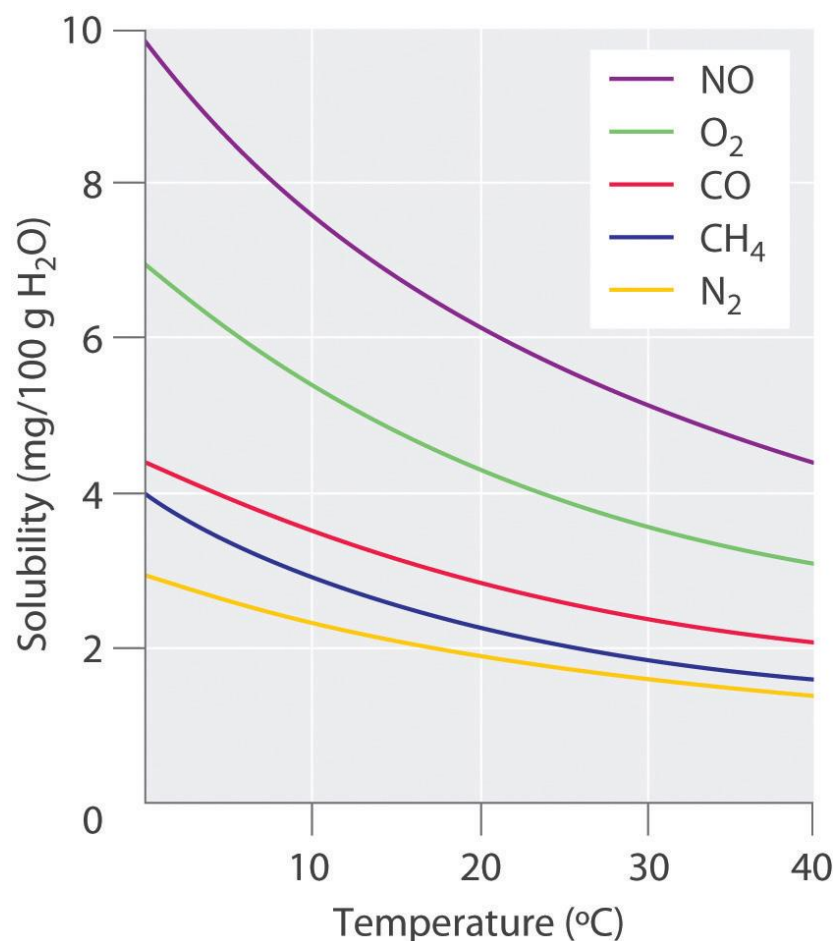
Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 13.10

"Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm". Attractive intermolecular interactions in the gas phase are essentially zero for most substances.

When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic process ($\Delta H_{\text{soln}} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas.^[1]

Figure 13.10 Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm

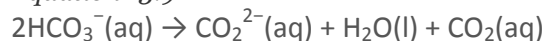


The solubilities of all gases decrease with increasing temperature.

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called “boiler scale,” a deposit that can seriously decrease the capacity of hot water pipes (Figure 13.11 "Boiler Scale in a Water Pipe"). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex and will be described in more detail in Chapter 17 "Solubility and Complexation Equilibria", but the driving force is the loss of dissolved CO₂ from solution. Hard water contains dissolved Ca²⁺ and HCO₃⁻ (bicarbonate) ions. Calcium bicarbonate [Ca(HCO₃)₂] is rather soluble in water,

but calcium carbonate (CaCO_3) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

Equation 13.9



Heating the solution decreases the solubility of CO_2 , which escapes into the gas phase above the solution.

In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.

Calcium carbonate (CaCO_3) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved CO_2 is driven into the gas phase at high temperatures.

In *thermal pollution*, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of O_2 at higher temperatures (Figure 13.10 "Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm"), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.

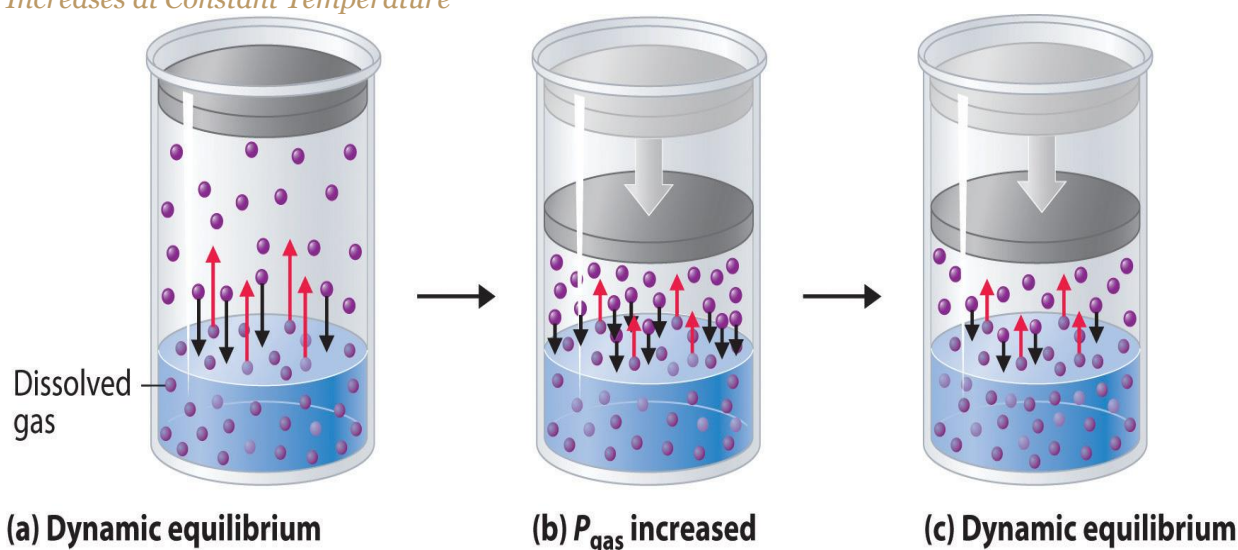
A similar effect is seen in the rising temperatures of bodies of water such as the Chesapeake Bay, the largest estuary in North America, where global warming has been implicated as the cause (For more information on global warming, see Chapter 5 "Energy Changes in Chemical Reactions", Section 5.5 "Energy Sources and the Environment".) For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter

feeders, which then decreased light transmission to allow the eelgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 13.12 "A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature", which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

Figure 13.12 A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature



(a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (For more information on vapor pressure, see Chapter 11 "Liquids", Section 11.3 "Unique

Properties of Liquids".) (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

Equation 13.10

$$C = kP$$

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k is the *Henry's law constant*, which must be determined experimentally for each combination of gas, solvent, and temperature. Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore $\text{mol}/(\text{L}\cdot\text{atm}) = \text{M}/\text{atm}$. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 13.6 "Henry's Law Constants for Selected Gases in Water at 20°C".

As the data in Table 13.6 "Henry's Law Constants for Selected Gases in Water at 20°C" demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost twice as soluble as N_2 . Although London dispersion forces are too weak to explain such a large difference, O_2 is paramagnetic and hence more polarizable than N_2 , which explains its high solubility.

Table 13.6 Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [$\text{mol}/(\text{L}\cdot\text{atm})$] $\times 10^{-4}$
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14
CO_2	392

Gases that react chemically with water, such as HCl and the other hydrogen halides, H₂S, and NH₃, do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give H⁺(aq) and Cl⁻(aq), *not* dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

Note the Pattern

Gases that react with water do not obey Henry's law.

Henry's law has important applications. For example, bubbles of CO₂ form as soon as a carbonated beverage is opened because the drink was bottled under CO₂ at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO₂ above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N₂ from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N₂ to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O₂ in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O₂ concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O₂ reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O₂ and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O₂ molecules. Although the concentration of dissolved O₂ in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O₂ concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O₂ result in dissolved oxygen concentrations comparable to those in normal blood.

EXAMPLE 7

The Henry's law constant for O_2 in water at $25^\circ C$ is $1.27 \times 10^{-3} \text{ M/atm}$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at $25^\circ C$ at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2 , and pressure

Asked for: solubility

Strategy:

A Use Dalton's law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton's law of partial pressures, see Chapter 10 "Gases", Section 10.5 "Mixtures of Gases".)

B Use Henry's law to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2 :

$$P_A = X_A P_t = (0.21)(1.00 \text{ atm}) = 0.21 \text{ atm}$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$CO_2 = kPO_2 = (1.27 \times 10^{-3} \text{ M/atm})(0.21 \text{ atm}) = 2.7 \times 10^{-4} \text{ M}$$

Exercise

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved CO_2 in a soft drink

- bottled under a pressure of 5.0 atm of CO_2 .
- in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately $3 \times 10^{-4} \text{ atm}$).

The Henry's law constant for CO_2 in water at $25^\circ C$ is $3.4 \times 10^{-2} \text{ M/atm}$.

Answer:

- 0.17 M
- $1 \times 10^{-5} \text{ M}$

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using **fractional crystallization**, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. **Henry's law** describes the relationship between the pressure and the solubility of a gas.

KEY TAKEAWAY

- The solubility of a solid may increase or decrease with increasing temperature, whereas the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

CONCEPTUAL PROBLEMS

1. Use the kinetic molecular theory of gases discussed in Chapter 10 "Gases" to explain why the solubility of virtually all gases in liquids decreases with increasing temperature.
2. An industrial plant uses water from a nearby stream to cool its reactor and returns the water to the stream after use. Over a period of time, dead fish start to appear downstream from the plant, but there is no evidence for any leaks of potentially toxic chemicals into the stream. What other factor might be causing the fish to die?
3. One manufacturer's instructions for setting up an aquarium specify that if boiled water is used, the water must be cooled to room temperature and allowed to stand overnight before fish are added. Why is it necessary for the water to stand?
4. Using a carbonated beverage as an example, discuss the effect of temperature on the "fizz." How does the "foaminess" of a carbonated beverage differ between Los Angeles, California, and Denver, Colorado?
5. A common laboratory technique for degassing a solvent is to place it in a flask that is sealed to the atmosphere and then evacuate the flask to remove any gases above the liquid. Why is this procedure effective? Why does the temperature of the solvent usually decrease substantially during this process?

ANSWERS

- 1.
- 2.
3. When water is boiled, all of the dissolved oxygen and nitrogen are removed. When the water is cooled to room temperature, it initially contains very little dissolved oxygen. Allowing the water to stand overnight allows oxygen in the air to dissolve, so that the fish will not suffocate.
- 4.
5. Evacuating the flask to remove gases decreases the partial pressure of oxygen above the solution. According to Henry's law, the solubility of any gas decreases as its partial pressure above the solution decreases. Consequently, dissolved oxygen escapes from solution into the gas phase, where it is removed by the vacuum

pump. Filling the flask with nitrogen gas and repeating this process several times effectively removes almost all of the dissolved oxygen. The temperature of the solvent decreases because some solvent evaporates as well during this process. The heat that is required to evaporate some of the liquid is initially removed from the rest of the solvent, decreasing its temperature.

NUMERICAL PROBLEMS

- The solubility of CO_2 in water at 0°C and 1 atm is 0.335 g/100 g of H_2O . At 20°C and 1 atm, the solubility of CO_2 in water is 0.169 g/100 g of H_2O .
 - What volume of CO_2 would be released by warming 750 g of water saturated with CO_2 from 0°C to 20°C ?
 - What is the value of the Henry's law constant for CO_2 under each set of conditions?
- The solubility of O_2 in 100 g of H_2O at varying temperatures and a pressure of 1 atm is given in the following table:

Solubility (g)	Temperature ($^\circ\text{C}$)
0.0069	0
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- What is the value of the Henry's law constant at each temperature?
- Does Henry's law constant increase or decrease with increasing temperature?
- At what partial pressure of O_2 would the concentration of O_2 in water at 0°C be the same as the concentration in water at 20°C at a partial pressure of 1 atm?
- Assuming that air is 20% O_2 by volume, at what atmospheric pressure would the O_2 concentration be the same at 20°C as it is at atmospheric pressure and 0°C ?

ANSWER

- 0.678 L CO_2
 - $k_{0^\circ\text{C}} = 7.61 \times 10^{-2} \text{ M/atm}$, $k_{20^\circ\text{C}} = 3.84 \times 10^{-2} \text{ M/atm}$

[1] The phenomenon is similar to that involved in the increase in vapor pressure of a pure liquid with increasing temperature, as discussed in Chapter 11 "Liquids". In the case of vapor

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13.4 Effects of Temperature and Pressure on Solubility

LEARNING OBJECTIVE

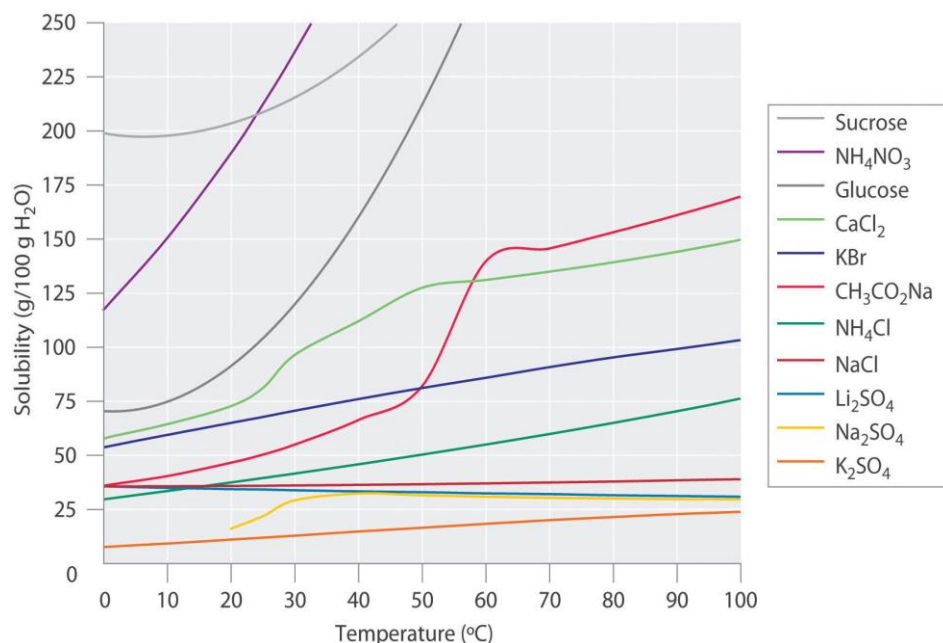
1. To understand the relationship among temperature, pressure, and solubility.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

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The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C . According to the temperature curves in Figure 13.9 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature", both compounds dissolve in water at 80°C , and all 50 g of KBr remains in solution at 0°C . Only about 36 g of $\text{CH}_3\text{CO}_2\text{Na}$ are soluble in 100 g of water at 0°C , however, so approximately 114 g (150 g – 36 g) of

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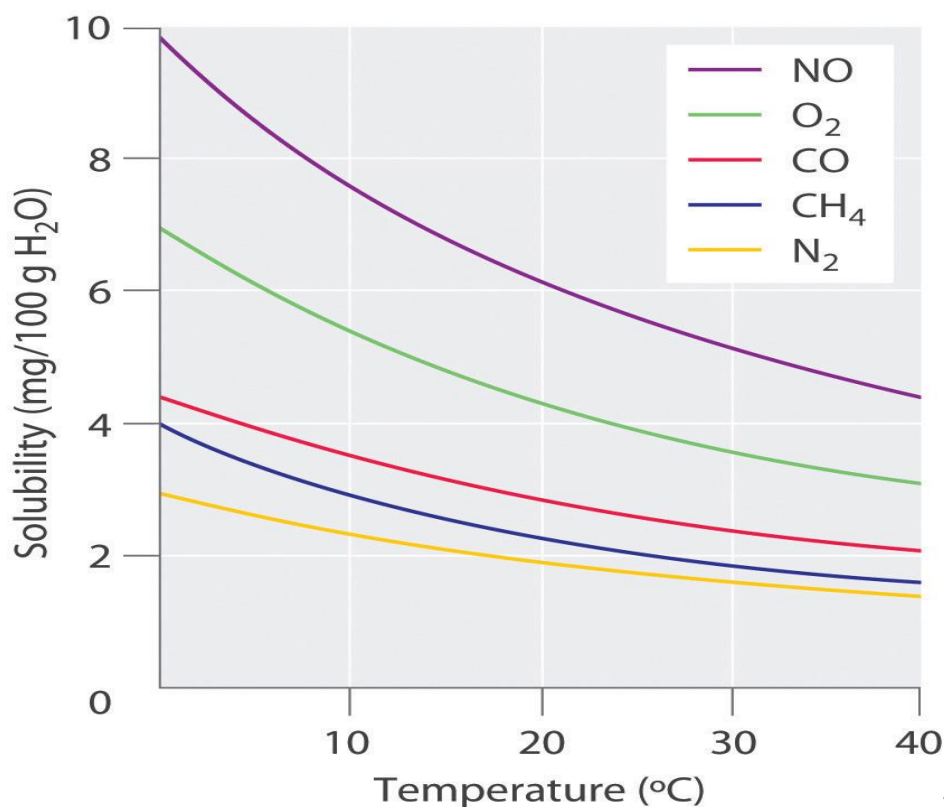
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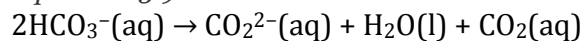


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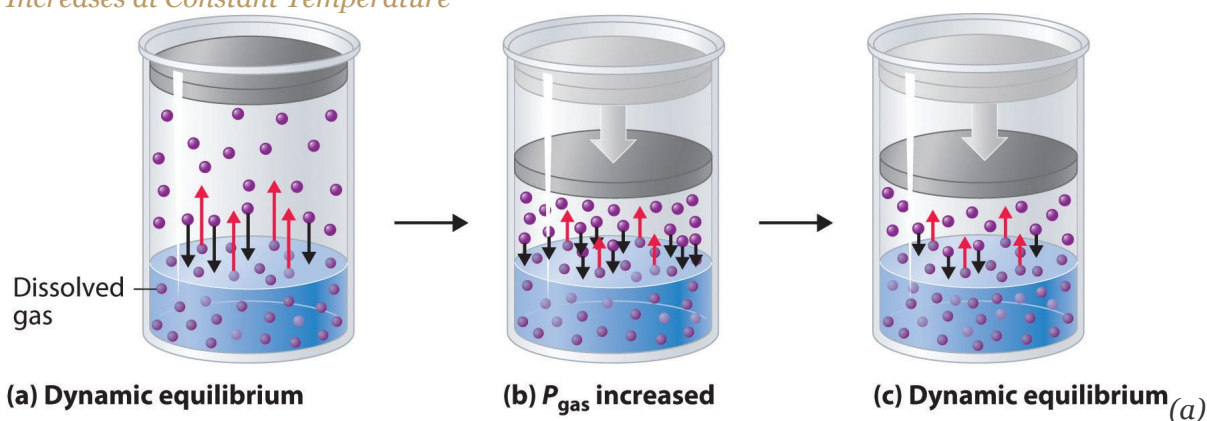
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External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 13.12 "A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature", which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

Figure 13.12 A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature



When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (For more information on vapor pressure, see Chapter 11 "Liquids", Section 11.3 "Unique Properties of Liquids".) (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

Equation 13.10

$$C = kP$$

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k is the *Henry's law constant*, which must be determined experimentally for each combination of gas, solvent, and temperature. Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore $\text{mol}/(\text{L}\cdot\text{atm}) = \text{M}/\text{atm}$. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 13.6 "Henry's Law Constants for Selected Gases in Water at 20°C".

As the data in Table 13.6 "Henry's Law Constants for Selected Gases in Water at 20°C" demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost twice as soluble as N_2 . Although London dispersion forces are too weak to explain such a large difference, O_2 is paramagnetic and hence more polarizable than N_2 , which explains its high solubility.

Table 13.6 Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant $[\text{mol}/(\text{L}\cdot\text{atm})] \times 10^{-4}$
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14
CO_2	392

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S , and NH_3 , do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $\text{H}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$, *not* dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

Note the Pattern

Gases that react with water do not obey Henry's law.

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N_2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

EXAMPLE 7

The Henry's law constant for O_2 in water at 25°C is $1.27 \times 10^{-3} \text{ M/atm}$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2 , and pressure

Asked for: solubility

Strategy:

A Use Dalton's law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton's law of partial pressures, see Chapter 10 "Gases", Section 10.5 "Mixtures of Gases".)

B Use Henry's law to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2 :

$$P_A = X_A P_t = (0.21)(1.00 \text{ atm}) = 0.21 \text{ atm}$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$CO_2 = k_{PO_2} = (1.27 \times 10^{-3} \text{ M/atm})(0.21 \text{ atm}) = 2.7 \times 10^{-4} \text{ M}$$

Exercise

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved CO_2 in a soft drink

- bottled under a pressure of 5.0 atm of CO_2 .
- in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately 3×10^{-4} atm).

The Henry's law constant for CO_2 in water at $25^\circ C$ is $3.4 \times 10^{-2} \text{ M/atm}$.

Answer:

- 0.17 M
- $1 \times 10^{-5} \text{ M}$

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using **fractional crystallization**, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. **Henry's law** describes the relationship between the pressure and the solubility of a gas.

KEY TAKEAWAY

- The solubility of a solid may increase or decrease with increasing temperature, whereas the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

CONCEPTUAL PROBLEMS

1. Use the kinetic molecular theory of gases discussed in Chapter 10 "Gases" to explain why the solubility of virtually all gases in liquids decreases with increasing temperature.
2. An industrial plant uses water from a nearby stream to cool its reactor and returns the water to the stream after use. Over a period of time, dead fish start to appear downstream from the plant, but there is no evidence for any leaks of potentially toxic chemicals into the stream. What other factor might be causing the fish to die?
3. One manufacturer's instructions for setting up an aquarium specify that if boiled water is used, the water must be cooled to room temperature and allowed to stand overnight before fish are added. Why is it necessary for the water to stand?
4. Using a carbonated beverage as an example, discuss the effect of temperature on the "fizz." How does the "foaminess" of a carbonated beverage differ between Los Angeles, California, and Denver, Colorado?
5. A common laboratory technique for degassing a solvent is to place it in a flask that is sealed to the atmosphere and then evacuate the flask to remove any gases above the liquid. Why is this procedure effective? Why does the temperature of the solvent usually decrease substantially during this process?

ANSWERS

- 1.
- 2.
3. When water is boiled, all of the dissolved oxygen and nitrogen are removed. When the water is cooled to room temperature, it initially contains very little dissolved oxygen. Allowing the water to stand overnight allows oxygen in the air to dissolve, so that the fish will not suffocate.
- 4.
5. Evacuating the flask to remove gases decreases the partial pressure of oxygen above the solution. According to Henry's law, the solubility of any gas decreases as its partial pressure above the solution decreases. Consequently, dissolved oxygen escapes from solution into the gas phase, where it is removed by the vacuum pump. Filling the flask with nitrogen gas and repeating this process several times effectively removes almost all of the dissolved oxygen. The temperature of the solvent decreases because some solvent evaporates as well during this process. The heat that is required to evaporate some of the liquid is initially removed from the rest of the solvent, decreasing its temperature.

NUMERICAL PROBLEMS

1. The solubility of CO_2 in water at 0°C and 1 atm is 0.335 g/100 g of H_2O . At 20°C and 1 atm, the solubility of CO_2 in water is 0.169 g/100 g of H_2O .
 - a. What volume of CO_2 would be released by warming 750 g of water saturated with CO_2 from 0°C to 20°C ?
 - b. What is the value of the Henry's law constant for CO_2 under each set of conditions?
2. The solubility of O_2 in 100 g of H_2O at varying temperatures and a pressure of 1 atm is given in the following table:

Solubility (g)	Temperature ($^\circ\text{C}$)
0.0069	0
0.0054	10
0.0043	20

- a. What is the value of the Henry's law constant at each temperature?
- b. Does Henry's law constant increase or decrease with increasing temperature?
- c. At what partial pressure of O_2 would the concentration of O_2 in water at 0°C be the same as the concentration in water at 20°C at a partial pressure of 1 atm?
- d. Assuming that air is 20% O_2 by volume, at what atmospheric pressure would the O_2 concentration be the same at 20°C as it is at atmospheric pressure and 0°C ?

ANSWER

1.
 - a. 0.678 L CO_2
 - b. $k_{0^\circ\text{C}} = 7.61 \times 10^{-2} \text{ M/atm}$, $k_{20^\circ\text{C}} = 3.84 \times 10^{-2} \text{ M/atm}$

[1] The phenomenon is similar to that involved in the increase in vapor pressure of a pure liquid with increasing temperature, as discussed in Chapter 11 "Liquids". In the case of vapor pressure, however, it is attractive forces between *solvent* molecules that are being overcome by the added thermal energy when the temperature is increased.

13.6 Aggregate Particles in Aqueous Solution

LEARNING OBJECTIVE

1. To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about $1\text{ }\mu\text{m}$ (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 13.9 "Properties of Liquid Solutions, Colloids, and Suspensions".

Table 13.9 Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word *colloid* (from the Greek *kólla*, meaning "glue") to describe these substances, as well as the words *sol* and *gel* to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture

from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,^[1] whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 13.22 "Tyndall Effect, the Scattering of Light by Colloids".

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called *albumin*, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

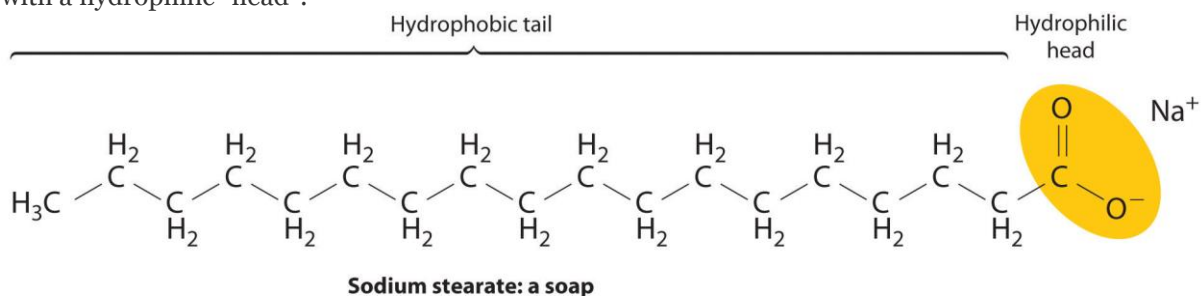
In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a "donut" shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen

to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine, Figure 5.16 "The Structures of 10 Amino Acids"). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 13.23 "Sickle-Cell Anemia"). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 13.24 "Formation of New Land by the Destabilization of a Colloid Suspension". Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

Emulsions

Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic “tail” with a hydrophilic “head”:



Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate $[\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2^- \text{Na}^+]$, and detergents, such as sodium dodecyl sulfate $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+]$, whose structures are as follows:



Sodium stearate:
a soap



Sodium dodecyl sulfate:
a detergent

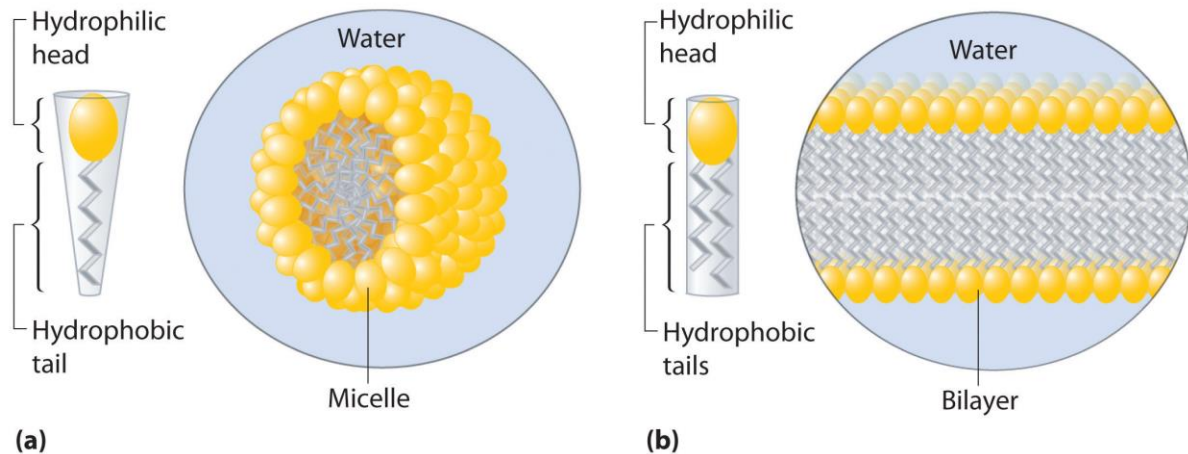
When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called *bile* into the small intestine. Bile contains a variety of *bile salts*, detergent-like molecules that emulsify the fats.

Micelles

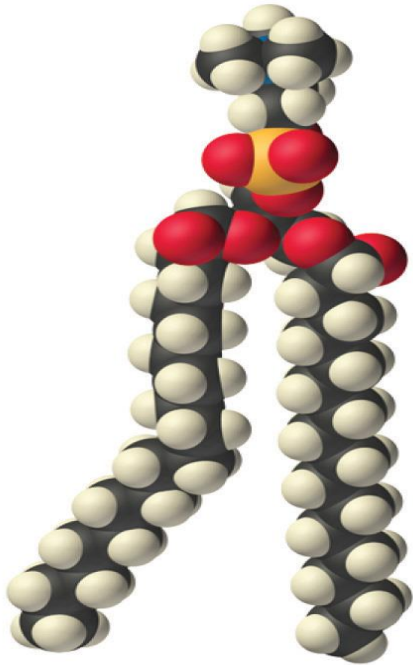
Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micelles, which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (part (a) in Figure 13.25 "Micelles and a Phospholipid Bilayer").

Figure 13.25 *Micelles and a Phospholipid Bilayer*



- (a)** Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior.
- (b)** Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and *two* hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in part (b) in Figure 13.25 "Micelles and a Phospholipid Bilayer", the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



Phosphatidylcholine: a phospholipid

A cell membrane is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cell is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A **suspension** is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a **colloid** are smaller and do not separate on standing. A colloid can be classified as a **sol**, a dispersion of solid particles in a liquid or solid; a **gel**, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an **aerosol**, a dispersion of solid or liquid particles in a gas; or an **emulsion**, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the **Tyndall effect**. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. **Emulsions** are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called **micelles**. **Phospholipids** are a class of detergent-like molecules that have two

hydrophobic tails attached to a hydrophilic head. A **bilayer** is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. **Cells** are collections of molecules that are surrounded by a phospholipid bilayer called a **cell membrane** and are able to reproduce themselves.

KEY TAKEAWAY

- Colloids and suspensions are mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures.

CONCEPTUAL PROBLEMS

- How does a colloid differ from a suspension? Which has a greater effect on solvent properties, such as vapor pressure?
- Is homogenized milk a colloid or a suspension? Is human plasma a colloid or a suspension? Justify your answers.
- How would you separate the components of an emulsion of fat dispersed in an aqueous solution of sodium chloride?

[1] The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893).

13.7 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

- ♦ Scuba divers utilize high-pressure gas in their tanks to allow them to breathe under water. At depths as shallow as 100 ft (30 m), the pressure exerted by water is 4.0 atm. At 25°C the values of Henry's law constants for N_2 , O_2 , and He in blood are as follows: $N_2 = 6.5 \times 10^{-4} \text{ mol}/(\text{L}\cdot\text{atm})$, $O_2 = 1.28 \times 10^{-3} \text{ mol}/(\text{L}\cdot\text{atm})$, and $He = 3.7 \times 10^{-4} \text{ mol}/(\text{L}\cdot\text{atm})$.
 - What would be the concentration of nitrogen and oxygen in blood at sea level where the air is 21% oxygen and 79% nitrogen?
 - What would be the concentration of nitrogen and oxygen in blood at a depth of 30 m, assuming that the diver is breathing compressed air?
- ♦ Many modern batteries take advantage of lithium ions dissolved in suitable electrolytes. Typical batteries have lithium concentrations of 0.10 M. Which aqueous solution has the higher concentration of ion pairs: 0.08 M LiCl or 1.4 M LiCl? Why? Does an increase in the number of ion pairs correspond to a higher or lower

van't Hoff factor? Batteries rely on a high concentration of unpaired Li^+ ions. Why is using a more concentrated solution not an ideal strategy in this case?

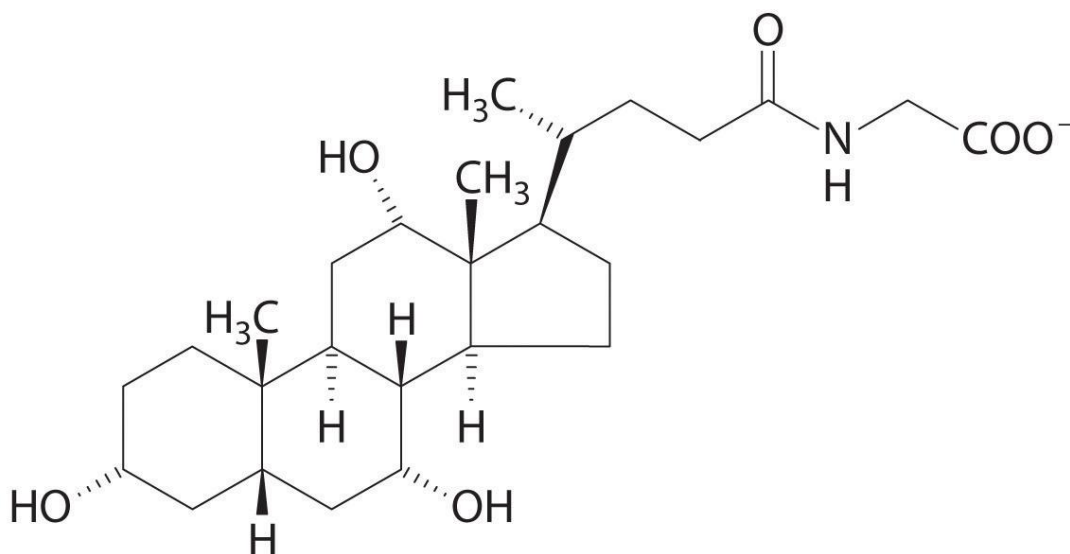
- Hydrogen sulfide, which is extremely toxic to humans, can be detected at a concentration of 2.0 ppb. At this level, headaches, dizziness, and nausea occur. At higher concentrations, however, the sense of smell is lost, and the lack of warning can result in coma and death can result. What is the concentration of H_2S in milligrams per liter at the detection level? The lethal dose of hydrogen sulfide by inhalation for rats is $7.13 \times 10^{-4} \text{ g/L}$. What is this lethal dose in ppm? The density of air is 1.2929 g/L.
- One class of antibiotics consists of cyclic polyethers that can bind alkali metal cations in aqueous solution. Given the following antibiotics and cation selectivities, what conclusion can you draw regarding the relative sizes of the cavities?

Antibiotic	Cation Selectivity
nigericin	$\text{K}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Li}^+$
lasalocid	$\text{Ba}^{2+} \gg \text{Cs}^+ > \text{Rb}^+, \text{K}^+ > \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$

- Phenylpropanolamine hydrochloride is a common nasal decongestant. An aqueous solution of phenylpropanolamine hydrochloride that is sold commercially as a children's decongestant has a concentration of $6.67 \times 10^{-3} \text{ M}$. If a common dose is 1.0 mL/12 lb of body weight, how many moles of the decongestant should be given to a 26 lb child?
- The "freeze-thaw" method is often used to remove dissolved oxygen from solvents in the laboratory. In this technique, a liquid is placed in a flask that is then sealed to the atmosphere, the liquid is frozen, and the flask is evacuated to remove any gas and solvent vapor in the flask. The connection to the vacuum pump is closed, the liquid is warmed to room temperature and then refrozen, and the process is repeated. Why is this technique effective for degassing a solvent?
- Suppose that, on a planet in a galaxy far, far away, a species has evolved whose biological processes require even more oxygen than we do. The partial pressure of oxygen on this planet, however, is much less than that on Earth. The chemical composition of the "blood" of this species is also different. Do you expect their "blood" to have a higher or lower value of the Henry's law constant for oxygen at standard temperature and pressure? Justify your answer.
- A car owner who had never taken general chemistry decided that he needed to put some ethylene glycol antifreeze in his car's radiator. After reading the directions on the container, however, he decided that "more

must be better.” Instead of using the recommended mixture (30% ethylene glycol/70% water), he decided to reverse the amounts and used a 70% ethylene glycol/30% water mixture instead. Serious engine problems developed. Why?

9. The ancient Greeks produced “Attic ware,” pottery with a characteristic black and red glaze. To separate smaller clay particles from larger ones, the powdered clay was suspended in water and allowed to settle. This process yielded clay fractions with coarse, medium, and fine particles, and one of these fractions was used for painting. Which size of clay particles forms a suspension, which forms a precipitate, and which forms a colloidal dispersion? Would the colloidal dispersion be better characterized as an emulsion? Why or why not? Which fraction of clay particles was used for painting?
10. The Tyndall effect is often observed in movie theaters, where it makes the beam of light from the projector clearly visible. What conclusions can you draw about the quality of the air in a movie theater where you observe a large Tyndall effect?
11. Aluminum sulfate is the active ingredient in styptic pencils, which can be used to stop bleeding from small cuts. The Al^{3+} ions induce aggregation of colloids in the blood, which facilitates formation of a blood clot. How can Al^{3+} ions induce aggregation of a colloid? What is the probable charge on the colloidal particles in blood?
12. ♦ The liver secretes bile, which is essential for the digestion of fats. As discussed in Chapter 5 “Energy Changes in Chemical Reactions”, fats are biomolecules with long hydrocarbon chains. The globules of fat released by partial digestion of food particles in the stomach and lower intestine are too large to be absorbed by the intestine unless they are emulsified by bile salts, such as glycocholate. Explain why a molecule like glycocholate is effective at creating an aqueous dispersion of fats in the digestive tract.



Glycocholate (a bile salt)

ANSWERS

1.
 - a. 1 atm: 2.7×10^{-4} M O₂ and 5.1×10^{-4} M N₂
 - b. 4 atm: 1.1×10^{-3} M O₂ and 2.1×10^{-3} M N₂
- 2.
3. 2.6×10^{-6} mg/L, 550 ppm
- 4.
5. 1.4×10^{-5} mol
- 6.
7. To obtain the same concentration of dissolved oxygen in their "blood" at a lower partial pressure of oxygen, the value of the Henry's law constant would have to be higher.
- 8.
9. The large, coarse particles would precipitate, the medium particles would form a suspension, and the fine ones would form a colloid. A colloid consists of solid particles in a liquid medium, so it is not an emulsion, which consists of small particles of one liquid suspended in another liquid. The finest particles would be used for painting.

Chapter 14

Chemical Kinetics

The gases, liquids, solids, and solutions that you learned to describe quantitatively in , , and , respectively, are systems whose chemical compositions do not change with time. Now we will present a quantitative description of a far more common situation in which the chemical composition of a system is *not* constant with time. An example of such a system is the stratosphere, where chemicals rising from the ground level initiate reactions that lead to decreases in the concentration of stratospheric ozone—the so-called ozone hole. (For more information about the ozone hole, see , .) Another example involves the production of polyethylene, in which the properties of the plastic are determined by the relative speeds of events that occur during the polymerization reaction. (For more information about the polymerization reaction, see , .) The techniques you are about to learn will enable you to describe the speed of many such changes and predict how the composition of each system will change in response to changing conditions.

The Belousov-Zhabotinsky reaction is, a chemical reaction that oscillates in time and space. When a very thin layer of an acidic solution containing potassium bromate (KBrO_3), cerium ammonium nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$, malonic acid ($\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$), and an indicator is poured into a shallow dish, local fluctuations in the concentration of the reactants and a complex series of reactions cause striking geometric patterns of concentric circles and spirals to propagate across the dish.

We begin with a discussion of chemical kinetics, which is the study of reaction rates, or the changes in the concentrations of reactants and products with time. As you learn about the factors that affect reaction rates, the methods chemists use for reporting and calculating those rates, and the clues that reaction rates provide about events at the molecular level, you will also discover the answers to questions such as the following: How can normally stable substances such as flour and coal cause devastating explosions? How do archaeologists use isotopic composition to estimate the ages of ancient artifacts? How do the catalysts used in catalytic converters, some laundry detergents, and meat tenderizers work?

Summary

Chemical kinetics is the study of **reaction rates**, the changes in the concentrations of reactants and products with time.

14.1 Factors That Affect Reaction Rates

LEARNING OBJECTIVE

1. To understand the factors that affect reaction rates.

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors: reactant concentrations, temperature, physical states and surface areas of reactants, and solvent and catalyst properties if either are present. By studying the kinetics of a reaction, chemists gain insights into how to control reaction conditions to achieve a desired outcome.

Concentration Effects

Two substances cannot possibly react with each other unless their constituent particles (molecules, atoms, or ions) come into contact. If there is no contact, the reaction rate will be zero. Conversely, the more reactant particles that collide per unit time, the more often a reaction between them can occur.

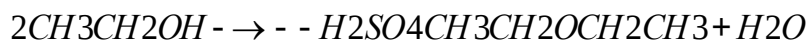
Consequently, the reaction rate usually increases as the concentration of the reactants increases. One example of this effect is the reaction of sucrose (table sugar) with sulfuric acid, which is shown in Figure 14.1 "The Effect of Concentration on Reaction Rates".

Temperature Effects

You learned in Chapter 10 "Gases" that increasing the temperature of a system increases the average kinetic energy of its constituent particles. As the average kinetic energy increases, the particles move faster, so they collide more frequently per unit time and possess greater energy when they collide. Both of these factors increase the reaction rate. Hence the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate of virtually all reactions decreases with decreasing temperature. For example, refrigeration retards the rate of growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce. Figure 14.2 "The Effect of Temperature on Reaction Rates" shows how temperature affects the light emitted by two chemiluminescent light sticks.

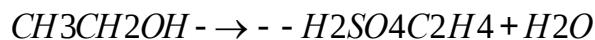
In systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100°C, ethanol is converted to diethyl ether:

Equation 14.1



At 180°C, however, a completely different reaction occurs, which produces ethylene as the major product:

Equation 14.2



Phase and Surface Area Effects

When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix). If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen. If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases. The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

Automobile engines use surface area effects to increase reaction rates. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigorous reaction (Figure 14.3 "The Effect of Surface Area on Reaction Rates"). Similar phenomena are partially responsible for dust explosions that occasionally destroy grain elevators or coal mines.

Solvent Effects

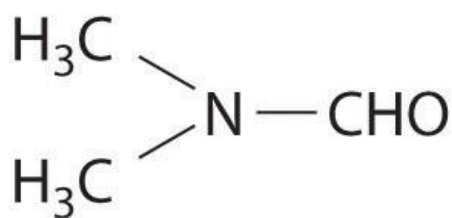
The nature of the solvent can also affect the reaction rates of solute particles. For example, a sodium acetate solution reacts with methyl iodide in an exchange reaction to give methyl acetate and sodium iodide.

Equation 14.3

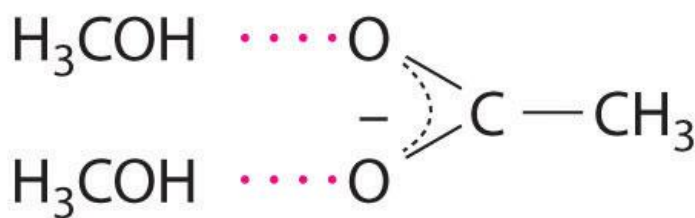


This reaction occurs 10 million times more rapidly in the organic solvent dimethylformamide [DMF; $(\text{CH}_3)_2\text{NCHO}$] than it does in methanol (CH_3OH). Although both are organic solvents with similar dielectric constants (36.7 for DMF versus 32.6 for methanol), methanol is able to hydrogen bond with

acetate ions, whereas DMF cannot. Hydrogen bonding reduces the reactivity of the oxygen atoms in the acetate ion.



DMF
(dimethylformamide)



methanol

acetate ion

Solvent viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time. Thus the reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

Catalyst Effects

You learned in Chapter 3 "Chemical Reactions" that a catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. Consider, for example, the decomposition of hydrogen peroxide in the presence and absence of different catalysts (Figure 14.4 "The Effect of Catalysts on Reaction Rates"). Because most catalysts are highly selective, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur.

The Effect of Catalysts on Reaction Rates

A solution of hydrogen peroxide (H_2O_2) decomposes in water so slowly that the change is not noticeable (left). Iodide ion acts as a catalyst for the decomposition of H_2O_2 , producing oxygen gas. The solution turns brown because of the reaction of H_2O_2 with I^- , which generates small amounts of I_3^- (center). The enzyme catalase is about 3 billion times more effective than iodide as a catalyst. Even in the presence of very small amounts of enzyme, the decomposition is vigorous (right).

Most of the bulk chemicals produced in industry are formed with catalyzed reactions. Recent estimates indicate that about 30% of the gross national product of the United States and other industrialized nations relies either directly or indirectly on the use of catalysts.

Summary

Factors that influence the reaction rates of chemical reactions include the concentration of reactants, temperature, the physical state of reactants and their dispersion, the solvent, and the presence of a catalyst.

KEY TAKEAWAY

- The reaction rate depends on the concentrations of the reactants, the temperature of the reaction, the phase and surface area of the reactants, the solvent, and the presence or the absence of a catalyst.

CONCEPTUAL PROBLEMS

1. What information can you obtain by studying the chemical kinetics of a reaction? Does a balanced chemical equation provide the same information? Why or why not?
2. If you were tasked with determining whether to proceed with a particular reaction in an industrial facility, why would studying the chemical kinetics of the reaction be important to you?
3. What is the relationship between each of the following factors and the reaction rate: reactant concentration, temperature of the reaction, physical properties of the reactants, physical and chemical properties of the solvent, and the presence of a catalyst?
4. A slurry is a mixture of a finely divided solid with a liquid in which it is only sparingly soluble. As you prepare a reaction, you notice that one of your reactants forms a slurry with the solvent, rather than a solution. What effect will this have on the reaction rate? What steps can you take to try to solve the problem?
5. Why does the reaction rate of virtually all reactions increase with an increase in temperature? If you were to make a glass of sweetened iced tea the old-fashioned way, by adding sugar and ice cubes to a glass of hot tea, which would you add first?
6. In a typical laboratory setting, a reaction is carried out in a ventilated hood with air circulation provided by outside air. A student noticed that a reaction that gave a high yield of a product in the winter gave a low yield of that same product in the summer, even though his technique did not change and the reagents and concentrations used were identical. What is a plausible explanation for the different yields?
7. A very active area of chemical research involves the development of solubilized catalysts that are not made inactive during the reaction process. Such catalysts are expected to increase reaction rates significantly relative to the same reaction run in the presence of a heterogeneous catalyst. What is the reason for anticipating that the relative rate will increase?

8. Water has a dielectric constant more than two times greater than that of methanol (80.1 for H_2O and 33.0 for CH_3OH). Which would be your solvent of choice for a substitution reaction between an ionic compound and a polar reagent, both of which are soluble in either methanol or water? Why?

ANSWERS

1. Kinetics gives information on the reaction rate and reaction mechanism; the balanced chemical equation gives only the stoichiometry of the reaction.
- 2.
3. Reaction rates generally increase with increasing reactant concentration, increasing temperature, and the addition of a catalyst. Physical properties such as high solubility also increase reaction rates. Solvent polarity can either increase or decrease the reaction rate of a reaction, but increasing solvent viscosity generally decreases reaction rates.
- 4.
5. Increasing the temperature increases the average kinetic energy of molecules and ions, causing them to collide more frequently and with greater energy, which increases the reaction rate. First dissolve sugar in the hot tea, and then add the ice.

14.2 Reaction Rates and Rate Laws

LEARNING OBJECTIVES

1. To determine the reaction rate.
2. To understand the meaning of a rate law.

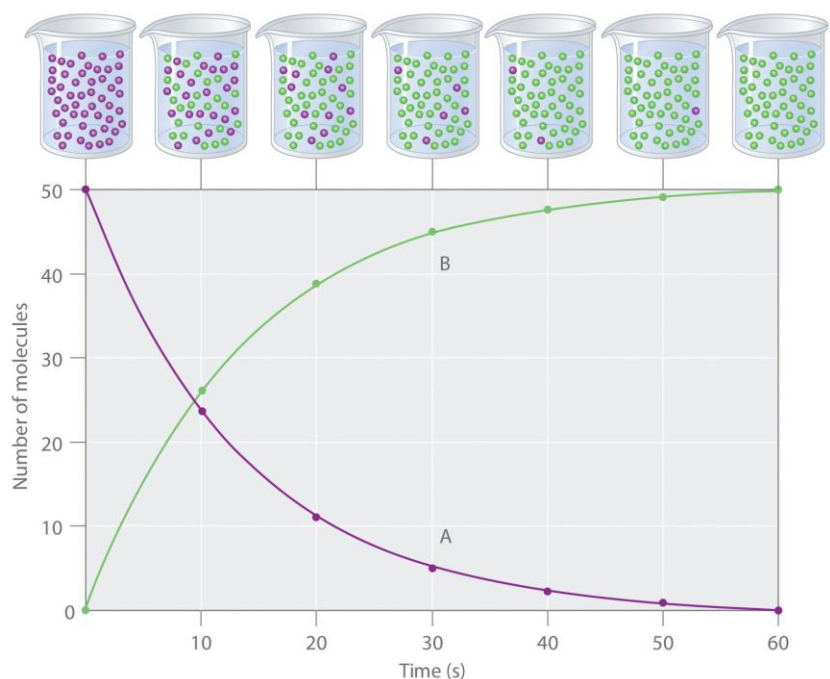
The factors discussed in Section 14.1 "Factors That Affect Reaction Rates" affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Reaction Rates

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the *change* in the concentration per unit time.

The progress of a simple reaction ($A \rightarrow B$) is shown in Figure 14.5 "The Progress of a Simple Reaction ($A \rightarrow B$)", where the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 14.5 "The Progress of a Simple Reaction ($A \rightarrow B$)". The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

Figure 14.5 *The Progress of a Simple Reaction ($A \rightarrow B$)*



The mixture initially contains only A molecules (purple). With increasing time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

Equation 14.4

$$\text{rate} = \frac{D[B]}{Dt} = - \frac{D[A]}{Dt}$$

Just as in Chapter 4 "Reactions in Aqueous Solution" and Chapter 5 "Energy Changes in Chemical Reactions", square brackets indicate molar concentrations, and the capital Greek delta (Δ) means "change in." Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of $\Delta[A]/\Delta t$ to convert that expression to a positive number. The reaction rate we would calculate for the reaction $A \rightarrow B$ using Equation 14.4 would be different for each interval. (This is not true for every reaction, as you will see later.) A much greater change occurs in [A]

and [B] during the first 10 s interval, for example, than during the last, which means that the reaction rate is fastest at first. This is consistent with the concentration effects described in Section 14.1 "Factors That Affect Reaction Rates" because the concentration of A is greatest at the beginning of the reaction.

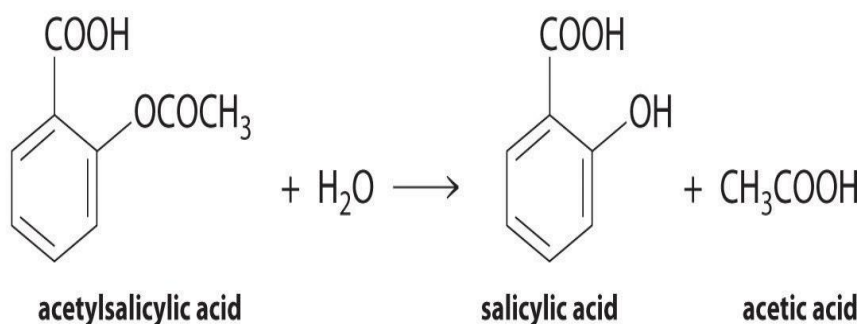
Note the Pattern

Reaction rates generally decrease with time as reactant concentrations decrease.

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 14.4 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world. (More than 25,000,000 kg are produced annually worldwide.) Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid.

Figure 14.6



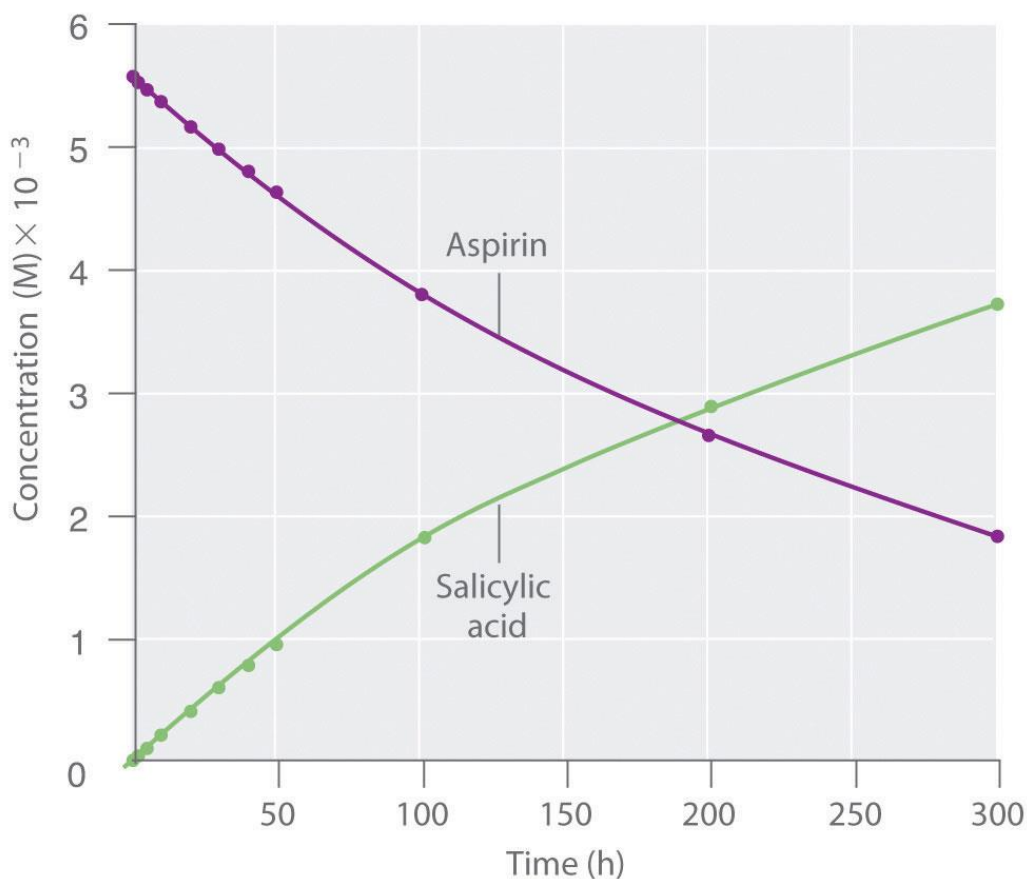
Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 14.1 "Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*" and are shown in the graph in Figure 14.7 "The Hydrolysis of Aspirin". These data were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

Table 14.1 Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}
*The reaction at pH 7.0 is very slow. It is <i>much</i> faster under acidic conditions, such as those found in the stomach.		

Figure 14.7 *The Hydrolysis of Aspirin*



This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1 "Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*". The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

We can calculate the average reaction rate for a given time interval from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_i). Using salicylic acid, for example, we find the reaction rate for the interval between $t = 0$ h and $t = 2.0$ h (recall that change is always calculated as final minus initial):

$$\begin{aligned} \text{rate}(t = 0 - 2.0 \text{ h}) &= [\text{salicylic acid}]_2 - [\text{salicylic acid}]_0 \div 2.0 \text{ h} - 0 \\ &= 0.040 \times 10^{-3} \text{ M} - 0 \text{ M} \div 2.0 \text{ h} = 2.0 \times 10^{-5} \text{ M/h} \end{aligned}$$

We can also calculate the reaction rate from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned} \text{rate}(t = 0 - 2.0 \text{ h}) &= -[\text{aspirin}]_2 - [\text{aspirin}]_0 \div 2.0 \text{ h} - 0 \text{ h} \\ &= -(5.51 \times 10^{-3} \text{ M}) - (5.55 \times 10^{-3} \text{ M}) \div 2.0 \text{ h} = 2 \times 10^{-5} \text{ M/h} \end{aligned}$$

If we now calculate the reaction rate during the last interval given in Table 14.1 "Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*" (the interval between 200 h and 300 h after the start of the reaction), we find that the reaction rate is significantly slower than it was during the first interval ($t = 0 - 2.0$ h):

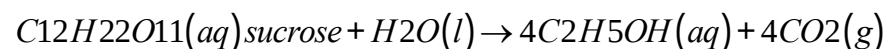
$$\begin{aligned} \text{rate}(t = 200 - 300 \text{ h}) &= [\text{salicylic acid}]_{300} - [\text{salicylic acid}]_{200} \div 300 \text{ h} - 200 \text{ h} \\ &= (3.73 \times 10^{-3} \text{ M}) - (2.91 \times 10^{-3} \text{ M}) \div 100 \text{ h} = 8.2 \times 10^{-6} \text{ M/h} \end{aligned}$$

You should verify from the data in Table 14.1 "Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*" that you get the same rate using the concentrations of aspirin measured at 200 h and 300 h.)

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Let us look at a reaction in which the coefficients are *not* all the same: the fermentation of sucrose to ethanol and carbon dioxide, which we encountered in Chapter 3 "Chemical Reactions".

Equation 14.5



The coefficients show us that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, we can find the reaction rate by looking at the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as you learned in Chapter 10 "Gases", the volume of CO_2 gas formed will

depend on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

Equation 14.6

$$\Delta[C_2H_5OH]/\Delta t = -4\Delta[sucrose]/\Delta t$$

The concentration of the reactant—in this case sucrose—*decreases* with increasing time, so the value of $\Delta[sucrose]$ is negative. Consequently, a minus sign is inserted in front of $\Delta[sucrose]$ in Equation 14.6 so that the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with increasing time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product that has the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 14.5) corresponds to sucrose, so the reaction rate is generally defined as follows:

Equation 14.7

$$rate = -\Delta[sucrose]/\Delta t = 1/4(\Delta[C_2H_5OH]/\Delta t)$$

EXAMPLE 1

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:



Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.

B For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution:

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, we define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B We know from the balanced chemical equation that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that we divide the rate of change of $[N_2O_5]$ and $[NO_2]$ by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2 , we must divide the rate of production of NO_2 by 4. The reaction rate expressions are as follows:

$$rate = \frac{d[O_2]}{dt} = \frac{d[NO_2]}{4dt} = -\frac{d[N_2O_5]}{2dt}$$

Exercise

The key step in the industrial production of sulfuric acid is the reaction of SO_2 with O_2 to produce SO_3 .
 $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer:

$$rate = -\frac{d[O_2]}{dt} = -\frac{d[SO_2]}{2dt} = \frac{d[SO_3]}{2dt}$$

EXAMPLE 2

Using the reaction shown in Example 1, calculate the reaction rate from the following data taken at 56°C :

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$			
Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A Using the equations in Example 1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution:

A We are asked to calculate the reaction rate in the interval between $t_1 = 240$ s and $t_2 = 600$ s. From Example 1, we see that we can evaluate the reaction rate using any of three expressions:

$$rate = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5 ,

$$rate = -\frac{\Delta[N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2(600 \text{ s} - 240 \text{ s})}$$

B Substituting actual values into the expression,

$$rate = -\frac{0.0197 \text{ M} - 0.0388 \text{ M}}{2(360 \text{ s})} = 2.65 \times 10^{-5} \text{ M/s}$$

Similarly, we can use NO_2 to calculate the reaction rate:

$$rate = \frac{\Delta[NO_2]}{4\Delta t} = \frac{[NO_2]_{600} - [NO_2]_{240}}{4(600 \text{ s} - 240 \text{ s})} \\ = \frac{0.0699 \text{ M} - 0.0314 \text{ M}}{4(360 \text{ s})} = 2.67 \times 10^{-5} \text{ M/s}$$

If we allow for experimental error, this is the same rate we obtained using the data for N_2O_5 , as it should be because the reaction rate should be the same no matter which concentration is used. We can also use the data for O_2 :

$$rate = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{600} - [O_2]_{240}}{600 \text{ s} - 240 \text{ s}} \\ = \frac{0.0175 \text{ M} - 0.00792 \text{ M}}{360 \text{ s}} = 2.66 \times 10^{-5} \text{ M/s}$$

Again, this is the same value we obtained from the N_2O_5 and NO_2 data. Thus the reaction rate does not depend on which reactant or product is used to measure it.

Exercise

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$			
Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer: $9.0 \times 10^{-6} \text{ M/s}$

Instantaneous Rates of Reaction

So far, we have determined average reaction rates over particular intervals of time. We can also determine the instantaneous rate of a reaction, which is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate.^[1]

Think of the distinction between the instantaneous and average rates of a reaction as being similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although you may travel for a long time at 65 mph on an interstate highway during a long trip, there may be times when you travel only 25 mph in construction zones or 0 mph if you stop for meals or gas. Thus your average speed on the trip may be only 50 mph, whereas your instantaneous speed on the interstate at a given moment may be 65 mph. Whether you are able to stop the car in time to avoid an accident depends on your instantaneous speed, not your average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval normally has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

In chemical kinetics, we generally focus on one particular instantaneous rate, which is the initial reaction rate, $t = 0$. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to $t = 0$.

Rate Laws

In Section 14.1 "Factors That Affect Reaction Rates", you learned that reaction rates generally decrease with time because reactant concentrations decrease as reactants are converted to products. You also learned that reaction rates generally increase when reactant concentrations are increased. We now examine the mathematical expressions called rate laws, which describe the relationships between reactant rates and reactant concentrations. Rate laws are laws as defined in Chapter 1 "Introduction to Chemistry"; that is, they are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives.

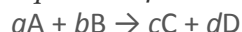
A differential rate law expresses the reaction rate in terms of *changes* in the concentration of one or more reactants ($\Delta[R]$) over a specific time interval (Δt). In contrast, an integrated rate law describes the reaction rate in terms of the *initial* concentration ($[R]_0$) and the *measured* concentration of one or more

reactants ($[R]$) after a given amount of time (t); we will discuss integrated rate laws in Section 14.3 "Methods of Determining Reaction Order". The integrated rate law can be found by using calculus to integrate the differential rate law, although the method of doing so is beyond the scope of this text. *Whether you use a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).*

Reaction Orders

For a reaction with the general equation

Equation 14.8



the experimentally determined rate law usually has the following form:

Equation 14.9

$$\text{rate} = k[A]^m[B]^n$$

The *proportionality constant* (k) is called the rate constant, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular value of the rate constant under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of k , however, does *not* change as the reaction progresses under a given set of conditions.

Thus the reaction rate depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers m and n , respectively. The values of m and n are derived from experimental measurements of the changes in reactant concentrations over time and indicate the reaction order, the degree to which the reaction rate depends on the concentration of each reactant; m and n need not be integers. For example, Equation 14.9 tells us that Equation 14.8 is m th order in reactant A and n th order in reactant B. It is important to remember that n and m are not related to the stoichiometric coefficients a and b in the balanced chemical equation and must be determined experimentally. The *overall reaction order* is the sum of all the exponents in the rate law: $m + n$.

Note the Pattern

Under a given set of conditions, the value of the rate constant does not change as the reaction progresses.

Although differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, integrated rate laws are used to determine the reaction order and the value of the rate constant from experimental measurements. (We present general forms for integrated rate laws in Section

14.3 "Methods of Determining Reaction Order".) To illustrate how chemists interpret a differential rate law, we turn to the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone. This reaction produces *t*-butanol according to the following equation:

Equation 14.10



Combining the rate expression in Equation 14.4 and Equation 14.9 gives us a general expression for the differential rate law:

Equation 14.11

$$\text{rate} = - \frac{d[A]}{dt} = k[A]^m[B]^n$$

Inserting the identities of the reactants into Equation 14.11 gives the following expression for the differential rate law for the reaction:

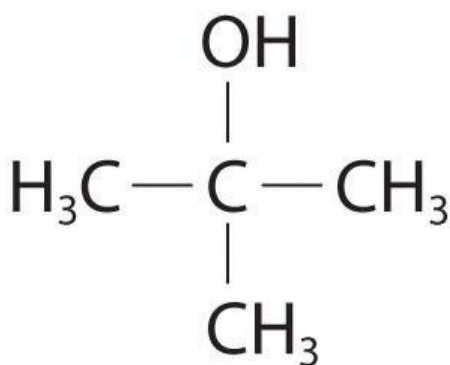
Equation 14.12

$$\text{rate} = - \frac{d[(\text{CH}_3)_3\text{CBr}]}{dt} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n$$

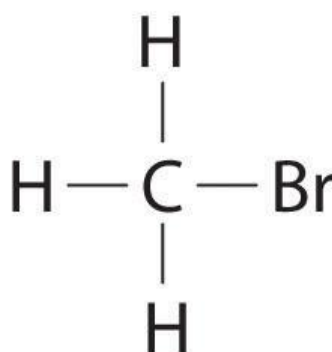
Experiments done to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(\text{CH}_3)_3\text{CBr}$ but is independent of the concentration of water. Thus *m* and *n* in Equation 14.12 are 1 and 0, respectively, and

Equation 14.13

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]^1[\text{H}_2\text{O}]^0 = k[(\text{CH}_3)_3\text{CBr}]$$



t-butanol



methyl bromide

Because

the exponent for the reactant is 1, the reaction is *first order* in $(\text{CH}_3)_3\text{CBr}$. It is *zeroth order* in water because the exponent for $[\text{H}_2\text{O}]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus the overall reaction order is $1 + 0 = 1$. What the reaction orders tell us in practical terms is that doubling the concentration of $(\text{CH}_3)_3\text{CBr}$ doubles the

reaction rate of the hydrolysis reaction, halving the concentration of $(\text{CH}_3)_3\text{CBr}$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has *no effect* on the reaction rate. (Again, when you work with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of k , m , and n in the rate law *must* be determined experimentally.) Experimental data show that k has the value $5.15 \times 10^{-4} \text{ s}^{-1}$ at 25°C . The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

Equation 14.14

$$\text{rate} = - \frac{d[\text{CH}_3\text{Br}]}{dt} = k'[\text{CH}_3\text{Br}]$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 14.14 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often change reaction conditions to obtain clues about what is occurring during a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. For methyl bromide, in contrast, the differential rate law becomes $\text{rate} = k''[\text{CH}_3\text{Br}][\text{OH}^-]$, with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, which again provides clues as to how the reactions differ on a molecular level.

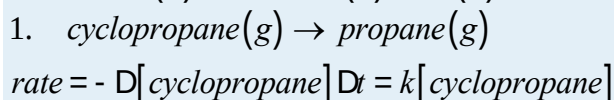
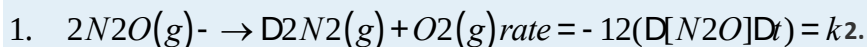
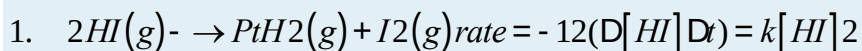
Note the Pattern

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements.

EXAMPLE 3

We present three reactions and their experimentally determined differential rate laws. For each reaction, give the *units* of the rate constant, give the reaction *order* with respect to each reactant, give the *overall*

reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.



Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:

A Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.

B Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Sum all exponents to obtain the overall reaction order.

C Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution:

1. **A** $[\text{HI}]^2$ will give units of (moles per liter)². For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

$$kM^2 = M/s \Rightarrow k = M/sM^2 = 1/M \cdot s = M^{-1} \cdot s^{-1}$$

B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

C If the concentration of HI is doubled, the reaction rate will increase from $k[\text{HI}]_0^2$ to $k(2[\text{HI}]_0)^2 = 4k[\text{HI}]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

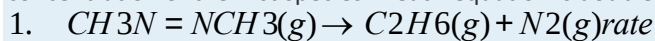
3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M \cdot s^{-1} = M/s$.

B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

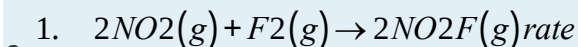
C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

Exercise

Given the following two reactions and their experimentally determined differential rate laws: determine the *units* of the rate constant if time is in seconds, determine the reaction *order* with respect to each reactant, give the *overall reaction order*, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.



$$= - \frac{d[CH_3N=NCH_3]}{dt} = k[CH_3N=NCH_3]$$



$$= - \frac{d[F_2]}{dt} = - \frac{1}{2} \frac{d[NO_2]}{dt} = k[NO_2][F_2]$$

Answer:

- s^{-1} ; first order in $CH_3N=NCH_3$; first order overall; doubling $[CH_3N=NCH_3]$ will double the reaction rate.
- $M^{-1} \cdot s^{-1}$; first order in NO_2 , first order in F_2 ; second order overall; doubling $[NO_2]$ will double the reaction rate.

Summary

Reaction rates are reported either as the **average rate** over a period of time or as the **instantaneous rate** at a single time.

The **rate law** for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a **differential rate law**,

describing the change in reactant or product concentrations as a function of time, or as an **integrated rate law**, describing the actual concentrations of reactants or products as a function of time.

The **rate constant** (k) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The power to which a concentration is raised in a rate law indicates the **reaction order**, the degree to which the reaction rate depends on the concentration of a particular reactant.

KEY TAKEAWAYS

- Reaction rates can be determined over particular time intervals or at a given point in time.
- A rate law describes the relationship between reactant rates and reactant concentrations.

KEY EQUATIONS

general definition of rate for $A \rightarrow B$

$$\text{Equation 14.4 : rate} = D[B]/Dt = -D[A]/Dt$$

$$\text{Equation 14.9 : rate} = k[A]^m[B]^n$$

general form of rate law when A and B are reactants

CONCEPTUAL PROBLEMS

1. Explain why the reaction rate is generally fastest at early time intervals. For the second-order $A + B \rightarrow C$, what would the plot of the concentration of C versus time look like during the course of the reaction?
2. Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?
3. Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order of $10^{10} \text{ L}/(\text{mol}\cdot\text{s})$. Would you expect the reactions to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+ + \text{N}(\text{CH}_3)_3 \rightarrow \text{H}_2\text{O} + \text{HN}(\text{CH}_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?
4. What information can you get from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?

5. During the hydrolysis reaction $A + H_2O \rightarrow B + C$, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How do you expect this effect to be reflected in the overall reaction order?

ANSWERS

1. Reactant concentrations are highest at the beginning of a reaction. The plot of $[C]$ versus t is a curve with a slope that becomes steadily less positive.
- 2.
3. Faster in a less viscous solvent because the rate of diffusion is higher; the H_3O^+/OH^- reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.
- 4.
- 5.

NUMERICAL PROBLEMS

1. The reaction rate of a particular reaction in which A and B react to make C is as follows:

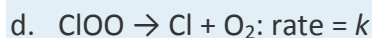
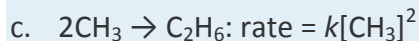
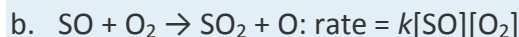
$$rate = - \frac{d[A]}{dt} = 12 \left(\frac{d[C]}{dt} \right)$$

Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?

2. While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?
3. Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

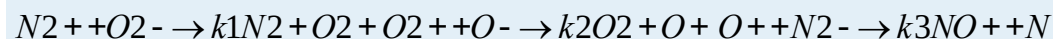
Time (s)	[A] (M)
120	0.158
240	0.089
360	0.062

4. Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.
 - a. $C_2H_5I \rightarrow C_2H_4 + HI$: $rate = k[C_2H_5I]$



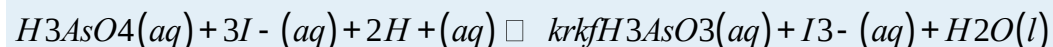
5. Cleavage of C_2H_6 to produce two $\text{CH}_3\cdot$ radicals is a gas-phase reaction that occurs at 700°C . This reaction is first order, with $k = 5.46 \times 10^{-4} \text{ s}^{-1}$. How long will it take for the reaction to go to 15% completion? to 50% completion?

6. Three chemical processes occur at an altitude of approximately 100 km in Earth's atmosphere.



Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = $k[\text{N}_2][\text{O}_2]$, which one of the steps is rate limiting?

7. The oxidation of aqueous iodide by arsenic acid to give I_3^- and arsenous acid proceeds via the following reaction:



Write an expression for the initial rate of decrease of $[\text{I}_3^-]$, $-\Delta[\text{I}_3^-]/\Delta t$. When the reaction rate of the forward reaction is equal to that of the reverse reaction: $k_f/k_r = [\text{H}_3\text{AsO}_3][\text{I}_3^-]/[\text{H}_3\text{AsO}_4][\text{I}^-]^3[\text{H}^+]^2$. Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

ANSWER

5. 298 s; 1270 s

[1] If you have studied calculus, you may recognize that the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

14.3 Methods of Determining Reaction Order

LEARNING OBJECTIVE

1. To know how to determine the reaction order from experimental data.

In the examples in this text, the exponents in the rate law are almost always the positive integers: 1 and 2 or even 0.

Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the

reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data.

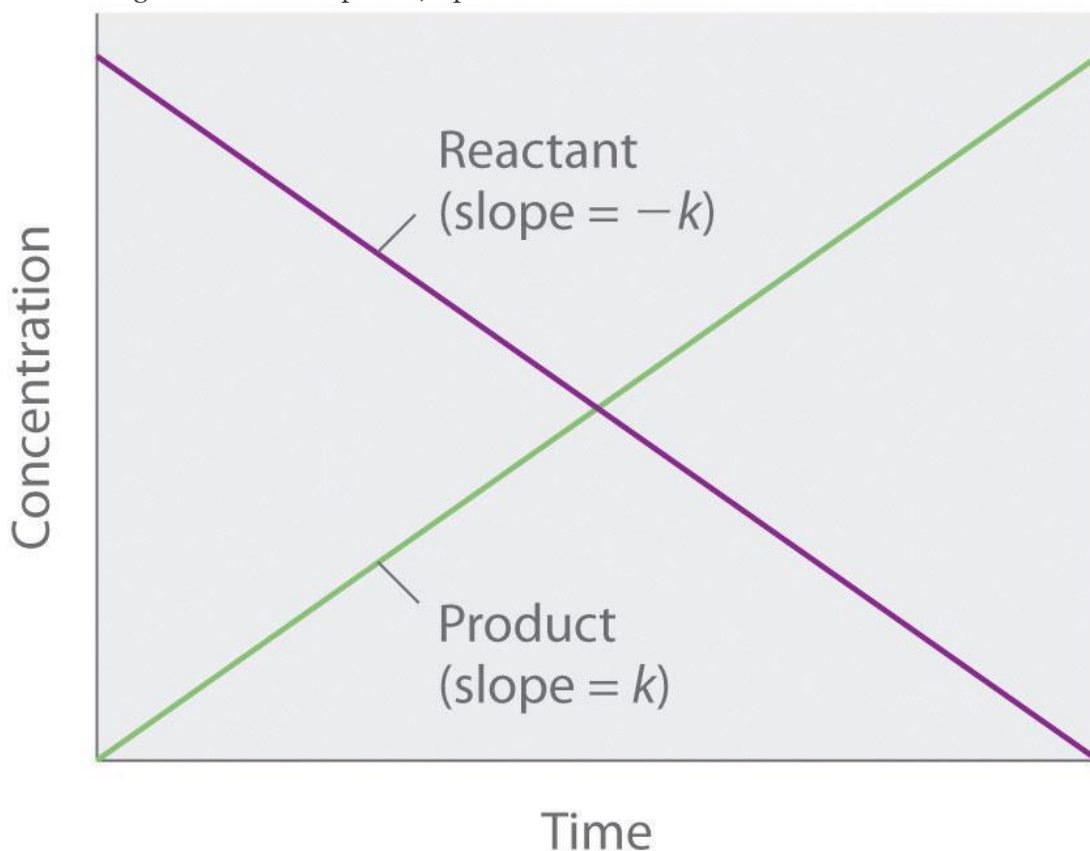
Zeroth-Order Reactions

A zeroth-order reaction is one whose rate is independent of concentration; its differential rate law is $\text{rate} = k$. We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

Equation 14.15

$$\text{rate} = -\frac{d[A]}{dt} = k[\text{reactant}]^0 = k(1) = k$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k , a positive value.



The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

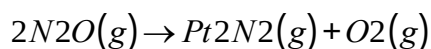
Equation 14.16

$$[A] = [A]_0 - kt$$

where $[A]_0$ is the initial concentration of reactant A. (Equation 14.16 has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = [A]$, $mx = -kt$, and $b = [A]_0$.) In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2 , which occurs at temperatures ranging from 200°C to 400°C:

Equation 14.17



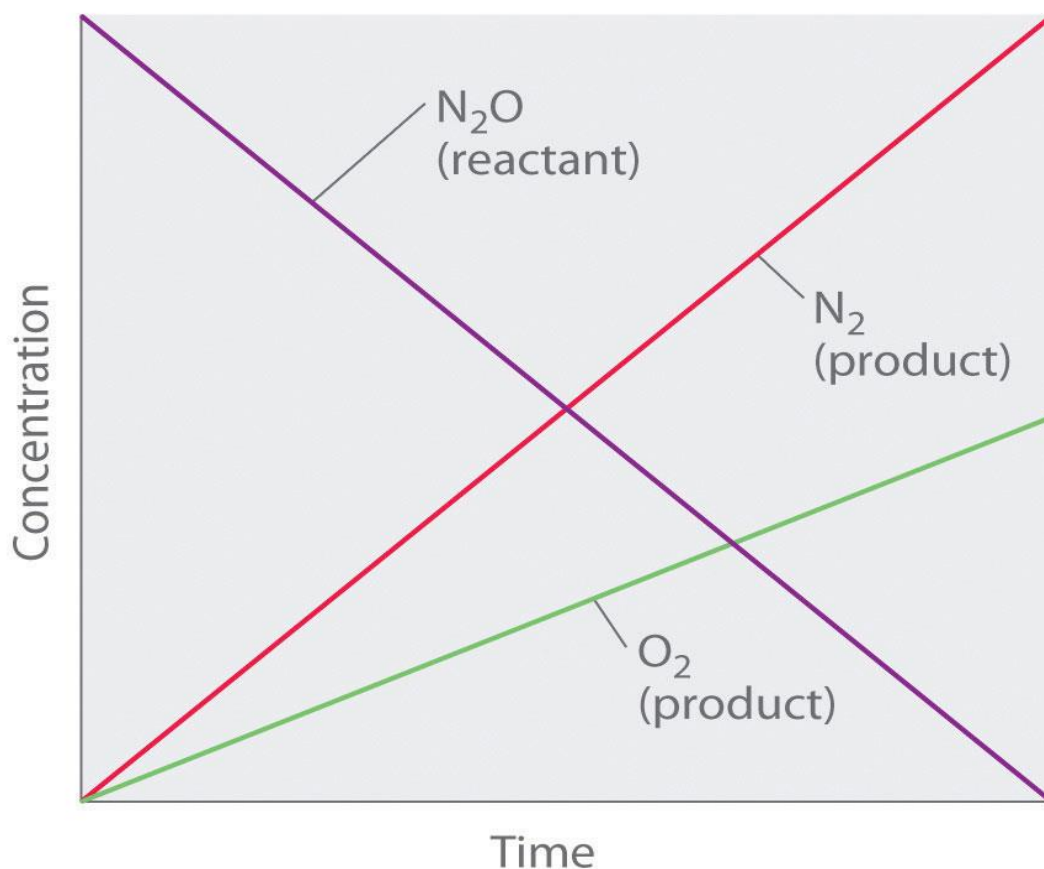
Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt *surface* available (not the *amount* of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate.^[1] The reaction rate is as follows:

Equation 14.18

$$\begin{aligned} \text{rate} &= - \frac{1}{2} \frac{d[N_2O]}{dt} \\ &= \frac{d[N_2]}{dt} = \frac{d[O_2]}{dt} \\ &= k[N_2O]_0 = k \end{aligned}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 14.8 "A Zeroth-Order Reaction", the change in the concentrations of all species with time is linear. Most important, the exponent (o) corresponding to the N_2O concentration in the experimentally derived rate law is *not* the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, *the rate law must be determined experimentally*.

Figure 14.8 A Zeroth-Order Reaction



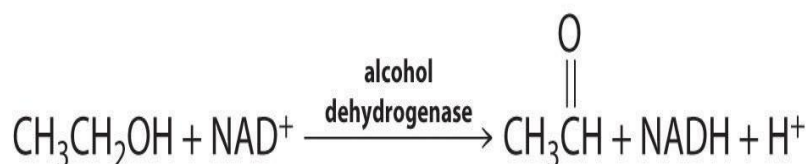
This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Note the Pattern

If a plot of reactant concentration versus time is linear, then the reaction is zeroth order in that reactant.

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the enzyme alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

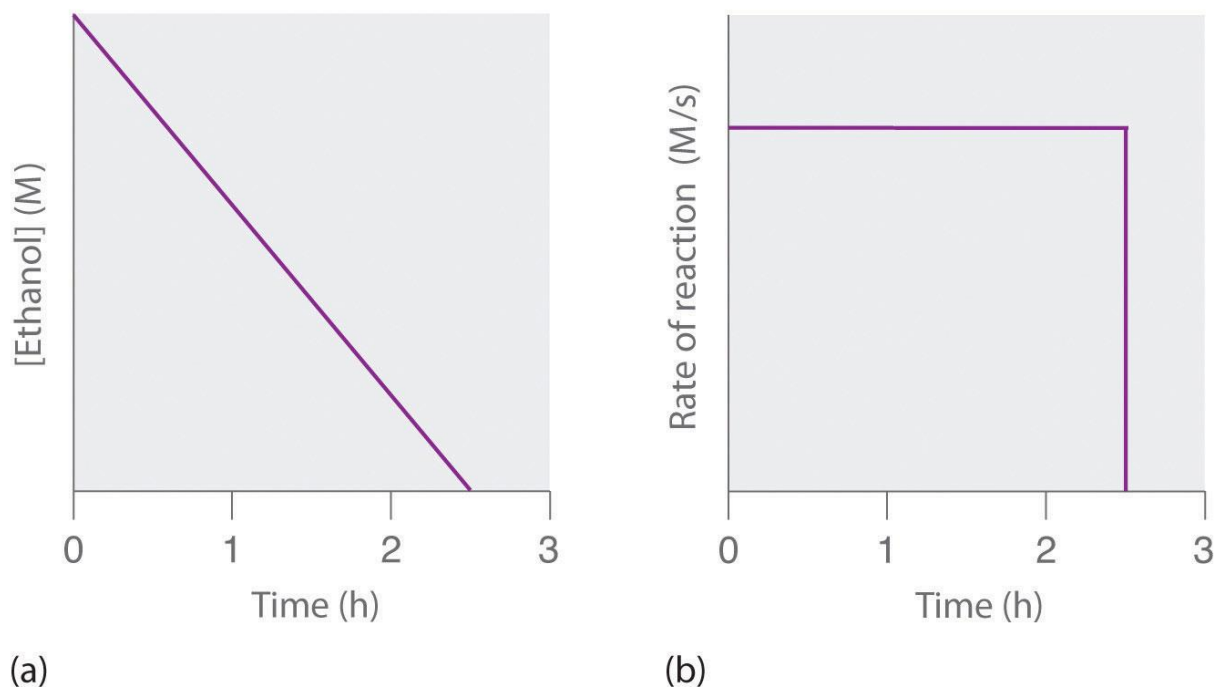
Figure 14.9



where NAD^+ (nicotinamide adenine dinucleotide) and $NADH$ (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (part (a) in Figure 14.10 "The Catalyzed Oxidation of Ethanol"). An average 70 kg person

typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver.^[2] When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 14.10 "The Catalyzed Oxidation of Ethanol").

Figure 14.10 *The Catalyzed Oxidation of Ethanol*



(a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a first-order reaction, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form $A \rightarrow \text{products}$. The differential rate for a first-order reaction is as follows:

Equation 14.19

$$\text{rate} = - \frac{d[A]}{dt} = k[A]$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

Equation 14.20

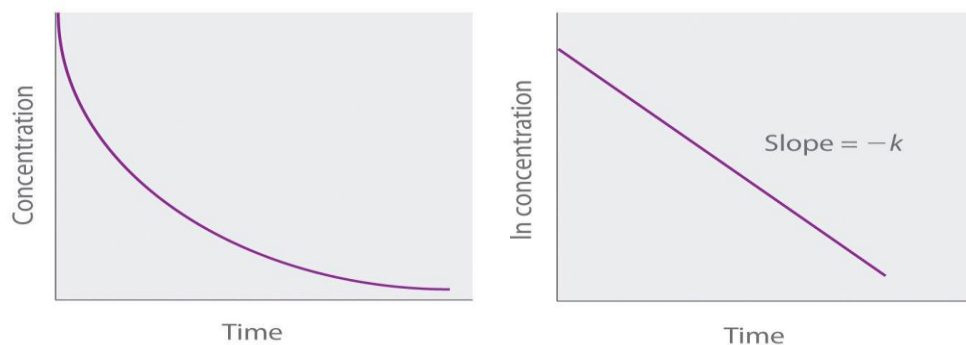
$$[A] = [A]_0 e^{-kt}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. (Essential Skills 6 in Chapter 11 "Liquids", Section 11.9 "Essential Skills 6", discusses natural logarithms.) Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 14.20 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 14.20 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t :

Equation 14.21

$$\ln[A] = \ln[A]_0 - kt$$

Because Equation 14.21 has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 14.19) or the integrated rate law (Equation 14.21) can be used to determine whether a particular reaction is first order.

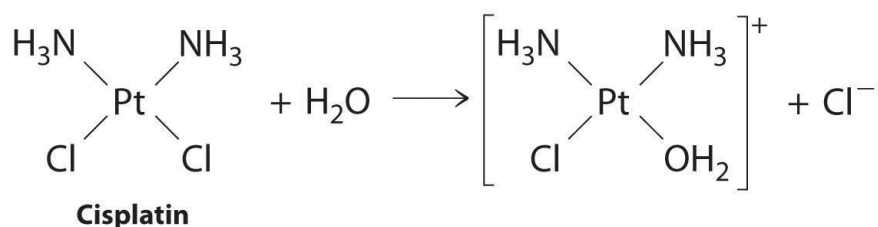


Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. In this chapter, we have already encountered two examples of first-order reactions: the hydrolysis of aspirin (Figure 14.6) and the reaction of *t*-butyl bromide with water to give *t*-butanol (Equation 14.10). Another reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin.

Cisplatin, the first “inorganic” anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

Figure 14.11



Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 14.11 is important because cisplatin, the form in which the drug is administered, is *not* the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 14.11 have been studied extensively to find ways of maximizing the concentration of the active species.

Note the Pattern

If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 14.2 "Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C". The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin. Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 14.2 "Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C" shows that the reaction rate doubles $[(1.8 \times 10^{-5} \text{ M/min}) \div (9.0 \times 10^{-6} \text{ M/min}) = 2.0]$ when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 $[(4.5 \times 10^{-5} \text{ M/min}) \div (9.0 \times 10^{-6} \text{ M/min}) = 5.0]$ when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is $\text{rate} = k[\text{cisplatin}]^1$. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 14.2 "Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C". For example, substituting the values for Experiment 3 into Equation 14.19,

$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Table 14.2 Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	[Cisplatin] ₀ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

EXAMPLE 4

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:



Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

Experiment	[CH ₃ CH ₂ Cl] ₀ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

B Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution:

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to [CH₃CH₂Cl]. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to [CH₃CH₂Cl].

B This behavior is characteristic of a first-order reaction, for which the rate law is $\text{rate} = k[\text{CH}_3\text{CH}_2\text{Cl}]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8} \text{ M/s} = k(0.010 \text{ M})1.6 \times 10^{-6} \text{ s}^{-1} = k$$

Exercise

Sulfuryl chloride (SO₂Cl₂) decomposes to SO₂ and Cl₂ by the following reaction:

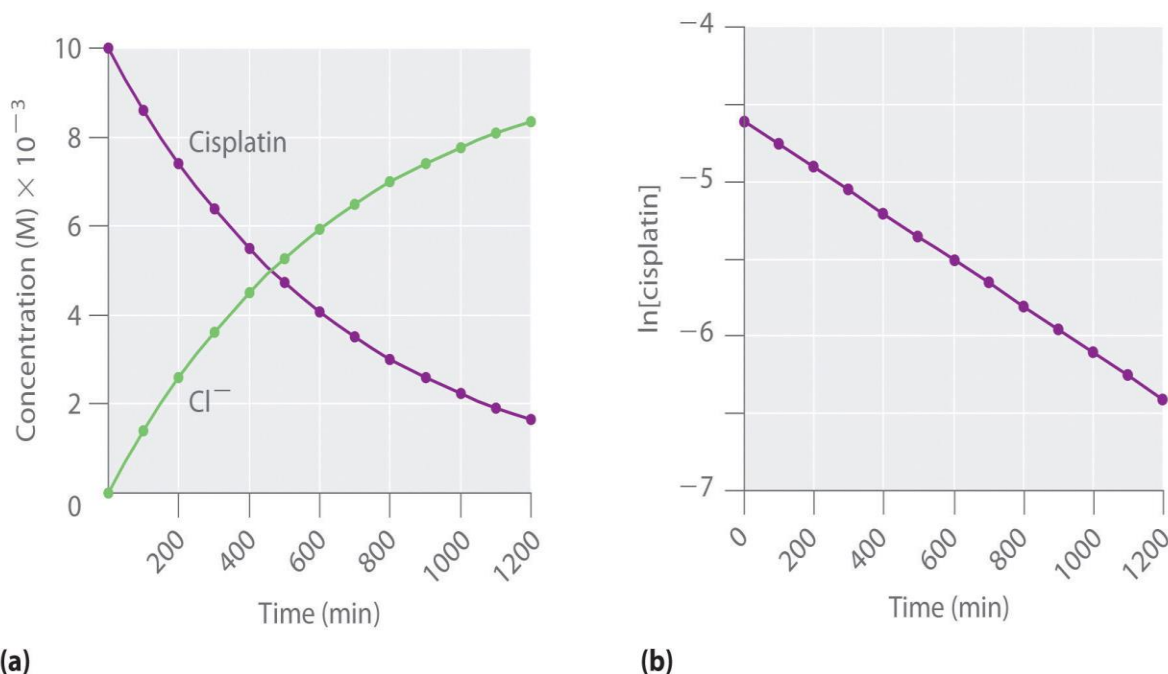


Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Experiment	[SO ₂ Cl ₂] ₀ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer: first order; $k = 2.2 \times 10^{-5} \text{ s}^{-1}$

Figure 14.12 *The Hydrolysis of Cisplatin, a First-Order Reaction*



These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Part (a) in Figure 14.12 "The Hydrolysis of Cisplatin, a First-Order Reaction" shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C. The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of

cisplatin versus time, we obtain the plot shown in part (b) in Figure 14.12 "The Hydrolysis of Cisplatin, a First-Order Reaction". The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 14.12 "The Hydrolysis of Cisplatin, a First-Order Reaction" for $t = 100 \text{ min}$ ($[\text{cisplatin}] = 0.0086 \text{ M}$) and $t = 1000 \text{ min}$ ($[\text{cisplatin}] = 0.0022 \text{ M}$),

$$\begin{aligned} \text{slope} - k &= \frac{\ln [\text{cisplatin}]_{1000} - \ln [\text{cisplatin}]_{100}}{1000 \text{ min} - 100 \text{ min}} \\ &= \frac{\ln 0.0022 - \ln 0.0086}{1000 \text{ min} - 100 \text{ min}} = \frac{-6.12 - (-4.76)}{900 \text{ min}} = -1.51 \times 10^{-3} \text{ min}^{-1} = -1.5 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 14.12 "The Hydrolysis of Cisplatin, a First-Order Reaction" are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

EXAMPLE 5

Refer back to Example 4. If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C , what is the concentration of ethyl chloride after 10 h ? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ? (Recall that we calculated the rate constant for this reaction in Example 4.)

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A Substitute values for the initial concentration ($[\text{A}]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ($[\text{A}]$) at the given time t .

B Given a concentration $[\text{A}]$, solve the integrated rate law for time t .

Solution:

The exponential form of the integrated rate law for a first-order reaction (Equation 14.20) is $[\text{A}] = [\text{A}]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having calculated the rate constant in Example 4 ($k = 1.6 \times 10^{-6} \text{ s}^{-1}$), we can use the rate law to calculate the concentration of the reactant at a given time t . Substituting the known values into the integrated rate law,

$$[CH_3CH_2Cl]_{10 \text{ h}} = [CH_3CH_2Cl]_0 e^{-kt} \\ = 0.0200 \text{ M} (e^{-(1.6 \times 10^{-6} \text{ s}^{-1})(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min})}) = 0.0189 \text{ M}$$

We could also have used the logarithmic form of the integrated rate law (Equation 14.21):

$$\ln[CH_3CH_2Cl]_{10 \text{ h}} - \ln[CH_3CH_2Cl]_0 = -kt \\ = \ln 0.0200 - (1.6 \times 10^{-6} \text{ s}^{-1})(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min}) = -3.912 \\ -0.0576 = -3.970 = e^{-3.970} \text{ M} = 0.0189 \text{ M}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t . Equation 14.21 gives the following:

$$\ln[CH_3CH_2Cl]_0 - \ln[CH_3CH_2Cl]_t = kt \\ [t = \ln 4.0] / (1.6 \times 10^{-6} \text{ s}^{-1}) = 8.7 \times 10^5 \text{ s} = 240 \text{ h} = 2.4 \times 10^2$$

Exercise

In the exercise in Example 4, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C . Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C . How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer: 0.0252 M; 29 h

Second-Order Reactions

The simplest kind of second-order reaction is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form $2A \rightarrow \text{products}$. A second kind of second-order reaction has a reaction rate that is proportional to the *product* of the concentrations of two reactants. Such reactions generally have the form $A + B \rightarrow \text{products}$. An example of the former is a *dimerization reaction*, in which two smaller molecules, each called a *monomer*, combine to form a larger molecule (a *dimer*).

The differential rate law for the simplest second-order reaction in which $2A \rightarrow \text{products}$ is as follows:

Equation 14.22

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse

(M⁻¹·s⁻¹). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

Equation 14.23

$$1[A] = 1[A]_0 + kt$$

Because Equation 14.23 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of $1/[A]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

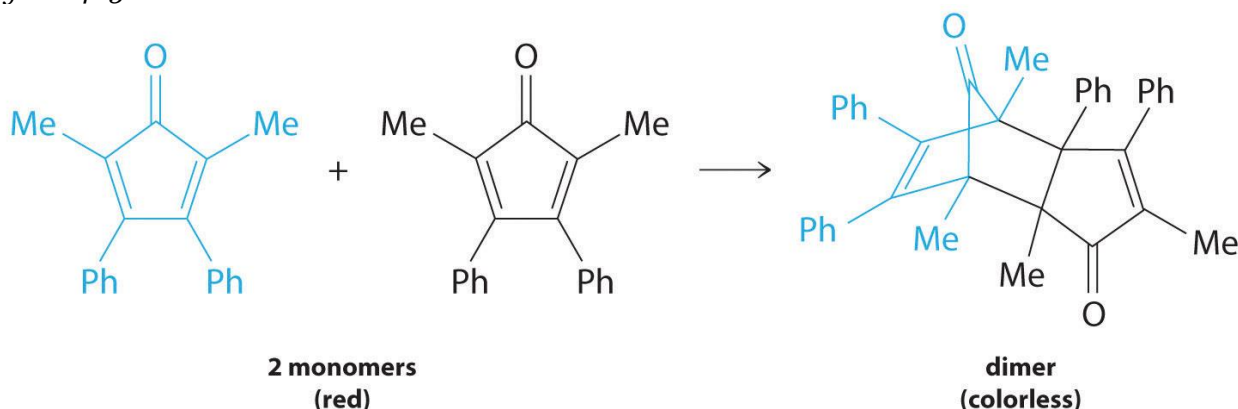
Note the Pattern

Second-order reactions generally have the form 2A → products or A + B → products.

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO₂ to NO and O₂ and the decomposition of HI to I₂ and H₂. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

Figure 14.13



For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively.^[3] Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the

synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 14.22) or the integrated rate law (Equation 14.23).

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 14.3 "Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M". From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$5.0 \times 10^{-5} \text{ M/min} / 1.8 \times 10^{-5} \text{ M/min} = 2.8$$

$$\text{and } 3.4 \times 10^{-3} \text{ M} / 2.0 \times 10^{-3} \text{ M} = 1.7$$

Table 14.3 Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

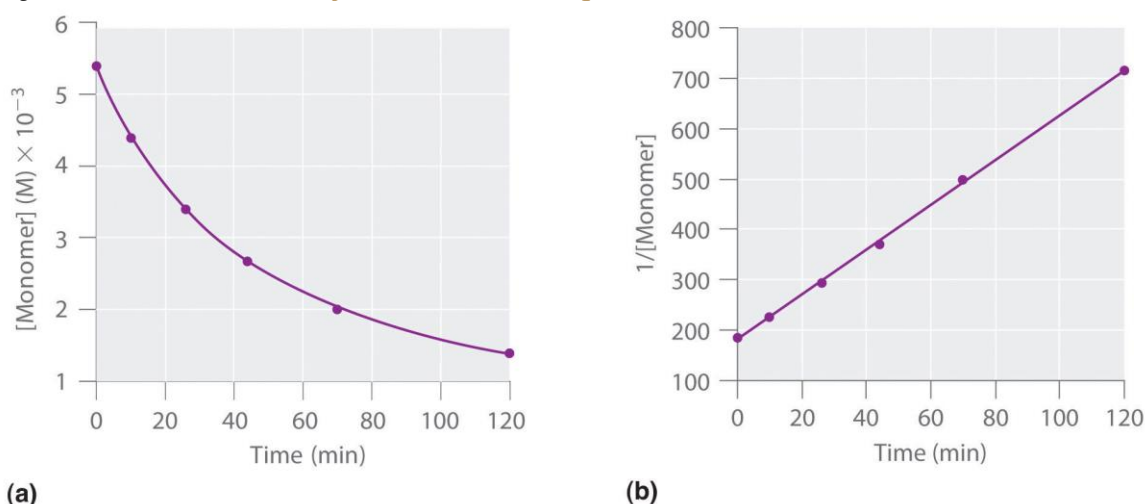
This means that the reaction is second order in the monomer. Using Equation 14.22 and the data from any row in Table 14.3 "Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M", we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\begin{aligned} \text{rate} &= 8.0 \times 10^{-5} \text{ M/min} = k[A]^2 \\ &= k(4.4 \times 10^{-3} \text{ M})^2 = k \end{aligned}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in part (a) in Figure

14.14 "Dimerization of a Monomeric Compound, a Second-Order Reaction". The measurements show that the concentration of the monomer (initially $5.4 \times 10^{-3} \text{ M}$) decreases with increasing time. This graph also shows that the reaction *rate* decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of $1/[\text{monomer}]$ versus t should be a straight line, as shown in part (b) in Figure 14.14 "Dimerization of a Monomeric Compound, a Second-Order Reaction". Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1 \text{ M}^{-1}\cdot\text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. *The reaction order must always be determined experimentally.*

Figure 14.14 *Dimerization of a Monomeric Compound, a Second-Order Reaction*



These plots correspond to dimerization of the monomer in Figure 14.13 " " as (a) the experimentally determined concentration of monomer versus time and (b) $1/[\text{monomer}]$ versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the *same order*, the reaction with the largest rate constant is the fastest.

Because the units of the rate constants for zeroth-, first-, and second-order reactions are different,

however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

The differential and integrated rate laws for zeroth-, first-, and second-order reactions and their

corresponding graphs are shown in Figure 14.16 "Properties of Reactions That Obey Zeroth-, First-, and

Second-Order Rate Laws" in Section 14.4 "Using Graphs to Determine Rate Laws, Rate Constants, and Reaction Orders".

EXAMPLE 6

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.



Experimental data for the reaction at 300°C and four initial concentrations of NO₂ are listed in the following table:

Experiment	[NO ₂] ₀ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.

B Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (*k*).

Solution:

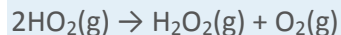
A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO₂ concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate $[(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0]$, which means that the reaction rate is proportional to [NO₂]². Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to [NO₂]². This behavior is characteristic of a second-order reaction.

B We have rate = $k[\text{NO}_2]^2$. We can calculate the rate constant (*k*) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\begin{aligned} \text{rate} &= 5.40 \times 10^{-5} \text{ M/s} \\ &= k[\text{NO}_2]^2 = k(0.010 \text{ M})^2 = k \end{aligned}$$

Exercise

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:



The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Experiment	$[\text{HO}_2]_0 \text{ (M)}$	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer: second order in HO_2 ; $k = 1.4 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$

Note the Pattern

If a plot of reactant concentration versus time is not linear but a plot of $1/\text{reaction concentration}$ versus time is linear, then the reaction is second order.

EXAMPLE 7

If a flask that initially contains 0.056 M NO_2 is heated at 300°C , what will be the concentration of NO_2 after 1.0 h ? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration?

Use the integrated rate law for a second-order reaction (Equation 14.23) and the rate constant calculated in Example 6.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A Given k , t , and $[\text{A}]_0$, use the integrated rate law for a second-order reaction to calculate $[\text{A}]$.

B Setting $[\text{A}]$ equal to $1/10$ of $[\text{A}]_0$, use the same equation to solve for t .

Solution:

A We know k and $[\text{NO}_2]_0$, and we are asked to determine $[\text{NO}_2]$ at $t = 1 \text{ h}$ (3600 s). Substituting the appropriate values into Equation 14.23,

$$1[\text{NO}_2]_{3600} = 1[\text{NO}_2]_0 + kt$$

$$= 10.056 \text{ M} + [(0.54 \text{ M} - 1 \times 10^{-4} \text{ M}) - 1](3600 \text{ s}) = 2.0 \times 10^{-3} \text{ M}$$

Thus $[\text{NO}_2]_{3600} = 5.1 \times 10^{-4} \text{ M}$.

B In this case, we know k and $[\text{NO}_2]_0$, and we are asked to calculate at what time $[\text{NO}_2] = 0.1[\text{NO}_2]_0 = 0.1(0.056 \text{ M}) = 0.0056 \text{ M}$. To do this, we solve Equation 14.23 for t , using the concentrations given.

$$t = (1/[\text{NO}_2]) - (1/[\text{NO}_2]_0)k$$

$$= (1/0.0056 \text{ M}) - (1/0.056 \text{ M})0.54 \text{ M} \cdot 1 \times 10^{-4} \text{ s}^{-1} = 3.0 \times 10^2 \text{ s} = 5.0 \text{ min}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise

In the exercise in Example 6, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2 , calculate the concentration of HO_2 that remains after 1.0 h at 25°C . How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 14.23) and the rate constant calculated in the exercise in Example 6.

Answer: $2.0 \times 10^{-13} \text{ M}$; $6.4 \times 10^{-6} \text{ s}$

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $\text{A} + \text{B} \rightarrow \text{products}$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

Equation 14.24

$$\text{rate} = -\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = k[\text{A}][\text{B}]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant. We presented one example at the end of Section 14.2 "Reaction Rates and Rate Laws", the reaction of CH_3Br with OH^- to produce CH_3OH .

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding reaction mechanisms can simplify what might seem to be a confusing variety of chemical

reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law.

This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow \text{products}$, for example, we need to determine k and the exponents m and n in the following equation:

Equation 14.25

$$\text{rate} = k[A]^m[B]^n$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments.

Rate data for a hypothetical reaction of the type $A + B \rightarrow \text{products}$ are given in Table 14.4 "Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow \text{Products}$ ". The general rate law for the reaction is given in Equation 14.25. We can obtain m or n directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 14.4 "Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow \text{Products}$ ".

Table 14.4 Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow \text{Products}$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

$$\text{rate}_1 = k[A_1]^m[B_1]^n \quad \text{rate}_3 = k[A_3]^m[B_3]^n$$

Inserting the appropriate values from Table 14.4 "Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow \text{Products}$ ",

$$\frac{8.5 \times 10^{-3} \text{ M/min}}{3.4 \times 10^{-3} \text{ M/min}} = \frac{k[0.50 \text{ M}]^m[0.50 \text{ M}]^n}{k[1.00 \text{ M}]^m[0.50 \text{ M}]^n}$$

Because 1.00 to any power is 1, $[1.00 \text{ M}]^m = 1.00 \text{ M}$. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for m .

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for n .

$$\frac{\text{rate}_5}{\text{rate}_1} = \frac{k[A]^m[B]^n}{k[A]^m[B]^n}$$

Substituting the appropriate values from Table 14.4 "Rate Data for a Hypothetical Reaction of the Form A + B → Products",

$$\frac{8.5 \times 10^{-3} \text{ M/min}}{8.5 \times 10^{-3} \text{ M/min}} = \frac{k[0.50 \text{ M}]^m[0.50 \text{ M}]^n}{k[0.50 \text{ M}]^m[1.00 \text{ M}]^n}$$

Canceling leaves $1.0 = [0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$\text{rate} = k[A]^2[B]^0 = k[A]^2$$

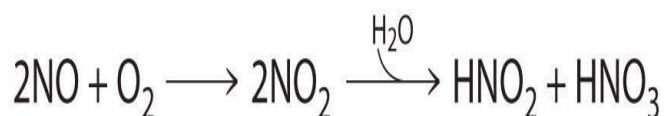
We can now calculate the rate constant by inserting the data from any row of Table 14.4 "Rate Data for a Hypothetical Reaction of the Form A + B → Products" into the experimentally determined rate law and solving for k . Using Experiment 2, we obtain

$$19 \times 10^{-3} \text{ M/min} = k(0.75 \text{ M})^2 3.4 \times 10^{-2} \text{ M}^{-1} \cdot \text{min}^{-1} = k$$

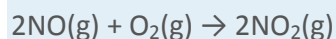
You should verify that using data from any other row of Table 14.4 "Rate Data for a Hypothetical Reaction of the Form A + B → Products" gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

EXAMPLE 8

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O₂ to give NO₂, which then reacts rapidly with water to give nitrous acid and nitric acid:



These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O₂ at 25°C:



Determine the rate law for the reaction and calculate the rate constant.

Experiment	[NO] ₀ (M)	[O ₂] ₀ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.

B Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for k .

Solution:

A Comparing Experiments 1 and 2 shows that as [O₂] is doubled at a constant value of [NO], the reaction rate approximately doubles. Thus the reaction rate is proportional to [O₂]¹, so the reaction is first order in O₂. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and [O₂] is held constant. That is, the reaction rate is proportional to [NO]², which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{7.98 \times 10^{-3} \text{ M/s}}{(0.0235 \text{ M})^2(0.0125 \text{ M})} = 1.16 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$$

The overall reaction order ($m + n$) is 3, so this is a third-order reaction, a reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

Exercise

The peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:
 $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 3\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_3^-(\text{aq})$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

Experiment	$[\text{S}_2\text{O}_8^{2-}]_0$ (M)	$[\text{I}^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer: rate = $k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$; $k = 20 \text{ M}^{-1}\cdot\text{s}^{-1}$

Summary

The reaction rate of a **zeroth-order reaction** is independent of the concentration of the reactants. The reaction rate of a **first-order reaction** is directly proportional to the concentration of one reactant. The reaction rate of a simple **second-order reaction** is proportional to the square of the concentration of one reactant. Knowing the **rate law** of a reaction gives clues to the **reaction mechanism**.

KEY TAKEAWAY

- Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data.

KEY EQUATIONS

zeroth-order reaction

Equation 14.15: $\text{rate} = -\frac{d[A]}{dt} = k$

Equation 14.16: $[A] = [A]_0 - kt$

first-order reaction

Equation 14.19: $\text{rate} = -\frac{d[A]}{dt} = k[A]$

Equation 14.20: $[A] = [A]_0 e^{-kt}$

Equation 14.21: $\ln[A] = \ln[A]_0 - kt$

second-order reaction

Equation 14.22: $\text{rate} = -\frac{d[A]}{dt} = k[A]^2$

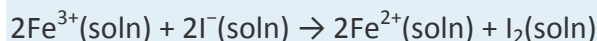
Equation 14.23: $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

CONCEPTUAL PROBLEMS

1. What are the characteristics of a zeroth-order reaction? Experimentally, how would you determine whether a reaction is zeroth order?
2. Predict whether the following reactions are zeroth order and explain your reasoning.
 - a. a substitution reaction of an alcohol with HCl to form an alkyl halide and water
 - b. catalytic hydrogenation of an alkene
 - c. hydrolysis of an alkyl halide to an alcohol
 - d. enzymatic conversion of nitrate to nitrite in a soil bacterium
3. In a first-order reaction, what is the advantage of using the integrated rate law expressed in natural logarithms over the rate law expressed in exponential form?
4. If the reaction rate is directly proportional to the concentration of a reactant, what does this tell you about (a) the reaction order with respect to the reactant and (b) the overall reaction order?
5. The reaction of NO with O₂ is found to be second order with respect to NO and first order with respect to O₂. What is the overall reaction order? What is the effect of doubling the concentration of each reagent on the reaction rate?

NUMERICAL PROBLEMS

1. Iodide reduces Fe(III) according to the following reaction:

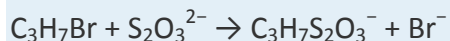


Experimentally, it was found that doubling the concentration of Fe(III) doubled the reaction rate, and doubling the iodide concentration increased the reaction rate by a factor of 4. What is the reaction order with respect to each species? What is the overall rate law? What is the overall reaction order?

2. Benzoyl peroxide is a medication used to treat acne. Its rate of thermal decomposition at several concentrations was determined experimentally, and the data were tabulated as follows:

Experiment	[Benzoyl Peroxide] ₀ (M)	Initial Rate (M/s)
1	1.00	2.22×10^{-4}
2	0.70	1.64×10^{-4}
3	0.50	1.12×10^{-4}
4	0.25	0.59×10^{-4}

3. What is the reaction order with respect to benzoyl peroxide? What is the rate law for this reaction?
4. 1-Bromopropane is a colorless liquid that reacts with S₂O₃²⁻ according to the following reaction:



The reaction is first order in 1-bromopropane and first order in $\text{S}_2\text{O}_3^{2-}$, with a rate constant of $8.05 \times 10^{-4} \text{ M}^{-1}\cdot\text{s}^{-1}$. If you began a reaction with 40 mmol/100 mL of $\text{C}_3\text{H}_7\text{Br}$ and an equivalent concentration of $\text{S}_2\text{O}_3^{2-}$, what would the initial reaction rate be? If you were to decrease the concentration of each reactant to 20 mmol/100 mL, what would the initial reaction rate be?

5. The experimental rate law for the reaction $3\text{A} + 2\text{B} \rightarrow \text{C} + \text{D}$ was found to be $\Delta[\text{C}]/\Delta t = k[\text{A}]^2[\text{B}]$ for an overall reaction that is third order. Because graphical analysis is difficult beyond second-order reactions, explain the procedure for determining the rate law experimentally.

ANSWERS

1. First order in Fe^{3+} ; second order in I^- ; third order overall; rate = $k[\text{Fe}^{3+}][\text{I}^-]^2$.
- 2.
3. $1.29 \times 10^{-4} \text{ M/s}$; $3.22 \times 10^{-5} \text{ M/s}$

[1] At very low concentrations of N_2O , where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration.

[2] Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol.

[3] The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by "dimer."

14.4 Using Graphs to Determine Rate Laws, Rate Constants, and Reaction Orders

LEARNING OBJECTIVE

1. To use graphs to analyze the kinetics of a reaction.

In Section 14.3 "Methods of Determining Reaction Order", you learned that the integrated rate law for each common type of reaction (zeroth, first, or second order in a single reactant) can be plotted as a straight line. Using these plots offers an alternative to the methods described for showing how reactant concentration changes with time and determining reaction order. We will illustrate the use of these graphs by considering the thermal decomposition of NO_2 gas at elevated temperatures, which occurs according to the following reaction:

Equation 14.26

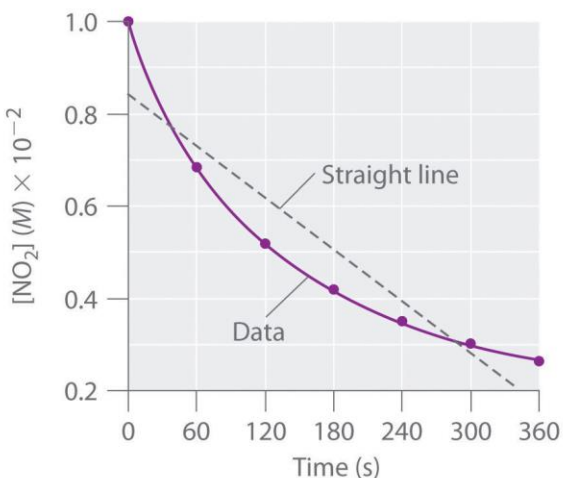


Experimental data for this reaction at 330°C are listed in Table 14.5 "Concentration of NO"; they are provided as $[\text{NO}_2]$, $\ln[\text{NO}_2]$, and $1/[\text{NO}_2]$ versus time to correspond to the integrated rate laws for zeroth-, first-, and second-order reactions, respectively. The actual concentrations of NO_2 are plotted versus time in part (a) in Figure 14.15 "The Decomposition of NO". Because the plot of $[\text{NO}_2]$ versus t is not a straight line, we know the reaction is not zeroth order in NO_2 . A plot of $\ln[\text{NO}_2]$ versus t (part (b) in Figure 14.15 "The Decomposition of NO") shows us that the reaction is not first order in NO_2 because a first-order reaction would give a straight line. Having eliminated zeroth-order and first-order behavior, we construct a plot of $1/[\text{NO}_2]$ versus t (part (c) in Figure 14.15 "The Decomposition of NO"). This plot is a straight line, indicating that the reaction is second order in NO_2 .

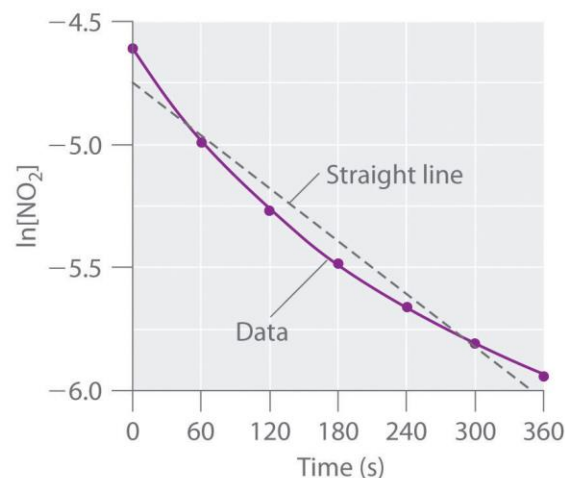
Table 14.5 Concentration of NO_2 as a Function of Time at 330°C

Time (s)	$[\text{NO}_2]$ (M)	$\ln[\text{NO}_2]$	$1/[\text{NO}_2]$ (M^{-1})
0	1.00×10^{-2}	-4.605	100
60	6.83×10^{-3}	-4.986	146
120	5.18×10^{-3}	-5.263	193
180	4.18×10^{-3}	-5.477	239
240	3.50×10^{-3}	-5.655	286
300	3.01×10^{-3}	-5.806	332
360	2.64×10^{-3}	-5.937	379

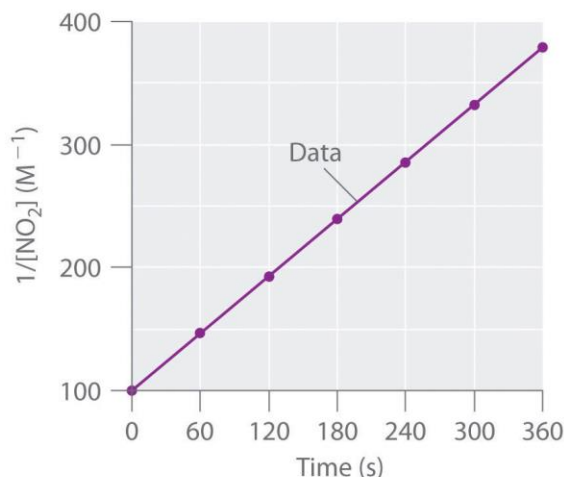
Figure 14.15 The Decomposition of NO_2



(a)



(b)

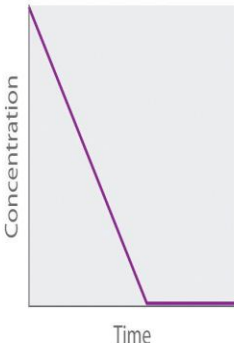
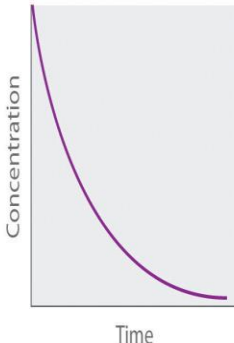
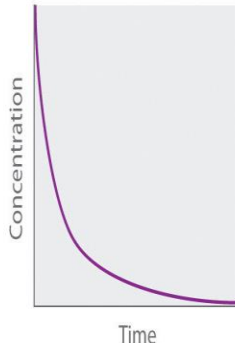
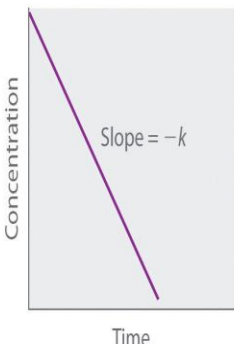
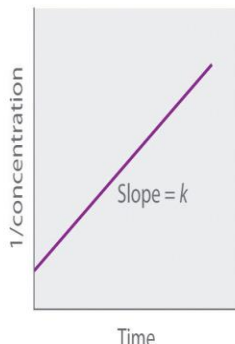


(c)

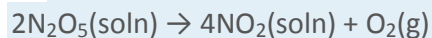
These plots show the decomposition of a sample of NO_2 at 330°C as (a) the concentration of NO_2 versus t , (b) the natural logarithm of $[\text{NO}_2]$ versus t , and (c) $1/[\text{NO}_2]$ versus t .

We have just determined the reaction order using data from a single experiment by plotting the concentration of the reactant as a function of time. Because of the characteristic shapes of the lines shown in Figure 14.16 "Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws", the graphs can be used to determine the reaction order of an unknown reaction. In contrast, the method described in Section 14.3 "Methods of Determining Reaction Order" required multiple experiments at different NO_2 concentrations as well as accurate initial rates of reaction, which can be difficult to obtain for rapid reactions.

Figure 14.16 Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws

	Zeroth Order	First Order	Second Order																								
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant																											
Relative rate vs. concentration	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>1</td></tr><tr><td>3</td><td>1</td></tr></table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>2</td></tr><tr><td>3</td><td>3</td></tr></table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>4</td></tr><tr><td>3</td><td>9</td></tr></table>	[A], M	Rate, M/s	1	1	2	4	3	9
[A], M	Rate, M/s																										
1	1																										
2	1																										
3	1																										
[A], M	Rate, M/s																										
1	1																										
2	2																										
3	3																										
[A], M	Rate, M/s																										
1	1																										
2	4																										
3	9																										
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k, rate constant	M/s	1/s	M ⁻¹ ·s ⁻¹																								

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:



This reaction is carried out in a CCl_4 solution at 45°C . The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus t , $\ln$ concentration versus t , and $1/\text{concentration}$ versus t and then determine the rate law and calculate the rate constant.

Time (s)	$[\text{N}_2\text{O}_5]$ (M)	$\ln[\text{N}_2\text{O}_5]$	$1/[\text{N}_2\text{O}_5]$ (M^{-1})
0	0.0365	-3.310	27.4
600	0.0274	-3.597	36.5
1200	0.0206	-3.882	48.5
1800	0.0157	-4.154	63.7
2400	0.0117	-4.448	85.5
3000	0.00860	-4.756	116
3600	0.00640	-5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

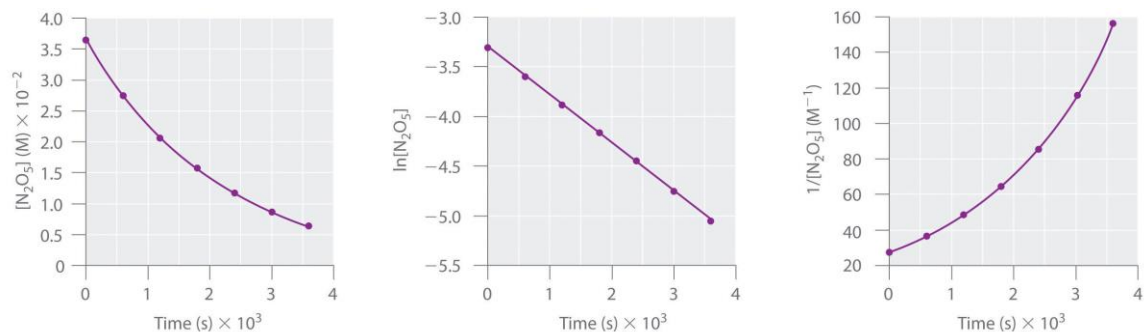
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 14.16 "Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws" to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[\text{N}_2\text{O}_5]$ versus t , $\ln[\text{N}_2\text{O}_5]$ versus t , and $1/[\text{N}_2\text{O}_5]$ versus t :



of $\ln[\text{N}_2\text{O}_5]$ versus t gives a straight line, whereas the plots of $[\text{N}_2\text{O}_5]$ versus t and $1/[\text{N}_2\text{O}_5]$ versus t do not. This means that the decomposition of N_2O_5 is first order in $[\text{N}_2\text{O}_5]$.

B The rate law for the reaction is therefore
 $\text{rate} = k[\text{N}_2\text{O}_5]$

Calculating the rate constant is straightforward because we know that the slope of the plot of $\ln[A]$ versus t for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[\text{N}_2\text{O}_5]$ versus t . Using the points for $t = 0$ and 3000 s ,

$$\text{slope} = \frac{\ln[\text{N}_2\text{O}_5]_{3000} - \ln[\text{N}_2\text{O}_5]_0}{3000 \text{ s} - 0 \text{ s}}$$

$$= \frac{(-4.756) - (-3.310)}{3000 \text{ s}} = -4.820 \times 10^{-4} \text{ s}^{-1}$$

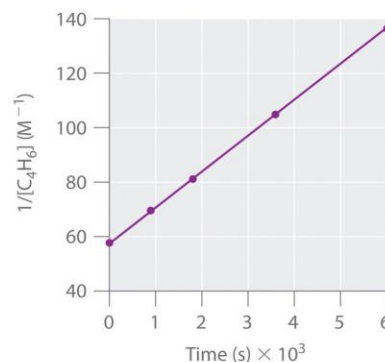
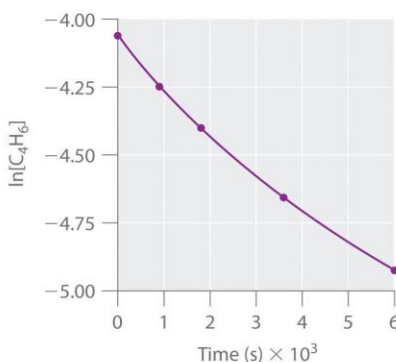
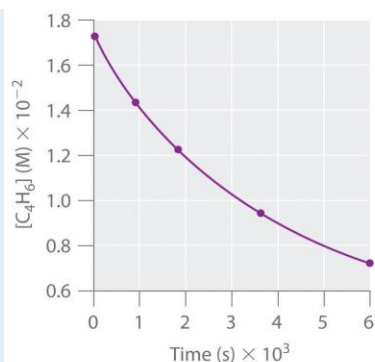
Thus $k = 4.820 \times 10^{-4} \text{ s}^{-1}$.

Exercise

1,3-Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, C_4H_6) is a volatile and reactive organic molecule used in the production of rubber. Above room temperature, it reacts slowly to form products. Concentrations of C_4H_6 as a function of time at 326°C are listed in the following table along with $\ln[\text{C}_4\text{H}_6]$ and the reciprocal concentrations. Graph the data as concentration versus t , $\ln$ concentration versus t , and $1/\text{concentration}$ versus t . Then determine the reaction order in C_4H_6 , the rate law, and the rate constant for the reaction.

Time (s)	$[\text{C}_4\text{H}_6] \text{ (M)}$	$\ln[\text{C}_4\text{H}_6]$	$1/[\text{C}_4\text{H}_6] \text{ (M}^{-1}\text{)}$
0	1.72×10^{-2}	-4.063	58.1
900	1.43×10^{-2}	-4.247	69.9
1800	1.23×10^{-2}	-4.398	81.3
3600	9.52×10^{-3}	-4.654	105
6000	7.30×10^{-3}	-4.920	137

Answer:



second order in C₄H₆; rate = $k[\text{C}_4\text{H}_6]^2$; $k = 1.3 \times 10^{-2} \text{ M}^{-1}\cdot\text{s}^{-1}$

Summary

For a zeroth-order reaction, a plot of the concentration of any reactant versus time is a straight line with a slope of $-k$. For a first-order reaction, a plot of the natural logarithm of the concentration of a reactant versus time is a straight line with a slope of $-k$. For a second-order reaction, a plot of the inverse of the concentration of a reactant versus time is a straight line with a slope of k .

KEY TAKEAWAY

- Plotting the concentration of a reactant as a function of time produces a graph with a characteristic shape that can be used to identify the reaction order in that reactant.

CONCEPTUAL PROBLEMS

- Compare first-order differential and integrated rate laws with respect to the following. Is there any information that can be obtained from the integrated rate law that cannot be obtained from the differential rate law?
 - the magnitude of the rate constant
 - the information needed to determine the order
 - the shape of the graphs
- In the single-step, second-order reaction $2\text{A} \rightarrow \text{products}$, how would a graph of $[\text{A}]$ versus time compare to a plot of $1/[\text{A}]$ versus time? Which of these would be the most similar to the same set of graphs for A during the single-step, second-order reaction $\text{A} + \text{B} \rightarrow \text{products}$? Explain.
- For reactions of the same order, what is the relationship between the magnitude of the rate constant and the reaction rate? If you were comparing reactions with different orders, could the same arguments be made? Why?

ANSWERS

1.
 - a. For a given reaction under particular conditions, the magnitude of the first-order rate constant does not depend on whether a differential rate law or an integrated rate law is used.
 - b. The differential rate law requires multiple experiments to determine reactant order; the integrated rate law needs only one experiment.
 - c. Using the differential rate law, a graph of concentration versus time is a curve with a slope that becomes less negative with time, whereas for the integrated rate law, a graph of $\ln[\text{reactant}]$ versus time gives a straight line with slope $= -k$. The integrated rate law allows you to calculate the concentration of a reactant at any time during the reaction; the differential rate law does not.
- 2.
3. The reaction rate increases as the rate constant increases. We cannot directly compare reaction rates and rate constants for reactions of different orders because they are not mathematically equivalent.

NUMERICAL PROBLEMS

1. One method of using graphs to determine reaction order is to use relative rate information. Plotting the log of the relative rate versus log of relative concentration provides information about the reaction. Here is an example of data from a zeroth-order reaction:

Relative [A] (M)	Relative Rate (M/s)
1	1
2	1
3	1

2. Varying [A] does not alter the reaction rate. Using the relative rates in the table, generate plots of $\log(\text{rate})$ versus $\log(\text{concentration})$ for zeroth-, first- and second-order reactions. What does the slope of each line represent?
3. The table below follows the decomposition of N_2O_5 gas by examining the partial pressure of the gas as a function of time at 45°C . What is the reaction order? What is the rate constant? How long would it take for the pressure to reach 105 mmHg at 45°C ?

Time (s)	Pressure (mmHg)

Time (s)	Pressure (mmHg)
0	348
400	276
1600	156
3200	69
4800	33

14.6 Reaction Rates—A Microscopic View

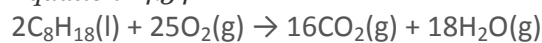
LEARNING OBJECTIVE

1. To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the *mechanism* of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the **reaction mechanism**.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

Equation 14.34

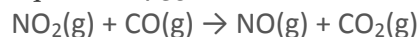


For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an elementary reaction, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the mechanism of the reaction. *The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

Equation 14.35



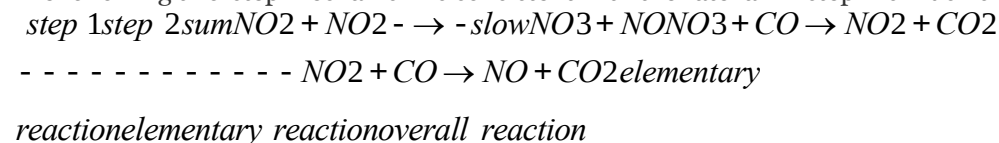
From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

Equation 14.36

$$\text{rate} = k[\text{NO}_2]^2$$

The fact that the reaction is second order in $[\text{NO}_2]$ and independent of $[\text{CO}]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be rate = $k[\text{NO}_2][\text{CO}]$.

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:



According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an intermediate in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

Note the Pattern

The sum of the elementary reactions in a reaction mechanism must give the overall balanced chemical equation of the reaction.

Using Molecularity to Describe a Rate Law

The molecularity of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as *unimolecular*; if there are two reactant molecules, it is *bimolecular*; and if there are three reactant molecules (a relatively rare situation), it is *termolecular*. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed

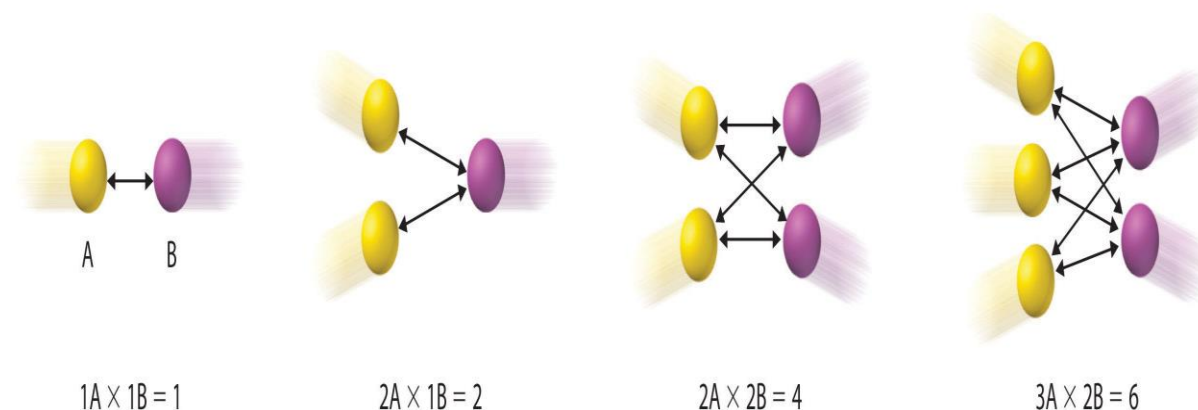
experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order *of the elementary reaction* is the same as its molecularity (Table 14.7 "Common Types of Elementary Reactions and Their Rate Laws"). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction ($A \rightarrow \text{products}$) is $\text{rate} = k[A]$. For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 14.19 "The Basis for Writing Rate Laws of Elementary Reactions". For a bimolecular elementary reaction of the form $A + B \rightarrow \text{products}$, the general rate law is $\text{rate} = k[A][B]$.

Table 14.7 Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
$A \rightarrow \text{products}$	unimolecular	$\text{rate} = k[A]$	first
$2A \rightarrow \text{products}$	bimolecular	$\text{rate} = k[A]^2$	second
$A + B \rightarrow \text{products}$	bimolecular	$\text{rate} = k[A][B]$	second
$2A + B \rightarrow \text{products}$	termolecular	$\text{rate} = k[A]^2[B]$	third
$A + B + C \rightarrow \text{products}$	termolecular	$\text{rate} = k[A][B][C]$	third

Figure 14.19 The Basis for Writing Rate Laws of Elementary Reactions



This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step.

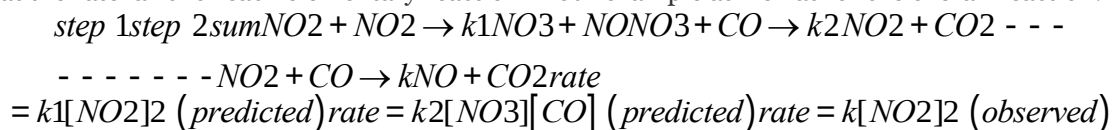
Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation not necessarily reveal the individual elementary reactions by which the reaction occurs, we *cannot* obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the *slowest* overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the rate-determining step, that must give the experimentally determined rate law for the overall reaction.^[1] The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.



Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow.

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

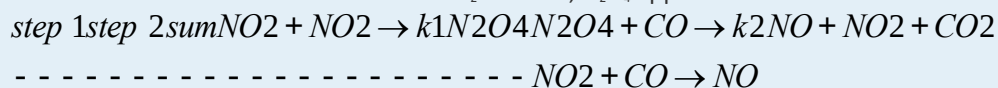


The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1 . That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

EXAMPLE 12

In an alternative mechanism for the reaction of NO_2 with CO , N_2O_4 appears as an intermediate.



Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law ($\text{rate} = k[\text{NO}_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A Determine the rate law for each elementary reaction in the reaction.

B Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution:

A The rate law for step 1 is $\text{rate} = k_1[\text{NO}_2]^2$; for step 2, it is $\text{rate} = k_2[\text{N}_2\text{O}_4][\text{CO}]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: $\text{rate} = k_1[\text{NO}_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4 , directly.

Exercise A

Iodine monochloride (ICl) reacts with H_2 as follows:



The experimentally determined rate law is $\text{rate} = k[\text{ICl}][\text{H}_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

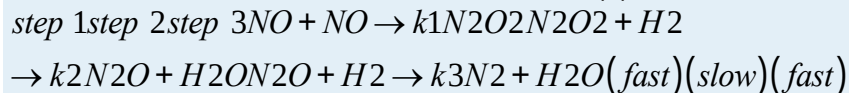
Answer:



This mechanism is consistent with the experimental rate law *if* the first step is the rate-determining step.

Exercise B

The reaction between NO and H₂ occurs via a three-step process:



Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction: $\text{rate} = k[\text{NO}]^2[\text{H}_2]^2$?

Answer:

- $\text{rate} = k_1[\text{NO}]^2$;
- $\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$;
- $\text{rate} = k_3[\text{N}_2\text{O}][\text{H}_2]$;
- $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- step 2
- Yes, because the rate of formation of $[\text{N}_2\text{O}_2] = k_1[\text{NO}]^2$. Substituting $k_1[\text{NO}]^2$ for $[\text{N}_2\text{O}_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

Chain Reactions

Many reaction mechanisms, like those discussed so far, consist of only two or three elementary reactions. Many others consist of long series of elementary reactions. The most common mechanisms are chain reactions, in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process. Chain reactions occur in fuel combustion, explosions, the formation of many polymers, and the tissue changes associated with aging. They are also important in the chemistry of the atmosphere.

Chain reactions are described as having three stages. The first is *initiation*, a step that produces one or more reactive intermediates. Often these intermediates are radicals, species that have an unpaired valence electron. In the second stage, *propagation*, reactive intermediates are continuously consumed and regenerated while products are formed. Intermediates are also consumed but not regenerated in the final stage of a chain reaction, *termination*, usually by forming stable products.

Let us look at the reaction of methane with chlorine at elevated temperatures (400°C–450°C), a chain reaction used in industry to manufacture methyl chloride (CH₃Cl), dichloromethane (CH₂Cl₂), chloroform (CHCl₃), and carbon tetrachloride (CCl₄):



Direct chlorination generally produces a mixture of all four carbon-containing products, which must then be separated by distillation. In our discussion, we will examine only the chain reactions that lead to the preparation of CH₃Cl.

In the initiation stage of this reaction, the relatively weak Cl–Cl bond cleaves at temperatures of about 400°C to produce chlorine atoms (Cl·):

$$\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$$

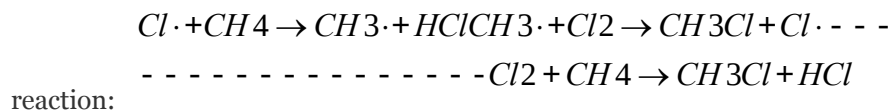
During propagation, a chlorine atom removes a hydrogen atom from a methane molecule to give HCl and CH₃·, the methyl radical:

$$\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{CH}_3\cdot + \text{HCl}$$

The methyl radical then reacts with a chlorine molecule to form methyl chloride and another chlorine atom, Cl·:

$$\text{CH}_3\cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$$

The sum of the propagation reactions is the same as the overall balanced chemical equation for the



Without a chain-terminating reaction, propagation reactions would continue until either the methane or the chlorine was consumed. Because radical species react rapidly with almost anything, however, including each other, they eventually form neutral compounds, thus terminating the chain reaction in any of three ways:



Here is the overall chain reaction, with the desired product (CH₃Cl) in bold:

<i>Initiation:</i>	$\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$
	$\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{CH}_3\cdot + \text{HCl}$
<i>Propagation:</i>	$\text{CH}_3\cdot + \text{Cl}_2 \rightarrow \textbf{CH}_3\text{Cl} + \text{Cl}\cdot$
<i>Termination:</i>	$\text{CH}_3\cdot + \text{Cl}\cdot \rightarrow \textbf{CH}_3\text{Cl}$

	$\text{CH}_3\cdot + \text{CH}_3\cdot \rightarrow \text{H}_3\text{CCH}_3$
	$\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$

The chain reactions responsible for explosions generally have an additional feature: the existence of one or more *chain branching steps*, in which one radical reacts to produce two or more radicals, each of which can then go on to start a new chain reaction. Repetition of the branching step has a cascade effect such that a single initiation step generates large numbers of chain reactions. The result is a very rapid reaction or an explosion.

The reaction of H_2 and O_2 , used to propel rockets, is an example of a chain branching reaction:

<i>Initiation:</i>	$\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2\cdot + \text{H}\cdot$
	$\text{HO}_2\cdot + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{OH}\cdot$
<i>Propagation:</i>	$\text{OH}\cdot + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}\cdot$
	$\text{H}\cdot + \text{O}_2 \rightarrow \text{OH}\cdot + \cdot\text{O}\cdot$
<i>Termination:</i>	$\cdot\text{O}\cdot + \text{H}_2 \rightarrow \text{OH}\cdot + \text{H}\cdot$

Termination reactions occur when the extraordinarily reactive $\text{H}\cdot$ or $\text{OH}\cdot$ radicals react with a third species. The complexity of a chain reaction makes it unfeasible to write a rate law for the overall reaction.

Summary

A **reaction mechanism** is the microscopic path by which reactants are transformed into products. Each step is an **elementary reaction**. Species that are formed in one step and consumed in another are **intermediates**. Each elementary reaction can be described in terms of its **molecularity**, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the **rate-determining step**. **Chain reactions** consist of three kinds of reactions: initiation, propagation, and termination. Intermediates in chain reactions are often **radicals**, species that have an unpaired valence electron.

KEY TAKEAWAY

- A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law.

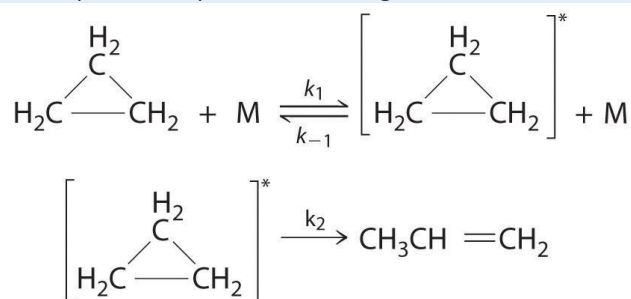
CONCEPTUAL PROBLEMS

1. How does the term *molecularity* relate to elementary reactions? How does it relate to the overall balanced chemical equation?

- What is the relationship between the reaction order and the molecularity of a reaction? What is the relationship between the reaction order and the balanced chemical equation?
- When you determine the rate law for a given reaction, why is it valid to assume that the concentration of an intermediate does not change with time during the course of the reaction?
- If you know the rate law for an overall reaction, how would you determine which elementary reaction is rate determining? If an intermediate is contained in the rate-determining step, how can the experimentally determined rate law for the reaction be derived from this step?
- Give the rate-determining step for each case.
 - Traffic is backed up on a highway because two lanes merge into one.
 - Gas flows from a pressurized cylinder fitted with a gas regulator and then is bubbled through a solution.
 - A document containing text and graphics is downloaded from the Internet.
- Before being sent on an assignment, an aging James Bond was sent off to a health farm where part of the program's focus was to purge his body of radicals. Why was this goal considered important to his health?

NUMERICAL PROBLEMS

- Cyclopropane, a mild anesthetic, rearranges to propylene via a collision that produces and destroys an energized species. The important steps in this rearrangement are as follows:



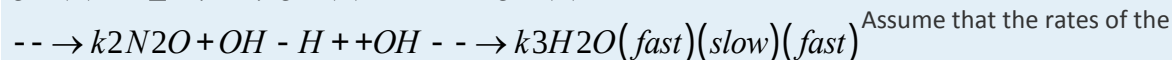
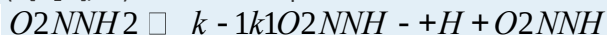
where

M is any molecule, including cyclopropane. Only those cyclopropane molecules with sufficient energy (denoted with an asterisk) can rearrange to propylene. Which step determines the rate constant of the overall reaction?

- Above approximately 500 K, the reaction between NO_2 and CO to produce CO_2 and NO follows the second-order rate law $\Delta[\text{CO}_2]/\Delta t = k[\text{NO}_2][\text{CO}]$. At lower temperatures, however, the rate law is $\Delta[\text{CO}_2]/\Delta t = k'[\text{NO}_2]^2$, for which it is known that NO_3 is an intermediate in the mechanism. Propose a complete low-temperature mechanism for the reaction based on this rate law. Which step is the slowest?

3. Nitramide (O_2NNH_2) decomposes in aqueous solution to N_2O and H_2O . What is the experimental rate law

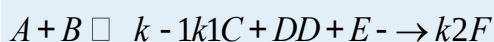
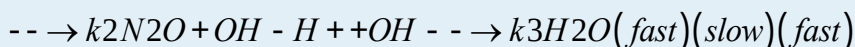
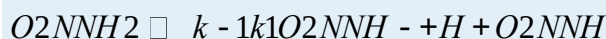
($\Delta[\text{N}_2\text{O}]/\Delta t$) for the decomposition of nitramide if the mechanism for the decomposition is as follows?



Assume that the rates of the

forward and reverse reactions in the first equation are equal.

4. The following reactions are given:



What is the relationship between the relative magnitudes of k_{-1} and k_2 if these reactions have the rate law

$\Delta[\text{F}]/\Delta t = k[\text{A}][\text{B}][\text{E}]/[\text{C}]$? How does the magnitude of k_1 compare to that of k_2 ? Under what conditions would

you expect the rate law to be $\Delta[\text{F}]/\Delta t = k'[\text{A}][\text{B}]$? Assume that the rates of the forward and reverse reactions

in the first equation are equal.

ANSWERS

1. The k_2 step is likely to be rate limiting; the rate cannot proceed any faster than the second step.

$$\text{rate} = k_2 k_1 [\text{O}_2\text{NNH}_2] / k_{-1} [\text{H}^+] = k [\text{O}_2\text{NNH}_2] [\text{H}^+]$$

[1] This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other.

14.7 The Collision Model of Chemical Kinetics

LEARNING OBJECTIVE

1. To understand why and how chemical reactions occur.

In Section 14.6 "Reaction Rates—A Microscopic View", you saw that it is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the *collision model of chemical kinetics*, which is a useful tool for understanding the behavior of reacting chemical species. According to the collision model, a chemical reaction can occur only when the reactant molecules, atoms, or ions collide with more than a certain amount of kinetic energy and in the proper orientation.

The collision model explains why, for example, most collisions between molecules do *not* result in a chemical reaction. Nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO₂ a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide. The collision model also explains why such chemical reactions occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates.

Activation Energy

In Chapter 10 "Gases", we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of activation energy (E_a). We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

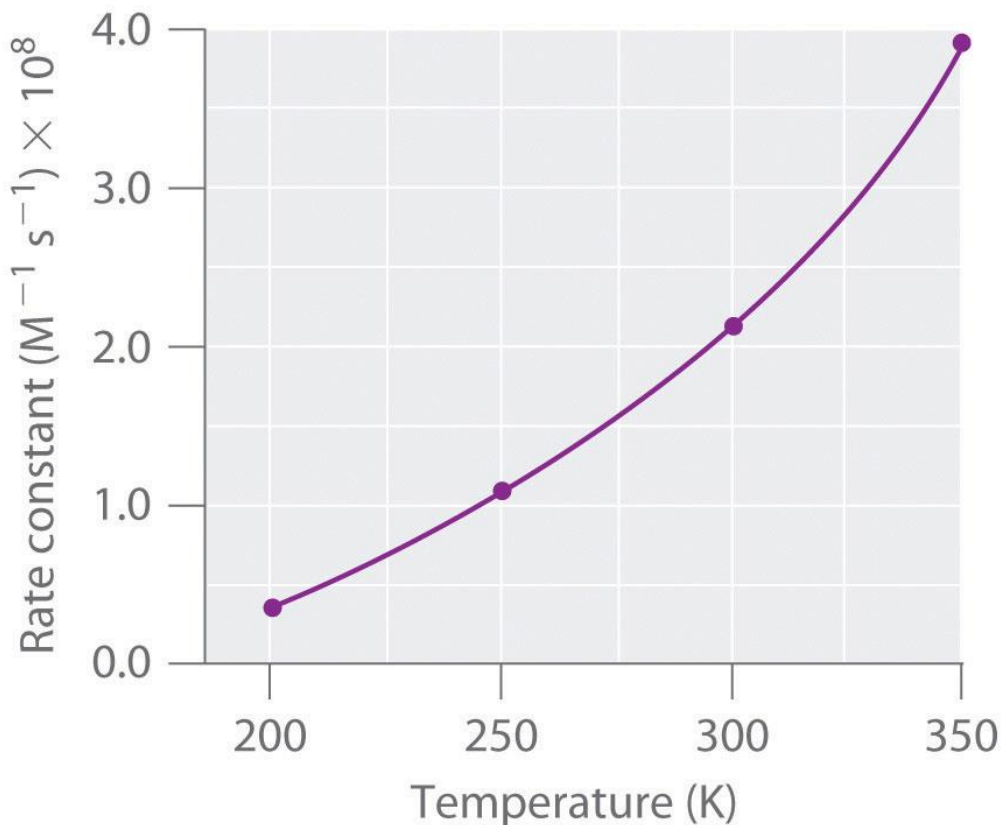
Equation 14.37



Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

The reaction rate, not the rate constant, will vary with concentration. The rate constant, however, does vary with temperature. Figure 14.20 "Rate Constant versus Temperature for the Reaction of NO with O" shows a plot of the rate constant of the reaction of NO with O₃ at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (Chapter 11 "Liquids") and of conductivity versus temperature (Chapter 12 "Solids"). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

Figure 14.20 Rate Constant versus Temperature for the Reaction of NO with O₃



The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases.

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and

empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the activation energy, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the activated complex or the transition state of the reaction. The activated complex is *not* a reaction intermediate; it does not last long enough to be detected readily.

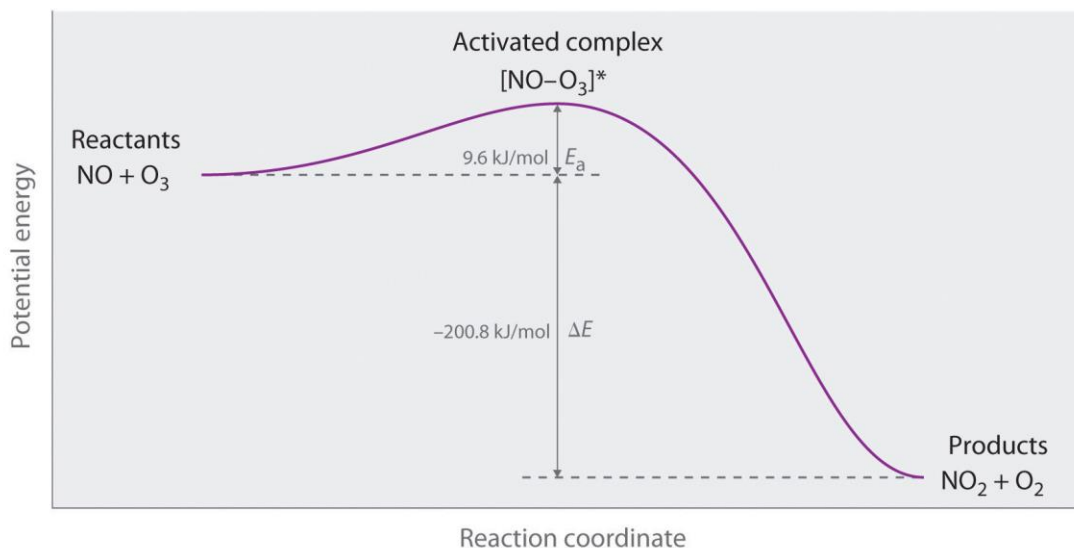
Note the Pattern

Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.

Graphing Energy Changes during a Reaction

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 14.21 "Energy of the Activated Complex for the NO–O" shows a plot for the NO–O₃ system, in which the vertical axis is potential energy and the horizontal axis is the *reaction coordinate*, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is -200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

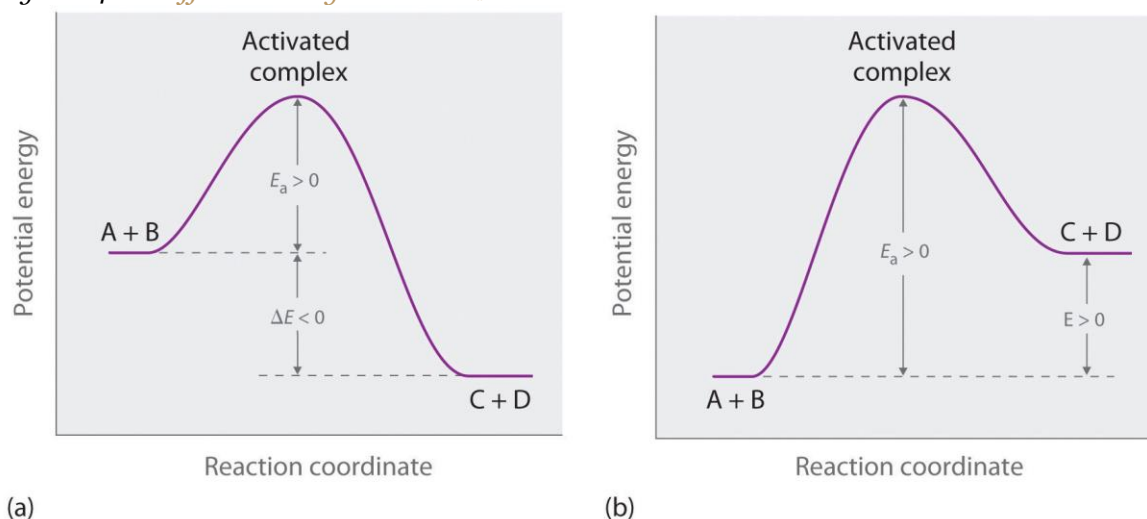
Figure 14.21 *Energy of the Activated Complex for the NO–O₃ System*



The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex.

Part (a) in Figure 14.22 "Differentiating between " illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, part (b) in Figure 14.22 "Differentiating between " illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and $\Delta E > 0$. Although the energy changes that result from a reaction can be positive, negative, or even zero, in all cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is always positive.

Figure 14.22 Differentiating between E_a and ΔE



The potential energy diagrams for a reaction with (a) $\Delta E < 0$ and (b) $\Delta E > 0$ illustrate the change in the

potential energy of the system as reactants are converted to products. E_a is always positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE .

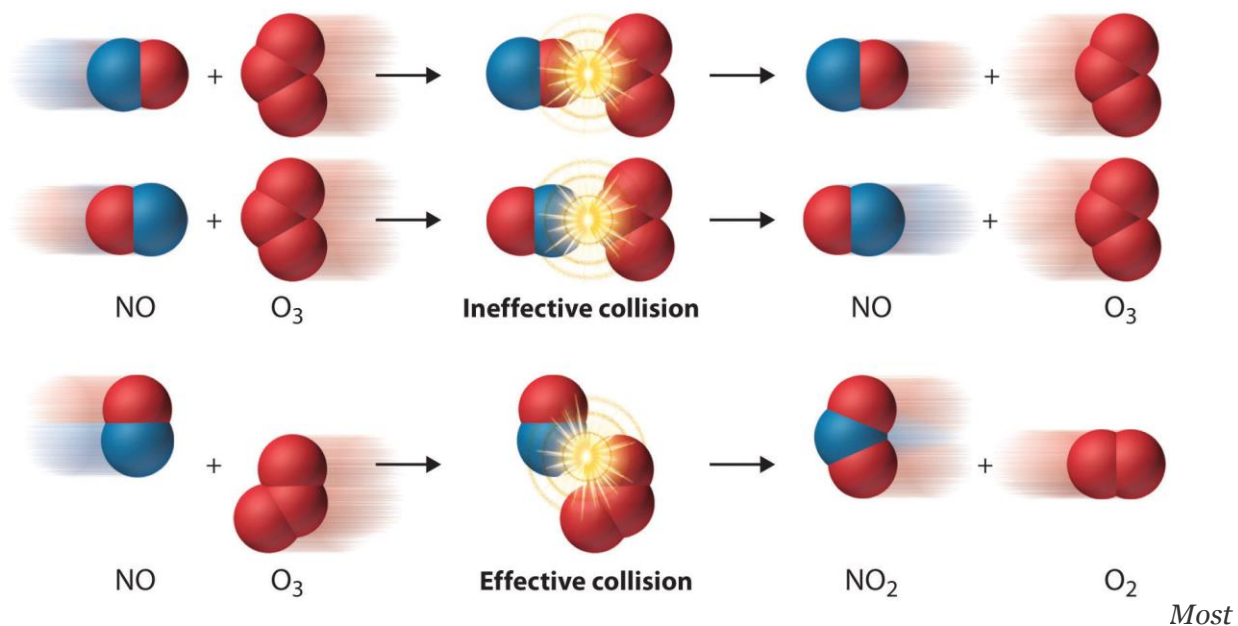
Note the Pattern

For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. (For more information on spontaneous reactions, see Chapter 18 "Chemical Thermodynamics".) *For two similar reactions under comparable conditions, the reaction with the smallest E_a will occur more rapidly.*

Even when the energy of collisions between two reactant species is greater than E_a , however, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2 , a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 14.23 "The Effect of Molecular Orientation on the Reaction of NO and O_3 "). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a , most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the steric factor (p), and, in general, its value can range from 0 (no orientations of molecules result in reaction) to 1 (all orientations result in reaction).

Figure 14.23 *The Effect of Molecular Orientation on the Reaction of NO and O_3*

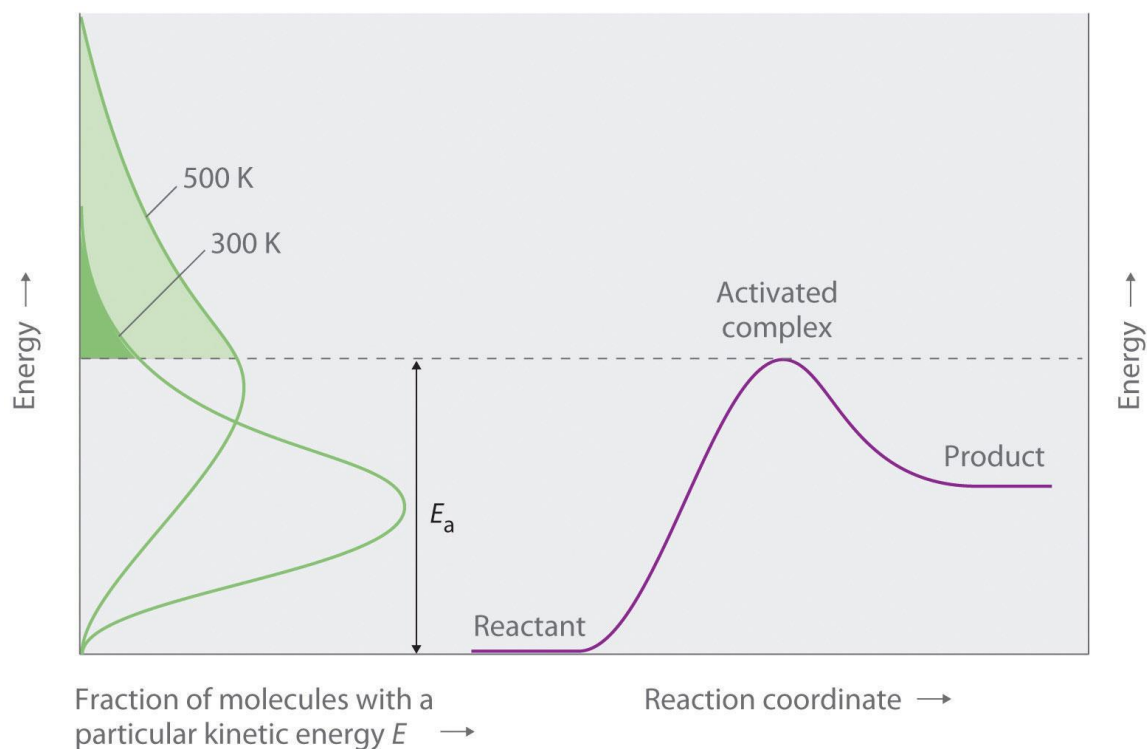


collisions of NO and O₃ molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O₃ are likely to produce NO₂ and O₂, even if the molecules collide with $E > E_a$.

The Arrhenius Equation

Figure 14.24 "Surmounting the Energy Barrier to a Reaction" shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a ; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a . Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

Figure 14.24 Surmounting the Energy Barrier to a Reaction



This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have $E > E_a$ and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K.

For an $A + B$ elementary reaction, all the factors that affect the reaction rate can be summarized in a single series of relationships:
 $\text{rate} = (\text{collision frequency})(\text{steric factor})(\text{fraction of collisions with } E > E_a)$

where

Equation 14.38

$$\text{rate} = k[A][B]$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A , called the frequency factor:

Equation 14.39

$$k = Ae^{-E_a / RT}$$

The frequency factor is used to convert concentrations to collisions per second.^[1] Equation 14.39 is known as the Arrhenius equation and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 14.39,

Equation 14.40

$$\ln k = \ln A + (-E_a/RT) = \ln A + [(-E_a/R)(1/T)]$$

Equation 14.40 is the equation of a straight line, $y = mx + b$, where $y = \ln k$ and $x = 1/T$. This means that a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a .

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining E_a from reaction rates measured at several temperatures is illustrated in Example 13.

EXAMPLE 13

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of $\ln$ [chirping rate] versus $1/T$ in Figure 14.25 "Graphical Determination of ", to calculate E_a for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Frequency (f ; chirps/min)	$\ln f$	T (K)	$1/T$ (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}

Frequency (f ; chirps/min)	$\ln f$	T (K)	$1/T$ (K)
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:

A From the plot of $\ln f$ versus $1/T$ in Figure 14.25 "Graphical Determination of ", calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.

B Express Equation 14.40 in terms of k_1 and T_1 and then in terms of k_2 and T_2 .

C Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1 .

D Using measured data from the table, solve the equation to obtain the ratio k_2/k_1 . Using the value listed in the table for k_1 , solve for k_2 .

Solution:

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of $\ln f$ versus $1/T$ should give a straight line (Figure 14.25 "Graphical Determination of "). Also, the slope of the plot of $\ln f$ versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 14.25 "Graphical

Determination of " to estimate the slope:

$$\text{slope} = \frac{\Delta \ln f}{\Delta (1/T)} = \frac{5.30 - 4.37}{3.4 \times 10^{-3} \text{ K}^{-1} - 3.48 \times 10^{-3} \text{ K}^{-1}} = -6.6 \times 10^3 \text{ K}$$

A computer best-fit line through all the points has a slope of $-6.67 \times 10^3 \text{ K}$, so our estimate is very close.

We now use it to solve for the activation energy:

$$E_a = -(\text{slope})(R) = -(-6.67 \times 10^3 \text{ K})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 55 \text{ kJ mol}^{-1}$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 14.40 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - E_a/RT_1$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - E_a/RT_2$$

C These two equations contain four known quantities (E_a , T_1 , T_2 , and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\ln k_2 - \ln k_1 = (\ln A - E_a/RT_2) - (\ln A - E_a/RT_1) = -E_a/RT_2 + E_a/RT_1$$

Then

$$\ln k_2/k_1 = E_a/R(1/T_1 - 1/T_2)$$

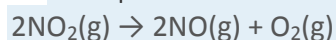
D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for $T_1 = 296$ K, where $f = 158$, and using the E_a calculated previously,

$$\ln k_2/k_1 = E_a/R(1/T_1 - 1/T_2) \\ = 55 \text{ kJ/mol} / 8.314 \text{ J/(K}\cdot\text{mol)} (1000 \text{ J/kJ}) (1/296 \text{ K} - 1/308 \text{ K}) = 0.87$$

Thus $k_{308}/k_{296} = 2.4$ and $k_{308} = (2.4)(158) = 380$, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

Exercise

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2 :



Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

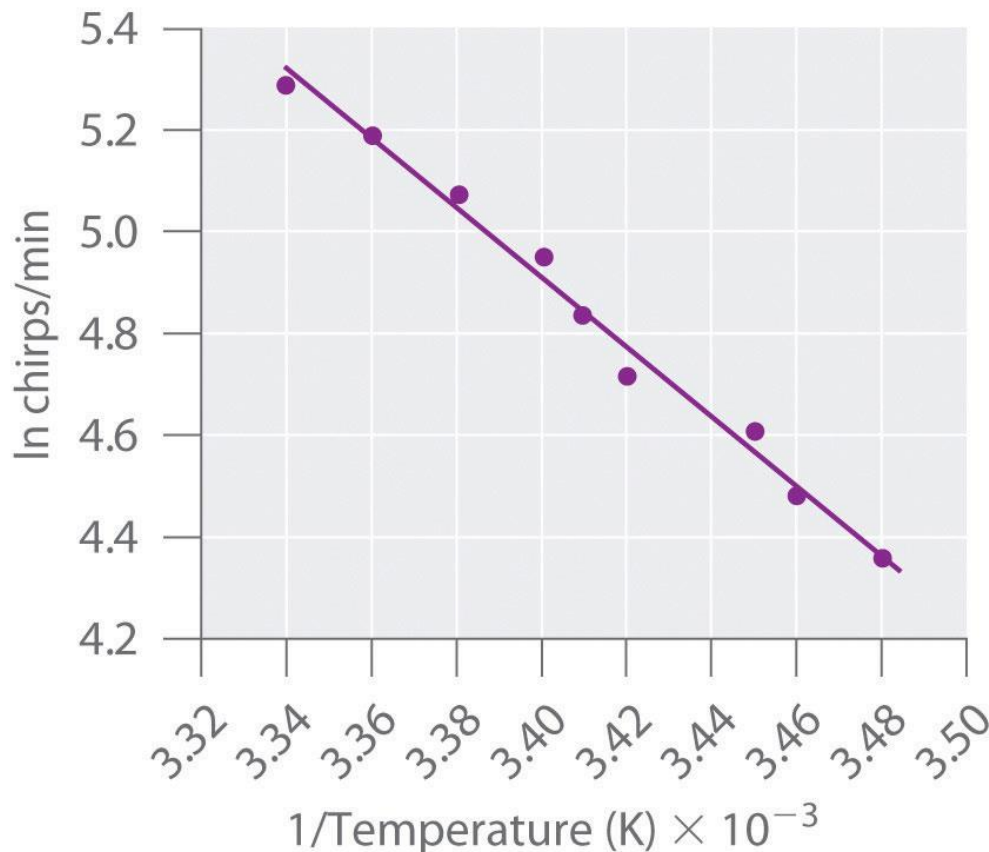
T (K)	k ($\text{M}^{-1}\cdot\text{s}^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer: $E_a = 114 \text{ kJ/mol}$; $k_{700} = 18,600 \text{ M}^{-1}\cdot\text{s}^{-1} = 1.86 \times 10^4 \text{ M}^{-1}\cdot\text{s}^{-1}$.

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C ?

Answer: about 51 kJ/mol

Figure 14.25 Graphical Determination of E_a for Tree Cricket Chirping



When the natural logarithm of the rate of tree cricket chirping is plotted versus $1/T$, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol .

Summary

A minimum energy (**activation energy**, E_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the **activated complex**, or **transition state**, of the reaction. At a given temperature, the higher the E_a , the slower the reaction. The fraction of orientations that result in a reaction is the **steric factor**. The **frequency factor**, steric factor, and activation energy are related to the rate constant in the **Arrhenius equation**: $k = Ae^{-E_a/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

KEY TAKEAWAY

- For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation.

KEY EQUATION

Arrhenius equation

$$\text{Equation 14.39: } k = Ae^{-E_a/RT}$$

CONCEPTUAL PROBLEMS

1. Although an increase in temperature results in an increase in kinetic energy, this increase in kinetic energy is not sufficient to explain the relationship between temperature and reaction rates. How does the activation energy relate to the chemical kinetics of a reaction? Why does an increase in temperature increase the reaction rate despite the fact that the average kinetic energy is still less than the activation energy?
2. For any given reaction, what is the relationship between the activation energy and each of the following?
 - a. electrostatic repulsions
 - b. bond formation in the activated complex
 - c. the nature of the activated complex
3. If you are concerned with whether a reaction will occur rapidly, why would you be more interested in knowing the magnitude of the activation energy than the change in potential energy for the reaction?
4. The product C in the reaction $A + B \rightarrow C + D$ can be separated easily from the reaction mixture. You have been given pure A and pure B and are told to determine the activation energy for this reaction to determine whether the reaction is suitable for the industrial synthesis of C. How would you do this? Why do you need to know the magnitude of the activation energy to make a decision about feasibility?
5. Above E_a , molecules collide with enough energy to overcome the energy barrier for a reaction. Is it possible for a reaction to occur at a temperature less than that needed to reach E_a ? Explain your answer.
6. What is the relationship between A , E_a , and T ? How does an increase in A affect the reaction rate?
7. Of two highly exothermic reactions with different values of E_a , which would need to be monitored more carefully: the one with the smaller value or the one with the higher value? Why?

NUMERICAL PROBLEMS

1. What happens to the approximate rate of a reaction when the temperature of the reaction is increased from 20°C to 30°C? What happens to the reaction rate when the temperature is raised to 70°C? For a given reaction at room temperature (20°C), what is the shape of a plot of reaction rate versus temperature as the temperature is increased to 70°C?
2. Acetaldehyde, used in silvering mirrors and some perfumes, undergoes a second-order decomposition between 700 and 840 K. From the data in the following table, would you say that acetaldehyde follows the general rule that each 10 K increase in temperature doubles the reaction rate?

T (K)	k ($M^{-1}\cdot s^{-1}$)
720	0.024
740	0.051
760	0.105
800	0.519

3. Bromoethane reacts with hydroxide ion in water to produce ethanol. The activation energy for this reaction is 90 kJ/mol. If the reaction rate is 3.6×10^{-5} M/s at 25°C, what would the reaction rate be at the following temperatures?
 - a. 15°C
 - b. 30°C
 - c. 45°C
4. An enzyme-catalyzed reaction has an activation energy of 15 kcal/mol. How would the value of the rate constant differ between 20°C and 30°C? If the enzyme reduced the E_a from 25 kcal/mol to 15 kcal/mol, by what factor has the enzyme increased the reaction rate at each temperature?
5. The data in the following table are the rate constants as a function of temperature for the dimerization of 1,3-butadiene. What is the activation energy for this reaction?

T (K)	k ($M^{-1}\cdot min^{-1}$)
529	1.4
560	3.7
600	25
645	82

6. The reaction rate at 25°C is 1.0×10^{-4} M/s. Increasing the temperature to 75°C causes the reaction rate to increase to 7.0×10^{-2} M/s. Estimate E_a for this process. If E_a were 25 kJ/mol and the reaction rate at 25°C is 1.0×10^{-4} M/s, what would be the reaction rate at 75°C?

ANSWERS

1. The reaction rate will approximately double: 20°C to 30°C, the reaction rate increases by about $2^1 = 2$; 20°C to 70°C, the reaction rate increases by about $2^5 = 32$ -fold. A plot of reaction rate versus temperature will give an exponential increase: $\text{rate} \propto 2^{\Delta T/10}$.
- 2.
3.
 - a. 1.0×10^{-5} M/s
 - b. 6.6×10^{-5} M/s
 - c. 3.5×10^{-4} M/s
- 4.
5. 100 kJ/mol
- 6.

[1] Because the frequency of collisions depends on the temperature, A is actually *not* constant. Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time.

14.8 Catalysis

LEARNING OBJECTIVE

1. To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

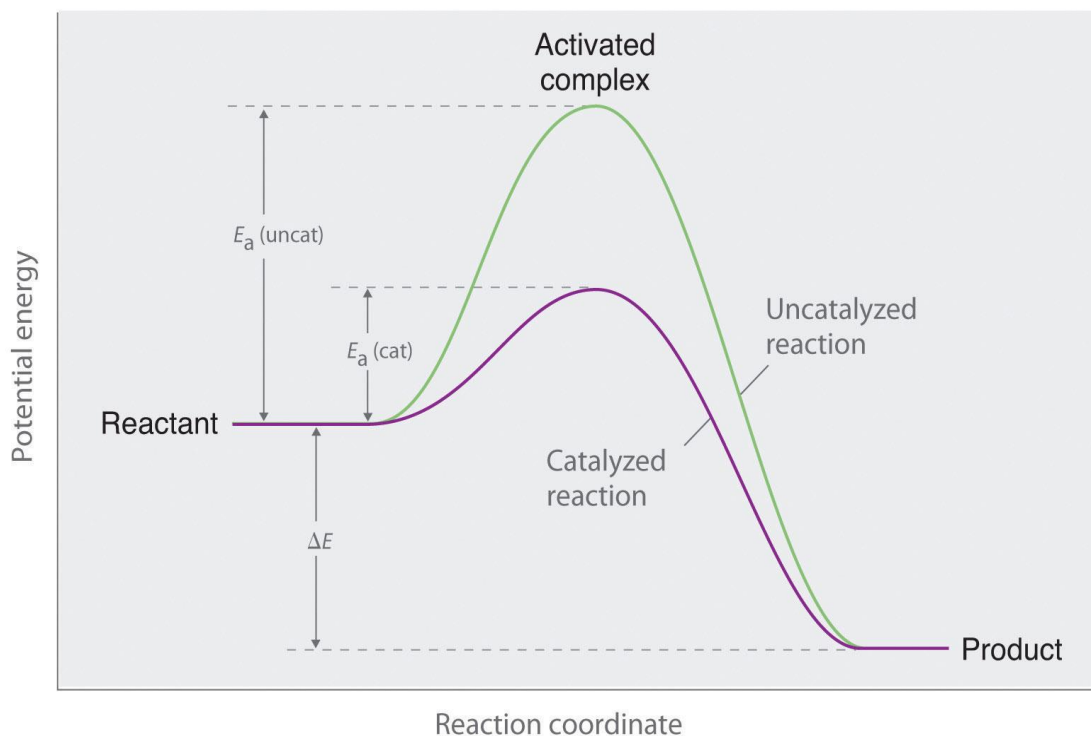
Chapter 3 "Chemical Reactions" described catalysts as substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it *must* appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a , but the *net* change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is *not* affected by the presence of a catalyst (Figure 14.26 "Lowering the Activation Energy of a Reaction by a Catalyst"). Nevertheless, because of its

lower E_a , the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of *both* the forward *and* the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, **homogeneous catalysts**, and **enzymes**.

Note the Pattern

A catalyst affects E_a , not ΔE .

Figure 14.26 Lowering the Activation Energy of a Reaction by a Catalyst



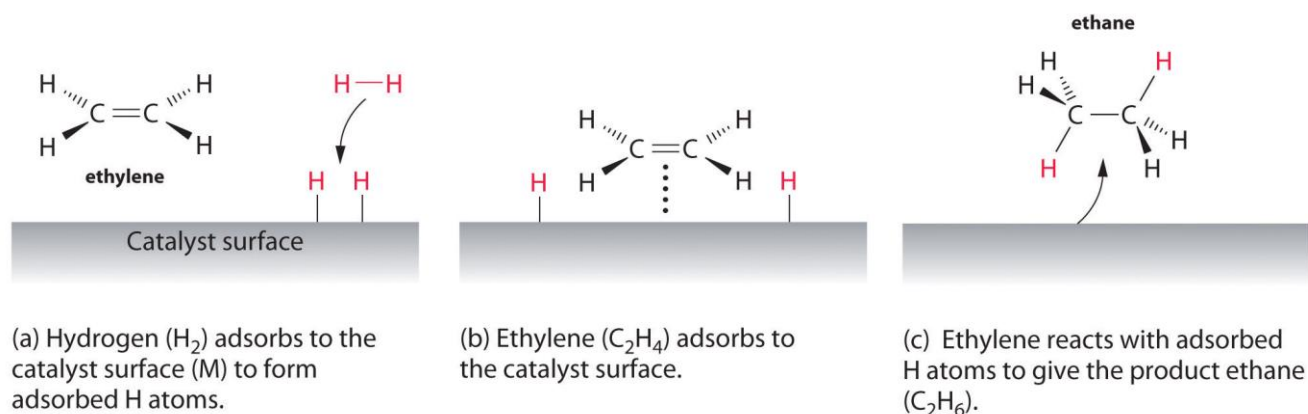
This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE).

Heterogeneous Catalysis

In heterogeneous catalysis, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called *adsorption* in such a way that a chemical bond in the reactant becomes weak and then breaks. *Poisons* are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 14.27 "Hydrogenation of Ethylene on a Heterogeneous Catalyst", the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called *desorption*. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H₂ is substantially lower on the catalyst surface.

Figure 14.27 *Hydrogenation of Ethylene on a Heterogeneous Catalyst*



When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H₂. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released.

Figure 14.27 "Hydrogenation of Ethylene on a Heterogeneous Catalyst" shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 14.8 "Some Commercially Important Reactions that Employ Heterogeneous Catalysts". Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here,

they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 14.8 Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V ₂ O ₅ or Pt	$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$	H ₂ SO ₄
Haber process	Fe, K ₂ O, Al ₂ O ₃	$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$	NH ₃
Ostwald process	Pt and Rh	$4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$	HNO ₃
water–gas shift reaction	Fe, Cr ₂ O ₃ , or Cu	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	H ₂ for NH ₃ , CH ₃ OH, and other fuels
steam reforming	Ni	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	H ₂
methanol synthesis	ZnO and Cr ₂ O ₃	$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$	CH ₃ OH

Homogeneous Catalysis

In homogeneous catalysis, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 14.9 "Some Commercially Important Reactions that Employ Homogeneous Catalysts"), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 14.9 Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	[Rh(CO) ₂ I ₂] ⁻	CO + CH ₃ OH	CH ₃ CO ₂ H
hydroperoxide process	Mo(VI) complexes	CH ₃ CH=CH ₂ + R–O–O–H	$\begin{array}{c} \text{CH}_3\text{CH} \quad \text{CH}_2 \\ \quad \diagdown \quad \diagup \\ \quad \quad \text{O} \end{array} + \text{ROH}$ propylene oxide

Commercial Process	Catalyst	Reactants	Final Product
hydroformylation	Rh/PR ₃ complexes	RCH=CH ₂ + CO + H ₂	RCH ₂ CH ₂ CHO
adiponitrile process	Ni/PR ₃ complexes	2HCN + CH ₂ =CHCH=CH ₂	NCCH ₂ CH ₂ CH ₂ CH ₂ CN used to synthesize nylon
olefin polymerization	(RC ₅ H ₅) ₂ ZrCl ₂	CH ₂ =CH ₂	-(CH ₂ CH ₂ -) _n : high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a substrate.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37°C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be *proteases*, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombardier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 14.28 "A Catalytic Defense Mechanism").

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most

widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In **heterogeneous catalysis**, catalysts provide a surface to which reactants bind in a process of adsorption. In **homogeneous catalysis**, catalysts are in the same phase as the reactants. **Enzymes** are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a **substrate**. **Enzyme inhibitors** cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

KEY TAKEAWAY

- Catalysts allow a reaction to proceed via a pathway that has a lower activation energy.

CONCEPTUAL PROBLEMS

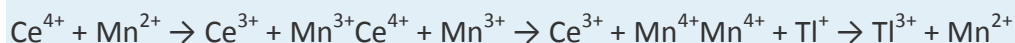
1. What effect does a catalyst have on the activation energy of a reaction? What effect does it have on the frequency factor (A)? What effect does it have on the change in potential energy for the reaction?
2. How is it possible to affect the product distribution of a reaction by using a catalyst?
3. A heterogeneous catalyst works by interacting with a reactant in a process called *adsorption*. What occurs during this process? Explain how this can lower the activation energy.
4. What effect does increasing the surface area of a heterogeneous catalyst have on a reaction? Does increasing the surface area affect the activation energy? Explain your answer.
5. Identify the differences between a heterogeneous catalyst and a homogeneous catalyst in terms of the following.
 - a. ease of recovery
 - b. collision frequency
 - c. temperature sensitivity
 - d. cost

6. An area of intensive chemical research involves the development of homogeneous catalysts, even though homogeneous catalysts generally have a number of operational difficulties. Propose one or two reasons why a homogenous catalyst may be preferred.

7. Consider the following reaction between cerium(IV) and thallium(I) ions:



This reaction is slow, but Mn^{2+} catalyzes it, as shown in the following mechanism:



In what way does Mn^{2+} increase the reaction rate?

8. The text identifies several factors that limit the industrial applications of enzymes. Still, there is keen interest in understanding how enzymes work for designing catalysts for industrial applications. Why?

9. Most enzymes have an optimal pH range; however, care must be taken when determining pH effects on enzyme activity. A decrease in activity could be due to the effects of changes in pH on groups at the catalytic center or to the effects on groups located elsewhere in the enzyme. Both examples are observed in chymotrypsin, a digestive enzyme that is a protease that hydrolyzes polypeptide chains. Explain how a change in pH could affect the catalytic activity due to (a) effects at the catalytic center and (b) effects elsewhere in the enzyme. (*Hint*: remember that enzymes are composed of functional amino acids.)

ANSWERS

1. A catalyst lowers the activation energy of a reaction. Some catalysts can also orient the reactants and thereby increase the frequency factor. Catalysts have no effect on the change in potential energy for a reaction.

2.

3. In adsorption, a reactant binds tightly to a surface. Because intermolecular interactions between the surface and the reactant weaken or break bonds in the reactant, its reactivity is increased, and the activation energy for a reaction is often decreased.

4.

5.

- Heterogeneous catalysts are easier to recover.
- Collision frequency is greater for homogeneous catalysts.
- Homogeneous catalysts are often more sensitive to temperature.
- Homogeneous catalysts are often more expensive.

6.

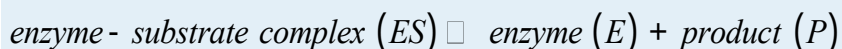
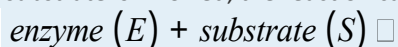
7. The Mn^{2+} ion donates two electrons to Ce^{4+} , one at a time, and then accepts two electrons from Ti^+ . Because Mn can exist in three oxidation states separated by one electron, it is able to couple one-electron and two-electron transfer reactions.

8.

9.

NUMERICAL PROBLEMS

1. At some point during an enzymatic reaction, the concentration of the activated complex, called an enzyme–substrate complex (ES), and other intermediates involved in the reaction is nearly constant. When a single substrate is involved, the reaction can be represented by the following sequence of equations:

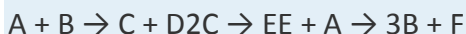


This can also be shown as follows:



Using molar concentrations and rate constants, write an expression for the rate of disappearance of the enzyme–substrate complex. Typically, enzyme concentrations are small, and substrate concentrations are high. If you were determining the rate law by varying the substrate concentrations under these conditions, what would be your apparent reaction order?

2. A particular reaction was found to proceed via the following mechanism:



What is the overall reaction? Is this reaction catalytic, and if so, what species is the catalyst? Identify the intermediates.

3. A particular reaction has two accessible pathways (A and B), each of which favors conversion of X to a different product (Y and Z, respectively). Under uncatalyzed conditions pathway A is favored, but in the presence of a catalyst pathway B is favored. Pathway B is reversible, whereas pathway A is not. Which product is favored in the presence of a catalyst? without a catalyst? Draw a diagram illustrating what is occurring with and without the catalyst.
4. The kinetics of an enzyme-catalyzed reaction can be analyzed by plotting the reaction rate versus the substrate concentration. This type of analysis is referred to as a Michaelis–Menten treatment. At low

substrate concentrations, the plot shows behavior characteristic of first-order kinetics, but at very high substrate concentrations, the behavior shows zeroth-order kinetics. Explain this phenomenon.

ANSWERS

1. $D[ES]Dt = -(k_2 + k_{-1})[ES] + k_1[E][S] + k_{-2}[E][P] \approx 0$; *zeroth*
2. order in substrate.
- 3.
4. In both cases, the product of pathway A is favored. All of the Z produced in the catalyzed reversible pathway B will eventually be converted to X as X is converted irreversibly to Y by pathway A.

14.9 End-of-Chapter Material

APPLICATION PROBLEMS

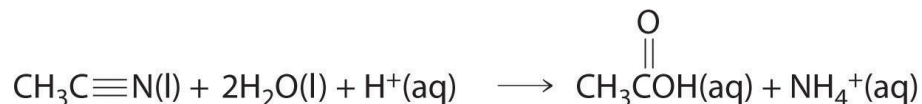
Problems marked with a ♦ involve multiple concepts.

1. Atmospheric chemistry in the region below the clouds of Venus appears to be dominated by reactions of sulfur and carbon-containing compounds. Included in representative elementary reactions are the following:

$$SO_2 + CO \rightarrow SO + CO_2$$

$$SO + CO \rightarrow S + CO_2$$

$$SO_2 + SO \rightarrow S + SO_3$$
 For each elementary reaction, write an expression for the net rate of reaction in terms of the concentrations of reactants and products.
2. In acid, nitriles hydrolyze to produce a carboxylic acid and ammonium ion. For example, acetonitrile, a substance used to extract fatty acids from fish liver oils, is hydrolyzed to acetic acid via the following reaction:



Express the reaction rate in terms of changes in the concentrations of each reactant and each product with time.

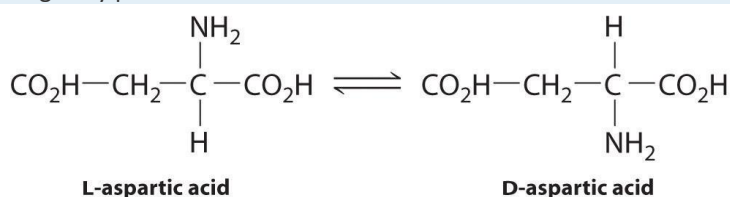
3. ♦ Ozone production occurs at lower altitudes according to the elementary reaction $O + O_2 \rightarrow O_3$, with an estimated rate of ozone production of 4.86×10^{31} molecules·s⁻¹ worldwide. What is the overall reaction order? If the reaction rate of loss of O_3 due to absorption of UV light (Equation 3.36) is 0.89×10^{31} molecules·s⁻¹, and 0.06×10^{31} molecules·s⁻¹ of ozone is transported to other atmospheric regions, is ozone being produced faster than it is being destroyed? Measurements show that ozone concentrations are not increasing rapidly. What conclusion can you draw from these data?

4. ♦ The water in a fishery became polluted when toxic waste was dumped into its pond, causing the fish population to substantially decline. The percentage of fish that survived is recorded in the following table.

Day	1	2	3	4	5
% survival	79	55	38	31	19

5. What is the reaction order of live fish $\rightarrow$ dead fish? What is the rate constant? If the fish continue to die at this rate, how many fish will be alive after 10 days?
6. Until 200 yr ago, manufactured iron contained charcoal produced from freshly cut wood that was added during the smelting process. As a result of this practice, older samples of iron can be dated accurately using the carbon-14 method. An archaeologist found a cast iron specimen that she believed dated to the period between 480 and 221 BC in Hunan, China. Radiocarbon dating of the sample indicated a 24% reduction in carbon-14 content. Was the archaeologist correct?
7. ♦ Because of its short half-life, ^{32}P -labeled compounds must be shipped as quickly as possible so that they can be used as radioactive tags in biological studies. A 50 g sample that contained 0.60% ^{32}P by mass was shipped at 11 a.m. on Monday morning. The package was delivered to a chemist via an overnight delivery service such that it arrived the next day.
- What would be the mass of ^{32}P remaining in the sample if he received the package on Tuesday afternoon but was unable to use it until 9 a.m. on Wednesday?
 - What would be the mass of ^{32}P present in the sample if the shipper had not delivered the sample until Friday afternoon and then it sat on a loading dock until 9 a.m. on Monday morning?
 - The late shipment was used immediately on Monday morning, but the biological samples were not analyzed until Thursday at 5 p.m. What percentage of the sample still consists of ^{32}P ?
8. ♦ Tritium (^3H) is a radioactive isotope that is commonly used to follow biochemical reactions.
- Using the data in Table 14.6 "Half-Lives and Applications of Some Radioactive Isotopes", calculate the radioactive decay constant (k) for tritium.
 - Use the value of k to determine the mass of tritium that is still present in a 5.00 g sample of NaB_3H_4 that is 17.57 yr old.

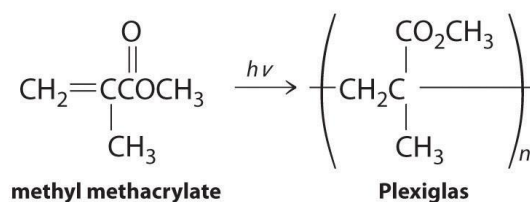
9. ♦ L-Aspartic acid is an amino acid found in fossil bone. It can convert to a geometrically different form (D-aspartic acid) at 20°C, with a half-life corresponding to the conversion of L → D of 14,000–20,000 yr. If the temperature of an archaeological site is constant, then the extent of the conversion can be used to date fossils. In one such case, archaeologists dated the arrival of humans on the North American continent to be 20,000 yr ago, but the conversion of L-aspartic acid to D-aspartic acid in human fossils indicated that Paleo-Indians were living in California at least 48,000 yr ago. What would be the relative concentrations of the L- and D-forms that produced this result? Carbon-14 has a half-life of approximately 5730 yr. What percentage of the carbon-14 originally present would have been found in the bones?



The

- technique described is frequently used in conjunction with radiocarbon dating. In cases where the results from the two techniques are in gross disagreement, what information can you get by comparing the two results?
10. ♦ Peroxides are able to initiate the radical polymerization of alkenes. Polyethylene, for example, is a high-molecular-weight polymer used as a film in packaging, as kitchenware, and as tubing. It is produced by heating ethylene at high pressure in the presence of oxygen or peroxide. It is formed by the following radical process:
- $$\text{RO}\cdot + \text{CH}_2 = \text{CH}_2 \rightarrow \text{RO}-\text{CH}_2-\text{CH}_2\cdot$$
- $$\text{RO}-\text{CH}_2-\text{CH}_2\cdot + \text{CH}_2 = \text{CH}_2 \rightarrow \text{RO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\cdot$$
- Label the steps that correspond to initiation and propagation.
 - Show all available chain-terminating steps.
 - The polymerization of styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$) occurs by a similar process to produce polystyrene, which is used as a packaging material. Draw the structure of the polymer that results from five propagation cycles.
11. Lucite and Plexiglas are transparent polymers used as a glass substitute when a plastic material is preferred for safety. The compound used to synthesize Lucite and Plexiglas is methyl methacrylate, which is shown here. During the polymerization reaction, light produces a radical initiator from hydrogen peroxide ($\text{H}_2\text{O}_2 \rightarrow$

2HO·). Show the mechanism for the polymerization, being sure to include the initiation and propagation steps.

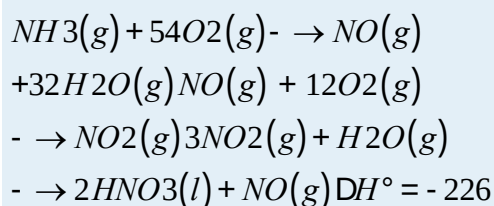


12. At

higher altitudes ozone is converted to O_2 by the reaction $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$, with a rate constant at 220 K of $6.8 \times 10^{-16} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$.

- What is the overall reaction order?
- What is E_a for this reaction if $A = 8 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$?
If Cl is present, the rate constant at 220 K becomes $3.7 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, with $A = 4.7 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$.
- Calculate E_a for the depletion of ozone in the presence of Cl.
- Show an energy-level diagram for these two processes, clearly labeling reactants, products, and activation energies.
- If you were an environmental scientist using these data to explain the effects of Cl on ozone concentration, what would be your conclusions?

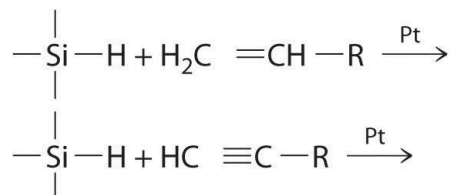
12. ♦ Nitric acid is produced commercially by the catalytic oxidation of ammonia by air over platinum gauze at approximately 900°C. The following reactions occur:



$$\Delta H^\circ = -57.1 \text{ kJ/mol} \quad \Delta H^\circ = -71.7 \text{ kJ/mol}$$

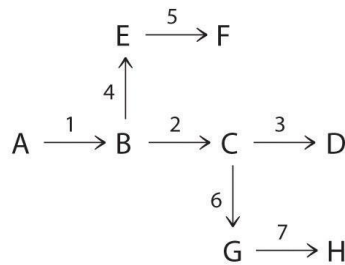
Why is platinum gauze rather than platinum wire used for the initial reaction? The reaction $4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ has $\Delta H^\circ = -316.6 \text{ kJ/mol}$. What would occur if the catalyst were not present? If the gas leaving the catalyst is not free of NH_3 , the following reaction takes place: $6\text{NO}(\text{g}) + 4\text{NH}_3(\text{g}) \rightarrow 5\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$. If this occurs, what will be the overall reaction?

13. Figure 14.27 "Hydrogenation of Ethylene on a Heterogeneous Catalyst" illustrates the mechanism for the reduction of ethylene on a platinum surface to produce ethane. Industrially important silanes are synthesized using a related mechanism and are used to increase adhesion between layers of glass fiber and between layers of silicone rubber. Predict the products of the following reactions:



14. In catalysis, if a molecule forms strong bonds to the catalyst, then the catalyst may become poisoned. Experiments on various catalysts showed the following results:
- Fe, Ru, and Os form weak bonds with N_2 ; however, O_2 , alkynes, alkenes, CO, H_2 , and CO_2 interact more strongly.
 - CO_2 and H_2 form weak bonds with a Co or Ni surface.
 - Rh, Pd, Ir, and Pt form weak bonds with H_2 but do not bond with CO_2 .
 - Cu, Ag, and Au form weak bonds with CO and ethylene.
 - Explain why Fe was chosen as a catalyst to convert nitrogen and hydrogen to ammonia. Why is Fe more suitable than Ru or Os?
 - Because alkenes generally interact more strongly with metal surfaces than does H_2 , what catalyst would you choose for hydrogenation of an alkene such as ethylene?
 - Although platinum is used in catalytic converters for automobile exhaust, it was not found to be a particularly effective catalyst for the reaction of H_2 with a mixture of carbon monoxide and carbon dioxide to produce methane. Why?
 - If you were interested in developing a catalyst to reversibly bind ethylene, which of the catalysts listed here would you choose?
14. Nonstoichiometric metal oxides can be effective catalysts for oxidation–reduction reactions. One such catalyst is Ni_{1-x}O , found to be effective for converting CO to CO_2 when oxygen is present. Why is it so effective?
15. The chemical reactions in an organism can be controlled by regulating the activity of certain enzymes. Efficient regulation results in an enzyme being active only when it is needed. For example, if a cell needed

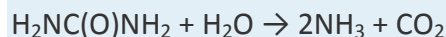
histidine, the nine enzymes needed to synthesize histidine would all be active. If the cell had adequate histidine, however, those enzymes would be inactive. The following diagram illustrates a situation in which three amino acids (D, F, H) are all synthesized from a common species, A. The numbers above the arrows refer to the enzymes that catalyze each step. Which enzymes would need to be regulated to produce D? F? H?



◆ 16.

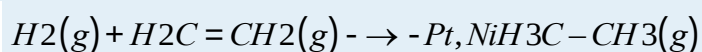
Because phosphorus-32 is incorporated into deoxyribonucleic acid (DNA), it can be used to detect DNA fragments. Consequently, it is used extensively in biological research, including the Human Genome Project, whose goal was to determine the complete sequence of human DNA. If you were to start with a 20 g sample of phosphorus that contained 10% ^{32}P by mass, converted it into DNA via several chemical steps that had an overall yield of 75% and took 25 days, and then incorporated it into bacteria and allowed them to grow for 5 more days, what mass of ^{32}P would be available for analysis at the end of this time?

17. The enzyme urease contains two atoms of nickel and catalyzes the hydrolysis of urea by the following reaction:



Urease is one of the most powerful catalysts known. It lowers the activation energy for the hydrolysis of urea from 137 kJ/mol to only 37 kJ/mol. Calculate the ratio of the reaction rate of the catalyzed reaction to the reaction rate of the uncatalyzed reaction at 37°C. Assume that the frequency factor is the same for both reactions.

16. As noted in Section 14.8 "Catalysis", the reaction rate for the hydrogenation of ethylene to give ethane can be increased by heterogeneous catalysts such as Pt or Ni:

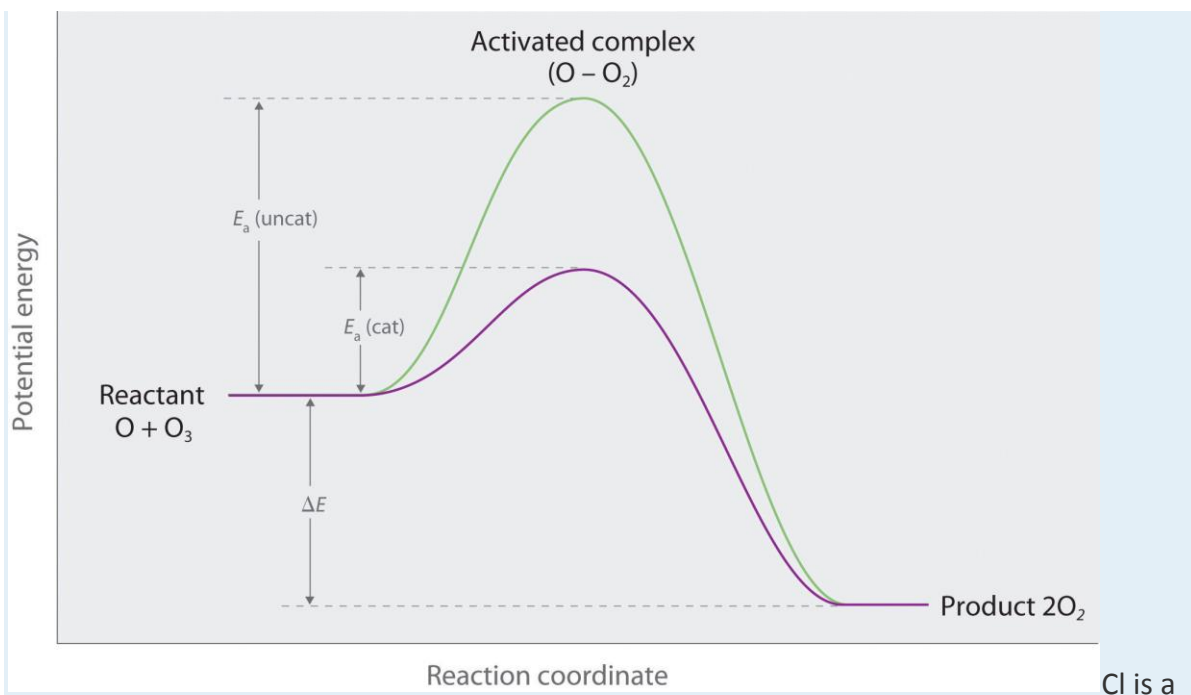


The activation energy for the uncatalyzed reaction is large (188 kJ/mol), so the reaction is very slow at room temperature. In the presence of finely divided metallic Ni, the activation energy is only 84 kJ/mol. Calculate

the ratio of the reaction rate of the catalyzed reaction to the reaction rate of the uncatalyzed reaction at 75°C.

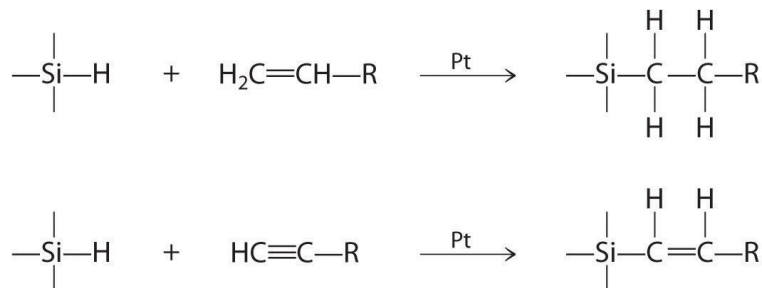
ANSWERS

1. $\text{rate} = k_f[\text{SO}_2][\text{CO}] - k_r[\text{SO}][\text{CO}_2]$; $\text{rate} = k_f[\text{SO}][\text{CO}] - k_r[\text{S}][\text{CO}_2]$; $\text{rate} = k_f[\text{SO}][\text{SO}_2] - k_r[\text{S}][\text{SO}_3]$
- 2.
3. The reaction is second order: first order in O and first order in O₃. Ozone is being produced faster than it is being destroyed. If ozone concentrations are not increasing, then either some other reaction must be consuming some of the ozone produced in this reaction or the ozone-producing reaction does not operate at this rate continuously.
- 4.
5. Yes; the object is about 2300 yr old.
- 6.
7.
 - a. $k = 0.05626 \text{ yr}^{-1}$
 - b. 0.487 g of ³H
- 8.
- 9.
- 10.
11.
 - a. second order, first order in O and first order in O₃;
 - b. 17 kJ/mol;
 - c. 0.44 kJ/mol;
 - d.



potent catalyst for ozone destruction because there is a large decrease in E_a when Cl is present.

12.



13.

14. Ni_{1-x}O is a nonstoichiometric oxide that contains a fraction of Ni(I) sites. These can react with oxygen to form a Ni(III)-oxide site, which is reduced by CO to give Ni(I) and CO_2 .

15.

16. 0.35 g of ^{32}P

17.

18. 4.1×10^{15}

$Z \square BX^- \rightarrow AY$

Chapter 15

Chemical Equilibrium

In Chapter 14 "Chemical Kinetics", we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches chemical equilibrium, the point at which the composition of the system no longer changes with time.

The reaction of O_2 with N_2 at high temperature in an internal combustion engine produces small amounts of NO , which reacts with atmospheric O_2 to form NO_2 , an important component of smog. The reddish-brown color of NO_2 is responsible for the characteristic color of smog.

We introduced the concept of equilibrium in Chapter 11 "Liquids", where you learned that a liquid and a vapor are in equilibrium when the number of molecules evaporating from the surface of the liquid per unit time is the same as the number of molecules condensing from the vapor phase. Vapor pressure is an example of a *physical equilibrium* because only the physical form of the substance changes. Similarly, in Chapter 13 "Solutions", we discussed saturated solutions, another example of a physical equilibrium, in which the rate of dissolution of a solute is the same as the rate at which it crystallizes from solution. In this chapter, we describe the methods chemists use to quantitatively describe the composition of chemical systems at equilibrium, and we discuss how factors such as temperature and pressure influence the equilibrium composition. As you study these concepts, you will also learn how urban smog forms and how reaction conditions can be altered to produce H_2 rather than the combustion products CO_2 and H_2O from the methane in natural gas. You will discover how to control the composition of the gases emitted in automobile exhaust and how synthetic polymers such as the polyacrylonitrile used in sweaters and carpets are produced on an industrial scale.

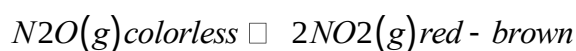
15.1 The Concept of Chemical Equilibrium

LEARNING OBJECTIVE

1. To understand what is meant by chemical equilibrium.

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). You may recall from Chapter 14 "Chemical Kinetics" that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = $-9.3^\circ C$; bp = $21.2^\circ C$) is heated from $-78.4^\circ C$ to $25^\circ C$, the red-brown color of NO_2 appears (Figure 15.1 "The "). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

Equation 15.1

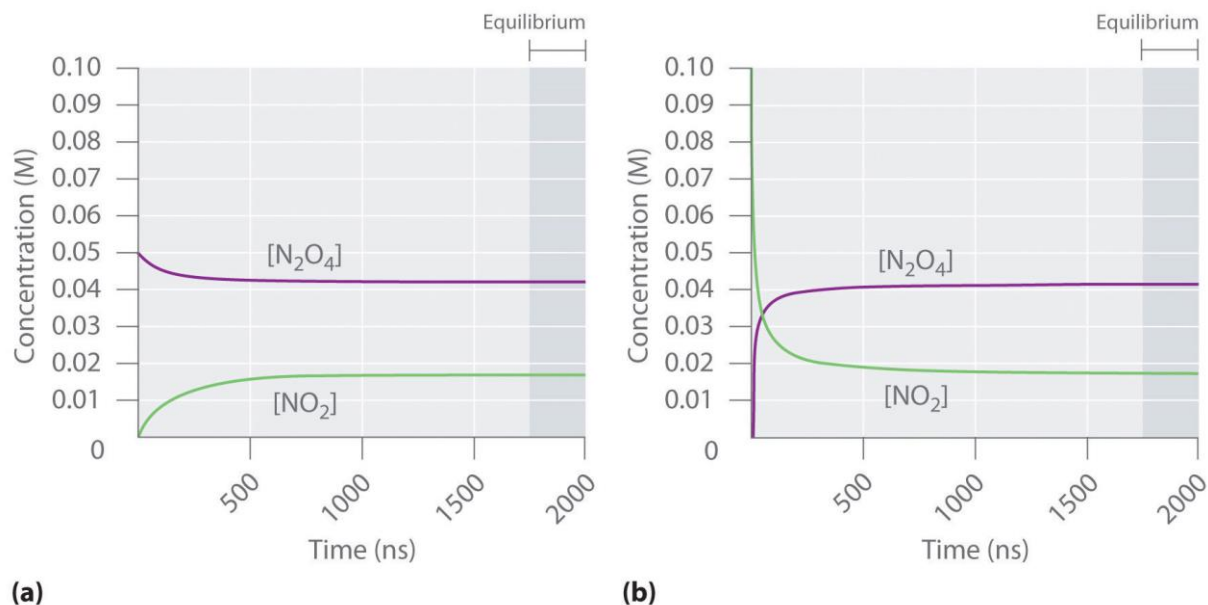


The double arrow indicates that both the forward and reverse reactions are occurring simultaneously; it is read "is in equilibrium with."

Figure 15.1 The system at Different Temperatures At dry ice temperature ($-78.4^\circ C$), the system contains essentially pure solid N_2O_4 , which is colorless. (center) As the system is warmed above the melting point of N_2O_4 ($-9.3^\circ C$), the N_2O_4 melts and then evaporates, and some of the vapor dissociates to red-brown NO_2 . (right) Eventually the sample reaches room temperature, and a mixture of gaseous N_2O_4 and NO_2 is present. The composition of the mixture and hence the color do not change further with time: the system has reached equilibrium at the new temperature.

Figure 15.2 "The Composition of N" shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 in part (a) in Figure 15.2 "The Composition of N", in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition, as shown in part (b) in Figure 15.2 "The Composition of N". Thus equilibrium can be approached from *either direction* in a chemical reaction.

Figure 15.2 The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature

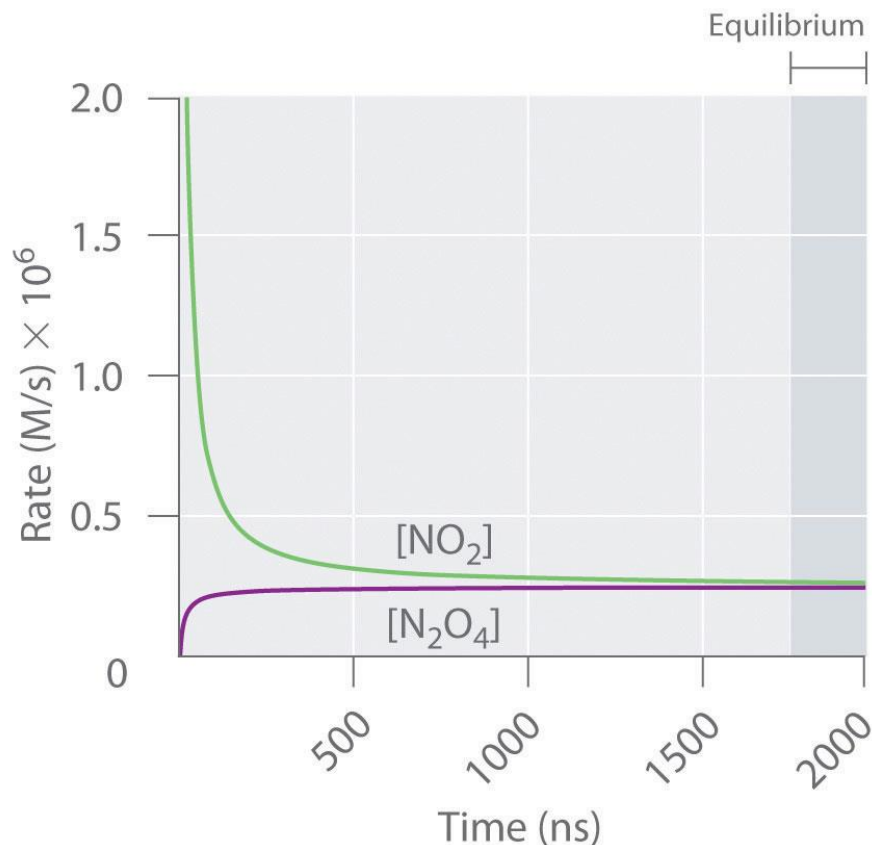


(a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2 . The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4 . The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: $[\text{N}_2\text{O}_4] = 0.0422 \text{ M}$ and $[\text{NO}_2] = 0.0156 \text{ M}$ at equilibrium.

Figure 15.3 "The Forward and Reverse Reaction Rates as a Function of Time for the " shows the forward and reverse reaction rates for a sample that initially contains pure NO_2 . Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6 \text{ M/s}$), but it decreases rapidly as the concentration of NO_2 decreases. (Recall from Chapter 14 "Chemical Kinetics" that the reaction rate of the dimerization reaction is expected to decrease rapidly because the reaction is second order in NO_2 : $\text{rate} = k_r[\text{NO}_2]^2$, where k_r is the rate constant for the reverse reaction shown in Equation 15.1.) As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2 —because the reaction is only first order in N_2O_4 ($\text{rate} = k_f[\text{N}_2\text{O}_4]$, where k_f is the rate constant for the forward reaction in Equation 15.1). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at *different* rates, then the system is *not* at equilibrium.

Figure 15.3 *The Forward and Reverse Reaction Rates as a Function of Time for the $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$*

System Shown in Part (b) in Figure 15.2 "The Composition of N"



The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

Note the Pattern

At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

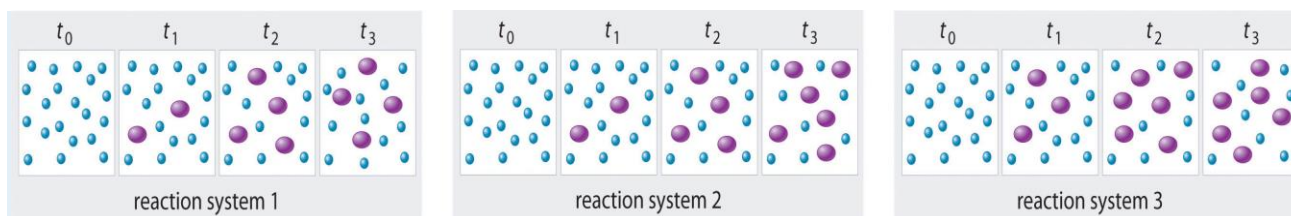
EXAMPLE 1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation $2A \rightleftharpoons B$,

where the blue circles are A and the purple ovals are B. Each set

of panels shows the changing composition of one of the three reaction mixtures as a function of time.

Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

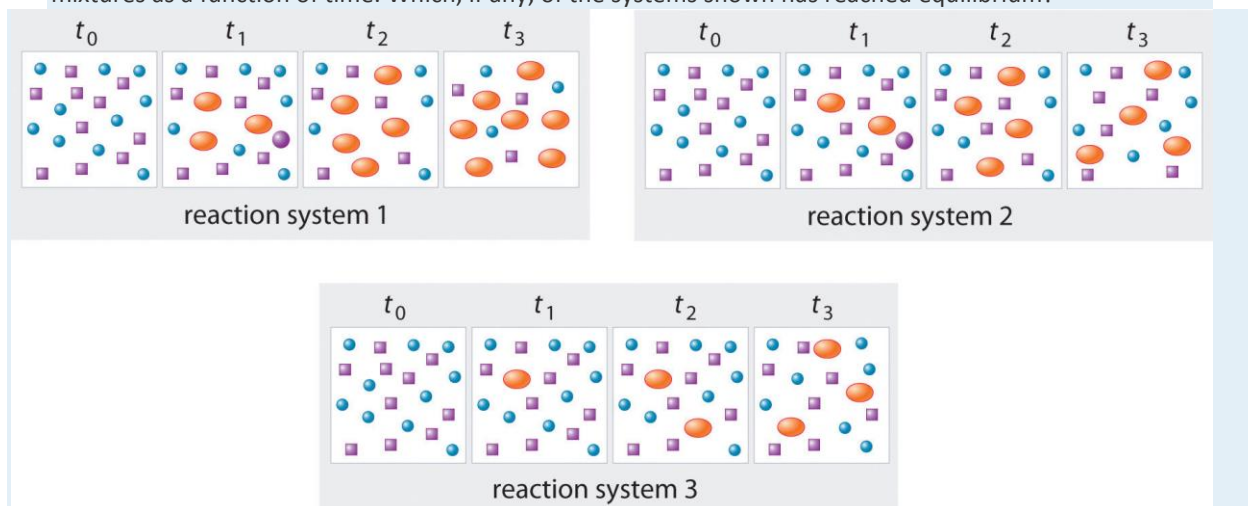
Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3 .

Thus systems 1 and 3 are at equilibrium by t_3 . In system 2, the concentrations of A and B are still changing between t_2 and t_3 , so system 2 may not yet have reached equilibrium by t_3 . Thus system 2 took the longest to reach chemical equilibrium.

Exercise

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is $A + B \rightleftharpoons C$. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer: system 2

Summary

Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

KEY TAKEAWAY

- At equilibrium, the forward and reverse reactions of a system proceed at equal rates.

CONCEPTUAL PROBLEMS

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the concentrations or amounts of the reactants and the products?
2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.
3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of NaCl in water. What is occurring on a microscopic level? What is happening on a macroscopic level?
4. Which of these systems exists in a state of chemical equilibrium?
 - a. oxygen and hemoglobin in the human circulatory system
 - b. iodine crystals in an open beaker
 - c. the combustion of wood
 - d. the amount of ^{14}C in a decomposing organism

ANSWER

- 1.
- 2.
3. Both forward and reverse reactions occur but at the same rate. Na^+ and Cl^- ions continuously leave the surface of an NaCl crystal to enter solution, while at the same time Na^+ and Cl^- ions in solution precipitate on the surface of the crystal.

15.2 The Equilibrium Constant

LEARNING OBJECTIVES

1. To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
2. To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the system described in Equation 15.1, the decomposition of N_2O_4 to NO_2 . Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

Equation 15.2

$$\text{forward rate} = k_f[\text{N}_2\text{O}_4]$$

Equation 15.3

$$\text{reverse rate} = k_r[\text{NO}_2]^2$$

At equilibrium, the forward rate equals the reverse rate:

Equation 15.4

$$k_f[\text{N}_2\text{O}_4] = k_r[\text{NO}_2]^2$$

so

Equation 15.5

$$k_f/k_r = [\text{NO}_2]^2/[\text{N}_2\text{O}_4]$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

Equation 15.6

$$K = k_f/k_r$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: *under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.*

Note the Pattern

The equilibrium constant is equal to the rate constant for the *forward* reaction divided by the rate constant for the *reverse* reaction.

Table 15.1 "Initial and Equilibrium Concentrations for " lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 15.1. At equilibrium the magnitude of the quantity $[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C , which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 15.1 Initial and Equilibrium Concentrations for *for NO₂ / N₂O₄* Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[\text{N}_2\text{O}_4]$ (M)	$[\text{NO}_2]$ (M)	$[\text{N}_2\text{O}_4]$ (M)	$[\text{NO}_2]$ (M)	$K = [\text{NO}_2]^2/[\text{N}_2\text{O}_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for *any* reversible reaction of the general form

Equation 15.7



where A and B are reactants, C and D are products, and a , b , c , and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

Equation 15.8

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where K is the equilibrium constant for the reaction. Equation 15.7 is called the equilibrium equation, and the right side of Equation 15.8 is called the equilibrium constant expression. The relationship shown in Equation 15.8 is true for *any* pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 15.2 "Equilibrium Constants for Selected Reactions*", for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl , which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 15.2 Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$	300	4.1×10^{18}
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	300	4.2×10^{13}
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$	300	2.7×10^8
$H_2(g) + D_2(g) \rightleftharpoons 2HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2I(g)$	800	4.6×10^{-7}
$Br_2(g) \rightleftharpoons 2Br(g)$	1000	4.0×10^{-7}

Reaction	Temperature (K)	Equilibrium Constant (<i>K</i>)
$\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g})$	1000	1.8×10^{-9}
$\text{F}_2(\text{g}) \rightleftharpoons 2\text{F}(\text{g})$	500	7.4×10^{-13}
*Equilibrium constants vary with temperature. The <i>K</i> values shown are for systems at the indicated temperatures.		

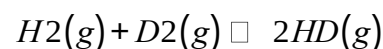
You will also notice in Table 15.2 "Equilibrium Constants for Selected Reactions*" that equilibrium constants have no units, even though Equation 15.8 suggests that the units of concentration might not always cancel because the exponents may vary. In fact, equilibrium constants are calculated using "effective concentrations," or *activities*, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M. As shown in Equation 15.9, the units of concentration cancel, which makes *K* unitless as well:

Equation 15.9

$$[A]_{\text{measured}}/[A]_{\text{standard state}} = MM = \text{mol} / \text{Lmol} / \text{L}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

Equation 15.10

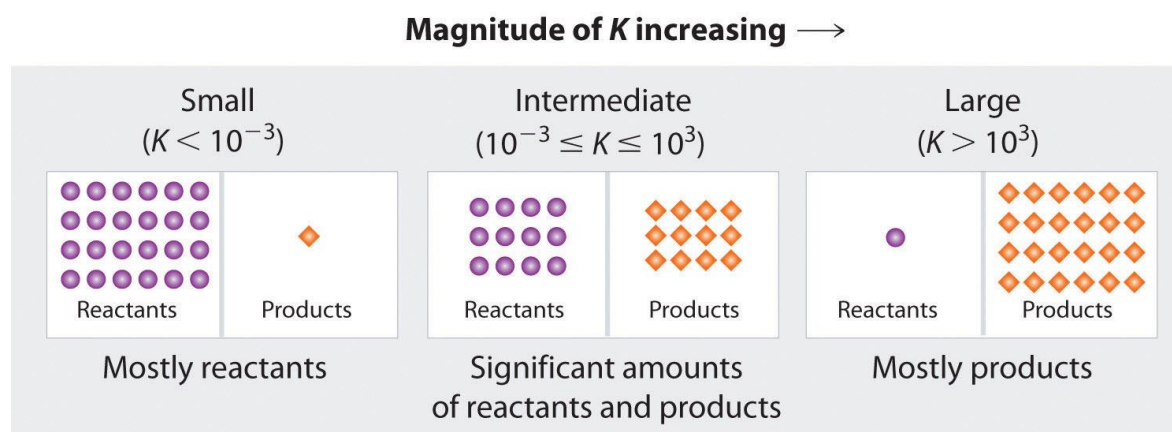


The equilibrium constant expression for this reaction is $[\text{HD}]^2/[\text{H}_2][\text{D}_2]$, and *K* is between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H₂, D₂, and HD contains significant concentrations of both product and reactants.

Figure 15.4 "The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant" summarizes the relationship between the magnitude of *K* and the relative concentrations of reactants and products at equilibrium for a general reaction, written as *reactants* $\rightleftharpoons$ *products*. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equation 15.9 and Equation 15.8), when $k_f \gg k_r$, *K* is a large number, and the concentration of products at equilibrium predominate. This

corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very small number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

Figure 15.4 *The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant*



Composition of equilibrium mixture

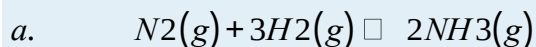
The larger the K , the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

Note the Pattern

A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

EXAMPLE 2

Write the equilibrium constant expression for each reaction.



Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 15.8. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

a. The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

b. $[NH_3]^2/[N_2][H_2]^3$

c. The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2 , with a coefficient of 12. Thus the equilibrium constant expression is as follows:

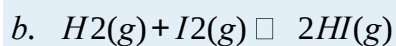
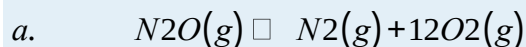
d. $[CO_2]/[CO][O_2]^{1/2}$

e. This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2 . The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$[CO]^2[O_2][CO_2]^2$$

Exercise

Write the equilibrium constant expression for each reaction.



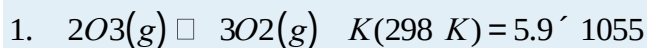
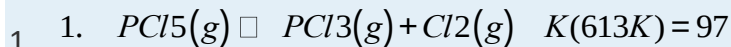
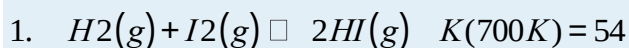
Answer:

a. $[N_2][O_2]^{1/2}/[N_2O]$

a. $[CO_2]^{16}/[H_2O]^{18}[C_8H_{18}]^2[O_2]^{25}$

EXAMPLE 3

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.



Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

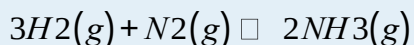
Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

- Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
- System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
- Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:



Values of the equilibrium constant at various temperatures were reported as $K_{25^\circ\text{C}} = 3.3 \times 10^8$, $K_{177^\circ\text{C}} = 2.6 \times 10^3$, and $K_{327^\circ\text{C}} = 4.1$.

- At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
- Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer:

- 327°C, where K is smallest
- 25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the

chemical reaction is written. For example, if we write the reaction described in Equation 15.7 in reverse, we obtain the following:

Equation 15.11



The corresponding equilibrium constant K' is as follows:

Equation 15.12

$$K' = \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

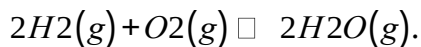
This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

Equation 15.13

$K = \frac{[NO_2]^2}{[N_2O_4]}$ but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K' is given by the inverse expression:

Equation 15.14

$K' = \frac{[N_2O_4]}{[NO_2]^2}$ Consider another example, the formation of water:



Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2 , is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2 .

Note the Pattern

The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction $2NO_2 \rightleftharpoons N_2O_4$ as $NO_2 \rightleftharpoons \frac{1}{2}N_2O_4$, for which the equilibrium constant K'' is as follows:

Equation 15.15

$$K' = [N_2O_4]^{1/2} / [NO_2]$$

The values for K' (Equation 15.14) and K'' are related as follows:

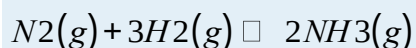
Equation 15.16

$$K' = (K'')^{1/2} = K''^{-1/2}$$

In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by n , then the new equilibrium constant is the original equilibrium constant raised to the n th power.

EXAMPLE 4

At 745 K, K is 0.118 for the following reaction:



What is the equilibrium constant for each related reaction at 745 K?

- $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
- $12N_2(g) + 32H_2(g) \rightleftharpoons 8NH_3(g)$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_2(g)$ with $H_2(g)$ to produce $NH_3(g)$ at 745 K is as follows:

$$a. \quad K = [NH_3]^2 / [N_2][H_2]^3 = 0.118$$

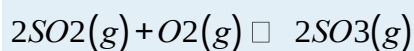
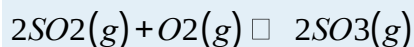
This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$b. \quad K' = 1/K = [N_2][H_2]^3 / [NH_3]^2 = 10.118 = 8.47$$

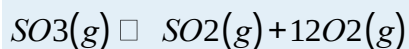
In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = [NH_3][N_2]^{1/2} / [H_2]^{3/2} = K^{1/2} = K^{-1/2} = 0.118^{-1/2} = 0.344 \text{ Exercise}$$

At 527°C, the equilibrium constant for the reaction



is 7.9×10^4 . Calculate the equilibrium constant for the following reaction at the same temperature:



Answer: 3.6×10^{-3}

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, we can write the equilibrium constant expression as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

Equation 15.17

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

Equation 15.18

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$$

Like K , K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity.^[1]

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the temperature (T):

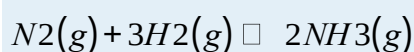
Equation 15.19

$$K_p = K(RT)^{\Delta n}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in kelvins. According to Equation 15.19, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4 , there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction, $K_p = K(RT)^1 = KRT$.

EXAMPLE 5

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:



What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn . Then use Equation 15.19 to calculate K from K_p .

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We

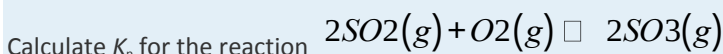
know K , and $T = 745$ K. Thus, from Equation 15.16, we have the following:

$$K_p = K(RT)^{-\Delta n} = K(RT)^2$$

$$= 0.118 \{ [0.08206 (L \cdot atm) / (mol \cdot K)] [745 K] \}^2 = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise



at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer: $K_p = 1.2 \times 10^3$

Homogeneous and Heterogeneous Equilibria

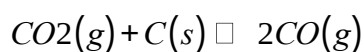
When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and

products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.^[2] (Recall from Chapter 11 "Liquids", for example, that the density of water, and thus its volume, changes by only a few percentage points between 0°C and 100°C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

Equation 15.20



The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

Equation 15.21

$$K = [\text{CO}]^2 / [\text{CO}_2][\text{C}]$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

Equation 15.22

$$[\text{C}] = 2.26 \text{ g/cm}^3 / 12.01 \text{ g/mol} \times 1000 \text{ cm}^3/\text{L} = 188 \text{ mol/L} = 188 \text{ M}$$

We can rearrange Equation 15.18 so that the constant terms are on one side:

Equation 15.23

$$K[\text{C}] = K(188) = [\text{CO}]^2 / [\text{CO}_2]$$

Incorporating the constant value of [C] into the equilibrium equation for the reaction in Equation 15.17,

Equation 15.24

$$K' = [\text{CO}]^2 / [\text{CO}_2]$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

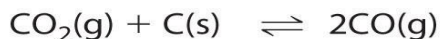
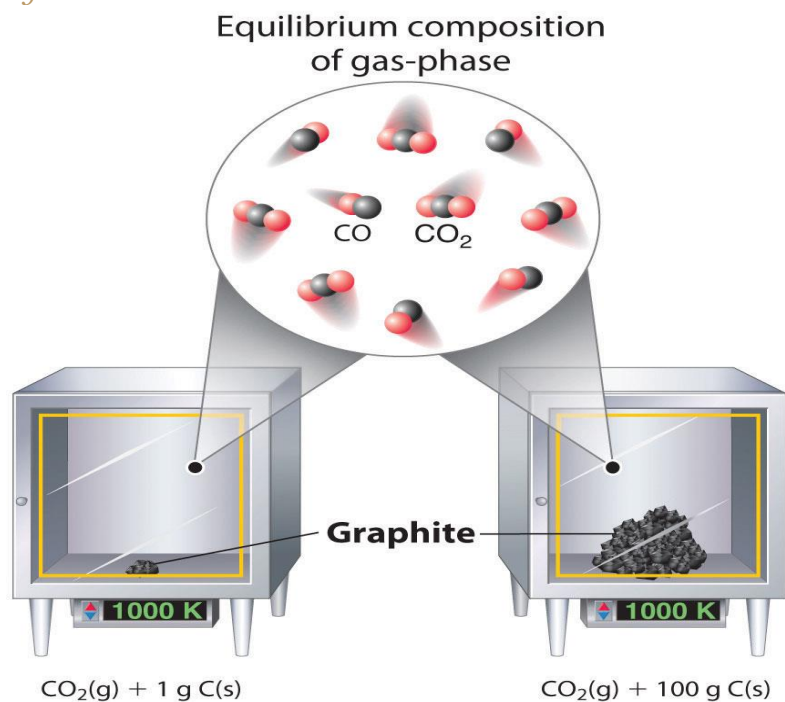
Equation 15.25

$$K_p = (P_{\text{CO}})^2 / P_{\text{CO}_2}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO₂, the system described in Equation 15.17 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 15.5 "Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System", it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

Figure 15.5 Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System

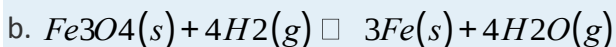
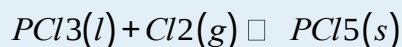


In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

EXAMPLE 6

Write each expression for K , incorporating all constants, and K_p for the following equilibrium reactions.

a.



Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution:

a. This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

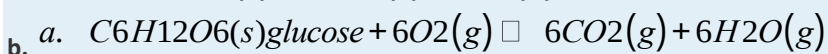
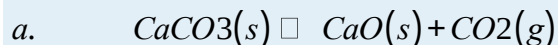
b. $K = 1/[Cl_2]$ and $K_p = 1/PCl_2$

This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = [H_2O]^4/[H_2]^4 \text{ and } K_p = (PH_2O)^4/(PH_2)^4$$

Exercise

Write the expressions for K and K_p for the following reactions.



Answer:

$$K = [CO_2]^6/[H_2O]^6[O_2]^6; K_p = (PCO_2)^6/(PH_2O)^6(PO_2)^6$$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

Note the Pattern

The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

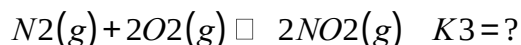
Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2 . As we stated in Section 15.1 "The Concept of Chemical Equilibrium", this reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO . The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.



Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2 :



The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \quad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \quad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

What is the relationship between K_1 , K_2 , and K_3 , all at 100°C ? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3 . Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1 K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3 :

$$K_3 = K_1 K_2 = (2.0 \times 10^{-25})(6.4 \times 10^9) = 1.3 \times 10^{-15}$$

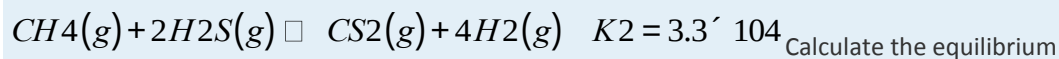
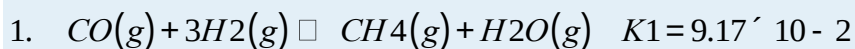
The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the *sum* of the ΔH values for the individual reactions.

Note the Pattern

To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

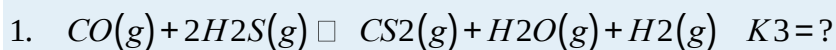
EXAMPLE 7

The following reactions occur at 1200°C:



Calculate the equilibrium

constant for the following reaction at the same temperature.



Given: two balanced equilibrium equations, values of K , and an equilibrium equation for the overall reaction

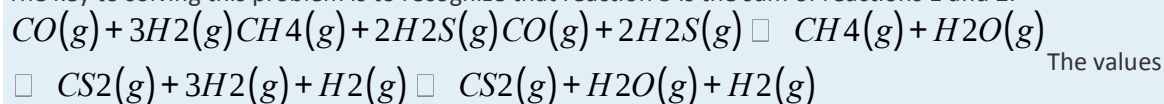
Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:



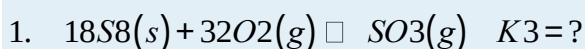
The values

for K_1 and K_2 are given, so it is straightforward to calculate K_3 :

$$K_3 = K_1 K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3$$

Exercise

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.



Answer: $K_3 = 1.1 \times 10^{66}$

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the **equilibrium constant (K)**, a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K . For a system at equilibrium, the **law of mass action** relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the **equilibrium equation**. The ratio is called the **equilibrium constant expression**. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a **homogeneous equilibrium**; a system whose reactants, products, or both are in more than one phase is a **heterogeneous equilibrium**. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

KEY TAKEAWAYS

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.

KEY EQUATIONS

Definition of equilibrium constant in terms of forward and reverse rate constants

Equation 15.6: $K = k_f/k_r$

Equilibrium constant expression (law of mass action)

Equation 15.8 : $K = [C]^c [D]^d [A]^a [B]^b$

Equilibrium constant expression for reactions involving gases using partial pressures

Equation 15.17 : $K_p = (P_C)^c (P_D)^d (P_A)^a (P_B)^b$

Relationship between K_p and K

Equation 15.19: $K_p = K(RT)^{\Delta n}$

CONCEPTUAL PROBLEMS

1. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?
2. Which of the following equilibria are homogeneous and which are heterogeneous?

[1] The "effective pressure" is called the *fugacity*, just as activity is the effective concentration.

[2] The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1.

15.3 Solving Equilibrium Problems

LEARNING OBJECTIVE

1. To solve quantitative problems involving chemical equilibria.

There are two fundamental kinds of equilibrium problems: (1) those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and (2) those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 "The Equilibrium Constant" that the equilibrium constant for the decomposition of $\text{CaCO}_3(\text{s})$ to $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$ is $K = [\text{CO}_2]$. At 800°C , the concentration of CO_2 in equilibrium with solid CaCO_3 and CaO is $2.5 \times 10^{-3} \text{ M}$. Thus K at 800°C is 2.5×10^{-3} . (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of *n*-butane, an additive used to increase the volatility of gasoline, to isobutane (2-methylpropane). This reaction can be written as follows:

Equation 15.26



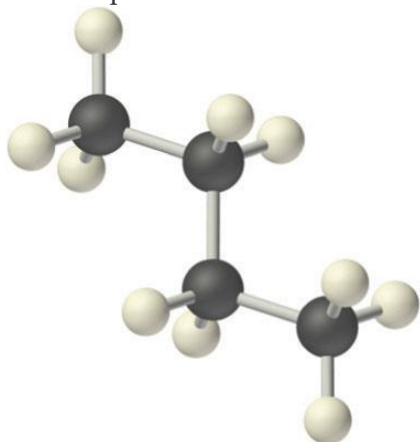
and the equilibrium constant $K = [\text{isobutane}]/[n\text{-butane}]$. At equilibrium, a mixture of *n*-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M *n*-butane.

Substituting these concentrations into the equilibrium constant expression,

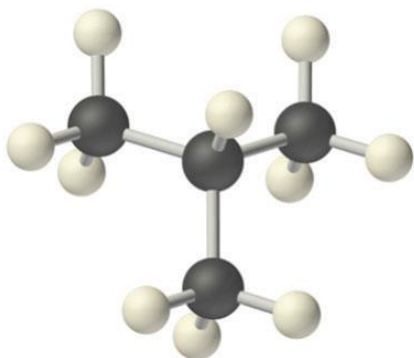
Equation 15.27

$$K = [\text{isobutane}]/[n\text{-butane}] = 0.041\text{ M}/0.016\text{ M} = 2.6$$

Thus the equilibrium constant for the reaction as written is 2.6.



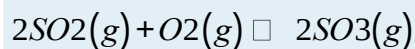
n-butane



isobutane (2-methylpropane)

EXAMPLE 8

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:



A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained $5.0 \times 10^{-2} \text{ M SO}_3$, $3.5 \times 10^{-3} \text{ M O}_2$, and $3.0 \times 10^{-3} \text{ M SO}_2$. Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy:

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K .

Solution:

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

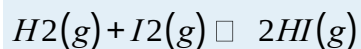
$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p , we use Equation 16.18, where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n} = 7.9 \times 10^4 [(0.08206 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K})(800 \text{ K})]^{-1} = 1.2 \times 10^3$$

Exercise

Hydrogen gas and iodine react to form hydrogen iodide via the reaction



A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained $1.37 \times 10^{-2} \text{ M HI}$, $6.47 \times 10^{-3} \text{ M H}_2$, and $5.94 \times 10^{-4} \text{ M I}_2$. Calculate K and K_p for this reaction.

Answer: $K = 48.8$; $K_p = 48.8$

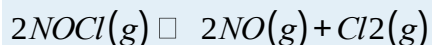
Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced

chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 9 shows one way to do this.

EXAMPLE 9

A 1.00 mol sample of NOCl was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl₂.

Calculate K at this temperature. The equation for the decomposition of NOCl to NO and Cl₂ is as follows:



Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

B Calculate all possible initial concentrations from the data given and insert them in the table.

C Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

D Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution:

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$$

To obtain the concentrations of NOCl, NO, and Cl₂ at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.



	[NOCl]	[NO]	[Cl ₂]
initial			
change			
final			

B Initially, the system contains 1.00 mol of NOCl in a 2.00 L container. Thus $[\text{NOCl}]_i = 1.00 \text{ mol} / 2.00 \text{ L} = 0.500 \text{ M}$. The initial concentrations of NO and Cl₂ are 0 M because initially no products are present.

Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl₂ in a 2.00 L container, so

$[\text{Cl}_2]_f = 0.056 \text{ mol} / 2.00 \text{ L} = 0.028 \text{ M}$. We insert these values into the following table:

$2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$			
	[NOCl]	[NO]	[Cl ₂]
initial	0.500	0	0
change			
final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl₂, the substance for which initial and final concentrations are known:

$$\Delta[\text{Cl}_2] = [0.028 \text{ M (final)} - 0.00 \text{ M (initial)}] = +0.028 \text{ M}$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl₂, so the change in the NO concentration is as follows:

$$\begin{aligned} \Delta[\text{NO}] &= (0.028 \text{ mol Cl}_2 / \text{L}) \\ &\quad / (2 \text{ mol NO} / 1 \text{ mol Cl}_2) = 0.056 \text{ M} \end{aligned}$$

Similarly, 2 mol of NOCl are consumed for every 1 mol of Cl₂ produced, so the change in the NOCl concentration is as follows:

$$\Delta[\text{NOCl}] = 0.028 \text{ mol Cl}_2 / \text{L} \times -2 \text{ mol NOCl} / 1 \text{ mol Cl}_2 = -0.056 \text{ M}$$

We insert these values into our table:

$2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$			
	[NOCl]	[NO]	[Cl ₂]
initial	0.500	0	0
change	-0.056	+0.056	+0.028
final			0.028

D We sum the numbers in the [NOCl] and [NO] columns to obtain the final concentrations of NO and NOCl:
 $[\text{NO}]_f = 0.000 \text{ M} + 0.056 \text{ M} = 0.056 \text{ M}$
 $[\text{NOCl}]_f = 0.500 \text{ M} + (-0.056 \text{ M}) = 0.444 \text{ M}$

We can now complete the table:

$2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$			
	[NOCl]	[NO]	[Cl ₂]
initial	0.500	0	0
change	-0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.056)^2 (0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

Exercise

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH₃) by reacting 0.1248 M H₂ and 0.0416 M N₂ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH₃.

What is K for the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ at this

temperature? What is K_p ?

Answer: $K = 0.105$; $K_p = 2.61 \times 10^{-5}$

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of *n*-butane to isobutane (Equation 15.26), for which $K = 2.6$ at 25°C. If we begin with a 1.00 M sample of *n*-butane, we can determine the concentration of *n*-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 9.

$n\text{-butane}(g) \rightleftharpoons \text{isobutane}(g)$		
	[<i>n</i> -Butane]	[Isobutane]
initial		
change		
final		

The initial concentrations of the reactant and product are both known: $[n\text{-butane}]_i = 1.00 \text{ M}$ and $[isobutane]_i = 0 \text{ M}$. We need to calculate the equilibrium concentrations of both n -butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the *change* in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane ($\Delta[isobutane]$) as $+x$, then the change in the concentration of n -butane is $\Delta[n\text{-butane}] = -x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n -butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$n\text{-butane}(g) \rightleftharpoons isobutane(g)$		
	[n-Butane]	[Isobutane]
initial	1.00	0
change	$-x$	$+x$
final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of n -butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[isobutane]}{[n\text{-butane}]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for x ,

$$x = 2.6(1.00 - x) \quad x + 2.6x = 2.6 \quad 2.6x = 2.6 \quad x = 0.72$$

We obtain the final concentrations by substituting this x value into the expressions for the final

concentrations of n -butane and isobutane listed in the table:

$$[n\text{-butane}]_f = (1.00 - x) \text{ M} = (1.00 - 0.72) \text{ M} = 0.28 \text{ M} \quad [isobutane]_f = (0.00 + x) \text{ M} = (0.00 + 0.72) \text{ M} = 0.72 \text{ M}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

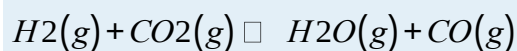
$$K = \frac{[isobutane]}{[n\text{-butane}]} = \frac{0.72 \text{ M}}{0.28 \text{ M}} = 2.6$$

This is the same K we were given, so we can be confident of our results.

Example 10 illustrates a common type of equilibrium problem that you are likely to encounter.

EXAMPLE 10

The *water–gas shift reaction* is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:



$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K , and initial concentrations

Asked for: final concentrations

Strategy:

A Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x . From the values in the table, calculate the final concentrations.

B Write the equilibrium equation for the reaction. Substitute appropriate values from the table to obtain x .

C Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K .

Solution:

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150$ M. Just as before, we will focus on the *change* in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x , then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x . For example, 1 mol of CO is produced for every 1 mol of H_2O , so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$				
	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
initial	0.0150	0.0150	0	0
change	$-x$	$-x$	$+x$	$+x$

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$				
	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
final	$(0.0150 - x)$	$(0.0150 - x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x :

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)^2} = 0.106$$

$$(0.0150 - x)^2 = x^2 \quad (0.0150 - x)^2 = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$x^2(0.0150 - x)^2 = (x(0.0150 - x))^2 = 0.106$$

(The quadratic formula is presented in Essential Skills 7 in Section 15.7 "Essential Skills".) Taking the

square root of the middle and right terms,

$$x(0.0150 - x) = \sqrt{0.106} = 0.326$$

$$= (0.326)(0.0150) - 0.326x = 0.00489 = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

$$[H_2]_f = [H_2]_i - [CO]_f = 0.0150 - 0.00369 = 0.0113 \text{ M}$$

$$[CO_2]_f = [CO_2]_i - [CO]_f = 0.0150 - 0.00369 = 0.0113 \text{ M}$$

$$[H_2O]_f = [H_2O]_i + [CO]_f = 0 + 0.00369 = 0.00369 \text{ M}$$

$$[CO]_f = [CO]_i + [CO]_f = 0 + 0.00369 = 0.00369 \text{ M}$$

$$[H_2O]_f = [H_2O]_i + [CO]_f = 0 + 0.00369 = 0.00369 \text{ M}$$

$$[CO]_f = [CO]_i + [CO]_f = 0 + 0.00369 = 0.00369 \text{ M}$$

$$[CO]_f = [CO]_i + [CO]_f = 0 + 0.00369 = 0.00369 \text{ M}$$

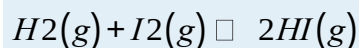
We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:



$K = 54$ at 425°C . If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer: $[\text{HI}]_f = 0.270\text{ M}$; $[\text{H}_2]_f = [\text{I}_2]_f = 0.037\text{ M}$

In Example 10, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 11.

EXAMPLE 11

In the water–gas shift reaction shown in Example 10, a sample containing 0.632 M CO_2 and 0.570 M H_2 is allowed to equilibrate at 700 K . At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (x) and the final concentrations.

B Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x .

C Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K .

Solution:

A $[\text{CO}_2]_i = 0.632\text{ M}$ and $[\text{H}_2]_i = 0.570\text{ M}$. Again, x is defined as the change in the concentration of H_2O : $\Delta[\text{H}_2\text{O}] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O , the change in the concentration of CO is the same as the change in the concentration of H_2O , so $\Delta[\text{CO}] = +x$. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[\text{H}_2] = \Delta[\text{CO}_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.



	[H ₂]	[CO ₂]	[H ₂ O]	[CO]
initial	0.570	0.632	0	0
change	-x	-x	+x	+x
final	(0.570 - x)	(0.632 - x)	x	x

B We can now use the equilibrium equation and the known K value to solve for x :

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 10, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)} = 0.148, -0.2$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148$ M, and $\Delta[H_2] = \Delta[CO_2] = -0.148$ M.

C The final concentrations of all species in the reaction mixture are as follows:

$$\begin{aligned} [H_2O]_f &= [H_2O]_i + \Delta[H_2O] = 0 \text{ M} + 0.148 \text{ M} = 0.148 \text{ M} \\ [CO]_f &= [CO]_i + \Delta[CO] = 0 \text{ M} + 0.148 \text{ M} = 0.148 \text{ M} \end{aligned}$$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise

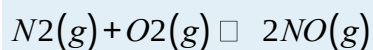
The exercise in Example 8 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C . If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C , what is the final concentration of each substance in the reaction mixture?

Answer: $[HI]_f = 0.0882$ M; $[H_2]_f = 0.156$ M; $[I_2]_f = 9.2 \times 10^{-4}$ M

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^3$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 12.

EXAMPLE 12

Atmospheric nitrogen and oxygen react to form nitric oxide:



$K_p = 2.0 \times 10^{-31}$ at 25°C . What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{\text{N}_2} = 0.78 \text{ atm}$ and $P_{\text{O}_2} = 0.21 \text{ atm}$)?

Given: balanced equilibrium equation and values of K_p , P_{O_2} , and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.

B Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).

C Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K .

Solution:

A Because we are given K_p and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

initial P	0.78	0.21	0
change in P	$-x$	$-x$	$+2x$
final P	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = (P_{NO})^2(P_{N_2})(P_{O_2}) = (2x)^2(0.78 - x)(0.21 - x) = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78 - x) =$

0.78 and $(0.21 - x) = 0.21$. Substituting these expressions into our original equation,

$$(2x)^2(0.78)(0.21) = 2.0 \times 10^{-31} \\ 20.16x^2 = 2.0 \times 10^{-31} \\ x^2 = 9.9 \times 10^{-17} \\ x = 9.9 \times 10^{-9}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

$$P_{NO} = 2x = 1.98 \times 10^{-8} \text{ atm} \\ P_{N_2} = (0.78 - x) \approx 0.78 \text{ atm} \\ P_{O_2} = (0.21 - x) \approx 0.21 \text{ atm}$$

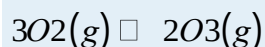
From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21 . When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^3$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C . We can verify our results by substituting them into the original equilibrium equation:

$$K_p = (P_{NO})^2(P_{N_2})(P_{O_2}) = (1.98 \times 10^{-8})^2(0.78)(0.21) = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

Exercise

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:



$K_p = 2.5 \times 10^{-59}$ at 25°C . What ozone partial pressure is in equilibrium with oxygen in the

atmosphere ($P_{O_2} = 0.21 \text{ atm}$)?

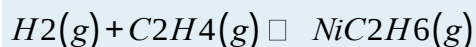
Answer: $4.8 \times 10^{-31} \text{ atm}$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds

100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 13.

EXAMPLE 13

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:



$K = 9.6 \times 10^{18}$ at $25^\circ C$. If a mixture of $0.200\text{ M } H_2$ and $0.155\text{ M } C_2H_4$ is maintained at $25^\circ C$ in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K , and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

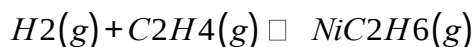
A Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.

B Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).

C Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M . Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be $0.200\text{ M} - 0.155\text{ M} = 0.045\text{ M}$. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 12. If we define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.



	[H ₂]	[C ₂ H ₄]	[C ₂ H ₆]
initial	0.200	0.155	0
assuming 100% reaction	0.045	0	0.155
change	+x	+x	-x
final	(0.045 + x)	(0 + x)	(0.155 - x)

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified $[(0.045 + x) = 0.045 \text{ and } (0.155 - x) = 0.155]$ as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18} = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

$$[C_2H_6]_f = (0.155 - x) \text{ M} = 0.155 \text{ M} \quad [C_2H_4]_f = x \text{ M} = 3.6 \times 10^{-19} \text{ M} \quad [H_2]_f = (0.045 + x) \text{ M} = 0.045 \text{ M}$$

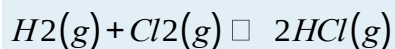
We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

Exercise

Hydrogen reacts with chlorine gas to form hydrogen chloride:



$K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H₂ and 0.392 M Cl₂ is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer: [H₂]_f = 4.8×10^{-32} M; [Cl₂]_f = 0.135 M; [HCl]_f = 0.514 M

Summary

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the

quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

KEY TAKEAWAY

- Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

CONCEPTUAL PROBLEMS

- Describe how to determine the magnitude of the equilibrium constant for a reaction when not all concentrations of the substances are known.
- Calculations involving systems with very small or very large equilibrium constants can be dramatically simplified by making certain assumptions about the concentrations of products and reactants. What are these assumptions when K is (a) very large and (b) very small? Illustrate this technique using the system $A + 2B \rightleftharpoons C$ for which you are to calculate the concentration of the product at equilibrium starting with only A and B. Under what circumstances should simplifying assumptions not be used?

NUMERICAL PROBLEMS

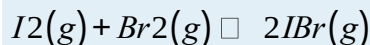
Please be sure you are familiar with the topics discussed in Essential Skills 7 (Section 15.7 "Essential Skills") before proceeding to the Numerical Problems.

- In the equilibrium reaction $A + B \rightleftharpoons C$, what happens to K if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction $2A \rightleftharpoons B + C$?
- The following table shows the reported values of the equilibrium PO_2 at three temperatures for the reaction $Ag_2O(s) \rightleftharpoons 2Ag(s) + \frac{1}{2}O_2(g)$, for which $\Delta H^\circ = 31 \text{ kJ/mol}$. Are these data consistent with what you would expect to occur? Why or why not?

$T (^\circ\text{C})$	$PO_2 (\text{mmHg})$
150	182
184	143
191	126

- Starting with pure A, if the total equilibrium pressure is 0.969 atm for the

4. Solid ammonium carbamate ($\text{NH}_4\text{CO}_2\text{NH}_2$) dissociates completely to ammonia and carbon dioxide when it vaporizes:
5. 3.5×10^{-2} . If you begin with 50 mL of a 0.896 M solution of IO_4^- that is diluted to 250 mL with water, how many moles of H_4IO_6^- are formed at equilibrium?
6. Iodine and bromine react to form IBr, which then sublimes. At 184.4°C , the overall reaction proceeds according to the following equation:



$K_p = 1.2 \times 10^2$. If you begin the reaction with 7.4 g of I_2 vapor and 6.3 g of Br_2 vapor in a 1.00 L container, what is the concentration of $\text{IBr}(g)$ at equilibrium? What is the partial pressure of each gas at equilibrium? What is the total pressure of the system?

7. For the reaction $\text{C}(s) + 12\text{N}_2(g) + 52\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{NH}_2(g)$,
 $K = 1.8 \times 10^{-6}$. If you begin the reaction with 1.0

mol of N_2 , 2.0 mol of H_2 , and sufficient $\text{C}(s)$ in a 2.00 L container, what are the concentrations of N_2 and CH_3NH_2 at equilibrium? What happens to K if the concentration of H_2 is doubled?

15.4 Nonequilibrium Conditions

LEARNING OBJECTIVE

1. To predict in which direction a reaction will proceed.

In Section 15.3 "Solving Equilibrium Problems", we saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the reaction quotient (Q). The expression for the reaction quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at *any* time during the reaction of *any* mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction: $Q = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$

the reaction quotient is defined as follows:

Equation 15.28

$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ The reaction quotient (Q_p), which is analogous to K_p , can be written for any reaction that involves gases by using the partial pressures of the components.

To understand how information is obtained using a reaction quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

Equation 15.29

$$Q = \frac{[NO_2]^2}{[N_2O_4]}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

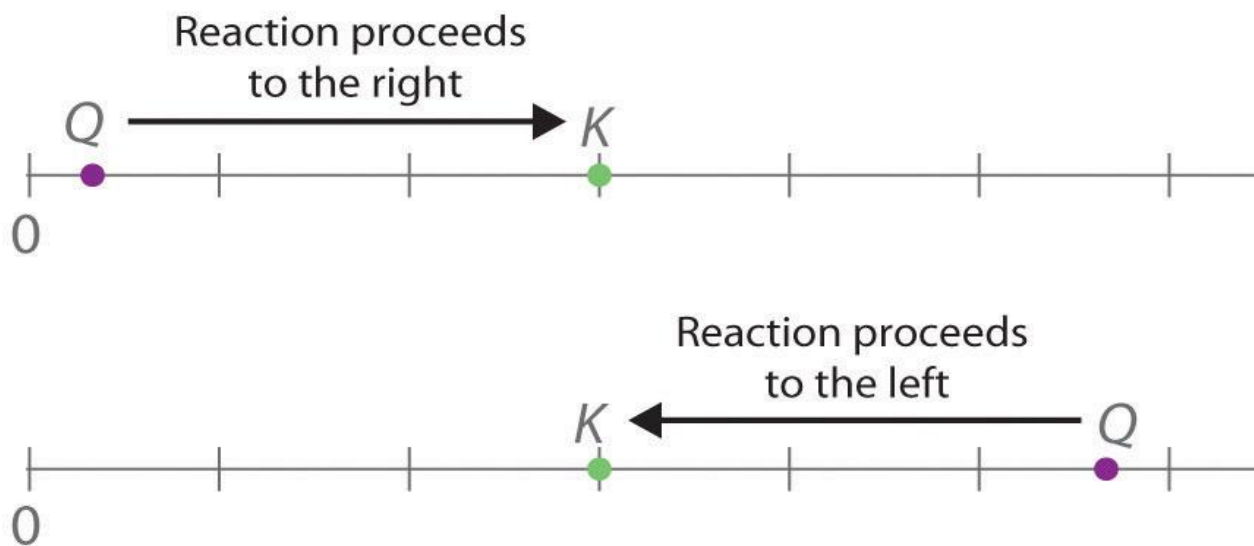
Experiment	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$Q = [NO_2]^2/[N_2O_4]$
1	0	0.0400	$0/0.0400 = 0$
2	0.0600	0	$(0.0600)^2/0 = \text{undefined}$
3	0.0200	0.0600	$(0.0200)^2/0.0600 = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K .

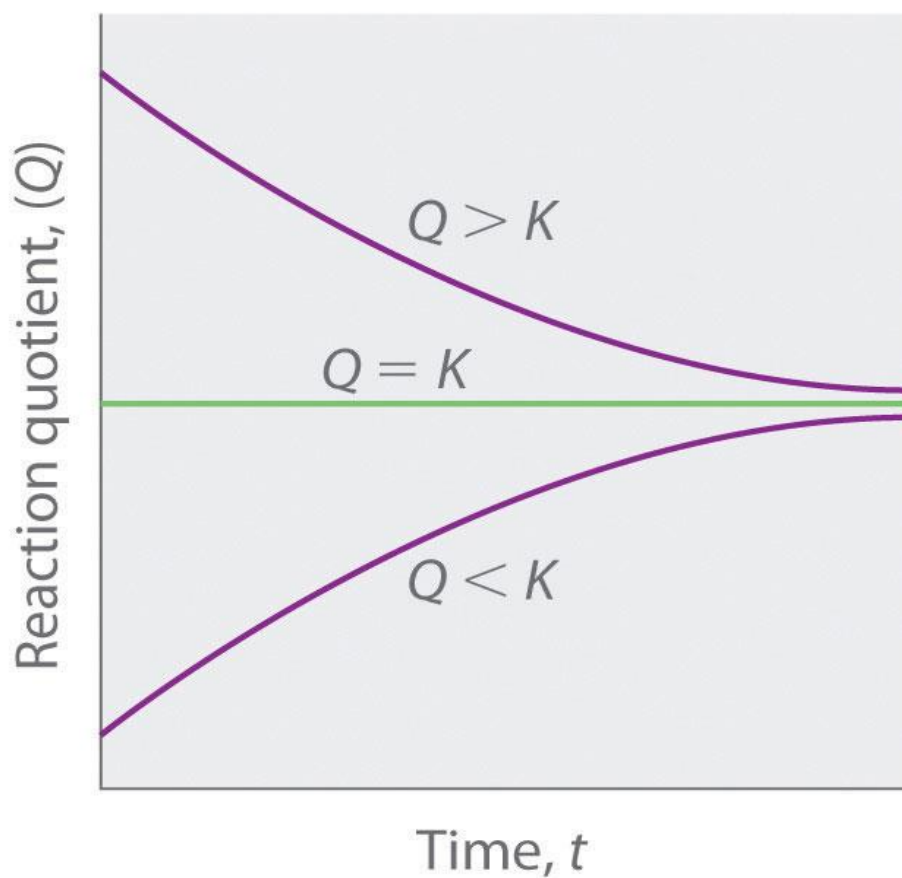
Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K . If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is *less than* the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is *greater than* at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of

products. These points are illustrated graphically in Figure 15.6 "Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of ".

Figure 15.6 Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K



(a) Q versus K , t_0 to t



(b) Q versus K , t_0 to t_∞

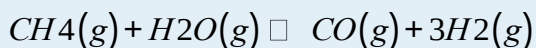
(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K . (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

Note the Pattern

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

EXAMPLE 14

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a *steam-reforming* reaction:



$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4 , 8.0×10^{-3} mol of H_2O , 1.6×10^{-2} mol of CO , and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O ?

Given: balanced chemical equation, K , amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A Calculate the molar concentrations of the reactants and the products.

B Use Equation 15.28 to determine Q . Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have

1.2×10^{-2} mol of CH_4 in a 2.0 L container, so

$$[\text{CH}_4] = 1.2 \times 10^{-2} \text{ mol} / 2.0 \text{ L} = 6.0 \times 10^{-3} \text{ M}$$

We can calculate the other concentrations in a similar way: $[\text{H}_2\text{O}] = 4.0 \times 10^{-3} \text{ M}$, $[\text{CO}] = 8.0 \times 10^{-3} \text{ M}$, and $[\text{H}_2] = 3.0 \times 10^{-3} \text{ M}$.

B We now compute Q and compare it with K :

$$\begin{aligned} Q &= [\text{CO}][\text{H}_2]^3 / [\text{CH}_4][\text{H}_2\text{O}] \\ &= (8.0 \times 10^{-3})(3.0 \times 10^{-3})^3 / (6.0 \times 10^{-3})(4.0 \times 10^{-3}) = 9.0 \times 10^{-6} \end{aligned}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4 .

Exercise

In the water–gas shift reaction introduced in Example 10, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:



$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O , 0.0080 mol of CO_2 , and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer: $Q = 0.96$ ($Q > K$), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K , such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

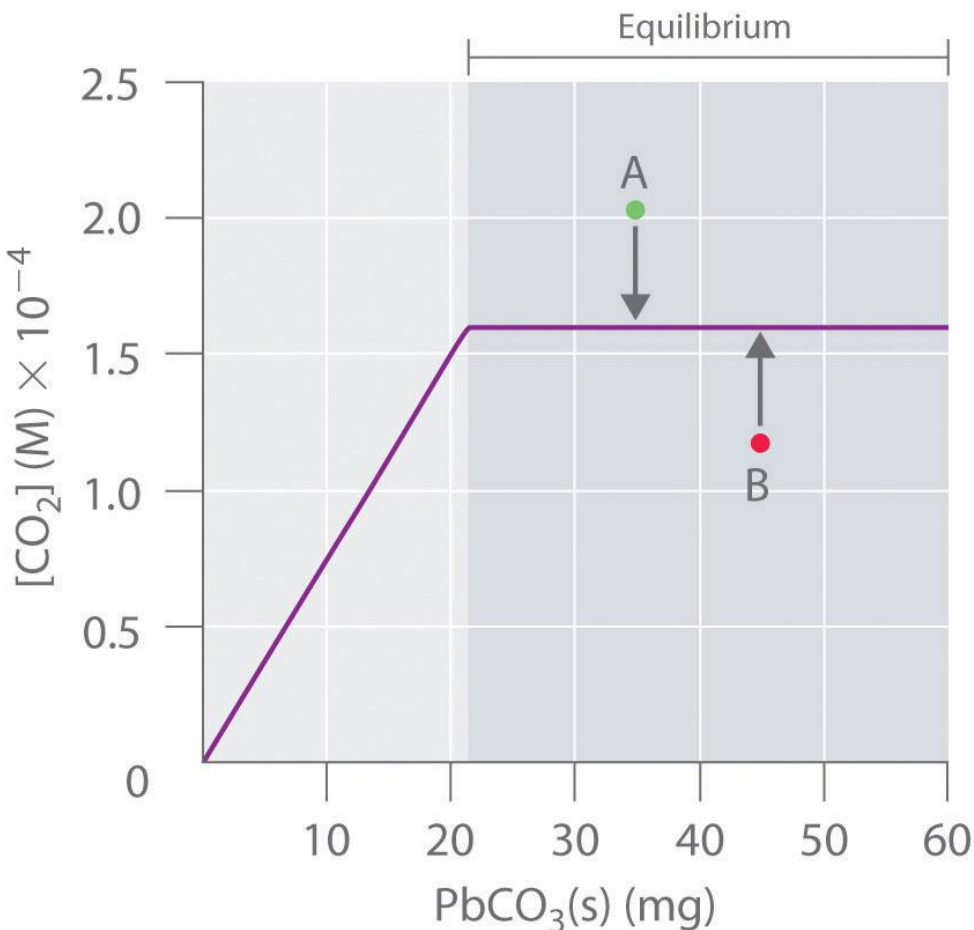
Equation 15.30



Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 15.7 "The Concentration of Gaseous CO_2 ", which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K . Thus the left portion of the graph represents a system that is *not* at equilibrium because it contains only $CO_2(g)$ and $PbO(s)$. In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any

CO₂ concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough PbCO₃ and PbO are present. For example, the point labeled *A* in Figure 15.7 "The Concentration of Gaseous CO" lies above the horizontal line, so it corresponds to a [CO₂] that is greater than the equilibrium concentration of CO₂ ($Q > K$). To reach equilibrium, the system must decrease [CO₂], which it can do only by reacting CO₂ with solid PbO to form solid PbCO₃. Thus the reaction in Equation 15.30 will proceed to the left as written, until [CO₂] = K . Conversely, the point labeled *B* in Figure 15.7 "The Concentration of Gaseous CO" lies below the horizontal line, so it corresponds to a [CO₂] that is less than the equilibrium concentration of CO₂ ($Q < K$). To reach equilibrium, the system must increase [CO₂], which it can do only by decomposing solid PbCO₃ to form CO₂ and solid PbO. The reaction in Equation 15.30 will therefore proceed to the right as written, until [CO₂] = K .

Figure 15.7 The Concentration of Gaseous CO₂ in a Closed System at Equilibrium as a Function of the Amount of Solid PbCO₃ Added



Initially the concentration of $\text{CO}_2(\text{g})$ increases linearly with the amount of solid PbCO_3 added, as PbCO_3 decomposes to $\text{CO}_2(\text{g})$ and solid PbO . Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid PbCO_3 has no effect on $[\text{CO}_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

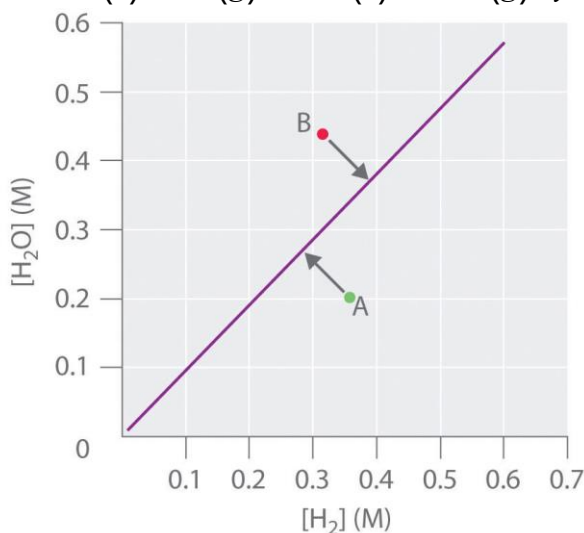
Equation 15.31



and the equilibrium constant K is $[\text{H}_2\text{O}]/[\text{H}_2]$. If $[\text{H}_2\text{O}]$ is doubled at equilibrium, then $[\text{H}_2]$ must also be doubled for the system to remain at equilibrium. A plot of $[\text{H}_2\text{O}]$ versus $[\text{H}_2]$ at equilibrium is a straight line with a slope of K (Figure 15.8 "The Concentration of Water Vapor versus the Concentration of Hydrogen for the "). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 15.31 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For

example, point A in Figure 15.8 "The Concentration of Water Vapor versus the Concentration of Hydrogen for the " lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction in Equation 15.31 will proceed to the right as written, consuming H_2 and producing H_2O , which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 15.8 "The Concentration of Water Vapor versus the Concentration of Hydrogen for the " lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 15.31 will proceed to the left as written, consuming H_2O and producing H_2 , which causes the concentration ratio to move down and to the right toward the equilibrium line.

Figure 15.8 The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO(s) + H_2(g) \rightleftharpoons Cd(s) + H_2O(g)$ System at Equilibrium



For any equilibrium concentration of $H_2O(g)$, there is only one equilibrium concentration of $H_2(g)$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K .

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

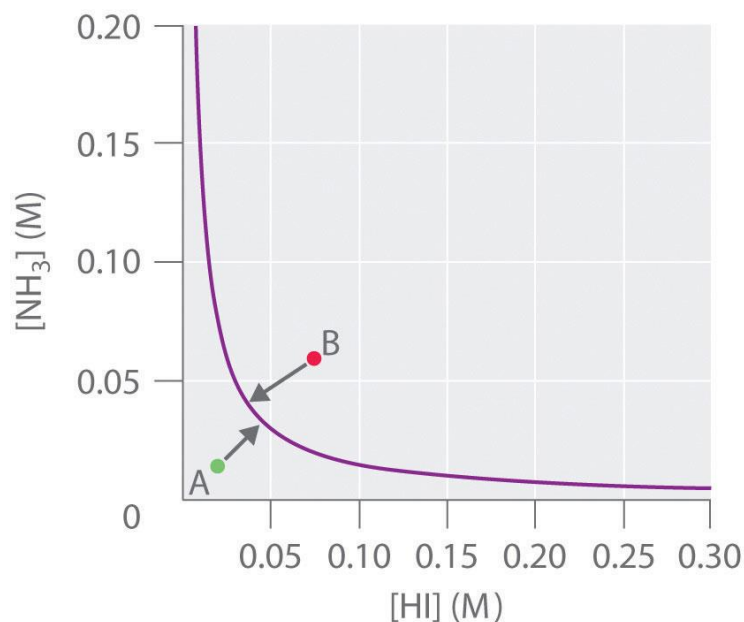
Equation 15.32



For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH_3 , the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 15.9 "The Concentration of NH_3 ". As a result, for a given

concentration of either HI or NH_3 , only a *single* equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[\text{NH}_3] = [\text{HI}] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure 15.9 "The Concentration of NH") corresponds to $Q < K$, and the reaction in Equation 15.32 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 15.9 "The Concentration of NH") corresponds to $Q > K$, and the reaction in Equation 15.32 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

Figure 15.9 The Concentration of $\text{NH}_3(\text{g})$ versus the Concentration of $\text{HI}(\text{g})$ for the $\text{NH}_4\text{I}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HI}(\text{g})$ System at Equilibrium



Only one equilibrium concentration of $\text{NH}_3(\text{g})$ is possible for any given equilibrium concentration of $\text{HI}(\text{g})$. In this case, the two are inversely proportional. Thus a large $[\text{HI}]$ at equilibrium requires a small $[\text{NH}_3]$ at equilibrium and vice versa.

Le Châtelier's Principle

When a system at equilibrium is perturbed in some way, the effects of the perturbation can be predicted qualitatively using Le Châtelier's principle (named after the French chemist Henri Louis Le Châtelier, 1850–1936).^[1] This principle can be stated as follows: *if a stress is applied to a system at equilibrium, the*

composition of the system will change to counteract the applied stress. Stress occurs when any change in a system affects the magnitude of Q or K . In Equation 15.32, for example, increasing $[\text{NH}_3]$ produces a stress on the system that requires a decrease in $[\text{HI}]$ for the system to return to equilibrium. As a further example, consider esters, which are one of the products of an equilibrium reaction between a carboxylic acid and an alcohol. (For more information on this type of reaction, see Chapter 3 "Chemical Reactions", Section 3.5 "Classifying Chemical Reactions".) Esters are responsible for the scents we associate with fruits (such as oranges and bananas), and they are also used as scents in perfumes. Applying a stress to the reaction of a carboxylic acid and an alcohol will change the composition of the system, leading to an increase or a decrease in the amount of ester produced. In Section 15.5 "Factors That Affect Equilibrium" and Section 15.6 "Controlling the Products of Reactions", we explore how chemists control reactions conditions to affect equilibrium concentrations.

Note the Pattern

In all reactions, if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress (Le Châtelier's principle).

EXAMPLE 15

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

- $2\text{HgO}(\text{s}) \rightleftharpoons 2\text{Hg}(\text{l}) + \text{O}_2(\text{g})$: the amount of **HgO** is doubled.
- $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$: the concentration of **H₂S** is tripled.
- $n\text{-butane}(\text{g}) \rightleftharpoons \text{isobutene}(\text{g})$: the concentration of **isobutane** is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

- Because HgO(s) and Hg(l) are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [\text{O}_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2 , so no compensatory change is necessary.
- NH_4HS does not appear in the equilibrium constant expression because it is a solid. Thus $K = [\text{NH}_3][\text{H}_2\text{S}]$, which means that the concentrations of the products are inversely proportional. If adding H_2S triples the H_2S concentration, for example, then the NH_3 concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals K .
- For this reaction, $K = [\text{isobutane}]/[n\text{-butane}]$, so halving the concentration of isobutane means that the n -butane concentration must also decrease by about half if the system is to maintain equilibrium.

Exercise

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

- $\text{HBr(g)} + \text{NaH(s)} \rightleftharpoons \text{NaBr(s)} + \text{H}_2\text{(g)}$: the concentration of HBr is decreased by a factor of 3.
- $6\text{Li(s)} + \text{N}_2\text{(g)} \rightleftharpoons 2\text{Li}_3\text{N(s)}$: the amount of Li is tripled.
- $\text{SO}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{SO}_2\text{Cl}_2\text{(l)}$: the concentration of Cl_2 is doubled.

Answer:

- $K = [\text{H}_2]/[\text{HBr}]$; $[\text{H}_2]$ must decrease by about a factor of 3.
- $K = 1/[\text{N}_2]$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.
- $K = 1/[\text{SO}_2][\text{Cl}_2]$; $[\text{SO}_2]$ must decrease by about half.

Summary

The **reaction quotient (Q or Q_p)** has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$.

Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and

pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium. **Le Châtelier's principle** states that if a stress is applied to a system at equilibrium, the composition of the system will adjust to counteract the stress.

KEY TAKEAWAY

- The reaction quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction.

KEY EQUATION

Reaction quotient

Equation 15.28 : $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

CONCEPTUAL PROBLEMS

- During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using Figure 15.8 "The Concentration of Water Vapor versus the Concentration of Hydrogen for the " and Figure 15.9 "The Concentration of NH_3 as your guides, sketch the shape of each graph using appropriate labels.
 - $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$
 - $2\text{MgO}(s) \rightleftharpoons 2\text{Mg}(s) + \text{O}_2(g)$
- Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?
 - $2\text{NaHCO}_3(s) \rightleftharpoons \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \textbf{H}_2\text{O}(g)$: $[\text{CO}_2]$ is doubled.
 - $\textbf{N}_2\text{F}_4(g) \rightleftharpoons 2\text{NF}_2(g)$: $[\text{NF}_2]$ is decreased by a factor of 2.
 - $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons \textbf{2HI}(g)$: $[\text{I}_2]$ is doubled.
- Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?
 - $\text{CS}_2(g) + \textbf{4H}_2(g) \rightleftharpoons \text{CH}_4(g) + 2\text{H}_2\text{S}(g)$: $[\text{CS}_2]$ is doubled.
 - $\textbf{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$: $[\text{Cl}_2]$ is decreased by a factor of 2.
 - $4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + \textbf{6H}_2\text{O}(g)$: $[\text{NO}]$ is doubled.

ANSWER

3.

a.

$$K = [CH_4][H_2S]^2[CS_2][H_2]^4;$$

doubling $[CS_2]$ would require decreasing $[H_2]$ by a factor of $2\sqrt{4}$ @ 1.189

b. $K = [PCl_3][Cl_2][PCl_5];$

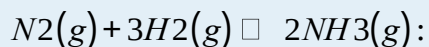
if $[Cl_2]$ is halved, $[PCl_5]$ must also be halved. $K = [PCl_3][Cl_2][PCl_5];$ if $[Cl_2]$ is halved, $[PCl_5]$ must also

c. $K = [NO]^4[H_2O]^6[NH_3][O_2]^5;$ if $[NO]$ is doubled,

$[H_2O]$ is multiplied by $22/3$ @ 1.587.

NUMERICAL PROBLEMS

1. The data in the following table were collected at 450°C for the reaction

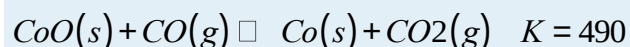
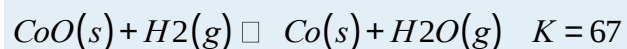


	Equilibrium Partial Pressure (atm)		
P (atm)	NH ₃	N ₂	H ₂
30 (equilibrium)	1.740	6.588	21.58
100	15.20	19.17	65.13
600	321.6	56.74	220.8

2. The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?
3. For the reaction $2A \rightleftharpoons B + 3C$, K at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

Experiment	A	B	C
1	2.50 M	2.50 M	2.50 M
2	1.30 atm	1.75 atm	14.15 atm
3	12.61 mol	18.72 mol	6.51 mol

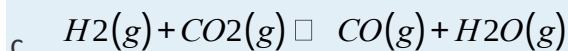
4. The following two reactions are carried out at 823 K:



Write the equilibrium expression for each reaction.

a. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of H_2 or CO plus 0.500 mol CoO.

b. Using the information provided, calculate K_p for the following reaction:



Describe the shape of the graphs of [reactants] versus [products] as the amount of CoO changes.

5. Hydrogen iodide (HI) is synthesized via $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$,

for which $K_p = 54.5$ at 425°C . Given a 2.0 L vessel containing 1.12×10^{-2} mol of H_2 and 1.8×10^{-3} mol of I_2 at equilibrium, what is the concentration of HI? Excess hydrogen is added to the vessel so that the vessel now contains 3.64×10^{-1} mol of H_2 . Calculate Q and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

ANSWERS

1. Not at equilibrium; in both cases, the sum of the equilibrium partial pressures is *less* than the total pressure, so the reaction will proceed to the right to decrease the pressure.

2.

3.

a. $K = [H_2O][H_2]$; $K = [CO_2][CO]$

b.

$P_{H_2O} = 21.0 \text{ atm}$;

$P_{H_2} = 0.27 \text{ atm}$;

$P_{CO_2} = 21.3 \text{ atm}$;

$P_{CO} = 0.07 \text{ atm}$

c. $K_p = 0.14$

d. The amount of CoO has no effect on the shape of a graph of products versus reactants *as long as some solid CoO is present*.

15.5 Factors That Affect Equilibrium

LEARNING OBJECTIVE

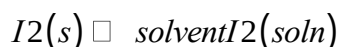
1. To predict the effects of stresses on a system at equilibrium.

Chemists use various strategies to increase the yield of the desired products of reactions. When synthesizing an ester, for example, how can a chemist control the reaction conditions to obtain the maximum amount of the desired product? Only three types of stresses can change the composition of an equilibrium mixture: (1) a change in the concentrations (or partial pressures) of the components by adding or removing reactants or products, (2) a change in the total pressure or volume, and (3) a change in the temperature of the system. In this section, we explore how changes in reaction conditions can affect the equilibrium composition of a system. We will explore each of these possibilities in turn.

Changes in Concentration

If we add a small volume of carbon tetrachloride (CCl_4) solvent to a flask containing crystals of iodine, we obtain a saturated solution of I_2 in CCl_4 , along with undissolved crystals:

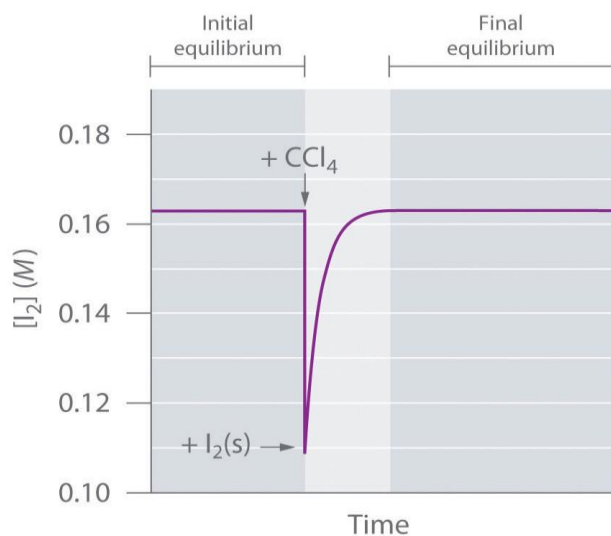
Equation 15.33



The system reaches equilibrium, with $K = [\text{I}_2]$. If we add more CCl_4 , thereby diluting the solution, Q is now less than K . Le Châtelier's principle tells us that the system will react to relieve the stress—but how?

Adding solvent stressed the system by decreasing the concentration of dissolved I_2 . Hence more crystals will dissolve, thereby increasing the concentration of dissolved I_2 until the system again reaches equilibrium if enough solid I_2 is available (Figure 15.10 "The Concentration of Dissolved I"). By adding solvent, we drove the reaction shown in Equation 15.33 to the right as written.

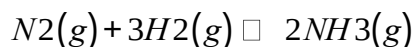
Figure 15.10 The Concentration of Dissolved I_2 as a Function of Time Following the Addition of More Solvent to a Saturated Solution in Contact with Excess Solid I_2



The concentration of I_2 decreases initially due to dilution but returns to its original value as long as solid I_2 is present.

We encounter a more complex system in the reaction of hydrogen and nitrogen to form ammonia:

Equation 15.34



The K_p for this reaction is 2.14×10^{-2} at about 540 K. Under one set of equilibrium conditions, the partial pressure of ammonia is $P_{NH_3} = 0.454 \text{ atm}$, that of hydrogen is $P_{H_2} = 2.319 \text{ atm}$, and that of nitrogen is $P_{N_2} = 0.773 \text{ atm}$. If an additional 1 atm of hydrogen is added to the reactor to give $P_{H_2} =$

3.319 atm, how will the system respond? Because the stress is an increase in P_{H_2} , the system must respond in some way that decreases the partial pressure of hydrogen to counteract the stress. The reaction will therefore proceed to the right as written, consuming H_2 and N_2 and forming additional NH_3 . Initially, the partial pressures of H_2 and N_2 will decrease, and the partial pressure of NH_3 will increase until the system eventually reaches a new equilibrium composition, which will have a net increase in P_{H_2} .

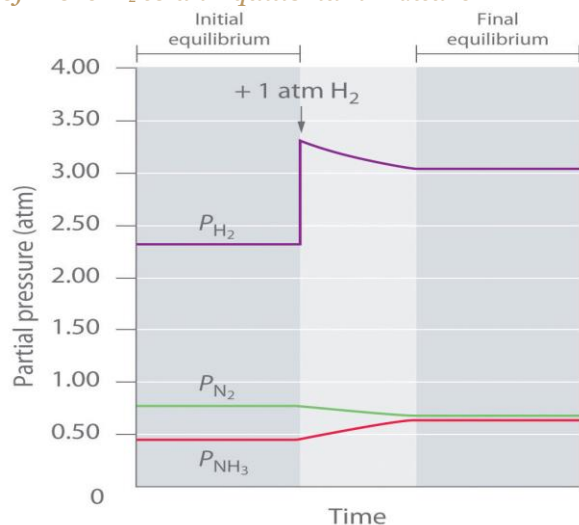
We can confirm that this is indeed what will happen by evaluating Q_p under the new conditions and comparing its value with K_p . The equations used to evaluate K_p and Q_p have the same form: substituting the values after adding hydrogen into the expression for Q_p results in the following:

$$Q_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} \\ = \frac{(0.454)^2}{(0.773)(2.319 + 1.00)^3} = 7.29 \times 10^{-3}$$

Thus $Q_p < K_p$, which tells us that the ratio of products to reactants is less than at equilibrium. To reach equilibrium, the reaction must proceed to the right as written: the partial pressures of the products will increase, and the partial pressures of the reactants will decrease. Q_p will thereby increase until it equals K_p ,

and the system will once again be at equilibrium. Changes in the partial pressures of the various substances in the reaction mixture (Equation 15.34) as a function of time are shown in Figure 15.11 "The Partial Pressures of H".

Figure 15.11 The Partial Pressures of H_2 , N_2 , and NH_3 as a Function of Time Following the Addition of More H_2 to an Equilibrium Mixture



Some of the added hydrogen is consumed by reacting with nitrogen to produce more ammonia, allowing the system to reach a new equilibrium composition.

We can force a reaction to go essentially to completion, regardless of the magnitude of K , by continually removing one of the products from the reaction mixture. Consider, for example, the *methanation* reaction, in which hydrogen reacts with carbon monoxide to form methane and water:

Equation 15.35



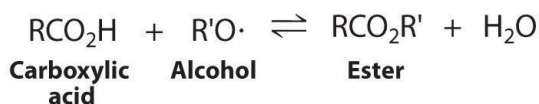
This reaction is used for the industrial production of methane, whereas the reverse reaction is used for the production of H_2 (Example 14). The expression for Q has the following form:

Equation 15.36

$$Q = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

Regardless of the magnitude of K , if either H_2O or CH_4 can be removed from the reaction mixture so that $[H_2O]$ or $[CH_4]$ is approximately zero, then $Q \approx 0$. In other words, when product is removed, the system is stressed ($Q \ll K$), and more product will form to counter the stress. Because water (bp = 100°C) is much less volatile than methane, hydrogen, or carbon monoxide (all of which have boiling points below -100°C), passing the gaseous reaction mixture through a cold coil will cause the water vapor to condense

to a liquid that can be drawn off. Continuing to remove water from the system forces the reaction to the right as the system attempts to equilibrate, thus enriching the reaction mixture in methane. This technique, referred to as *driving a reaction to completion*, can be used to force a reaction to completion even if K is relatively small. For example, esters are usually synthesized by removing water. The products of the condensation reaction are shown here. In Chapter 19 "Electrochemistry", we will describe the thermodynamic basis for the change in the equilibrium position caused by changes in the concentrations of reaction components.



EXAMPLE 16

For each equilibrium system, predict the effect of the indicated stress on the specified quantity.

- a. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$: (1) the effect of removing O_2 on PSO_3 (2) the effect of removing O_2 on PCO_2

$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$: (1) the effect of removing CO_2 on the amount of CaCO_3 ; (2) the effect of adding CaCO_3 on PCO_2

Given: balanced chemical equations and changes

Asked for: effects of indicated stresses

Strategy:

Use Q and K to predict the effect of the stress on each reaction.

Solution:

- a. (1) Removing O_2 will decrease PCO_2 thereby decreasing the denominator in the reaction quotient and making $Q_p > K_p$. The reaction will proceed to the left as written, increasing the partial pressures of SO_2 and O_2 until Q_p once again equals K_p . (2) Removing O_2 will decrease PCO_2 and thus increase Q_p , so the reaction will proceed to the left. The partial pressure of SO_3 will decrease.
- b. K_p and Q_p are both equal to PCO_2 . (1) Removing CO_2 from the system causes more CaCO_3 to react to produce CO_2 , which increases PCO_2 to the partial pressure required by K_p . (2) Adding (or removing) solid CaCO_3 has no effect on PCO_2 because it does not appear in the expression for K_p (or Q_p).

Exercise

For each equilibrium system, predict the effect that the indicated stress will have on the specified quantity.

- a. $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$: (1) the effect of adding CO on $[H_2]$; (2) the effect of adding CO_2 on $[H_2]$
- b. $CuO(s) + CO(g) \rightleftharpoons Cu(s) + CO_2(g)$:
- c. (1) the effect of adding CO on the amount of Cu; (2) the effect of adding CO_2 on $[CO]$

Answer:

- a. (1) $[H_2]$ increases; (2) $[H_2]$ decreases.
- b. (1) the amount of Cu increases; (2) $[CO]$ increases.

Changes in Total Pressure or Volume

Because liquids are relatively incompressible, changing the pressure above a liquid solution has little effect on the concentrations of dissolved substances. Consequently, changes in external pressure have very little effect on equilibrium systems that contain only solids or liquids. In contrast, because gases are highly compressible, their concentrations vary dramatically with pressure. From the ideal gas law, $PV = nRT$, described in Chapter 11 "Liquids", the concentration (C) of a gas is related to its pressure as follows:

Equation 15.37

$$C = n/V = P/RT$$

Hence the concentration of any gaseous reactant or product is directly proportional to the applied pressure (P) and inversely proportional to the total volume (V). Consequently, the equilibrium compositions of systems that contain gaseous substances are quite sensitive to changes in pressure, volume, and temperature.

These principles can be illustrated using the reversible dissociation of gaseous N_2O_4 to gaseous NO_2 (Equation 15.1). The syringe shown in Figure 15.12 "The Effect of Changing the Volume (and Thus the Pressure) of an Equilibrium Mixture of N" initially contains an equilibrium mixture of colorless N_2O_4 and red-brown NO_2 . Decreasing the volume by 50% causes the mixture to become darker because all concentrations have doubled. Decreasing the volume also constitutes a stress, however, as we can see by examining the effect of a change in volume on Q . At equilibrium, $Q = K = [NO_2]^2/[N_2O_4]$ (Equation 15.13).

If the volume is decreased by half, the concentrations of the substances in the mixture are doubled, so the new reaction quotient is as follows:

Equation 15.38

$$Q = (2[NO_2])^2 / (2[N_2O_4]) = 4[NO_2]^2 / 2[N_2O_4] = 2K$$

Because Q is now greater than K , the system is no longer at equilibrium. The stress can be relieved if the reaction proceeds to the left, consuming 2 mol of NO_2 for every 1 mol of N_2O_4 produced. This will decrease the concentration of NO_2 and increase the concentration of N_2O_4 , causing Q to decrease until it once again equals K . Thus, as shown in part (c) in Figure 15.12 "The Effect of Changing the Volume (and Thus the Pressure) of an Equilibrium Mixture of N ", the intensity of the brown color due to NO_2 decreases with time following the change in volume.

The syringe with a total volume of 15 mL contains an equilibrium mixture of N_2O_4 and NO_2 ; the red-brown color is proportional to the NO_2 concentration. (b) If the volume is rapidly decreased by a factor of 2 to 7.5 mL, the initial effect is to double the concentrations of all species present, including NO_2 . Hence the color becomes more intense. (c) With time, the system adjusts its composition in response to the stress as predicted by Le Châtelier's principle, forming colorless N_2O_4 at the expense of red-brown NO_2 , which decreases the intensity of the color of the mixture.

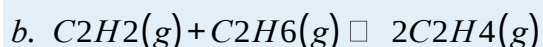
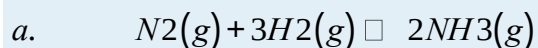
Note the Pattern

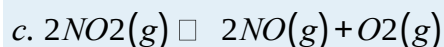
Increasing the pressure of a system (or decreasing the volume) favors the side of the reaction that has fewer gaseous molecules and vice versa.

In general, if a balanced chemical equation contains different numbers of gaseous reactant and product molecules, the equilibrium will be sensitive to changes in volume or pressure. Increasing the pressure on a system (or decreasing the volume) will favor the side of the reaction that has fewer gaseous molecules and vice versa.

EXAMPLE 17

For each equilibrium system, write the reaction quotient for the system if the pressure is decreased by a factor of 2 (i.e., if the volume is doubled) at constant temperature and then predict the direction of the reaction.





Given: balanced chemical equations

Asked for: direction of reaction if pressure is halved

Strategy:

Use Le Châtelier's principle to predict the effect of the stress.

Solution:

a. Two moles of gaseous products are formed from 4 mol of gaseous reactants. Decreasing the pressure will cause the reaction to shift to the left because that side contains the larger number of moles of gas. Thus the pressure increases, counteracting the stress. K for this reaction is $[\text{NH}_3]^2/[\text{N}_2][\text{H}_2]^3$. When the pressure is decreased by a factor of 2, the concentrations are halved, which means that the new reaction quotient is as follows:

b. $Q = [1/2\text{NH}_3]^2/[1/2\text{N}_2][1/2\text{H}_2]^3 = 1/4\text{NH}_3^2/1/16[\text{N}_2][\text{H}_2]^3 = 4K$ Two moles of gaseous products form from 2 mol of gaseous reactants. Decreasing the pressure will have no effect on the equilibrium composition because both sides of the balanced chemical equation have the same number of moles of gas. Here $K = [\text{C}_2\text{H}_4]^2/[\text{C}_2\text{H}_2][\text{C}_2\text{H}_6]$. The new reaction quotient is as follows:

$$Q = [\text{C}_2\text{H}_4]^2/[\text{C}_2\text{H}_2][\text{C}_2\text{H}_6] = [1/2\text{C}_2\text{H}_4]^2/[1/2\text{C}_2\text{H}_2][1/2\text{C}_2\text{H}_6]$$

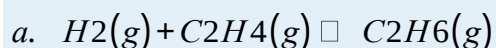
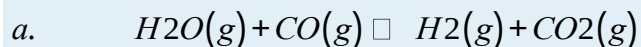
c. $= 1/4[\text{C}_2\text{H}_4]^2/1/4[\text{C}_2\text{H}_2][\text{C}_2\text{H}_6] = K$

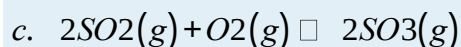
Three moles of gaseous products are formed from 2 mol of gaseous reactants. Decreasing the pressure will favor the side that contains more moles of gas, so the reaction will shift toward the products to increase the pressure. For this reaction $K = [\text{NO}]^2[\text{O}_2]/[\text{NO}_2]^2$. Under the new reaction conditions the reaction quotient is as follows:

$$Q = [1/2\text{NO}]^2/[1/2\text{O}_2][1/2\text{NO}_2]^2 = 1/8[\text{NO}]^2[\text{O}_2]/1/4[\text{NO}_2]^2 = 1/2K$$

Exercise

For each equilibrium system, write a new reaction quotient for the system if the pressure is increased by a factor of 2 (i.e., if the volume is halved) at constant temperature and then predict the direction in which the reaction will shift.





Answer:

- a. $Q = K$; no effect
- b. $Q = 1/2 K$; to the right
- c. $Q = 1/2 K$; to the right

Changes in Temperature

In all the cases we have considered so far, the magnitude of the equilibrium constant, K or K_p , was constant. Changes in temperature can, however, change the value of the equilibrium constant without immediately affecting the reaction quotient ($Q \neq K$). In this case, the system is no longer at equilibrium; the composition of the system will change until Q equals K at the new temperature.

To predict how an equilibrium system will respond to a change in temperature, we must know something about the enthalpy change of the reaction (ΔH_{rxn}). As you learned in Chapter 5 "Energy Changes in Chemical Reactions", heat is released to the surroundings in an exothermic reaction ($\Delta H_{\text{rxn}} < 0$), and heat is absorbed from the surroundings in an endothermic reaction ($\Delta H_{\text{rxn}} > 0$). We can express these changes in the following way:

Equation 15.39

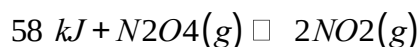
Exothermic: reactants $\rightleftharpoons$ products + heat ($\Delta H < 0$) Equation 15.40

Endothermic: reactants + heat $\rightleftharpoons$ products ($\Delta H > 0$)

Thus heat can be thought of as a product in an exothermic reaction and as a reactant in an endothermic reaction. Increasing the temperature of a system corresponds to adding heat. Le Châtelier's principle predicts that an exothermic reaction will shift to the left (toward the reactants) if the temperature of the system is increased (heat is added). Conversely, an endothermic reaction will shift to the right (toward the products) if the temperature of the system is increased. If a reaction is thermochemically neutral ($\Delta H_{\text{rxn}} = 0$), then a change in temperature will not affect the equilibrium composition.

We can examine the effects of temperature on the dissociation of N_2O_4 to NO_2 , for which $\Delta H = +58$ kJ/mol. This reaction can be written as follows:

Equation 15.41



Increasing the temperature (adding heat to the system) is a stress that will drive the reaction to the right, as illustrated in Figure 15.13 "The Effect of Temperature on the Equilibrium between Gaseous N". Thus increasing the temperature increases the ratio of NO_2 to N_2O_4 at equilibrium, which increases K .

A tube containing a mixture of N_2O_4 and NO_2 in the same proportion at room temperature is red-brown due to the NO_2 present. (left) Immersing the tube in ice water causes the mixture to become lighter in color due to a shift in the equilibrium composition toward colorless N_2O_4 . (right) In contrast, immersing the same tube in boiling water causes the mixture to become darker due to a shift in the equilibrium composition toward the highly colored NO_2 .

The effect of increasing the temperature on a system at equilibrium can be summarized as follows: *increasing the temperature increases the magnitude of the equilibrium constant for an endothermic reaction, decreases the equilibrium constant for an exothermic reaction, and has no effect on the equilibrium constant for a thermally neutral reaction.* Table 15.3 "Temperature Dependence of " shows the temperature dependence of the equilibrium constants for the synthesis of ammonia from hydrogen and nitrogen, which is an exothermic reaction with $\Delta H^\circ = -91.8 \text{ kJ/mol}$. The values of both K and K_p decrease dramatically with increasing temperature, as predicted for an exothermic reaction.

Table 15.3 Temperature Dependence of K and K_p for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Temperature (K)	K	K_p
298	3.3×10^8	5.6×10^5
400	3.9×10^4	3.6×10^1
450	2.6×10^3	1.9
500	1.7×10^2	1.0×10^{-1}
550	2.6×10^1	1.3×10^{-2}
600	4.1	1.7×10^{-3}

Note the Pattern

Increasing the temperature causes endothermic reactions to favor products and exothermic reactions to favor reactants.

EXAMPLE 18

For each equilibrium reaction, predict the effect of decreasing the temperature:



Given: balanced chemical equations and values of ΔH_{rxn}

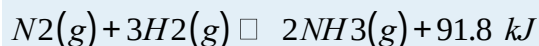
Asked for: effects of decreasing temperature

Strategy:

Use Le Châtelier's principle to predict the effect of decreasing the temperature on each reaction.

Solution:

a. The formation of NH_3 is exothermic, so we can view heat as one of the products:



If the temperature of the mixture is decreased, heat (one of the products) is being removed from the system, which causes the equilibrium to shift to the right. Hence the formation of ammonia is favored at lower temperatures.

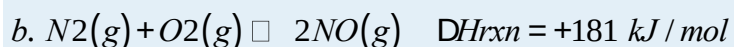
b. The decomposition of calcium carbonate is endothermic, so heat can be viewed as one of the reactants:



If the temperature of the mixture is decreased, heat (one of the reactants) is being removed from the system, which causes the equilibrium to shift to the left. Hence the thermal decomposition of calcium carbonate is less favored at lower temperatures.

Exercise

For each equilibrium system, predict the effect of increasing the temperature on the reaction mixture:



Answer:

a. Reaction shifts to the left.

b. Reaction shifts to the right.

Summary

Three types of stresses can alter the composition of an equilibrium system: adding or removing reactants or products, changing the total pressure or volume, and changing the temperature of the system. A

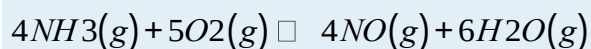
reaction with an unfavorable equilibrium constant can be driven to completion by continually removing one of the products of the reaction. Equilibria that contain different numbers of gaseous reactant and product molecules are sensitive to changes in volume or pressure; higher pressures favor the side with fewer gaseous molecules. Removing heat from an exothermic reaction favors the formation of products, whereas removing heat from an endothermic reaction favors the formation of reactants.

KEY TAKEAWAY

- Equilibria are affected by changes in concentration, total pressure or volume, and temperature.

CONCEPTUAL PROBLEMS

- If an equilibrium reaction is endothermic in the forward direction, what is the expected change in the concentration of each component of the system if the temperature of the reaction is increased? If the temperature is decreased?
- Write the equilibrium equation for the following system:



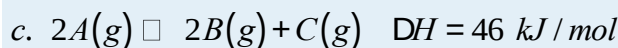
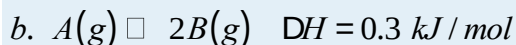
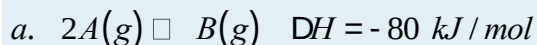
Would you expect the equilibrium to shift toward the products or reactants with an increase in pressure? Why?

- The reaction rate approximately doubles for every 10°C rise in temperature. What happens to K ?
- The formation of $\text{A}_2\text{B}_2(g)$ via the equilibrium reaction $2\text{AB}(g) \rightleftharpoons \text{A}_2\text{B}_2(g)$ is exothermic. What happens to the ratio k_f/k_r if the temperature is increased? If both temperature and pressure are increased?
- In each system, predict the effect that the indicated change will have on the specified quantity at equilibrium:
 - $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$

NUMERICAL PROBLEMS

- For each equilibrium reaction, describe how Q and K change when the pressure is increased, the temperature is increased, the volume of the system is increased, and the concentration(s) of the reactant(s) is increased.
 - $\text{A}(g) \rightleftharpoons \text{B}(g) \quad \Delta H = -20.6 \text{ kJ/mol}$
 - $2\text{A}(g) \rightleftharpoons \text{B}(g) \quad \Delta H = 0.3 \text{ kJ/mol}$
 - $\text{A}(g) + \text{B}(g) \rightleftharpoons 2\text{C}(g) \quad \Delta H = 46 \text{ kJ/mol}$

2. For each equilibrium reaction, describe how Q and K change when the pressure is decreased, the temperature is increased, the volume of the system is decreased, and the concentration(s) of the reactant(s) is increased.

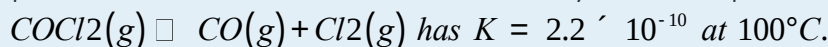


3. Le Châtelier's principle states that a system will change its composition to counteract stress. For the system $CO(g) + C \rightleftharpoons CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, write the equilibrium constant expression K_p . What changes in the values of Q and K would you anticipate when (a) the volume is doubled, (b) the pressure is increased by a factor of 2, and (c) $COCl_2$ is removed from the system?

4. For the equilibrium system $3O_2(g) \rightleftharpoons 2O_3(g)$, $\Delta H^\circ = 284 \text{ kJ}$, write the equilibrium constant expression K_p . What happens to the values of Q and K if the reaction temperature is increased? What happens to these values if both the temperature and pressure are increased?

5. Carbon and oxygen react to form CO_2 gas via $C(s) + O_2(g) \rightleftharpoons CO_2(g)$, for which $K = 1.2 \times 10^{69}$.

Would you expect K to increase or decrease if the volume of the system were tripled? Why?



6. The reaction *Starting with an initial $PCOCl_2$ of 1.0*

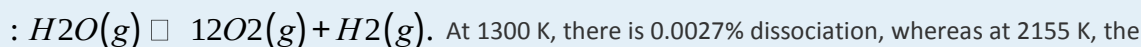
7. atm, you determine the following values of P_{CO} at three successive time intervals: 6.32×10^{-6} atm, 1.78×10^{-6} atm, and 1.02×10^{-5} atm. Based on these data, in which direction will the reaction proceed after each measurement? If chlorine gas is added to the system, what will be the effect on Q ?

8. The following table lists experimentally determined partial pressures at three temperatures for the reaction $Br_2(g) \rightleftharpoons 2Br(g)$.

T (K)	1123	1173	1273
P_{Br_2} (atm)	3.000	0.3333	6.755×10^{-2}
P_{Br} (atm)	3.477×10^{-2}	2.159×10^{-2}	2.191×10^{-2}

9. Is this an endothermic or an exothermic reaction? Explain your reasoning.

10. The dissociation of water vapor proceeds according to the following reaction



dissociation is 1.18%. Calculate K and K_p . Is this an endothermic reaction or an exothermic reaction? How do

the magnitudes of the two equilibria compare? Would increasing the pressure improve the yield of H_2 gas at either temperature? (Hint: assume that the system initially contains 1.00 mol of H_2O in a 1.00 L container.)

11. When 1.33 mol of CO_2 and 1.33 mol of H_2 are mixed in a 0.750 L container and heated to $395^\circ C$, they react according to the following equation: $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$. If $K = 0.802$, what are the equilibrium concentrations of each component of the equilibrium mixture? What happens to K if H_2O is removed during the course of the reaction?
12. The equilibrium reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ has $K_p = 2.2 \times 10^9$ at 298 K. If you begin with 2.0 mol of Br_2 and 2.0 mol of H_2 in a 5.0 L container, what is the partial pressure of HBr at equilibrium? What is the partial pressure of H_2 at equilibrium? If H_2 is removed from the system, what is the effect on the partial pressure of Br_2 ?
13. Iron(II) oxide reacts with carbon monoxide according to the following equation:
 $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$. At $800^\circ C$, $K = 0.34$; at $1000^\circ C$, $K = 0.40$.
 - a. A 20.0 L container is charged with 800.0 g of CO_2 , 1436 g of FeO , and 1120 g of iron. What are the equilibrium concentrations of all components of the mixture at each temperature?
 - b. What are the partial pressures of the gases at each temperature?
 - c. If CO were removed, what would be the effect on PCO_2 at each temperature?
14. The equilibrium constant K for the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ is 1.9 at 1000 K and 0.133 at 298 K.
 - a. If excess C is allowed to react with 25.0 g of CO_2 in a 3.00 L flask, how many grams of CO are produced at each temperature?
 - b. What are the partial pressures of each gas at 298 K? at 1000 K?
 - c. Would you expect K to increase or decrease if the pressure were increased at constant temperature and volume?
15. Data for the oxidation of methane, $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$, in a closed 5.0 L vessel are listed in the following table. Fill in the blanks and determine the missing values of Q and K (indicated by ?) as the reaction is driven to completion.

	CH_4	O_2	CO_2	H_2O	Q	K
initial (moles)	0.45	0.90	0	0	?	
at equilibrium						1.29

	CH ₄	O ₂	CO ₂	H ₂ O	Q	K
add 0.50 mol of methane	0.95				?	
new equilibrium						?
remove water				0	?	
new equilibrium						1.29

ANSWERS

1.

2.

3.

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{Cl}_2}}{P_{\text{CO}_2}}$$

None of the changes would affect K ; (a) Q doubles; (b) Q is halved; Q decreases.

4.

5. K would not change; it does not depend on volume.

6.

7.

8.

9. $[\text{CO}] = [\text{H}_2\text{O}] = 0.839 \text{ M}$, $[\text{CO}_2] = [\text{H}_2] = 0.930 \text{ M}$; no effect on K

10.

11.

a. At 800°C, $[\text{CO}] = 0.678 \text{ M}$, $[\text{CO}_2] = 0.231 \text{ M}$; at 1000°C, $[\text{CO}] = 0.645 \text{ M}$, $[\text{CO}_2] = 0.264 \text{ M}$

b. At 800°C, $P_{\text{CO}} = 59.7 \text{ atm}$, $P_{\text{CO}_2} = 20.3 \text{ atm}$; at 1000°C, $P_{\text{CO}} = 67.4 \text{ atm}$, $P_{\text{CO}_2} = 27.6 \text{ atm}$.

c. Removing CO would cause the reaction to shift to the right, causing P_{CO_2} to decrease.

12.

13.

	CH ₄	O ₂	CO ₂	H ₂ O	Q	K
initial (moles)	0.45	0.90	0	0	0	1.29
at equilibrium	0.215	0.43	0.235	0.47	K	1.29
add 0.50 mol of methane	0.715	0.43	0.235	0.47	0.39	1.29
new equilibrium	0.665	0.33	0.285	0.57	K	1.29

	CH ₄	O ₂	CO ₂	H ₂ O	Q	K
remove water	0.665	0.33	0.285	0	0	1.29
new equilibrium	0.57	0.14	0.38	0.19	K	1.29

15.6 Controlling the Products of Reactions

LEARNING OBJECTIVE

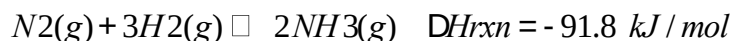
1. To understand different ways to control the products of a reaction.

Whether in the synthetic laboratory or in industrial settings, one of the primary goals of modern chemistry is to control the identity and quantity of the products of chemical reactions. For example, a process aimed at synthesizing ammonia is designed to maximize the amount of ammonia produced using a given amount of energy. Alternatively, other processes may be designed to minimize the creation of undesired products, such as pollutants emitted from an internal combustion engine. To achieve these goals, chemists must consider the competing effects of the reaction conditions that they can control.

One way to obtain a high yield of a desired compound is to make the reaction rate of the desired reaction much faster than the reaction rates of any other possible reactions that might occur in the system. Altering reaction conditions to control reaction rates, thereby obtaining a single product or set of products, is called kinetic control. A second approach, called thermodynamic control, consists of adjusting conditions so that at equilibrium only the desired products are present in significant quantities.

An example of thermodynamic control is the Haber-Bosch process^[1] used to synthesize ammonia via the following reaction:

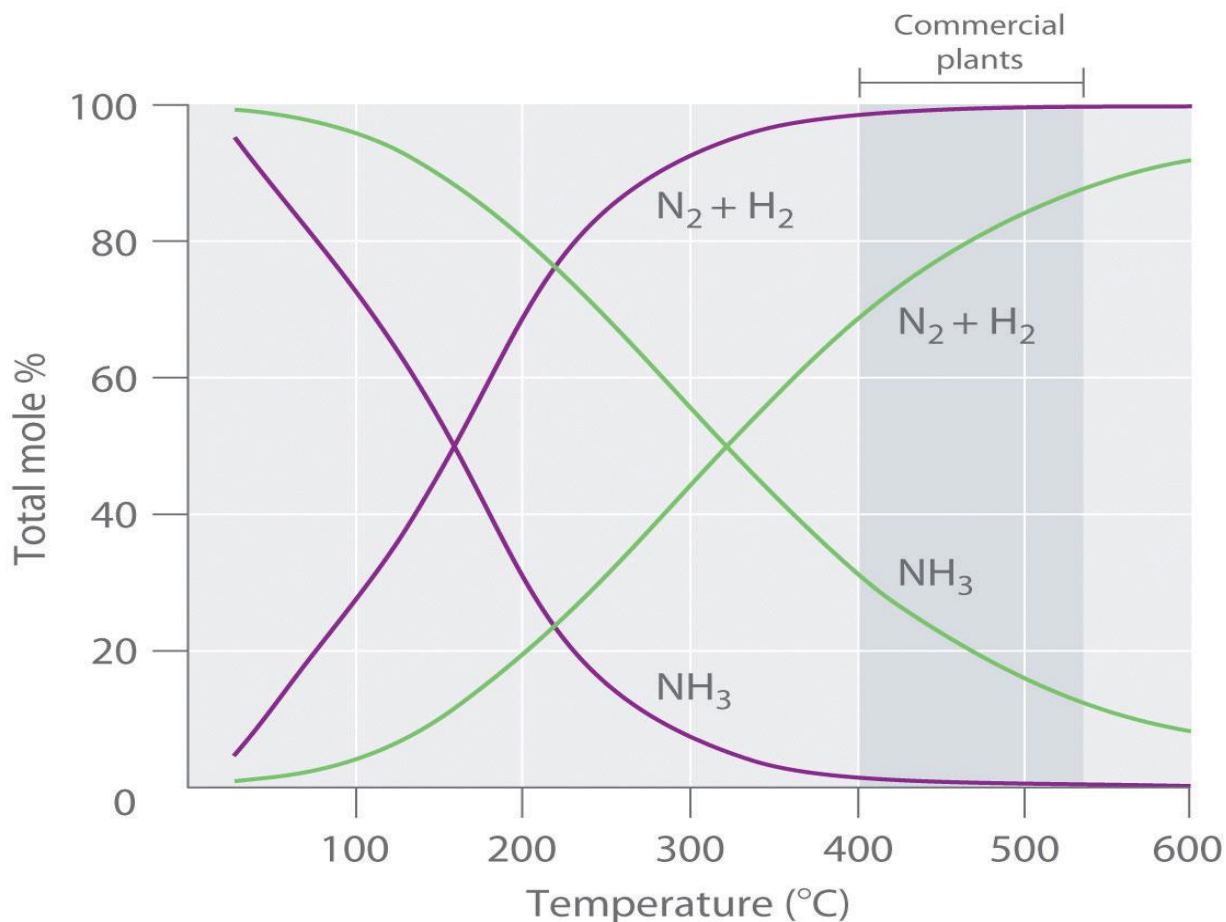
Equation 15.42



Because the reaction converts 4 mol of gaseous reactants to only 2 mol of gaseous product, Le Châtelier's principle predicts that the formation of NH₃ will be favored when the pressure is increased. The reaction is exothermic, however ($\Delta H_{\text{rxn}} = -91.8 \text{ kJ/mol}$), so the equilibrium constant decreases with increasing temperature, which causes an equilibrium mixture to contain only relatively small amounts of ammonia at high temperatures (Figure 15.14 "Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen"). Taken together, these considerations suggest that the maximum yield of NH₃ will be obtained if the reaction is carried out at as low a temperature and as high a pressure as possible.

Unfortunately, at temperatures less than approximately 300°C, where the equilibrium yield of ammonia would be relatively high, the reaction is too *slow* to be of any commercial use. The industrial process therefore uses a mixed oxide ($\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$) catalyst that enables the reaction to proceed at a significant rate at temperatures of 400°C–530°C, where the formation of ammonia is less unfavorable than at higher temperatures.

Figure 15.14 *Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen*

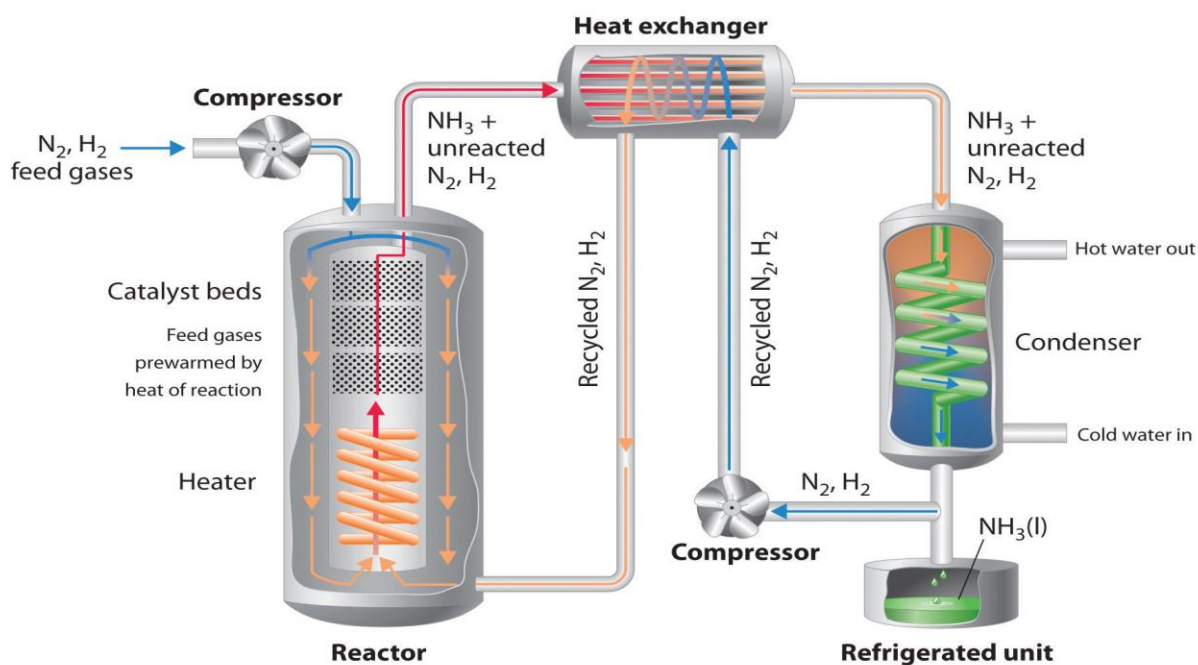


At all temperatures, the total pressure in the systems was initially either 4 atm (purple curves) or 200 atm (green curves). Note the dramatic **decrease** in the proportion of NH_3 at equilibrium at higher temperatures in both cases, as well as the large **increase** in the proportion of NH_3 at equilibrium at any temperature for the system at higher pressure (green) versus lower pressure (purple). Commercial plants that use the Haber-Bosch process to synthesize ammonia on an industrial scale operate at temperatures of 400°C–530°C (indicated by the darker gray band) and total pressures of 130–330 atm.

Because of the low value of the equilibrium constant at high temperatures (e.g., $K = 0.039$ at 800 K), there is no way to produce an equilibrium mixture that contains large proportions of ammonia at high temperatures. We can, however, control the temperature and the pressure while using a catalyst to convert a fraction of the N_2 and H_2 in the

reaction mixture to NH_3 , as is done in the Haber-Bosch process. This process also makes use of the fact that the product—ammonia—is less volatile than the reactants. Because NH_3 is a liquid at room temperature at pressures greater than 10 atm, cooling the reaction mixture causes NH_3 to condense from the vapor as liquid ammonia, which is easily separated from unreacted N_2 and H_2 . The unreacted gases are recycled until complete conversion of hydrogen and nitrogen to ammonia is eventually achieved. Figure 15.15 "A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process" is a simplified layout of a Haber-Bosch process plant.

Figure 15.15 A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process

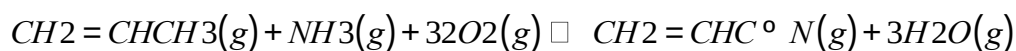


A

3:1 mixture of gaseous H_2 and N_2 is compressed to 130–330 atm, heated to 400°C–530°C, and passed over an $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ catalyst, which results in partial conversion to gaseous NH_3 . The resulting mixture of gaseous NH_3 , H_2 , and N_2 is passed through a heat exchanger, which uses the hot gases to prewarm recycled N_2 and H_2 , and a condenser to cool the NH_3 , giving a liquid that is readily separated from unreacted N_2 and H_2 . (Although the normal boiling point of NH_3 is -33°C , the boiling point increases rapidly with increasing pressure, to 20°C at 8.5 atm and 126°C at 100 atm.) The unreacted N_2 and H_2 are recycled to form more NH_3 .

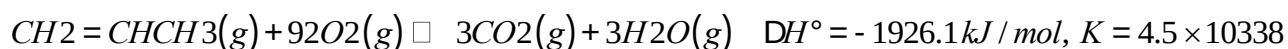
The Sohio acrylonitrile process, in which propene and ammonia react with oxygen to form acrylonitrile, is an example of a kinetically controlled reaction:

Equation 15.43

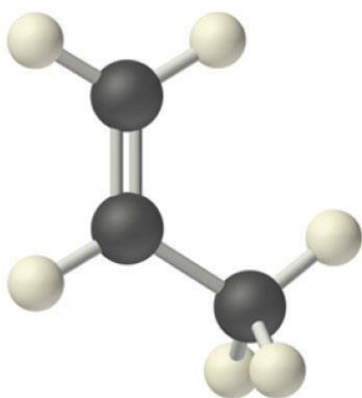
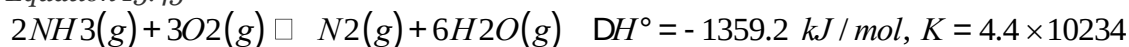


Like most oxidation reactions of organic compounds, this reaction is highly exothermic ($\Delta H^\circ = -519 \text{ kJ/mol}$) and has a very large equilibrium constant ($K = 1.2 \times 10^{94}$). Nonetheless, the reaction shown in Equation 15.43 is not the reaction a chemist would expect to occur when propene or ammonia is heated in the presence of oxygen. Competing combustion reactions that produce CO_2 and N_2 from the reactants, such as those shown in Equation 15.44 and Equation 15.45, are even more exothermic and have even larger equilibrium constants, thereby reducing the yield of the desired product, acrylonitrile:

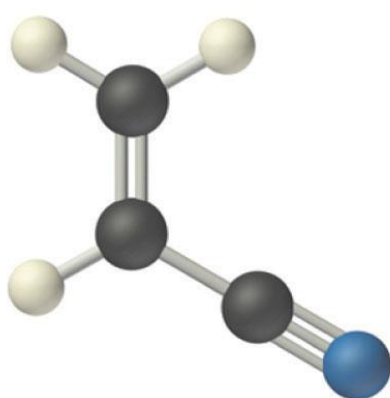
Equation 15.44



Equation 15.45



propene



acrylonitrile

In fact, the formation of acrylonitrile in Equation 15.43 is accompanied by the release of approximately 760 kJ/mol of heat due to partial combustion of propene during the reaction.

The Sohio process uses a catalyst that selectively accelerates the rate of formation of acrylonitrile without significantly affecting the reaction rates of competing combustion reactions. Consequently, acrylonitrile is formed more rapidly than CO_2 and N_2 under the optimized reaction conditions (approximately 1.5 atm and 450°C). The reaction mixture is rapidly cooled to prevent further oxidation or combustion of acrylonitrile, which is then washed out of the vapor with a liquid water spray. Thus controlling the kinetics of the reaction causes the desired product to be formed under conditions where equilibrium is not established. In industry, this reaction is carried out on an enormous scale. Acrylonitrile is the building block of the polymer called *polyacrylonitrile*, found in all the products referred to collectively as *acrylics*, whose wide range of uses includes the synthesis of fibers woven into clothing and carpets.

Note the Pattern

Controlling the amount of product formed requires that both thermodynamic and kinetic factors be considered.

EXAMPLE 19

Recall that methanation is the reaction of hydrogen with carbon monoxide to form methane and water:



This reaction is the reverse of the steam reforming of methane described in Example 14. The reaction is exothermic ($\Delta H^\circ = -206 \text{ kJ/mol}$), with an equilibrium constant at room temperature of $K_p = 7.6 \times 10^{24}$.

Unfortunately, however, CO and H₂ do not react at an appreciable rate at room temperature. What conditions would you select to maximize the amount of methane formed per unit time by this reaction?

Given: balanced chemical equation and values of ΔH° and K

Asked for: conditions to maximize yield of product

Strategy:

Consider the effect of changes in temperature and pressure and the addition of an effective catalyst on the reaction rate and equilibrium of the reaction. Determine which combination of reaction conditions will result in the maximum production of methane.

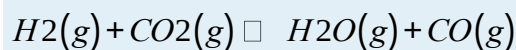
Solution:

The products are highly favored at equilibrium, but the rate at which equilibrium is reached is too slow to be useful. You learned in Chapter 14 "Chemical Kinetics" that the reaction rate can often be increased dramatically by increasing the temperature of the reactants. Unfortunately, however, because the reaction is quite exothermic, an increase in temperature will shift the equilibrium to the left, causing more reactants to form and relieving the stress on the system by absorbing the added heat. If we increase the temperature too much, the equilibrium will no longer favor methane formation. (In fact, the equilibrium constant for this reaction is very temperature sensitive, decreasing to only 1.9×10^{-3} at 1000°C.) To increase the reaction rate, we can try to find a catalyst that will operate at lower temperatures where equilibrium favors the formation of products. Higher pressures will also favor the formation of products because 4 mol of gaseous reactant are converted to only 2 mol of gaseous product. Very high pressures should not be needed, however, because the equilibrium constant favors the formation of products. Thus optimal conditions for the reaction include carrying it out at temperatures greater than room temperature (but not too high), adding a catalyst, and using pressures greater than atmospheric pressure.

Industrially, catalytic methanation is typically carried out at pressures of 1–100 atm and temperatures of 250°C–450°C in the presence of a nickel catalyst. (At 425°C, K_p is 3.7×10^3 , so the formation of products is still favored.) The synthesis of methane can also be favored by removing either H_2O or CH_4 from the reaction mixture by condensation as they form.

Exercise

As you learned in Example 10, the water–gas shift reaction is as follows:



$K_p = 0.106$ and $\Delta H = 41.2$ kJ/mol at 700 K. What reaction conditions would you use to maximize the yield of carbon monoxide?

Answer: high temperatures to increase the reaction rate and favor product formation, a catalyst to increase the reaction rate, and atmospheric pressure because the equilibrium will not be greatly affected by pressure

Summary

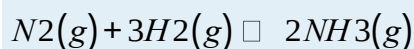
Changing conditions to affect the reaction rates to obtain a single product is called **kinetic control** of the system. In contrast, **thermodynamic control** is adjusting the conditions to ensure that only the desired product or products are present in significant concentrations at equilibrium.

KEY TAKEAWAY

- Both kinetic and thermodynamic factors can be used to control reaction products.

CONCEPTUAL PROBLEMS

- A reaction mixture will produce either product A or B depending on the reaction pathway. In the absence of a catalyst, product A is formed; in the presence of a catalyst, product B is formed. What conclusions can you draw about the forward and reverse rates of the reaction that produces A versus the reaction that produces B in (a) the absence of a catalyst and (b) the presence of a catalyst?
- Describe how you would design an experiment to determine the equilibrium constant for the synthesis of ammonia:



The forward reaction is exothermic ($\Delta H^\circ = -91.8$ kJ). What effect would an increase in temperature have on the equilibrium constant?

3. What effect does a catalyst have on each of the following?
 - a. the equilibrium position of a reaction
 - b. the rate at which equilibrium is reached
 - c. the equilibrium constant?
4. How can the ratio Q/K be used to determine in which direction a reaction will proceed to reach equilibrium?
5. Industrial reactions are frequently run under conditions in which competing reactions can occur. Explain how a catalyst can be used to achieve reaction selectivity. Does the ratio Q/K for the selected reaction change in the presence of a catalyst?

NUMERICAL PROBLEMS

1. The oxidation of acetylene via $2C_2H_2(g) + 5O_2(g) \rightleftharpoons 4CO_2(g) + 2H_2O(l)$ has $\Delta H^\circ = -2600$ kJ. What strategy would you use with regard to temperature, volume, and pressure to maximize the yield of product?
2. The oxidation of carbon monoxide via $CO(g) + 1/2 O_2(g) \rightleftharpoons CO_2(g)$ has $\Delta H^\circ = -283$ kJ. If you were interested in maximizing the yield of CO_2 , what general conditions would you select with regard to temperature, pressure, and volume?
3. You are interested in maximizing the product yield of the system $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K = 280$ and $\Delta H^\circ = -158$ kJ. What general conditions would you select with regard to temperature, pressure, and volume? If SO_2 has an initial concentration of 0.200 M and the amount of O_2 is stoichiometric, what amount of SO_3 is produced at equilibrium?

ANSWER

1. Use low temperature and high pressure (small volume).

[1] Karl Bosch (1874–1940) was a German chemical engineer who was responsible for designing the process that took advantage of Fritz Haber's discoveries regarding the $N_2 + H_2/NH_3$ equilibrium to make ammonia synthesis via this route cost-effective. He received the Nobel Prize in Chemistry in 1931 for his work. The industrial process is called either the Haber process or the Haber-Bosch process.

15.7 Essential Skills

TOPIC

- The quadratic formula

Previous Essential Skills sections introduced many of the mathematical operations you need to solve chemical problems. We now introduce the quadratic formula, a mathematical relationship involving sums of powers in a single variable that you will need to apply to solve some of the problems in this chapter.

The Quadratic Formula

Mathematical expressions that involve a sum of powers in one or more variables (e.g., x) multiplied by coefficients (such as a) are called *polynomials*. Polynomials of a single variable have the general form $a_n x^n + \dots + a_2 x^2 + a_1 x + a_0$

The highest power to which the variable in a polynomial is raised is called its *order*. Thus the polynomial shown here is of the n th order. For example, if n were 3, the polynomial would be third order.

A *quadratic equation* is a second-order polynomial equation in a single variable x :
 $ax^2 + bx + c = 0$

According to the fundamental theorem of algebra, a second-order polynomial equation has two solutions—called *roots*—that can be found using a method called *completing the square*. In this method, we solve for x by first adding $-c$ to both sides of the quadratic equation and then divide both sides by a :

$$x^2 + bx = -c/a$$

We can convert the left side of this equation to a perfect square by adding $b^2/4a^2$, which is equal to $(b/2a)^2$:

$$\text{Left side: } x^2 + bx + b^2/4a^2 = (x + b/2a)^2$$

Having added a value to the left side, we must now add that same value, $b^2/4a^2$, to the right side:

$$(x + b/2a)^2 = -c/a + b^2/4a^2$$

The common denominator on the right side is $4a^2$. Rearranging the right side, we obtain the following:

$$(x + b/2a)^2 = b^2 - 4ac / 4a^2$$

Taking the square root of both sides and solving for x ,

$$x + b/2a = \pm \sqrt{b^2 - 4ac} / 2a$$

$$x = -b/2a \pm \sqrt{b^2 - 4ac} / 2a$$

This equation, known as the *quadratic formula*, has two roots:

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

$$\text{and } x = \frac{-b - \sqrt{b^2 - 4ac}}{2a}$$

Thus we can obtain the solutions to a quadratic equation by substituting the values of the coefficients (a , b , c) into the quadratic formula.

When you apply the quadratic formula to obtain solutions to a quadratic equation, it is important to remember that one of the two solutions may not make sense or neither may make sense. There may be times, for example, when a negative solution is not reasonable or when both solutions require that a square root be taken of a negative number. In such cases, we simply discard any solution that is unreasonable and only report a solution that is reasonable. Skill Builder ES1 gives you practice using the quadratic formula.

SKILL BUILDER ES1

Use the quadratic formula to solve for x in each equation. Report your answers to three significant figures.

a. $x^2 + 8x - 5 = 0$

b. $2x^2 - 6x + 3 = 0$

$3x^2 - 5x - 4 = 6$

$2x(-x + 2) + 1 = 0$

$3x(2x + 1) - 4 = 5$

Solution:

a. $x = \frac{-8 \pm \sqrt{8^2 - 4(1)(-5)}}{2(1)} = 0.583$

and $x = \frac{-8 \pm \sqrt{8^2 - 4(1)(-5)}}{2(1)} = -8.58$

b. $x = \frac{-(-6) \pm \sqrt{(-6)^2 - 4(2)(3)}}{2(2)} = 2.37$

and $x = \frac{-(-6) \pm \sqrt{(-6)^2 - 4(2)(3)}}{2(2)} = 0.634$

$x = \frac{-(-5) \pm \sqrt{(-5)^2 - 4(3)(-10)}}{2(3)} = 2.84$

and $x = \frac{-(-5) \pm \sqrt{(-5)^2 - 4(3)(-10)}}{2(3)} = -1.17$

$x = \frac{-4 \pm \sqrt{4^2 - 4(-2)(1)}}{2(-2)} = -0.225$

and $x = \frac{-4 \pm \sqrt{4^2 - 4(-2)(1)}}{2(-2)} = 2.22$

$x = \frac{-4 \pm \sqrt{4^2 - 4(-2)(1)}}{2(-2)} = -0.225$

and $x = \frac{-4 \pm \sqrt{4^2 - 4(-2)(1)}}{2(-2)} = 2.22$

$x = \frac{-1 \pm \sqrt{1^2 - 4(2)(-3)}}{2(2)} = 1.00$ and $x = \frac{-1 \pm \sqrt{1^2 - 4(2)(-3)}}{2(2)} = 1.50$

$x = \frac{-1 \pm \sqrt{1^2 - 4(2)(-3)}}{2(2)} = 1.50$

15.8 End-of-Chapter Material

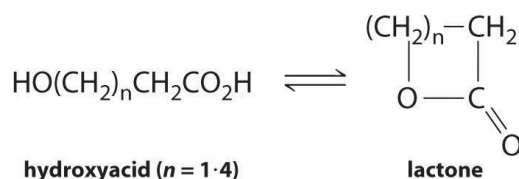
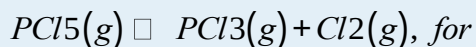
APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. ♦ The total concentrations of dissolved Al in a soil sample represent the sum of “free” Al^{3+} and bound forms of Al that are stable enough to be considered definite chemical species. The distribution of aluminum among its possible chemical forms can be described using equilibrium constants such as the following:

$$K_1 = [\text{AlOH}^{2+}]/[\text{Al}^{3+}][\text{OH}^-] = 1.0 \times 10^9 \quad K_2 = [\text{AlSO}_4^+]/[\text{Al}^{3+}][\text{SO}_4^{2-}] = 1.0 \times 10^3 \quad K_3 = [\text{AlF}^{2+}]/[\text{Al}^{3+}][\text{F}^-] = 1.0 \times 10^7$$

- Write an equilibrium equation for each expression.
 - Which anion has the highest affinity for Al^{3+} : OH^- , SO_4^{2-} , or F^- ? Explain your reasoning.
 - A 1.0 M solution of Al^{3+} is mixed with a 1.0 M solution of each of the anions. Which mixture has the lowest Al^{3+} concentration?
2. Many hydroxy acids form lactones (cyclic esters) that contain a 5- or 6-membered ring. Common hydroxy acids found in nature are glycolic acid, a constituent of cane sugar juice; lactic acid, which has the characteristic odor and taste of sour milk; and citric acid, found in fruit juices. The general reaction for lactone formation can be written as follows:

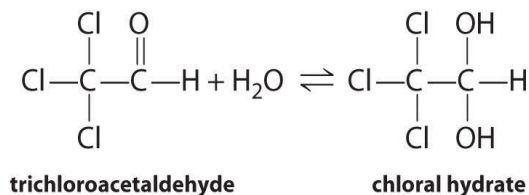


Use

the information in the following table to calculate the equilibrium constant for lactone formation for each hydroxy acid given and determine which ring size is most stable.

	At Equilibrium		
Hydroxy Acid Formula	Size of Lactone Ring (atoms)	Hydroxy Acid (M)	Lactone (M)
$\text{HOCH}_2\text{CH}_2\text{COOH}$	4	4.99×10^{-3}	5.00×10^{-5}
$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{COOH}$	5	8.10×10^{-5}	2.19×10^{-4}
$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	6	5.46×10^{-2}	5.40×10^{-9}
$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	7	9.90×10^{-3}	1.00×10^{-4}

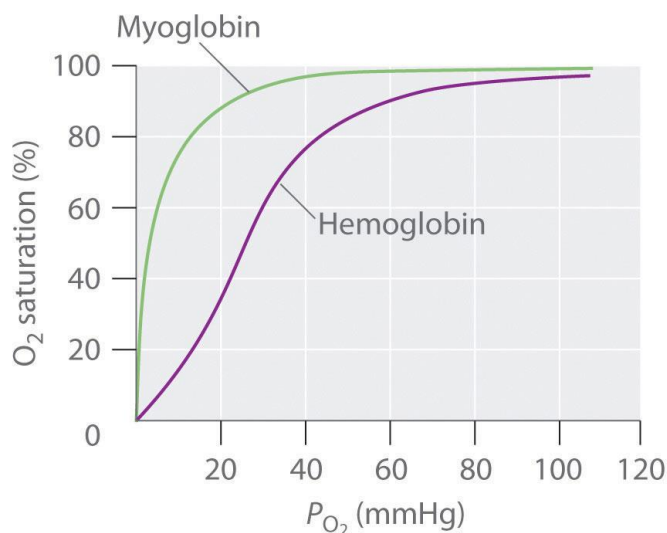
3. ♦ Phosphorus pentachloride, an important reagent in organic chemistry for converting alcohols to alkyl chlorides ($\text{ROH} \rightarrow \text{RCl}$), is hydrolyzed in water to form phosphoric acid and hydrogen chloride. In the gaseous state, however, PCl_5 can decompose at 250°C according to $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, for which $K = 0.0420$.
- Are products or reactants favored in the decomposition of $\text{PCl}_5(\text{g})$?
 - If a 2.00 L flask containing 104.1 g PCl_5 is heated to 250°C , what is the equilibrium concentration of each species in this reaction?
 - What effect would an increase in pressure have on the equilibrium position? Why?
 - If a 1.00×10^3 L vessel containing 2.00×10^3 kg of PCl_3 with a constant chlorine pressure of 2.00 atm is allowed to reach equilibrium, how many kilograms of PCl_5 are produced? What is the percent yield of PCl_5 ?
4. ♦ Carbon disulfide (CS_2) is used in the manufacture of rayon and in electronic vacuum tubes. However, extreme caution must be used when handling CS_2 in its gaseous state because it is extremely toxic and can cause fatal convulsions. Chronic toxicity is marked by psychic disturbances and tremors. CS_2 is used to synthesize H_2S at elevated T via the following reaction:
- $\text{CS}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g}) \quad K = 3.3 \times 10^4$
If the equilibrium concentration of methane in this reaction is 2.5×10^{-2} M and the initial concentration of each reactant is 0.1635 M, what is the concentration of H_2S at equilibrium?
 - Exposure to CS_2 concentrations greater than 300 ppm for several hours can start to produce adverse effects. After working for several hours in a laboratory that contains large quantities of CS_2 , you notice that the fume hoods were off and there was not enough ventilation to remove any CS_2 vapor. Given the equilibrium $\text{CS}_2(\text{l}) \rightleftharpoons \text{CS}_2(\text{g})$, where $T = 20^\circ\text{C}$ and $K_p = 0.391$, determine whether you are in any danger.
5. ♦ Chloral hydrate, a sedative commonly referred to as “knockout drops,” is in equilibrium with trichloroacetaldehyde in highly concentrated aqueous solutions:



The

equilibrium constant for this reaction as written is 3×10^4 . Are the products or the reactants favored? Write an equilibrium expression for this reaction. How could you drive this reaction to completion?

6. Hydrogen cyanide is commercially produced in the United States by the following reaction : $\text{CH}_4(g) + \text{NH}_3(g) + 3\text{O}_2(g) \rightarrow \text{HCN}(g) + 3\text{H}_2\text{O}(g)$, where HCN is continuously removed from the system. This reaction is carried out at approximately 1100°C in the presence of a catalyst; however, the high temperature causes other reactions to occur. Why is it necessary to run this reaction at such an elevated temperature? Does the presence of the catalyst affect the equilibrium position?
7. ♦ Hemoglobin transports oxygen from the lungs to the capillaries and consists of four subunits, each capable of binding a single molecule of O_2 . In the lungs, *PO₂ is relatively high (100 mmHg), so hemoglobin becomes nearly saturated with O₂.*
In the tissues, however, PO₂ is relatively low (40
8. *mmHg), so hemoglobin releases about half of its bound oxygen. Myoglobin, a protein in muscle, resembles a single subunit of hemoglobin. The plots show the percent O₂ saturation versus PO₂ for*
9. hemoglobin and myoglobin. Based on these plots, which molecule has the higher affinity for oxygen? What advantage does hemoglobin have over myoglobin as the oxygen transporter? Why is it advantageous to have myoglobin in muscle tissue? Use equilibrium to explain why it is more difficult to exercise at high altitudes where the partial pressure of oxygen is lower.



1. Sodium sulfate is widely used in the

recycling industry as well as in the detergent and glass industries. This compound combines with H_2SO_4 via $Na_2SO_4(s) + H_2SO_4(g) \rightleftharpoons 2NaHSO_4(s)$. Sodium hydrogen

10. sulfate is used as a cleaning agent because it is water soluble and acidic.
 - a. Write an expression for K for this reaction.
 - b. Relate this equilibrium constant to the equilibrium constant for the related reaction: $2Na_2SO_4(s) + 2H_2SO_4(g) \rightleftharpoons 4NaHSO_4(s)$.
 - c. The dissolution of Na_2SO_4 in water produces the equilibrium reaction $SO_4^{2-}(aq) + H_2O(l) \rightleftharpoons HSO_4^-(aq) + OH^-(aq)$ with $K = 8.33 \times 10^{-13}$. What is the concentration of OH^- in a solution formed from the dissolution of 1.00 g of sodium sulfate to make 150.0 mL of aqueous solution? Neglect the autoionization of water in your answer.
11. ♦ One of the Venera orbiter satellites measured S_2 concentrations at the surface of Venus. The resulting thermochemical data suggest that S_2 formation at the planet's surface occurs via the following equilibrium reaction: $4CO(g) + 2SO_2(g) \rightleftharpoons 4CO_2(g) + S_2(g)$. Write an expression for K for this

a reaction and then relate this expression to those for the following reactions:

- a. $2\text{CO}(g) + \text{SO}_2(g) \rightleftharpoons 2\text{CO}_2(g) + 12\text{S}_2(g)$
 a. $\text{CO}(g) + 12\text{SO}_2(g) \rightleftharpoons \text{CO}_2(g) + 14\text{S}_2(g)$

At 450°C, the equilibrium pressure of CO_2 is 85.0 atm, SO_2 is 1.0 atm, CO is 1.0 atm, and S_2 is 3.0×10^{-8} atm. What are K and K_p at this temperature? What is the concentration of S_2 ?

12. ♦ Until the early part of the 20th century, commercial production of sulfuric acid was carried out by the “lead-chamber” process, in which SO_2 was oxidized to H_2SO_4 in a lead-lined room. This process may be summarized by the following sequence of reactions:

- a. $\text{NO}(g) + \text{NO}_2(g) + 2\text{H}_2\text{SO}_4(l) \rightleftharpoons 2\text{NOHSO}_4(s) + \text{H}_2\text{O}(l) \quad K_1$
 a. $2\text{NOHSO}_4(s) + \text{SO}_2(g) + 2\text{H}_2\text{O}(l) \rightleftharpoons 3\text{H}_2\text{SO}_4(l) + 2\text{NO}(g) \quad K_2$

Write the equilibrium constant expressions for reactions 1 and 2 and the sum of the reactions (reaction 3).

- b. Show that $K_3 = K_1 \times K_2$.
 c. If insufficient water is added in reaction 2 such that the reaction becomes $\text{NOHSO}_4(s) + 12\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons 32\text{H}_2\text{SO}_4(l) + \text{NO}(g)$, does K_3 still equal $K_1 \times K_2$?
 d. Based on part c, write the equilibrium constant expression for K_2 .

13. Phosgene (carbonic dichloride, COCl_2) is a colorless, highly toxic gas with an odor similar to that of moldy hay.

Used as a lethal gas in war, phosgene can be immediately fatal; inhalation can cause *either pneumonia or pulmonary edema*. For the equilibrium reaction $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$, K_p is

14. 0.680 at -10°C . If the initial pressure of COCl_2 is 0.681 atm, what is the partial pressure of each component of this equilibrium system? Is the formation of products or reactant favored in this reaction?

15. ♦ British bituminous coal has a high sulfur content and produces much smoke when burned. In 1952, burning of this coal in London led to elevated levels of smog containing high concentrations of sulfur dioxide, a lung irritant, and more than 4000 people died. Sulfur dioxide emissions can be converted to SO_3 and ultimately to H_2SO_4 , which is the cause of acid rain. The initial reaction is $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$, for which $K_p = 44$.

- a. Given this K_p , are product or reactants favored in this reaction?
 b. What is the partial pressure of each species under equilibrium conditions if the initial pressure of each reactant is 0.50 atm?

c. Would an increase in pressure favor the formation of product or reactants? Why?

16. Oxyhemoglobin is the oxygenated form of hemoglobin, the oxygen-carrying pigment of red blood cells.

Hemoglobin is built from α and β protein chains. Assembly of the oxygenated (oxy) and deoxygenated (deoxy) β -chains has been studied with the following results:

$$4b(\text{oxy}) \rightleftharpoons b_4(\text{oxy}) \quad K = 9.07 \times 10^{15}$$

$$4b(\text{deoxy}) \rightleftharpoons b_4(\text{deoxy}) \quad K = 9.20 \times 10^{13}$$

Is it more likely that hemoglobin β chains assemble in an oxygenated or deoxygenated state? Explain your answer.

17. ♦ Inorganic weathering reactions can turn silicate rocks, such as diopside ($\text{CaMgSi}_2\text{O}_6$), to carbonate via the following reaction:



Write an expression for the equilibrium constant. Although this reaction occurs on both Earth and Venus, the high surface temperature of Venus causes the reaction to be driven in one direction on that planet. Predict whether high temperatures will drive the reaction to the right or the left and then justify your answer. The estimated partial pressure of carbon dioxide on Venus is 85 atm due to the dense Venusian atmosphere. How does this pressure influence the reaction?

18. Silicon and its inorganic compounds are widely used to manufacture textile glass fibers, cement, ceramic products, and synthetic fillers. Two of the most important industrially utilized silicon halides are SiCl_4 and SiHCl_3 , formed by reaction of elemental silicon with HCl at temperatures greater than 300°C :



Which of these two reactions is favored by increasing $[\text{HCl}]$? by decreasing the volume of the system?

19. ♦ The first step in the utilization of glucose in humans is the conversion of glucose to glucose-6-phosphate via the transfer of a phosphate group from ATP (adenosine triphosphate), which produces glucose-6-phosphate and ADP (adenosine diphosphate):

a. $\text{glucose} + \text{ATP} \rightleftharpoons \text{glucose-6-phosphate} + \text{ADP}$ $K = 680$ at 25°C Is the formation of products or reactants favored in this reaction?

b. Would K increase, decrease, or remain the same if the glucose concentration were doubled?

c. If $-RT \ln K = -RT' \ln K'$, what would K be if the temperature were decreased to 0°C ?

- d. Is the formation of products favored by an increase or a decrease in the temperature of the system?
20. In the presence of O_2 , the carbon atoms of glucose can be fully oxidized to CO_2 with a release of free energy almost 20 times greater than that possible under conditions in which O_2 is not present. In many animal cells, the TCA cycle (tricarboxylic acid cycle) is the second stage in the complete oxidation of glucose. One reaction in the TCA cycle is the conversion of citrate to isocitrate, for which $K = 0.08$ in the forward direction. Speculate why the cycle continues despite this unfavorable value of K . What happens if the citrate concentration increases?
21. ♦ Soil is an open system, subject to natural inputs and outputs that may change its chemical composition. Aqueous-phase, adsorbed, and solid-phase forms of $Al(III)$ are of critical importance in controlling the acidity of soils, although industrial effluents, such as sulfur and nitrogen oxide gases, and fertilizers containing nitrogen can also have a large effect. Dissolution of the mineral gibbsite, which contains Al^{3+} in the form $Al(OH)_3(s)$, occurs in soil according to the following reaction:
- $$Al(OH)_3(s) + 3H^+(aq) \rightleftharpoons Al^{3+}(aq) + 3H_2O(l)$$
- When gibbsite is in a highly crystalline state, $K = 9.35$ for this reaction at 298 K. In the microcrystalline state, $K = 8.11$. Is this change consistent with the increased surface area of the microcrystalline state?

ANSWERS

- 1.
- 2.
- 3.
- a. reactant
- b. $[Cl_2] = [PCl_3] = 0.0836 \text{ M}$; $[PCl_5] = 0.166 \text{ M}$
- c. increasing pressure favors reactant (PCl_5)
- d. $1.59 \times 10^3 \text{ kg}$; 52.5%
- 4.
- Products are favored;*
5. $K = \frac{[chloral\ hydrate][Cl_3CHO][H_2O]}{[CH_3CHO]^3}$;
high concentrations of water will favor chloral hydrate
6. formation.

7.

8.

9.

a. 1. $K = \frac{[CO_2]^4[S_2][CO]^4[SO_2]^2}{[CO]^2[S_2]^{1/2}[CO]^2[SO_2]} = K^{1/2}$
 $K^2 = [CO_2]^4[S_2]^2[CO]^4[SO_2]^2 = K^{1/4}$ $K_p = 1.6$; $K = 93$; $[S_2] = 5.1 \times 10^{-10} \text{ M}$

10.

$$PCO = PCl_2 = 0.421 \text{ atm};$$

11. $PCOCl_2 = 0.260 \text{ atm};$

reactants are slightly favored.

Chapter 16

Aqueous Acid–Base Equilibria

Many vital chemical and physical processes take place exclusively in aqueous solution, including the complex biochemical reactions that occur in living organisms and the reactions that rust and corrode steel objects, such as bridges, ships, and automobiles. Among the most important reactions in aqueous solution are those that can be categorized as acid–base, precipitation, and complexation reactions. So far, our discussions of these reactions have been largely qualitative. In this chapter and Chapter 17 "Solubility and Complexation Equilibria", however, we take a more quantitative approach to understanding such reactions, using the concept of chemical equilibrium that we developed in Chapter 15 "Chemical Equilibrium" for simple gas-phase reactions. We will begin by revisiting acid–base reactions in a qualitative fashion and then develop quantitative methods to describe acid–base equilibria. In Chapter 17 "Solubility and Complexation Equilibria", we will use the same approach to describe the equilibria involved in the dissolution of sparingly soluble solids and the formation of metal complexes.

Indicators are used to monitor changes in pH. *The pH of a solution can be monitored using an acid–base indicator, a substance that undergoes a color change within a specific pH range that is characteristic of that indicator.*

In Chapter 4 "Reactions in Aqueous Solution", we described how acid rain can adversely affect the survival of marine life and plant growth. Many significant phenomena, such as acid rain, can be understood only in terms of the acid–base behavior of chemical species. As we expand our discussion of acid–base behavior in this chapter, you will learn

why lemon slices are served with fish, why the strengths of acids and bases can vary over many orders of magnitude, and why rhubarb leaves are toxic to humans. You will also understand how the pH of your blood is kept constant, even though you produce large amounts of acid when you exercise.

16.1 The Autoionization of Water

LEARNING OBJECTIVES

1. To understand the autoionization reaction of liquid water.
2. To know the relationship among pH, pOH, and pK_w .

As you learned in Chapter 4 "Reactions in Aqueous Solution" and Chapter 8 "Ionic versus Covalent Bonding", acids and bases can be defined in several different ways (Table 16.1 "Definitions of Acids and Bases"). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can *donate* a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can *accept* a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton, as we demonstrated in Chapter 4 "Reactions in Aqueous Solution". Consequently, all Brønsted–Lowry acid–base reactions actually involve *two* conjugate acid–base pairs and the transfer of a *proton* from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, discussed in Chapter 8 "Ionic versus Covalent Bonding", focuses on accepting or donating *pairs of electrons* rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table 16.1 Definitions of Acids and Bases

	Acids	Bases
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because this chapter deals with acid–base equilibria in *aqueous solution*, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which

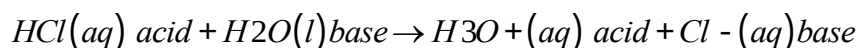
definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

In Chapter 4 "Reactions in Aqueous Solution", we also introduced the acid–base properties of water, its *autoionization reaction*, and the definition of pH. The purpose of this section is to review those concepts and describe them using the concepts of chemical equilibrium developed in Chapter 15 "Chemical Equilibrium".

Acid–Base Properties of Water

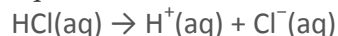
The structure of the water molecule, with its polar O–H bonds and two lone pairs of electrons on the oxygen atom, was described in Chapter 4 "Reactions in Aqueous Solution" and Chapter 8 "Ionic versus Covalent Bonding", and the structure of liquid water was discussed in Chapter 13 "Solutions". Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). As you learned in Chapter 4 "Reactions in Aqueous Solution", the proton, in turn, reacts with a water molecule to form the *hydronium ion* (H_3O^+):

Equation 16.1



In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 16.1 is often written in a simpler form by removing H_2O from each side:

Equation 16.2



In Equation 16.2, the hydronium ion is represented by H^+ , although free H^+ ions do not exist in liquid water.

Water can also act as an acid, as shown in Equation 16.3. In this equilibrium reaction, H_2O donates a proton to NH_3 , which acts as a base:

Equation 16.3

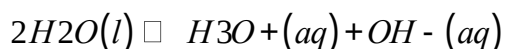


Thus water is amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 16.3 is an equilibrium reaction as indicated by the double arrow.

The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

Equation 16.4



The equilibrium constant K for this reaction can be written as follows:

Equation 16.5

$$K = [\text{H}_3\text{O}^+][\text{OH}^-]/[\text{H}_2\text{O}]^2$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25°C , the concentrations of the hydronium ion and the hydroxide ion are equal: $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.003 \times 10^{-7} \text{ M}$. Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb. We can calculate $[\text{H}_2\text{O}]$ at 25°C from the density of water at this temperature (0.997 g/mL):

Equation 16.6

$$[\text{H}_2\text{O}] = \text{mol/L} = (0.997 \text{ g/mL})(1 \text{ mol}/18.02 \text{ g})(1000 \text{ mL}) = 55.3 \text{ M}$$

With so few water molecules dissociated, the equilibrium of the autoionization reaction (Equation 16.4) lies far to the left. Consequently, $[\text{H}_2\text{O}]$ is essentially unchanged by the autoionization reaction and can be treated as a constant. Incorporating this constant into the equilibrium expression allows us to rearrange Equation 16.5 to define a new equilibrium constant, the ion-product constant of liquid water (K_w):

Equation 16.7

$$K[\text{H}_2\text{O}]^2 K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Substituting the values for $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ at 25°C into this expression,

Equation 16.8

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14} \text{ M}$. Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0°C to 4.99×10^{-13} at 100°C .

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+ and OH^- concentrations from the dissociation of water are so small ($1.003 \times 10^{-7} M$) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.

The Relationship among pH, pOH, and pK_w

The *pH scale* is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall from Chapter 4 "Reactions in Aqueous Solution" that pH and the H^+ (H_3O^+) concentration are related as follows:

Equation 16.9

$$pH = -\log_{10}[H^+]$$

Equation 16.10

$$[H^+] = 10^{-pH}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. (Refer to Essential Skills 3 in Chapter 4 "Reactions in Aqueous Solution", Section 4.10 "Essential Skills 3", if you need to refresh your memory about how to use logarithms.) Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7} M$), whereas acidic solutions have $pH < 7.00$ (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have $pH > 7.00$ (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous *pOH scale* to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

Equation 16.11

$$pOH = -\log_{10}[OH^-]$$

Equation 16.12

The constant K_w can also be expressed using this notation, where $pK_w = -\log K_w$.

Because a neutral solution has $[\text{OH}^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25°C is $7.00 + 7.00 = 14.00$. We can show that the sum of pH and pOH is equal to 14.00 for *any* aqueous solution at 25°C by taking the negative logarithm of both sides of Equation 16.7:

Equation 16.13

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

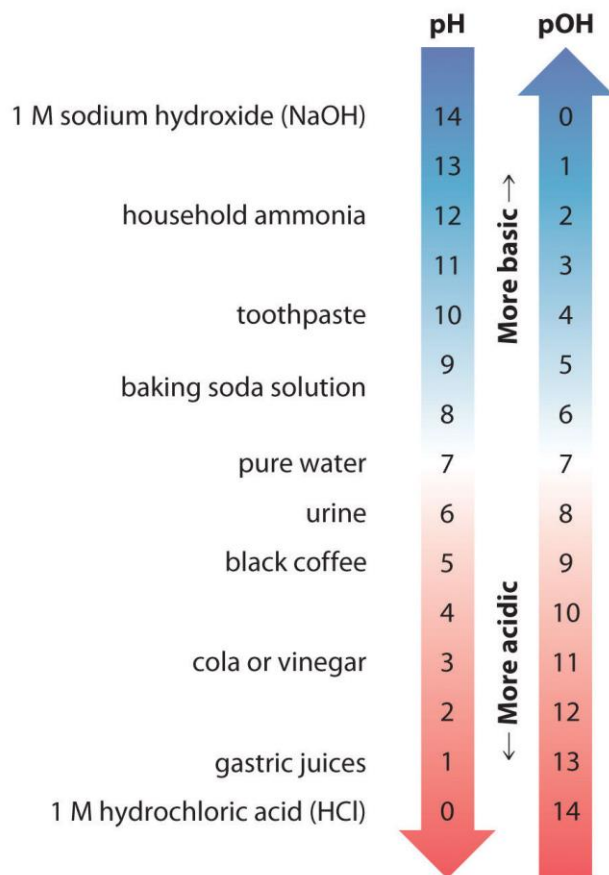
$$\begin{aligned} -\log K_w pK_w &= -\log([\text{H}_3\text{O}^+][\text{OH}^-]) \\ &= (-\log[\text{H}_3\text{O}^+]) + (-\log[\text{OH}^-]) = \text{pH} + \text{pOH} \end{aligned}$$

Thus at any temperature, $\text{pH} + \text{pOH} = \text{p}K_w$, so at 25°C, where $K_w = 1.0 \times 10^{-14}$, $\text{pH} + \text{pOH} = 14.00$. More generally, the pH of any neutral solution is half of the $\text{p}K_w$ at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 16.1 "The Inverse Relationship between the pH and pOH Scales" over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

Note the Pattern

For any neutral solution, $\text{pH} + \text{pOH} = 14.00$ (at 25°C) and $\text{pH} = 14 - \text{pOH}$.

Figure 16.1 *The Inverse Relationship between the pH and pOH Scales*



As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease.

Common substances have pH values that range from extremely acidic to extremely basic.

EXAMPLE 1

The K_w for water at 100°C is 4.99×10^{-13} . Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100°C . Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w , pH, and pOH

Strategy:

A Calculate pK_w by taking the negative logarithm of K_w .

B For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 16.7 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A Because pK_w is the negative logarithm of K_w , we can write
 $pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12} , so pK_w must be between 12 and 13.

B Equation 16.7 shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$K_w x = [H_3O^+][OH^-] = (x)(x) = x^2 = K_w \quad \quad \quad x = 4.99 \times 10^{-7} \quad \quad \quad x = 7.06 \times 10^{-7} M$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$pH = pOH = -\log(7.06 \times 10^{-7}) = 6.15 \text{ (to two decimal places)}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w . In this case, we know that $pK_w = 12.302$, and from Equation 16.13, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can use Equation 16.13 directly, setting $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$pK_w = pH + pOH = y + y = 2y = pK_w / 2 = 12.302 / 2 = 6.15 = pH = pOH$$

Exercise

Humans maintain an internal temperature of about 37°C . At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37°C . Report pH and pOH values to two decimal places.

Answer: $pK_w = 13.45$ $pH = pOH = 6.73$

Summary

Water is **amphiprotic**: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The *autoionization* of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the **ion-product constant of liquid water (K_w)** and is defined as $K_w = [H_3O^+][OH^-]$. At 25°C , K_w is 1.01×10^{-14} ; hence $pH + pOH = pK_w = 14.00$.

KEY TAKEAWAY

- For any neutral solution, $pH + pOH = 14.00$ (at 25°C) and $pH = 1/2 pK_w$.

KEY EQUATIONS

Ion-product constant of liquid water

Equation 16.7: $K_w = [H_3O^+][OH^-]$

Definition of pH

Equation 16.9: $pH = -\log_{10}[H^+]$

Equation 16.10: $[H^+] = 10^{-pH}$

Definition of pOH

Equation 16.11: $pOH = -\log_{10}[OH^-]$

Equation 16.12: $[OH^-] = 10^{-pOH}$

Relationship among pH, pOH, and pK_w

Equation 16.13: $pK_w = pH + pOH$

CONCEPTUAL PROBLEMS

1. What is the relationship between the value of the equilibrium constant for the autoionization of liquid water and the tabulated value of the ion-product constant of liquid water (K_w)?
2. The density of liquid water decreases as the temperature increases from 25°C to 50°C. Will this effect cause K_w to increase or decrease? Why?
3. Show that water is amphiprotic by writing balanced chemical equations for the reactions of water with HNO_3 and NH_3 . In which reaction does water act as the acid? In which does it act as the base?
4. Write a chemical equation for each of the following.
 - a. Nitric acid is added to water.
 - b. Potassium hydroxide is added to water.
 - c. Calcium hydroxide is added to water.
 - d. Sulfuric acid is added to water.
5. Show that K for the sum of the following reactions is equal to K_w .
 - a. $HMnO_4(aq) \rightleftharpoons H^+(aq) + MnO_4^-(aq)$

ANSWERS

1.
$$K_{\text{auto}} = [H_3O^+][OH^-]/[H_2O]^2, K_w = [H_3O^+][OH^-] = K_{\text{auto}}[H_2O]^2$$
- 2.
3. $H_2O(l) + HNO_3(g) \rightarrow H_3O^+(aq) + NO_3^-(aq)$; water is the base
 $H_2O(l) + NH_3(g) \rightarrow OH^-(aq) + NH_4^+(aq)$; water is the acid

NUMERICAL PROBLEMS

1. The autoionization of sulfuric acid can be described by the following chemical equation:

$$\text{At } 25^\circ\text{C}, K = 3 \times 10^{-4}.$$

Write an equilibrium constant expression *for* H_2SO_4 that is analogous to K_w . The density of H_2SO_4 is 1.8 g/cm^3 at 25°C . What is the concentration of H_3SO_4^+ ? What fraction of H_2SO_4 is ionized?

2. An aqueous solution of a substance is found to have $[\text{H}_3\text{O}^+] = 2.48 \times 10^{-8} \text{ M}$. Is the solution acidic, neutral, or basic?
3. The pH of a solution is 5.63. What is its pOH? What is the $[\text{OH}^-]$? Is the solution acidic or basic?
4. State whether each solution is acidic, neutral, or basic.
- $[\text{H}_3\text{O}^+] = 8.6 \times 10^{-3} \text{ M}$
 - $[\text{H}_3\text{O}^+] = 3.7 \times 10^{-9} \text{ M}$
 - $[\text{H}_3\text{O}^+] = 2.1 \times 10^{-7} \text{ M}$
 - $[\text{H}_3\text{O}^+] = 1.4 \times 10^{-6} \text{ M}$
5. Calculate the pH and the pOH of each solution.
- 0.15 M HBr
 - 0.03 M KOH
 - $2.3 \times 10^{-3} \text{ M HNO}_3$
 - $9.78 \times 10^{-2} \text{ M NaOH}$
 - 0.00017 M HCl
 - 5.78 M HI
6. Calculate the pH and the pOH of each solution.
- 25.0 mL of $2.3 \times 10^{-2} \text{ M HCl}$, diluted to 100 mL
 - 5.0 mL of 1.87 M NaOH, diluted to 125 mL
 - 5.0 mL of 5.98 M HCl added to 100 mL of water
 - 25.0 mL of 3.7 M HNO_3 added to 250 mL of water
 - 35.0 mL of 0.046 M HI added to 500 mL of water
 - 15.0 mL of 0.0087 M KOH added to 250 mL of water.
7. The pH of stomach acid is approximately 1.5. What is the $[\text{H}^+]$?
8. Given the pH values in parentheses, what is the $[\text{H}^+]$ of each solution?

- a. household bleach (11.4)
 - b. milk (6.5)
 - c. orange juice (3.5)
 - d. seawater (8.5)
 - e. tomato juice (4.2)
9. A reaction requires the addition of 250.0 mL of a solution with a pH of 3.50. What mass of HCl (in milligrams) must be dissolved in 250 mL of water to produce a solution with this pH?
 10. If you require 333 mL of a pH 12.50 solution, how would you prepare it using a 0.500 M sodium hydroxide stock solution?

ANSWERS

1. $KH_2SO_4 = [H_3SO_4^+][HSO_4^-] = K[H_2SO_4]^2$; $[H_3SO_4^+] = 0.3 \text{ M}$; the fraction ionized is 0.02.
- 1.
2. $pOH = 8.37$; $[OH^-] = 4.3 \times 10^{-9} \text{ M}$; acidic
- 3.
- 4.
- a. $pH = 0.82$; $pOH = 13.18$
- b. $pH = 12.5$; $pOH = 1.5$
- c. $pH = 2.64$; $pOH = 11.36$
- d. $pH = 12.990$; $pOH = 1.010$
- e. $pH = 3.77$; $pOH = 10.23$
- f. $pH = -0.762$; $pOH = 14.762$
- 5.
- 6.
- 7.
8. 2.9 mg HCl

16.2 A Qualitative Description of Acid–Base Equilibria

LEARNING OBJECTIVES

1. To understand the concept of conjugate acid–base pairs.

2. To know the relationship between acid or base strength and the magnitude of K_a , K_b , pK_a , and pK_b .
3. To understand the leveling effect.

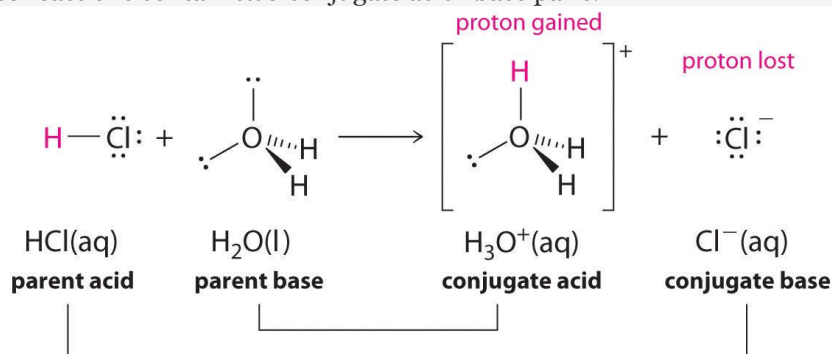
We now turn our attention to acid–base reactions to see how the concepts of chemical equilibrium and equilibrium constants can deepen our understanding of this kind of chemical behavior. We begin with a qualitative description of acid–base equilibria in terms of the Brønsted–Lowry model and then proceed to a quantitative description in Section 16.4 "Quantitative Aspects of Acid–Base Equilibria".

Conjugate Acid–Base Pairs

We discussed the concept of conjugate acid–base pairs in Chapter 4 "Reactions in Aqueous Solution", using the reaction of ammonia, the base, with water, the acid, as an example. In aqueous solutions, acids and bases can be defined in terms of the transfer of a proton from an acid to a base. Thus for every acidic species in an aqueous solution, there exists a species derived from the acid by the loss of a proton. These two species that differ by only a proton constitute a conjugate acid–base pair. For example, in the reaction of HCl with water (Equation 16.1), HCl, the *parent acid*, donates a proton to a water molecule, the *parent base*, thereby forming Cl^- . Thus HCl and Cl^- constitute a conjugate acid–base pair. By convention, we always write a conjugate acid–base pair as the acid followed by its conjugate base. In the reverse reaction, the Cl^- ion in solution acts as a base to accept a proton from H_3O^+ , forming H_2O and HCl. Thus H_3O^+ and H_2O constitute a second conjugate acid–base pair. In general, any acid–base reaction must contain *two* conjugate acid–base pairs, which in this case are HCl/Cl^- and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.

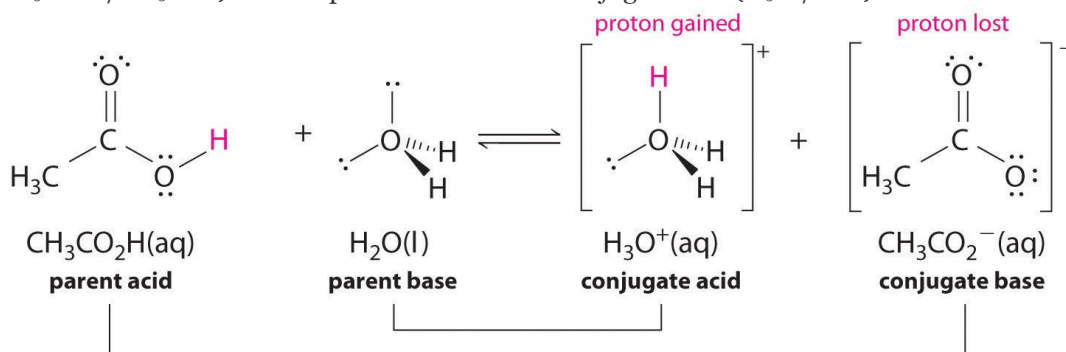
Note the Pattern

All acid–base reactions contain *two* conjugate acid–base pairs.



Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the

base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$) and the parent base and its conjugate acid ($\text{H}_3\text{O}^+/\text{H}_2\text{O}$).



In the reaction of ammonia with water to give ammonium ions and hydroxide ions (Equation 16.3), ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are $\text{NH}_4^+/\text{NH}_3$ and $\text{H}_2\text{O}/\text{OH}^-$. Some common conjugate acid–base pairs are shown in Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs".

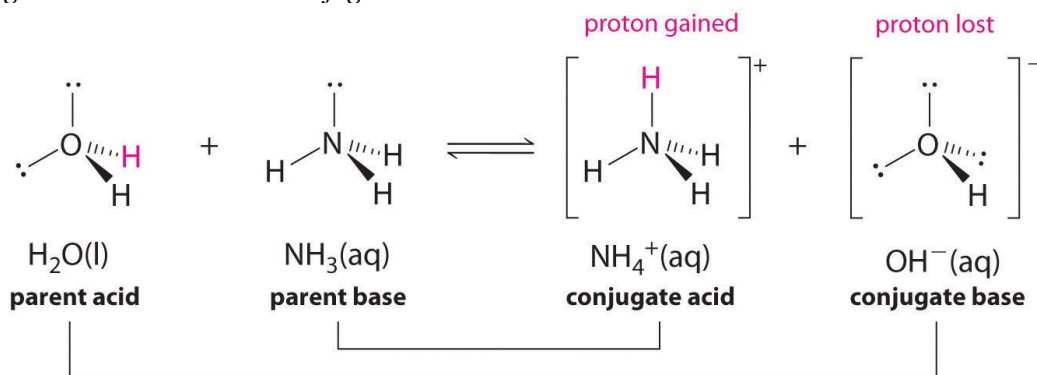


Figure 16.2 *The Relative Strengths of Some Common Conjugate Acid–Base Pairs*

ACID		BASE	
negligible	OH^-	O^{2-}	strong
	HS^-	S^{2-}	
← Relative acid strength increasing	H_2O	OH^-	Relative base strength increasing →
	HPO_4^{2-}	PO_4^{3-}	
	HCO_3^-	CO_3^{2-}	
	NH_4^+	NH_3	
	HCN	CN^-	
	H_2PO_4^-	HPO_4^{2-}	
	HSO_3^-	SO_3^{2-}	
	H_2S	HS^-	
	H_2CO_3	HCO_3^-	
	$\text{C}_5\text{H}_5\text{NH}^+$	$\text{C}_5\text{H}_5\text{N}$	
	$\text{CH}_3\text{CO}_2\text{H}$	CH_3CO_2^-	
	HF	F^-	
	H_3PO_4	H_2PO_4^-	
	H_2SO_3	HSO_3^-	
	HSO_4^-	SO_4^{2-}	
	H_3O^+	H_2O	
strong	HNO_3	NO_3^-	negligible
	H_2SO_4	HSO_4^-	
	HCl	Cl^-	
	HBr	Br^-	

The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Acid–Base Equilibrium Constants: K_a , K_b , pK_a , and pK_b

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A^- is its conjugate base, is as follows:

Equation 16.14



The equilibrium constant for this dissociation is as follows:

Equation 16.15

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}_2\text{O}][\text{HA}]}$$

As we noted earlier, the concentration of water is essentially constant for all reactions in aqueous solution, so $[H_2O]$ in Equation 16.15 can be incorporated into a new quantity, the acid ionization constant (K_a), also called the *acid dissociation constant*:

Equation 16.16

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Thus the numerical values of K and K_a differ by the concentration of water (55.3 M). Again, for simplicity, H_3O^+ can be written as H^+ in Equation 16.16. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form H_3O^+ . The larger the K_a , the stronger the acid and the higher the H^+ concentration at equilibrium.^[1] The values of K_a for a number of common acids are given in Table 16.2 "Values of".

Table 16.2 Values of K_a , pK_a , K_b , and pK_b for Selected Acids (HA) and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	-9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	-2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	-1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	NO_2^-	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2^-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	HOCl	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	-12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	-21.0
*The number in parentheses indicates the ionization step referred to for a polyprotic acid.						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH⁺ is its conjugate acid:

Equation 16.17



The equilibrium constant for this reaction is the base ionization constant (K_b), also called the *base dissociation constant*:

Equation 16.18

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Once again, the concentration of water is constant, so it does not appear in the equilibrium constant expression; instead, it is included in the K_b . The larger the K_b , the stronger the base and the higher the OH⁻ concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 16.3 "Values of".

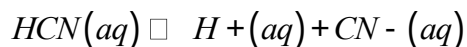
Table 16.3 Values of K_b , pK_b , K_a , and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH⁺)

Base	B	K_b	pK_b	BH ⁺	K_a	pK_a
hydroxide ion	OH ⁻	1.0	0.00*	H ₂ O	1.0×10^{-14}	14.00
phosphate ion	PO ₄ ³⁻	2.1×10^{-2}	1.68	HPO ₄ ²⁻	4.8×10^{-13}	12.32
dimethylamine	(CH ₃) ₂ NH	5.4×10^{-4}	3.27	(CH ₃) ₂ NH ₂ ⁺	1.9×10^{-11}	10.73
methylamine	CH ₃ NH ₂	4.6×10^{-4}	3.34	CH ₃ NH ₃ ⁺	2.2×10^{-11}	10.66
trimethylamine	(CH ₃) ₃ N	6.3×10^{-5}	4.20	(CH ₃) ₃ NH ⁺	1.6×10^{-10}	9.80
ammonia	NH ₃	1.8×10^{-5}	4.75	NH ₄ ⁺	5.6×10^{-10}	9.25
pyridine	C ₅ H ₅ N	1.7×10^{-9}	8.77	C ₅ H ₅ NH ⁺	5.9×10^{-6}	5.23
aniline	C ₆ H ₅ NH ₂	7.4×10^{-10}	9.13	C ₆ H ₅ NH ₃ ⁺	1.3×10^{-5}	4.87
water	H ₂ O	1.0×10^{-14}	14.00	H ₃ O ⁺	1.0*	0.00
*As in Table 16.2 "Values of".						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base.

Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN⁻ with water to produce a basic solution:

Equation 16.19



Equation 16.20



The equilibrium constant expression for the ionization of HCN is as follows:

Equation 16.21

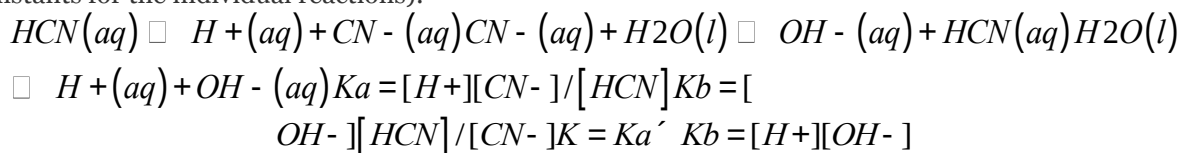
$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

The corresponding expression for the reaction of cyanide with water is as follows:

Equation 16.22

$$K_b = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]}$$

If we add Equation 16.19 and Equation 16.20, we obtain the following (recall from Chapter 15 "Chemical Equilibrium" that the equilibrium constant for the *sum* of two reactions is the *product* of the equilibrium constants for the individual reactions):



In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w :

Equation 16.23

$$K_a K_b = K_w$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pK_w , we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

Equation 16.24

$$pK_a = -\log_{10} K_a$$

Equation 16.25

$$K_a = 10^{-pK_a}$$

and pK_b as

Equation 16.26

$$pK_b = -\log_{10} K_b$$

Equation 16.27

$$K_b = 10^{-pK_b}$$

Similarly, Equation 16.23, which expresses the relationship between K_a and K_b , can be written in logarithmic form as follows:

Equation 16.28

$$pK_a + pK_b = pK_w$$

At 25°C, this becomes

Equation 16.29

$$pK_a + pK_b = 14.00$$

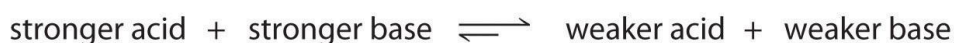
The values of pK_a and pK_b are given for several common acids and bases in Table 16.2 "Values of " and Table 16.3 "Values of ", respectively, and a more extensive set of data is provided in Chapter 27 "Appendix C: Dissociation Constants and p" and Chapter 28 "Appendix D: Dissociation Constants and p". Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs". The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a . This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b . At the bottom left of Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs" are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

Note the Pattern

The conjugate base of a strong acid is a weak base and vice versa.

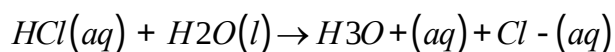
We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: *an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:*



In an acid–base reaction, the proton always reacts with the stronger base.

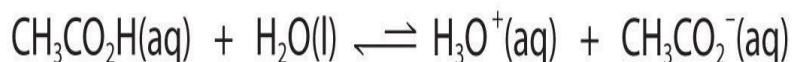
For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^- ; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

Equation 16.30



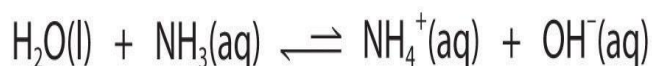
In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

Figure 16.3



Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

Figure 16.4



Note the Pattern

All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

EXAMPLE 2

- Calculate K_b and $\text{p}K_b$ of the butyrate ion ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2^-$). The $\text{p}K_a$ of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
- Calculate K_a and $\text{p}K_a$ of the dimethylammonium ion $[(\text{CH}_3)_2\text{NH}_2^+]$. The base ionization constant K_b of dimethylamine $[(\text{CH}_3)_2\text{NH}]$ is 5.4×10^{-4} at 25°C .

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b , K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 16.23. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 16.28 and Equation 16.29. Use the relationships $pK = -\log K$ and $K = 10^{-pK}$ (Equation 16.24 and Equation 16.26) to convert between K_a and pK_a or K_b and pK_b .

Solution:

a. We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 16.29: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b ,

$$4.83 + pK_b = 14.00 = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

b. In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b , we can use Equation 16.23: $K_a K_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a ,

$$K_a(5.4 \times 10^{-4})K_b = 1.01 \times 10^{-14} = 1.9 \times 10^{-11}$$

Because $pK_a = -\log K_a$, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b + pK_a = -\log(5.4 \times 10^{-4}) = 3.27 \\ = 14.00 = 10.73 = 10 - pK_a = 10 - 10.73 = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a , pK_a , K_b , or pK_b), we can calculate the other three.

Exercise

Lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$] is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer: $K_a = 1.4 \times 10^{-4}$ for lactic acid; $pK_b = 10.14$ and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 16.2 "Values of " that acids like H_2SO_4 and HNO_3 lie *above* the hydronium ion, meaning that they have $\text{p}K_a$ values less than zero and are stronger acids than the H_3O^+ ion.^[2] In fact, all six of the common strong acids that we first encountered in Chapter 4 "Reactions in Aqueous Solution" have $\text{p}K_a$ values less than zero, which means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water.

Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 10^8 greater than K_a for HNO_3 , the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I^- or NO_3^- . In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+ , *regardless of the identity of the strong acid*. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO_3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O . Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid *in this solvent*. This result clearly tells us that HI is a stronger acid than HNO_3 . The relative order of acid strengths and approximate K_a and $\text{p}K_a$ values for the strong acids at the top of Table 16.2 "Values of " were determined using measurements like this and different nonaqueous solvents.

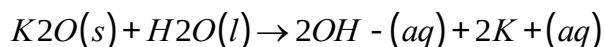
Note the Pattern

In aqueous solutions, $[\text{H}_3\text{O}^+]$ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O .

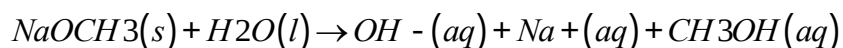
The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH^- is leveled to the strength of OH^- because OH^- is the strongest base that can exist in equilibrium with water. Salts such as K_2O , NaOCH_3 (sodium methoxide), and NaNH_2 (sodamide, or sodium amide), whose

anions are the conjugate bases of species that would lie below water in Table 16.3 "Values of", are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

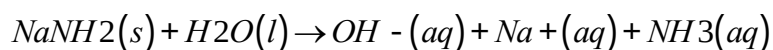
Equation 16.31



Equation 16.32



Equation 16.33

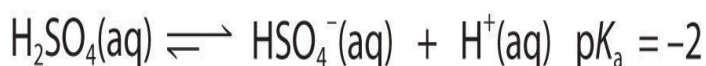


Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

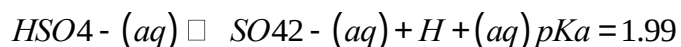
Polyprotic Acids and Bases

As you learned in Chapter 4 "Reactions in Aqueous Solution", *polyprotic acids* such as H_2SO_4 , H_3PO_4 , and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4 , for example:

Figure 16.5



Equation 16.34



The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

Note the Pattern

For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-} . Just like water, HSO_4^- can therefore act as *either* an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a *polyprotic base* that is capable of accepting two protons in a stepwise manner:

Figure 16.6

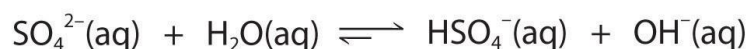


Figure 16.7



Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by $\text{p}K_{\text{a}} + \text{p}K_{\text{b}} = \text{p}K_{\text{w}}$. Consider, for example, the $\text{HSO}_4^-/\text{SO}_4^{2-}$ conjugate acid–base pair. From Table 16.2 "Values of ", we see that the $\text{p}K_{\text{a}}$ of HSO_4^- is 1.99. Hence the $\text{p}K_{\text{b}}$ of SO_4^{2-} is $14.00 - 1.99 = 12.01$. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Figure 16.6 lies to the left. The HSO_4^- ion is also a very weak base [$\text{p}K_{\text{a}}$ of $\text{H}_2\text{SO}_4 = 2.0$, $\text{p}K_{\text{b}}$ of $\text{HSO}_4^- = 14 - (-2.0) = 16$], which is consistent with what we expect for the conjugate base of a strong acid. Thus the equilibrium shown in Figure 16.7 also lies almost completely to the left. Once again, equilibrium favors the formation of the weaker acid–base pair.

EXAMPLE 3

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $\text{NH}_4^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$
- $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}(\text{aq}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CO}_2^-(\text{aq}) + \text{HCN}(\text{aq})$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

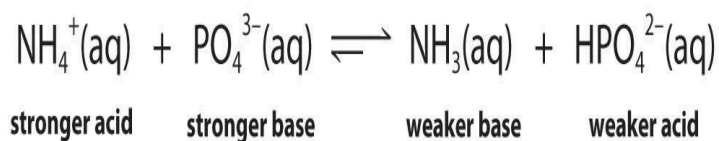
Identify the conjugate acid–base pairs in each reaction. Then refer to Table 16.2 "Values of ", Table 16.3

"Values of ", and Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs" to

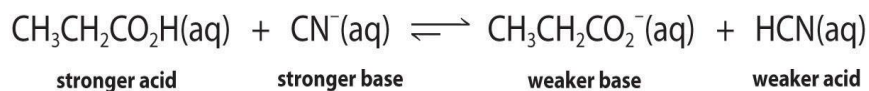
determine which is the stronger acid and base. Equilibrium always favors the formation of the weaker acid–base pair.

Solution:

a. The conjugate acid–base pairs are $\text{NH}_4^+/\text{NH}_3$ and $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$. According to Table 16.2 "Values of " and Table 16.3 "Values of ", NH_4^+ is a stronger acid ($\text{p}K_a = 9.25$) than HPO_4^{2-} ($\text{p}K_a = 12.32$), and PO_4^{3-} is a stronger base ($\text{p}K_b = 1.68$) than NH_3 ($\text{p}K_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:



b. The conjugate acid–base pairs are $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}/\text{CH}_3\text{CH}_2\text{CO}_2^-$ and HCN/CN^- . According to Table 16.2 "Values of ", HCN is a weak acid ($\text{p}K_a = 9.21$) and CN^- is a moderately weak base ($\text{p}K_b = 4.79$). Propionic acid ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$) is not listed in Table 16.2 "Values of ", however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties *are* listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-\text{CH}_2\text{CH}_3$ versus $-\text{CH}_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the $\text{p}K_a$ of propionic acid to be similar in magnitude to the $\text{p}K_a$ of acetic acid. (In fact, the $\text{p}K_a$ of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN . Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:



Exercise

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- a. $H_2O(l) + HS^-(aq) \rightleftharpoons OH^-(aq) + H_2S(aq)$
 b. $HCO_2^-(aq) + HSO_4^-(aq) \rightleftharpoons HCO_2H(aq) + SO_4^{2-}(aq)$

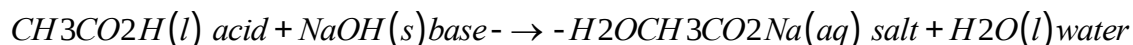
Answer:

- a. left
 b. left

Acid–Base Properties of Solutions of Salts

We can also use the relative strengths of conjugate acid–base pairs to understand the acid–base properties of solutions of salts. In Chapter 4 "Reactions in Aqueous Solution", you learned that a *neutralization reaction* can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation, such as Na^+ , replaces the proton on the acid. An example is the reaction of CH_3CO_2H , a weak acid, with $NaOH$, a strong base:

Equation 16.35



Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as $NaCl$ dissolves in water, it produces $Na^+(aq)$ and $Cl^-(aq)$ ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The Cl^- ion is the conjugate base of the strong acid HCl , so it has essentially no basic character. Consequently, dissolving $NaCl$ in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

Figure 16.8

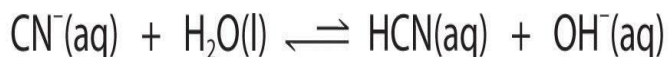
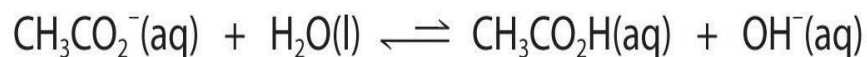


Figure 16.9



Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table 16.2 "Values of " and Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs", we can see that CN^- is a stronger base ($\text{p}K_{\text{b}} = 4.79$) than acetate ($\text{p}K_{\text{b}} = 9.24$), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs"). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

Figure 16.10

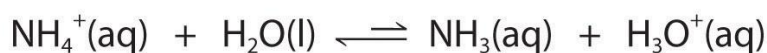


Figure 16.11

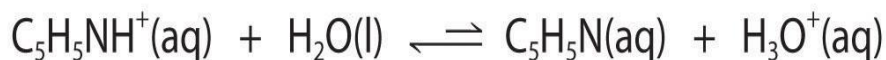
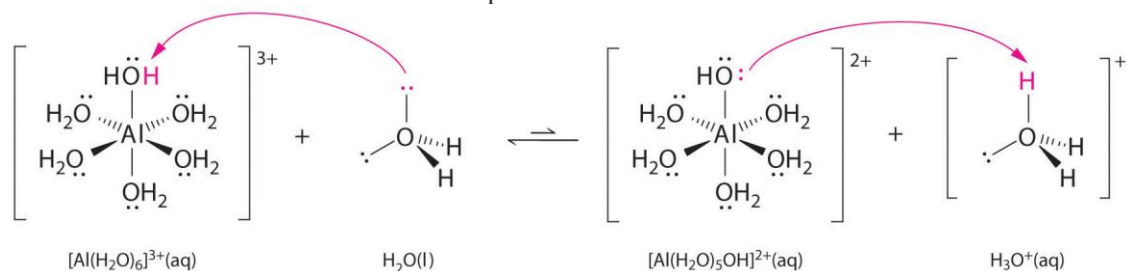


Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs" shows that H_3O^+ is a stronger acid than either NH_4^+ or $\text{C}_5\text{H}_5\text{NH}^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at

25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2 "The Relative Strengths of Some Common Conjugate Acid–Base Pairs", indicating that the pyridinium ion is more acidic than the ammonium ion.

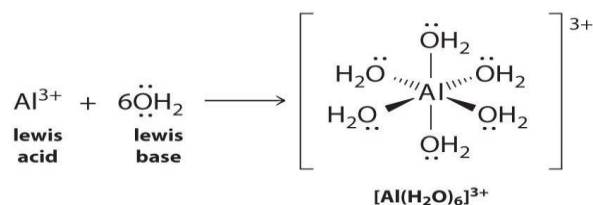
What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation *and* the anion can react separately with water to produce an acid and a base, respectively? According to Figure 16.10, the ammonium ion will lower the pH, while according to Figure 16.9, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base ($pK_a \approx pK_b$). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the cation is a stronger acid than the anion is a base, the final solution has a $pH < 7.00$. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a $pH > 7.00$.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+ . Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure 16.12 "Effect of a Metal Ion on the Acidity of Water"), as discussed in Chapter 4 "Reactions in Aqueous Solution". A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

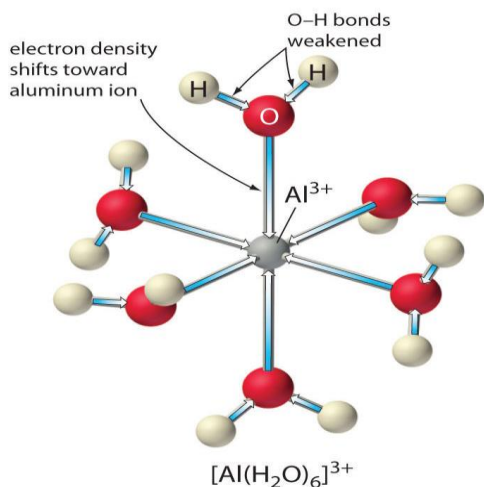


Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the O–H bonds, as shown in part (b) in Figure 16.12 "Effect of a Metal Ion on the Acidity of Water". With less electron density between the O atoms and the H atoms, the O–H bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.

Figure 16.12 Effect of a Metal Ion on the Acidity of Water



(a)



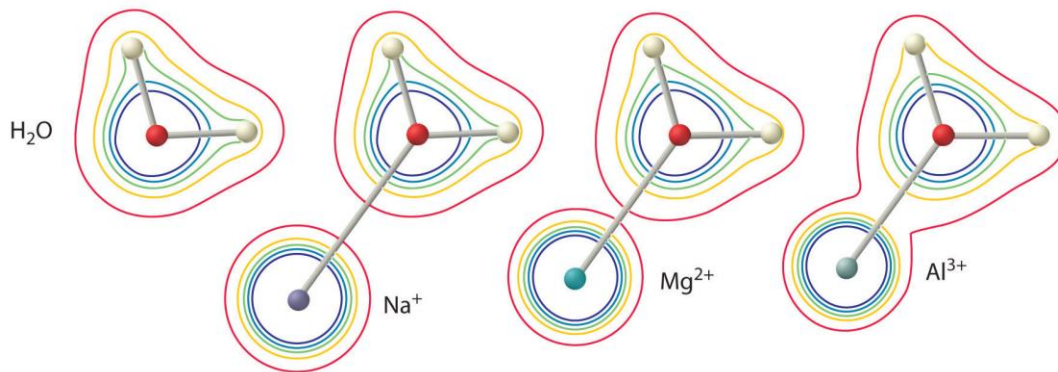
(b)

(a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

The magnitude of this effect depends on the following two factors (Figure 16.13 "The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule"):

1. **The charge on the metal ion.** A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^{+}) of the same radius.
2. **The radius of the metal ion.** For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

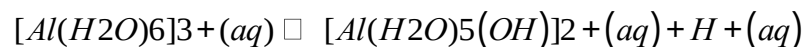
Figure 16.13 *The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule*



The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+ , Mg^{2+} , and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+} , are acidic:

Equation 16.36



The $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the *charge-to-radius ratio* of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as Li^+ and Mg^{2+} or Ca^{2+} and Y^{3+} , have different sizes and charges but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

Note the Pattern

Solutions of small, highly charged metal ions in water are acidic.

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactions. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

Note the Pattern

A hydrolysis reaction is an acid–base reaction.

EXAMPLE 4

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

- a. KNO_3
- b. $\text{CrBr}_3 \cdot 6\text{H}_2\text{O}$
- c. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.

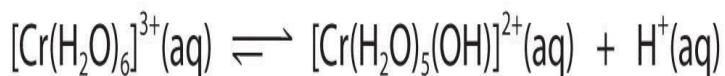
B If the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

a. **A** The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.

B The NO_3^- anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1 "Definitions of Acids and Bases"). Hence neither the cation nor the anion will react with water to produce H^+ or OH^- , and the solution will be neutral.

b. **A** The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ complex, which will behave as a weak acid:



B The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

c. **A** The Na^+ ion, like the K^+ , is a very weak acid, so it should not affect the acidity of the solution.

B In contrast, SO_4^{2-} is the conjugate base of HSO_4^- , which is a weak acid. Hence the SO_4^{2-} ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

Exercise

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

- a. KI
- b. $\text{Mg}(\text{ClO}_4)_2$
- c. NaHS

Answer:

- a. neutral
- b. acidic
- c. basic (due to the reaction of HS^- with water to form H_2S and OH^-)

Summary

Two species that differ by only a proton constitute a **conjugate acid–base pair**. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the **acid ionization constant (K_a)**. Similarly, the equilibrium constant for the reaction of a weak base with water is the **base ionization constant (K_b)**. For any conjugate acid–base pair, $K_a K_b = K_w$. Smaller values of $\text{p}K_a$ correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of $\text{p}K_b$ correspond to larger base ionization constants and hence stronger bases. At 25°C , $\text{p}K_a + \text{p}K_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the **leveling effect**. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base. A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a **hydrolysis reaction**.

KEY TAKEAWAYS

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

KEY EQUATIONS

Acid ionization constant

Equation 16.16: $K_a = \frac{[H_3O^+][A^-]}{[HA]}$

Base ionization constant

Equation 16.18: $K_b = \frac{[BH^+][OH^-]}{[B]}$

Relationship between K_a and K_b of a conjugate acid–base pair

Equation 16.23: $K_a K_b = K_w$

Definition of pK_a

Equation 16.24: $pK_a = -\log_{10} K_a$

Equation 16.25: $K_a = 10^{-pK_a}$

Definition of pK_b

Equation 16.26: $pK_b = -\log_{10} K_b$

Equation 16.27: $K_b = 10^{-pK_b}$

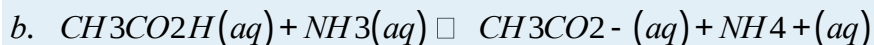
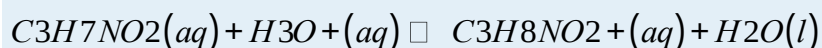
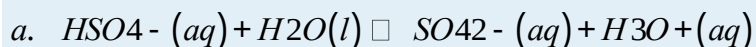
Relationship between pK_a and pK_b of a conjugate acid–base pair

Equation 16.28: $pK_a + pK_b = pK_w$

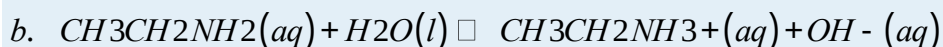
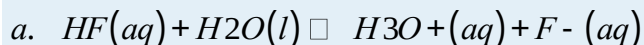
Equation 16.29: $pK_a + pK_b = 14.00$ (at 25°C)

CONCEPTUAL PROBLEMS

Identify the conjugate acid–base pairs in each equilibrium.



1. Identify the conjugate acid–base pairs in each equilibrium.



- c. $C_3H_7NO_2(aq) + OH^-(aq) \rightleftharpoons C_3H_6NO_2^-(aq) + H_2O(l)$
- d. $CH_3CO_2H(aq) + 2HF(aq) \rightleftharpoons CH_3C(OH)_2^+(aq) + HF_2^-(aq)$
2. Salts such as NaH contain the hydride ion (H^-). When sodium hydride is added to water, it produces hydrogen gas in a highly vigorous reaction. Write a balanced chemical equation for this reaction and identify the conjugate acid–base pairs.
3. Write the expression for K_a for each reaction.
- a. $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$
- b. *formic acid*(aq) + $H_2O(l) \rightleftharpoons$ *formate*(aq) + $H_3O^+(aq)$
- c. $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
4. Write an expression for the ionization constant K_b for each reaction.
- a. $OCH_3^-(aq) + H_2O(l) \rightleftharpoons HOCH_3(aq) + OH^-(aq)$
- b. $NH_2^-(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + OH^-(aq)$
- c. $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$
5. Predict whether each equilibrium lies primarily to the left or to the right.
- a. $HBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Br^-(aq)$
- b. $NaH(soln) + NH_3(l) \rightleftharpoons H_2(soln) + NaNH_2(soln)$
- c. $OCH_3^-(aq) + NH_3(aq) \rightleftharpoons CH_3OH(aq) + NH_2^-(aq)$
- d. $NH_3(aq) + HCl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$
6. Species that are strong bases in water, such as CH_3^- , NH_2^- , and S^{2-} , are leveled to the strength of OH^- , the conjugate base of H_2O . Because their relative base strengths are indistinguishable in water, suggest a method for identifying which is the strongest base. How would you distinguish between the strength of the acids HIO_3 , H_2SO_4 , and $HClO_4$?
7. Is it accurate to say that a 2.0 M solution of H_2SO_4 , which contains two acidic protons per molecule, is 4.0 M in H^+ ? Explain your answer.
8. The alkalinity of soil is defined by the following equation: $\text{alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$. The source of both HCO_3^- and CO_3^{2-} is H_2CO_3 . Explain why the basicity of soil is defined in this way.
9. Why are aqueous solutions of salts such as $CaCl_2$ neutral? Why is an aqueous solution of $NaNH_2$ basic?
10. Predict whether aqueous solutions of the following are acidic, basic, or neutral.
- a. Li_3N

- b. NaH
 - c. KBr
 - d. $\text{C}_2\text{H}_5\text{NH}_3^+\text{Cl}^-$
11. When each compound is added to water, would you expect the pH of the solution to increase, decrease, or remain the same?
- a. LiCH_3
 - b. MgCl_2
 - c. K_2O
 - d. $(\text{CH}_3)_2\text{NH}_2^+\text{Br}^-$
12. Which complex ion would you expect to be more acidic— $\text{Pb}(\text{H}_2\text{O})_4^{2+}$ or $\text{Sn}(\text{H}_2\text{O})_4^{2+}$? Why?
13. Would you expect $\text{Sn}(\text{H}_2\text{O})_4^{2+}$ or $\text{Sn}(\text{H}_2\text{O})_6^{4+}$ to be more acidic? Why?
14. Is it possible to arrange the hydrides LiH, RbH, KH, CsH, and NaH in order of increasing base strength in aqueous solution? Why or why not?

ANSWER

- 1.
- a. $\text{HSO}_4^- (\text{aq}) \text{ acid } 1 + \text{H}_2\text{O} (\text{l}) \text{ base } 2$
 - ☐ $\text{SO}_4^{2-} (\text{aq}) \text{ base } 1 + \text{H}_3\text{O}^+ (\text{aq}) \text{ acid } 2$
 - b. $\text{C}_3\text{H}_7\text{NO}_2 (\text{aq}) \text{ base } 2 + \text{H}_3\text{O}^+ (\text{aq}) \text{ acid } 1$
 - ☐ $\text{C}_3\text{H}_8\text{NO}_2 + (\text{aq}) \text{ acid } 2 + \text{H}_2\text{O} (\text{l}) \text{ base } 1$
- 2.
- a. $\text{HOAc} (\text{aq}) \text{ acid } 1 + \text{NH}_3 (\text{aq}) \text{ base } 2$ ☐ $\text{CH}_3\text{CO}_2^- (\text{aq}) \text{ base } 1 + \text{NH}_4^+ (\text{aq}) \text{ acid } 2$
 - a. $\text{SbF}_5 (\text{aq}) \text{ acid } 1 + 2\text{HF} (\text{aq}) \text{ base } 2$ ☐ $\text{H}_2\text{F}^+ (\text{aq}) \text{ acid } 2 + \text{SbF}_6^- (\text{aq}) \text{ base } 1$

NUMERICAL PROBLEMS

1. Arrange these acids in order of increasing strength.
- acid A: $\text{p}K_a = 1.52$
 - acid B: $\text{p}K_a = 6.93$
 - acid C: $\text{p}K_a = 3.86$

Given solutions with the same initial concentration of each acid, which would have the highest percent ionization?

2. Arrange these bases in order of increasing strength:

○ base A: $pK_b = 13.10$

○ base B: $pK_b = 8.74$

○ base C: $pK_b = 11.87$

Given solutions with the same initial concentration of each base, which would have the highest percent ionization?

3. Calculate the K_a and the pK_a of the conjugate acid of a base with each pK_b value.

a. 3.80

b. 7.90

c. 13.70

d. 1.40

e. -2.50

4. Benzoic acid is a food preservative with a pK_a of 4.20. Determine the K_b and the pK_b for the benzoate ion.

5. Determine K_a and pK_a of boric acid $[B(OH)_3]$, solutions of which are occasionally used as an eyewash; the pK_b of its conjugate base is 4.80.

ANSWERS

1. acid B < acid C < acid A (strongest)

2.

3.

a. $K_a = 6.3 \times 10^{-11}$; $pK_a = 10.20$

b. $K_a = 7.9 \times 10^{-7}$; $pK_a = 6.10$

c. $K_a = 0.50$; $pK_a = 0.30$

d. $K_a = 2.5 \times 10^{-13}$; $pK_a = 12.60$

e. $K_a = 3.2 \times 10^{-17}$; $pK_a = 16.50$

4.

5. $K_a = 6.3 \times 10^{-10}$ $pK_a = 9.20$

16.3 Molecular Structure and Acid–Base Strength

LEARNING OBJECTIVE

1. To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the A–H or B–H⁺ bond, the less likely the bond is to break to form H⁺ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	<	HCl	<	HBr	<	HI
H–X Bond Energy (kJ/mol)	570		432		366		298
pK _a	3.20		–6.1		–8.9		–9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, *acid strengths of binary hydrides increase as we go down a column of the periodic table*. For example, the order of acidity for the binary hydrides of Group 16 is as follows, with pK_a values in parentheses: H₂O (14.00 = pK_w) < H₂S (7.05) < H₂Se (3.89) < H₂Te (2.6).

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base (A[–] or B) contains one more lone pair of electrons than the parent acid (AH or BH⁺). *Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H⁺ and makes the parent acid a stronger acid*. Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pK_a values in parentheses: CH₄ (~50) << NH₃ (~36) < H₂O (14.00) < HF (3.20). Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH₄ is CH₃[–], and the conjugate base of HF is F[–]. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F[–] ion than carbon can stabilize the negative charge in the CH₃[–] ion. Consequently, HF has a greater tendency to dissociate to form H⁺ and F[–] than does methane to form H⁺ and CH₃[–], making HF a much stronger acid than CH₄.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E[−] and H⁺. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, *acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.*

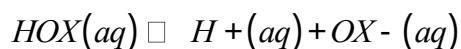
Note the Pattern

Acid strengths of binary hydrides *increase* as we go *down* a column or *from left to right* across a row of the periodic table.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an *inductive effect*, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

Equation 16.37



The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pK _a
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H⁺.

The acidity of oxoacids, with the general formula HOXO_n (*n* = 0–3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure 16.14 "The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit",

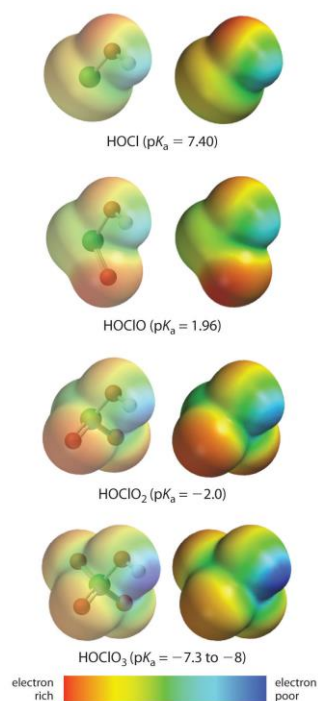
the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

Note the Pattern

Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure 16.14 "The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit" show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure 16.14 "The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit" and Figure 16.15 "The Relationship between Delocalization of the Negative Charge in the Oxoanions of Chlorine and the Number of Terminal Oxygen Atoms", blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from HClO to HClO₄ (also written as HOClO₃), while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H⁺ ions, thereby increasing the strength of the acid.

Figure 16.14 The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit



These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities.

Source: Chlorine oxoacids pK_a values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole, 1993).

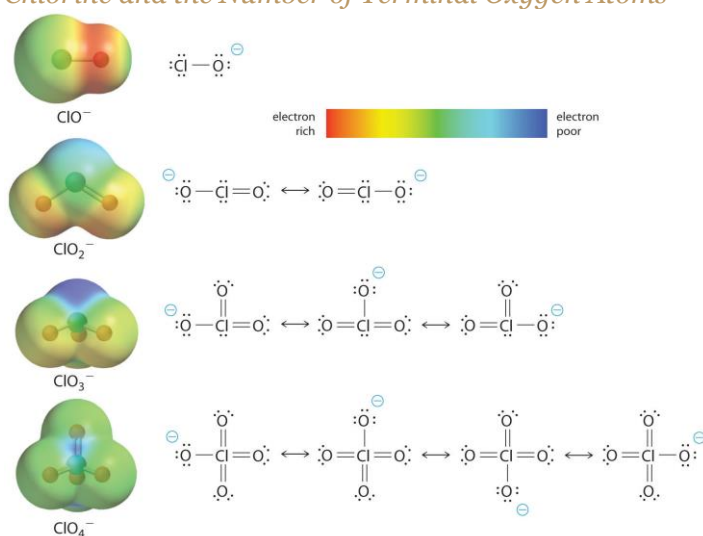
At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure 16.15 "The Relationship between Delocalization of the Negative Charge in the Oxoanions of Chlorine and the Number of Terminal Oxygen Atoms", the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms. The electrostatic potential plots in Figure 16.15 "The Relationship between Delocalization of the Negative Charge in the Oxoanions of Chlorine and the Number of Terminal Oxygen Atoms" demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO^- is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^- , indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single

oxygen atom (Figure 16.15 "The Relationship between Delocalization of the Negative Charge in the Oxoanions of Chlorine and the Number of Terminal Oxygen Atoms"). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.

Note the Pattern

Electron delocalization in the conjugate base increases acid strength.

Figure 16.15 The Relationship between Delocalization of the Negative Charge in the Oxoanions of Chlorine and the Number of Terminal Oxygen Atoms



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and HClO_4 is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which

causes electrons to be drawn from oxygen to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.

Careful inspection of the data in Table 16.4 "Values of p" shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $(\text{HO})_2\text{C}=\text{O}$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid (H_3PO_4), for which $\text{p}K_{\text{a}1} = 2.16$. Instead, the tabulated value of $\text{p}K_{\text{a}1}$ for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see in Section 16.6 "Buffers", however, H_2CO_3 is only a minor component of the aqueous solutions of CO_2 that are referred to as carbonic acid. Similarly, if phosphorous acid (H_3PO_3) actually had the structure $(\text{HO})_3\text{P}$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as HOCl ($\text{p}K_{\text{a}} = 7.40$). In fact, the $\text{p}K_{\text{a}1}$ for phosphorous acid is 1.30, and the structure of phosphorous acid is $(\text{HO})_2\text{P}(=\text{O})\text{H}$ with one H atom directly bonded to P and one $\text{P}=\text{O}$ bond. Thus the $\text{p}K_{\text{a}1}$ for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4 . Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

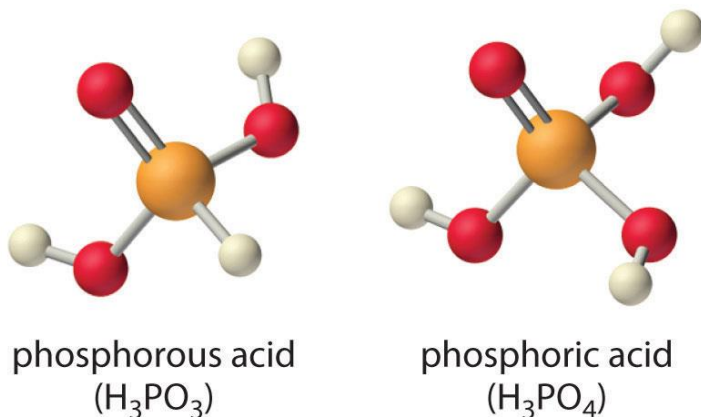
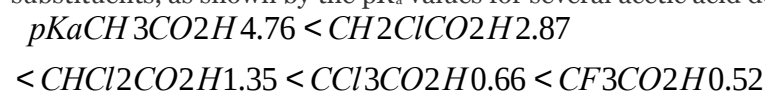


Table 16.4 Values of $\text{p}K_{\text{a}}$ for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	$\text{p}K_{\text{a}1}$	$\text{p}K_{\text{a}2}$	$\text{p}K_{\text{a}3}$
carbonic acid*	" H_2CO_3 "	6.35	10.33	
citric acid	$\text{HO}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$	3.13	4.76	6.40
malonic acid	$\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$	2.85	5.70	
oxalic acid	$\text{HO}_2\text{CCO}_2\text{H}$	1.25	3.81	

phosphoric acid	H ₃ PO ₄	2.16	7.21	12.32
phosphorous acid	H ₃ PO ₃	1.3	6.70	
succinic acid	HO ₂ CCH ₂ CH ₂ CO ₂ H	4.21	5.64	
sulfuric acid	H ₂ SO ₄	-2.0	1.99	
sulfurous acid*	"H ₂ SO ₃ "	1.85	7.21	
Polyprotic Bases	Formula	p K_{b1}	p K_{b2}	
ethylenediamine	H ₂ N(CH ₂) ₂ NH ₂	4.08	7.14	
piperazine	HN(CH ₂ CH ₂) ₂ NH	4.27	8.67	
propylenediamine	H ₂ N(CH ₂) ₃ NH ₂	3.45	5.12	
*H₂CO₃ and H₂SO₃ are at best minor components of aqueous solutions of CO₂(g) and SO₂(g), respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.				

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pK_a values for several acetic acid derivatives:



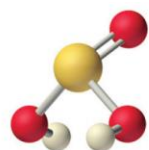
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the –CH₃ group of acetic acid by a –CF₃ group results in about a 10,000-fold increase in acidity!

EXAMPLE 5

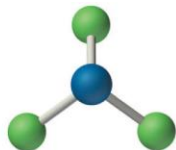
Arrange the compounds of each series in order of increasing acid or base strength.

- sulfuric acid [H₂SO₄, or (HO)₂SO₂], fluorosulfonic acid (FSO₃H, or FSO₂OH), and sulfurous acid [H₂SO₃, or (HO)₂SO]
- ammonia (NH₃), trifluoramine (NF₃), and hydroxylamine (NH₂OH)

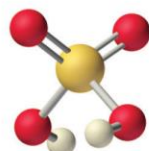
The structures are shown here.



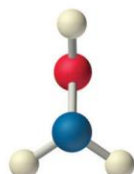
sulfurous acid
(H_2SO_3)



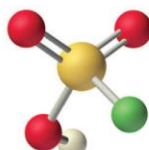
trifluoramine
(NF_3)



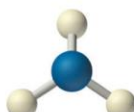
sulfuric acid
(H_2SO_4)



hydroxylamine
(NH_2OH)



fluorosulfonic acid
(FSO_3H)



ammonia
(NH_3)

Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

a. Although both sulfuric acid and sulfurous acid have two -OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an -OH by -F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S-OH bond and the O-H bond. Because its O-H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured $\text{p}K_a$ values for these acids:

b. $\text{p}K_a \text{H}_2\text{SO}_3 1.85 < \text{H}_2\text{SO}_4 - 2 < \text{FSO}_3\text{H} - 10$

c. The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH_3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3 . Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured $\text{p}K_b$ values:

$$\text{p}K_b \text{NF}_3 \ll \text{NH}_2\text{OH} 8.06 < \text{NH}_3 4.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has not been measured.

Exercise

Arrange the compounds of each series in order of

- decreasing acid strength: H_3PO_4 , $\text{CH}_3\text{PO}_3\text{H}_2$, and HClO_3 .
- increasing base strength: CH_3S^- , OH^- , and CF_3S^- .

Answer:

- $\text{HClO}_3 > \text{CH}_3\text{PO}_3\text{H}_2 > \text{H}_3\text{PO}_4$
- $\text{CF}_3\text{S}^- < \text{CH}_3\text{S}^- < \text{OH}^-$

Summary

The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B– H^+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+ , making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an *inductive effect*, which can weaken an O–H bond and allow hydrogen to be more easily lost as H^+ ions.

KEY TAKEAWAY

- Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound.

CONCEPTUAL PROBLEMS

- Section 16.3 "Molecular Structure and Acid–Base Strength" presented several factors that affect the relative strengths of acids and bases. For each pair, identify the most important factor in determining which is the stronger acid or base in aqueous solution.
 - $\text{CH}_3\text{CCl}_2\text{CH}_2\text{CO}_2\text{H}$ versus $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
 - $\text{CH}_3\text{CO}_2\text{H}$ versus $\text{CH}_3\text{CH}_2\text{OH}$
 - HClO versus HBrO
 - $\text{CH}_3\text{C}(=\text{O})\text{NH}_2$ versus $\text{CH}_3\text{CH}_2\text{NH}_2$
 - H_3AsO_4 versus H_3AsO_3
- The stability of the conjugate base is an important factor in determining the strength of an acid. Which would you expect to be the stronger acid in aqueous solution— $\text{C}_6\text{H}_5\text{NH}_3^+$ or NH_4^+ ? Justify your reasoning.
- Explain why H_2Se is a weaker acid than HBr .
- Arrange the following in order of decreasing acid strength in aqueous solution: H_3PO_4 , $\text{CH}_3\text{PO}_3\text{H}_2$, and HClO_3 .
- Arrange the following in order of increasing base strength in aqueous solution: CH_3S^- , OH^- , and CF_3S^- .
- Arrange the following in order of increasing acid strength in aqueous solution: HClO_2 , HNO_2 , and HNO_3 .
- Do you expect H_2SO_3 or H_2SeO_3 to be the stronger acid? Why?
- Give a plausible explanation for why CF_3OH is a stronger acid than CH_3OH in aqueous solution. Do you expect $\text{CHCl}_2\text{CH}_2\text{OH}$ to be a stronger or a weaker acid than CH_3OH ? Why?
- Do you expect Cl_2NH or NH_3 to be the stronger base in aqueous solution? Why?

ANSWERS

-
-
-
-
- $\text{CF}_3\text{S}^- < \text{CH}_3\text{S}^- < \text{OH}^-$ (strongest base)
-

- 7.
- 8.
9. NH_3 ; Cl atoms withdraw electron density from N in Cl_2NH .

16.4 Quantitative Aspects of Acid–Base Equilibria

LEARNING OBJECTIVE

1. To use K_a and K_b values to calculate the percent ionization and the pH of a solution of an acid or a base.

This section presents a quantitative approach to analyzing acid–base equilibria. You will learn how to determine the values of K_a and K_b , how to use K_a or K_b to calculate the percent ionization and the pH of an aqueous solution of an acid or a base, and how to calculate the equilibrium constant for the reaction of an acid with a base from the K_a and K_b of the reactants.

Determining K_a and K_b

The ionization constants K_a and K_b are equilibrium constants that are calculated from experimentally measured concentrations, just like the equilibrium constants discussed in Chapter 15 "Chemical Equilibrium". Before proceeding further, it is important to understand exactly what is meant when we describe the concentration of an aqueous solution of a weak acid or a weak base. Suppose, for example, we have a bottle labeled 1.0 M acetic acid or 1.0 M ammonia. As you learned in Chapter 4 "Reactions in Aqueous Solution", such a solution is usually prepared by dissolving 1.0 mol of acetic acid or ammonia in water and adding enough water to give a final volume of exactly 1.0 L. If, however, we were to list the actual concentrations of all the species present in either solution, we would find that *none* of the values is exactly 1.0 M because a weak acid such as acetic acid or a weak base such as ammonia always reacts with water to some extent. The extent of the reaction depends on the K_a or the K_b , the concentration of the acid or the base, and the temperature. Consequently, only the *total concentration* of both the ionized and unionized species is equal to 1.0 M.

The *analytical concentration* (C) is defined as the *total* concentration of all forms of an acid or a base that are present in solution, regardless of their state of protonation. Thus a "1.0 M" solution of acetic acid has an analytical concentration of 1.0 M, which is the sum of the *actual* concentrations of unionized acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) and the ionized form (CH_3CO_2^-):

Equation 16.38



As we shall see shortly, if we know the analytical concentration and the K_a , we can calculate the actual values of $[CH_3CO_2H]$ and $[CH_3CO_2^-]$.

The equilibrium equations for the reaction of acetic acid and ammonia with water are as follows:

Equation 16.39
$$K_a = [H^+][CH_3CO_2^-] / [CH_3CO_2H]$$

Equation 16.40

$$K_b = [NH_4^+][OH^-] / [NH_3]$$

where K_a and K_b are the ionization constants for acetic acid and ammonia, respectively. In addition to the analytical concentration of the acid (or the base), we must have a way to measure the concentration of at least *one* of the species in the equilibrium constant expression to determine the K_a (or the K_b). There are two common ways to obtain the concentrations: (1) measure the electrical conductivity of the solution, which is related to the total concentration of ions present, and (2) measure the pH of the solution, which gives $[H^+]$ or $[OH^-]$.

Example 6 and Example 7 illustrate the procedure for determining K_a for a weak acid and K_b for a weak base. In both cases, we will follow the procedure developed in Chapter 15 "Chemical Equilibrium": the analytical concentration of the acid or the base is the *initial* concentration, and the stoichiometry of the reaction with water determines the *change* in concentrations. The *final* concentrations of all species are calculated from the initial concentrations and the changes in the concentrations. Inserting the final concentrations into the equilibrium constant expression enables us to calculate the K_a or the K_b .

EXAMPLE 6

Electrical conductivity measurements indicate that 0.42% of the acetic acid molecules in a 1.00 M solution are ionized at 25°C. Calculate K_a and pK_a for acetic acid at this temperature.

Given: analytical concentration and percent ionization

Asked for: K_a and pK_a

Strategy:

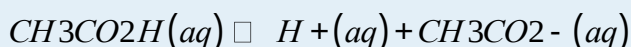
A Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

B Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

C Substitute the final concentrations into the equilibrium constant expression and calculate the K_a . Take the negative logarithm of K_a to obtain the pK_a .

Solution:

A The balanced equilibrium equation for the dissociation of acetic acid is as follows:



and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

B To calculate the K_a , we need to know the equilibrium concentrations of CH_3CO_2H , $CH_3CO_2^-$, and H^+ . The most direct way to do this is to construct a table that lists the initial concentrations and the changes in concentrations that occur during the reaction to give the final concentrations, using the procedure introduced in Chapter 15 "Chemical Equilibrium". The initial concentration of unionized acetic acid ($[CH_3CO_2H]_i$) is the analytical concentration, 1.00 M, and the initial acetate concentration ($[CH_3CO_2^-]_i$) is zero. The initial concentration of H^+ is not zero, however; $[H^+]_i$ is 1.00×10^{-7} M due to the autoionization of water. The measured percent ionization tells us that 0.42% of the acetic acid molecules are ionized at equilibrium. Consequently, the change in the concentration of acetic acid is $\Delta[CH_3CO_2H] = -(4.2 \times 10^{-3})(1.00 \text{ M}) = -0.0042 \text{ M}$. Conversely, the change in the acetate concentration is $\Delta[CH_3CO_2^-] = +0.0042 \text{ M}$ because every 1 mol of acetic acid that ionizes gives 1 mol of acetate. Because one proton is produced for each acetate ion formed, $\Delta[H^+] = +0.0042 \text{ M}$ as well. These results are summarized in the following table.

$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$			
	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	1.00	1.00×10^{-7}	0
change	-0.0042	+0.0042	+0.0042
final			

The final concentrations of all species are therefore as follows:

$$[CH_3CO_2H]_f = [CH_3CO_2H]_i + \Delta[CH_3CO_2H] = 1.00 \text{ M}$$

$$+(-0.0042 \text{ M}) = 0.9958 \text{ M} \quad [CH_3CO_2^-]_f = [CH_3CO_2^-]_i + \Delta[CH_3CO_2^-] = 0 \text{ M}$$

$$\begin{aligned}
 &+ (0.0042 \text{ M}) = 0.0042 \text{ M} \\
 &[H^+] = [H^+]_i \\
 &+ D[H^+] = 1.00 \times 10^{-7} \text{ M} + (0.0042 \text{ M}) = 0.0042 \text{ M}
 \end{aligned}$$

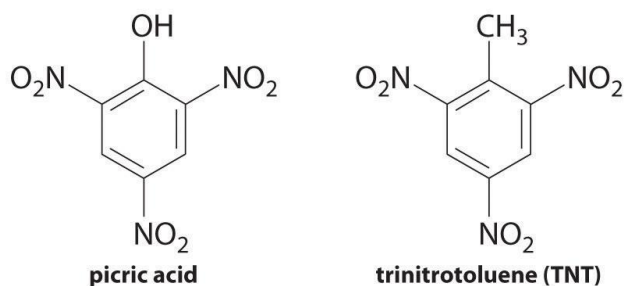
C We can now calculate K_a by inserting the final concentrations into the equilibrium constant expression:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.0042)(0.0042)}{1.00} = 1.8 \times 10^{-5}$$

The pK_a is the negative logarithm of K_a : $pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74$.

Exercise

Picric acid is the common name for 2,4,6-trinitrophenol, a derivative of phenol (C_6H_5OH) in which three H atoms are replaced by nitro ($-NO_2$) groups. The presence of the nitro groups removes electron density from the phenyl ring, making picric acid a much stronger acid than phenol ($pK_a = 9.99$). The nitro groups also make picric acid potentially explosive, as you might expect based on its chemical similarity to 2,4,6-trinitrotoluene, better known as TNT. A 0.20 M solution of picric acid is 73% ionized at 25°C. Calculate K_a and pK_a for picric acid.



Answer: $K_a = 0.39$; $pK_a = 0.41$

EXAMPLE 7

A 1.0 M aqueous solution of ammonia has a pH of 11.63 at 25°C. Calculate K_b and pK_b for ammonia.

Given: analytical concentration and pH

Asked for: K_b and pK_b

Strategy:

A Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

B Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

C Substitute the final concentrations into the equilibrium constant expression and calculate the K_b . Take the negative logarithm of K_b to obtain the pK_b .

Solution:

A The balanced equilibrium equation for the reaction of ammonia with water is as follows:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ and the equilibrium constant expression is as follows:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Remember that water does not appear in the equilibrium constant expression for K_b .

B To calculate K_b , we need to know the equilibrium concentrations of NH_3 , NH_4^+ , and OH^- . The initial concentration of NH_3 is the analytical concentration, 1.0 M, and the initial concentrations of NH_4^+ and OH^- are 0 M and 1.00×10^{-7} M, respectively. In this case, we are given the pH of the solution, which allows us to calculate the final concentration of one species (OH^-) directly, rather than the change in concentration. Recall that $pK_w = pH + pOH = 14.00$ at 25°C. Thus $pOH = 14.00 - pH = 14.00 - 11.63 = 2.37$, and $[OH^-]_f = 10^{-2.37} = 4.3 \times 10^{-3}$ M. Our data thus far are listed in the following table.

$NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$			
	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	1.0	0	1.00×10^{-7}
change			
final			4.3×10^{-3}

The final $[OH^-]$ is much greater than the initial $[H^+]$, so the change in $[OH^-]$ is as follows:

$$\Delta[OH^-] = (4.3 \times 10^{-3} \text{ M}) - (1.00 \times 10^{-7} \text{ M}) \approx 4.3 \times 10^{-3} \text{ M}$$

The stoichiometry of the reaction tells us that 1 mol of NH_3 is converted to NH_4^+ for each 1 mol of OH^- formed, so

$$\Delta[NH_4^+] = +4.3 \times 10^{-3} \text{ M} \text{ and } \Delta[NH_3] = -4.3 \times 10^{-3} \text{ M}$$

We can now insert these values for the changes in concentrations into the table, which enables us to complete the table.

$H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$			
	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	1.0	0	1.00×10^{-7}

$H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$			
	[NH₃]	[NH₄⁺]	[OH⁻]
change	-4.3×10^{-3}	$+4.3 \times 10^{-3}$	$+4.3 \times 10^{-3}$
final	1.0	4.3×10^{-3}	4.3×10^{-3}

C Inserting the final concentrations into the equilibrium constant expression gives K_b :

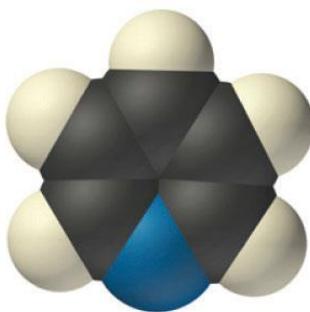
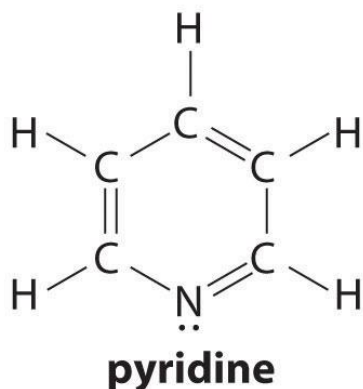
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(4.3 \times 10^{-3})(4.3 \times 10^{-3})}{1.0} = 1.8 \times 10^{-5}$$

and $pK_b = -\log K_b = 4.74$.

The K_b and the pK_b for ammonia are almost exactly the same as the K_a and the pK_a for acetic acid at 25°C. In other words, ammonia is almost exactly as strong a base as acetic acid is an acid. Consequently, the extent of the ionization reaction in an aqueous solution of ammonia at a given concentration is the same as in an aqueous solution of acetic acid at the same concentration.

Exercise

The pH of a 0.050 M solution of pyridine (C₅H₅N) is 8.96 at 25°C. Calculate K_b and pK_b for pyridine.



Answer: $K_b = 1.7 \times 10^{-9}$; $pK_b = 8.77$

Calculating Percent Ionization from K_a or K_b

When carrying out a laboratory analysis, chemists frequently need to know the concentrations of all species in solution. Because the reactivity of a weak acid or a weak base is usually very different from the reactivity of its conjugate base or acid, we often need to know the percent ionization of a solution of an acid or a base to understand a chemical reaction. The percent ionization is defined as follows:

Equation 16.41

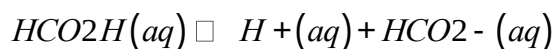
$$\text{percent ionization of acid} = \frac{[H^+]}{[HA]} \times 100$$

Equation 16.42

$$\text{percent ionization of base} = \frac{[OH^-]}{[B]} \times 100$$

One way to determine the concentrations of species in solutions of weak acids and bases is a variation of the tabular method we used previously to determine K_a and K_b values. As a demonstration, we will calculate the concentrations of all species and the percent ionization in a 0.150 M solution of formic acid at 25°C. The data in Table 16.2 "Values of " show that formic acid ($K_a = 1.8 \times 10^{-4}$ at 25°C) is a slightly stronger acid than acetic acid. The equilibrium equation for the ionization of formic acid in water is as follows:

Equation 16.43



and the equilibrium constant expression for this reaction is as follows:

Equation 16.44

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]}$$

We set the initial concentration of HCO_2H equal to 0.150 M, and that of HCO_2^- is 0 M. The initial concentration of H^+ is 1.00×10^{-7} M due to the autoionization of water. Because the equilibrium constant for the ionization reaction is small, the equilibrium will lie to the left, favoring the unionized form of the acid. Hence we can define x as the amount of formic acid that dissociates.

If the change in $[HCO_2H]$ is $-x$, then the change in $[H^+]$ and $[HCO_2^-]$ is $+x$. The final concentration of each species is the sum of its initial concentration and the change in concentration, as summarized in the following table.

$HCO_2H(aq) \rightleftharpoons H^+(aq) + HCO_2^-(aq)$			
	$[HCO_2H]$	$[H^+]$	$[HCO_2^-]$
initial	0.150	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	$(1.00 \times 10^{-7} + x)$	x

We can calculate x by substituting the final concentrations from the table into the equilibrium constant expression:

$$K_a = [H^+][HCO_2^-] / [HCO_2H] = (1.00 \times 10^{-7} + x)x / 0.150 - x$$

Because the ionization constant K_a is small, x is likely to be small compared with the initial concentration of formic acid: $(0.150 - x) M \approx 0.150 M$. Moreover, $[H^+]$ due to the autoionization of water ($1.00 \times 10^{-7} M$) is likely to be negligible compared with $[H^+]$ due to the dissociation of formic acid: $(1.00 \times 10^{-7} + x) M \approx x M$. Inserting these values into the equilibrium constant expression and solving for x ,

$$K_a = x^2 / 0.150x = 1.8 \times 10^{-4} = 5.2 \times 10^{-3}$$

We can now calculate the concentrations of the species present in a 0.150 M formic acid solution by inserting this value of x into the expressions in the last line of the table:

$$[HCO_2H] / [HCO_2^-] / [H^+] = (0.150 - x) M = 0.145 M = x = 5.2$$

$$\times 10^{-3} M = (1.00 \times 10^{-7} + x) M = 5.2 \times 10^{-3} M$$

Thus the pH of the solution is $-\log(5.2 \times 10^{-3}) = 2.28$. We can also use these concentrations to calculate the fraction of the original acid that is ionized. In this case, the percent ionization is the ratio of $[H^+]$ (or $[HCO_2^-]$) to the analytical concentration, multiplied by 100 to give a percentage:

$$\text{percent ionization} = [H^+] / C_{HA} \times 100 = 5.2 \times 10^{-3} M / 0.150 \times 100 = 3.5\%$$

Always check to make sure that any simplifying assumption was valid. As a general rule of thumb, approximations such as those used here are valid *only* if the quantity being neglected is no more than about 5% of the quantity to which it is being added or from which it is being subtracted. If the quantity that was neglected is much greater than about 5%, then the approximation is probably not valid, and you should go back and solve the problem using the quadratic formula. In the previous demonstration, both simplifying assumptions were justified: the percent ionization is only 3.5%, which is well below the approximately 5% limit, and the $1.00 \times 10^{-7} M [H^+]$ due to the autoionization of water is much, much less than the $5.2 \times 10^{-3} M [H^+]$ due to the ionization of formic acid.

As a general rule, the $[H^+]$ contribution due to the autoionization of water can be ignored as long as the product of the acid or the base ionization constant and the analytical concentration of the acid or the base is at least 10 times greater than the $[H^+]$ or $[OH^-]$ from the autoionization of water—that is, if

Equation 16.45

$$K_a C_{HA} \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6}$$

or

Equation 16.46

$$K_b C_B \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6}$$

By substituting the appropriate values for the formic acid solution into Equation 16.45, we see that the simplifying assumption is valid in this case:

Equation 16.47

$$K_a C_{\text{HA}} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5} > 1.0 \times 10^{-6}$$

Doing this simple calculation before solving this type of problem saves time and allows you to write simplified expressions for the final concentrations of the species present. In practice, it is necessary to include the $[\text{H}^+]$ contribution due to the autoionization of water only for extremely dilute solutions of very weak acids or bases.

Example 8 illustrates how the procedure outlined previously can be used to calculate the pH of a solution of a weak base.

EXAMPLE 8

Calculate the pH and percent ionization of a 0.225 M solution of ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$), which is used in the synthesis of some dyes and medicines. The $\text{p}K_b$ of ethylamine is 3.19 at 20°C .

Given: concentration and $\text{p}K_b$

Asked for: pH and percent ionization

Strategy:

A Write the balanced equilibrium equation for the reaction and the equilibrium constant expression.

Calculate K_b from $\text{p}K_b$.

B Use Equation 16.45 to see whether you can ignore $[\text{H}^+]$ due to the autoionization of water. Then use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for $[\text{OH}^-]$. Use Equation 16.42 to calculate the percent ionization.

C Use the relationship $K_w = [\text{OH}^-][\text{H}^+]$ to obtain $[\text{H}^+]$. Then calculate the pH of the solution.

Solution:

A We begin by writing the balanced equilibrium equation for the reaction:



The corresponding equilibrium constant expression is as follows:

$$K_b = \frac{[\text{CH}_3\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$$

From the $\text{p}K_b$, we have $K_b = 10^{-3.19} = 6.5 \times 10^{-4}$.

B To calculate the pH, we need to determine the H^+ concentration. Unfortunately, H^+ does not appear in either the chemical equation or the equilibrium constant expression. However, $[H^+]$ and $[OH^-]$ in an aqueous solution are related by $K_w = [H^+][OH^-]$. Hence if we can determine $[OH^-]$, we can calculate $[H^+]$ and then the pH. The initial concentration of $CH_3CH_2NH_2$ is 0.225 M, and the initial $[OH^-]$ is 1.00×10^{-7} M. Because ethylamine is a weak base, the extent of the reaction will be small, and it makes sense to let x equal the amount of $CH_3CH_2NH_2$ that reacts with water. The change in $[CH_3CH_2NH_2]$ is therefore $-x$, and the change in both $[CH_3CH_2NH_3^+]$ and $[OH^-]$ is $+x$. To see whether the autoionization of water can safely be ignored, we substitute K_b and C_b into Equation 16.46:

$$K_b C_b = (6.5 \times 10^{-4})(0.225) = 1.5 \times 10^{-4} > 1.0 \times 10^{-6}$$

Thus the simplifying assumption is valid, and we will not include $[OH^-]$ due to the autoionization of water in our calculations.

$H_2O(l) + CH_3CH_2NH_2(aq) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$			
	$[CH_3CH_2NH_2]$	$[CH_3CH_2NH_3^+]$	$[OH^-]$
initial	0.225	0	1.00×10^{-7}
change	$-x$	$+x$	$+x$
final	$(0.225 - x)$	x	x

Substituting the quantities from the last line of the table into the equilibrium constant expression,

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]} = \frac{(x)(x)}{0.225 - x} = 6.5 \times 10^{-4}$$

As before, we assume the amount of $CH_3CH_2NH_2$ that ionizes is small compared with the initial concentration, so $[CH_3CH_2NH_2]_f = 0.225 - x \approx 0.225$. With this assumption, we can simplify the equilibrium equation and solve for x :

$$K_b = \frac{x^2}{0.225} = 6.5 \times 10^{-4} = 0.012 = \frac{[CH_3CH_2NH_3^+]_f [OH^-]_f}{[CH_3CH_2NH_2]_f}$$

The percent ionization is therefore

$$\text{percent ionization} = \frac{[OH^-]_f}{C_b} \times 100 = \frac{0.012 \text{ M}}{0.225 \text{ M}} \times 100 = 5.4\%$$

which is at the upper limit of the approximately 5% range that can be ignored. The final hydroxide concentration is thus 0.012 M.

C We can now determine the $[H^+]$ using the expression for K_w :

$$K_w 1.01 \times 10^{-14} = 4 \times 10^{-13} \text{ M} = [OH^-][H^+] = (0.012 \text{ M})[H^+] = [H^+]$$

The pH of the solution is $-\log(8.4 \times 10^{-13}) = 12.08$. Alternatively, we could have calculated pOH as $-\log(0.012) = 1.92$ and determined the pH as follows:

$$pH + pOH = pK_w = 14.00 = 14.00 - 1.92 = 12.08$$

The two methods are equivalent.

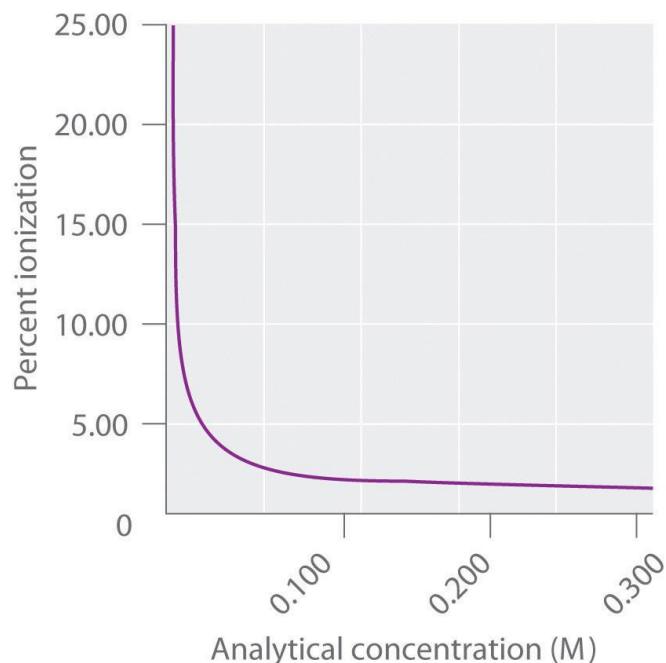
Exercise

Aromatic amines, in which the nitrogen atom is bonded directly to a phenyl ring ($-\text{C}_6\text{H}_5$) tend to be much weaker bases than simple alkylamines. For example, aniline ($\text{C}_6\text{H}_5\text{NH}_2$) has a pK_b of 9.13 at 25°C . What is the pH of a 0.050 M solution of aniline?

Answer: 8.78

The previous examples illustrate a key difference between solutions of strong acids and bases and solutions of weak acids and bases. Because strong acids and bases ionize essentially completely in water, the percent ionization is always approximately 100%, regardless of the concentration. In contrast, the percent ionization in solutions of weak acids and bases is small and depends on the analytical concentration of the weak acid or base. As illustrated for benzoic acid in Figure 16.16 "The Relationship between the Analytical Concentration of a Weak Acid and Percent Ionization", the percent ionization of a weak acid or a weak base actually *increases* as its analytical concentration decreases. The percent ionization also increases as the magnitude of K_a and K_b increases.

Figure 16.16 The Relationship between the Analytical Concentration of a Weak Acid and Percent Ionization



As shown here for benzoic acid ($C_6H_5CO_2H$), the percent ionization decreases as the analytical concentration of a weak acid increases.

Unlike the K_a or the K_b , the percent ionization is not a constant for weak acids and bases but depends on *both* the K_a or the K_b *and* the analytical concentration. Consequently, the procedure in Example 8 must be used to calculate the percent ionization and pH for solutions of weak acids and bases. Example 9 and its corresponding exercise demonstrate that the combination of a dilute solution and a relatively large K_a or K_b can give a percent ionization much greater than 5%, making it necessary to use the quadratic equation to determine the concentrations of species in solution.

Note the Pattern

The percent ionization in a solution of a weak acid or a weak base *increases* as the analytical concentration *decreases* and as the K_a or the K_b *increases*.

EXAMPLE 9

Benzoic acid ($C_6H_5CO_2H$) is used in the food industry as a preservative and medically as an antifungal agent. Its pK_a at $25^\circ C$ is 4.20, making it a somewhat stronger acid than acetic acid. Calculate the percentage of benzoic acid molecules that are ionized in each solution.

- a 0.0500 M solution
- a 0.00500 M solution

Given: concentrations and pK_a

Asked for: percent ionization

Strategy:

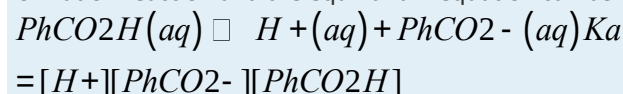
A Write both the balanced equilibrium equation for the ionization reaction and the equilibrium equation (Equation 16.15). Use Equation 16.25 to calculate the K_a from the pK_a .

B For both the concentrated solution and the dilute solution, use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for $[C_6H_5CO_2^-]_f$ for each solution.

C Use the values of $[C_6H_5CO_2^-]_f$ and Equation 16.41 to calculate the percent ionization.

Solution:

A If we abbreviate benzoic acid as $PhCO_2H$ where $Ph = -C_6H_5$, the balanced equilibrium equation for the ionization reaction and the equilibrium equation can be written as follows:



From the pK_a , we have $K_a = 10^{-4.20} = 6.3 \times 10^{-5}$.

a. **B** For the more concentrated solution, we set up our table of initial concentrations, changes in concentrations, and final concentrations:

$PhCO_2H(aq) \rightleftharpoons H^+(aq) + PhCO_2^-(aq)$			
	$[PhCO_2H]$	$[H^+]$	$[PhCO_2^-]$
initial	0.0500	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.0500 - x)$	$(1.00 \times 10^{-7} + x)$	x

b. Inserting the expressions for the final concentrations into the equilibrium equation and making our usual assumptions, that $[PhCO_2^-]$ and $[H^+]$ are negligible due to the autoionization of water,

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]} = 1.8 \times 10^{-3}$$

c.
$$= \frac{(x)(x)}{0.0500 - x} = x = 2.0 \times 10^{-5}$$

d. This value is less than 5% of 0.0500, so our simplifying assumption is justified, and $[PhCO_2^-]$ at equilibrium is 1.8×10^{-3} M. We reach the same conclusion using C_{HA} : $K_a C_{HA} = (6.3 \times 10^{-5})(0.0500) = 3.2 \times 10^{-6} > 1.0 \times 10^{-6}$.

e. **C** The percent ionized is the ratio of the concentration of $PhCO_2^-$ to the analytical concentration, multiplied by 100:

f.
$$\text{percent ionized} = \frac{[\text{PhCO}_2^-]}{[\text{PhCO}_2^-] + [\text{PhCO}_2\text{H}]} \times 100 = \frac{1.8 \times 10^{-5}}{1.8 \times 10^{-5} + 0.0500} \times 100 = 3.6\%$$

g. Because only 3.6% of the benzoic acid molecules are ionized in a 0.0500 M solution, our simplifying assumptions are confirmed.

h. **B** For the more dilute solution, we proceed in exactly the same manner. Our table of concentrations is therefore as follows:

$\text{PhCO}_2\text{H}(aq) \rightleftharpoons \text{H}^+(aq) + \text{PhCO}_2^-(aq)$			
	$[\text{PhCO}_2\text{H}]$	$[\text{H}^+]$	$[\text{PhCO}_2^-]$
initial	0.00500	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.00500 - x)$	$(1.00 \times 10^{-7} + x)$	x

i. Inserting the expressions for the final concentrations into the equilibrium equation and making our usual simplifying assumptions,

j.
$$K_a = \frac{[\text{H}^+][\text{PhCO}_2^-]}{[\text{PhCO}_2\text{H}]} = \frac{(x)(x)}{0.00500 - x} \approx \frac{x^2}{0.00500} = 6.3 \times 10^{-5}$$

k. Unfortunately, this number is greater than 10% of 0.00500, so our assumption that the fraction of benzoic acid that is ionized in this solution could be neglected and that $(0.00500 - x) \approx x$ is not valid. Furthermore, we see that $K_a C_{\text{HA}} = (6.3 \times 10^{-5})(0.00500) = 3.2 \times 10^{-7} < 1.0 \times 10^{-6}$. Thus the relevant equation is as follows:

l.
$$x^2 + 6.3 \times 10^{-5}x - 3.2 \times 10^{-7} = 0$$

m. which must be solved using the quadratic formula. Multiplying out the quantities,

n.
$$x^2 + (6.3 \times 10^{-5})x - (3.2 \times 10^{-7}) = 0$$

o. Rearranging the equation to fit the standard quadratic equation format,

p.
$$x^2 + (6.3 \times 10^{-5})x - (3.2 \times 10^{-7}) = 0$$

q. This equation can be solved by using the quadratic formula:

r.
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(6.3 \times 10^{-5}) \pm \sqrt{(6.3 \times 10^{-5})^2 - 4(1)(-3.2 \times 10^{-7})}}{2(1)}$$

$$= 5.3 \times 10^{-4} \text{ or } -5.9 \times 10^{-4}$$

s.

t. Because a negative x value corresponds to a negative $[\text{PhCO}_2^-]$, which is not physically meaningful, we use the positive solution: $x = 5.3 \times 10^{-4}$. Thus $[\text{PhCO}_2^-] = 5.3 \times 10^{-4} \text{ M}$.

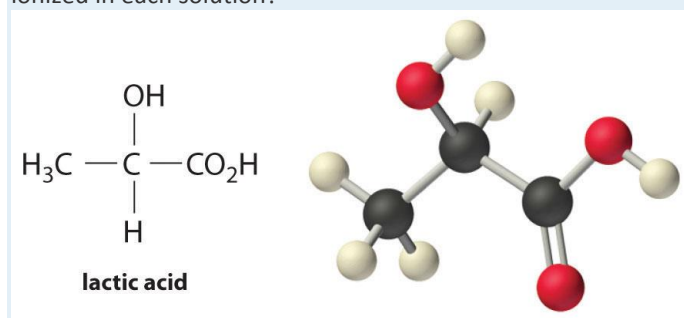
u. **C** The percent ionized is therefore

v.
$$\text{percent ionized} = \frac{[\text{PhCO}_2^-]}{[\text{PhCO}_2^-] + [\text{CPhCO}_2\text{H}]} \times 100$$

w. In the more dilute solution ($C = 0.00500 \text{ M}$), 11% of the benzoic acid molecules are ionized versus only 3.6% in the more concentrated solution ($C = 0.0500 \text{ M}$). Decreasing the analytical concentration by a factor of 10 results in an approximately threefold increase in the percentage of benzoic acid molecules that are ionized.

Exercise

Lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$) is a weak acid with a $\text{p}K_a$ of 3.86 at 25°C . What percentage of the lactic acid is ionized in each solution?



a. a 0.10 M solution

b. a 0.0020 M solution

Answer:

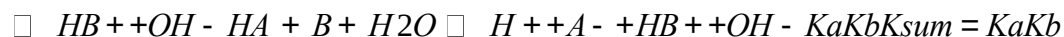
a. 3.7%

b. 23%

Determining K_{eq} from K_a and K_b

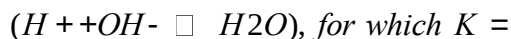
In Section 16.2 "A Qualitative Description of Acid–Base Equilibria", you learned how to use K_a and K_b values to qualitatively predict whether reactants or products are favored in an acid–base reaction. Tabulated values of K_a (or $\text{p}K_a$) and K_b (or $\text{p}K_b$), plus the K_w , enable us to quantitatively determine the direction and extent of reaction for a weak acid and a weak base by calculating K for the reaction. To illustrate how to do this, we begin by writing the dissociation equilibria for a weak acid and a weak base and then summing them:

Equation 16.48



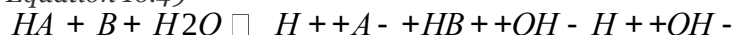
The overall reaction has H_2O on the left and H^+ and OH^- on the right, which means it involves the autoionization of water ($\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$) in addition to the acid–base equilibrium in which we

are interested. We can obtain an equation that includes only the acid–base equilibrium by simply *adding the equation for the reverse of the autoionization of water*



$1/K_w$, to the overall equilibrium in Equation 16.48 and canceling:

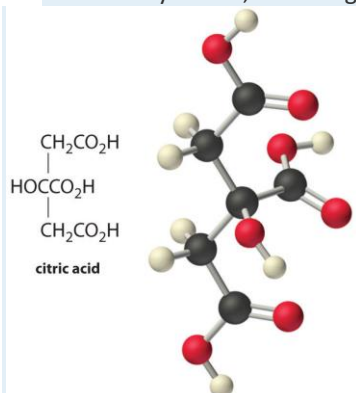
Equation 16.49



Thus the equilibrium constant for the reaction of a weak acid with a weak base is the product of the ionization constants of the acid and the base divided by K_w . Example 10 illustrates how to calculate the equilibrium constant for the reaction of a weak acid with a weak base.

EXAMPLE 10

Fish tend to spoil rapidly, even when refrigerated. The cause of the resulting “fishy” odor is a mixture of amines, particularly methylamine (CH_3NH_2), a volatile weak base ($\text{p}K_b = 3.34$). Fish is often served with a wedge of lemon because lemon juice contains citric acid, a triprotic acid with $\text{p}K_a$ values of 3.13, 4.76, and 6.40 that can neutralize amines. Calculate the equilibrium constant for the reaction of excess citric acid with methylamine, assuming that only the first dissociation constant of citric acid is important.



Given: $\text{p}K_b$ for base and $\text{p}K_a$ for acid

Asked for: K

Strategy:

A Write the balanced equilibrium equation and the equilibrium constant expression for the reaction.

B Convert pK_a and pK_b to K_a and K_b and then use Equation 16.49 to calculate K .

Solution:

A If we abbreviate citric acid as $H_3\text{citrate}$, the equilibrium equation for its reaction with methylamine is as follows:



The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CH_3NH_3^+][H_2\text{citrate}^-]}{[CH_3NH_2][H_3\text{citrate}]}$$

B Equation 16.49 is $K = (K_a K_b) / K_w$. Converting pK_a and pK_b to K_a and K_b gives $K_a = 10^{-3.13} = 7.4 \times 10^{-4}$ for citric acid and $K_b = 10^{-3.34} = 4.6 \times 10^{-4}$ for methylamine. Substituting these values into the equilibrium equation, $K = K_a K_b / K_w = (7.4 \times 10^{-4})(4.6 \times 10^{-4}) / 1.01 \times 10^{-14} = 3.4 \times 10^7$

The value of pK can also be calculated directly by taking the negative logarithm of both sides of Equation 16.49, which gives

$$pK = pK_a + pK_b - pK_w = 3.13 + 3.34 - 14.00 = -7.53$$

Thus $K = 10^{-(-7.53)} = 3.4 \times 10^7$, in agreement with the earlier value. In either case, the K values show that the reaction of citric acid with the volatile, foul-smelling methylamine lies very far to the right, favoring the formation of a much less volatile salt with no odor. This is one reason a little lemon juice helps make less-than-fresh fish more appetizing.

Exercise

Dilute aqueous ammonia solution, often used as a cleaning agent, is also effective as a deodorizing agent.

To see why, calculate the equilibrium constant for the reaction of aqueous ammonia with butyric acid ($CH_3CH_2CH_2CO_2H$), a particularly foul-smelling substance associated with the odor of rancid butter and smelly socks. The pK_b of ammonia is 4.75, and the pK_a of butyric acid is 4.83.

Answer: 2.6×10^4

Summary

If the concentration of one or more of the species in a solution of an acid or a base is determined experimentally, K_a and K_b can be calculated, and K_a , pK_a , K_b , and pK_b can be used to quantitatively describe the composition of solutions of acids and bases. The concentrations of all species present in solution can

be determined, as can the pH of the solution and the percentage of the acid or base that is ionized. The equilibrium constant for the reaction of a weak acid with a weak base can be calculated from K_a (or pK_a), K_b (or pK_b), and K_w .

KEY TAKEAWAY

- For a solution of a weak acid or a weak base, the percent ionization increases as the K_a or the K_b increases and as the analytical concentration decreases.

KEY EQUATIONS

Percent ionization of acid

$$\text{Equation 16.41: } \frac{[H^+]}{C_{HA}} \times 100$$

Percent ionization of base

$$\text{Equation 16.42: } \frac{[OH^-]}{C_B} \times 100$$

Equilibrium constant for reaction of a weak acid with a weak base

$$\text{Equation 16.49: } K = K_a K_b / K_w$$

CONCEPTUAL PROBLEMS

- Explain why the analytical concentration (C) of H_2SO_4 is equal to $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$.
- Write an expression for the analytical concentration (C) of H_3PO_4 in terms of the concentrations of the species actually present in solution.
- For relatively dilute solutions of a weak acid such as acetic acid (CH_3CO_2H), the concentration of undissociated acetic acid in solution is often assumed to be the same as the analytical concentration. Explain why this is a valid practice.
- How does dilution affect the percent ionization of a weak acid or a weak base?
- What is the relationship between the K_a of a weak acid and its percent ionization? Does a compound with a large pK_a value have a higher or a lower percent ionization than a compound with a small pK_a value (assuming the same analytical concentration in both cases)? Explain.
- For a dilute solution of a weak acid (HA), show that the pH of the solution can be approximated using the following equation (where C_{HA} is the analytical concentration of the weak acid):

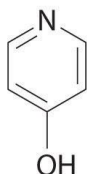
$$pH = -\log K_a \times CHA - - - - - \ddot{O}$$

Under what conditions is this approximation valid?

NUMERICAL PROBLEMS

1. The pK_a of NH_3 is estimated to be 35. Its conjugate base, the amide ion (NH_2^-), can be isolated as an alkali metal salt, such as sodium amide ($NaNH_2$). Calculate the pH of a solution prepared by adding 0.100 mol of sodium amide to 1.00 L of water. Does the pH differ appreciably from the pH of a NaOH solution of the same concentration? Why or why not?
2. Phenol is a topical anesthetic that has been used in throat lozenges to relieve sore throat pain. Describe in detail how you would prepare a 2.00 M solution of phenol (C_6H_5OH) in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of phenol with water? Use the information in Chapter 27 "Appendix C: Dissociation Constants and p" to calculate the pH of the phenol solution.
3. Describe in detail how you would prepare a 1.50 M solution of methylamine in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of methylamine with water? Use the information in Table 16.3 "Values of " to calculate the pH of the solution.
4. A 0.200 M solution of diethylamine, a substance used in insecticides and fungicides, is only 3.9% ionized at 25°C. Write an equation showing the equilibrium reaction and then calculate the pK_b of diethylamine. What is the pK_a of its conjugate acid, the diethylammonium ion? What is the equilibrium constant expression for the reaction of diethylammonium chloride with water?
5. A 1.00 M solution of fluoroacetic acid (FCH_2CO_2H) is 5% dissociated in water. What is the equilibrium constant expression for the dissociation reaction? Calculate the concentration of each species in solution and then calculate the pK_a of FCH_2CO_2H .
6. The pK_a of 3-chlorobutanoic acid ($CH_3CHClCH_2CO_2H$) is 4.05. What percentage is dissociated in a 1.0 M solution? Do you expect the pK_a of butanoic acid to be greater than or less than the pK_a of 3-chlorobutanoic acid? Why?
7. The pK_a of the ethylammonium ion ($C_2H_5NH_3^+$) is 10.64. What percentage of ethylamine is ionized in a 1.00 M solution of ethylamine?

8. The pK_a of Cl_3CCO_2H is 0.64. What is the pH of a 0.580 M solution? What percentage of the Cl_3CCO_2H is dissociated?
9. The pH of a 0.150 M solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is 2.70. What is the pK_b of the conjugate base, aniline ($C_6H_5NH_2$)? Do you expect the pK_b of $(CH_3)_2CHNH_2$ to be greater than or less than the pK_b of $C_6H_5NH_2$? Why?
10. What is the pH of a 0.620 M solution of $CH_3NH_3^+Br^-$ if the pK_b of CH_3NH_2 is 10.62?
11. The pK_b of 4-hydroxypyridine is 10.80 at 25°C. What is the pH of a 0.0250 M solution?



12. The pK_a values of formic acid and the methylammonium ion are 3.75 and 10.62, respectively. Calculate K for the following reaction:
13. $HCO_2^-(aq) + CH_3NH_3^+(aq) \rightleftharpoons HCO_2H(aq) + CH_3NH_2(aq)$
14. The pK_a values of butanoic acid and the ammonium ion are 4.82 and 9.24, respectively. Calculate K for the following reaction:
15. $CH_3CH_2CH_2CO_2^-(aq) + NH_4^+(aq) \rightleftharpoons CH_3CH_2CH_2CO_2H(aq) + NH_3(aq)$
16. Use the information in Table 16.2 "Values of " to calculate the pH of a 0.0968 M solution of calcium formate.
17. Calculate the pH of a 0.24 M solution of sodium lactate. The pK_a of lactic acid is 3.86.
18. Use the information in Table 16.3 "Values of " to determine the pH of a solution prepared by dissolving 750.0 mg of methylammonium chloride ($CH_3NH_3^+Cl^-$) in enough water to make 150.0 mL of solution.
19. Use the information in Table 16.2 "Values of " to determine the pH of a solution prepared by dissolving 855 mg of sodium nitrite ($NaNO_2$) in enough water to make 100.0 mL of solution.

ANSWERS

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.

- 7.
- 8.
9. $pK_b = 9.43$; $(CH_3)_2CHNH_2$ will be a stronger base and have a lower pK_b ; aniline is a weaker base because the lone pair on the nitrogen atom can be delocalized on the aromatic ring.
- 10.
- 11.
- 12.
13. 3.8×10^{-5}
- 14.
- 15.
- 16.
17. 8.18

16.5 Acid–Base Titrations

LEARNING OBJECTIVE

1. To calculate the pH at any point in an acid–base titration.

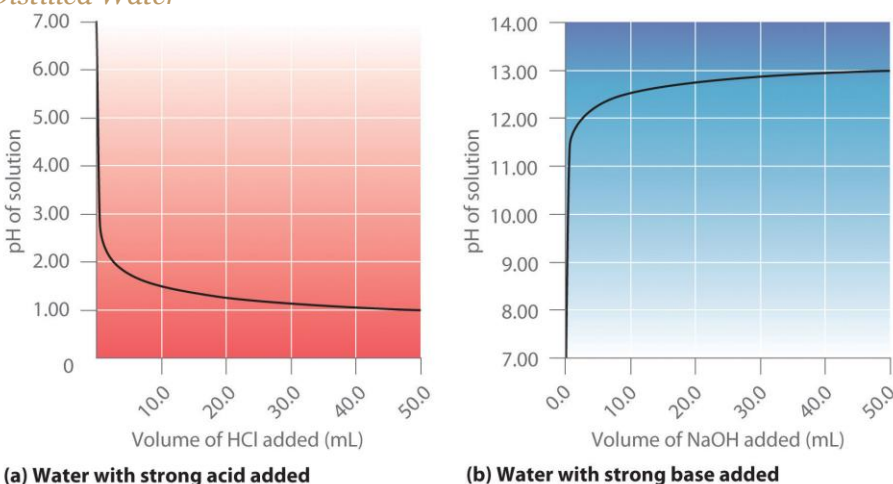
In Chapter 4 "Reactions in Aqueous Solution", you learned that in an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the *titrant*) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the *unknown*). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titration of Strong Acids and Bases

Part (a) of Figure 16.17 "Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water" shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to

50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in part (b) in Figure 16.17 "Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water". As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

Figure 16.17 *Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water*



(a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M NaOH.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H^+ because of the neutralization reaction: $(OH^- + H^+ \rightarrow H_2O)$

(in part (a) in Figure 16.18 "The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid"). Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the H^+ ions originally present have been consumed. (For more information on titrations and the equivalence point, see Chapter 4 "Reactions in Aqueous Solution", Section 4.9 "Quantitative Analysis Using

Titration".) For the titration of a monoprotic strong acid (HCl) with a *monobasic* strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

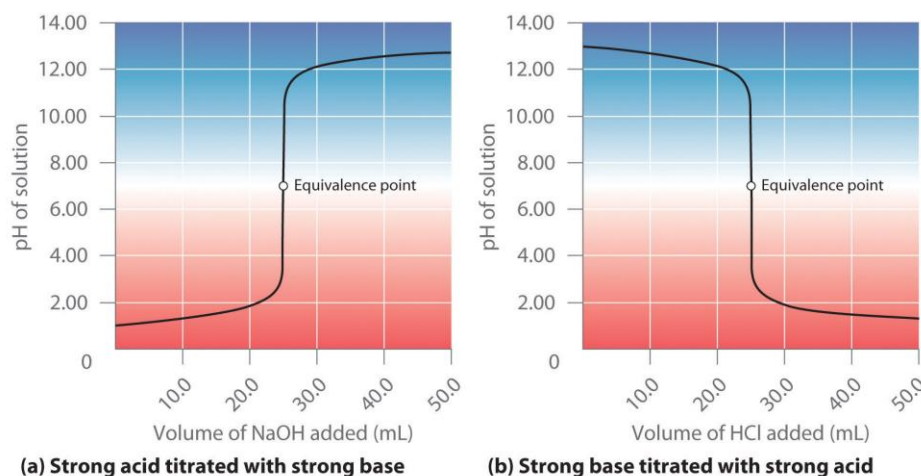
Equation 16.50

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b :

$$\begin{aligned} \text{moles of base} &= (\text{volume})_b (\text{molarity})_b = V_b M_b \\ &= \text{moles of acid} = (\text{volume})_a (\text{molarity})_a = V_a M_a \end{aligned}$$

$$V_b(0.20 \text{ M}) = (0.0500 \text{ L})(0.10 \text{ M}) = 0.025 \text{ L} = 25 \text{ mL}$$

Figure 16.18 The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid



(a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M NaOH, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more.

At the equivalence point (when 25.0 mL of NaOH solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more NaOH produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M NaOH.

As shown in part (b) in Figure 16.18 "The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid", the titration of 50.0 mL of a 0.10 M solution of NaOH with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in part (a) in Figure 16.18 "The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid". The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on *only* the concentrations of the acid and base, *not* their identities.

Note the Pattern

The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

EXAMPLE 11

Calculate the pH of the solution after 24.90 mL of 0.200 M NaOH has been added to 50.00 mL of 0.100 M HCl.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A Calculate the number of millimoles of H^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.

B Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution:

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of H^+ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$(50.00 \text{ mL})(0.100 \text{ mmol HCl/mL}) \\ = 5.00 \text{ mmol HCl} = 5.00 \text{ mmol H}^+$$

The number of millimoles of NaOH added is as follows:

$$24.90 \text{ mL} \times 0.200 \text{ mmol NaOH/mL} = 4.98 \text{ mmol NaOH} = 4.98 \text{ mmol OH}^-$$

Thus H^+ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of OH^- to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess H^+ is $5.00 \text{ mmol} - 4.98 \text{ mmol} = 0.02 \text{ mmol}$ of H^+ .

B The final volume of the solution is $50.00 \text{ mL} + 24.90 \text{ mL} = 74.90 \text{ mL}$, so the final concentration of H^+ is as follows:

$$[\text{H}^+] = 0.02 \text{ mmol H}^+ / 74.90 \text{ mL} = 3 \times 10^{-4} \text{ M}$$

The pH is $-\log[\text{H}^+] = -\log(3 \times 10^{-4}) = 3.5$, which is significantly less than the pH of 7.00 for a neutral solution.

Exercise

Calculate the pH of a solution prepared by adding 40.00 mL of 0.237 M HCl to 75.00 mL of a 0.133 M solution of NaOH.

Answer: 11.6

Titration of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b . As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned in Section 16.4 "Quantitative Aspects of Acid–Base Equilibria", $[\text{H}^+]$ of a solution of a weak acid (HA) is *not* equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, $[\text{H}^+]$ is less than $[\text{HA}]$. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration. Part (a) in Figure 16.19 "The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid" shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure 16.18 "The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid". Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part

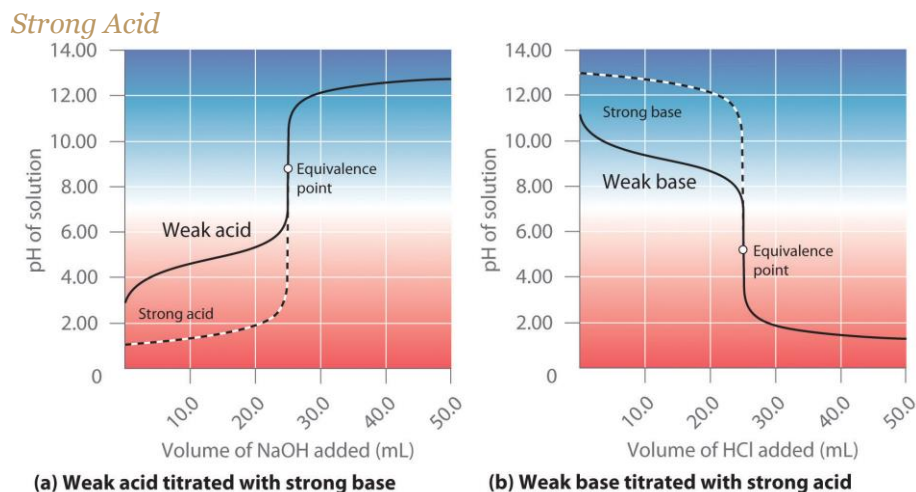
of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

Note the Pattern

The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b .

The titration curve in part (a) in Figure 16.19 "The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid" was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of NaOH. The procedure is illustrated in the following subsection and Example 12 for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$).

Figure 16.19 *The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid*



(a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH_3 , the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then

again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained Section 16.4 "Quantitative Aspects of Acid–Base Equilibria", if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a table of initial concentrations, changes in concentrations, and final concentrations. In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$			
	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.100 - x)$	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = [H^+][CH_3CO_2^-] / [CH_3CO_2H] = (x)(x) / (0.100 - x) \approx x^2 / 0.100 = 1.74 \times 10^{-5}$$

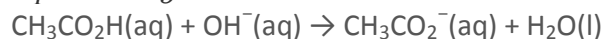
Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}$ M. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure 16.19 "The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid"). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

Equation 16.51



All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the *amounts* of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation (Equation 16.15) to determine $[H^+]$ of the resulting solution.

Step 1: To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of CH_3CO_2H in the original solution and the amount of OH^- in the NaOH solution that was added. The acetic acid solution contained

$$(50.00 \text{ mL}) (0.100 \text{ mmol } CH_3CO_2H / \text{mL}) = 5.00 \text{ mmol } CH_3CO_2H$$

The NaOH solution contained

$$(5.00 \text{ mL}) (0.200 \text{ mmol } NaOH / \text{mL}) = 1.00 \text{ mmol } NaOH$$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:
 $5.00 \text{ mmol } CH_3CO_2H - 1.00 \text{ mmol } OH^- = 4.00 \text{ mmol } CH_3CO_2H$

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following table, which shows the numbers of moles of the various species, *not* their concentrations.

$CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$			
	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	-1.00 mmol	-1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^- , but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of

OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2: To calculate $[\text{H}^+]$ at equilibrium following the addition of NaOH, we must first calculate $[\text{CH}_3\text{CO}_2\text{H}]$ and $[\text{CH}_3\text{CO}_2^-]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$\begin{aligned} \text{final volume}[\text{CH}_3\text{CO}_2\text{H}][\text{CH}_3\text{CO}_2^-] &= 50.00 \text{ mL} + 5.00 \text{ mL} \\ &= 55.00 \text{ mL} = 4.00 \text{ mmol CH}_3\text{CO}_2\text{H} / 55.00 \text{ mL} = 7.27 \times 10^{-2} \text{ M} \\ &\quad .00 \text{ mmol CH}_3\text{CO}_2^- / 55.00 \text{ mL} = 1.82 \times 10^{-2} \text{ M} \end{aligned}$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid

(1.74×10^{-5}), we can use Equation 16.15 to calculate $[\text{H}^+]$ at equilibrium:

$$\begin{aligned} K_a &= [\text{CH}_3\text{CO}_2^-][\text{H}^+][\text{CH}_3\text{CO}_2\text{H}] \\ [\text{H}^+] &= K_a[\text{CH}_3\text{CO}_2\text{H}][\text{CH}_3\text{CO}_2^-] \\ &= (1.74 \times 10^{-5})(7.27 \times 10^{-2} \text{ M}) / 1.82 \times 10^{-2} = 6.95 \times 10^{-5} \text{ M} \end{aligned}$$

Calculating $-\log[\text{H}^+]$ gives $\text{pH} = -\log(6.95 \times 10^{-5}) = 4.158$.

Comparing the titration curves for HCl and acetic acid in part (a) in Figure 16.19 "The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid", we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example 12, we calculate another point for constructing the titration curve of acetic acid.

EXAMPLE 12

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and $\text{CH}_3\text{CO}_2\text{H}$. Determine which species, if either, is present in excess.

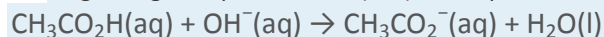
B Tabulate the results showing initial numbers, changes, and final numbers of millimoles.

C If excess acetate is present after the reaction with OH^- , write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.

D Calculate K_b using the relationship $K_w = K_a K_b$ (Equation 16.23). Calculate $[\text{OH}^-]$ and use this to calculate the pH of the solution.

Solution:

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:



The initial numbers of millimoles of OH^- and $\text{CH}_3\text{CO}_2\text{H}$ are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol OH}^- / \text{mL}) = 5.00 \text{ mmol OH}^-$$

$$50.00 \text{ mL}(0.100 \text{ CH}_3\text{CO}_2\text{H} / \text{mL}) = 5.00 \text{ mmol CH}_3\text{CO}_2\text{H}$$

The number of millimoles of OH^- equals the number of millimoles of $\text{CH}_3\text{CO}_2\text{H}$, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{CO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$			
	$[\text{CH}_3\text{CO}_2\text{H}]$	$[\text{OH}^-]$	$[\text{CH}_3\text{CO}_2^-]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	-5.00 mmol	-5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base *with water* to calculate $[\text{H}^+]$ at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[\text{CH}_3\text{CO}_2^-] = 5.00 \text{ mmol CH}_3\text{CO}_2^- / (50.00 + 25.00) \text{ mL} = 6.67 \times 10^{-2} \text{ M}$$

The equilibrium reaction of acetate with water is as follows:



The equilibrium constant for this reaction is $K_b = K_w/K_a$, where K_a is the acid ionization constant of acetic acid. We therefore define x as $[OH^-]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$H_2O(l) + CH_3CO_2^-(aq) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$			
	$[CH_3CO_2^-]$	$[CH_3CO_2H]$	$[OH^-]$
initial	0.0667	0	1.00×10^{-7}
change	$-x$	$+x$	$+x$
final	$(0.0667 - x)$	x	x

D Substituting the expressions for the final values from this table into Equation 16.18,

$$K_b = [CH_3CO_2H][OH^-] / [CH_3CO_2^-] = (x)(x) / (0.0667 - x) \approx x^2 / 0.0667$$

We can obtain K_b by rearranging Equation 16.23 and substituting the known values:

$$K_b = K_w K_a = 1.01 \times 10^{-14} / 1.74 \times 10^{-5} = 5.80 \times 10^{-10} = x^2 / 0.0667$$

which we can solve to get $x = 6.22 \times 10^{-6}$. Thus $[OH^-] = 6.22 \times 10^{-6}$ M, and the pH of the final solution is 8.794 (part (a) in Figure 16.19 "The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid"). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce OH^- .

Exercise

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

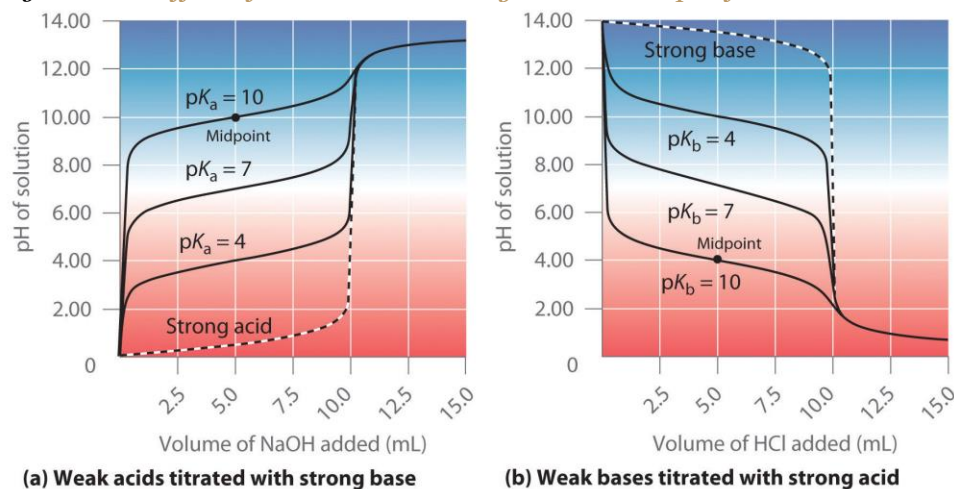
Answer: 9.23

As shown in part (b) in Figure 16.19 "The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid", the titration curve for NH_3 , a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is *less* than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure 16.20 "Effect of Acid or Base Strength on the Shape of Titration Curves" illustrates the shape of titration curves as a function of the pK_a or the pK_b . As the acid or the base being titrated becomes

weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

Figure 16.20 *Effect of Acid or Base Strength on the Shape of Titration Curves*



Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to $pK_a = 10$ and $pK_b = 10$.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in part (a) in Figure 16.20 "Effect of Acid or Base Strength on the Shape of Titration Curves" and part (b) in Figure 16.20 "Effect of Acid or Base Strength on the Shape of Titration Curves" for the two shallowest curves. By definition, at the midpoint of the titration of an acid, $[HA] = [A^-]$. Recall from Equation 16.15 that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides, $-\log K_a = -\log[H_3O^+]$

From the definitions of pK_a and pH , we see that this is identical to

Equation 16.52

$$pK_a = pH$$

Thus *the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid*, as indicated in part (a) in Figure 16.20 "Effect of Acid or Base Strength on the Shape of Titration Curves" for the weakest acid where we see that the midpoint for $pK_a = 10$ occurs at $pH = 10$. Titration methods can therefore be used to determine both the concentration *and* the pK_a (or the pK_b) of a weak acid (or a weak base).

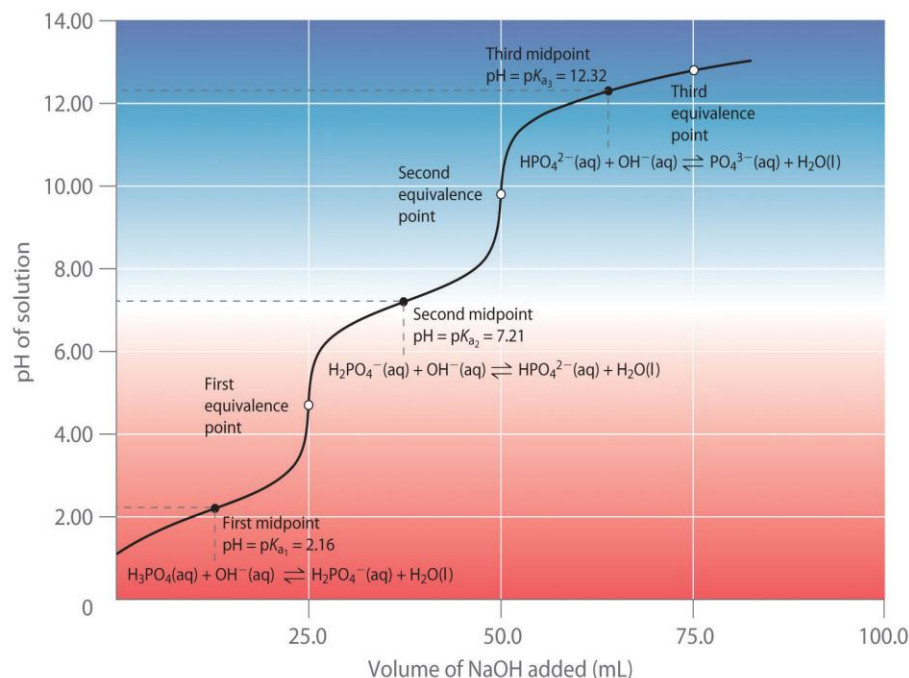
Note the Pattern

The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titration of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the overall titration curve shows well-resolved "steps" corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 16.21 "Titration Curve for Phosphoric Acid (H)" and shows two well-defined steps: the first midpoint corresponds to pK_{a1} , and the second midpoint corresponds to pK_{a2} . Because HPO_4^{2-} is such a weak acid, pK_{a3} has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

Figure 16.21 Titration Curve for Phosphoric Acid (H_3PO_4), a Typical Polyprotic Acid

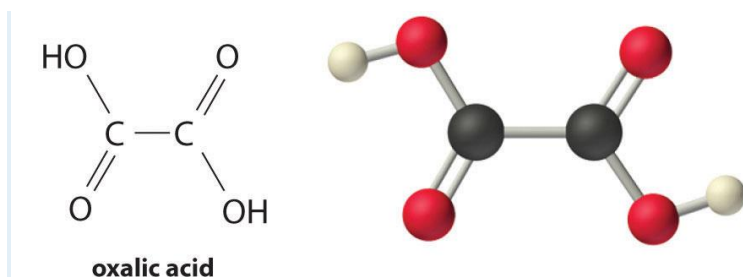


The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each K_a is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at $\text{pH} \approx 4.6$ and H_2PO_4^- at $\text{pH} \approx 9.8$. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at $\text{pH} \approx 13$, is not well defined.

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 16.21 "Titration Curve for Phosphoric Acid (H)". The initial pH is high, but as acid is added, the pH decreases in steps if the successive $\text{p}K_b$ values are well separated. Table 16.4 "Values of $\text{p}K_b$ " lists the ionization constants and $\text{p}K_b$ values for some common polyprotic acids and bases.

EXAMPLE 13

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$), a diprotic acid (abbreviated as H_2ox). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($^-\text{O}_2\text{CCO}_2^-$, abbreviated ox^{2-}).^[1]



Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.

B Calculate the concentrations of all the species in the final solution. Use Equation 16.16 to determine $[H^+]$ and convert this value to pH.

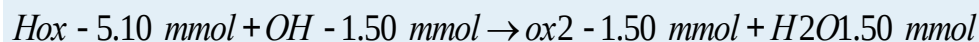
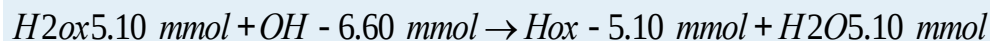
Solution:

A Table 16.4 "Values of p" gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.0 \text{ mL}(0.0510 \text{ mmol } H_2Ox/mL) = 5.10 \text{ mmol } H_2Ox$$

$$55.0 \text{ mL}(0.120 \text{ mmol } NaOH/mL) = 6.60 \text{ mmol } NaOH$$

The strongest acid (H_2Ox) reacts with the base first. This leaves $(6.60 - 5.10) = 1.50$ mmol of OH^- to react with Hox^- , forming ox^{2-} and H_2O . The reactions can be written as follows:



In tabular form,

	H_2Ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	-5.10 mmol	-5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	-1.50 mmol	-1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[\text{H}^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 12:

final volume of solution = $100.0 \text{ mL} + 55.0 \text{ mL} = 155.0 \text{ mL}$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[\text{Hox}^-] = [\text{ox}^{2-}] = \frac{3.60 \text{ mmol Hox}^-}{155.0 \text{ mL}} = 2.32 \times 10^{-2} \text{ M} = 1.50 \text{ mmol ox}^{2-} / 155.0 \text{ mL} = 9.68 \times 10^{-3} \text{ M}$$

We can now calculate $[\text{H}^+]$ at equilibrium using the following equation:

$$K_{a2} = [\text{ox}^{2-}][\text{H}^+][\text{Hox}^-]$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-} ,

$$[\text{H}^+] = \frac{K_{a2}[\text{Hox}^-]}{[\text{ox}^{2-}]} = \frac{(1.6 \times 10^{-4})(2.32 \times 10^{-2})}{9.68 \times 10^{-3}} = 3.7 \times 10^{-4} \text{ M}$$

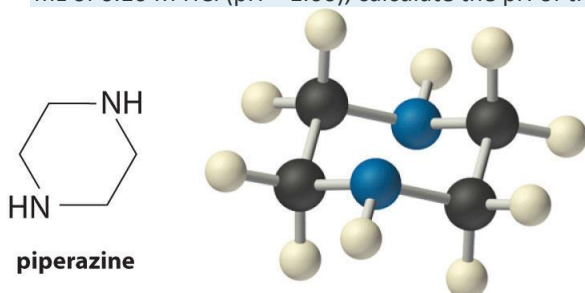
So

$$\text{pH} = -\log[\text{H}^+] = -\log(3.7 \times 10^{-4}) = 3.43$$

This answer makes chemical sense because the pH is between the first and second $\text{p}K_a$ values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than $\text{p}K_{a1}$), but we added only enough to titrate less than half of the second, less acidic proton, with $\text{p}K_{a2}$. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to $\text{p}K_{a2}$.

Exercise

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine ($\text{p}K_{b1} = 4.27$, $\text{p}K_{b2} = 8.67$). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:



where the protonated form is designated by HIn and the conjugate base by In^- . The ionization constant for the deprotonation of indicator HIn is as follows:

Equation 16.53

$$K_{\text{in}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

The $\text{p}K_{\text{in}}$ (its $\text{p}K_{\text{a}}$) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH (Figure 16.22 "Naturally Occurring pH Indicators in Red Cabbage Juice"). In all cases, though, a good indicator must have the following properties:

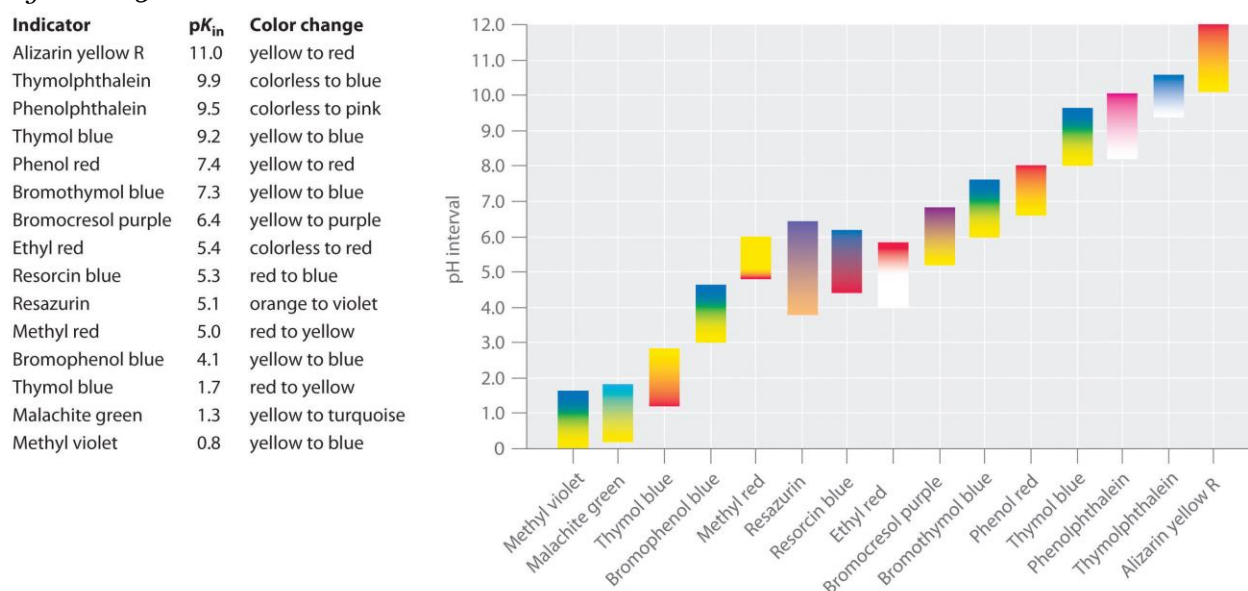
- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a $\text{p}K_{\text{in}}$ that is within one pH unit of the expected pH at the equivalence point of the titration.

Figure 16.22 Naturally Occurring pH Indicators in Red Cabbage Juice

Red cabbage juice contains a mixture of substances whose color depends on the pH. Each test tube contains a solution of red cabbage juice in water, but the pH of the solutions varies from pH = 2.0 (far left) to pH = 11.0 (far right). At pH = 7.0, the solution is blue.

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure 16.23 "Some Common Acid–Base Indicators" shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Figure 16.23 *Some Common Acid–Base Indicators*



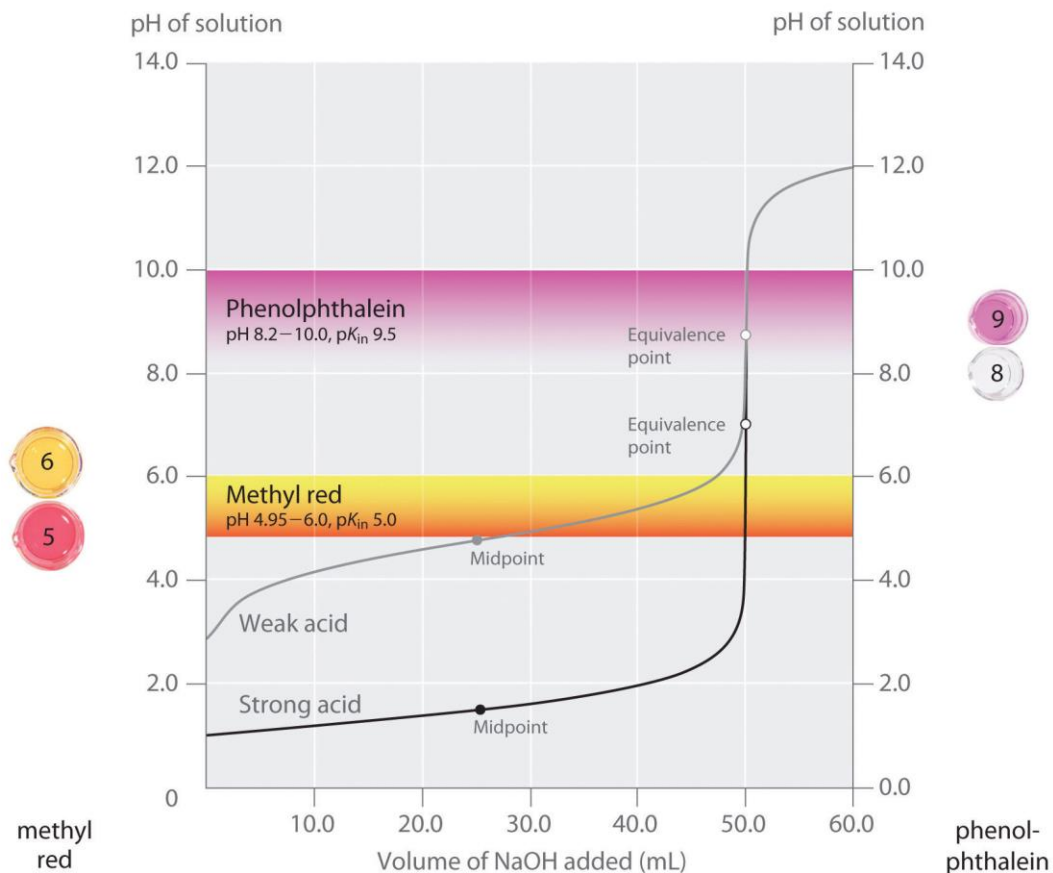
Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes.

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In^- increases, the color of the solution slowly changes from the characteristic color of HIn to that of In^- . As we will see in Section 16.6 "Buffers", the $[In^-]/[HIn]$ ratio changes from 0.1 at a pH one unit *below* pK_{in} to 10 at a pH one unit *above* pK_{in} . Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pK_{in} value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the

wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure 16.24 "Choosing the Correct Indicator for an Acid–Base Titration". This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M NaOH. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of NaOH has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the HCl titration, the phenolphthalein indicator will turn pink when about 50 mL of NaOH has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the *midpoint* of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of NaOH will therefore cause the methyl red indicator to change color, resulting in a huge error.

Figure 16.24 Choosing the Correct Indicator for an Acid–Base Titration



The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M NaOH. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pK_{in} for methyl red (5.0) is very close to the pK_a of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pK_{in} between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with $pK_{in} > 7.0$, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with $pK_{in} < 7.0$, should be used.

The existence of many different indicators with different colors and pK_{in} values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH

electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure 16.25 "pH Paper").

Summary

The shape of a **titration curve**, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The **equivalence point** of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the **midpoint**, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration *and* the pK_a (or the pK_b) of a weak acid (or a weak base). **Acid–base indicators** are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

KEY TAKEAWAY

- Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a , and the pK_b of the system.

CONCEPTUAL PROBLEMS

1. Why is the portion of the titration curve that lies below the equivalence point of a solution of a weak acid displaced upward relative to the titration curve of a strong acid? How are the slopes of the curves different at the equivalence point? Why?
2. Predict whether each solution will be neutral, basic, or acidic at the equivalence point of each titration.
 - a. An aqueous solution of NaOH is titrated with 0.100 M HCl.
 - b. An aqueous solution of ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) is titrated with 0.150 M HNO_3
 - c. An aqueous solution of aniline hydrochloride ($\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$) is titrated with 0.050 M KOH.

3. The pK_a values of phenol red, bromophenol blue, and phenolphthalein are 7.4, 4.1, and 9.5, respectively. Which indicator is best suited for each acid–base titration?
- titrating a solution of $Ba(OH)_2$ with 0.100 M HCl
 - titrating a solution of trimethylamine (Me_3N) with 0.150 M HNO_3
 - titrating a solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) with 0.050 M KOH
4. For the titration of any strong acid with any strong base, the pH at the equivalence point is 7.0. Why is this not usually the case in titrations of weak acids or weak bases?
5. Why are the titration curves for a strong acid with a strong base and a weak acid with a strong base identical in shape above the equivalence points but not below?
6. Describe what is occurring on a molecular level during the titration of a weak acid, such as acetic acid, with a strong base, such as NaOH, at the following points along the titration curve. Which of these points corresponds to $pH = pK_a$?
- at the beginning of the titration
 - at the midpoint of the titration
 - at the equivalence point
 - when excess titrant has been added
7. On a molecular level, describe what is happening during the titration of a weak base, such as ammonia, with a strong acid, such as HCl, at the following points along the titration curve. Which of these points corresponds to $pOH = pK_b$?
- at the beginning of the titration
 - at the midpoint of the titration
 - at the equivalence point
 - when excess titrant has been added
8. For the titration of a weak acid with a strong base, use the K_a expression to show that $pH = pK_a$ at the midpoint of the titration.
9. Chemical indicators can be used to monitor pH rapidly and inexpensively. Nevertheless, electronic methods are generally preferred. Why?
10. Why does adding ammonium chloride to a solution of ammonia in water decrease the pH of the solution?

11. Given the equilibrium system $\text{CH}_3\text{CO}_2\text{H}(\text{aq}) \rightleftharpoons \text{CH}_3\text{CO}_2^-(\text{aq}) + \text{H}^+(\text{aq})$, explain what happens to the position of the equilibrium and the pH in each case.
 - a. Dilute HCl is added.
 - b. Dilute NaOH is added.
 - c. Solid sodium acetate is added.
12. Given the equilibrium system $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$, explain what happens to the position of the equilibrium and the pH in each case.
 - a. Dilute HCl is added.
 - b. Dilute NaOH is added.
 - c. Solid $\text{CH}_3\text{NH}_3^+\text{Cl}^-$ is added.

ANSWER

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.
- 7.
- 8.
- 9.
- 10.
11.
 - a. shifts to left; pH decreases
 - b. shifts to right; pH increases
 - c. shifts to left; pH increases
- 12.

NUMERICAL PROBLEMS

1. Calculate the pH of each solution.
 - a. A volume of 25.0 mL of 6.09 M HCl is added to 100.0 mL of distilled water

- b. A volume of 5.0 mL of 2.55 M NaOH is added to 75.0 mL of distilled water.
2. What is the pH of a solution prepared by mixing 50.0 mL of 0.225 M HCl with 100.0 mL of a 0.184 M solution of NaOH?
3. What volume of 0.50 M HCl is needed to completely neutralize 25.00 mL of 0.86 M NaOH?
4. Calculate the final pH when each pair of solutions is mixed.
- a. 100 mL of 0.105 M HCl and 100 mL of 0.115 M sodium acetate
- b. 50 mL of 0.10 M HCl and 100 mL of 0.15 M sodium acetate
- c. 100 mL of 0.109 M acetic acid and 100 mL of 0.118 M NaOH
- d. 100 mL of 0.998 M acetic acid and 50.0 mL of 0.110 M NaOH
5. Calculate the final pH when each pair of solutions is mixed.
- a. 100 mL of 0.983 M HCl and 100 mL of 0.102 M sodium fluoride
- b. 50.0 mL of 0.115 M HCl and 100 mL of 0.109 M sodium fluoride
- c. 100 mL of 0.106 M hydrofluoric acid and 50.0 mL of 0.996 M NaOH
- d. 100 mL of 0.107 M sodium acetate and 50.0 mL of 0.987 M acetic acid
6. Calcium carbonate is a major contributor to the “hardness” of water. The amount of CaCO_3 in a water sample can be determined by titrating the sample with an acid, such as HCl, which produces water and CO_2 . Write a balanced chemical equation for this reaction. Generate a plot of solution pH versus volume of 0.100 M HCl added for the titration of a solution of 250 mg of CaCO_3 in 200.0 mL of water with 0.100 M HCl; assume that the HCl solution is added in 5.00 mL increments. What volume of HCl corresponds to the equivalence point?
7. For a titration of 50.0 mL of 0.288 M NaOH, you would like to prepare a 0.200 M HCl solution. The only HCl solution available to you, however, is 12.0 M.
- a. How would you prepare 500 mL of a 0.200 M HCl solution?
- b. Approximately what volume of your 0.200 M HCl solution is needed to neutralize the NaOH solution?
- c. After completing the titration, you find that your “0.200 M” HCl solution is actually 0.187 M. What was the exact volume of titrant used in the neutralization?
8. While titrating 50.0 mL of a 0.582 M solution of HCl with a solution labeled “0.500 M KOH,” you overshoot the endpoint. To correct the problem, you add 10.00 mL of the HCl solution to your flask and then carefully continue the titration. The total volume of titrant needed for neutralization is 71.9 mL.

- a. What is the actual molarity of your KOH solution?
- b. What volume of titrant was needed to neutralize 50.0 mL of the acid?
9. Complete the following table and generate a titration curve showing the pH versus volume of added base for the titration of 50.0 mL of 0.288 M HCl with 0.321 M NaOH. Clearly indicate the equivalence point.

Base Added (mL)	10.0	30.0	40.0	45.0	50.0	55.0	65.0	75.0
pH								

10. The following data were obtained while titrating 25.0 mL of 0.156 M NaOH with a solution labeled "0.202 M HCl." Plot the pH versus volume of titrant added. Then determine the equivalence point from your graph and calculate the exact concentration of your HCl solution.

Volume of HCl (mL)	5	10	15	20	25	30	35
pH	11.46	11.29	10.98	4.40	2.99	2.70	2.52

11. Fill in the data for the titration of 50.0 mL of 0.241 M formic acid with 0.0982 M KOH. The pK_a of formic acid is 3.75. What is the pH of the solution at the equivalence point?

Volume of Base Added (mL)	0	5	10	15	20	25
pH						

12. Glycine hydrochloride, which contains the fully protonated form of the amino acid glycine, has the following structure:
- a. Given 50.0 mL of solution that is 0.430 M glycine hydrochloride, how many milliliters of 0.150 M KOH are needed to fully deprotonate the carboxylic acid group?
- b. How many additional milliliters of KOH are needed to deprotonate the ammonium group?
- c. What is the pH of the solution at each equivalence point?
- d. How many milliliters of titrant are needed to obtain a solution in which glycine has no net electrical charge? The pH at which a molecule such as glycine has no net charge is its *isoelectric point*. What is the isoelectric point of glycine?
13. What is the pH of a solution prepared by adding 38.2 mL of 0.197 M HCl to 150.0 mL of 0.242 M pyridine? The pK_b of pyridine is 8.77.
14. What is the pH of a solution prepared by adding 40.3 mL of 0.289 M NaOH to 150.0 mL of 0.564 M succinic acid ($\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$)? (For succinic acid, $pK_{a1} = 4.21$ and $pK_{a2} = 5.64$).

ANSWERS

- 1.
- 2.
3. 43 mL
- 4.
- 5.
- 6.
- 7.
- a. dilute 8.33 mL of 12.0 M HCl to 500.0 mL
- b. 72 mL
- c. 77.0 mL
- 8.
- 9.
- 10.
11. pH at equivalence point = 8.28

Volume of Base Added (mL)	0	5	10	15	20	25
pH	2.19	2.38	2.70	2.89	3.04	3.15

[1] Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH, as we shall see in Chapter 17 "Solubility and Complexation Equilibria". As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.

16.6 Buffers

LEARNING OBJECTIVES

1. To understand how adding a common ion affects the position of an acid–base equilibrium.
2. To know how to use the Henderson-Hasselbalch equation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or “buffer,” other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A⁻) or a weak base (B) and its conjugate acid (BH⁺), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H⁺). Le Châtelier's principle can be used to predict the effect on the equilibrium position of the solution.

A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate.

Recall that the dissociation reaction of acetic acid is as follows:

Equation 16.54



and the equilibrium constant expression is as follows:

Equation 16.55

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

Sodium acetate (CH₃CO₂Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na⁺ and CH₃CO₂⁻ ions. If sodium acetate is added to a solution of acetic acid, Le Châtelier's principle predicts that the equilibrium in Equation 16.54 will shift to the left, consuming some of the added CH₃CO₂⁻ and some of the H⁺ ions originally present in solution:



Because Na⁺ is a spectator ion, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which [H⁺] is less than the initial value. Because [H⁺] has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding *any* base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, [H⁺] increases. Once again the equilibrium is temporarily disturbed, but the excess H⁺ ions react with the conjugate base (CH₃CO₂⁻), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower [CH₃CO₂⁻] than before. In both cases, *only the equilibrium composition has*

changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case CH_3CO_2^- , will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is called the common ion effect.

Note the Pattern

Adding a common ion to a system at equilibrium affects the equilibrium composition but not the ionization constant.

EXAMPLE 14

In Section 16.4 "Quantitative Aspects of Acid–Base Equilibria", we calculated that a 0.150 M solution of formic acid at 25°C ($\text{p}K_a = 3.75$) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?

b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, $\text{p}K_a$, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.

B Substitute the expressions for the final concentrations into the expression for K_a . Calculate $[\text{H}^+]$ and the pH of the solution.

C Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

a. **A** Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than

formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:



The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

$\text{HCO}_2\text{H}(aq) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_2^-(aq)$			
	$[\text{HCO}_2\text{H}]$	$[\text{H}^+]$	$[\text{HCO}_2^-]$
initial	0.150	1.00×10^{-7}	0.100
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	x	$(0.100 + x)$

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$K_a = [\text{H}^+][\text{HCO}_2^-] / [\text{HCO}_2\text{H}]$$

$$= (x)(0.100 + x) / 0.150 - x = x(0.100) / 0.150 = 10^{-3.75} = 1.8 \times 10^{-4}$$

Rearranging and solving for x ,

$$x = (1.8 \times 10^{-4}) \times 0.150 / 0.100 = 2.7 \times 10^{-4} = [\text{H}^+]$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover, $K_a C_{\text{HA}} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$, which is greater than 1.0×10^{-6} , so again, our assumption is justified. The final pH is $-\log(2.7 \times 10^{-4}) = 3.57$, compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Châtelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

b. **C** Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$\text{HCO}_2\text{H}(aq) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_2^-(aq)$			
	$[\text{HCO}_2\text{H}]$	$[\text{H}^+]$	$[\text{HCO}_2^-]$

$HCO_2H(aq) \rightleftharpoons H^+(aq) + HCO_2^-(aq)$			
	$[HCO_2H]$	$[H^+]$	$[HCO_2^-]$
initial	0.150	0.200	0
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	$(0.200 + x)$	x

c. To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[HCO_2^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$d. \quad K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]}$$

$$d. \quad = \frac{(0.200 + x)(x)}{0.150 - x} = x(0.200)0.150 = 1.80 \times 10^{-4}$$

e. Rearranging and solving for x ,

$$f. \quad a. \quad x = (1.80 \times 10^{-4})^{1/2} (0.150 M / 0.200 M) = 1.35 \times 10^{-4} = [HCO_2^-]$$

again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$g. \quad a. \quad \text{percent ionization} = \frac{1.35 \times 10^{-4} M}{0.150 M} \times 100 = 0.0900\%$$

h. Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 ($3.45\% / 0.0900\%$). Again, this is consistent with Le Châtelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

Exercise

As you learned in Example 8, a 0.225 M solution of ethylamine ($CH_3CH_2NH_2$, $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

- the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
- the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer:

$$a. \quad 11.16$$

$$b. \quad 1.3\%$$

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

Equation 16.56



If the equilibrium constant for the reaction as written in Equation 16.56 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = 1/K_b = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 16.56 to shift to the left, consuming the added OH^- . As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Châtelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is $pK_a = pK_w - pK_b = 14.0 - 5.0 = 9.0$. Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

Equation 16.57



Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 16.57 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the *pH range* over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 16.26 "Effect of Buffer Concentration on the Capacity of a Buffer", when NaOH is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M NaOH to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of NaOH solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the NaOH solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 14 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \rightleftharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

Equation 16.58

$$K_a = [H^+][A^-] / [HA]$$

This equation can be rearranged as follows:

Equation 16.59

$$[H^+] = K_a [HA] / [A^-]$$

Taking the logarithm of both sides and multiplying both sides by -1 ,

Equation 16.60

$$- \log[H^+] = - \log K_a - \log([HA] / [A^-]) = - \log K_a + \log([A^-] / [HA])$$

Replacing the negative logarithms in Equation 16.60,

Equation 16.61

$$pH = pK_a + \log([A^-] / [HA])$$

or, more generally,

Equation 16.62

$$pH = pK_a + \log([base] / [acid])$$

Equation 16.61 and Equation 16.62 are both forms of the Henderson-Hasselbalch equation, named after the two early-20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch equation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch equation is easily interpreted without the need for calculations:

1. **[base] = [acid]**. Under these conditions, $[\text{base}]/[\text{acid}] = 1$ in Equation 16.62. Because $\log 1 = 0$, $\text{pH} = \text{p}K_a$, *regardless of the actual concentrations of the acid and base*. Recall from Section 16.5 "Acid–Base Titrations" that this corresponds to the midpoint in the titration of a weak acid or a weak base.
2. **[base]/[acid] = 10**. In Equation 16.62, because $\log 10 = 1$, $\text{pH} = \text{p}K_a + 1$.
3. **[base]/[acid] = 100**. In Equation 16.62, because $\log 100 = 2$, $\text{pH} = \text{p}K_a + 2$.

Each time we increase the $[\text{base}]/[\text{acid}]$ ratio by 10, the pH of the solution increases by 1 pH unit.

Conversely, if the $[\text{base}]/[\text{acid}]$ ratio is 0.1, then $\text{pH} = \text{p}K_a - 1$. Each additional factor-of-10 decrease in the $[\text{base}]/[\text{acid}]$ ratio causes the pH to decrease by 1 pH unit.

Note the Pattern

If $[\text{base}] = [\text{acid}]$ for a buffer, then $\text{pH} = \text{p}K_a$. Changing this ratio by a factor of 10 either way changes the pH by ± 1 unit.

EXAMPLE 15

What is the pH of a solution that contains

- a. 0.135 M HCO_2H and 0.215 M HCO_2Na ? (The $\text{p}K_a$ of formic acid is 3.75.)
- b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na ?
- c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The $\text{p}K_b$ of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and $\text{p}K_a$; concentration of base, conjugate acid, and $\text{p}K_b$

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch equation (Equation 16.61 or Equation 16.62) to calculate the pH.

Solution:

a. According to the Henderson-Hasselbalch equation, the pH of a solution that contains both a weak acid and its conjugate base is $pH = pK_a + \log([A^-]/[HA])$. Inserting the given values into the equation,

$$pH = 3.75 + \log(0.2150.135) = 3.75 + \log 1.593 = 3.95$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

b. This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch equation,

$$pH = 3.75 + \log(0.02150.0135) = 3.75 + \log 1.593 = 3.95$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends *only* on the *ratio* of the concentrations of the conjugate base and the acid, *not* on the magnitude of the concentrations. Because the $[A^-]/[HA]$ ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

c. In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy⁺). We will therefore use Equation 16.62, the more general form of the Henderson-Hasselbalch equation, in which “base” and “acid” refer to the appropriate species of the conjugate acid–base pair. We are given $[base] = [Py] = 0.119$ M and $[acid] = [HPy^+] = 0.234$ M. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related: $pK_a + pK_b = pK_w$. Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch equation,

$$pH = pK_a + \log([base]/[acid]) = 5.23 + \log(0.119/0.234) = 5.23 - 0.294 = 4.94$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Exercise

What is the pH of a solution that contains

- 0.333 M benzoic acid and 0.252 M sodium benzoate?
- 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer:

a. 4.08

b. 9.68

The Henderson-Hasselbalch equation can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 16.

EXAMPLE 16

The buffer solution in Example 15 contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?

b. What is the final pH if 5.00 mL of 1.00 M NaOH are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 14. Then calculate the amount of acid or base added.

B Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch equation (Equation 16.62) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

a. **A** We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100 \text{ mL}(0.135 \text{ mmol } \text{HCO}_2\text{H/mL}) = 13.5 \text{ mmol } \text{HCO}_2\text{H}$$

$$100 \text{ mL}(0.215 \text{ mmol } \text{HCO}_2^-/\text{mL}) = 21.5 \text{ mmol } \text{HCO}_2^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00 \text{ mL}(1.00 \text{ mmol } \text{H}^+/\text{mL}) = 5.00 \text{ mmol } \text{H}^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:



	[HCO ₂ ⁻]	[H ⁺]	[HCO ₂ H]
initial	21.5 mmol	5.00 mmol	13.5 mmol
change	-5.00 mmol	-5.00 mmol	+5.00 mmol
final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H⁺ in solution is given as “~0 mmol.” For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final [H⁺] and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 14 or the Henderson–Hasselbalch equation. Because we have performed *many* equilibrium calculations in this chapter, we’ll take the latter approach. The Henderson–Hasselbalch equation requires the concentrations of HCO₂⁻ and HCO₂H, which can be calculated using the number of millimoles (*n*) of each and the total volume (*V_T*). Substituting these values into the Henderson–Hasselbalch equation,

$$pH = pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right)$$

$$= pK_a + \log\left(\frac{nHCO_2^- / V_T}{nHCO_2H / V_T}\right) = pK_a + \log\left(\frac{nHCO_2^-}{nHCO_2H}\right)$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$pH = pK_a + \log\left(\frac{nHCO_2^-}{nHCO_2H}\right)$$

$$= 3.75 + \log\left(\frac{16.5 \text{ mmol}}{18.5 \text{ mmol}}\right) = 3.75 - 0.050 = 3.70$$

Once again, this result makes sense on two levels. First, the addition of HCl has decreased the pH from 3.95, as expected. Second, the ratio of HCO₂⁻ to HCO₂H is slightly less than 1, so the pH should be between the *pK_a* and *pK_a – 1*.

b. **A** The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO₂H and 21.5 mmol of HCO₂⁻. The number of millimoles of OH⁻ in 5.00 mL of 1.00 M NaOH is as follows:

$$5.00 \text{ mL}(1.00 \text{ mmol OH}^- / \text{mL}) = 5.00 \text{ mmol OH}^-$$

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.



	[HCO ₂ H]	[OH ⁻]	[HCO ₂ ⁻]
initial	13.5 mmol	5.00 mmol	21.5 mmol
change	-5.00 mmol	-5.00 mmol	+5.00 mmol
final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH⁻ in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO₂⁻ and HCO₂H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$pH = pK_a + \log\left(\frac{nHCO_2^-}{nHCO_2H}\right) = 3.75 + \log\left(\frac{26.5 \text{ mmol}}{8.5 \text{ mmol}}\right) = 3.75 + 0.494 = 4.24$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO₂⁻/HCO₂H ratio between 1 and 10.

Exercise

The buffer solution from Example 15 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

- What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
- What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer:

- 5.30
- 4.42

Note the Pattern

Only the *amounts* (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch equation, *not* their concentrations.

Note the Pattern

The most effective buffers contain equal concentrations of an acid and its conjugate base.

The results obtained in Example 16 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or NaOH solution to 100 mL of an *unbuffered* solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would

lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M NaOH would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH. A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 16.27

"Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid" for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of CH_3CO_2^- to $\text{CH}_3\text{CO}_2\text{H}$ from 1:1 reduces the buffer capacity of the solution.

The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $\text{pH} = \text{pK}_a \pm 1$).

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5 "Acid–Base Titrations". Consider the schematic titration curve of a weak acid with a strong base shown in Figure 16.28 "The Relationship between Titration Curves and Buffers". As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a , which is why buffer solutions usually have a pH that is within ± 1 pH units of the pK_a of the acid component of the buffer.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a . In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b . However, we can calculate either K_a or K_b from the other because they are related by K_w .

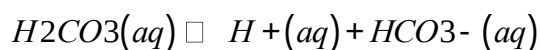
Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $\text{CO}_2/\text{HCO}_3^-$ system, which dominates the buffering action of blood plasma.

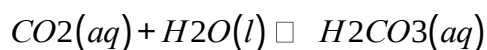
The acid–base equilibrium in the $\text{CO}_2/\text{HCO}_3^-$ buffer system is usually written as follows:

Equation 16.63



with $K_a = 4.5 \times 10^{-7}$ and $\text{p}K_a = 6.35$ at 25°C . In fact, Equation 16.63 is a grossly oversimplified version of the $\text{CO}_2/\text{HCO}_3^-$ system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3 . Thus Equation 16.63 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C . As shown in Equation 16.64, CO_2 is in equilibrium with H_2CO_3 , but the equilibrium lies far to the left, with an $\text{H}_2\text{CO}_3/\text{CO}_2$ ratio less than 0.01 under most conditions:

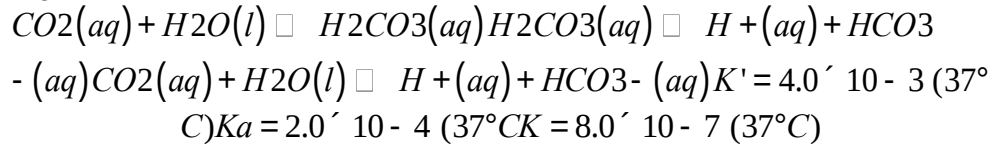
Equation 16.64



with $K' = 4.0 \times 10^{-3}$ at 37°C . The true $\text{p}K_a$ of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4} , which makes it a much stronger acid than Equation 16.63 suggests.

Adding Equation 16.63 and Equation 16.64 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

Equation 16.65



The K value for the reaction in Equation 16.65 is the product of the *true* ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

Equation 16.66

$K = [H^+][HCO_3^-] / [CO_2] = 8.0 \times 10^{-7}$ The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law, $[CO_2] = kPCO_2$, where k is the Henry's law constant for CO_2 , which is $3.0 \times 10^{-5} \text{ M/mmHg}$ at $37^\circ C$. (For more information about Henry's law, see Chapter 13 "Solutions", Section 13.4 "Effects of Temperature and Pressure on Solubility".) Substituting this expression for $[CO_2]$ in Equation 16.66,

Equation 16.67

$$K = [H^+][HCO_3^-] / (3.0 \times 10^{-5} \text{ M/mmHg})(PCO_2)$$

where PCO_2 is in mmHg. Taking the negative logarithm of both sides and rearranging,

Equation 16.68

$$pH = 6.10 + \log [HCO_3^-] / (3.0 \times 10^{-5} \text{ M/mmHg})(PCO_2)$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 16.29 "Buffering in Blood: pH versus $[HCO_3^-]$ " plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of PCO_2 , with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of PCO_2 , indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines.

According to Equation 16.65, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2 . Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in PCO_2 . Because the change in $[HCO_3^-] / PCO_2$ is

small, Equation 16.68 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form $[\text{HCO}_3^-]$, but CO_2 is replenished by the body, again limiting the change in both $[\text{HCO}_3^-]/\text{PCO}_2$

and pH. The $\text{CO}_2/\text{HCO}_3^-$ buffer system is an example of an *open* system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower PCO_2 at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[\text{HCO}_3^-]$. The increase in pH and decrease in $[\text{HCO}_3^-]$ in response to the decrease in PCO_2 are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the **common ion effect**. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its **buffer capacity** depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the **Henderson-Hasselbalch equation**, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $\text{CO}_2/\text{HCO}_3^-$ system, which dominates the buffering action of blood plasma.

KEY EQUATIONS

Henderson-Hasselbalch equation

Equation 16.61: $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$

Equation 16.62: $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$

KEY TAKEAWAY

- The common ion effect allows solutions to act as buffers, whose pH can be calculated using the Henderson-Hasselbalch equation.

CONCEPTUAL PROBLEMS

1. Explain why buffers are crucial for the proper functioning of biological systems.
2. What is the role of a buffer in chemistry and biology? Is it correct to say that buffers prevent a change in $[\text{H}_3\text{O}^+]$? Explain your reasoning.
3. Explain why the most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base.
4. Which region of the titration curve of a weak acid or a weak base corresponds to the region of the smallest change in pH per amount of added strong acid or strong base?
5. If you were given a solution of sodium acetate, describe two ways you could convert the solution to a buffer.
6. Why are buffers usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base?
7. The titration curve for a monoprotic acid can be divided into four regions: the starting point, the region around the midpoint of the titration, the equivalence point, and the region after the equivalence point. For which region would you use each approach to describe the behavior of the solution?
 - a. a buffer
 - b. a solution of a salt of a weak base
 - c. a solution of a weak acid
 - d. diluting a strong base
8. Which of the following will produce a buffer solution? Explain your reasoning in each case.
 - a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
 - b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
 - c. mixing 100 mL of 0.1 M hydrofluoric acid and 100 mL of 0.1 M HCl
 - d. mixing 100 mL of 0.1 M hydrofluoric acid and 50 mL of 0.1 M NaOH
 - e. mixing 100 mL of 0.1 M sodium fluoride and 50 mL of 0.1 M NaOH.
9. Which of the following will produce a buffer solution? Explain your reasoning in each case.
 - a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate

- b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
 - c. mixing 100 mL of 0.1 M acetic acid and 100 mL of 0.1 M NaOH
 - d. mixing 100 mL of 0.1 M acetic acid and 50 mL of 0.1 M NaOH
 - e. mixing 100 mL of 0.1 M sodium acetate and 50 mL of 0.1 M acetic acid
10. Use the definition of K_b for a weak base to derive the following expression, which is analogous to the Henderson-Hasselbalch equation but for a weak base (B) rather than a weak acid (HA):
11. $pOH = pK_b - \log([base][acid])$
12. Why do biological systems use overlapping buffer systems to maintain a constant pH?
13. The CO_2/HCO_3^- buffer system of blood has an effective pK_a of approximately 6.1, yet the normal pH of blood is 7.4. Why is CO_2/HCO_3^- an effective buffer when the pK_a is more than 1 unit below the pH of blood? What happens to the pH of blood when the CO_2 pressure increases? when the O_2 pressure increases?
14. Carbon dioxide produced during respiration is converted to carbonic acid (H_2CO_3). The pK_{a1} of carbonic acid is 6.35, and its pK_{a2} is 10.33. Write the equations corresponding to each pK value and predict the equilibrium position for each reaction.

ANSWER

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.
- 7.
- 8.
- 9.
- a. Not a buffer; the HCl completely neutralizes the sodium acetate to give acetic acid and NaCl(aq).
- b. Buffer; the HCl neutralizes only half of the sodium acetate to give a solution containing equal amounts of acetic acid and sodium acetate.
- c. Not a buffer; the NaOH completely neutralizes the acetic acid to give sodium acetate.

- d. Buffer; the NaOH neutralizes only half of the acetic acid to give a solution containing equal amounts of acetic acid and sodium acetate.
- e. Buffer; the solution will contain a 2:1 ratio of sodium acetate and acetic acid.

NUMERICAL PROBLEMS

1. Benzenesulfonic acid ($pK_a = 0.70$) is synthesized by treating benzene with concentrated sulfuric acid. Calculate the following:
 - a. the pH of a 0.286 M solution of benzenesulfonic acid
 - b. the pH after adding enough sodium benzenesulfonate to give a final benzenesulfonate concentration of 0.100 M
2. Phenol has a pK_a of 9.99. Calculate the following:
 - a. the pH of a 0.195 M solution
 - b. the percent increase in the concentration of phenol after adding enough solid sodium phenoxide (the sodium salt of the conjugate base) to give a total phenoxide concentration of 0.100 M
3. Salicylic acid is used in the synthesis of acetylsalicylic acid, or aspirin. One gram dissolves in 460 mL of water to create a saturated solution with a pH of 2.40.
 - a. What is the K_a of salicylic acid?
 - b. What is the final pH of a saturated solution that is also 0.238 M in sodium salicylate?
 - c. What is the final pH if 10.00 mL of 0.100 M HCl are added to 150.0 mL of the buffered solution?
 - d. What is the final pH if 10.00 mL of 0.100 M NaOH are added to 150.0 mL of the buffered solution?
4. An intermediate used in the synthesis of perfumes is valeric acid, also called pentanoic acid. The pK_a of pentanoic acid is 4.84 at 25°C.
 - a. What is the pH of a 0.259 M solution of pentanoic acid?

- b. Sodium pentanoate is added to make a buffered solution. What is the pH of the solution if it is 0.210 M in sodium pentanoate?
- c. What is the final pH if 8.00 mL of 0.100 M HCl are added to 75.0 mL of the buffered solution?
- d. What is the final pH if 8.00 mL of 0.100 M NaOH are added to 75.0 mL of the buffered solution?

ANSWER

- 1.
- 2.
- 3.
- a. 1.35×10^{-3}
- b. 4.03
- c. 3.88
- d. 4.30

16.6 Buffers

LEARNING OBJECTIVES

- 1. To understand how adding a common ion affects the position of an acid–base equilibrium.
- 2. To know how to use the Henderson-Hasselbalch equation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or “buffer,” other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Châtelier's principle can be used to predict the effect on the equilibrium position of the solution.

A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate.

Recall that the dissociation reaction of acetic acid is as follows:

Equation 16.54

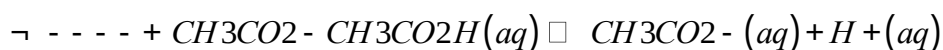


and the equilibrium constant expression is as follows:

Equation 16.55

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Châtelier's principle predicts that the equilibrium in Equation 16.54 will shift to the left, consuming some of the added $CH_3CO_2^-$ and some of the H^+ ions originally present in solution:



Because Na^+ is a spectator ion, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding *any* base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, *only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same*. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is called the common ion effect.

Note the Pattern

Adding a common ion to a system at equilibrium affects the equilibrium composition but not the ionization constant.

EXAMPLE 14

In Section 16.4 "Quantitative Aspects of Acid–Base Equilibria", we calculated that a 0.150 M solution of formic acid at 25°C ($pK_a = 3.75$) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?

b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a , and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.

B Substitute the expressions for the final concentrations into the expression for K_a . Calculate $[H^+]$ and the pH of the solution.

C Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

a. **A** Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:



The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

$\text{HCO}_2\text{H}(aq) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_2^-(aq)$			
	$[\text{HCO}_2\text{H}]$	$[\text{H}^+]$	$[\text{HCO}_2^-]$
initial	0.150	1.00×10^{-7}	0.100
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	x	$(0.100 + x)$

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$K_a = \frac{[\text{H}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

$$= \frac{(x)(0.100 + x)}{0.150 - x} \approx \frac{x(0.100)}{0.150} = 10^{-3.75} = 1.8 \times 10^{-4}$$

Rearranging and solving for x ,

$$x = \frac{(1.8 \times 10^{-4})(0.150)}{0.100} = 2.7 \times 10^{-4} = [\text{H}^+]$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover, $K_a C_{\text{HA}} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$, which is greater than 1.0×10^{-6} , so again, our assumption is justified. The final pH is $-\log(2.7 \times 10^{-4}) = 3.57$, compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Châtelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

b. **C** Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$\text{HCO}_2\text{H}(aq) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_2^-(aq)$			
	$[\text{HCO}_2\text{H}]$	$[\text{H}^+]$	$[\text{HCO}_2^-]$
initial	0.150	0.200	0
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	$(0.200 + x)$	x

c. To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[HCO_2^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = [H^+][HCO_2^-] / [HCO_2H]$$

d.
$$= (0.200 + x)(x) / 0.150 - x =$$

$$x(0.200) / 0.150 = 1.80 \times 10^{-4}$$

e. Rearranging and solving for x ,

a.
$$x = (1.80 \times 10^{-4}) \times 0.150 / 0.200 = 1.35 \times 10^{-4} = [HCO_2^-]$$

f. Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

g. a.
$$\text{percent ionization} = 1.35 \times 10^{-4} / 0.150 \times 100 = 0.0900\%$$

h. Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 ($3.45\% / 0.0900\%$). Again, this is consistent with Le Châtelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

Exercise

As you learned in Example 8, a 0.225 M solution of ethylamine ($CH_3CH_2NH_2$, $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$

b. the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer:

a. 11.16

b. 1.3%

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

Equation 16.56



If the equilibrium constant for the reaction as written in Equation 16.56 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = 1/K_b = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 16.56 to shift to the left, consuming the added OH^- . As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Châtelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the $\text{p}K_b$ of the base is 5.0, the $\text{p}K_a$ of its conjugate acid is $\text{p}K_a = \text{p}K_w - \text{p}K_b = 14.0 - 5.0 = 9.0$. Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

Equation 16.57



Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 16.57 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the *pH range* over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 16.26 "Effect of Buffer Concentration on the Capacity of a Buffer", when NaOH is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M NaOH to 100.0 mL of distilled water results in a very large change

in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of NaOH solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the NaOH solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 14 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \rightleftharpoons H^+ + A^-$,

for which the equilibrium constant expression is as follows:

Equation 16.58

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

This equation can be rearranged as follows:

Equation 16.59

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

Taking the logarithm of both sides and multiplying both sides by -1 ,

Equation 16.60

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) = -\log K_a + \log([A^-][HA])$$

Replacing the negative logarithms in Equation 16.60,

Equation 16.61

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

or, more generally,

Equation 16.62

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

Equation 16.61 and Equation 16.62 are both forms of the Henderson-Hasselbalch equation, named after the two early-20th-century chemists who first noticed that this rearranged version of the equilibrium

constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch equation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch equation is easily interpreted without the need for calculations:

1. **[base] = [acid]**. Under these conditions, $[\text{base}]/[\text{acid}] = 1$ in Equation 16.62. Because $\log 1 = 0$, $\text{pH} = \text{p}K_a$, *regardless of the actual concentrations of the acid and base*. Recall from Section 16.5 "Acid–Base Titrations" that this corresponds to the midpoint in the titration of a weak acid or a weak base.
2. **[base]/[acid] = 10**. In Equation 16.62, because $\log 10 = 1$, $\text{pH} = \text{p}K_a + 1$.
3. **[base]/[acid] = 100**. In Equation 16.62, because $\log 100 = 2$, $\text{pH} = \text{p}K_a + 2$.

Each time we increase the $[\text{base}]/[\text{acid}]$ ratio by 10, the pH of the solution increases by 1 pH unit.

Conversely, if the $[\text{base}]/[\text{acid}]$ ratio is 0.1, then $\text{pH} = \text{p}K_a - 1$. Each additional factor-of-10 decrease in the $[\text{base}]/[\text{acid}]$ ratio causes the pH to decrease by 1 pH unit.

Note the Pattern

If $[\text{base}] = [\text{acid}]$ for a buffer, then $\text{pH} = \text{p}K_a$. Changing this ratio by a factor of 10 either way changes the pH by ± 1 unit.

EXAMPLE 15

What is the pH of a solution that contains

- a. 0.135 M HCO_2H and 0.215 M HCO_2Na ? (The $\text{p}K_a$ of formic acid is 3.75.)
- b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na ?
- c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The $\text{p}K_b$ of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and $\text{p}K_a$; concentration of base, conjugate acid, and $\text{p}K_b$

Asked for: pH

strategy:

Substitute values into either form of the Henderson-Hasselbalch equation (Equation 16.61 or Equation 16.62) to calculate the pH.

Solution:

a. According to the Henderson-Hasselbalch equation, the pH of a solution that contains both a weak acid and its conjugate base is $pH = pK_a + \log([A^-]/[HA])$. Inserting the given values into the equation,

$$pH = 3.75 + \log(0.2150/0.135) = 3.75 + \log 1.593 = 3.95$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

b. This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch equation,

$$pH = 3.75 + \log(0.02150/0.0135) = 3.75 + \log 1.593 = 3.95$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends *only* on the *ratio* of the concentrations of the conjugate base and the acid, *not* on the magnitude of the concentrations. Because the $[A^-]/[HA]$ ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

c. In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy⁺). We will therefore use Equation 16.62, the more general form of the Henderson-Hasselbalch equation, in which “base” and “acid” refer to the appropriate species of the conjugate acid–base pair. We are given $[base] = [Py] = 0.119$ M and $[acid] = [HPy^+] = 0.234$ M. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related: $pK_a + pK_b = pK_w$. Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$= 5.23 + \log(0.119/0.234) = 5.23 - 0.294 = 4.94$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Exercise

What is the pH of a solution that contains

- 0.333 M benzoic acid and 0.252 M sodium benzoate?
- 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer:

a. 4.08

b. 9.68

The Henderson-Hasselbalch equation can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 16.

EXAMPLE 16

The buffer solution in Example 15 contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?

b. What is the final pH if 5.00 mL of 1.00 M NaOH are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 14. Then calculate the amount of acid or base added.

B Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch equation (Equation 16.62) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

a. **A** We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100 \text{ mL}(0.135 \text{ mmol } \text{HCO}_2\text{H/mL}) = 13.5 \text{ mmol } \text{HCO}_2\text{H}$$

$$100 \text{ mL}(0.215 \text{ mmol } \text{HCO}_2^-/\text{mL}) = 21.5 \text{ mmol } \text{HCO}_2^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00 \text{ mL}(1.00 \text{ mmol } \text{H}^+/\text{mL}) = 5.00 \text{ mmol } \text{H}^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:



	[HCO ₂ ⁻]	[H ⁺]	[HCO ₂ H]
initial	21.5 mmol	5.00 mmol	13.5 mmol
change	-5.00 mmol	-5.00 mmol	+5.00 mmol
final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H⁺ in solution is given as “~0 mmol.” For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final [H⁺] and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 14 or the Henderson–Hasselbach equation. Because we have performed *many* equilibrium calculations in this chapter, we’ll take the latter approach. The Henderson–Hasselbalch equation requires the concentrations of HCO₂⁻ and HCO₂H, which can be calculated using the number of millimoles (*n*) of each and the total volume (*V_T*). Substituting these values into the Henderson–Hasselbalch equation,

$$pH = pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) = pK_a + \log\left(\frac{nHCO_2^- / V_T}{nHCO_2H / V_T}\right) = pK_a + \log\left(\frac{nHCO_2^-}{nHCO_2H}\right)$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$pH = pK_a + \log\left(\frac{nHCO_2^-}{nHCO_2H}\right) = 3.75 + \log\left(\frac{16.5 \text{ mmol}}{18.5 \text{ mmol}}\right) = 3.75 - 0.050 = 3.70$$

Once again, this result makes sense on two levels. First, the addition of HCl has decreased the pH from 3.95, as expected. Second, the ratio of HCO₂⁻ to HCO₂H is slightly less than 1, so the pH should be between the *pK_a* and *pK_a – 1*.

b. **A** The procedure for solving this part of the problem is exactly the same as that used in part (a).

We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO₂H and 21.5 mmol of HCO₂⁻. The number of millimoles of OH⁻ in 5.00 mL of 1.00 M NaOH is as follows:

$$5.00 \text{ mL}(1.00 \text{ mmol OH}^- / \text{mL}) = 5.00 \text{ mmol OH}^-$$

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.



	[HCO ₂ H]	[OH ⁻]	[HCO ₂ ⁻]
initial	13.5 mmol	5.00 mmol	21.5 mmol
change	-5.00 mmol	-5.00 mmol	+5.00 mmol
final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH⁻ in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO₂⁻ and HCO₂H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$pH = pK_a + \log(nHCO_2^- / nHCO_2H)$$

$$= 3.75 + \log(26.5 \text{ mmol} / 8.5 \text{ mmol}) = 3.75 + 0.494 = 4.24$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO₂⁻/HCO₂H ratio between 1 and 10.

Exercise

The buffer solution from Example 15 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

- What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
- What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer:

- 5.30
- 4.42

Note the Pattern

Only the *amounts* (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch equation, *not* their concentrations.

Note the Pattern

The most effective buffers contain equal concentrations of an acid and its conjugate base.

The results obtained in Example 16 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or NaOH solution to 100 mL of an *unbuffered* solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would

lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M NaOH would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH. A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 16.27

"Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid" for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of CH_3CO_2^- to $\text{CH}_3\text{CO}_2\text{H}$ from 1:1 reduces the buffer capacity of the solution.

The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $\text{pH} = \text{pK}_a \pm 1$).

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5 "Acid–Base Titrations". Consider the schematic titration curve of a weak acid with a strong base shown in Figure 16.28 "The Relationship between Titration Curves and Buffers". As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a , which is why buffer solutions usually have a pH that is within ± 1 pH units of the pK_a of the acid component of the buffer.

Figure 16.28 The Relationship between Titration Curves and Buffers

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the

weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a . In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b . However, we can calculate either K_a or K_b from the other because they are related by K_w .

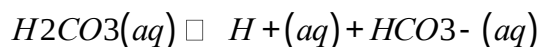
Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $\text{CO}_2/\text{HCO}_3^-$ system, which dominates the buffering action of blood plasma.

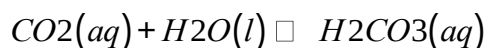
The acid–base equilibrium in the $\text{CO}_2/\text{HCO}_3^-$ buffer system is usually written as follows:

Equation 16.63



with $K_a = 4.5 \times 10^{-7}$ and $\text{p}K_a = 6.35$ at 25°C . In fact, Equation 16.63 is a grossly oversimplified version of the $\text{CO}_2/\text{HCO}_3^-$ system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3 . Thus Equation 16.63 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C . As shown in Equation 16.64, CO_2 is in equilibrium with H_2CO_3 , but the equilibrium lies far to the left, with an $\text{H}_2\text{CO}_3/\text{CO}_2$ ratio less than 0.01 under most conditions:

Equation 16.64



with $K' = 4.0 \times 10^{-3}$ at 37°C . The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4} , which makes it a much stronger acid than Equation 16.63 suggests. Adding Equation 16.63 and Equation 16.64 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

Equation 16.65

$$K_a K = 2.0 \times 10^{-4} \quad (37^\circ\text{C}) \quad K = 8.0 \times 10^{-7} \quad (37^\circ\text{C})$$

The K value for the reaction in Equation 16.65 is the product of the *true* ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $\text{CO}_2(\text{aq})$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

Equation 16.66

$$K = [\text{H}^+][\text{HCO}_3^-] / [\text{CO}_2] = 8.0 \times 10^{-7}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law, $[\text{CO}_2] = k P_{\text{CO}_2}$, where k is the Henry's law constant for CO_2 , which is $3.0 \times 10^{-5} \text{ M/mmHg}$ at 37°C . (For more information about Henry's law, see Chapter 13 "Solutions", Section 13.4 "Effects of Temperature and Pressure on Solubility".) Substituting this expression for $[\text{CO}_2]$ in Equation 16.66,

Equation 16.67

$$K = [\text{H}^+][\text{HCO}_3^-] / (3.0 \times 10^{-5} \text{ M/mmHg})(P_{\text{CO}_2})$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

Equation 16.68

$$\text{pH} = 6.10 + \log[\text{HCO}_3^-] - (3.0 \times 10^{-5} \text{ M/mmHg})(P_{\text{CO}_2})$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[\text{HCO}_3^-]$. Figure 16.29 "Buffering in Blood: pH versus $[\text{HCO}_3^-]$ " plots the relationship between pH and $[\text{HCO}_3^-]$ under physiological conditions for several different values of P_{CO_2} , with

normal pH and $[\text{HCO}_3^-]$ values indicated by the dashed lines.

Only those combinations of pH and $[\text{HCO}_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[\text{HCO}_3^-]$ are indicated by dashed lines.

According to Equation 16.65, adding a strong acid to the $\text{CO}_2/\text{HCO}_3^-$ system causes $[\text{HCO}_3^-]$ to decrease as HCO_3^- is converted to CO_2 . Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in $P\text{CO}_2$. Because the change in $[\text{HCO}_3^-]/P\text{CO}_2$

is small, Equation 16.68 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form $[\text{HCO}_3^-]$, but CO_2 is replenished by the body, again limiting the change in both $[\text{HCO}_3^-]/P\text{CO}_2$

and pH. The $\text{CO}_2/\text{HCO}_3^-$ buffer system is an example of an *open* system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower $P\text{CO}_2$ at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[\text{HCO}_3^-]$. The increase in pH and decrease in $[\text{HCO}_3^-]$ in response to the decrease in $P\text{CO}_2$ are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the **common ion effect**. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its **buffer capacity** depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the **Henderson-Hasselbalch equation**, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $\text{CO}_2/\text{HCO}_3^-$ system, which dominates the buffering action of blood plasma.

KEY EQUATIONS

Henderson-Hasselbalch equation

Equation 16.61: $pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$

Equation 16.62: $pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$

KEY TAKEAWAY

- The common ion effect allows solutions to act as buffers, whose pH can be calculated using the Henderson-Hasselbalch equation.

CONCEPTUAL PROBLEMS

1. Explain why buffers are crucial for the proper functioning of biological systems.
2. What is the role of a buffer in chemistry and biology? Is it correct to say that buffers prevent a change in $[H_3O^+]$? Explain your reasoning.
3. Explain why the most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base.
4. Which region of the titration curve of a weak acid or a weak base corresponds to the region of the smallest change in pH per amount of added strong acid or strong base?
5. If you were given a solution of sodium acetate, describe two ways you could convert the solution to a buffer.
6. Why are buffers usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base?
7. The titration curve for a monoprotic acid can be divided into four regions: the starting point, the region around the midpoint of the titration, the equivalence point, and the region after the equivalence point. For which region would you use each approach to describe the behavior of the solution?
 - a. a buffer
 - b. a solution of a salt of a weak base
 - c. a solution of a weak acid
 - d. diluting a strong base
8. Which of the following will produce a buffer solution? Explain your reasoning in each case.
 - a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
 - b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
 - c. mixing 100 mL of 0.1 M hydrofluoric acid and 100 mL of 0.1 M HCl

- d. mixing 100 mL of 0.1 M hydrofluoric acid and 50 mL of 0.1 M NaOH
 - e. mixing 100 mL of 0.1 M sodium fluoride and 50 mL of 0.1 M NaOH.
9. Which of the following will produce a buffer solution? Explain your reasoning in each case.
- a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
 - b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
 - c. mixing 100 mL of 0.1 M acetic acid and 100 mL of 0.1 M NaOH
 - d. mixing 100 mL of 0.1 M acetic acid and 50 mL of 0.1 M NaOH
 - e. mixing 100 mL of 0.1 M sodium acetate and 50 mL of 0.1 M acetic acid
10. Use the definition of K_b for a weak base to derive the following expression, which is analogous to the Henderson-Hasselbalch equation but for a weak base (B) rather than a weak acid (HA):
11. $pOH = pKb - \log([base][acid])$

Why do biological systems use overlapping buffer systems to maintain a constant pH?

12. The CO_2/HCO_3^- buffer system of blood has an effective pK_a of approximately 6.1, yet the normal pH of blood is 7.4. Why is CO_2/HCO_3^- an effective buffer when the pK_a is more than 1 unit below the pH of blood? What happens to the pH of blood when the CO_2 pressure increases? when the O_2 pressure increases?
13. Carbon dioxide produced during respiration is converted to carbonic acid (H_2CO_3). The pK_{a1} of carbonic acid is 6.35, and its pK_{a2} is 10.33. Write the equations corresponding to each pK value and predict the equilibrium position for each reaction.

ANSWER

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.
- 7.
- 8.
- 9.

- a. Not a buffer; the HCl completely neutralizes the sodium acetate to give acetic acid and NaCl(aq).
 - b. Buffer; the HCl neutralizes only half of the sodium acetate to give a solution containing equal amounts of acetic acid and sodium acetate.
 - c. Not a buffer; the NaOH completely neutralizes the acetic acid to give sodium acetate.
 - d. Buffer; the NaOH neutralizes only half of the acetic acid to give a solution containing equal amounts of acetic acid and sodium acetate.
 - e. Buffer; the solution will contain a 2:1 ratio of sodium acetate and acetic acid.
- 10.
- 11.
- 12.
- 13.

NUMERICAL PROBLEMS

1. Benzenesulfonic acid ($pK_a = 0.70$) is synthesized by treating benzene with concentrated sulfuric acid. Calculate the following:
 - a. the pH of a 0.286 M solution of benzenesulfonic acid
 - b. the pH after adding enough sodium benzenesulfonate to give a final benzenesulfonate concentration of 0.100 M
2. Phenol has a pK_a of 9.99. Calculate the following:
 - a. the pH of a 0.195 M solution
 - b. the percent increase in the concentration of phenol after adding enough solid sodium phenoxide (the sodium salt of the conjugate base) to give a total phenoxide concentration of 0.100 M
3. Salicylic acid is used in the synthesis of acetylsalicylic acid, or aspirin. One gram dissolves in 460 mL of water to create a saturated solution with a pH of 2.40.
 - a. What is the K_a of salicylic acid?
 - b. What is the final pH of a saturated solution that is also 0.238 M in sodium salicylate?
 - c. What is the final pH if 10.00 mL of 0.100 M HCl are added to 150.0 mL of the buffered solution?

- d. What is the final pH if 10.00 mL of 0.100 M NaOH are added to 150.0 mL of the buffered solution?
4. An intermediate used in the synthesis of perfumes is valeric acid, also called pentanoic acid. The pK_a of pentanoic acid is 4.84 at 25°C.
- a. What is the pH of a 0.259 M solution of pentanoic acid?
- b. Sodium pentanoate is added to make a buffered solution. What is the pH of the solution if it is 0.210 M in sodium pentanoate?
- c. What is the final pH if 8.00 mL of 0.100 M HCl are added to 75.0 mL of the buffered solution?
- d. What is the final pH if 8.00 mL of 0.100 M NaOH are added to 75.0 mL of the buffered solution?

ANSWER

1.
2.
3.
a. 1.35×10^{-3}
b. 4.03
c. 3.88
d. 4.30

16.7 End-of-Chapter Material

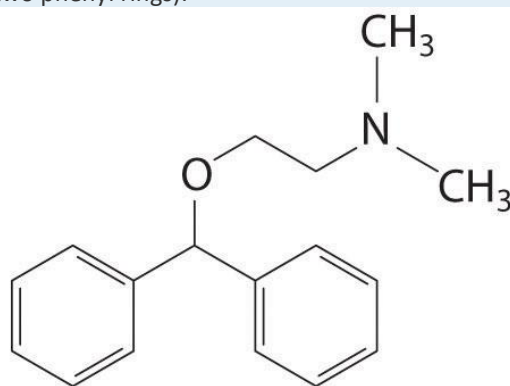
APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. The analytical concentration of lactic acid in blood is generally less than 1.2×10^{-3} M, corresponding to the sum of [lactate] and [lactic acid]. During strenuous exercise, however, oxygen in the muscle tissue is

depleted, and overproduction of lactic acid occurs. This leads to a condition known as lactic acidosis, which is characterized by elevated blood lactic acid levels (approximately 5.0×10^{-3} M). The pK_a of lactic acid is 3.86.

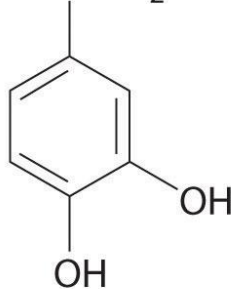
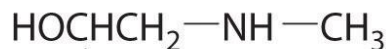
- a. What is the actual lactic acid concentration under normal physiological conditions?
- b. What is the actual lactic acid concentration during lactic acidosis?
2. When the internal temperature of a human reaches 105°F, immediate steps must be taken to prevent the person from having convulsions. At this temperature, K_w is approximately 2.94×10^{-14} .
 - a. Calculate the pK_w and the pH and pOH of a neutral solution at 105°F.
 - b. Is the pH greater than or less than that calculated in Exercise 1 for a neutral solution at a normal body temperature of 98.6°F?
3. ♦ The compound diphenhydramine (DPH) is the active ingredient in a number of over-the-counter antihistamine medications used to treat the runny nose and watery eyes associated with hay fever and other allergies. DPH is a derivative of trimethylamine (one methyl group is replaced by a more complex organic “arm” containing two phenyl rings):



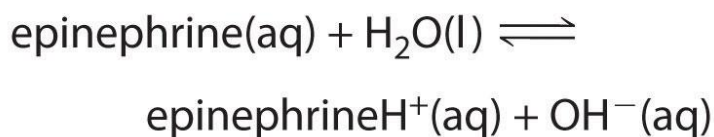
diphenhydramine

The compound is sold as the water-soluble hydrochloride salt (DPH^+Cl^-). A tablet of diphenhydramine hydrochloride contains 25.0 mg of the active ingredient. Calculate the pH of the solution if two tablets are dissolved in 100 mL of water. The pK_b of diphenhydramine is 5.47, and the formula mass of diphenhydramine hydrochloride is 291.81 amu.

4. ♦ Epinephrine, a secondary amine, is used to counter allergic reactions as well as to bring patients out of anesthesia and cardiac arrest. The pK_b of epinephrine is 4.31. What is the percent ionization in a 0.280 M solution? What is the percent ionization after enough solid epinephrine hydrochloride is added to make the final epinephrine H^+ concentration 0.982 M? What is the final pH of the solution?



epinephrine



5. ♦ Fluoroacetic acid is a poison that has been used by ranchers in the western United States. The ranchers place the poison in the carcasses of dead animals to kill coyotes that feed on them; unfortunately, however, eagles and hawks are also killed in the process. How many milliliters of 0.0953 M Ca(OH)_2 are needed to completely neutralize 50.0 mL of 0.262 M fluoroacetic acid solution ($\text{p}K_a = 2.59$)? What is the initial pH of the solution? What is the pH of the solution at the equivalence point?
6. Accidental ingestion of aspirin (acetylsalicylic acid) is probably the most common cause of childhood poisoning. Initially, salicylates stimulate the portion of the brain that controls breathing, resulting in hyperventilation (excessively intense breathing that lowers the PCO_2 in the lungs). Subsequently, a potentially serious rebound effect occurs, as the salicylates are converted to a weak acid, salicylic acid, in the body. Starting with the normal values of $\text{PCO}_2 = 40$ mmHg, $\text{pH} = 7.40$, and $[\text{HCO}_3^-] = 24$ mM, show what happens during the initial phase of respiratory stimulation and the subsequent phase of acid production. Why is the rebound effect dangerous?

ANSWER

- 1.
- 2.
- 3.
- 4.
5. 68.7 mL; 1.60; 7.85

Chapter 17

Solubility and Complexation Equilibria

Although focused exclusively on acid–base equilibria in aqueous solutions, equilibrium concepts can also be applied to many other kinds of reactions that occur in aqueous solution. In this chapter, we describe the equilibria involved in the solubility of ionic compounds and the formation of complex ions.

Solubility equilibria involving ionic compounds are important in fields as diverse as medicine, biology, geology, and industrial chemistry. Carefully controlled precipitation reactions of calcium salts, for example, are used by many organisms to produce structural materials, such as bone and the shells that surround mollusks and bird eggs. In contrast, uncontrolled precipitation reactions of calcium salts are partially or wholly responsible for the formation of scale in coffee makers and boilers, “bathtub rings,” and kidney stones, which can be excruciatingly painful. The principles discussed in this chapter will enable you to understand how these apparently diverse phenomena are related. Solubility equilibria are also responsible for the formation of caves and their striking features, such as stalactites and stalagmites, through a long process involving the repeated dissolution and precipitation of calcium carbonate. In addition to all of these phenomena, by the end of this chapter you will understand why barium sulfate is ideally suited for x-ray imaging of the digestive tract, and why soluble complexes of gadolinium can be used for imaging soft tissue and blood vessels using magnetic resonance imaging (MRI), even though most simple salts of both metals are toxic to humans.

17.1 Determining the Solubility of Ionic Compounds

LEARNING OBJECTIVE

1. To calculate the solubility of an ionic compound from its K_{sp} .

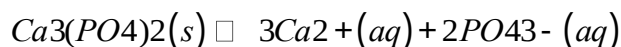
We begin our discussion of solubility and *complexation equilibria*—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of

calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:^[1]

Equation 17.1



The equilibrium constant for the dissolution of a sparingly soluble salt is the solubility product (K_{sp}) of the salt. Because the concentration of a pure solid such as $\text{Ca}_3(\text{PO}_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. (For more information on the equilibrium constant expression, see Chapter 15 "Chemical Equilibrium", Section 15.2 "The Equilibrium Constant".) The equilibrium constant expression for the dissolution of calcium phosphate is therefore

Equation 17.2

$$K[\text{Ca}_3(\text{PO}_4)_2] = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2[\text{Ca}_3(\text{PO}_4)_2] = K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33} , indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C"; they show that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equation 17.1, changes in pH can affect the solubility of a compound, as you will discover in Section 17.4 "Solubility and pH".

Note the Pattern

As with K , the concentration of a pure solid does not appear explicitly in K_{sp} .

Table 17.1 Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K_{sp}	Solid	Color	K_{sp}
Acetates			Iodides		
$\text{Ca}(\text{O}_2\text{CCH}_3)_2 \cdot 3\text{H}_2\text{O}$	white	4×10^{-3}	Hg_2I_2^*	yellow	5.2×10^{-29}
Bromides			PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}	Oxalates		
Hg_2Br_2^*	yellow	6.40×10^{-23}	$\text{Ag}_2\text{C}_2\text{O}_4$	white	5.40×10^{-12}
Carbonates			$\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	white	4.83×10^{-6}
CaCO_3	white	3.36×10^{-9}	PbC_2O_4	white	4.8×10^{-10}
PbCO_3	white	7.40×10^{-14}	Phosphates		
Chlorides			Ag_3PO_4	white	8.89×10^{-17}

Solid	Color	K_{sp}	Solid	Color	K_{sp}
AgCl	white	1.77×10^{-10}	$\text{Sr}_3(\text{PO}_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2^*	white	1.43×10^{-18}	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	pink	9.91×10^{-16}
PbCl_2	white	1.70×10^{-5}	Sulfates		
Chromates			Ag_2SO_4	white	1.20×10^{-5}
CaCrO_4	yellow	7.1×10^{-4}	BaSO_4	white	1.08×10^{-10}
PbCrO_4	yellow	2.8×10^{-13}	PbSO_4	white	2.53×10^{-8}
Fluorides			Sulfides		
BaF_2	white	1.84×10^{-7}	Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}	CdS	yellow	8.0×10^{-27}
Hydroxides			PbS	black	8.0×10^{-28}
$\text{Ca}(\text{OH})_2$	white	5.02×10^{-6}	ZnS	white	1.6×10^{-24}
$\text{Cu}(\text{OH})_2$	pale blue	1×10^{-14}			
$\text{Mn}(\text{OH})_2$	light pink	1.9×10^{-13}			
$\text{Cr}(\text{OH})_3$	gray-green	6.3×10^{-31}			
$\text{Fe}(\text{OH})_3$	rust red	2.79×10^{-39}			
*These contain the Hg_2^{2+} ion.					

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of *mass* of solute per 100 mL of solvent, K_{sp} , like K , is defined in terms of the *molar* concentrations of the component ions.

EXAMPLE 1

Calcium oxalate monohydrate $[\text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}]$, also written as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is a sparingly soluble salt that is the other major component of kidney stones [along with $\text{Ca}_3(\text{PO}_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp} .

Given: solubility in g/100 mL

Asked for: K_{sp}

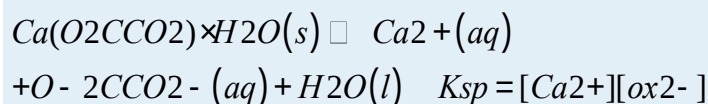
Strategy:

A Write the balanced dissolution equilibrium and the corresponding solubility product expression.

B Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp} .

Solution:

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:



Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine $[\text{Ca}^{2+}]$ and $[\text{ox}^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$7.36 \times 10^{-4} \text{ g} / 146.1 \text{ g/mol} = 5.04 \times 10^{-6} \text{ mol Ca}(\text{O}_2\text{CCO}_2)\cdot\text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$(5.04 \times 10^{-6} \text{ mol Ca}(\text{O}_2\text{CCO}_2)\cdot\text{H}_2\text{O} / 100 \text{ mL}) (1000 \text{ mL} / 1.00 \text{ L}) = 5.04 \times 10^{-5} \text{ mol/L} = 5.04 \times 10^{-5} \text{ M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both $5.04 \times 10^{-5} \text{ M}$. Inserting these values into the solubility product expression,

$$K_{sp} = [\text{Ca}^{2+}][\text{ox}^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

Exercise

One crystalline form of calcium carbonate (CaCO_3) is the mineral sold as “calcite” in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp} .

Answer: 4.5×10^{-9}

Note the Pattern

The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.

Calcite, a structural material for many organisms, is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth?

Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations as we did in Chapter 15 "Chemical Equilibrium", remembering that the concentration of the pure solid is essentially constant.

EXAMPLE 2

We saw that the K_{sp} for $\text{Ca}_3(\text{PO}_4)_2$ is 2.07×10^{-33} at 25°C . Calculate the aqueous solubility of $\text{Ca}_3(\text{PO}_4)_2$ in terms of the following:

- the molarity of ions produced in solution
- the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.

B Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

- a. **A** The dissolution equilibrium for $\text{Ca}_3(\text{PO}_4)_2$ (Equation 17.1) is shown in the following table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $\text{Ca}_3(\text{PO}_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in moles per liter, then the change in $[\text{Ca}^{2+}]$ will be $+3x$, and the change in $[\text{PO}_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$			
	$\text{Ca}_3(\text{PO}_4)_2$	$[\text{Ca}^{2+}]$	$[\text{PO}_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

- b. Although the *amount* of solid $\text{Ca}_3(\text{PO}_4)_2$ changes as some of it dissolves, its *molar concentration* does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

c.
$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 2.07 \times 10^{-33} = (3x)^3 (2x)^2$$

c.
$$2.07 \times 10^{-33} = 108x^5 = x^5 = x$$

- d. This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is $2x$ and $3x$, which means that $[\text{PO}_4^{3-}] = 2.28 \times 10^{-7}$ and $[\text{Ca}^{2+}] = 3.42 \times 10^{-7}$.

- e. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$[(1.14 \times 10^{-7} \text{ mol/L})(100 \text{ mL})(1 \text{ L}/1000 \text{ mL}) \div (310.18 \text{ g Ca}_3(\text{PO}_4)_2 / 1 \text{ mol})] = 3.54 \times 10^{-6} \text{ g Ca}_3(\text{PO}_4)_2$$

Exercise

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C . Calculate the following:

- the molarity of a saturated solution
- the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer:

- $1.28 \times 10^{-4} \text{ M}$
- 3.54 mg

The Ion Product

The ion product (Q) of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (Q) discussed for gaseous equilibria in Chapter 15 "Chemical Equilibrium". Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are *not* necessarily equilibrium concentrations.

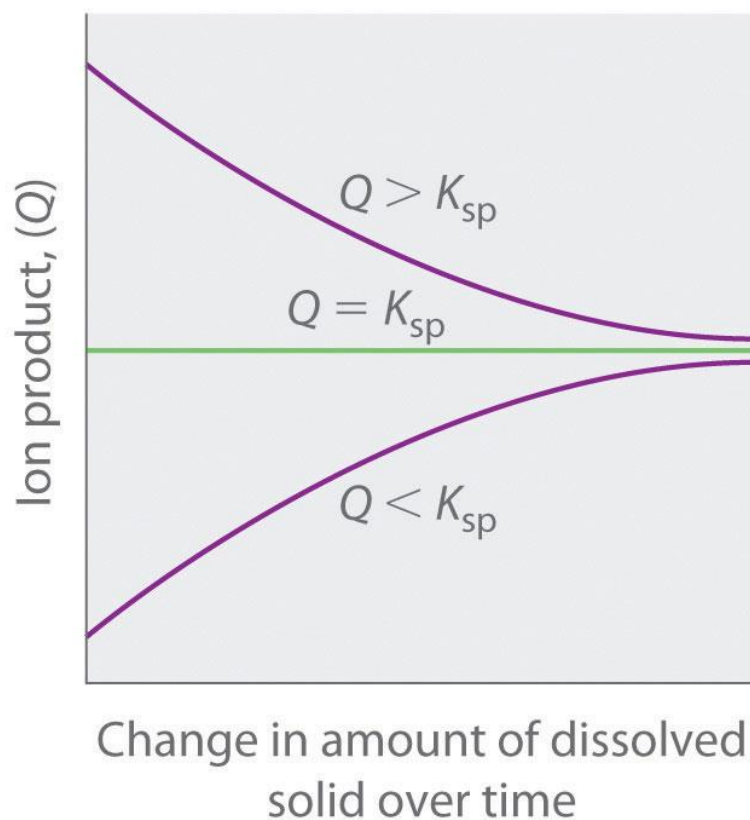
Note the Pattern

The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.

As summarized in Figure 17.1 "The Relationship between ", there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{\text{sp}}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{\text{sp}}$. The solution is saturated and at equilibrium.
- $Q > K_{\text{sp}}$. The solution is supersaturated, and ionic solid will precipitate.

Figure 17.1 *The Relationship between Q and K_{sp}*



If Q is less than K_{sp} , the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp} , the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

EXAMPLE 3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C , so it is ideally suited for this purpose because of its low solubility when a “barium milkshake” is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M BaCl_2 ? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

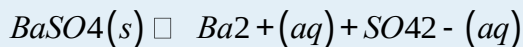
A Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp} .

B Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).

C Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution:

A The only slightly soluble salt that can be formed when these two solutions are mixed is BaSO_4 because NaCl is highly soluble. The equation for the precipitation of BaSO_4 is as follows:



The solubility product expression is as follows:

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product— $Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ —using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs.

The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original

100 mL of BaCl_2 solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles Ba}^{2+} = 100 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)$$

$$(3.2 \times 10^{-4} \text{ mol/L}) = 3.2 \times 10^{-5} \text{ mol Ba}^{2+}$$

$$[\text{Ba}^{2+}] = \frac{3.2 \times 10^{-5} \text{ mol Ba}^{2+}}{110 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)} = 2.9 \times 10^{-4} \text{ M Ba}^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of

Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles SO}_4^{2-} = 10.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)$$

$$(0.0020 \text{ mol/L}) = 2.0 \times 10^{-5} \text{ mol SO}_4^{2-}$$

$$[\text{SO}_4^{2-}] = \frac{2.0 \times 10^{-5} \text{ mol SO}_4^{2-}}{110 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)}$$

$$= 1.8 \times 10^{-4} \text{ M SO}_4^{2-}$$

We can now calculate Q :

$$Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (2.9 \times 10^{-4})(1.8 \times 10^{-4}) = 5.2 \times 10^{-8}$$

C We now compare Q with the K_{sp} . If $Q > K_{sp}$, then BaSO_4 will precipitate, but if $Q < K_{sp}$, it will not.

Because $Q > K_{sp}$, we predict that BaSO_4 will precipitate when the two solutions are mixed. In fact, BaSO_4 will

continue to precipitate until the system reaches equilibrium, which occurs when $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}} = 1.08 \times 10^{-10}$.

Exercise

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11} . If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5} M solution of $\text{Ca}(\text{NO}_3)_2$, will CaF_2 precipitate?

Answer: yes ($Q = 4.7 \times 10^{-11} > K_{\text{sp}}$)

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant.

Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. This dependency is another example of the common ion effect discussed in Chapter 16 "Aqueous Acid–Base Equilibria", Section 16.6 "Buffers": adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Châtelier's principle. As a result, *the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion.*^[2]

Consider, for example, the effect of adding a soluble salt, such as CaCl_2 , to a saturated solution of calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$. We have seen that the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{\text{sp}} = 2.07 \times 10^{-33}$). Thus a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$ in water contains $3 \times (1.14 \times 10^{-7} \text{ M}) = 3.42 \times 10^{-7}$ M Ca^{2+} and $2 \times (1.14 \times 10^{-7} \text{ M}) = 2.28 \times 10^{-7}$ M PO_4^{3-} , according to the stoichiometry shown in Equation 17.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16 "Aqueous Acid–Base Equilibria"). If CaCl_2 is added to a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$, the Ca^{2+} ion concentration will increase such that $[\text{Ca}^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{\text{sp}}$. The only way the system can return to equilibrium is for the reaction in Equation 17.1 to proceed to the left, resulting in precipitation of $\text{Ca}_3(\text{PO}_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{\text{sp}}$.

Note the Pattern

The common ion effect usually decreases the solubility of a sparingly soluble salt.

EXAMPLE 4

Calculate the solubility of calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ in 0.20 M CaCl_2 .

Given: concentration of CaCl_2 solution

Asked for: solubility of $\text{Ca}_3(\text{PO}_4)_2$ in CaCl_2 solution

Strategy:

A Write the balanced equilibrium equation for the dissolution of $\text{Ca}_3(\text{PO}_4)_2$. Tabulate the concentrations of all species produced in solution.

B Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $\text{Ca}_3(\text{PO}_4)_2$.

Solution:

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in moles per liter, then the change in $[\text{Ca}^{2+}]$ is once again $+3x$, and the change in $[\text{PO}_4^{3-}]$ is $+2x$. We can insert these values into the table.

$\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$			
	$\text{Ca}_3(\text{PO}_4)_2$	$[\text{Ca}^{2+}]$	$[\text{PO}_4^{3-}]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (0.20 + 3x)^3 (2x)^2 = 2.07 \times 10^{-33}$$

Because $\text{Ca}_3(\text{PO}_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x \ll 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$K_{sp} = (0.20)^3 (2x)^2 = 2.07 \times 10^{-33} = 6.5 \times 10^{-32} = 2.5 \times 10^{-16} \text{ M}$$

This value is the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in 0.20 M CaCl_2 at 25°C . It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Châtelier's principle. With one exception, this example is identical to Example 2—here the initial $[\text{Ca}^{2+}]$ was 0.20 M rather than 0.

Exercise

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C .

Answer: 2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

Summary

The equilibrium constant for a dissolution reaction, called the **solubility product (K_{sp})**, is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of *mass* of solute per 100 mL of solvent, K_{sp} is defined in terms of the *molar* concentrations of the component ions. In contrast, the **ion product (Q)** describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Châtelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

KEY TAKEAWAY

- The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium.

CONCEPTUAL PROBLEMS

1. Write an expression for K_{sp} for each salt.
 - a. AgI
 - b. CaF_2
 - c. PbCl_2
 - d. Ag_2CrO_4
2. Some species are not represented in a solubility product expression. Why?
3. Describe the differences between Q and K_{sp} .
4. How can an ion product be used to determine whether a solution is saturated?
5. When using K_{sp} to directly compare the solubilities of compounds, why is it important to compare only the K_{sp} values of salts that have the same stoichiometry?
6. Describe the effect of a common ion on the solubility of a salt. Is this effect similar to the common ion effect found in buffers? Explain your answer.
7. Explain why the presence of MgCl_2 decreases the molar solubility of the sparingly soluble salt MgCO_3 .

ANSWERS

1.
 - a. $K_{sp} = [\text{Ag}^+][\text{I}^-]$

- b. $K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$
- c. $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$
- d. $K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$
- 2.
- 3.
- 4.
5. For a 1:1 salt, the molar solubility is simply $\sqrt{K_{sp}}$. For a 2:1 salt, the molar solubility is $\sqrt[3]{K_{sp}/4}$. Consequently, the magnitudes of K_{sp} can be correlated with molar solubility only if the salts have the same stoichiometry.
- 6.
7. Because of the common ion effect. Adding a soluble Mg^{2+} salt increases $[\text{Mg}^{2+}]$ in solution, and Le Châtelier's principle predicts that this will shift the solubility equilibrium of MgCO_3 to the left, decreasing its solubility.

NUMERICAL PROBLEMS

1. Predict the molar solubility of each compound using the K_{sp} values given in Chapter 26 "Appendix B: Solubility-Product Constants (".
 - a. $\text{Cd}(\text{IO}_3)_2$
 - b. AgCN
 - c. HgI_2
2. Predict the molar solubility of each compound using the K_{sp} values given.
 - a. Li_3PO_4 : 2.37×10^{-11}
 - b. $\text{Ca}(\text{IO}_3)_2$: 6.47×10^{-6}
 - c. $\text{Y}(\text{IO}_3)_3$: 1.12×10^{-10}
3. A student prepared 750 mL of a saturated solution of silver sulfate (Ag_2SO_4). How many grams of Ag_2SO_4 does the solution contain? $K_{sp} = 1.20 \times 10^{-5}$.
4. Given the K_{sp} values in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C" and Chapter 26 "Appendix B: Solubility-Product Constants (", predict the molar concentration of each species in a saturated aqueous solution.
 - a. silver bromide
 - b. lead oxalate

- c. iron(II) carbonate
 - d. silver phosphate
 - e. copper(I) cyanide
5. Given the K_{sp} values in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C" and Chapter 26 "Appendix B: Solubility-Product Constants (", predict the molar concentration of each species in a saturated aqueous solution.
- a. copper(I) chloride
 - b. lanthanum(III) iodate
 - c. magnesium phosphate
 - d. silver chromate
 - e. strontium sulfate
6. Silicon dioxide, the most common binary compound of silicon and oxygen, constitutes approximately 60% of Earth's crust. Under certain conditions, this compound can react with water to form silicic acid, which can be written as either H_4SiO_4 or $Si(OH)_4$. Write a balanced chemical equation for the dissolution of SiO_2 in basic solution. Write an equilibrium constant expression for the reaction.
7. The K_{sp} of $Mg(OH)_2$ is 5.61×10^{-12} . If you tried to dissolve 24.0 mg of $Mg(OH)_2$ in 250 mL of water and then filtered the solution and dried the remaining solid, what would you predict to be the mass of the undissolved solid? You discover that only 1.0 mg remains undissolved. Explain the difference between your expected value and the actual value.
8. The K_{sp} of lithium carbonate is 8.15×10^{-4} . If 2.34 g of the salt is stirred with 500 mL of water and any undissolved solid is filtered from the solution and dried, what do you predict to be the mass of the solid? You discover that all of your sample dissolves. Explain the difference between your predicted value and the actual value.
9. You have calculated that 24.6 mg of $BaSO_4$ will dissolve in 1.0 L of water at 25°C. After adding your calculated amount to 1.0 L of water and stirring for several hours, you notice that the solution contains undissolved solid. After carefully filtering the solution and drying the solid, you find that 22.1 mg did not dissolve. According to your measurements, what is the K_{sp} of barium sulfate?
10. In a saturated silver chromate solution, the molar solubility of chromate is 6.54×10^{-5} . What is the K_{sp} ?
11. A saturated lead(II) chloride solution has a chloride concentration of 3.24×10^{-2} mol/L. What is the K_{sp} ?