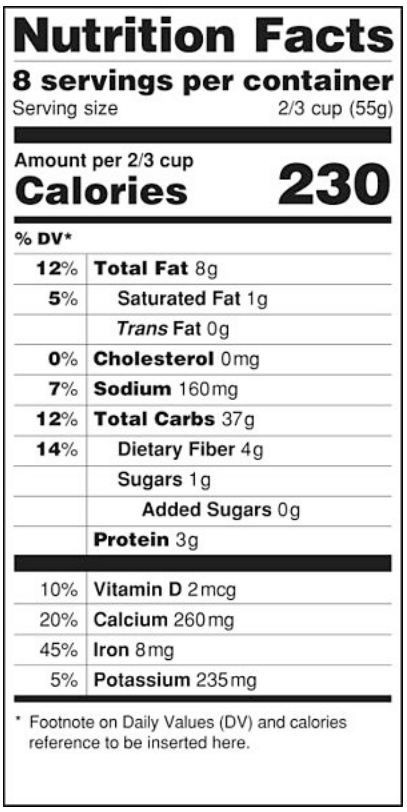


Figure 7.1 "Calories on Food Labels." This label expresses the energy content of the food, but in Calories (which are actually kilocalories).

Example 7.5

Problem

The label in Figure 7.1 "Calories on Food Labels" states that the serving has 38 Cal. How many joules is this?

Solution

We recognize that with a capital C, the Calories unit is actually kilocalories. To determine the number of joules, we convert first from kilocalories to calories (using the definition of the *kilo-* prefix) and then from calories to joules (using the relationship between calories and joules). So:

$$38 \cancel{\text{kcal}} \times \frac{1,000 \cancel{\text{cal}}}{1 \cancel{\text{kcal}}} \times \frac{4.184 \text{ J}}{1 \cancel{\text{cal}}} = 160,000 \text{ J}$$

Test Yourself

A serving of breakfast cereal usually has 110 Cal. How many joules of energy is this?

Answer

460,000 J

In the study of energy, we use the term **system** to describe the part of the universe under study: a beaker, a flask, or a container whose contents are being observed and measured. An **isolated system** is a system that does not allow a transfer of energy or matter into or out of the system. A good approximation of an isolated system is a closed, insulated thermos-type bottle. The fact that the thermos-type bottle is closed keeps matter from moving in or out, and the fact that it is insulated keeps energy from moving in or out.

One of the fundamental ideas about the total energy of an isolated system is that is does not increase or decrease. When this happens to a quantity, we say that the quantity is *conserved*. The statement that the total energy of an isolated system does not change is called the **law of conservation of energy**. As a scientific law, this concept occupies the highest level of understanding we have about the natural universe.

Key Takeaways

- Energy is the ability to do work and uses the unit joule.
- The law of conservation of energy states that the total energy of an isolated system does not increase or decrease.

Exercises

Questions

1. Define *energy*. How is work related to energy?
2. Give two units of energy and indicate which one is preferred.
3. Express the quantity of 422 J in calories.
4. Express the quantity of 3.225 kJ in calories.
5. Express the quantity 55.69 cal in joules.
6. Express the quantity 965.33 kcal in joules.
7. How does a Calorie differ from a calorie?
8. Express the quantity 965.33 Cal in joules.
9. What is the law of conservation of energy?
10. What does the word *conserved* mean as applied to the law of conservation of energy?

Answers

1. Energy is the ability to do work. Work is a form of energy.
3. 101 cal
5. 233.0 J
7. A Calorie is actually a kilocalorie, or 1,000 calories.
9. The total energy of an isolated system does not increase or decrease.

Media Attributions

- "Calories on Food Labels" by U.S. Food and Drug Administration © Public Domain

Stoichiometry Calculations Using Enthalpy

Learning Objectives

1. Perform stoichiometry calculations using energy changes from thermochemical equations.

In Chapter 5 “Stoichiometry and the Mole”, we related quantities of one substance to another in a chemical equation by performing calculations that used the balanced chemical equation; the balanced chemical equation provided equivalences that we used to construct conversion factors. For example, observe the following balanced chemical equation:

$$2\,\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{H_2O}(\ell)$$

In this equation, we recognize the following equivalences:

$$2\ \mathrm{mol\ H_2} \Leftrightarrow 1\ \mathrm{mol\ O_2} \Leftrightarrow 2\ \mathrm{mol\ H_2O}$$

Where ⇔ is the mathematical symbol for “is equivalent to.” In our thermochemical equation, however, we have another quantity — energy change:

$$2\,\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{H_2O}(\ell) \qquad \Delta H = -570\ \mathrm{kJ}$$

This new quantity allows us to add another equivalence to our list:

$$2\ \mathrm{mol\ H_2} \Leftrightarrow 1\ \mathrm{mol\ O_2} \Leftrightarrow 2\ \mathrm{mol\ H_2O} \Leftrightarrow -570\ \mathrm{kJ}$$

That is, we can now add an energy amount to the equivalences — the enthalpy change of a balanced chemical reaction. This equivalence can also be used to construct conversion factors so that we can relate enthalpy change to amounts of substances reacted or produced.

Note that these equivalences address a concern. When an amount of energy is listed for a balanced chemical reaction, what amount(s) of reactants or products does it refer to? The answer is that relates to the number of moles of the substance as indicated by its coefficient in the balanced chemical reaction. Thus, 2 mol of H_2 are related to −570 kJ, while 1 mol of O_2 is related to −570 kJ. This is why the unit on the energy change is kJ, not kJ/mol.

For example, consider the following thermochemical equation:

$$\mathrm{H_2(g)} + \mathrm{Cl_2(g)} \rightarrow 2\,\mathrm{HCl(g)} \qquad \Delta H = -184.6\ \mathrm{kJ}$$

The equivalences for this thermochemical equation are:

$$1 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } Cl_2 \Leftrightarrow 2 \text{ mol HCl} \Leftrightarrow -184.6 \text{ kJ}$$

Suppose we asked how much energy is given off when 8.22 mol of H_2 react. We would construct a conversion factor between the number of moles of H_2 and the energy given off, −184.6 kJ:

$$8.22 \cancel{\text{ mol } H_2} \times \frac{-184.6 \text{ kJ}}{1 \cancel{\text{ mol } H_2}} = -1,520 \text{ kJ}$$

The negative sign means that this much energy is given off.

Example 7.6

Problem

Determine how much energy is given off when 222.4 g of N_2 reacts in the following thermochemical equation:

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \qquad \Delta H = -91.8 \text{ kJ}$$

Solution

The balanced thermochemical equation relates the energy change to moles, not grams, so we first convert the amount of N_2 to moles and then use the thermochemical equation to determine the energy change:

$$222.4 \cancel{\text{ g } N_2} \times \frac{1 \cancel{\text{ mol } N_2}}{28.00 \cancel{\text{ g } N_2}} \times \frac{-91.8 \text{ kJ}}{1 \cancel{\text{ mol } N_2}} = -729 \text{ kJ}$$

Test Yourself

Determine how much heat is given off when 1.00 g of H_2 reacts in the following thermochemical equation:

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \qquad \Delta H = -91.8 \text{ kJ}$$

Answer

−15.1 kJ

Like any stoichiometric quantity, we can start with energy and determine an amount, rather than the other way around.

Example 7.7

Problem

Determine what mass of NO can be made if 558 kJ of energy are supplied, given the following thermochemical equation:

$$\mathrm{N_2(g) + O_2(g) \rightarrow 2\,NO(g)} \qquad \Delta H = 180.6\ \mathrm{kJ}$$

Solution

This time, we start with an amount of energy:

$$558\ \cancel{\mathrm{kJ}} \times \frac{2\ \cancel{\mathrm{mol\ NO}}}{180.6\ \cancel{\mathrm{kJ}}} \times \frac{30.0\ \mathrm{g\ NO}}{1\ \cancel{\mathrm{mol\ NO}}} = 185\ \mathrm{g\ NO}$$

Test Yourself

Given the following equation, how many grams of N_2 will react if 100.0 kJ of energy are supplied?

$$\mathrm{N_2(g) + O_2(g) \rightarrow 2\,NO(g)} \qquad \Delta H = 180.6\ \mathrm{kJ}$$

Answer

15.5 g

Chemistry Is Everywhere: Welding with Chemical Reactions

One very energetic reaction is called the *thermite reaction*. Its classic reactants are aluminum metal and iron(III) oxide; the reaction produces iron metal and aluminum oxide:

$$\mathrm{2\,Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2\,Fe(s)} \qquad \Delta H = -850.2\ \mathrm{kJ}$$

When properly done, the reaction gives off so much energy that the iron product comes off as a *liquid*. (Iron normally melts at 1,536°C.) If carefully directed, the liquid iron can fill spaces between two or more metal parts and, after it quickly cools, can weld the metal parts together.

Thermite reactions are used for this purpose even today. For civilian purposes, they are used to re-weld broken locomotive axles that cannot be easily removed for repair. They are used to weld railroad tracks together. Thermite reactions can also be used to separate thin pieces of metal if, for whatever reason, a torch doesn't work.

Figure 7.2 "Thermite Reaction." A small clay pot contains a thermite mixture. It is reacting at high temperature in the photo and will eventually produce molten metal to join the railroad tracks below it.

Thermite reactions are also used for military purposes. Thermite mixtures are frequently used with additional components as incendiary devices — devices that start fires. Thermite reactions are also useful in disabling enemy weapons: a piece of artillery doesn't work so well when it has a hole melted into its barrel because of a thermite reaction!

Key Takeaways

- The energy change of a chemical reaction can be used in stoichiometry calculations.

Exercises

Questions

1. Write the equivalences that this balanced thermochemical equation implies:

$$\mathrm{PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g) \quad \Delta H = -87.9\ kJ}$$

2. Write the equivalences that this balanced thermochemical equation implies:

$$\mathrm{2\,SO_3(g) \rightarrow 2\,SO_2(g) + O_2(g) \quad \Delta H = 197.9\ kJ}$$

3. How many kilojoules are given off when 17.8 mol of $CH_4(g)$ react in the following equation?

$$\mathrm{CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(\ell) \quad \Delta H = -890.1\ kJ}$$

4. How many kilojoules are absorbed when 0.772 mol of $N_2(g)$ reacts in the following equation?
$$\mathrm{N_2(g) + 2\,NO(g) \rightarrow 2\,N_2O(g) \quad \Delta H = 73.8\ kJ}$$
5. How many kilojoules are absorbed when 23.09 mol of $C_6H_6(\ell)$ are formed in the following equation?
$$\mathrm{6\,C(s) + 3\,H_2(g) \rightarrow C_6H_6(\ell) \quad \Delta H = 49.0\ kJ}$$
6. How many kilojoules are given off when 8.32 mol of Mg react in the following equation?
$$\mathrm{2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s) \quad \Delta H = -1,213\ kJ}$$
7. Glucose ($C_6H_{12}O_6$) is the main fuel metabolized in animal cells. How much energy is given off when 100.0 g of $C_6H_{12}O_6$ react in the following equation?
$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O \quad \Delta H = -2,799\ kJ}$$
8. How much energy is given off when 288 g of Fe are produced, given the following thermochemical equation?
$$\mathrm{2\,Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2\,Fe(s) \quad \Delta H = -850.2\ kJ}$$
9. How much energy is absorbed when 85.2 g of CO_2 are reacted in the following thermochemical equation?
$$\mathrm{2\,CO_2(g) \rightarrow 2\,CO(g) + O_2(g) \quad \Delta H = 566\ kJ}$$
10. How much energy is absorbed when 55.9 g of $Na^+(aq)$ are reacted in the following thermochemical equation?
$$\mathrm{2\,Na^+(aq) + SO_4{}^{2-}(aq) \rightarrow Na_2SO_4(s) \quad \Delta H = 819.8\ kJ}$$
11. $NaHCO_3$ decomposes when exposed to heat. What mass of $NaHCO_3$ is decomposed by 256 kJ, in the following thermochemical equation?
$$\mathrm{2\,NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(\ell) \quad \Delta H = 91.5\ kJ}$$
12. HgO decomposes when exposed to heat. What mass of O_2 can be made with 100.0 kJ, in the following thermochemical equation?
$$\mathrm{2\,HgO(s) \rightarrow 2\,Hg(\ell) + O_2(g) \quad \Delta H = 1816\ kJ}$$
13. What mass of SO_3 is needed to generate 1,566 kJ in the following thermochemical equation?
$$\mathrm{Fe_2O_3(s) + 3\,SO_3(g) \rightarrow Fe_2(SO_4)_3(s) \quad \Delta H = -570.2\ kJ}$$
14. What mass of HBr will be formed when 553 kJ of energy are given off in the following thermochemical equation?
$$\mathrm{H_2(g) + Br_2(\ell) \rightarrow 2\,HBr(g) \quad \Delta H = -72.6\ kJ}$$

Answers

1. 1 mol PCl_3 ⇔ 1 mol Cl_2 ⇔ 1 mol PCl_5 ⇔ −87.9 kJ
3. 15,800 kJ
5. 1,130 kJ
7. 1,554 kJ
9. 548 kJ
11. 470 g
13. 6.60×10^2 g

Media Attributions

- "Thermite Reaction" by Skatebiker © Public Domain

Enthalpy and Chemical Reactions

Learning Objectives

1. Define *enthalpy*.
2. Properly express the enthalpy change of chemical reactions.
3. Explain how enthalpy changes are measured experimentally.

Now that we have shown how energy, work, and heat are related, we are ready to consider energy changes in chemical reactions. A fundamental concept is that *every chemical reaction occurs with a concurrent change in energy*. Now we need to learn how to properly express these energy changes.

Our study of gases in Chapter 6 “Gases” and our definition of work in the section “Work and Heat” indicate that conditions like pressure, volume, and temperature affect the energy content of a system. What we need is a definition of energy that holds when some of these conditions are specified (somewhat similar to our definition of standard temperature and pressure in our study of gases). We define the **enthalpy change** (ΔH) as the heat of a process when pressure is held constant:

$$\Delta H \equiv q \text{ at constant pressure}$$

The letter *H* stands for “enthalpy,” a kind of energy, while the Δ implies a change in the quantity. We will always be interested in the change in *H*, rather than the absolute value of *H* itself.

When a chemical reaction occurs, there is a characteristic change in enthalpy. The enthalpy change for a reaction is typically written after a balanced chemical equation and on the same line. For example, when two moles of hydrogen react with one mole of oxygen to make two moles of water, the characteristic enthalpy change is 570 kJ. We write the equation as:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell) \quad \Delta H = -570 \text{ kJ}$$

A chemical equation that includes an enthalpy change is called a **thermochemical equation**. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

Example 7.8

Problem

Write the thermochemical equation for the reaction of $PCl_3(g)$ with $Cl_2(g)$ to make $PCl_5(g)$, which has an enthalpy change of −88 kJ.

Solution

$$\mathrm{PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g) \quad \Delta H = -88\ kJ}$$

Test Yourself

Write the thermochemical equation for the reaction of $N_2(g)$ with $O_2(g)$ to make $2NO(g)$, which has an enthalpy change of 181 kJ.

Answer

$$\mathrm{N_2(g) + O_2(g) \rightarrow 2\,NO\,(g) \quad \Delta H = 181\ kJ}$$

You may have noticed that the Δ*H* for a chemical reaction may be positive or negative. The number is assumed to be positive if it has no sign; a + sign can be added explicitly to avoid confusion. A chemical reaction that has a positive Δ*H* is said to be **endothermic**, while a chemical reaction that has a negative Δ*H* is said to be **exothermic**.

What does it mean if the Δ*H* of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy change that accompanies the reaction can be diagrammed as in part (a) in Figure 7.3 “Reaction Energy”: the energy of the reactants has some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in part (b) in Figure 7.3 “Reaction Energy.” If the enthalpy change of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

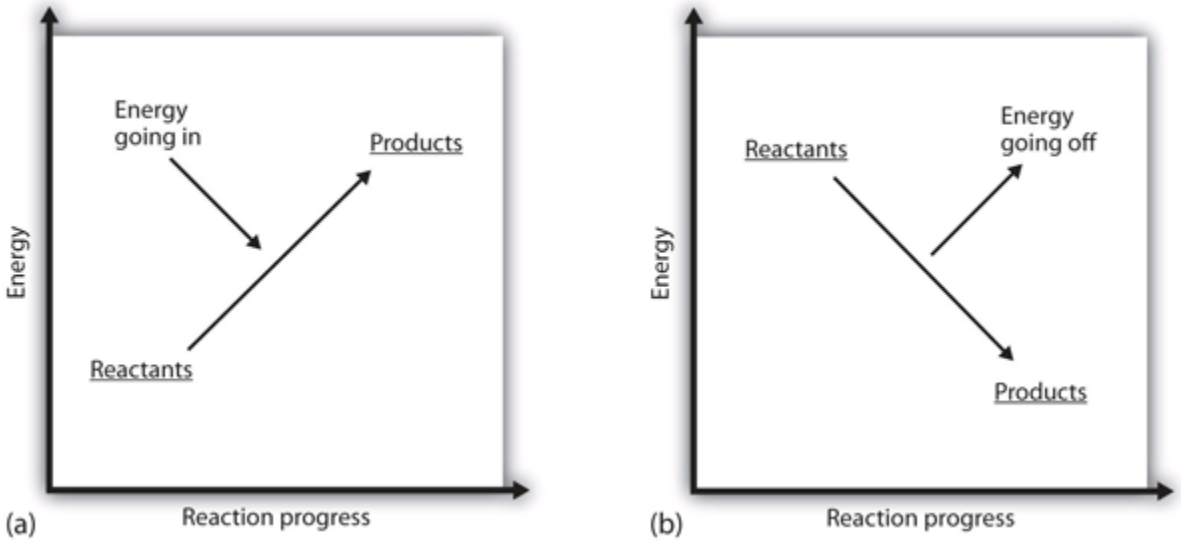


Figure 7.3 "Reaction Energy." Part (a): In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy). Part (b): In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).

Example 7.9

Problem

Consider this thermochemical equation:

$$2\,\mathrm{CO(g)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)} \quad \Delta H = -565\ \mathrm{kJ}$$

Is it exothermic or endothermic? How much energy is given off or absorbed?

Solution

By definition, a chemical reaction that has a negative ΔH is exothermic, meaning that this much energy — in this case, 565 kJ — is given off by the reaction.

Test Yourself

Consider this thermochemical equation:

$$\mathrm{CO_2(g)} + \mathrm{H_2(g)} \rightarrow \mathrm{CO(g)} + \mathrm{H_2O(g)} \quad \Delta H = 42\ \mathrm{kJ}$$

Is it exothermic or endothermic? How much energy is given off or absorbed?

Answer

Endothermic; 42 kJ are absorbed.

How are ΔH values measured experimentally? Actually, ΔH is not measured; q is measured. But the measurements are performed under conditions of constant pressure, so ΔH *is equal to the* q *measured.*

Experimentally, q is measured by taking advantage of the following equation:

$$q = mc\Delta T$$

We premeasure the mass of the chemicals in a system. Then we let the chemical reaction occur and measure the change in temperature (ΔT) of the system. If we know the specific heat of the materials in the system (typically, we do), we can calculate q. That value of q is numerically equal to the ΔH of the process, which we can scale up to a molar scale. The container in which the system resides is typically insulated, so any energy change goes into changing the temperature of the system, rather than being leaked from the system. The container is referred to as a **calorimeter**, and the process of measuring changes in enthalpy is called **calorimetry**.

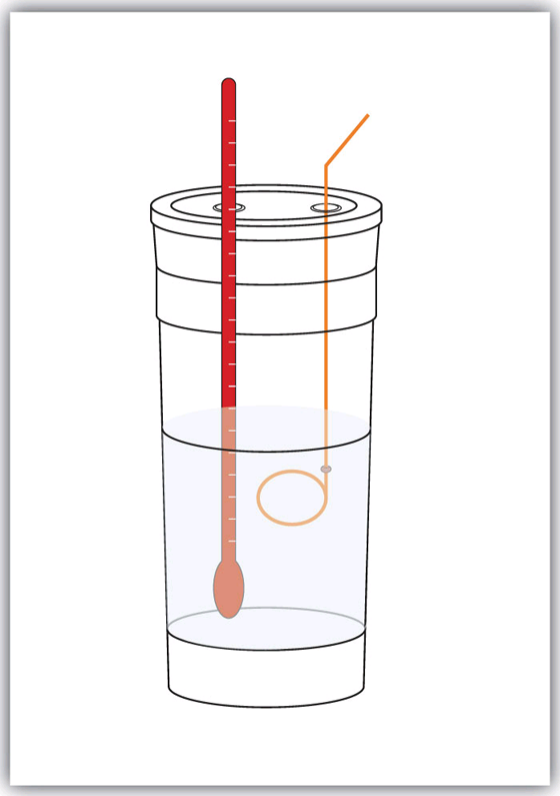


Figure 7.4 "Calorimeter." A simple calorimeter can be constructed from some nested foam coffee cups, a cover, a thermometer, and a stirrer.

For example, suppose 4.0 g of NaOH, or 0.10 mol of NaOH, are dissolved to make 100.0 mL of aqueous solution, while 3.65 g of HCl, or 0.10 mol of HCl, are dissolved to make another 100.0 mL of aqueous solution. The two solutions are mixed in an insulated calorimeter, a thermometer is inserted, and the calorimeter is covered (see Figure 7.4 "Calorimeter" for an example setup). The thermometer measures the temperature change as the following chemical reaction occurs:

$$\mathrm{NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)}$$

An observer notes that the temperature increases from 22.4°C to 29.1°C. Assuming that the heat capacities and densities of the solutions are the same as those of pure water, we now have the

information we need to determine the enthalpy change of the chemical reaction. The total amount of solution is 200.0 mL, and with a density of 1.00 g/mL, we thus have 200.0 g of solution. Using the equation for *q*, we substitute for our experimental measurements and the specific heat of water (see Table 7.1 “Enthalpies of Formation for Various Substances” in “Formation Reactions”):

$$q = (200.0\ \cancel{\text{g}}) \left(4.184 \cdot \frac{\text{J}}{\cancel{\text{g}} \cdot \cancel{^\circ\text{C}}} \right) (6.7\ \cancel{^\circ\text{C}})$$

Solving for *q*, we get:

$$q = 5,600\ \text{J} \equiv \Delta H \text{ for the reaction}$$

The heat *q* is equal to the Δ*H* for the reaction because the chemical reaction occurs at constant pressure. However, the reaction is giving off this amount of energy, so the actual sign on Δ*H* is negative:

$$\Delta H = -5,600\ \text{J for the reaction}$$

Thus, we have the following thermochemical equation for the chemical reaction that occurred in the calorimeter:

$$\frac{1}{10}\text{NaOH(aq)} + \frac{1}{10}\text{HCl(aq)} \rightarrow \frac{1}{10}\text{NaCl(aq)} + \frac{1}{10}\text{H}_2\text{O}(\ell) \quad \Delta H = -5,600\ \text{J}$$

The $\frac{1}{10}$ coefficients are present to remind us that we started with one-tenth of a mole of each reactant, so we make one-tenth of a mole of each product. Typically, however, we report thermochemical equations in terms of moles, not one-tenth of a mole. To scale up to molar quantities, we must multiply the coefficients by 10. However, when we do this, we get 10 times as much energy. Thus, we have:

$$\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(\ell) \quad \Delta H = -56,000\ \text{J}$$

The Δ*H* can be converted into kJ units, so our final thermochemical equation is:

$$\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(\ell) \quad \Delta H = -56\ \text{kJ}$$

We have just taken our experimental data from calorimetry and determined the enthalpy change of a chemical reaction. Similar measurements on other chemical reactions can determine the Δ*H* values of any chemical reaction you want to study.

Example 7.10

Problem

A 100 mL solution of 0.25 mol of Ca^{2+}(aq) was mixed with 0.50 mol of F^-(aq) ions, and CaF_2 was precipitated:

$$\text{Ca}^{2+}(\text{aq}) + 2\,\text{F}^-(\text{aq}) \rightarrow \text{CaF}_2(\text{s})$$

The temperature of the solution increased by 10.5°C. What was the enthalpy change for the chemical reaction? What was the enthalpy change for the production of 1 mol of CaF_2? Assume that the solution has the same density and specific heat as water.

Solution

Because we are given ΔT directly, we can determine the heat of the reaction, which is equal to ΔH:

$$q = (100\ \cancel{g})\left(4.184 \cdot \frac{\text{J}}{\cancel{g} \cdot \cancel{^\circ C}}\right)(10.5\ \cancel{^\circ C})$$

Solving for q, we get:

$$q = 4,400\ \text{J}$$

Therefore, ΔH = −4,400 J.

According to the stoichiometry of the reaction, exactly 0.25 mol of CaF_2 will form, so this quantity of heat is for 0.25 mol. For 1 mol of CaF_2, we need to scale up the heat by a factor of four:

$$q = 4,400\ \text{J} \times 4 = 17,600\ \text{J for 1 mol } \text{CaF}_2$$

On a molar basis, the change in enthalpy is:

$$\Delta H = -17,600\ \text{J} = -17.6\ \text{kJ}$$

Test Yourself

In a calorimeter at constant pressure, 0.10 mol of CH_4(g) and 0.20 mol of O_2(g) are reacted, according to the following equation:

$$\text{CH}_4(\text{g}) + 2\,\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\,\text{H}_2\text{O}(\ell)$$

The reaction warms 750.0 g of H_2O by 28.4°C. What is ΔH for the reaction on a molar scale?

Answer

−891 kJ

Key Takeaways

- Every chemical reaction occurs with a concurrent change in energy.
- The change in enthalpy equals heat at constant pressure.
- Enthalpy changes can be expressed by using thermochemical equations.
- Enthalpy changes are measured by using calorimetry.

Exercises

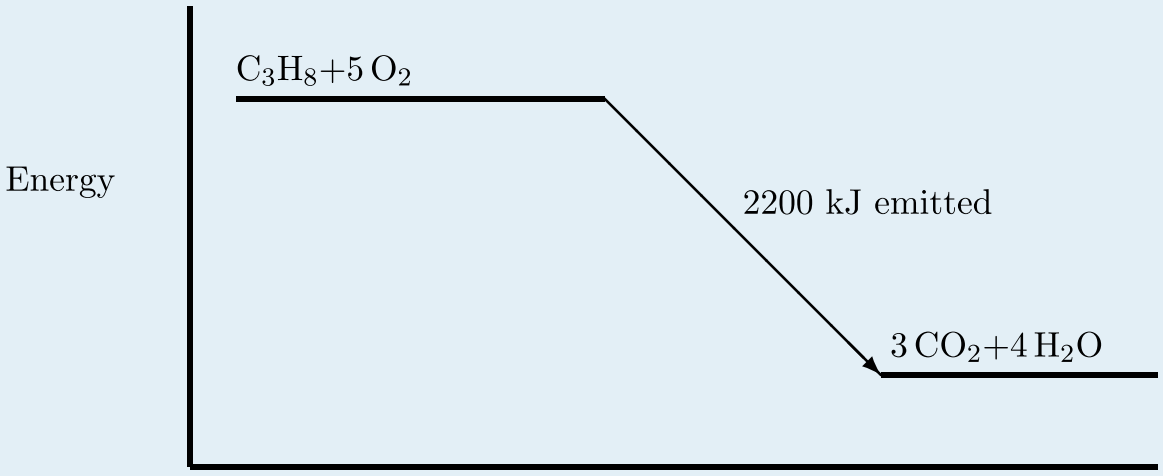
Questions

1. Under what circumstances are q and ΔH the same?

2. Under what circumstances are q and ΔH different?
3. Hydrogen gas and chlorine gas react to make hydrogen chloride gas with an accompanying enthalpy change of −184 kJ. Write a properly balanced thermochemical equation for this process.
4. Propane (C_3H_8) reacts with elemental oxygen gas to produce carbon dioxide and liquid water with an accompanying enthalpy change of −2,220 kJ. Write a properly balanced thermochemical equation for this process.
5. Nitrogen gas reacts with oxygen gas to make NO(g) while absorbing 180 kJ. Write a properly balanced thermochemical equation for this process.
6. Solid sodium reacts with chlorine gas to make solid sodium chloride while giving off 772 kJ. Write a properly balanced thermochemical equation for this process.
7. Hydrogen gas and chlorine gas react to make hydrogen chloride gas with an accompanying enthalpy change of −184 kJ. Is this process endothermic or exothermic?
8. Propane (C_3H_8) reacts with elemental oxygen gas to produce carbon dioxide while giving off 2,220 kJ of energy. Is this process endothermic or exothermic?
9. Nitrogen gas reacts with oxygen gas to make NO(g) while absorbing 180 kJ. Is this process exothermic or endothermic?
10. Sodium metal can react with nitrogen to make sodium azide (NaN_3) with a ΔH of 21.72 kJ. Is this process exothermic or endothermic?
11. Draw an energy level diagram for the chemical reaction in Exercise 8. (See Figure 7.3 “Reaction Energy” for an example.)
12. Draw an energy level diagram for the chemical reaction in Exercise 9. (See Figure 7.3 “Reaction Energy” for an example.)
13. In a 250 mL solution, 0.25 mol of KOH(aq) and 0.25 mol of HNO_3(aq) are combined. The temperature of the solution increases from 22.5°C to 35.9°C. Assume the solution has the same density and heat capacity of water. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?
14. In a 600 mL solution, 0.50 mol of $Ca(OH)_2$(aq) and 0.50 mol of H_2SO_4(aq) are combined. The temperature of the solution increases by 22.3°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis? Assume the solution has the same density and heat capacity of water.
15. To warm 400.0 g of H_2O, 0.050 mol of ethanol (C_2H_5OH) is burned. The water warms from 24.6°C to 65.6°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?
16. To warm 100.0 g of H_2O, 0.066 mol beeswax is burned. The water warms from 21.4°C to 25.5°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?

Answers

1. under conditions of constant pressure
3. $\mathrm{H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)} \quad \Delta H = -184\ \mathrm{kJ}$
5. $\mathrm{N_2(g) + O_2(g) \rightarrow 2\,NO(g)} \quad \Delta H = 180\ \mathrm{kJ}$
7. exothermic
9. endothermic



11.

13. heat of reaction = −14.0 kJ; ΔH = −56.0 kJ/mol of reactants

15. heat of reaction = −68.6 kJ; ΔH = −1,370 kJ/mole of ethanol

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Work and Heat

Learning Objectives

1. Define a type of work in terms of pressure and volume.
2. Define *heat*.
3. Relate the amount of heat to a temperature change.

We have already defined work as a force acting through a distance. It turns out that there are other equivalent definitions of work that are also important in chemistry.

When a certain volume of a gas expands, it works against an external pressure to expand (see Figure 7.5 “Volume versus Pressure”). That is, the gas must perform work. Assuming that the external pressure P_{ext} is constant, the amount of work done by the gas is given by the following equation:

$$w = -P_{\text{ext}} \times \Delta V$$

In which ΔV is the change in volume of the gas. This term is always the final volume minus the initial volume, as shown here:

$$\Delta V = V_{\text{final}} - V_{\text{initial}}$$

ΔV can be positive or negative, depending on whether V_{final} is larger (is expanding) or smaller (is contracting) than V_{initial}. The negative sign in the equation for work is important and implies that as volume expands (ΔV is positive), the gas in the system is *losing* energy as work. On the other hand, if the gas is contracting, ΔV is negative, and the two negative signs make the work positive, so energy is being added to the system.

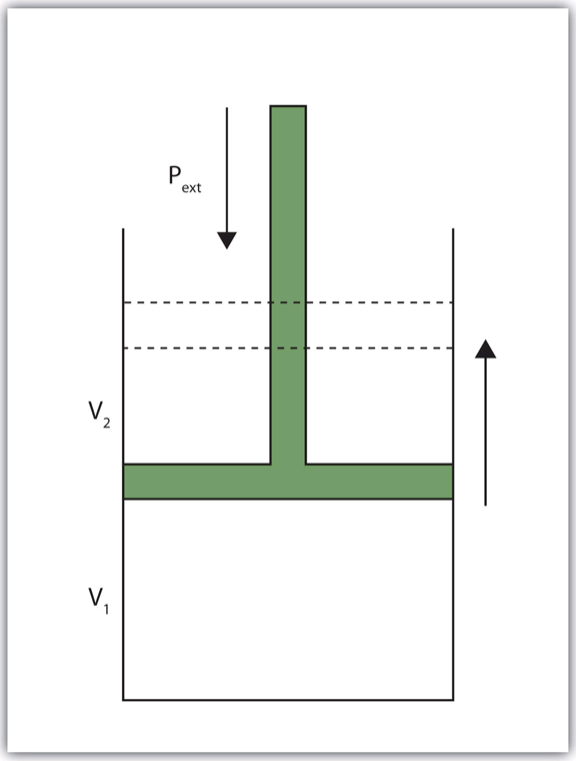

Figure 7.5 "Volume versus Pressure." When a gas expands against an external pressure, the gas does work.

Finally, let us consider units. Volume changes are usually expressed in units like litres, while pressures are usually expressed in atmospheres. When we use the equation to determine work, the unit for work comes out as litre·atmospheres, or L·atm. This is not a very common unit for work. However, there is a conversion factor between L·atm and the common unit of work, joules:

$$1 \text{ L} \cdot \text{atm} = 101.32 \text{ J}$$

Using this conversion factor and the previous equation for work, we can calculate the work performed when a gas expands or contracts.

Example 7.11

Problem

What is the work performed by a gas if it expands from 3.44 L to 6.19 L against a constant external pressure of 1.26 atm? Express the final answer in joules.

Solution

First we need to determine the change in volume, ΔV. A change is always the final value minus the initial value:

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 6.19 \text{ L} - 3.44 \text{ L} = 2.75 \text{ L}$$

Now we can use the definition of work to determine the work done:

$$w = -P_{\text{ext}} \cdot \Delta V = -(1.26 \text{ atm})(2.75 \text{ L}) = -3.47 \text{ L} \cdot \text{atm}$$

Now we construct a conversion factor from the relationship between litre·atmospheres and joules:

$$-3.47 \cancel{\text{ L} \cdot \text{atm}} \times \frac{101.32 \text{ J}}{1 \cancel{\text{ L} \cdot \text{atm}}} = -351 \text{ J}$$

We limit the final answer to three significant figures, as appropriate.

Test Yourself

What is the work performed when a gas expands from 0.66 L to 1.33 L against an external pressure of 0.775 atm?

Answer

−53 J

Heat is another aspect of energy. **Heat** is the transfer of energy from one body to another due to a difference in temperature. For example, when we touch something with our hands, we interpret that object as either hot or cold depending on how energy is transferred: If energy is transferred into your hands, the object feels hot. If energy is transferred from your hands to the object, your hands feel cold. Because heat is a measure of energy transfer, heat is also measured in joules.

For a given object, the amount of heat (q) involved is proportional to two things: the mass of the object (m) and the temperature change (ΔT) evoked by the energy transfer. We can write this mathematically as:

$$q \propto m \times \Delta T$$

where $\propto$ means "is proportional to." To make a proportionality an equality, we include a proportionality constant. In this case, the proportionality constant is labelled c and is called the **specific heat capacity**, or, more succinctly, specific heat:

$$q = mc\Delta T$$

where the mass, specific heat, and change in temperature are multiplied together. Specific heat is a measure of how much energy is needed to change the temperature of a substance; the larger the specific heat, the more energy is needed to change the temperature. The units for specific heat are $\frac{\text{J}}{\text{g} \cdot {}^{\circ}\text{C}}$ or $\frac{\text{J}}{\text{g} \cdot \text{K}}$, depending on what the unit of ΔT is. You may note a departure from the insistence that temperature be expressed in Kelvin. That is because a change in temperature has the same value, whether the temperatures are expressed in degrees Celsius or kelvins.

Example 7.12

Problem

Calculate the heat involved when 25.0 g of Fe increase temperature from 22°C to 76°C. The specific heat of Fe is 0.449 $\frac{\text{J}}{\text{g} \cdot^{\circ} \text{C}}$.

Solution

First we need to determine ΔT. A change is always the final value minus the initial value:

$$\Delta T = 76^{\circ}\text{C} - 22^{\circ}\text{C} = 54^{\circ}\text{C}$$

Now we can use the expression for q, substitute for all variables, and solve for heat:

$$q = (25.0 \cancel{\text{g}}) \left(0.449 \cdot \frac{\text{J}}{\cancel{\text{g}} \cdot \cancel{^{\circ}\text{C}}}\right) (54\cancel{^{\circ}\text{C}}) = 610 \text{ J}$$

Note how the g and °C units cancel, leaving J, a unit of heat. Also note that this value of q is inherently positive, meaning that energy is going into the system.

Test Yourself

Calculate the heat involved when 76.5 g of Ag increase temperature from 17.8°C to 144.5°C. The specific heat of Ag is 0.233 $\frac{\text{J}}{\text{g} \cdot^{\circ} \text{C}}$.

Answer

2,260 J

As with any equation, when you know all but one variable in the expression for q, you can determine the remaining variable by using algebra.

Example 7.13

Problem

It takes 5,408 J of heat to raise the temperature of 373 g of Hg by 104°C. What is the specific heat of Hg?

Solution

We can start with the equation for q, but now different values are given, and we need to solve for specific heat. Note that ΔT is given directly as 104°C. Substituting:

$$5,408 \text{ J} = (373 \text{ g}) c (104^{\circ}\text{C})$$

We divide both sides of the equation by 373 g and 104°C:

$$c = \frac{5408 \text{ J}}{(373 \text{ g})(104^\circ\text{C})}$$

Combining the numbers and bringing together all the units, we get:

$$c = 0.139 \cdot \frac{\text{J}}{\text{g} \cdot^\circ \text{C}}$$

Test Yourself

Gold has a specific heat of 0.129 $\frac{\text{J}}{\text{g} \cdot^\circ \text{C}}$. If 1,377 J are needed to increase the temperature of a sample of gold by 99.9°C, what is the mass of the gold?

Answer

107 g

Table 7.3 “Specific Heats of Various Substances” lists the specific heats of some substances. Specific heat is a physical property of substances, so it is a characteristic of the substance. The general idea is that the lower the specific heat, the less energy is required to change the temperature of the substance by a certain amount.

Table 7.3 Specific Heats of Various Substances

Substance	**Specific Heat** $\frac{\text{J}}{\text{g} \cdot^\circ \text{C}}$
water	4.184
iron	0.449
gold	0.129
mercury	0.139
aluminum	0.900
ethyl alcohol	2.419
magnesium	1.03
helium	5.171
oxygen	0.918

Key Takeaways

- Work can be defined as a gas changing volume against a constant external pressure.
- Heat is the transfer of energy due to temperature differences.
- Heat can be calculated in terms of mass, temperature change, and specific heat.

Exercises

Questions

1. Give two definitions of *work*.
2. What is the sign on work when a sample of gas increases its volume? Explain why work has that sign.
3. What is the work when a gas expands from 3.00 L to 12.60 L against an external pressure of 0.888 atm?
4. What is the work when a gas expands from 0.666 L to 2.334 L against an external pressure of 2.07 atm?
5. What is the work when a gas contracts from 3.45 L to 0.97 L under an external pressure of 0.985 atm?
6. What is the work when a gas contracts from 4.66 L to 1.22 L under an external pressure of 3.97 atm?
7. Like work, the sign on heat can be positive or negative. What is happening to the total energy of a system if heat is positive?
8. Like work, the sign on heat can be positive or negative. What is happening to the total energy of a system if heat is negative?
9. What is the heat when 55.6 g of Fe increase temperature from 25.6°C to 177.9°C? The heat capacity of Fe is in Table 7.3.
10. What is the heat when 0.444 g of Au increases temperature from 17.8°C to 222.5°C? The heat capacity of Au is in Table 7.3.
11. What is the heat when 245 g of H_2O cool from 355 K to 298 K? The heat capacity of H_2O is in Table 7.3.
12. What is the heat when 100.0 g of Mg cool from 725 K to 552 K? The heat capacity of Mg is in Table 7.3.
13. It takes 452 J of heat to raise the temperature of a 36.8 g sample of a metal from 22.9°C to 98.2°C. What is the heat capacity of the metal?
14. It takes 2,267 J of heat to raise the temperature of a 44.5 g sample of a metal from 33.9°C to 288.3°C. What is the heat capacity of the metal?
15. An experimenter adds 336 J of heat to a 56.2 g sample of Hg. What is its change in temperature? The heat capacity of Hg is in Table 7.3.
16. To a 0.444 g sample of H_2O, 23.4 J of heat are added. What is its change in temperature? The heat capacity of H_2O is in Table 7.3.
17. An unknown mass of Al absorbs 187.9 J of heat and increases its temperature from 23.5°C to 35.6°C. What is the mass of the aluminum? How many moles of aluminum is this?
18. A sample of He goes from 19.4°C to 55.9°C when 448 J of energy are added. What is the mass of the helium? How many moles of helium is this?

Answers

1. Work is a force acting through a distance or a volume changing against some pressure.

3. −864 J
5. 248 J
7. When heat is positive, the total energy of the system is increasing.
9. 3.80×10^3 J
11. −58,400 J
13. $0.163 \frac{\text{J}}{\text{g} \cdot^\circ \text{C}}$
15. 43.0°C
17. 17.3 g; 0.640 mol

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Hess's Law

Learning Objectives

1. Learn how to combine chemical equations and their enthalpy changes.

Now that we understand that chemical reactions occur with a simultaneous change in energy, we can apply the concept more broadly. To start, remember that some chemical reactions are rather difficult to perform. For example, consider the combustion of carbon to make carbon monoxide:

$$2\,\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO(g)} \quad \Delta H = ?$$

In reality, this is extremely difficult to do; given the opportunity, carbon will react to make another compound, carbon dioxide:

$$2\,\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

Is there a way around this? Yes. It comes from the understanding that chemical equations can be treated like algebraic equations, with the arrow acting like the equals sign. Like algebraic equations, chemical equations can be combined, and if the same substance appears on both sides of the arrow, it can be cancelled out (much like a spectator ion in ionic equations). For example, consider these two reactions:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)}$$

$$2\,\mathrm{CO_2(g)} \rightarrow 2\,\mathrm{CO(g)} + \mathrm{O_2(g)}$$

If we added these two equations by combining all the reactants together and all the products together, we would get:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} + 2\,\mathrm{CO_2(g)} \rightarrow 2\,\mathrm{CO_2(g)} + 2\,\mathrm{CO(g)} + \mathrm{O_2(g)}$$

We note that $2CO_2(g)$ appears on both sides of the arrow, so they cancel:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} + \cancel{2\,\mathrm{CO_2(g)}} \rightarrow \cancel{2\,\mathrm{CO_2(g)}} + 2\,\mathrm{CO(g)} + \mathrm{O_2(g)}$$

We also note that there are 2 mol of O_2 on the reactant side, and 1 mol of O_2 on the product side. We can cancel 1 mol of O_2 from both sides:

$$2\,\mathrm{C(s)} + \cancel{2}\mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO(g)} + \cancel{\mathrm{O_2(g)}}$$

What do we have left?

$$2\,\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO(g)}$$

This is the reaction we are looking for! So by algebraically combining chemical equations, we can generate new chemical equations that may not be feasible to perform.

What about the enthalpy changes? **Hess's law** states that when chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way. Two corollaries immediately present themselves:

1. If a chemical reaction is reversed, the sign on ΔH is changed.
2. If a multiple of a chemical reaction is taken, the same multiple of the ΔH is taken as well.

What are the equations being combined? The first chemical equation is the combustion of C, which produces CO_2:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)}$$

This reaction is two times the reaction to make CO_2 from C(s) and O_2(g), whose enthalpy change is known:

$$\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

According to the first corollary, the first reaction has an energy change of two times −393.5 kJ, or −787.0 kJ:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)} \quad \Delta H = -787.0\ \mathrm{kJ}$$

The second reaction in the combination is related to the combustion of CO(g):

$$2\,\mathrm{CO(g)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)} \quad \Delta H = -566.0\ \mathrm{kJ}$$

The second reaction in our combination is the *reverse* of the combustion of CO. When we reverse the reaction, we change the sign on the ΔH:

$$2\,\mathrm{CO_2(g)} \rightarrow 2\,\mathrm{CO(g)} + \mathrm{O_2(g)} \quad \Delta H = +566.0\ \mathrm{kJ}$$

Now that we have identified the enthalpy changes of the two component chemical equations, we can combine the ΔH values and add them:

$$\begin{array}{rcl} 2\,\mathrm{C(s)} + \cancel{2}\mathrm{O_2(g)} & \rightarrow & \cancel{2\,\mathrm{CO_2(g)}} \\ \cancel{2\,\mathrm{CO_2(g)}} & \rightarrow & 2\,\mathrm{CO(g)} + \cancel{\mathrm{O_2(g)}} \\ \hline 2\,\mathrm{C(s)} + \mathrm{O_2(g)} & \rightarrow & 2\,\mathrm{CO(g)} \end{array} \qquad \begin{array}{rcl} \Delta H & = & -787.0\ \mathrm{kJ} \\ \Delta H & = & +566.0\ \mathrm{kJ} \\ \Delta H & = & -787.0 + 566.0\ \mathrm{kJ} = -221.0\ \mathrm{kJ} \end{array}$$

Hess's law is very powerful. It allows us to combine equations to generate new chemical reactions whose enthalpy changes can be calculated, rather than directly measured.

Example 7.14

Problem

Determine the enthalpy change of:

$$\mathrm{C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O} \quad \Delta H = ?$$

from these reactions:

$$\mathrm{C_2H_2 + H_2 \rightarrow C_2H_4} \qquad \Delta H = -174.5\ \mathrm{kJ}$$

$$\mathrm{2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O} \qquad \Delta H = -1,692.2\ \mathrm{kJ}$$

$$\mathrm{2\,CO_2 + H_2 \rightarrow 2\,O_2 + C_2H_2} \qquad \Delta H = -167.5\ \mathrm{kJ}$$

Solution

We will start by writing chemical reactions that put the correct number of moles of the correct substance on the proper side. For example, our desired reaction has C_2H_4 as a reactant, and only one reaction from our data has C_2H_4. However, it has C_2H_4 as a product. To make it a reactant, we need to reverse the reaction, changing the sign on the ΔH:

$$\mathrm{C_2H_4 \rightarrow C_2H_2 + H_2} \quad \Delta H = +174.5\ \mathrm{kJ}$$

We need CO_2 and H_2O as products. The second reaction has them on the proper side, so let us include one of these reactions (with the hope that the coefficients will work out when all our reactions are added):

$$\mathrm{2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O} \quad \Delta H = -1,692.2\ \mathrm{kJ}$$

We note that we now have 4 mol of CO_2 as products; we need to get rid of 2 mol of CO_2. The last reaction has $2CO_2$ as a reactant. Let us use it as written:

$$\mathrm{2\,CO_2 + H_2 \rightarrow 2\,O_2 + C_2H_2} \quad \Delta H = -167.5\ \mathrm{kJ}$$

We combine these three reactions, modified as stated:

$$\begin{array}{rcl} \mathrm{C_2H_4} & \rightarrow & \mathrm{C_2H_2 + H_2} \\ \mathrm{2\,C_2H_2 + 5\,O_2} & \rightarrow & \mathrm{4\,CO_2 + 2\,H_2O} \\ \mathrm{2\,CO_2 + H_2} & \rightarrow & \mathrm{2\,O_2 + C_2H_2} \\ \hline \mathrm{C_2H_4 + 2\,C_2H_2 + 5\,O_2 + 2\,CO_2 + H_2} & \rightarrow & \mathrm{C_2H_2 + H_2 + 4\,CO_2 + 2\,H_2O + 2\,O_2 + C_2H_2} \end{array}$$

$\Delta H = +174.5\ \mathrm{kJ}$
$\Delta H = -1,692.2\ \mathrm{kJ}$
$\Delta H = -167.5\ \mathrm{kJ}$

What cancels? $2C_2H_2$, H_2, $2O_2$, and $2CO_2$. What is left is:

$$\mathrm{C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O}$$

Which is the reaction we are looking for. The ΔH of this reaction is the sum of the three ΔH values:

$$\Delta H = +174.5 - 1,692.2 - 167.5 = -1,685.2\ \mathrm{kJ}$$

Test Yourself

Given the following thermochemical equations:

$$\begin{array}{rcll} \mathrm{Pb + Cl_2} & \rightarrow & \mathrm{PbCl_2} & \Delta H = -223\ \mathrm{kJ} \\ \mathrm{PbCl_2 + Cl_2} & \rightarrow & \mathrm{PbCl_4} & \Delta H = -87\ \mathrm{kJ} \end{array}$$

Determine ΔH for:

$$\mathrm{2\,PbCl_2 \rightarrow Pb + PbCl_4}$$

Answer

+136 kJ

Key Takeaways

- Hess's law allows us to combine reactions algebraically and then combine their enthalpy changes the same way.

Exercises

Questions

1. Define Hess's law.
2. What does Hess's law require us to do to the Δ*H* of a thermochemical equation if we reverse the equation?
3. If the Δ*H* for $C_2H_4 + H_2 \rightarrow C_2H_6$ is −65.6 kJ, what is the Δ*H* for the reaction $C_2H_6 \rightarrow C_2H_4 + H_2$?
4. If the Δ*H* for $2Na + Cl_2 \rightarrow 2NaCl$ is −772 kJ, what is the Δ*H* for the reaction $2NaCl \rightarrow 2Na + Cl_2$?
5. If the Δ*H* for $C_2H_4 + H_2 \rightarrow C_2H_6$ is −65.6 kJ, what is the Δ*H* for the reaction $2C_2H_4 + 2H_2 \rightarrow 2C_2H_6$?
6. If the Δ*H* for $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ is −2,650 kJ, what is the Δ*H* for the reaction $6C_2H_6 + 21O_2 \rightarrow 12CO_2 + 18H_2O$?
7. The Δ*H* for $C_2H_4 + H_2O \rightarrow C_2H_5OH$ is −44 kJ. What is the Δ*H* for the reaction $2C_2H_5OH \rightarrow 2C_2H_4 + 2H_2O$?
8. The Δ*H* for $N_2 + O_2 \rightarrow 2NO$ is 181 kJ. What is the Δ*H* for the reaction $\mathrm{NO} \rightarrow \frac{1}{2}\mathrm{N_2} + \frac{1}{2}\mathrm{O_2}$?
9. Determine the Δ*H* for the reaction $Cu + Cl_2 \rightarrow CuCl_2$ given these data:

$$\begin{aligned} 2\,\mathrm{Cu} + \mathrm{Cl_2} &\rightarrow 2\,\mathrm{CuCl} & \Delta H &= -274\ \mathrm{kJ} \\ 2\,\mathrm{CuCl} + \mathrm{Cl_2} &\rightarrow 2\,\mathrm{CuCl_2} & \Delta H &= -166\ \mathrm{kJ} \end{aligned}$$

10. Determine Δ*H* for the reaction $2CH_4 \rightarrow 2H_2 + C_2H_4$ given these data:

$$\begin{aligned} \mathrm{CH_4} + 2\,\mathrm{O_2} &\rightarrow \mathrm{CO_2} + 2\,\mathrm{H_2O} & \Delta H &= -891\ \mathrm{kJ} \\ \mathrm{C_2H_4} + 3\,\mathrm{O_2} &\rightarrow 2\,\mathrm{CO_2} + 2\,\mathrm{H_2O} & \Delta H &= -1,411\ \mathrm{kJ} \\ 2\,\mathrm{H_2} + \mathrm{O_2} &\rightarrow 2\,\mathrm{H_2O} & \Delta H &= -571\ \mathrm{kJ} \end{aligned}$$

11. Determine Δ*H* for the reaction $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$ given these data:

$$4\,\mathrm{Fe} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{Fe_2O_3} \qquad \Delta H = -1,650\ \mathrm{kJ}$$
$$2\,\mathrm{S} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{SO_3} \qquad \Delta H = -792\ \mathrm{kJ}$$
$$2\,\mathrm{Fe} + 3\,\mathrm{S} + 6\,\mathrm{O_2} \rightarrow \mathrm{Fe_2(SO_4)_3} \qquad \Delta H = -2,583\ \mathrm{kJ}$$

12. Determine Δ*H* for the reaction $CaCO_3 \rightarrow CaO + CO_2$ given these data:

$$2\,\mathrm{Ca} + 2\,\mathrm{C} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{CaCO_3} \qquad \Delta H = -2,414\ \mathrm{kJ}$$
$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad \Delta H = -393.5\ \mathrm{kJ}$$
$$2\,\mathrm{Ca} + \mathrm{O_2} \rightarrow 2\,\mathrm{CaO} \qquad \Delta H = -1,270\ \mathrm{kJ}$$

Answers

1. If chemical equations are combined, their energy changes are also combined.
3. Δ*H* = 65.6 kJ
5. Δ*H* = −131.2 kJ
7. Δ*H* = 88 kJ
9. Δ*H* = −220 kJ
11. Δ*H* = 570 kJ

End-of-Chapter Material

Additional Exercises

1. What is the work when 124 mL of gas contract to 72.0 mL under an external pressure of 822 torr?
2. What is the work when 2,345 mL of gas contract to 887 mL under an external pressure of 348 torr?
3. A 3.77 L volume of gas is exposed to an external pressure of 1.67 atm. As the gas contracts, 156 J of work are added to the gas. What is the final volume of the gas?
4. A 457 mL volume of gas contracts when 773 torr of external pressure act on it. If 27.4 J of work are added to the gas, what is its final volume?
5. What is the heat when 1,744 g of Hg increase in temperature by 334°C? Express your final answer in kJ.
6. What is the heat when 13.66 kg of Fe cool by 622°C? Express your final answer in kJ.
7. What is final temperature when a 45.6 g sample of Al at 87.3°C gains 188 J of heat?
8. What is final temperature when 967 g of Au at 557°C lose 559 J of heat?
9. Plants take CO_2 and H_2O and make glucose ($C_6H_{12}O_6$) and O_2. Write a balanced thermochemical equation for this process. Use data in Table 7.1 “Enthalpies of Formation for Various Substances.”
10. Exercise 9 described the formation of glucose in plants, which take in CO_2 and H_2O and give off O_2. Is this process exothermic or endothermic? If exothermic, where does the energy go? If endothermic, where does the energy come from?
11. The basic reaction in the refining of aluminum is to take $Al_2O_3(s)$ and turn it into Al(s) and $O_2(g)$. Write the balanced thermochemical equation for this process. Use data in Table 7.1.
12. Is the enthalpy change of the reaction $H_2O(\ell) \rightarrow H_2O(g)$ zero or nonzero? Use data in Table 7.1 to determine the answer.
13. What mass of H_2O can be heated from 22°C to 80°C in the combustion of 1 mol of CH_4? You will need the balanced thermochemical equation for the combustion of CH_4. Use data in Table 7.1.
14. What mass of H_2O can be heated from 22°C to 80°C in the combustion of 1 mol of C_2H_6? You will need the balanced thermochemical equation for the combustion of C_2H_6. Use data in Table 7.1. Compare your answer to Exercise 13.
15. What is the enthalpy change for the unknown reaction?

$$\begin{aligned} \mathrm{Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)} \qquad & \Delta H = -359 \text{ kJ} \\ \mathrm{PbCl_2(s) + Cl_2(g) \rightarrow PbCl_4(\ell)} \qquad & \Delta H = ? \\ \mathrm{Pb(s) + 2\,Cl_2(g) \rightarrow PbCl_4(\ell)} \qquad & \Delta H = -329 \text{ kJ} \end{aligned}$$

16. What is the enthalpy change for the unknown reaction?

$$\mathrm{P\,(s)} + \frac{3}{2}\mathrm{Br_2}(\ell) \rightarrow \mathrm{PBr_3}(\ell) \qquad \Delta H = -185\ \mathrm{kJ}$$

$$\mathrm{PI_3(s)} \rightarrow \mathrm{P\,(s)} + \frac{3}{2}\mathrm{I_2(s)} \qquad \Delta H = ?$$

$$\mathrm{PI_3} + \frac{3}{2}\mathrm{Br_2}(\ell) \rightarrow \mathrm{PBr_3}(\ell) + \frac{3}{2}\mathrm{I_2(s)} \qquad \Delta H = -139\ \mathrm{kJ}$$

17. What is the Δ*H* for the reaction C(s, gra) → C(s, dia)? The label *gra* means graphite, and the label *dia* means diamond. What does your answer mean?
18. Without consulting any tables, determine the Δ*H* for the reaction $H_2O(\ell, 25°C) \rightarrow H_2O(\ell, 25°C)$. Explain your answer.

Answers

1. 5.70 J
3. 4.69 L
5. 80.97 kJ
7. 91.9°C
9. $6\,\mathrm{CO_2(g)} + 6\,\mathrm{H_2O}(\ell) \rightarrow \mathrm{C_6H_{12}O_6(s)} + 6\,\mathrm{O_2(g)} \quad \Delta H = 2,799\ \mathrm{kJ}$
11. $2\,\mathrm{Al_2O_3(s)} \rightarrow 4\,\mathrm{Al\,(s)} + 3\,\mathrm{O_2(g)} \quad \Delta H = 3,351.4\ \mathrm{kJ}$
13. 3,668 g
15. Δ*H* = 30 kJ
17. Δ*H* = 1.897 kJ; the reaction is endothermic.

Chapter 8. Electronic Structure

Normal light microscopes can magnify objects up to about 1,500 times. Electron microscopes can magnify objects up to 1,000,000 times. Why can electron microscopes magnify images so much?

A microscope's resolution depends on the wavelength of light used. The smaller the wavelength, the more a microscope can magnify. Light is a wave, and, as such, it has a wavelength associated with it. The wavelength of visible light, which is detected by the eyes, varies from about 700 nm to about 400 nm.

One of the startling conclusions about modern science is that electrons also act as waves. However, the wavelength of electrons is much, much shorter — about 0.5 to 1 nm. This allows electron microscopes to magnify 600–700 times more than light microscopes. This allows us to see even smaller features in a world that is invisible to the naked eye.

Atoms act the way they do because of their structure. We already know that atoms are composed of protons, neutrons, and electrons. Protons and neutrons are located in the nucleus, and electrons orbit around the nucleus. But we need to know the structural details to understand why atoms react the way they do.

Virtually everything we know about atoms ultimately comes from light. Before we can understand the composition of atoms (especially electrons), we need to understand the properties of light.

Light

Learning Objectives

1. Describe light with its frequency and wavelength.
2. Describe light as a particle of energy.

What we know as light is more properly called *electromagnetic radiation*. We know from experiments that light acts as a wave. As such, it can be described as having a frequency and a wavelength. The **wavelength** of light is the distance between corresponding points in two adjacent light cycles, and the **frequency** of light is the number of cycles of light that pass a given point in one second. Wavelength is typically represented by λ, the lowercase Greek letter *lambda*, while frequency is represented by ν, the lowercase Greek letter *nu* (although it looks like a Roman "vee," it is actually the Greek equivalent of the letter "en"). Wavelength has units of length (metres, centimetres, etc.), while frequency has units of *per second*, written as s^{-1} and sometimes called a *hertz* (Hz). Figure 8.01 "Characteristics of Light Waves" shows how these two characteristics are defined.

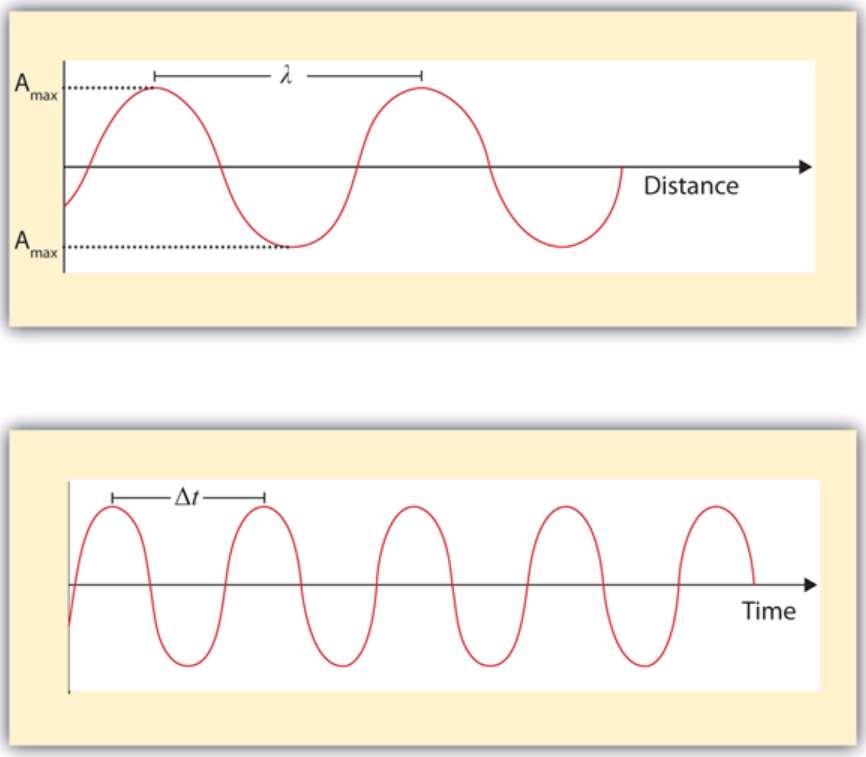

Figure 8.01 "Characteristics of Light Waves." Light acts as a wave and can be described by a wavelength λ and a frequency ν.

One property of waves is that their speed is equal to their wavelength times their frequency. That means we have:

$$\text{speed} = \lambda\nu$$

For light, however, speed is actually a universal constant when light is travelling through a vacuum (or, to a very good approximation, air). The measured speed of light (c) in a vacuum is 2.9979×10^8 m/s, or about 3.00×10^8 m/s. Thus, we have:

$$c = \lambda\nu$$

Because the speed of light is a constant, the wavelength and the frequency of light are related to each other: as one increases, the other decreases and vice versa. We can use this equation to calculate what one property of light has to be when given the other property.

Example 8.7

Problem

What is the frequency of light if its wavelength is 5.55×10^{-7} m?

Solution

We use the equation that relates the wavelength and frequency of light with its speed. We have:

$$3.00 \times 10^8 \text{ m/s} = (5.55 \times 10^{-7} \text{ m})\nu$$

We divide both sides of the equation by 5.55×10^{-7} m and get:

$$\nu = 5.41 \times 10^{14} \text{ s}^{-1}$$

Note how the m units cancel, leaving s in the denominator. A unit in a denominator is indicated by a −1 power — s^{-1} — and read as "per second."

Test Yourself

What is the wavelength of light if its frequency is 1.55×10^{10} s^{-1}?

Answer

0.0194 m, or 19.4 mm

Light also behaves like a package of energy. It turns out that for light, the energy of the "package" of energy is proportional to its frequency. (For most waves, energy is proportional to wave amplitude, or the height of the wave.) The mathematical equation that relates the energy (E) of light to its frequency is:

$$E = h\nu$$

Where ν is the frequency of the light, and h is a constant called **Planck's constant**. Its value is 6.626 ×

10^{-34} J·s — a very small number that is another fundamental constant of our universe, like the speed of light. The units on Planck's constant may look unusual, but these units are required so that the algebra works out.

Example 8.8

Problem

What is the energy of light if its frequency is 1.55×10^{10} s^{-1}?

Solution

Using the formula for the energy of light, we have:

$$E = (6.626 \times 10^{-34}\ \text{J} \cdot \text{s})(1.55 \times 10^{10}\ \text{s}^{-1})$$

Seconds are in the numerator and the denominator, so they cancel, leaving us with joules, the unit of energy. So:

$$E = 1.03 \times 10^{-23}\ \text{J}$$

This is an extremely small amount of energy — but this is for only one light wave.

Test Yourself

What is the frequency of a light wave if its energy is 4.156×10^{-20} J?

Answer

6.27×10^{13} s^{-1}

Because a light wave behaves like a little particle of energy, light waves have a particle-type name: the **photon**. It is not uncommon to hear light described as photons.

Wavelengths, frequencies, and energies of light span a wide range; the entire range of possible values for light is called the **electromagnetic spectrum**. We are mostly familiar with visible light, which is light having a wavelength range between about 400 nm and 700 nm. Light can have much longer and much shorter wavelengths than this, with corresponding variations in frequency and energy. Figure 8.02 "The Electromagnetic Spectrum" shows the entire electromagnetic spectrum and how certain regions of the spectrum are labelled. You may already be familiar with some of these regions; they are all light—with different frequencies, wavelengths, and energies.

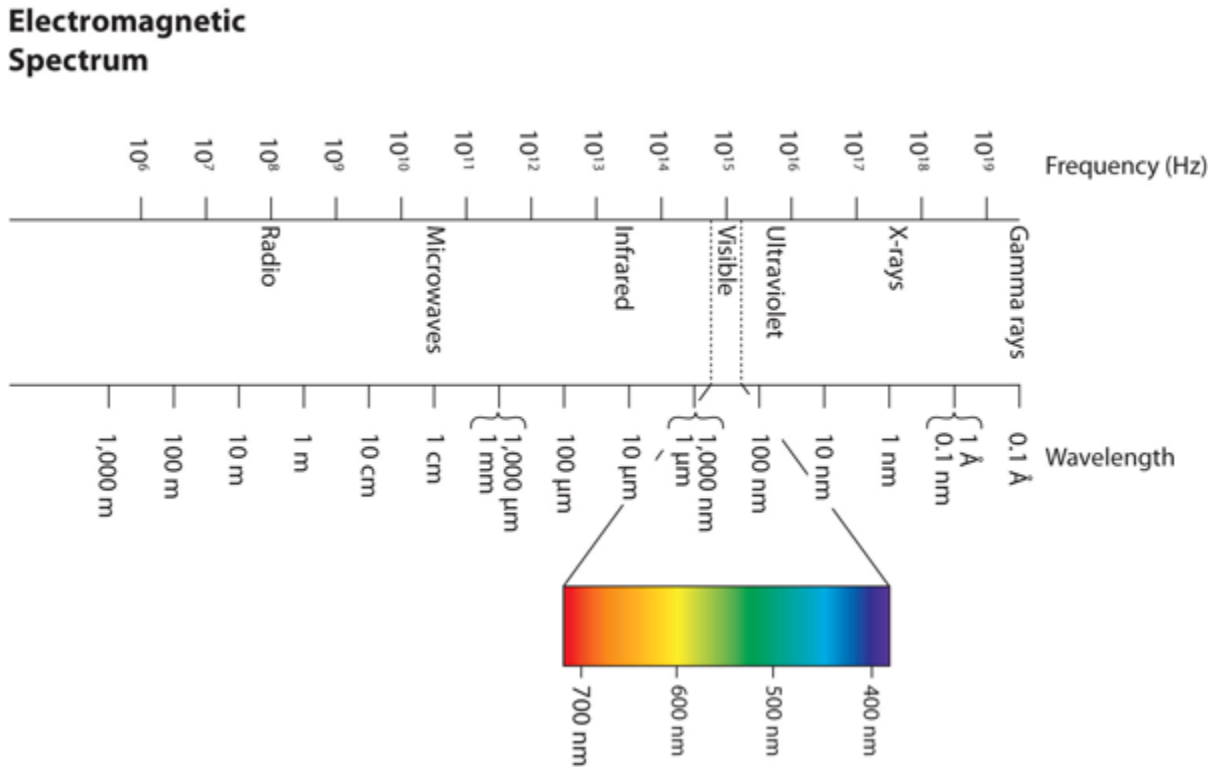

Figure 8.02 "The Electromagnetic Spectrum." The electromagnetic spectrum, with its various regions labelled. The borders of each region are approximate.

Key Takeaways

- Light acts like a wave, with a frequency and a wavelength.
- The frequency and wavelength of light are related by the speed of light, a constant.
- Light acts like a particle of energy, whose value is related to the frequency of light.

Exercises

Questions

1. Describe the characteristics of a light wave.
2. What is a characteristic of a particle of light?
3. What is the frequency of light if its wavelength is 7.33×10^{-5} m?
4. What is the frequency of light if its wavelength is 1.226 m?
5. What is the frequency of light if its wavelength is 733 nm?
6. What is the frequency of light if its wavelength is 8.528 cm?
7. What is the wavelength of light if its frequency is $8.19 \times 10^{14}\ s^{-1}$?

8. What is the wavelength of light if its frequency is $3.66 \times 10^{6}\ s^{-1}$?
9. What is the wavelength of light if its frequency is 1.009×10^{6} Hz?
10. What is the wavelength of light if its frequency is 3.79×10^{-3} Hz?
11. What is the energy of a photon if its frequency is $5.55 \times 10^{13}\ s^{-1}$?
12. What is the energy of a photon if its frequency is $2.06 \times 10^{18}\ s^{-1}$?
13. What is the energy of a photon if its wavelength is 5.88×10^{-4} m?
14. What is the energy of a photon if its wavelength is 1.888×10^{2} m?

Answers

1. Light has a wavelength and a frequency.
3. $4.09 \times 10^{12}\ s^{-1}$
5. $4.09 \times 10^{14}\ s^{-1}$
7. 3.66×10^{-7} m
9. 297 m
11. 3.68×10^{-20} J
13. 3.38×10^{-22} J

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Quantum Numbers for Electrons

Learning Objectives

1. Explain what spectra are.
2. Learn the quantum numbers that are assigned to electrons.

There are two fundamental ways of generating light: either heat an object up so hot it glows or pass an electrical current through a sample of matter (usually a gas). Incandescent lights and fluorescent lights generate light via these two methods, respectively.

A hot object gives off a continuum of light. We notice this when the visible portion of the electromagnetic spectrum is passed through a prism: the prism separates light into its constituent colours, and all colours are present in a continuous rainbow (part (a) in Figure 8.03 “Prisms and Light”). This image is known as a **continuous spectrum**. However, when electricity is passed through a gas and light is emitted and this light is passed though a prism, we see only certain lines of light in the image (part (b) in Figure 8.03 “Prisms and Light”). This image is called a line spectrum. It turns out that every element has its own unique, characteristic line spectrum.

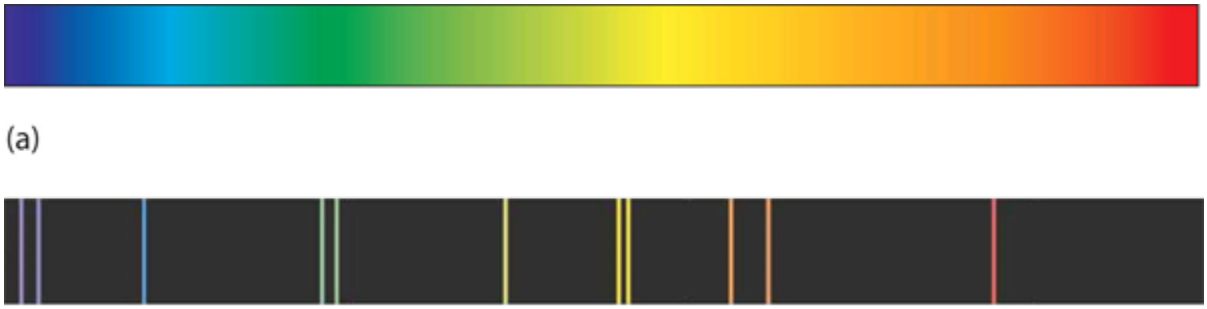

Figure 8.03 “Prisms and Light.” (a) A glowing object gives off a full rainbow of colours, which are noticed only when light is passed through a prism to make a continuous spectrum. (b) However, when electricity is passed through a gas, only certain colours of light are emitted. Here are the colours of light in the line spectrum of Hg.

Why does the light emitted from an electrically excited gas have only certain colours, while light given off by hot objects has a continuous spectrum? For a long time, it was not well explained. Particularly simple was the spectrum of hydrogen gas, which could be described easily by an equation; no other element has a spectrum that is so predictable (Figure 8.04 “Hydrogen Spectrum”). Late-nineteenth-century scientists found that the positions of the lines obeyed a pattern given by the following equation:

$$\frac{1}{\lambda} = (109,700\ \mathrm{cm}^{-1})\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

Where *n* = 3, 4, 5, 6,…, but they could not explain why this was so.

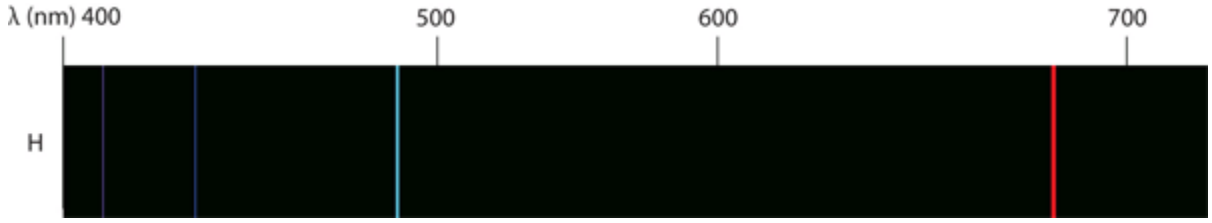

Figure 8.04 "Hydrogen Spectrum." The spectrum of hydrogen was particularly simple and could be predicted by a simple mathematical expression.

In 1913, the Danish scientist Niels Bohr suggested a reason why the hydrogen atom spectrum looked this way. He suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number *n* (the same *n* in the equation above and now called a **quantum number**). Quantities that have certain specific values are called **quantized**. Bohr suggested that the energy of the electron in hydrogen was quantized because it was in a specific orbit. Because the energies of the electron can have only certain values, the changes in energies can have only certain values (somewhat similar to a staircase: not only are the stair steps set at specific heights but the height between steps is fixed). Finally, Bohr suggested that the energy of light emitted from electrified hydrogen gas was equal to the energy difference of the electron's energy states:

$$E_{\mathrm{light}} = h\nu = \Delta E_{\mathrm{electron}}$$

This means that only certain frequencies (and thus, certain wavelengths) of light are emitted. Figure 8.05 "Bohr's Model of the Hydrogen Atom" shows a model of the hydrogen atom based on Bohr's ideas.

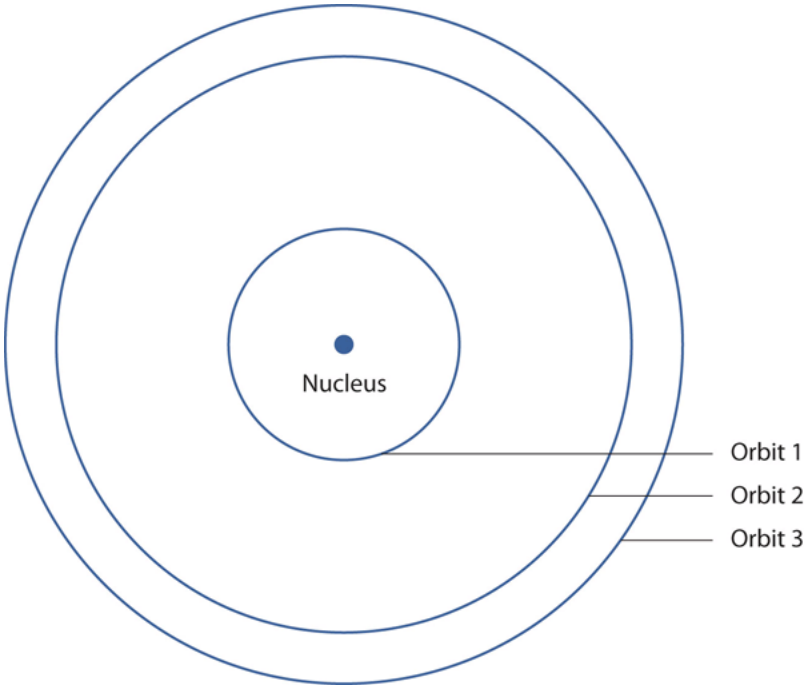

Figure 8.05 "Bohr's Model of the Hydrogen Atom." Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

Bohr's ideas were useful but were applied only to the hydrogen atom. However, later researchers generalized Bohr's ideas into a new theory called **quantum mechanics**, which explains the behaviour of electrons as if they were acting as a wave, not as particles. Quantum mechanics predicts two major things: quantized energies for electrons of all atoms (not just hydrogen) and an organization of electrons within atoms. Electrons are no longer thought of as being randomly distributed around a nucleus or restricted to certain orbits (in that regard, Bohr was wrong). Instead, electrons are collected into groups and subgroups that explain much about the chemical behaviour of the atom.

In the quantum-mechanical model of an atom, the state of an electron is described by four quantum numbers, not just the one predicted by Bohr. The first quantum number is called the **principal quantum number**. Represented by *n*, the principal quantum number largely determines the energy of an electron. Electrons in the same atom that have the same principal quantum number are said to occupy an **electron shell** of the atom. The principal quantum number can be any nonzero positive integer: 1, 2, 3, 4,….

Within a shell, there may be multiple possible values of the next quantum number, the **angular momentum quantum number**, represented by ℓ. The ℓ quantum number has a minor effect on the energy of the electron but also affects the spatial distribution of the electron in three-dimensional space — that is, the shape of an electron's distribution in space. The value of the ℓ quantum number can be any integer between 0 and $n - 1$:

$$\ell = 0, 1, 2, \ldots, n - 1$$

Thus, for a given value of *n*, there are different possible values of ℓ, as shown in Table 8.1.

Table 8.1 Possible Values of ℓ

If *n* equals	ℓ can be
1	0
2	0 or 1
3	0, 1, or 2
4	0, 1, 2, or 3

and so forth. Electrons within a shell that have the same value of ℓ are said to occupy a **subshell** in the atom. Commonly, instead of referring to the numerical value of ℓ, a letter represents the value of ℓ (to help distinguish it from the principal quantum number):

Table 8.2 Atomic Subshells as Defined by the Value of ℓ

If ℓ equals	The subshell is
0	*s*
1	*p*
2	*d*
3	*f*

The next quantum number is called the **magnetic quantum number**, represented by $m\ell$. For any value of ℓ, there are $2\ell + 1$ possible values of m_ℓ, ranging from $-\ell$ to ℓ:

$$-\ell \leq m_\ell \leq \ell$$

or

$$|m\ell| \leq \ell$$

The following explicitly lists the possible values of m_ℓ for the possible values of ℓ:

Table 8.3 Possible Values of *m*ℓ

If ℓ equals	The *m*ℓ values can be
0	0
1	−1, 0, or 1
2	−2, −1, 0, 1, or 2
3	−3, −2, −1, 0, 1, 2, or 3

The particular value of m_ℓ dictates the orientation of an electron's distribution in space. When ℓ is zero,

m_ℓ can be only zero, so there is only one possible orientation. When ℓ is 1, there are three possible orientations for an electron's distribution. When ℓ is 2, there are five possible orientations of electron distribution. This goes on and on for other values of ℓ, but we need not consider any higher values of ℓ here. Each value of m_ℓ designates a certain **orbital**. Thus, there is only one orbital when ℓ is zero, three orbitals when ℓ is 1, five orbitals when ℓ is 2, and so forth. The m_ℓ quantum number has no effect on the energy of an electron unless the electrons are subjected to a magnetic field — hence its name.

The ℓ quantum number dictates the general shape of electron distribution in space (Figure 8.06 "Electron Orbitals"). As shown in part (a), any *s* orbital is spherically symmetric, and there is only one orbital in any *s* subshell. Part (b) shows that any *p* orbital has a two-lobed, dumbbell-like shape; because there are three of them, we normally represent them as pointing along the *x*-, *y*-, and *z*-axes of Cartesian space. In part (c), we see that *d* orbitals are four-lobed rosettes; they are oriented differently in space (the one labelled d_z^2 has two lobes and a torus instead of four lobes, but it is equivalent to the other orbitals). When there is more than one possible value of m_ℓ, each orbital is labelled with one of the possible values. It should be noted that the diagrams in Figure 8.06 are estimates of the electron distribution in space, not surfaces electrons are fixed on.

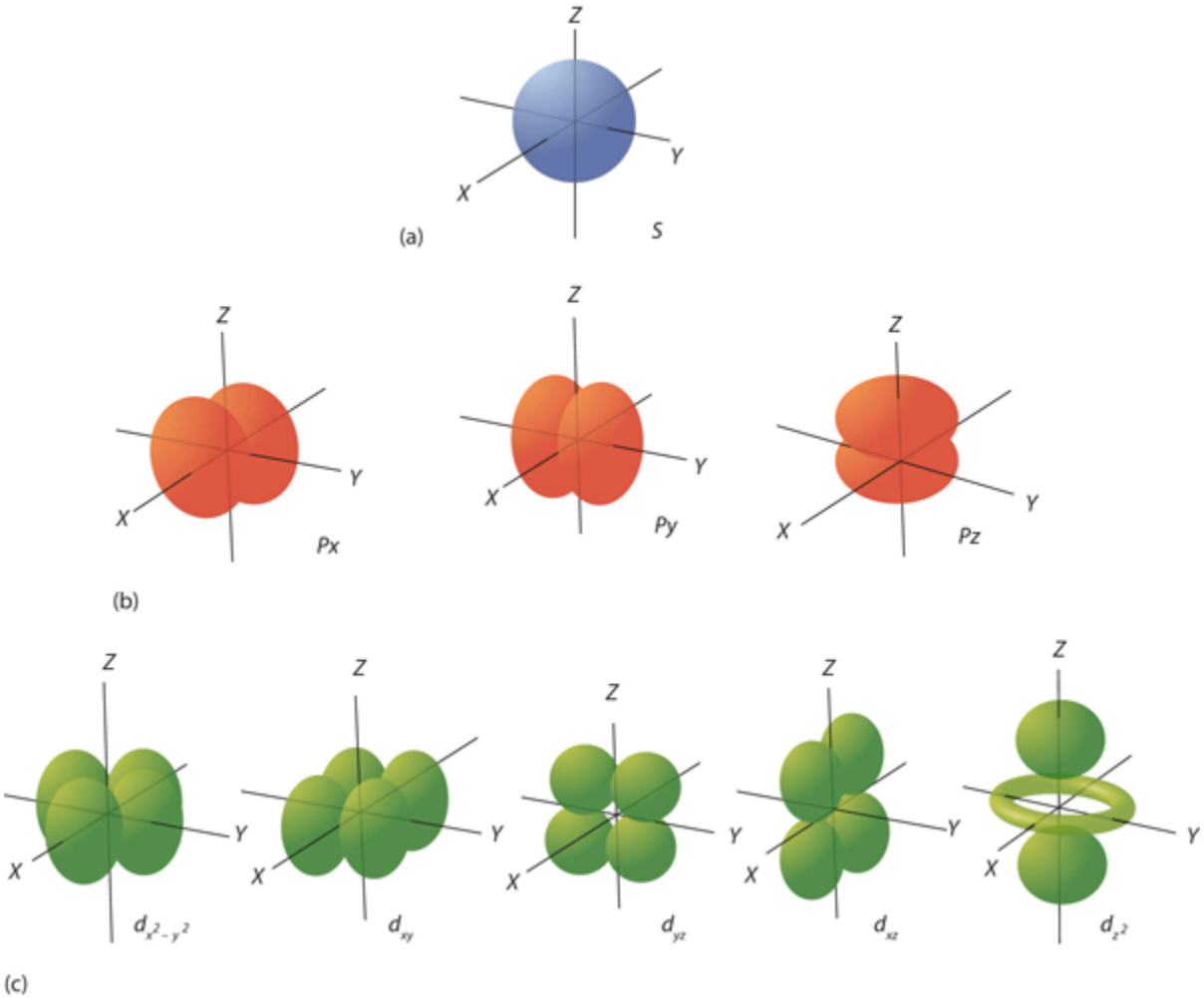

Figure 8.06 "Electron Orbitals." (a) The lone s orbital is spherical in distribution. (b) The three p orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five d orbitals are rosette in shape, except for the d_z^2 orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

The final quantum number is the **spin quantum number**, represented by m_s. Electrons and other subatomic particles behave as if they are spinning (we cannot tell if they really are, but they behave as if they are). Electrons themselves have two possible spin states, and because of mathematics, they are assigned the quantum numbers +½ and −½. These are the only two possible choices for the spin quantum number of an electron.

Example 8.3

Problems

Of the set of quantum numbers $\{n, \ell, m_\ell, m_s\}$, which are possible and which are not allowed?

1. $\{3, 2, 1, +½\}$
2. $\{2, 2, 0, −½\}$
3. $\{3, −1, 0, +½\}$

Solutions

1. The principal quantum number n must be an integer, which it is here. The quantum number ℓ must be less than n, which it is. The m_ℓ quantum number must be between $-\ell$ and ℓ, which it is. The spin quantum number is +½, which is allowed. Because this set of quantum numbers follows all restrictions, it is possible.
2. The quantum number n is an integer, but the quantum number ℓ must be less than n, which it is not. Thus, this is not an allowed set of quantum numbers.
3. The principal quantum number n is an integer, but ℓ is not allowed to be negative. Therefore, this is not an allowed set of quantum numbers.

Test Yourself

Of the set of quantum numbers $\{n, \ell, m_\ell, m_s\}$, which are possible and which are not allowed?

1. $\{4, 2, −2, 1\}$
2. $\{3, 1, 0, −½\}$

Answers

1. Spin must be either +½ or −½, so this set of quantum number is not allowed.
2. allowed

Chemistry Is Everywhere: Neon Lights

A neon light is basically an electrified tube with a small amount of gas in it. Electricity excites electrons in the gas atoms, which then give off light as the electrons go back into a lower energy state. However, many so-called “neon” lights don’t contain neon!

Although we know now that a gas discharge gives off only certain colours of light, without a prism or other component to separate the individual light colours, we see a composite of all the colours emitted. It is not unusual for a certain colour to predominate. True neon lights, with neon gas in them, have a reddish-orange light due to the large amount of red-, orange-, and yellow-coloured light emitted. However, if you use krypton instead of neon, you get a whitish light, while using argon yields a blue-purple light. A light filled with nitrogen gas glows purple, as does a helium lamp. Other gases — and mixtures of gases — emit other colours of light. Ironically, despite its importance in the development of modern electronic theory, hydrogen lamps emit little visible light and are rarely used for illumination purposes.

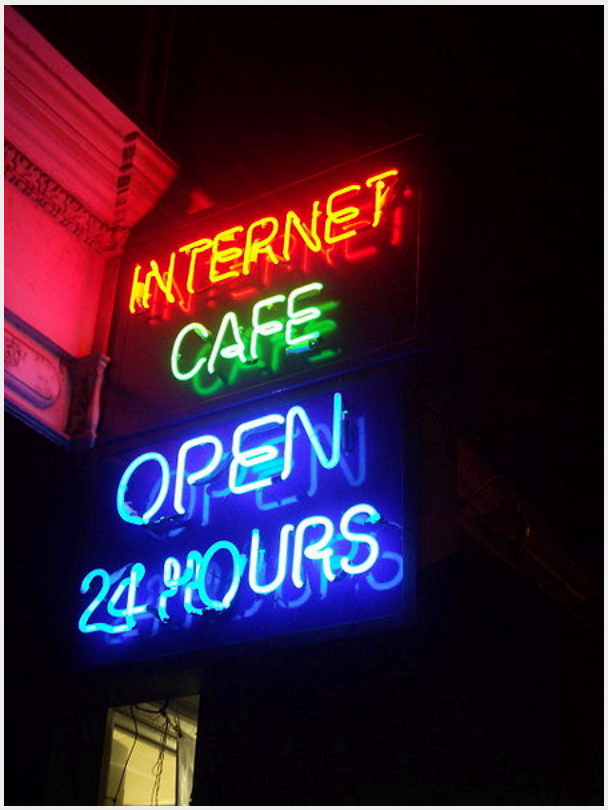

Figure 8.07 "Neon." The different colours of these "neon" lights are caused by gases other than neon in the discharge tubes.

Key Takeaways

- Electrons in atoms have quantized energies.
- The state of electrons in atoms is described by four quantum numbers.

Exercises

Questions

1. Differentiate between a continuous spectrum and a line spectrum.
2. Under what circumstances is a continuous spectrum formed? Under what circumstances is a line spectrum formed?
3. What is the wavelength of light from the hydrogen atom spectrum when $n = 3$?
4. What is the wavelength of light from the hydrogen atom spectrum when $n = 5$?
5. What are the restrictions on the principal quantum number?
6. What are the restrictions on the angular momentum quantum number?
7. What are the restrictions on the magnetic quantum number?
8. What are the restrictions on the spin quantum number?
9. What are the possible values for ℓ when $n = 5$?
10. What are the possible values for ℓ when $n = 1$?
11. What are the possible values for m_ℓ when $\ell = 3$?
12. What are the possible values for m_ℓ when $\ell = 6$?
13. Describe the shape of an *s* orbital.
14. Describe the shape of a *p* orbital.
15. Which of these sets of quantum numbers is allowed? If it is not, explain why.
    a. $\{4, 1, -2, +½\}$
    b. $\{2, 0, 0, -½\}$
16. Which of these sets of quantum numbers is allowed? If it is not, explain why.
    a. $\{5, 2, -1, -½\}$
    b. $\{3, -1, -1, -½\}$

Answers

1. A continuous spectrum is a range of light frequencies or wavelengths; a line spectrum shows only certain frequencies or wavelengths.
3. 6.56×10^{-7} m, or 656 nm
5. The principal quantum number is restricted to being a positive whole number.
7. The absolute value of m_ℓ must be less than or equal to ℓ: $|m_\ell| \leq \ell$.
9. ℓ can be 0, 1, 2, 3, or 4.
11. m_ℓ can be −3, −2, −1, 0, 1, 2, or 3.
13. An *s* orbital is spherical in shape.
15. a. Because $|m_\ell|$ must be less than ℓ, this set of quantum numbers is not allowed.
    b. Allowed.

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Organization of Electrons in Atoms

Learning Objectives

1. Learn how electrons are organized in atoms.
2. Represent the organization of electrons by an electron configuration.

Now that you know that electrons have quantum numbers, how are they arranged in atoms? The key to understanding electronic arrangement is summarized in the **Pauli exclusion principle**: no two electrons in an atom can have the same set of four quantum numbers. This dramatically limits the number of electrons that can exist in a shell or a subshell.

Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells–subshells with lower energies. Consider H, an atom with a single electron only. Under normal conditions, the single electron would go into the $n = 1$ shell, which has only a single *s* subshell with one orbital (because m_ℓ can equal only 0). The convention is to label the shell–subshell combination with the number of the shell and the letter that represents the subshell. Thus, the electron goes in the 1*s* shell–subshell combination. It is usually not necessary to specify the m_ℓ or m_s quantum numbers, but for the H atom, the electron has $m_\ell = 0$ (the only possible value) and an m_s of either +½ or −½.

The He atom has two electrons. The second electron can also go into the 1*s* shell–subshell combination but only if its spin quantum number is different from the first electron's spin quantum number. Thus, the sets of quantum numbers for the two electrons are {1, 0, 0, +½} and {1, 0, 0, −½}. Notice that the overall set is different for the two electrons, as required by the Pauli exclusion principle.

The next atom is Li, with three electrons. However, now the Pauli exclusion principle implies that we cannot put that electron in the 1*s* shell–subshell because no matter how we try, this third electron would have the same set of four quantum numbers as one of the first two electrons. So this third electron must be assigned to a different shell–subshell combination. However, the $n = 1$ shell doesn't have another subshell; it is restricted to having just $\ell = 0$, or an *s* subshell. Therefore, this third electron has to be assigned to the $n = 2$ shell, which has an *s* ($\ell = 0$) subshell and a *p* ($\ell = 1$) subshell. Again, we usually start with the lowest quantum number, so this third electron is assigned to the 2*s* shell–subshell combination of quantum numbers.

The Pauli exclusion principle has the net effect of limiting the number of electrons that can be assigned a shell–subshell combination of quantum numbers. For example, in any *s* subshell, no matter what the shell number, there can be a maximum of only two electrons. Once the *s* subshell is filled up, any additional electrons must go to another subshell in the shell (if it exists) or to higher-numbered shell. A similar analysis shows that a *p* subshell can hold a maximum of six electrons. A *d* subshell can hold a

maximum of 10 electrons, while an *f* subshell can have a maximum of 14 electrons. By limiting subshells to these maxima, we can distribute the available electrons to their shells and subshells.

Example 8.4

Problem

How would the six electrons for C be assigned to the *n* and ℓ quantum numbers?

Solution

The first two electrons go into the 1*s* shell–subshell combination. Two additional electrons can go into the 2*s* shell–subshell, but now this subshell is filled with the maximum number of electrons. The *n* = 2 shell also has a *p* subshell, so the remaining two electrons can go into the 2*p* subshell. The 2*p* subshell is not completely filled because it can hold a maximum of six electrons.

Test Yourself

How would the 11 electrons for Na be assigned to the *n* and ℓ quantum numbers?

Answer

Two 1*s* electrons, two 2*s* electrons, six 2*p* electrons, and one 3*s* electron.

Now that we see how electrons are partitioned among the shells and subshells, we need a more concise way of communicating this partitioning. Chemists use an **electron configuration** to represent the organization of electrons in shells and subshells in an atom. An electron configuration simply lists the shell and subshell labels, with a right superscript giving the number of electrons in that subshell. The shells and subshells are listed in the order of filling.

For example, an H atom has a single electron in the 1*s* subshell. Its electron configuration is:

$$\text{H: } 1s$$

He has two electrons in the 1*s* subshell. Its electron configuration is:

$$\text{He: } 1s^2$$

The three electrons for Li are arranged in the 1*s* subshell (two electrons) and the 2*s* subshell (one electron). The electron configuration of Li is:

$$\text{Li: } 1s^2 2s^1$$

Be has four electrons, two in the 1*s* subshell and two in the 2*s* subshell. Its electron configuration is:

$$\text{Be: } 1s^2 2s^2$$

Now that the 2*s* subshell is filled, electrons in larger atoms must go into the 2*p* subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2*p* subshell:

$$\begin{aligned} \text{B:} &\quad 1s^2 2s^2 2p^1 \\ \text{C:} &\quad 1s^2 2s^2 2p^2 \\ \text{N:} &\quad 1s^2 2s^2 2p^3 \\ \text{O:} &\quad 1s^2 2s^2 2p^4 \\ \text{F:} &\quad 1s^2 2s^2 2p^5 \\ \text{Ne:} &\quad 1s^2 2s^2 2p^6 \end{aligned}$$

Now that the 2*p* subshell is filled (all possible subshells in the $n = 2$ shell), the next electron for the next-larger atom must go into the $n = 3$ shell, *s* subshell.

Example 8.5

Problem

What is the electron configuration for Na, which has 11 electrons?

Solution

The first two electrons occupy the 1*s* subshell. The next two occupy the 2*s* subshell, while the next six electrons occupy the 2*p* subshell. This gives us 10 electrons so far, with 1 electron left. This last electron goes into the $n = 3$ shell, *s* subshell. Thus, the electron configuration of Na is $1s^2 2s^2 2p^6 3s^1$.

Test Yourself

What is the electron configuration for Mg, which has 12 electrons?

Answer

$1s^2 2s^2 2p^6 3s^2$

For larger atoms, the electron arrangement becomes more complicated. This is because after the 3*p* subshell is filled, filling the 4*s* subshell first actually leads to a lesser overall energy than filling the 3*d* subshell. Recall that while the principal quantum number largely dictates the energy of an electron, the angular momentum quantum number also has an impact on energy; by the time we get to the 3*d* and 4*s* subshells, we see overlap in the filling of the shells. Thus, after the 3*p* subshell is completely filled (which occurs for Ar), the next electron for K occupies the 4*s* subshell, not the 3*d* subshell:

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1, \textbf{ not } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$$

For larger and larger atoms, the order of filling the shells and subshells seems to become even more complicated. There are some useful ways to remember the order, like that shown in Figure 8.08 “Electron Shell Filling Order.” If you follow the arrows in order, they pass through the subshells in the order that they are filled with electrons in larger atoms. Initially, the order is the same as the expected

shell–subshell order, but for larger atoms, there is some shifting around of the principal quantum numbers. However, Figure 8.08 gives a valid ordering of filling subshells with electrons for most atoms.

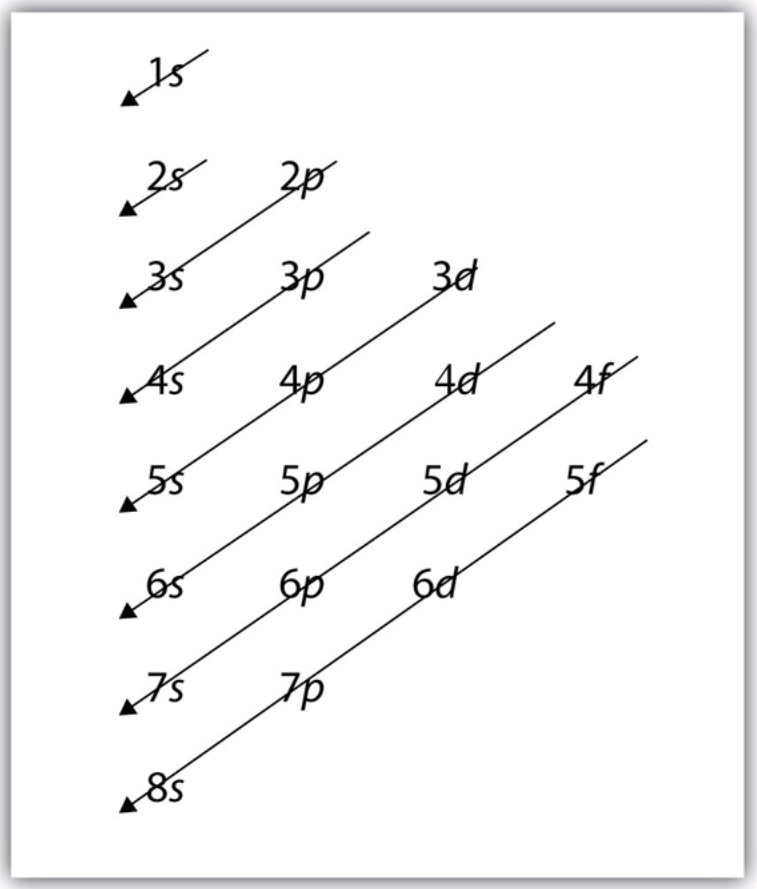

Figure 8.08 "Electron Shell Filling Order." Starting with the top arrow, follow each arrow. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms. The n = 5 and higher shells have more subshells, but only those subshells that are needed to accommodate the electrons of the known elements are given.

Example 8.6

Problem

What is the predicted electron configuration for Sn, which has 50 electrons?

Solution

We will follow the chart in Figure 8.08 "Electron Shell Filling Order" until we can accommodate 50 electrons in the subshells in the proper order:

$$\text{Sn: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$$

Verify by adding the superscripts, which indicate the number of electrons:

$$2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 10 + 2 = 50$$

Therefore, we have placed all 50 electrons in subshells in the proper order.

Test Yourself

What is the electron configuration for Ba, which has 56 electrons?

Answer

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$$

As the previous example demonstrated, electron configurations can get fairly long. An **abbreviated electron configuration** uses one of the elements from the last column of the periodic table, which contains what are called the *noble gases*, to represent the core of electrons up to that element. Then the remaining electrons are listed explicitly. For example, the abbreviated electron configuration for Li, which has three electrons, would be:

$$\text{Li: } [\text{He}]2s^1$$

Where [He] represents the two-electron core that is equivalent to He's electron configuration. The square brackets represent the electron configuration of a noble gas. This is not much of an abbreviation. However, consider the abbreviated electron configuration for W, which has 74 electrons:

$$\text{W: } [\text{Xe}]6s^2 4f^{14} 5d^4$$

This is a significant simplification over an explicit listing of all 74 electrons. So for larger elements, the abbreviated electron configuration can be a very useful shorthand.

Example 8.7

Problem

What is the abbreviated electron configuration for P, which has 15 electrons?

Solution

With 15 electrons, the electron configuration of P is:

$$\text{P: } 1s^2 2s^2 2p^6 3s^2 3p^3$$

The first immediate noble gas is Ne, which has an electron configuration of $1s^2 2s^2 2p^6$. Using the electron configuration of Ne to represent the first 10 electrons, the abbreviated electron configuration of P is:

$$\text{P: } [\text{Ne}]3s^2 3p^3$$

Test Yourself

What is the abbreviated electron configuration for Rb, which has 37 electrons?

Answer

$$[\mathrm{Kr}]5s^1$$

There are some exceptions to the rigorous filling of subshells by electrons. In many cases, an electron goes from a higher-numbered shell to a lower-numbered but later-filled subshell to fill the later-filled subshell. One example is Ag. With 47 electrons, its electron configuration is predicted to be:

$$\mathrm{Ag:}\ [\mathrm{Kr}]5s^2 4d^9$$

However, experiments have shown that the electron configuration is actually:

$$\mathrm{Ag:}\ [\mathrm{Kr}]5s^1 4d^{10}$$

This, then, qualifies as an exception to our expectations. At this point, you do not need to memorize the exceptions; but if you come across one, understand that it is an exception to the normal rules of filling subshells with electrons, which can happen.

Electron Configuration Energy Diagrams

We have just seen that electrons fill orbitals in shells and subshells in a regular pattern, but why does it follow this pattern? There are three principles which should be followed to properly fill electron orbital energy diagrams:

1. The aufbau principle
2. The Pauli exclusion principle
3. Hund's rule

The overall pattern of the electron shell filling order emerges from the **aufbau principle** (German for "building up"): electrons fill the lowest energy orbitals first. Increasing the principle quantum number, *n*, increases orbital energy levels, as the electron density becomes more spread out away from the nucleus. In many-electron atoms (all atoms except hydrogen), the energy levels of subshells varies due to electron-electron repulsions. The trend that emerges is that energy levels increase with value of the angular momentum quantum number, *l*, for orbitals sharing the same principle quantum number, *n*. This is demonstrated in Figure 8.09, where each line represents an orbital, and each set of lines at the same energy represents a subshell of orbitals.

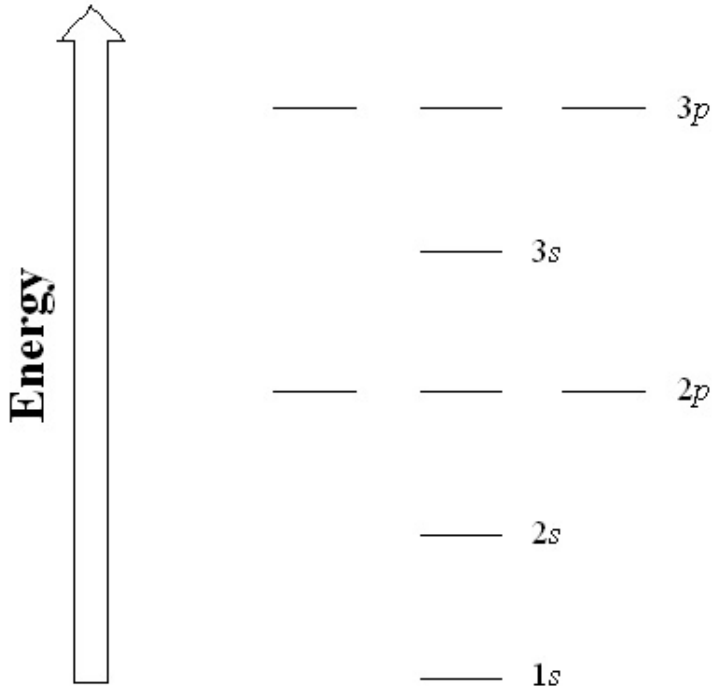

Figure 8.09 "Generic Energy Diagram of Orbitals in a Multi-Electron Atom." [Long Description]

As previously discussed, the Pauli exclusion principle states that we can only fill each orbital with a maximum of two electrons of opposite spin. But how should we fill multiple orbitals of the same energy level within a subshell (e.g., the three orbitals in the 2*p* subshell)? Orbitals of the same energy level are known as degenerate orbitals, and we fill them using **Hund's rule**: place one electron into each degenerate orbital first, before pairing them in the same orbital. Let's examine a few examples to demonstrate the use of the three principles.Boron is atomic number 5, and therefore has 5 electrons. First fill the lowest energy 1*s* orbital with two electrons of opposite spin, then the 2*s* orbital with 2 electrons of opposite spin and finally place the last electron into any of the three degenerate 2*p* orbitals (Figure 8.10).

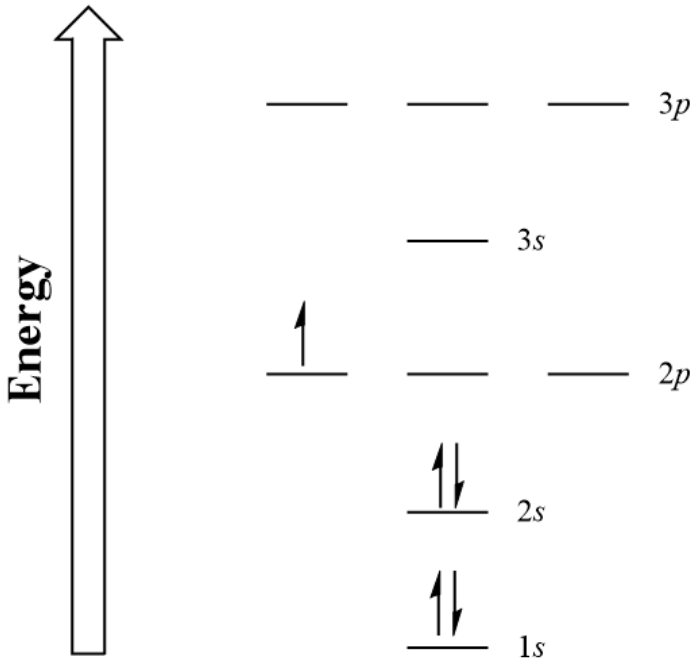

Figure 810 "Boron Electron Configuration Energy Diagram."

Moving across the periodic table, we follow Hund's rule and add an additional electron to each degenerate 2*p* orbital for each subsequent element (Figure 8.11). At oxygen we can finally pair up and fill one of the degenerate 2*p* orbitals.

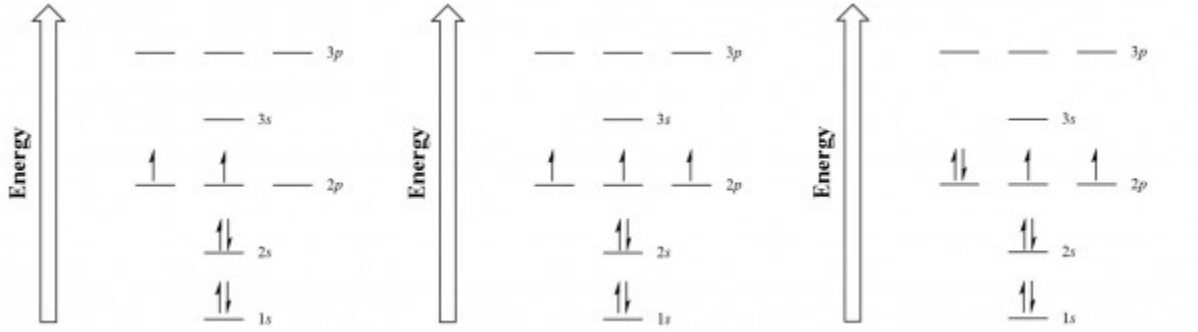

Figure 8.11 "Electron Configuration Energy Diagrams for Carbon, Nitrogen, and Oxygen." [Long Description]

Key Takeaways

- The Pauli exclusion principle limits the number of electrons in the subshells and shells.
- Electrons in larger atoms fill shells and subshells in a regular pattern that we can follow.
- Electron configurations are a shorthand method of indicating what subshells electrons occupy in atoms.
- Abbreviated electron configurations are a simpler way of representing electron configurations for larger atoms.
- Exceptions to the strict filling of subshells with electrons occur.

- Electron configurations are assigned from lowest to highest energy following the aufbau principle
- One electron is placed in each degenerate orbital before pairing electrons following Hund's rule.
- Electron configuration energy diagrams follow three principles: the aufbau principle, the Pauli exclusion principle and Hund's rule.

Exercises

Questions

1. Give two possible sets of four quantum numbers for the electron in an H atom.
2. Give the possible sets of four quantum numbers for the electrons in a Li atom.
3. How many subshells are completely filled with electrons for Na? How many subshells are unfilled?
4. How many subshells are completely filled with electrons for Mg? How many subshells are unfilled?
5. What is the maximum number of electrons in the entire $n = 2$ shell?
6. What is the maximum number of electrons in the entire $n = 4$ shell?
7. Write the complete electron configuration for each atom.
    a. Si, 14 electrons
    b. Sc, 21 electrons
8. Write the complete electron configuration for each atom.
    a. Br, 35 electrons
    b. Be, 4 electrons
9. Write the complete electron configuration for each atom.
    a. Cd, 48 electrons
    b. Mg, 12 electrons
10. Write the complete electron configuration for each atom.
    a. Cs, 55 electrons
    b. Ar, 18 electrons
11. Write the abbreviated electron configuration for each atom in Exercise 7.
12. Write the abbreviated electron configuration for each atom in Exercise 8.
13. Write the abbreviated electron configuration for each atom in Exercise 9.
14. Write the abbreviated electron configuration for each atom in Exercise 10.
15. Draw electron configuration energy diagrams for potassium and bromine.

Answers

1. {1, 0, 0, +½} and {1, 0, 0, −½}
3. Three subshells (1*s*, 2*s*, 2*p*) are completely filled, and one shell (3*s*) is partially filled.

5. 8 electrons

7. a. $1s^2 2s^2 2p^6 3s^2 3p^2$
   b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

9. a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$
   b. $1s^2 2s^2 2p^6 3s^2$

11. a. $[\mathrm{Ne}] 3s^2 3p^2$
    b. $[\mathrm{Ar}] 4s^2 3d^1$

13. a. $[\mathrm{Kr}] 5s^2 4d^{10}$
    b. $[\mathrm{Ne}] 3s^2$

15. Potassium:

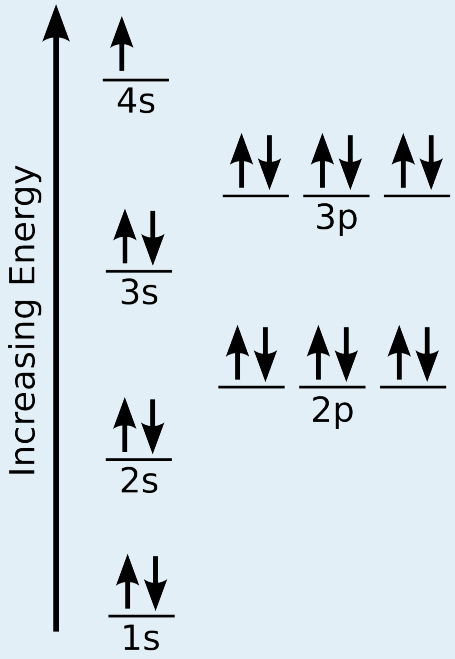

Figure 8.11a "Potassium Electron Configuration."

Bromine:

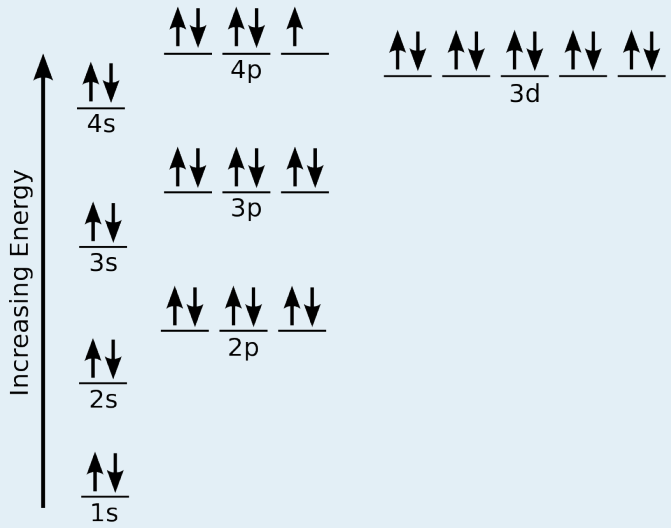

Figure 8.11b "Bromine Electron Configuration."

Long Descriptions

Figure 8.09 description: A blank diagram showing the different subshells of an atom and how many orbitals they contain. Remember that an orbital can hold two electrons. From lowest to highest energy, the subshells shown are:

- 1*s* (one orbital)
- 2*s* (one orbital)
- 2*p* (three orbitals)
- 3*s* (one orbital)
- 3*p* (three orbitals)

[Return to Figure 8.09]

Figure 8.11 description: Electron configuration energy diagrams for carbon, nitrogen, and oxygen.

Carbon's 1*s* and 2*s* subshells are full. In the 2*p* subshell, the first two orbitals have one electron each.

Nitrogen's 1*s* and 2*s* subshells are full. In the 2*p* subshell, each of the three orbitals has one electron.

Oxygen's 1*s* and 2*s* subshells are full. In the 2*p* subshell, the first orbital has two electrons, and the second and third orbitals have one electron each.

[Return to Figure 8.11]

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Electronic Structure and the Periodic Table

Learning Objectives

1. Relate the electron configurations of the elements to the shape of the periodic table.
2. Determine the expected electron configuration of an element by its place on the periodic table.

In Chapter 3 "Atoms, Molecules, and Ions", we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure 8.12 "The Periodic Table." The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

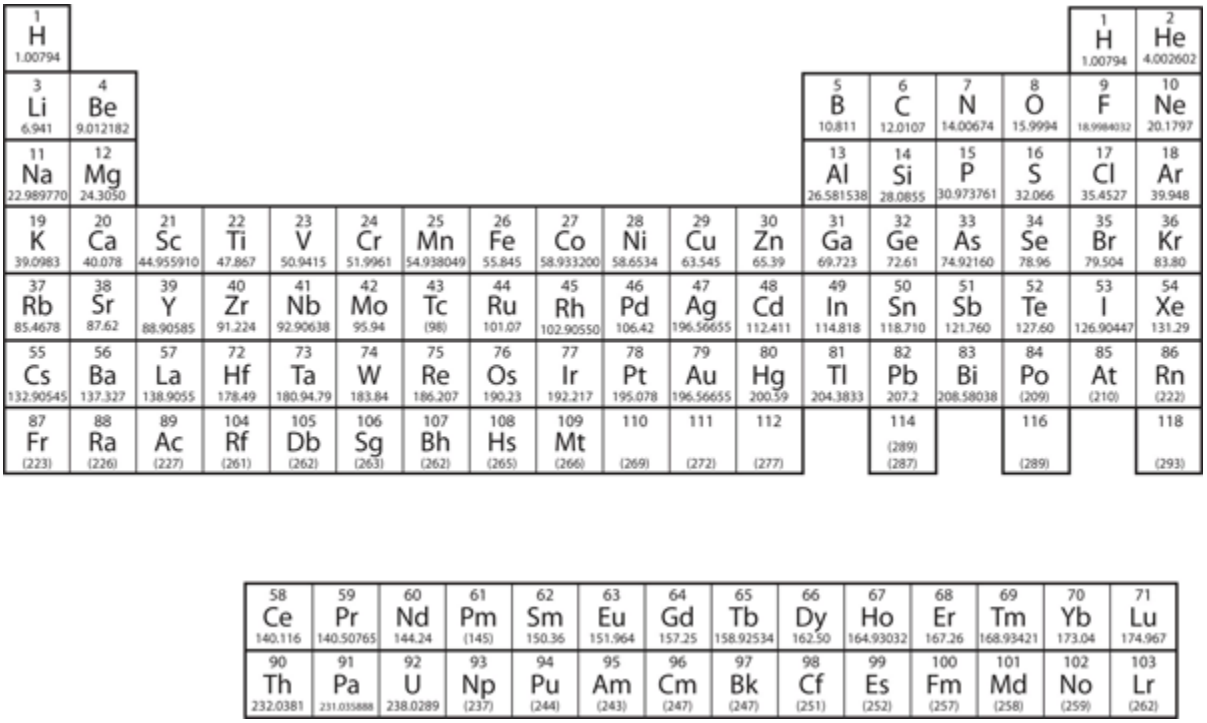

Figure 8.12 "The Periodic Table." View an accessible periodic table online.

Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations: *the shape of the periodic table mimics the filling of the subshells with electrons*.

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the n = 1 shell is filled. These two elements make up the first row of the periodic table (see Figure 8.13 "The 1*s* Subshell").

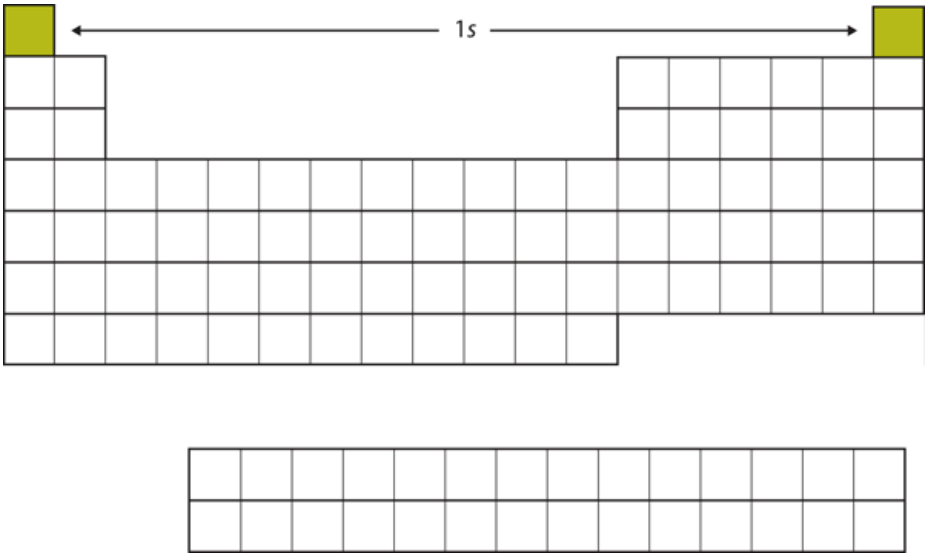

Figure 8.13 "The 1s Subshell." H and He represent the filling of the 1s subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 8.14 "The 2*s* Subshell" shows that these two elements are adjacent on the periodic table.

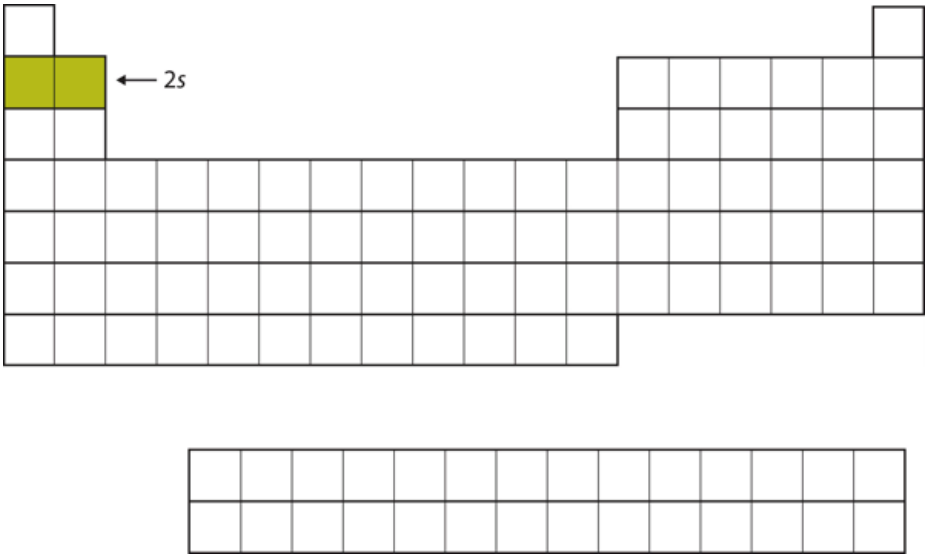

Figure 8.14 "The 2s Subshell." In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 8.15 "The 2*p* Subshell").

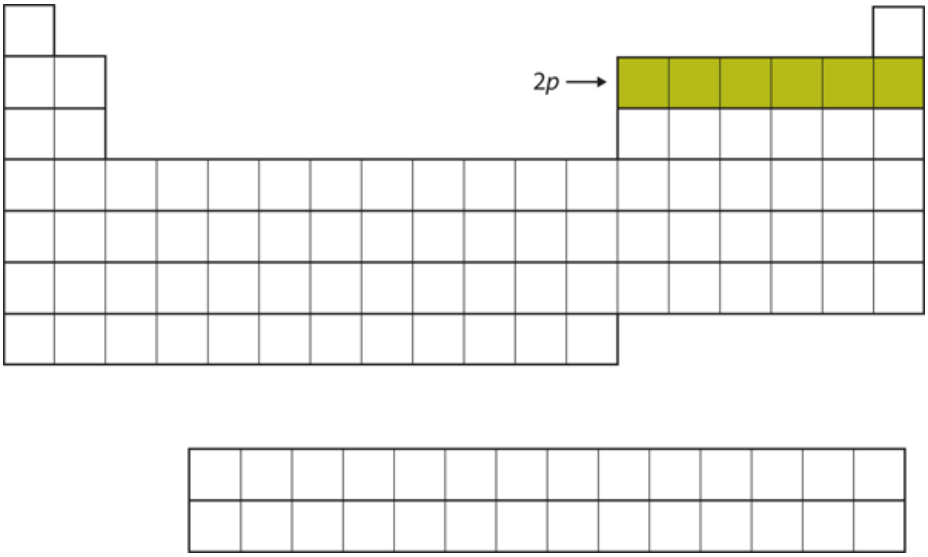

Figure 8.15 "The 2p Subshell." For B through Ne, the 2p subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 8.16 "The 3*s* Subshell").

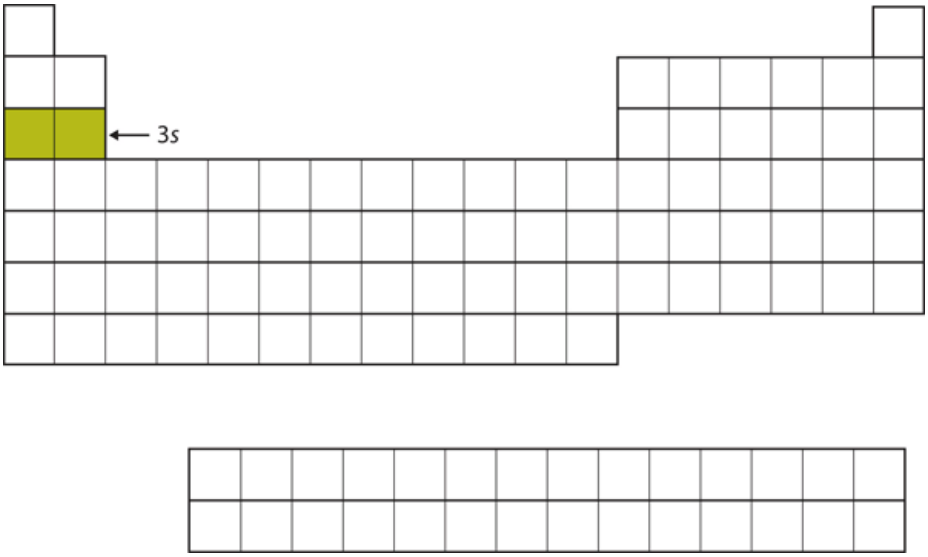

Figure 8.16 "The 3s Subshell." Now the 3s subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 8.17 "The 3*p* Subshell").

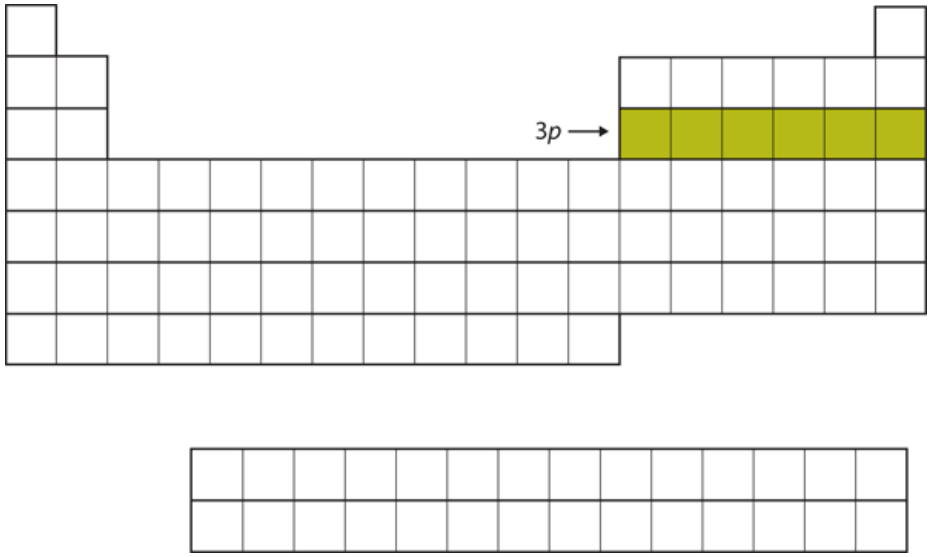

Figure 8.17 "The 3p Subshell." Next, the 3p subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell, which consists of K and Ca (Figure 8.18 "The 4*s* Subshell").

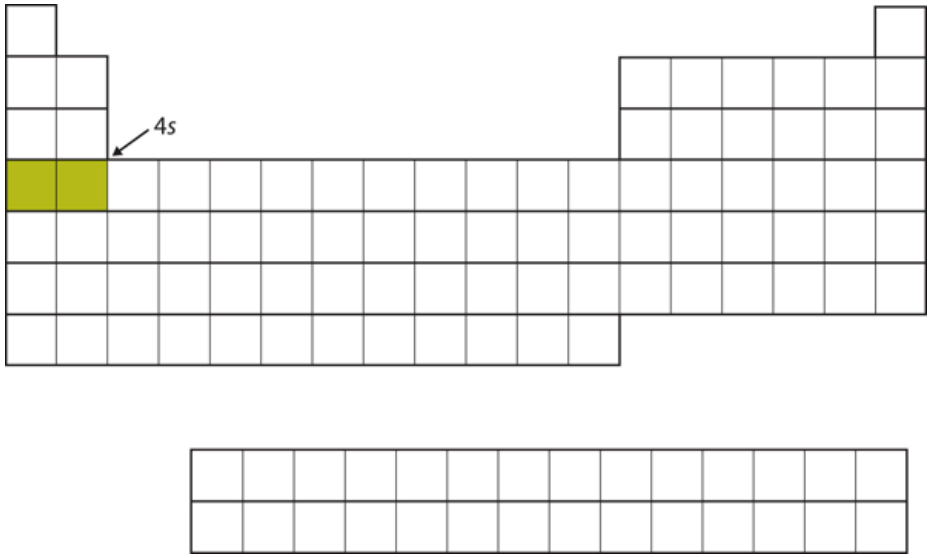

Figure 8.18 "The 4s Subshell." The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table, which consists of Sc to Zn (Figure 8.19 "The 3*d* Subshell").

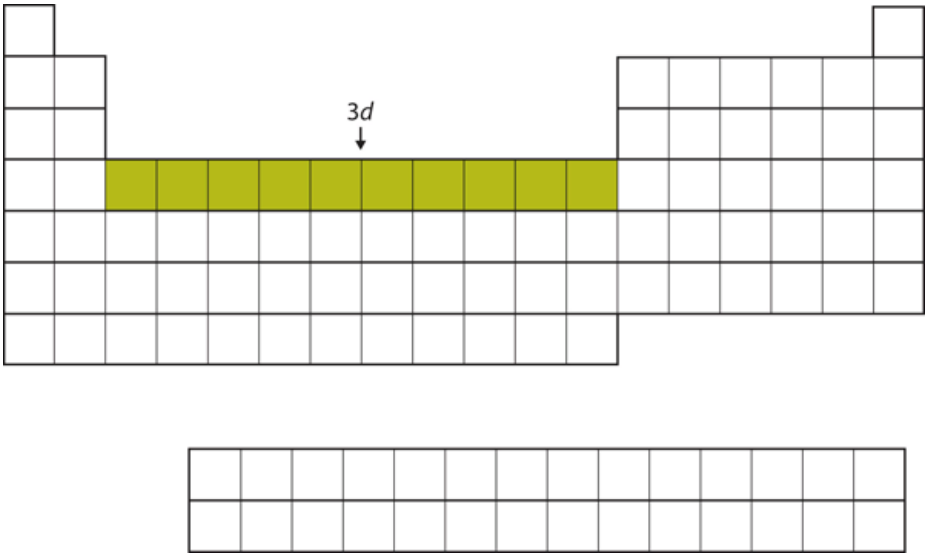

Figure 8.19 "The 3d Subshell." The 3d subshell is filled in the middle section of the periodic table.

And so forth. As we go across the rows of the periodic table, the overall shape of the table outlines how the electrons are occupying the shells and subshells.

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two columns of the periodic table are labelled the ***s* block**. Similarly, the ***p* block** are the right-most six columns of the periodic table, the ***d* block** is the middle 10 columns of the periodic table, while the ***f* block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 8.20 "Blocks on the Periodic Table" shows the blocks of the periodic table.

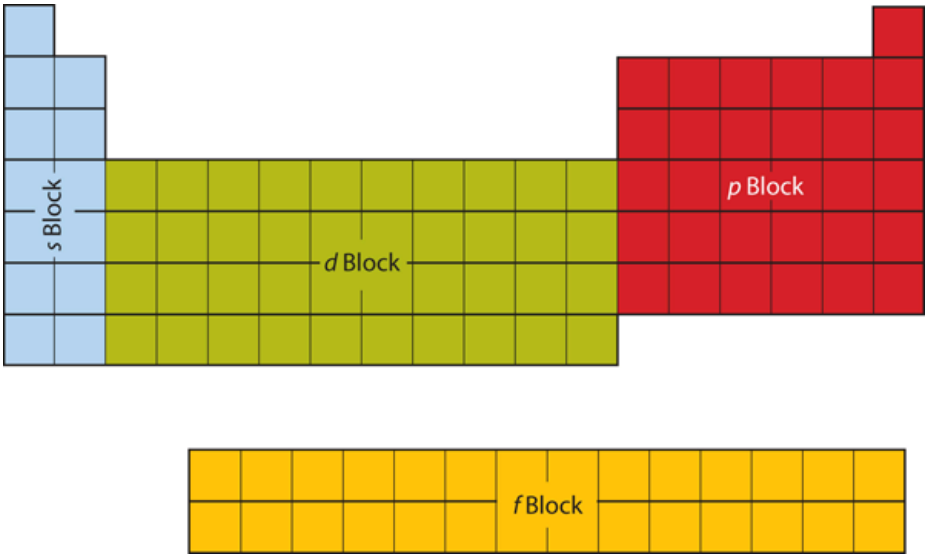

Figure 8.20 "Blocks on the Periodic Table." The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

Table 8.4 Electron Configurations of Elements in the First Column of the Periodic Table

Element	Electron Configuration
H	$1s^1$
Li	$1s^2 2s^1$
Na	[Ne]$3s^1$
K	[Ar]$4s^1$
Rb	[Kr]$5s^1$
Cs	[Xe]$6s^1$

They all have a similar electron configuration in their valence shells: a single *s* electron. Because much of the chemistry of an element is influenced by valence electrons, we would expect that these elements would have similar chemistry — *and they do*. The organization of electrons in atoms explains not only the shape of the periodic table but also the fact that elements in the same column of the periodic table have similar chemistry.

The same concept applies to the other columns of the periodic table. Elements in each column have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the *s* and *p* blocks. In the *d* and *f* blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 8.21 "Selenium on the Periodic Table." It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is [Ar]$4s^2 3d^{10} 4p^4$, as expected.

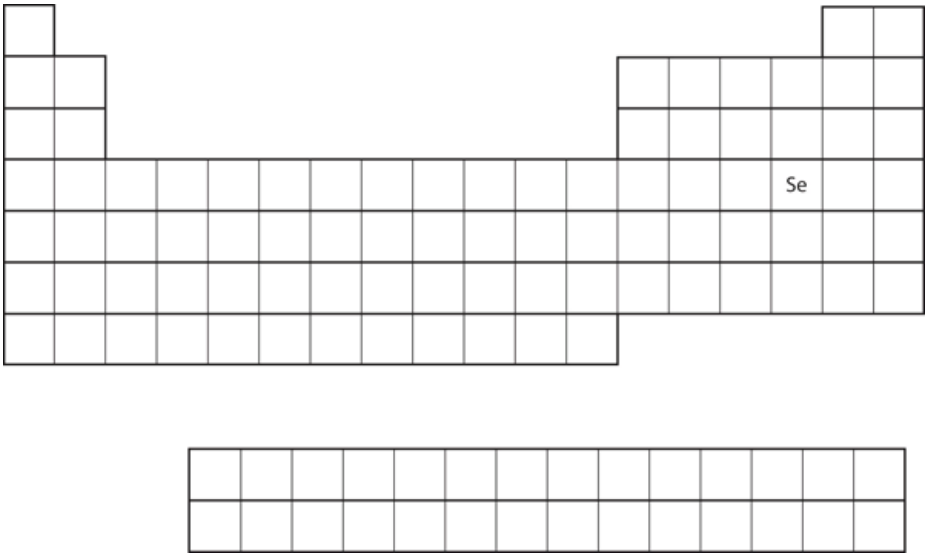

Figure 8.21 "Selenium on the Periodic Table."

Example 8.5

Problem

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. See Figure 8.22 "Various Elements on the Periodic Table."

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the *s* block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is [Ar]$4s^2$.
2. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in p^2. Tin's electron configuration is [Kr]$5s^2 4d^{10} 5p^2$.

Test Yourself

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. See Figure 8.22.

1. Ti
2. Cl

Answer

1. [Ar]$4s^2 3d^2$
2. [Ne]$3s^2 3p^5$

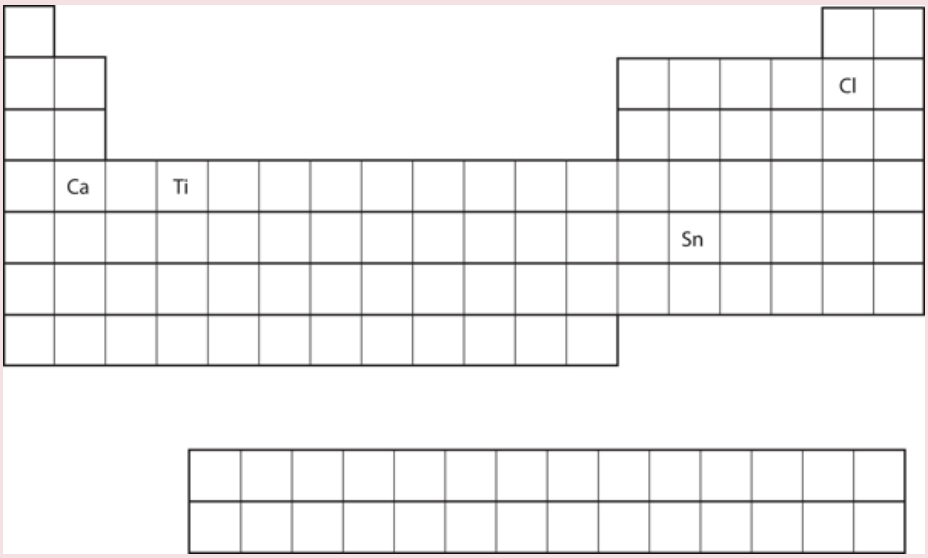

Figure 8.22 "Various Elements on the Periodic Table." [Long Description]

Food and Drink App: Artificial Colours

The colour of objects comes from a different mechanism than the colours of neon and other discharge lights. Although coloured lights produce their colours, objects are coloured because they preferentially reflect a certain colour from the white light that shines on them. A red tomato, for example, is bright red because it reflects red light while absorbing all the other colours of the rainbow.

Many foods, such as tomatoes, are highly coloured; in fact, the common statement "you eat with your eyes first" is an implicit recognition that the visual appeal of food is just as important as its taste. But what about processed foods?

Many processed foods have food colourings added to them. There are two types of food colourings: natural and artificial. Natural food colourings include caramelized sugar for brown; annatto, turmeric, and saffron for various shades of orange or yellow; betanin from beets for purple; and even carmine, a deep red dye that is extracted from the cochineal, a small insect that is a parasite on cacti in Central and South America. (That's right: you may be eating bug juice!)

Some colourings are artificial. In the United States, the Food and Drug Administration currently approves only seven compounds as artificial colourings in food, beverages, and cosmetics:

1. FD&C Blue #1: Brilliant Blue FCF
2. FD&C Blue #2: Indigotine
3. FD&C Green #3: Fast Green FCF
4. RD&C Red #3: Erythrosine
5. FD&C Red #40: Allura Red AC
6. FD&C Yellow #5: Tartrazine
7. FD&C Yellow #6: Sunset Yellow FCF

Lower-numbered colours are no longer on the market or have been removed for various reasons. Typically, these artificial colourings are large molecules that absorb certain colours of light very strongly, making them useful even at very low concentrations in foods and cosmetics. Even at such low amounts, some critics claim that a small portion of the population (especially children) is sensitive to artificial colourings and urge that their use be curtailed or halted. However, formal studies

of artificial colourings and their effects on behaviour have been inconclusive or contradictory. Despite this, most people continue to enjoy processed foods with artificial colouring (like those shown in the accompanying figure).

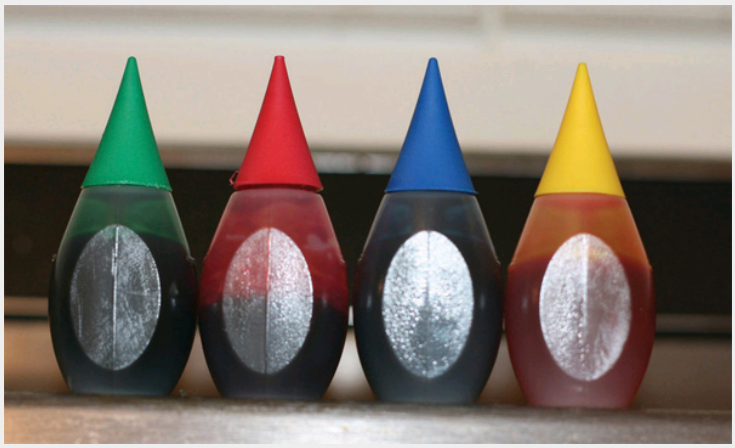

Figure 8.22a "Food Colouring." Artificial food colourings are found in a variety of food products, such as processed foods, candies, and egg dyes. Even pet foods have artificial food colouring in them, although it's likely that the animal doesn't care!

Key Takeaways

- The arrangement of electrons in atoms is responsible for the shape of the periodic table.
- Electron configurations can be predicted by the position of an atom on the periodic table.

Exercises

Questions

1. Where on the periodic table are *s* subshells being occupied by electrons?
2. Where on the periodic table are *d* subshells being occupied by electrons?
3. In what block is Ra found?
4. In what block is Br found?
5. What are the valence shell electron configurations of the elements in the second column of the periodic table?
6. What are the valence shell electron configurations of the elements in the next-to-last column of the periodic table?
7. What are the valence shell electron configurations of the elements in the first column of the *p* block?
8. What are the valence shell electron configurations of the elements in the last column of the *p* block?
9. From the element's position on the periodic table, predict the electron configuration of each of the following atoms:
    a. Sr
    b. S

10. From the element's position on the periodic table, predict the electron configuration of each of the following atoms:
    a. Fe
    b. Ba
11. From the element's position on the periodic table, predict the electron configuration of each of the following atoms:
    a. V
    b. Ar
12. From the element's position on the periodic table, predict the electron configuration of each of the following atoms:
    a. Cl
    b. K
13. From the element's position on the periodic table, predict the electron configuration of each of the following atoms:
    a. Ge
    b. C
14. From the element's position on the periodic table, predict the electron configuration of each of the following atoms:
    a. Mg
    b. I

Answers

1. the first two columns
3. the *s* block
5. ns^2
7. ns^2np^1
9. a. $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$
   b. $1s^22s^22p^63s^23p^4$
11. a. $1s^22s^22p^63s^23p^64s^23d^3$
    b. $1s^22s^22p^63s^23p^6$
13. a. $1s^22s^22p^63s^23p^64s^23d^{10}4p^2$
    b. $1s^22s^22p^2$

Long Descriptions

Figure 8.22 description: Various elements on the periodic table.

Ca (calcium) is in the second column from the left and the fourth row.

Ti (titanium) is in the fourth column from the left and the fourth row.

Cl (chlorine) is in the second column from the right and the second row.

Sn (tin) is in the fifth column from the right and the fifth row.

[Return to Figure 8.22]

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Periodic Trends

Learning Objectives

1. Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

One of the reasons the periodic table is so useful is because its structure allows us to qualitatively determine how some properties of the elements vary versus their position on the periodic table. The variation of properties versus position on the periodic table is called **periodic trends**. There is no other tool in science that allows us to judge relative properties of a class of objects like this, which makes the periodic table a very useful tool. Many periodic trends are general. There may be a few points where an opposite trend is seen, but there is an overall trend when considered across a whole row or down a whole column of the periodic table.

Effective Nuclear Charge

Many of the periodic properties of atoms depend on electron configuration; in particular, the valence electrons and their level of attraction to the nucleus.

Valence electrons are simultaneously attracted to the positive charge of the nucleus and screened (repelled) by the negative charges of other electrons. This net nuclear charge felt by valence electrons is known as its **effective nuclear charge**, Z_{eff} (pronounced “zed-effective”). The effective nuclear charge is always less than the actual nuclear charge, and can be roughly estimated using the following equation:

$$Z_{\text{eff}} = Z - S$$

Where Z is the nuclear charge (equal to the number of protons), and S is the screening constant which can be approximated to the number of non-valence or “core” electrons.

For example: try to approximate the effective nuclear charge of magnesium.

First, we must determine the electron configuration of magnesium to determine the number of core electrons:

$$\text{Mg} = 1s^2 2s^2 2p^6 3s^2 = [\text{Ne}]3s^2$$

Therefore, magnesium has 10 core electrons from its $1s^2$, $2s^2$, and $2p^6$ orbitals.

Magnesium is element 12, so it has 12 protons and a nuclear charge of 12:

$$Z_{\text{eff}} = 12 - 10$$
$$Z_{\text{eff}} = \ \ 2+$$

Moving left to right across a period on the periodic table, each subsequent element has an additional proton and valence electron, but the core electrons which are responsible for the majority of screening remain the same. This results in a trend that in general the effective nuclear charge increases from left to right across any period of the periodic table.

Moving from top to bottom down a column of the periodic table, we might expect the elements to have a similar effective nuclear charge as they all have the same number of valence electrons. However, we actually see a slight increase in Z_{eff} moving down a column of the periodic table. As the principal quantum number (n) increases, the orbital size increases making the core electron clouds more spread out. These core electron clouds that are more diffuse do not screen as well, giving a slight increase to Z_{eff} (see Figure 8.23 "Increasing Effective Nuclear Charge").

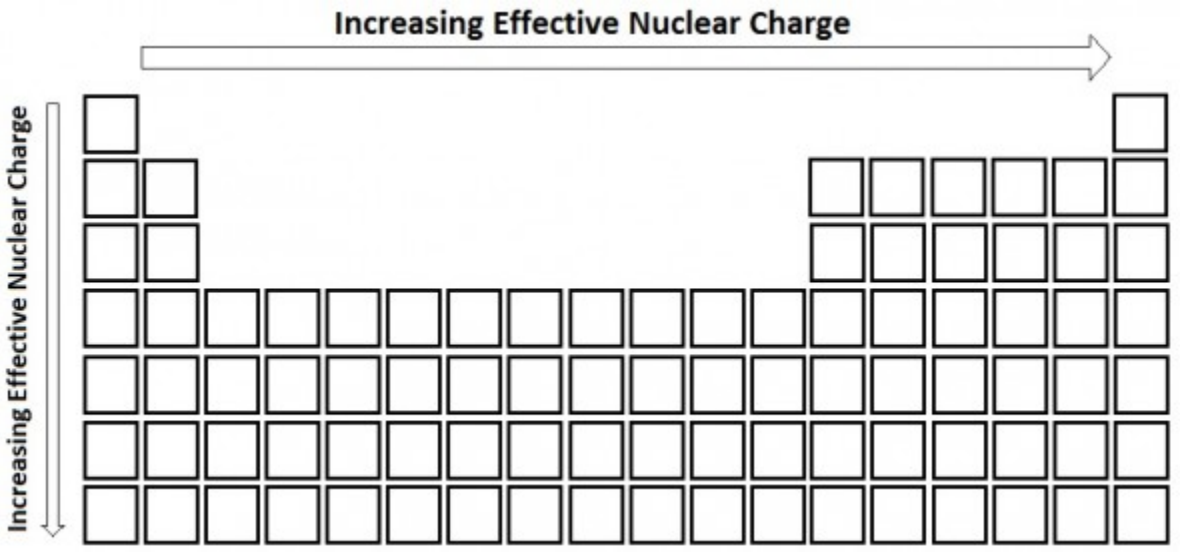

Figure 8.23 "Increasing Effective Nuclear Charge." The periodic trend for effective nuclear charge.

Atomic Radii

The **atomic radius** is an indication of the size of an atom. Although the concept of a definite radius of an atom is a bit fuzzy, atoms behave as if they have a certain radius. Such radii can be estimated from various experimental techniques, such as the x-ray crystallography of crystals.

As you go down a column of the periodic table, the atomic radii increase. This is because the valence electron shell is getting a larger and there is a larger principal quantum number, so the valence shell lies physically farther away from the nucleus. This trend can be summarized as follows:

$$\text{as } \downarrow \text{PT, atomic radius} \uparrow$$

Where PT stands for "periodic table." Going across a row on the periodic table, left to right, the trend is different. This is because although the valence shell maintains the same principal quantum number, the number of protons — and hence the nuclear charge — is increasing as you go across the row. The

increasing positive charge leads to a larger effective nuclear charge which casts a tighter grip on the valence electrons, so as you go across the periodic table, the atomic radii decrease. Again, we can summarize this trend as follows:

$$\text{as } \rightarrow \text{PT, atomic radius } \downarrow$$

Figure 8.24 "Atomic Radii Trends on the Periodic Table" shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

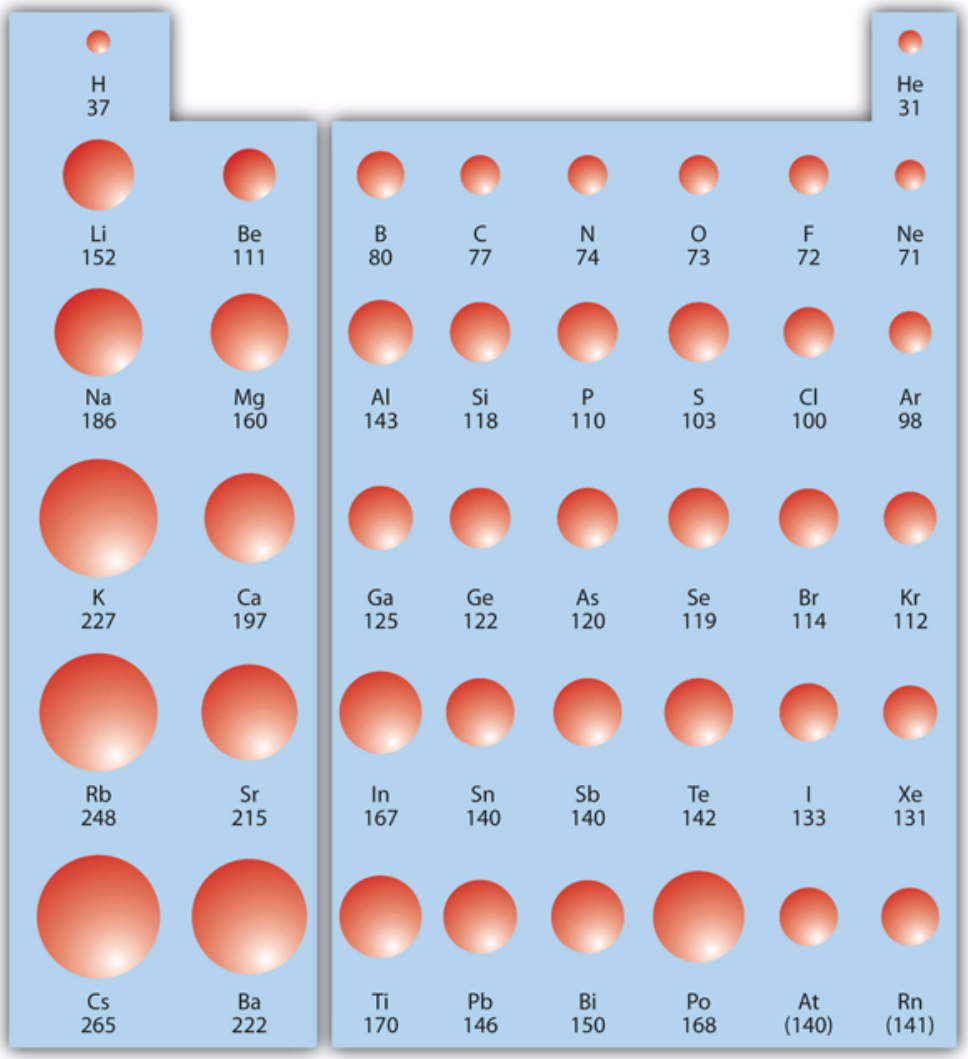

Figure 8.24 "Atomic Radii Trends on the Periodic Table." Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm. [Long Description]

Example 8.9

Problems

Referring only to a periodic table and not to Figure 8.24 “Atomic Radii Trends on the Periodic Table,” which atom is larger in each pair?

1. Si or S
2. S or Te

Solutions

1. Si is to the left of S on the periodic table, so it is larger because as you go across the row, the atoms get smaller.
2. S is above Te on the periodic table, so Te is larger because as you go down the column, the atoms get larger.

Test Yourself

Referring only to a periodic table and not to Figure 8.24 “Atomic Radii Trends on the Periodic Table,” which atom is smaller, Ca or Br?

Answer

Br

Ionization Energy

Ionization energy (IE) is the amount of energy required to remove an electron from an atom in the gas phase:

$$\mathrm{A\,(g)} \rightarrow \mathrm{A^{+}(g)} + \mathrm{e^{-}} \qquad \Delta H \equiv \mathrm{IE}$$

IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus:

$$\text{as} \ \downarrow \mathrm{PT}, \ \mathrm{IE} \downarrow$$

However, as you go across the periodic table and the electrons get drawn closer in, it takes more energy to remove an electron; as a result, IE increases:

$$\text{as} \ \rightarrow \mathrm{PT}, \ \mathrm{IE} \uparrow$$

Figure 8.25 “Ionization Energy Trends on the Periodic Table” shows values of IE versus position on the periodic table. Again, the trend isn’t absolute, but the general trends going across and down the periodic table should be obvious.

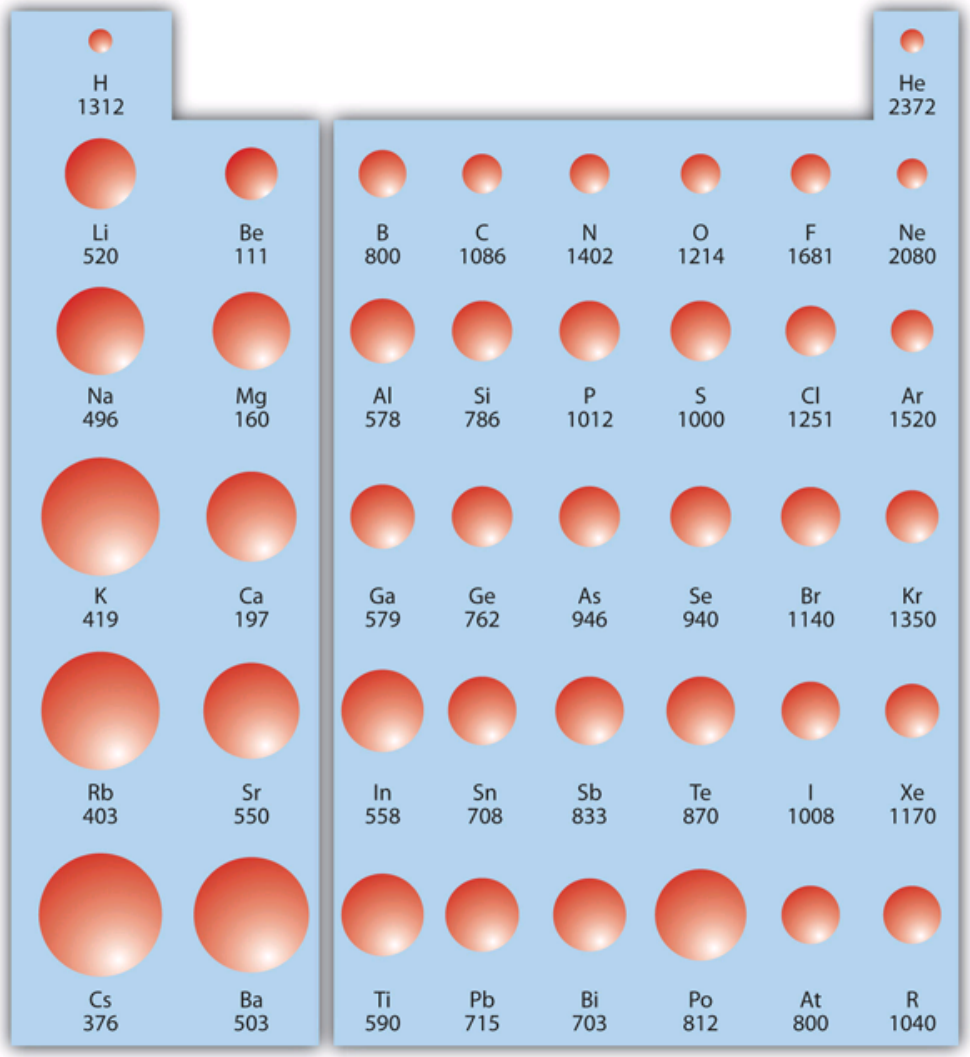

Figure 8.25 "Ionization Energy on the Periodic Table." Values are in kJ/mol. [Long Description]

IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

$$\begin{aligned} \text{IE}_1 \quad & \text{A}(\text{g}) \quad \rightarrow \quad \text{A}^{+}(\text{g}) + \text{e}^- \\ \text{IE}_2 \quad & \text{A}^{+}(\text{g}) \quad \rightarrow \quad \text{A}^{2+}(\text{g}) + \text{e}^- \\ \text{IE}_3 \quad & \text{A}^{2+}(\text{g}) \quad \rightarrow \quad \text{A}^{3+}(\text{g}) + \text{e}^- \end{aligned}$$

And so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^2 2s^2 2p^6 3s^2$:

$$\begin{array}{lllll} \mathrm{IE}_1 = & 738\ \mathrm{kJ/mol} & \mathrm{Mg(g)} & \rightarrow & \mathrm{Mg}^{+}\mathrm{(g)} + \mathrm{e}^{-} \\ \mathrm{IE}_2 = & 1,450\ \mathrm{kJ/mol} & \mathrm{Mg}^{+}\mathrm{(g)} & \rightarrow & \mathrm{Mg}^{2+}\mathrm{(g)} + \mathrm{e}^{-} \\ \mathrm{IE}_3 = & 7,734\ \mathrm{kJ/mol} & \mathrm{Mg}^{2+}\mathrm{(g)} & \rightarrow & \mathrm{Mg}^{3+}\mathrm{(g)} + \mathrm{e}^{-} \end{array}$$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3*s* subshell, but the third electron has to be removed from the $n = 2$ shell (specifically, the 2*p* subshell, which is lower in energy than the $n = 3$ shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. It is trends like this that demonstrate that electrons are organized in atoms in groups.

Example 8.10

Problems

Which atom in each pair has the larger IE?

1. Ca or Sr
2. K or K^+

Solutions

1. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
2. Because K^+ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in K^+ to be removed comes from another shell.

Test Yourself

Which atom has the lower ionization energy, C or F?

Answer

C

Electron Affinity

The opposite of IE is described by **electron affinity (EA)**, which is the energy change when a gas-phase atom accepts an electron:

$$\mathrm{A(g)} + \mathrm{e}^{-} \rightarrow \mathrm{A}^{-}\mathrm{(g)} \qquad \Delta H \equiv \mathrm{EA}$$

EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

$$\text{as} \rightarrow \text{PT, EA} \uparrow$$

There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure 8.26 “Electron Affinity on the Periodic Table” shows EA values versus position on the periodic table for the *s*– and *p*-block elements. The trend isn’t absolute, especially considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.

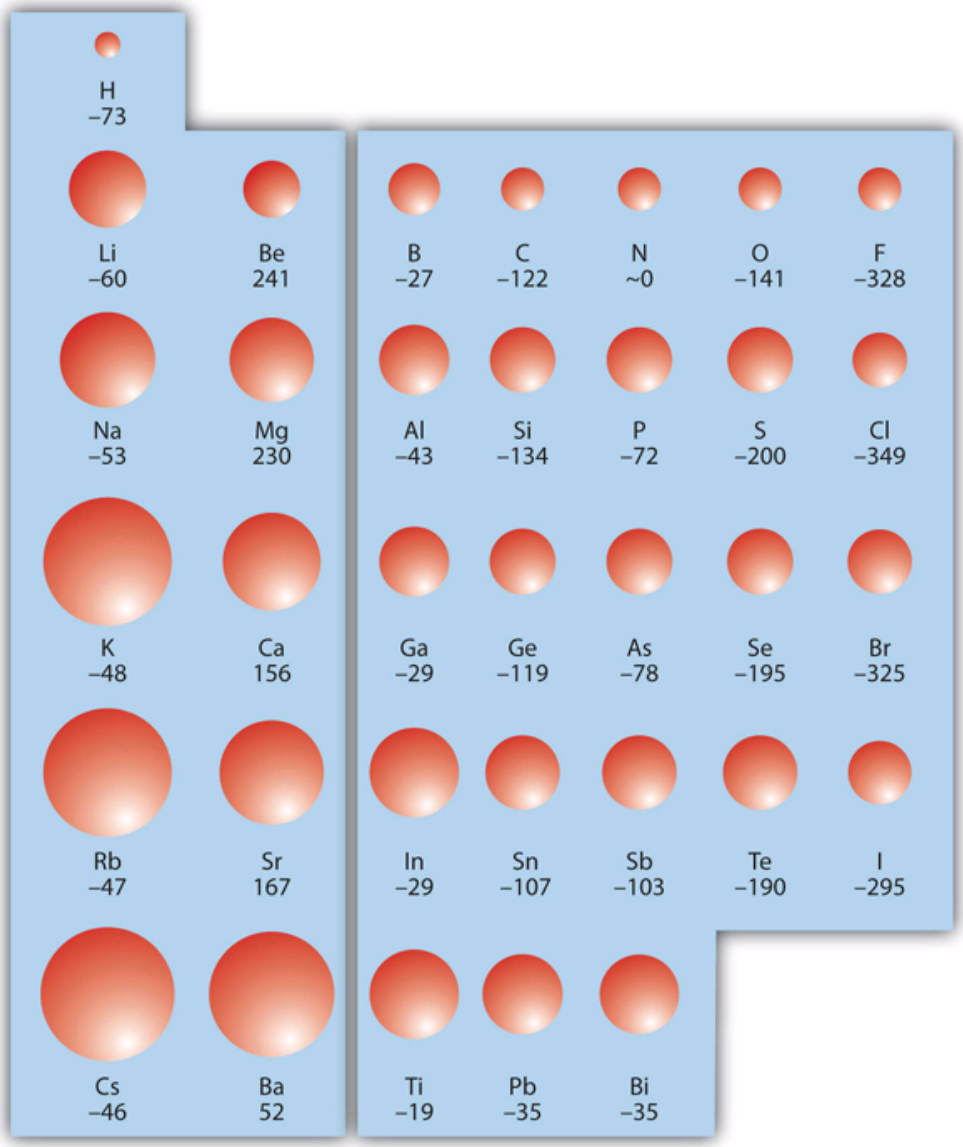

Figure 8.26 “Electron Affinity on the Periodic Table.” Values are in kJ/mol. [Long Description]

Example 8.11

Problems

Predict which atom in each pair will have the highest magnitude of EA.

1. C or F
2. Na or S

Solutions

1. C and F are in the same row on the periodic table, but F is farther to the right. Therefore, F should have the larger magnitude of EA.
2. Na and S are in the same row on the periodic table, but S is farther to the right. Therefore, S should have the larger magnitude of EA.

Test Yourself

Predict which atom will have the highest magnitude of EA, As or Br.

Answer

Br

Key Takeaways

- Certain properties — notably effective nuclear charge, atomic radius, IE, and EA — can be qualitatively understood by the positions of the elements on the periodic table.

Exercises

Questions

1. Write a chemical equation with an IE energy change.
2. Write a chemical equation with an EA energy change.
3. State the trends in atomic radii as you go across and down the periodic table.
4. State the trends in IE as you go across and down the periodic table.
5. Which atom of each pair is larger?
    a. Na or Cs

b. N or Bi

6. Which atom of each pair is larger?

   a. C or Ge
   b. Be or Ba

7. Which atom of each pair is larger?

   a. K or Cl
   b. Ba or Bi

8. Which atom of each pair is larger?

   a. Si or S
   b. H or He

9. Which atom has the higher IE?

   a. Na or S
   b. Ge or Br

10. Which atom has the higher IE?

    a. C or Ne
    b. Rb or I

11. Which atom has the higher IE?

    a. Li or Cs
    b. Se or O

12. Which atom has the higher IE?

    a. Al or Ga
    b. F or I

13. A third-row element has the following successive IEs: 738; 1,450; 7,734; and 10,550 kJ/mol. Identify the element.
14. A third-row element has the following successive IEs: 1,012; 1,903; 2,912; 4,940; 6,270; and 21,300 kJ/mol. Identify the element.
15. For which successive IE is there a large jump in IE for Ca?
16. For which successive IE is there a large jump in IE for Al?
17. Which atom has the greater magnitude of EA?

    a. C or F
    b. Al or Cl

18. Which atom has the greater magnitude of EA?

    a. K or Br
    b. Mg or S

Answers

1. $\mathrm{Na(g)} \rightarrow \mathrm{Na^{+}(g)} + \mathrm{e^{-}} \qquad \Delta H = \mathrm{IE}$ (answers will vary)
3. As you go across, atomic radii decrease; as you go down, atomic radii increase.

5. a. Cs
   b. Bi
7. a. K
   b. Ba
9. a. S
   b. Br
11. a. Li
    b. O
13. Mg
15. The third IE shows a large jump in Ca.
17. a. F
    b. Cl

Long Descriptions

Figure 8.24 description: Chart of atomic radii trends on the periodic table. The data has been compiled in the following table:

Table 8.5 Atomic Radii Trends on the Periodic Table

Row	Element	Atomic Radius (picometres)
First	H	37
First	He	31
Second	Li	152
Second	Be	111
Second	B	80
Second	C	77
Second	N	74
Second	O	73
Second	F	72
Second	Ne	71
Third	Na	186
Third	Mg	160
Third	Al	143
Third	Si	118
Third	P	110
Third	S	103
Third	Cl	100
Third	Ar	98
Fourth	K	227
Fourth	Ca	197
Fourth	Ga	125
Fourth	Ge	122
Fourth	As	120
Fourth	Se	119
Fourth	Br	114
Fourth	Kr	112
Fifth	Rb	248
Fifth	Sr	215

Fifth	In	167
Fifth	Sn	140
Fifth	Sb	140
Fifth	Te	142
Fifth	I	133
Fifth	Xe	131
Sixth	Cs	265
Sixth	Ba	222
Sixth	Ti	170
Sixth	Pb	146
Sixth	Bi	150
Sixth	Po	168
Sixth	At	(140)
Sixth	Rn	(141)

[Return to Figure 8.24]

Figure 8.25 description: Chart of ionization energy on the periodic table. The data has been compiled in the following table:

Table 8.6 Ionization Energy on the Periodic Table

Row	Element	Ionization Energy (kJ/mol)
First	H	1312
First	He	2372
Second	Li	520
Second	Be	111
Second	B	800
Second	C	1086
Second	N	1402
Second	O	1214
Second	F	1681
Second	Ne	2080
Third	Na	496
Third	Mg	160
Third	Al	578
Third	Si	786
Third	P	1012
Third	S	1000
Third	Cl	1251
Third	Ar	1520
Fourth	K	419
Fourth	Ca	197
Fourth	Ga	579
Fourth	Ge	762
Fourth	As	946
Fourth	Se	940
Fourth	Br	1140
Fourth	Kr	1350
Fifth	Rb	403
Fifth	Sr	550

Fifth	In	558
Fifth	Sn	708
Fifth	Sb	833
Fifth	Te	870
Fifth	I	1008
Fifth	Xe	1170
Sixth	Cs	376
Sixth	Ba	503
Sixth	Ti	590
Sixth	Pb	715
Sixth	Bi	703
Sixth	Po	812
Sixth	At	800
Sixth	Rn	1040

[Return to Figure 8.25]

Figure 8.26 description: Chart of electron affinity on the periodic table. The data has been compiled in the following table:

Table 8.7 Electron Affinity on the Periodic Table

Row	Element	Electron Affinity (kJ/mol)
First	H	−73
Second	Li	−60
Second	Be	241
Second	B	−27
Second	C	−122
Second	N	~0
Second	O	−141
Second	F	−328
Third	Na	−53
Third	Mg	230
Third	Al	−43
Third	Si	−134
Third	P	−72
Third	S	−200
Third	Cl	−349
Fourth	K	−48
Fourth	Ca	156
Fourth	Ga	−29
Fourth	Ge	−119
Fourth	As	−78
Fourth	Se	−195
Fourth	Br	−325
Fifth	Rb	−47
Fifth	Sr	167
Fifth	In	−29
Fifth	Sn	−107
Fifth	Sb	−103
Fifth	Te	−190

Fifth	I	−295
Sixth	Cs	−46
Sixth	Ba	52
Sixth	Ti	−19
Sixth	Pb	−35
Sixth	Bi	−35

[Return to Figure 8.26]

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End-of-Chapter Material

Additional Exercises

1. What is the frequency of light if its wavelength is 1.00 m?
2. What is the wavelength of light if its frequency is 1.00 s^{-1}?
3. What is the energy of a photon if its wavelength is 1.00 m?
4. What is the energy of a photon if its frequency is 1.00 s^{-1}?
5. If visible light is defined by the wavelength limits of 400 nm and 700 nm, what is the energy range for visible light photons?
6. Domestic microwave ovens use microwaves that have a wavelength of 122 mm. What is the energy of one photon of this microwave?
7. Use the equation for the wavelengths of the lines of light in the H atom spectrum to calculate the wavelength of light emitted when n is 7 and 8.
8. Use the equation for the wavelengths of the lines of light in the H atom spectrum to calculate the wavelengths of light emitted when n is 5 and 6.
9. Make a table of all the possible values of the four quantum numbers when the principal quantum number $n = 5$.
10. Make a table of all the possible values of m_ℓ and m_s when $\ell = 4$. What is the lowest value of the principal quantum number for this to occur?
11. a. Predict the electron configurations of Sc through Zn.
    b. From a source of actual electron configurations, determine how many exceptions there are from your predictions in part a.
12. a. Predict the electron configurations of Ga through Kr.
    b. From a source of actual electron configurations, determine how many exceptions there are from your predictions in part a.
13. Recently, Russian chemists reported experimental evidence of element 117. Use the periodic table to predict its valence shell electron configuration.
14. Bi (atomic number 83) is used in some stomach discomfort relievers. Using its place on the periodic table, predict its valence shell electron configuration.
15. Which atom has a higher ionization energy (IE), O or P?
16. Which atom has a higher IE, F or As?
17. Which atom has a smaller radius, As or Cl?
18. Which atom has a smaller radius, K or F?
19. How many IEs does an H atom have? Write the chemical reactions for the successive ionizations.
20. How many IEs does a Be atom have? Write the chemical reactions for the successive ionizations.
21. Based on what you know of electrical charges, do you expect Na^+ to be larger or smaller than Na?
22. Based on what you know of electrical charges, do you expect Cl^- to be larger or smaller than Cl?

Answers

1. $3.00 \times 10^{8}\ s^{-1}$
3. 1.99×10^{-22} J
5. 4.97×10^{-19} J to 2.84×10^{-19} J
7. 3.97×10^{-7} m and 3.89×10^{-7} m, respectively
9. **Table 8.8 All Possible Quantum Number Values When $n = 5$**

ℓ	m_ℓ	m_s
0	0	½ or −½
1	−1, 0, or 1	½ or −½
2	−2, −1, 0, 1, or 2	½ or −½
3	−3, −2, −1, 0, 1, 2, or 3	½ or −½
4	−4, −3, −2, −1, 0, 1, 2, 3, or 4	½ or −½

11. a. The electron configurations are predicted to end in $3d^1$, $3d^2$, $3d^3$, $3d^4$, $3d^5$, $3d^6$, $3d^7$, $3d^8$, $3d^9$, and $3d^{10}$.
    b. Cr and Cu are exceptions.
13. Element 117's valence shell electron configuration should be $7s^2 7p^5$.
15. O
17. Cl
19. H has only one IE: $H \rightarrow H^+ + e^-$
21. smaller

Chapter 9. Chemical Bonds

Diamond is the hardest natural material known on Earth. Yet diamond is just pure carbon. What is special about this element that makes diamond so hard?

Bonds. Chemical bonds.

In a perfect diamond crystal, each C atom makes four connections — bonds — to four other C atoms in a three-dimensional matrix. Four is the greatest number of bonds that is commonly made by atoms, so C atoms maximize their interactions with other atoms. This three-dimensional array of connections extends throughout the diamond crystal, making it essentially one large molecule. Breaking a diamond means breaking every bond at once.

Also, the bonds are moderately strong. There are stronger interactions known, but the carbon-carbon connection is fairly strong itself. Not only does a person have to break many connections at once, but also the bonds are strong connections from the start.

There are other substances that have bonding arrangements similar to those of the diamond. Silicon dioxide and boron nitride have some similarities, but neither of them comes close to the ultimate hardness of diamond.

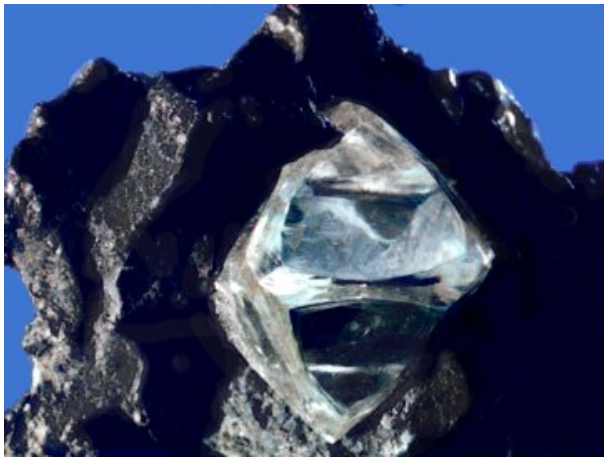


Figure 9.0 “Rough Diamond.” Diamond is the hardest known natural substance and is composed solely of the element carbon.

How do atoms make compounds? Typically they join together in such a way that they lose their identities as elements and adopt a new identity as a compound. These joins are called *chemical bonds*. But how do atoms join together? Ultimately, it all comes down to electrons. Before we discuss how electrons interact, we need to introduce a tool to simply illustrate electrons in an atom.

Media Attributions

- "Rough Diamond" by United States Geological Survey © Public Domain

Lewis Electron Dot Diagrams

Learning Objectives

1. Draw a Lewis electron dot diagram for an atom or a monatomic ion.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

A **Lewis electron dot diagram** (or electron dot diagram or a Lewis diagram or a Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (It does not matter what order the positions are used.) For example, the Lewis electron dot diagram for hydrogen is simply:

$$\mathrm{H}\cdot$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathrm{H}} \qquad \text{or} \qquad \cdot\mathrm{H} \qquad \text{or} \qquad \underset{\cdot}{\mathrm{H}}$$

The electron dot diagram for helium, with two valence electrons, is as follows:

$$\mathrm{He}\colon$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1*s* subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^2 2s^1$, so it has only one electron in its valence shell. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:

$$\mathrm{Li}\cdot$$

Beryllium has two valence electrons in its 2*s* shell, so its electron dot diagram is like that of helium:

$$\mathrm{Be}\colon$$

The next atom is boron. Its valence electron shell is $2s^2 2p^1$, so it has three valence electrons. The third electron will go on another side of the symbol:

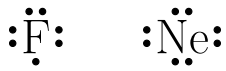
Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2*s* subshell and two in the 2*p* subshell. As usual, we will draw two dots together on one side, to represent the 2*s* electrons. However, conventionally, we draw the dots for the two *p* electrons on different sides. As such, the electron dot diagram for carbon is as follows:

With nitrogen, which has three *p* electrons, we put a single dot on each of the three remaining sides:

For oxygen, which has four *p* electrons, we now have to start doubling up on the dots on one other side of the symbol. When doubling up electrons, make sure that a side has no more than two electrons.

Fluorine and neon have seven and eight dots, respectively:



With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the $n = 3$ shell. By going through the periodic table, we see that the Lewis electron dot diagrams of atoms will never have more than eight dots around the atomic symbol.

Example 9.1

Problem

What is the Lewis electron dot diagram for each element?

1. aluminum
2. selenium

Solution

1. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3*s* electrons:

2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the $n = 4$ shell, there are six electrons. Its electron dot diagram is as follows:

Test Yourself

What is the Lewis electron dot diagram for each element?

1. phosphorus
2. argon

Answer

For atoms with partially filled *d* or *f* subshells, these electrons are typically omitted from Lewis electron dot diagrams. For example, the electron dot diagram for iron (valence shell configuration $4s^2 3d^6$) is as follows:

Elements in the same column of the periodic table have similar Lewis electron dot diagrams because they have the same valence shell electron configuration. Thus the electron dot diagrams for the first column of elements are as follows:

Monatomic ions are atoms that have either lost (for cations) or gained (for anions) electrons. Electron dot diagrams for ions are the same as for atoms, except that some electrons have been removed for cations, while some electrons have been added for anions. Thus in comparing the electron configurations and electron dot diagrams for the Na atom and the Na^+ ion, we note that the Na atom has a single valence electron in its Lewis diagram, while the Na^+ ion has lost that one valence electron:

Lewis dot diagram:		Na^+
Electron configuration:	$[Ne]3s^1$	[Ne]

Technically, the valence shell of the Na^+ ion is now the $n = 2$ shell, which has eight electrons in it. So why do we not put eight dots around Na^+? Conventionally, when we show electron dot diagrams for ions, we show the original valence shell of the atom, which in this case is the $n = 3$ shell and empty in the Na^+ ion.

In making cations, electrons are first lost from the *highest numbered shell*, not necessarily the last subshell filled. For example, in going from the neutral Fe atom to the Fe^{2+} ion, the Fe atom loses its two 4*s* electrons first, not its 3*d* electrons, despite the fact that the 3*d* subshell is the last subshell being filled. Thus we have:

Lewis dot diagram:	Fe:	Fe^{2+}
Electron configuration:	$[Ar]4s^2 3d^6$	$[Ar]3d^6$

Anions have extra electrons when compared to the original atom. Here is a comparison of the Cl atom with the Cl^- ion:

Lewis dot diagram:	:Cl·	:Cl:$^-$
Electron configuration:	$[Ne]3s^2 3p^5$	$[Ne]3s^2 3p^6$

Example 9.2

Problem

What is the Lewis electron dot diagram for each ion?

1. Ca^{2+}
2. O^{2-}

Solution

1. Having lost its two original valence electrons, the Lewis electron dot diagram is just Ca^{2+}.
2. The O^{2-} ion has gained two electrons in its valence shell, so its Lewis electron dot diagram is as follows:

:O:$^{2-}$

Test Yourself

The valence electron configuration of thallium, whose symbol is Tl, is $6s^2 5d^{10} 6p^1$. What is the Lewis electron dot diagram for the Tl^+ ion?

Answer

Tl:$^+$

Key Takeaways

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis electron dot diagrams for ions have fewer (for cations) or more (for anions) dots than the corresponding atom.

Exercises

Questions

1. Explain why the first two dots in a Lewis electron dot diagram are drawn on the same side of the atomic symbol.
2. Is it necessary for the first dot around an atomic symbol to go on a particular side of the atomic symbol?
3. What column of the periodic table has Lewis electron dot diagrams with two electrons?
4. What column of the periodic table has Lewis electron dot diagrams that have six electrons in them?
5. Draw the Lewis electron dot diagram for each element.
    a. strontium
    b. silicon
6. Draw the Lewis electron dot diagram for each element.
    a. krypton
    b. sulfur
7. Draw the Lewis electron dot diagram for each element.
    a. titanium
    b. phosphorus
8. Draw the Lewis electron dot diagram for each element.
    a. bromine
    b. gallium
9. Draw the Lewis electron dot diagram for each ion.
    a. Mg^{2+}
    b. S^{2-}
10. Draw the Lewis electron dot diagram for each ion.
    a. In^{+}
    b. Br^{-}
11. Draw the Lewis electron dot diagram for each ion.
    a. Fe^{2+}
    b. N^{3-}
12. Draw the Lewis electron dot diagram for each ion.
    a. H^{+}
    b. H^{-}

Answers

1. The first two electrons in a valence shell are *s* electrons, which are paired.
3. The second column of the periodic table.

5. a. $\mathrm{Sr}:$
   b. $\cdot\dot{\underset{\cdot}{\mathrm{Si}}}\cdot$
7. a. $\mathrm{Ti}:$
   b. $\cdot\dot{\mathrm{P}}:$
9. a. Mg^{2+}
   b. $:\ddot{\underset{\cdot\cdot}{\mathrm{S}}}\cdot^{2-}$
11. a. Fe^{2+}
    b. $:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:^{3-}$

Electron Transfer: Ionic Bonds

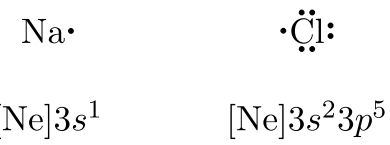
Learning Objectives

1. State the octet rule.
2. Define *ionic bond*.
3. Demonstrate electron transfer between atoms to form ionic bonds.

In the section "Lewis Electron Dot Diagrams", we saw how ions are formed by losing electrons to make cations or by gaining electrons to form anions. The astute reader may have noticed something: Many of the ions that form have eight electrons in their valence shell. Either atoms gain enough electrons to have eight electrons in the valence shell and become the appropriately charged anion, or they lose the electrons in their original valence shell. The *lower* shell, now the valence shell, has eight electrons in it, so the atom becomes positively charged. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of electrons. The trend that atoms like to have eight electrons in their valence shell is called the **octet rule**. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good rule of thumb for understanding the kinds of bonding arrangements that atoms can make.

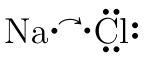
It is not impossible to violate the octet rule. Consider sodium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Na^+ ion. We *could* remove another electron by adding even more energy to the ion, to make the Na^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Na^+ ion has a complete octet in its new valence shell, the $n = 2$ shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Now consider an Na atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

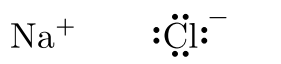


$$[\mathrm{Ne}]3s^1 \qquad [\mathrm{Ne}]3s^2 3p^5$$

For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to gain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

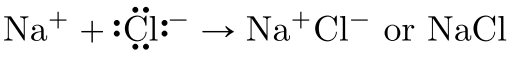


Resulting in two ions — the Na^+ ion and the Cl^- ion:



$$[Ne] \quad [Ne]3s^2 3p^6$$

Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:



Where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond**, and it is one of the main types of chemical bonds in chemistry. Ionic bonds are caused by electrons *transferring* from one atom to another.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:

The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:

Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:

The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:

These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the law of conservation of matter as well.

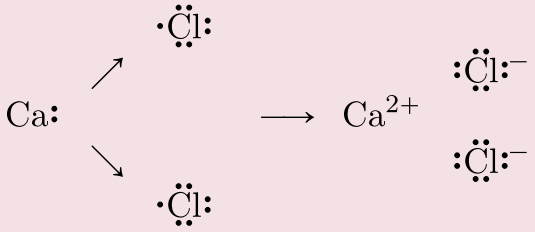
Example 9.3

Problem

With arrows, illustrate the transfer of electrons to form calcium chloride from Ca atoms and Cl atoms.

Solution

A Ca atom has two valence electrons, while a Cl atom has seven electrons. A Cl atom needs only one more to complete its octet, while Ca atoms have two electrons to lose. Thus we need two Cl atoms to accept the two electrons from one Ca atom. The transfer process looks like this:

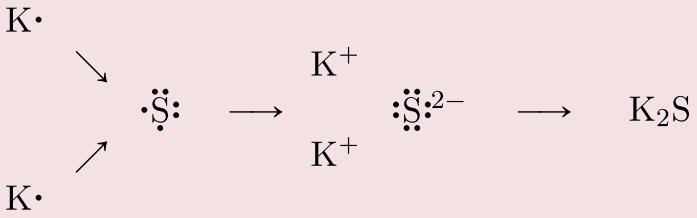


The oppositely charged ions attract each other to make $CaCl_2$.

Test Yourself

With arrows, illustrate the transfer of electrons to form potassium sulfide from K atoms and S atoms.

Answer



The strength of ionic bonding depends on two major characteristics: the magnitude of the charges and the size of the ion. The greater the magnitude of the charge, the stronger the ionic bond. The smaller the ion, the stronger the ionic bond (because a smaller ion size allows the ions to get closer together). The measured strength of ionic bonding is called the **lattice energy**. Some lattice energies are given in Table 9.1 “Lattice Energies of Some Ionic Compounds.”

Table 9.1 Lattice Energies of Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)
LiF	1,036
LiCl	853
NaCl	786
NaBr	747
MgF_2	2,957
Na_2O	2,481
MgO	3,791

Chemistry Is Everywhere: Salt

The element sodium is a very reactive metal; given the opportunity, it will react with the sweat on your hands and form sodium hydroxide, which is a very corrosive substance. The element chlorine is a pale yellow, corrosive gas that should not be inhaled due to its poisonous nature. Bring these two hazardous substances together, however, and they react to make the ionic compound sodium chloride, known simply as salt. Sodium, chlorine, and sodium chloride can be seen in Figure 9.1 below.

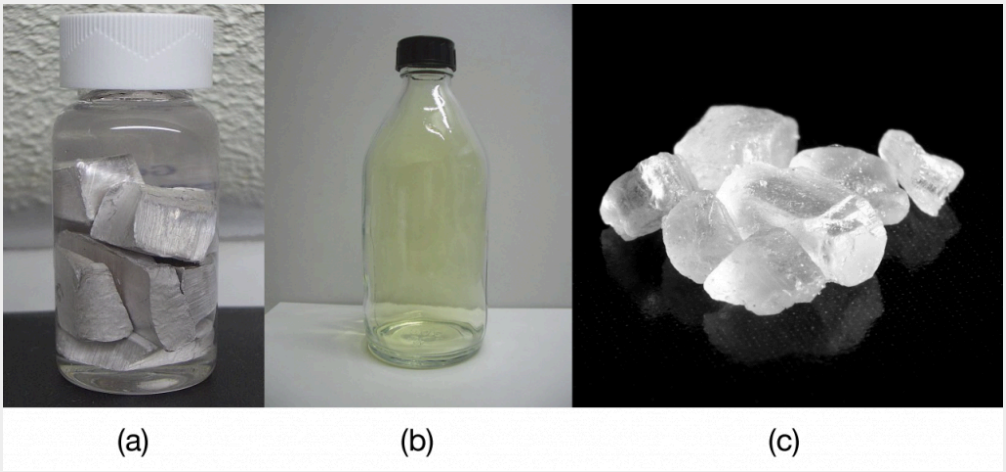


Figure 9.1 "Sodium Chloride." (a) Sodium is a very reactive metal. (b) Chlorine is a pale yellow, noxious gas. (c) Together, sodium and chlorine make sodium chloride — salt — which is necessary for our survival.

Salt is necessary for life. Na^+ ions are one of the main ions in the human body and are necessary to regulate the fluid balance in the body. Cl^- ions are necessary for proper nerve function and respiration. Both of these ions are supplied by salt. The taste of salt is one of the fundamental tastes; salt is probably the most ancient flavouring known, and one of the few rocks we eat.

The health effects of too much salt are still under debate, although a 2010 report by the US Department of Agriculture concluded that "excessive sodium intake … raises blood pressure, a well-accepted and extraordinarily common risk factor for stroke, coronary heart disease, and kidney disease."[1] It is clear that most people ingest more salt than their bodies need, and most nutritionists recommend curbing salt intake. Curiously, people who suffer from low salt (called *hyponatria*) do so not

1. U.S. Department of Agriculture Committee for Nutrition Policy and Promotion, "Report of the Dietary Guidelines Advisory Committee on the Dietary Guidelines for Americans," accessed January 5, 2010, https://www.dietaryguidelines.gov/sites/default/files/2019-05/2010DGACReport-camera-ready-Jan11-11.pdf.

because they ingest too little salt but because they drink too much water. Endurance athletes and others involved in extended strenuous exercise need to watch their water intake so their body's salt content is not diluted to dangerous levels.

Key Takeaways

- The tendency to form species that have eight electrons in the valence shell is called the octet rule.
- The attraction of oppositely charged ions caused by electron transfer is called an ionic bond.
- The strength of ionic bonding depends on the magnitude of the charges and the sizes of the ions.

Exercises

Questions

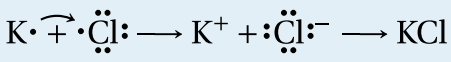
1. Comment on the possible formation of the K^{2+} ion. Why is its formation unlikely?
2. Comment on the possible formation of the Cl^{2-} ion. Why is its formation unlikely?
3. How many electrons does a Ba atom have to lose to have a complete octet in its valence shell?
4. How many electrons does a Pb atom have to lose to have a complete octet in its valence shell?
5. How many electrons does an Se atom have to gain to have a complete octet in its valence shell?
6. How many electrons does an N atom have to gain to have a complete octet in its valence shell?
7. With arrows, illustrate the transfer of electrons to form potassium chloride from K atoms and Cl atoms.
8. With arrows, illustrate the transfer of electrons to form magnesium sulfide from Mg atoms and S atoms.
9. With arrows, illustrate the transfer of electrons to form scandium fluoride from Sc atoms and F atoms.
10. With arrows, illustrate the transfer of electrons to form rubidium phosphide from Rb atoms and P atoms.
11. Which ionic compound has the higher lattice energy — KI or MgO? Why?
12. Which ionic compound has the higher lattice energy — KI or LiF? Why?
13. Which ionic compound has the higher lattice energy — BaS or MgO? Why?
14. Which ionic compound has the higher lattice energy — NaCl or NaI? Why?

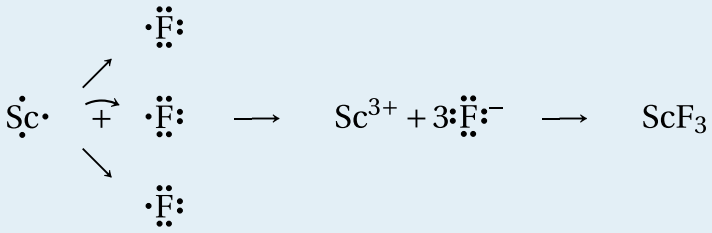
Answers

1. The K^{2+} ion is unlikely to form because the K^+ ion already satisfies the octet rule and is rather stable.

3. two

5. two

7. 

9. 

11. MgO, because the ions have a higher magnitude charge.

13. MgO, because the ions are smaller.

Media Attributions

Figure 9.1

- “Sodium metal chunks in oil” by Wilco Oelen © CC BY-SA (Attribution-ShareAlike)
- “Chlorine in bottle” by Wilco Oelen © CC BY-SA (Attribution-ShareAlike)
- “Salt Crystals” by Mark Schellhase © CC BY-SA (Attribution-ShareAlike)

Covalent Bonds

Learning Objectives

1. Define *covalent bond*.
2. Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons and another atom to gain one or more electrons. However, some atoms won't give up or gain electrons easily. Yet they still participate in compound formation. How?

There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**.

Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathrm{H}\cdot \qquad \cdot\mathrm{H}$$

The two H atoms can share their electrons:

$$\mathrm{H{:}H}$$

We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:

$$\mathrm{H{:}H}$$

$\nearrow$ 2 electrons on this H $\qquad$ $\nwarrow$ 2 electrons on this H

Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

$$\mathrm{H}\text{——}\mathrm{H}$$

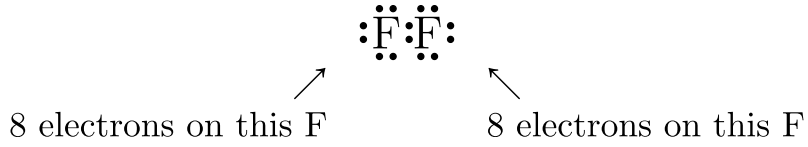
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**.

As another example, consider fluorine. F atoms have seven electrons in their valence shell:

$$:\ddot{\mathrm{F}}\cdot \quad \cdot\ddot{\mathrm{F}}:$$

These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.

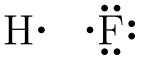
Note that each F atom has a complete octet around it now:



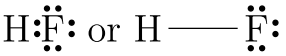
We can also write this using a dash to represent the shared electron pair:

There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone electron pairs**. Each F atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:



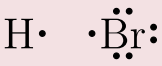
We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

Example 9.4

Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:



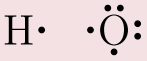
The two atoms can share their unpaired electron:

Test Yourself

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

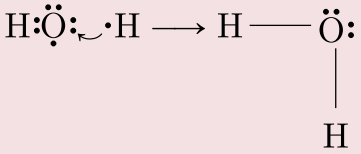
Answer

More than two atoms can participate in covalent bonding, although any given covalent bond will be between two atoms only. Consider H and O atoms:



The H and O atoms can share an electron to form a covalent bond:

The H atom has a complete valence shell. However, the O atom has only seven electrons around it, which is not a complete octet. We fix this by including a second H atom, whose single electron will make a second covalent bond with the O atom:



(It does not matter on what side the second H atom is positioned.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

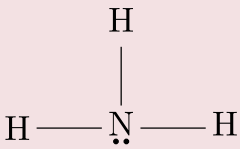
Example 9.5

Use a Lewis electron dot diagram to show the covalent bonding in NH_3.

Solution

The N atom has the following Lewis electron dot diagram:

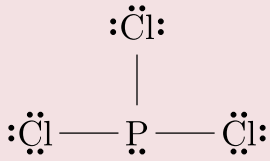
It has three unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of NH_3 is as follows:



Test Yourself

Use a Lewis electron dot diagram to show the covalent bonding in PCl_3.

Answer

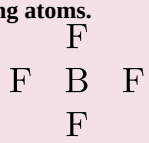


There is a simple set of steps for determining the Lewis electron dot diagram of a simple molecule. First, you must identify the central atom and the surrounding atoms. The **central atom** is the atom in the center of the molecule, while the **surrounding atoms** are the atoms making bonds to the central atom. The central atom is usually written first in the formula of the compound (H_2O is the notable exception). After the central and surrounding atoms have been identified, follow these steps:

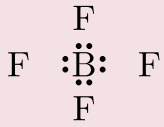
1. Count the total number of valence electrons. Add extra if the species has negative charges and remove some for every positive charge on the species.
2. Write the central atom and surround it with the surrounding atoms.
3. Put a pair of electrons between the central atom and each surrounding atom.
4. Complete the octets around the surrounding atoms (except for H).
5. Put the remaining electrons, if any, around the central atom.
6. Check that every atom has a full valence shell.

Let us try these steps to determine the electron dot diagram for BF_4^-. The B atom is the central atom, and the F atoms are the surrounding atoms. There is a negative sign on the species, so we have an extra electron to consider.

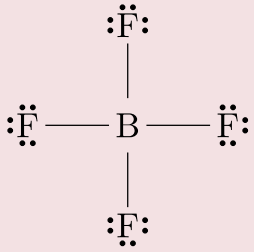
1. **Count the total number of valence electrons.** B has 3, each F has 7, and there is one extra electron: 3 + 7 + 7 + 7 + 7 + 1 = 32.
2. **Write the central atom surrounded by surrounding atoms.**



3. **Put a pair of electrons between the central atom and each surrounding atom.** This uses up eight electrons, so we have 32 − 8 = 24 electrons left.

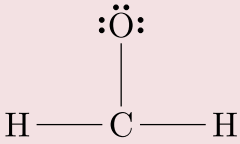


4. **Complete the octets around the surrounding atoms (except for H).** This uses up 24 more electrons, leaving 24 − 24 = 0 electrons left.



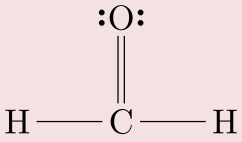
5. **Put the remaining electrons, if any, around the central atom.** There are no additional electrons to add to the central atom.
6. **Check.** The B atom has eight electrons around it, as does each F atom. Each atom has a complete octet. This is a good Lewis electron dot diagram for BF_4^-.

Sometimes, however, these steps don't work. If we were to follow these steps for the compound formaldehyde (CH_2O), we would get the following:



The H and O atoms have the proper number of electrons, but the C atom has only six electrons around it, not the eight electrons for an octet. How do we fix this?

We fix this by recognizing that two atoms can share more than one pair of electrons. In the case of CH_2O, the O and C atoms share two pairs of electrons, with the following Lewis electron dot diagram as a result:



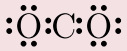
The bond between the C and O atoms is a **double bond** and represents two bonding pairs of electrons between the atoms. If using the rules for drawing Lewis electron dot diagrams don't work as written, a double bond may be required.

Example 9.6

What is the proper Lewis electron dot diagram for CO_2?

Solution

The central atom is a C atom, with O atoms as surrounding atoms. We have a total of 4 + 6 + 6 = 16 valence electrons. Following the rules for Lewis electron dot diagrams for compounds gives us:



The O atoms have complete octets around them, but the C atom has only four electrons around it. The way to solve this dilemma is to make a double bond between carbon and *each* O atom:

Each O atom still has eight electrons around it, but now the C atom also has a complete octet. This is an acceptable Lewis electron dot diagram for CO_2.

Test Yourself

What is the proper Lewis electron dot diagram for carbonyl sulfide (COS)?

Answer

It is also possible to have a **triple bond**, in which there are three pairs of electrons between two atoms. Good examples of this are elemental nitrogen (N_2) and acetylene (C_2H_2):

Acetylene is an interesting example of a molecule with two central atoms, which are both C atoms.

Polyatomic ions are bonded together with covalent bonds. Because they are ions, however, they participate in ionic bonding with other ions. So both major types of bonding can occur at the same time.

Food and Drink App: Vitamins and Minerals

Vitamins are nutrients that our bodies need in small amounts but cannot synthesize; therefore, they must be obtained from the diet. The word *vitamin* comes from "vital amine" because it was once thought that all these compounds had an amine group (NH_2) in it. This is not actually true, but the name stuck anyway.

All vitamins are covalently bonded molecules. Most of them are commonly named with a letter, although all of them also

have formal chemical names. Thus vitamin A is also called retinol, vitamin C is called ascorbic acid, and vitamin E is called tocopherol. There is no single vitamin B; there is a group of substances called the *B complex vitamins* that are all water soluble and participate in cell metabolism. If a diet is lacking in a vitamin, diseases such as scurvy or rickets develop. Luckily, all vitamins are available as supplements, so any dietary deficiency in a vitamin can be easily corrected.

A mineral is any chemical element other than carbon, hydrogen, oxygen, or nitrogen that is needed by the body. Minerals that the body needs in quantity include sodium, potassium, magnesium, calcium, phosphorus, sulfur, and chlorine. Essential minerals that the body needs in tiny quantities (so-called *trace elements*) include manganese, iron, cobalt, nickel, copper, zinc, molybdenum, selenium, and iodine. Minerals are also obtained from the diet. Interestingly, most minerals are consumed in ionic form, rather than as elements or from covalent molecules. Like vitamins, most minerals are available in pill form, so any deficiency can be compensated for by taking supplements.

Supplement Facts

Serving Size 1 Tablet

Each Tablet Contains	% Daily Value
Vitamin A 5000 I.U (50% as Beta Carotene)	100%
Vitamin C 60 mg	100%
Vitamin D 400 I.U.	100%
Vitamin E 30 I.U.	100%
Vitamin K 25 mcg	31%
Thiamin (Vitamin B1) 1.5 mg	100%
Riboflavin (Vitamin B2) 1.7 mg	100%
Niacin 20 mg	100%
Vitamin B6 2 mg	100%
Folic Acid 400 mcg	100%
Vitamin B12 6 mcg	100%
Biotin 30 mcg	10%
Pantothenic Acid 10 mg	100%
Calcium 160 mg	16%
Iron 18 mg	100%
Phosphorus 110 mg	11%
Iodine 150 mcg	100%
Magnesium 100 mg	25%
Zinc 15 mg	100%
Selenium 20 mcg	29%
Copper 2 mg	100%
Manganese 2 mg	100%
Chromium 120 mcg	100%
Molybdenum 75 mcg	100%
Chloride 72 mg	2%
Potassium 80 mg	2%
Boron 150 mcg	*
Nickel 5 mcg	*
Silicon 2 mg	*
Tin 10 mcg	*
Vanadium 10 mcg	*
Lutein 250 mcg	*

* Daily Value (DV) not stablished

Figure 9.2 Vitamin and Mineral Supplements.

Every entry down through pantothenic acid is a vitamin, and everything from calcium and below is a mineral.

Key Takeaways

- Covalent bonds are formed when atoms share electrons.

- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly represent the bonding in some molecules.

Exercises

Questions

1. How many electrons will be in the valence shell of an H atom when it makes a covalent bond?
2. How many electrons will be in the valence shell of a non-H atom when it makes a covalent bond?
3. What is the Lewis electron dot diagram of I_2? Circle the electrons around each atom to verify that each valence shell is filled.
4. What is the Lewis electron dot diagram of H_2S? Circle the electrons around each atom to verify that each valence shell is filled.
5. What is the Lewis electron dot diagram of NCl_3? Circle the electrons around each atom to verify that each valence shell is filled.
6. What is the Lewis electron dot diagram of SiF_4? Circle the electrons around each atom to verify that each valence shell is filled.
7. Draw the Lewis electron dot diagram for each substance.
    a. SF_2
    b. BH_4^-
8. Draw the Lewis electron dot diagram for each substance.
    a. PI_3
    b. OH^-
9. Draw the Lewis electron dot diagram for each substance.
    a. GeH_4
    b. ClF
10. Draw the Lewis electron dot diagram for each substance.
    a. AsF_3
    b. NH_4^+
11. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    a. SiO_2
    b. C_2H_4 (assume two central atoms)
12. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    a. CN^-
    b. C_2Cl_2 (assume two central atoms)
13. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    a. CS_2

b. NH_2CONH_2 (assume that the N and C atoms are the central atoms)

14. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.

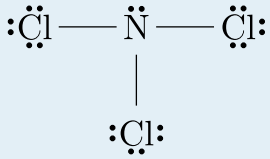
a. POCl

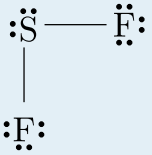
b. HCOOH (assume that the C atom and one O atom are the central atoms)

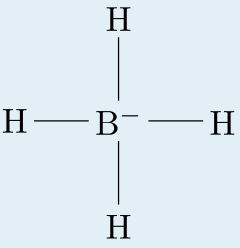
Answers

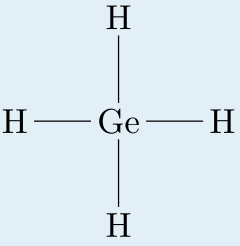
1. two

3. 

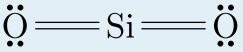
5. 

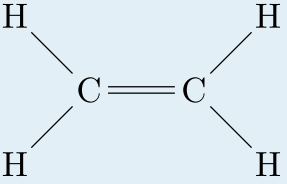
7. a. 

b. 

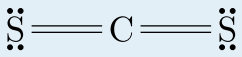
9. a. 

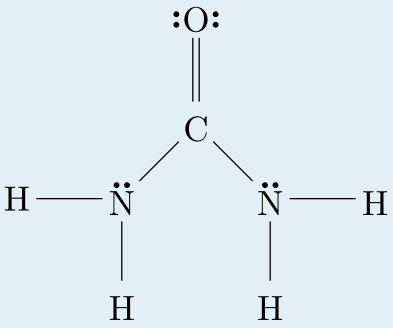
b. 

11. a. 

b. 

13.

a. 

b. 

Other Aspects of Covalent Bonds

Learning Objectives

1. Describe a nonpolar bond and a polar bond.
2. Use electronegativity to determine whether a bond between two elements will be nonpolar covalent, polar covalent, or ionic.
3. Describe the bond energy of a covalent bond.

Consider the H_2 molecule:

$$H{:}H$$

Because the nuclei of each H atom contain protons, the electrons in the bond are attracted to the nuclei (opposite charges attract). But because the two atoms involved in the covalent bond are both H atoms, each nucleus attracts the electrons by the same amount. Thus the electron pair is equally shared by the two atoms. The equal sharing of electrons in a covalent bond is called a **nonpolar covalent bond**.

Now consider the HF molecule:

$$H — \ddot{F}:$$

There are two different atoms involved in the covalent bond. The H atom has one proton in its nucleus that is attracting the bonding pair of electrons. However, the F atom has nine protons in its nucleus, with nine times the attraction of the H atom. The F atom attracts the electrons so much more strongly that the electrons remain closer to the F atom than to the H atom; the electrons are no longer equally balanced between the two nuclei.

Because the electrons in the bond are nearer to the F atom, this side of the molecule takes on a partial negative charge, which is represented by δ− (δ is the lowercase Greek letter delta). The other side of the molecule, the H atom, adopts a partial positive charge, which is represented by δ+:

$$\overset{\delta+}{H} — \overset{\delta-}{\ddot{F}:}$$

A covalent bond between different atoms that attract the shared electrons by different amounts and cause an imbalance of electron distribution is called a **polar covalent bond**.

Technically, any covalent bond between two different elements is polar. However, the degree of polarity is important. A covalent bond between two different elements may be so slightly imbalanced

that the bond is, essentially, nonpolar. A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity?

Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure 9.3 “Electronegativities of the Elements.”

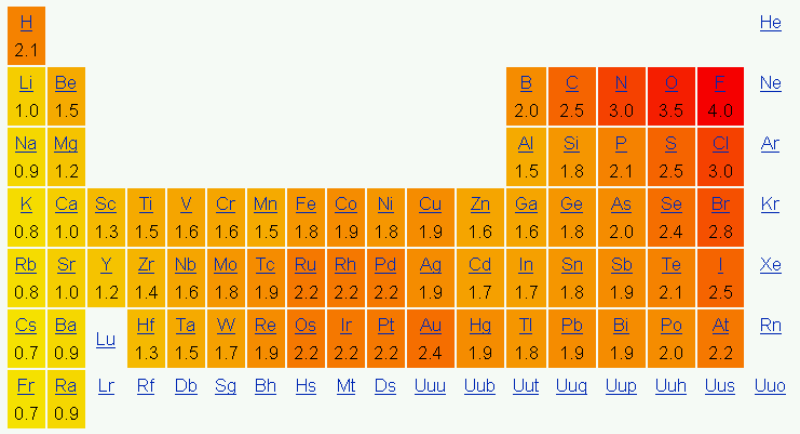


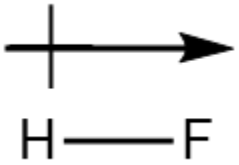
Figure 9.3 “Electronegativities of the Elements.” Electronegativities are used to determine the polarity of covalent bonds. (Source: from Joanjoc at Wikimedia Commons, public domain.)

The polarity of a covalent bond can be judged by determining the *difference* between the electronegativities of the two atoms involved in the covalent bond, as summarized in Table 9.2 “Electronegativities of Bond Types.”

Table 9.2 Electronegativities of Bond Types

Electronegativity Difference	Bond Type
0	nonpolar covalent
0–0.4	slightly polar covalent
0.4–1.9	definitely polar covalent
>1.9	likely ionic

The unequal sharing of electrons in a covalent bond is usually indicated by partial charge notation as seen earlier, or by a dipole arrow. Dipole arrows depict the unequal sharing by showing the flow of electron density. Dipole arrows have an end with a “+ sign” depicting an electropositive area from which electron density is being pulled, and an end with an arrowhead pointing to the more electronegative atom toward which electron density is being pulled.



Example 9.7

What is the polarity of each of the following bonds?

1. C–H
2. O–H

Solution

Using Figure 9.3 “Electronegativities of the Elements,” we can calculate the electronegativity differences of the atoms involved in the bond.

1. For the C–H bond, the difference in electronegativities is 2.5 − 2.1 = 0.4. Thus we predict that this bond will be slightly polar covalent.
2. For the O–H bond, the difference in electronegativities is 3.5 − 2.1 = 1.4, so we predict that this bond will be definitely polar covalent.

Test Yourself

What is the polarity of each of these bonds?

1. Rb–F
2. P–Cl

Answers

1. likely ionic
2. polar covalent

The polarity of a covalent bond can have significant influence on the properties of the substance. If the overall molecule is polar, the substance may have a higher melting point and boiling point than expected; also, it may or may not be soluble in various other substances, such as water or hexane.

It should be obvious that covalent bonds are stable because molecules exist. However, the bonds can be broken if enough energy is supplied to a molecule. To break most covalent bonds between any two given atoms, a certain amount of energy must be supplied. Although the exact amount of energy depends on the molecule, the approximate amount of energy to be supplied is similar if the atoms in the bond are the same. The approximate amount of energy needed to break a covalent bond is called the **bond energy** of the covalent bond. Table 9.3 “Bond Energies of Covalent Bonds” lists the bond energies of some covalent bonds.

Table 9.3 Bond Energies of Covalent Bonds

Bond	Energy (kJ/mol)
C–C	348
C=C	611
C≡C	837
C–O	351
C=O	799
C–Cl	328
C–H	414
F–F	159
H–Cl	431
H–F	569
H–H	436
N–N	163
N=N	418
N≡N	946
N–H	389
O–O	146
O=O	498
O–H	463
S–H	339
S=O	523
Si–H	293
Si–O	368

A few trends are obvious from Table 9.3. For bonds that involve the same two elements, a double bond is stronger than a single bond, and a triple bond is stronger than a double bond. The energies of multiple bonds are not exact multiples of the single-bond energy; for carbon-carbon bonds, the energy increases somewhat less than double or triple the C–C bond energy, while for nitrogen-nitrogen bonds the bond energy increases at a rate greater than the multiple of the N–N single bond energy. The bond energies in Table 9.3 are average values; the exact value of the covalent bond energy will vary slightly among molecules with these bonds but should be close to these values.

To be broken, covalent bonds always require energy; that is, covalent-bond *breaking* is always an *endothermic* process. Thus the Δ*H* for this process is positive:

$$\text{molecule OH} \rightarrow \text{molecule O} + \text{H} \qquad \Delta H \approx +463 \text{ kJ/mol}$$

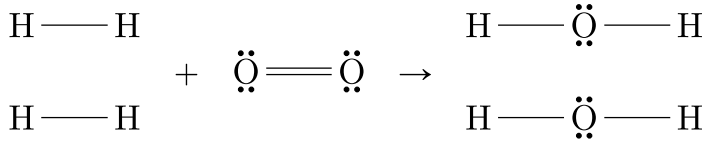
However, when making a covalent bond, energy is always given off; covalent-bond *making* is always an *exothermic* process. Thus Δ*H* for this process is negative:

$$\text{molecule S} + \text{H} \rightarrow \text{molecule SH} \qquad \Delta H \approx -339 \text{ kJ/mol}$$

Bond energies can be used to estimate the energy change of a chemical reaction. When bonds are broken in the reactants, the energy change for this process is endothermic. When bonds are formed in the products, the energy change for this process is exothermic. We combine the positive energy change with the negative energy change to estimate the overall energy change of the reaction. For example, in

$$2H_2 + O_2 \rightarrow 2H_2O$$

We can draw Lewis electron dot diagrams for each substance to see what bonds are broken and what bonds are formed:



(The lone electron pairs on the O atoms are omitted for clarity.) We are breaking two H–H bonds and one O–O double bond and forming four O–H single bonds. The energy required for breaking the bonds is as follows:

$$\begin{array}{rr} 2 \text{ H}\!-\!\text{H bonds:} & 2 \times (+436 \text{ kJ/mol}) \\ 1 \text{ O}\!=\!\text{O bond:} & +\,498 \text{ kJ/mol} \\ \hline \text{Total:} & +\,1,370 \text{ kJ/mol} \end{array}$$

The energy given off during the formation of the four O–H bonds is as follows:

$$\begin{array}{rr} 4 \text{ O}\!-\!\text{H bonds:} & 4 \times (-463 \text{ kJ/mol}) \\ \hline \text{Total:} & -1,852 \text{ kJ/mol} \end{array}$$

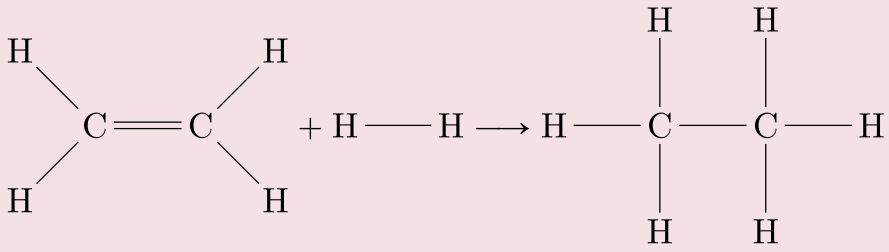
Combining these two numbers:

$$\begin{array}{rr} & +1,370 \text{ kJ/mol} \\ + & (-1,852 \text{ kJ/mol}) \\ \hline \text{Net Change:} & -482 \text{ kJ/ml} \approx \Delta H \end{array}$$

The actual Δ*H* is −572 kJ/mol; we are off by about 16% — although not ideal, a 16% difference is reasonable because we used estimated, not exact, bond energies.

Example 9.8

Estimate the energy change of this reaction:



Solution

Here, we are breaking a C–C double bond and an H–H single bond and making a C–C single bond and two C–H single bonds. Bond breaking is endothermic, while bond making is exothermic. For the bond breaking:

$$\begin{array}{rr} 1\ \mathrm{C{=\!=}C}: & +611\ \mathrm{kJ/mol} \\ 1\ \mathrm{H{-\!-}H}: & +436\ \mathrm{kJ/mol} \\ \hline \text{Total:} & +1,047\ \mathrm{kJ/mol} \end{array}$$

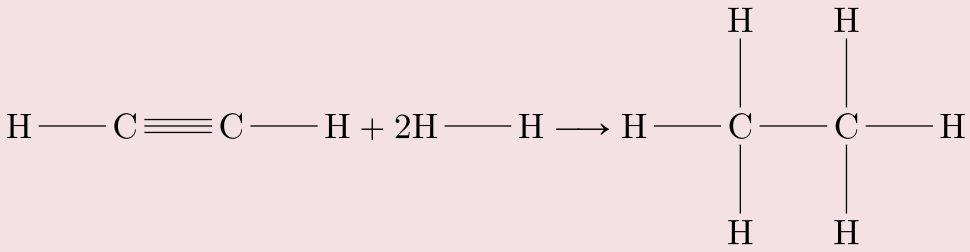
For the bond making:

$$\begin{array}{rr} 1\ \mathrm{C{-\!-}C}: & -348\ \mathrm{kJ/mol} \\ 2\ \mathrm{C{-\!-}H}: & 2 \times (-414\ \mathrm{kJ/mol}) \\ \hline \text{Total:} & -1,176\ \mathrm{kJ/mol} \end{array}$$

Overall, the energy change is +1,047 + (−1,176) = −129 kJ/mol.

Test Yourself

Estimate the energy change of this reaction:



Answer

−295 kJ/mol

Key Takeaways

- Covalent bonds can be nonpolar or polar, depending on the electronegativities of the atoms involved.
- Covalent bonds can be broken if energy is added to a molecule.
- The formation of covalent bonds is accompanied by energy given off.
- Covalent bond energies can be used to estimate the enthalpy changes of chemical reactions.

Exercises

Questions

1. Give an example of a nonpolar covalent bond. How do you know it is nonpolar?
2. Give an example of a polar covalent bond. How do you know it is polar?
3. How do you know which side of a polar bond has the partial negative charge? Identify the negatively charged side of each polar bond.
    a. H–Cl
    b. H–S
4. How do you know which side of a polar bond has the partial positive charge? Identify the positively charged side of each polar bond.
    a. H–Cl
    b. N–F
5. Label the bond between the given atoms as nonpolar covalent, slightly polar covalent, definitely polar covalent, or likely ionic.
    a. H and C
    b. C and F
    c. K and F
6. Label the bond between the given atoms as nonpolar covalent, slightly polar covalent, definitely polar covalent, or likely ionic.
    a. S and Cl
    b. P and O
    c. Cs and O
7. Which covalent bond is stronger: a C–C bond or a C–H bond?
8. Which covalent bond is stronger: an O–O double bond or an N–N double bond?
9. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

10. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.

$$HN{=}NH + 2H_2 \rightarrow 2NH_3$$

11. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

12. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Answers

1. H–H; it is nonpolar because the two atoms have the same electronegativities (answers will vary).

3. a. Cl side
   b. S side

5. a. slightly polar covalent
   b. definitely polar covalent
   c. likely ionic

7. C–H bond

9. −80 kJ

11. −798 kJ

Violations of the Octet Rule

Learning Objectives

1. Recognize the three major types of violations of the octet rule.

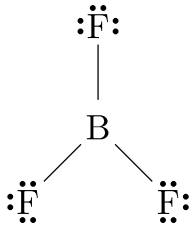
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless — quite the contrary. As with many rules, there are exceptions, or violations.

There are three violations to the octet rule. **Odd-electron molecules** represent the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

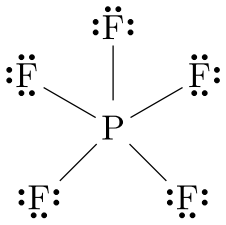
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:

Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called **expanded valence shell molecules**. Such compounds

are formed only by central atoms in the third row of the periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is PF_5. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:



Formally, the P atom has 10 electrons in its valence shell.

Example 9.9

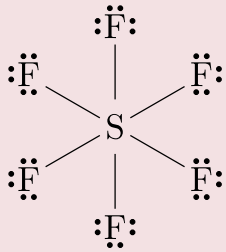
Identify each violation of the octet rule by drawing a Lewis electron dot diagram.

1. ClO
2. SF_6

Solution

1. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:

2. In SF_6, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:



Test Yourself

Identify the violation to the octet rule in XeF_2 by drawing a Lewis electron dot diagram.

Answer

The Xe atom has an expanded valence shell with more than eight electrons around it.

Key Takeaways

- There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules.

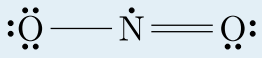
Exercises

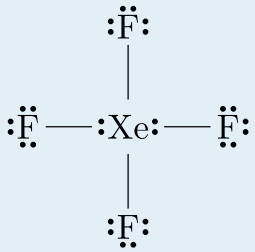
Questions

1. Why can an odd-electron molecule not satisfy the octet rule?
2. Why can an atom in the second row of the periodic table not form expanded valence shell molecules?
3. Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.
    a. NO_2
    b. XeF_4
4. Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.
    a. BCl_3
    b. ClO_2
5. Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.
    a. POF_3
    b. ClF_3
6. Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.
    a. SF_4
    b. BeH_2

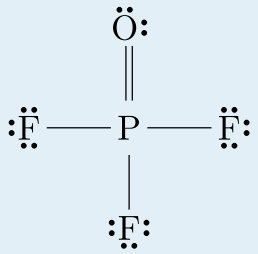
Answers

1. There is no way all electrons can be paired if there are an odd number of them.

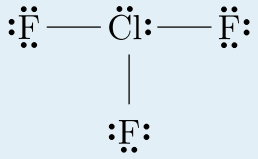
3. a. 

   b. 

5. a.



b.



Molecular Shapes and Polarity

Learning Objectives

1. Determine the shape of simple molecules.
2. Determine the polarity of molecules using net molecular dipoles.

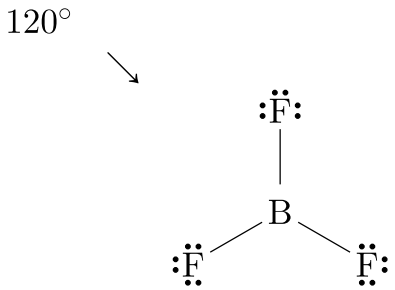
Molecules have shapes. There is an abundance of experimental evidence to that effect — from their physical properties to their chemical reactivity. Small molecules — molecules with a single central atom — have shapes that can be easily predicted.

The basic idea in molecular shapes is called **valence shell electron pair repulsion (VSEPR)**. It says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from each other as possible. VSEPR makes a distinction between **electron group geometry**, which expresses how electron groups (bonding and nonbonding electron pairs) are arranged, and **molecular geometry**, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

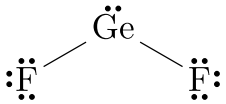
There are two types of **electron groups**: any type of bond — single, double, or triple — and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible — 180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle — 120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:



Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:



From an electron-group-geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups around the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 9.4 “Tetrahedral Geometry.” If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

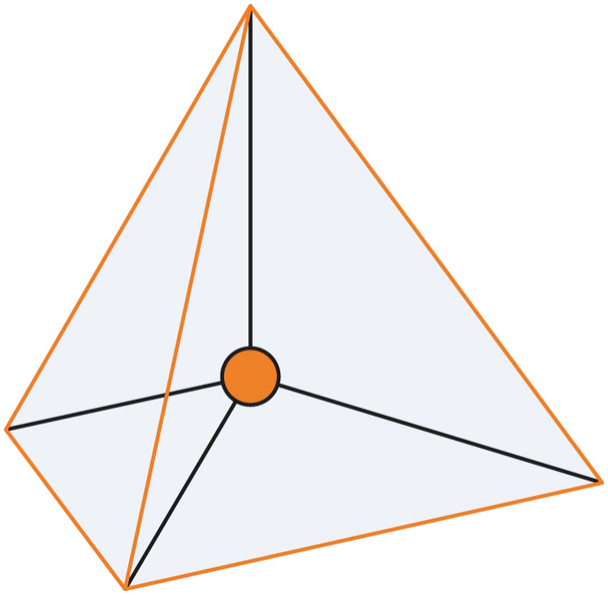
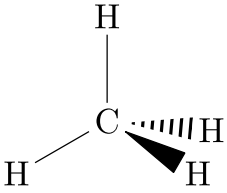
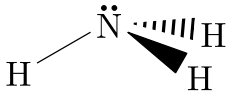


Figure 9.4 “Tetrahedral Geometry.” Four electron groups orient themselves in the shape of a tetrahedron.



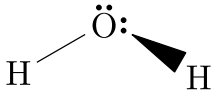
This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

NH_3 is an example of a molecule whose central atom has four electron groups but only three of them are bonded to surrounding atoms.



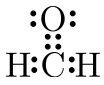
Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

H_2O is an example of a molecule with a central atom that has four electron groups but only two of them are bonded to surrounding atoms.

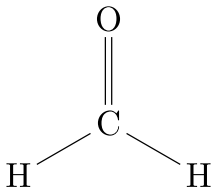


Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups around the central atom but only one electron group bonded to another atom is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. CH_2O has the following Lewis electron dot diagram.



The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape:



(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both *planar* and *triangular* describe the appropriate approximate shape of this molecule.

Example 9.10

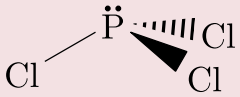
What is the approximate shape of each molecule?

1. PCl_3
2. NOF

Solution

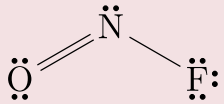
The first step is to draw the Lewis electron dot diagram of the molecule.

1. For PCl_3, the Lewis electron dot diagram is as follows:



   The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

2. The Lewis diagram for NOF is as follows:



   The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

Test Yourself

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

Table 9.4 “Summary of Molecular Shapes” summarizes the shapes of molecules based on their number of electron groups and surrounding atoms.

Table 9.4 Summary of Molecular Shapes

Number of Electron Groups on Central Atom	Number of Surrounding Atoms	Molecular Shape
any	1	linear
2	2	linear
3	3	trigonal planar
3	2	bent
4	4	tetrahedral
4	3	trigonal pyramidal
4	2	bent

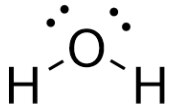
Molecular Polarity

The overall polarity of molecules with more than one bond is determined from both the polarity of the individual bonds and the shape of the molecule. Each bond's dipole moment can be treated as a **vector quantity**, having a magnitude and direction. Therefore the molecular polarity is the vector sum of the individual bond dipoles.

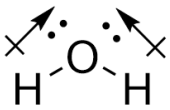
How to determine the vector sum

One method to determine the vector sum of dipole arrows is known as the tail-to-head method. Let's examine this method for a molecule of water.

1. First draw the Lewis electron dot diagram for water and determine its molecular shape. Water has four electron groups, but only two atoms attached to the central atom so it is bent.

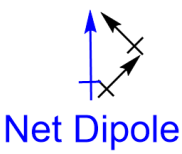


2. Draw in dipole arrows for all polar covalent bonds, starting the arrow at the more electropositive atom, and ending at the more electronegative atom.

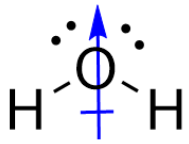


3. Connect the dipole arrows tail-to-head.

4. Draw a new line connecting the tail of the first vector. This is the net molecular dipole.



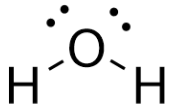
5. Now superimpose the net molecular dipole arrow onto the molecule.



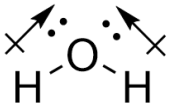
An alternative method for determining the vector sum

An alternative method to determine the vector sum of dipole arrows is known as the vector component method. Let's examine this method again for a molecule of water. The first two steps remain the same as the tail-to-head method:

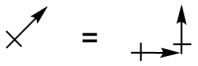
1. First draw the Lewis electron dot diagram for water and determine its molecular shape. Water has four electron groups, but only two atoms attached to the central atom so it is bent.



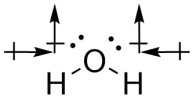
2. Draw in dipole arrows for all polar covalent bonds, starting the arrow at the more electropositive atom, and ending at the more electronegative atom.



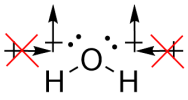
3. For dipole arrows at an angle, separate them into horizontal and vertical vector components.



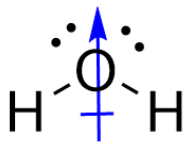
4. Superimpose the vector components onto the molecule.



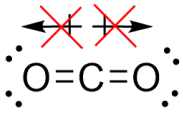
5. Cancel out any vector components that are of equal magnitude and pointing in the opposite direction.



6. The remaining vector components both point vertically, showing the net molecular dipole.



As a result of the vector quantity nature of bond dipoles, some molecules may contain polar bonds, yet have no net molecular dipole moment. For example, CO_2:



Key Takeaways

- The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.
- The molecular polarity can be established by determining the vector sum of all bond dipoles.

Exercises

Questions

1. What is the basic premise behind VSEPR?
2. What is the difference between electron group geometry and molecular geometry?
3. Identify the electron group geometry and molecular geometry of each molecule.
    a. H_2S
    b. $POCl_3$
4. Identify the electron group geometry and the molecular geometry of each molecule.
    a. CS_2
    b. H_2S
5. Identify the electron group geometry and the molecular geometry of each molecule.
    a. HCN
    b. CCl_4
6. Identify the electron group geometry and the molecular geometry of each molecule.
    a. BI_3
    b. PH_3
7. What is the geometry of each species?
    a. CN^-

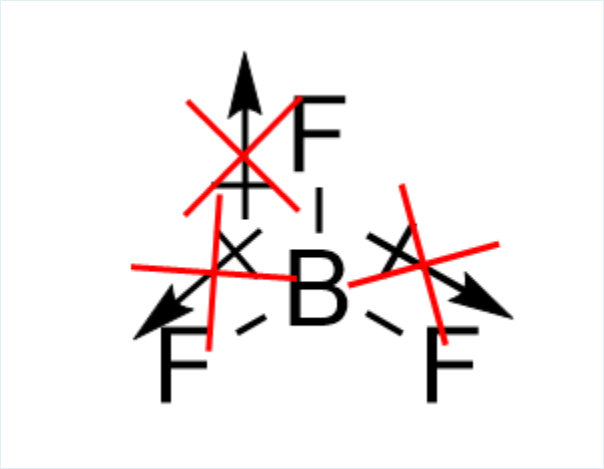
b. PO_4^{3-}

8. What is the geometry of each species?
   a. PO_3^{3-}
   b. NO_3^-
9. What is the geometry of each species?
   a. COF_2
   b. C_2Cl_2 (both C atoms are central atoms and are bonded to each other)
10. What is the geometry of each species?
    a. CO_3^{2-}
    b. N_2H_4 (both N atoms are central atoms and are bonded to each other)
11. Determine the net molecular dipole of each species:
    a. BF_3
    b. NH_3

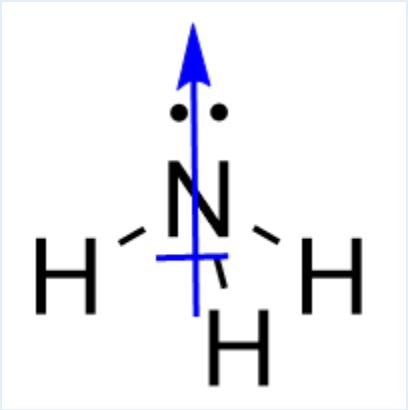
Answers

1. Electron pairs repel each other.

3. a. electron group geometry: tetrahedral; molecular geometry: bent
   b. electron group geometry: tetrahedral; molecular geometry: tetrahedral
5. a. electron group geometry: linear; molecular geometry: linear
   b. electron group geometry: tetrahedral; molecular geometry: tetrahedral
7. a. linear
   b. tetrahedral
9. a. trigonal planar
   b. linear and linear about each central atom
11. a. BF_3 = No net dipole moment



b. NH_3 =


N
H
H
H

Valence Bond Theory and Hybrid Orbitals

Jessie A. Key

Learning Objectives

1. Gain an understanding of valence bond theory.
2. Gain an understanding of hybrid orbitals.

Valence Bond Theory

Earlier we saw that covalent bonding requires the sharing of electrons between two atoms, so that each atom can complete its valence shell. But how does this sharing process occur? Remember that we can only estimate the likelihood of finding an electron in a certain area as a probability. This probability is represented as a distribution in space that we call an *atomic orbital* (Figure 9.5 “Representations of *s* and *p* atomic orbitals”).

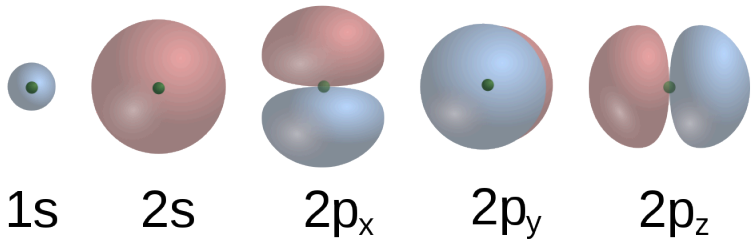


Figure 9.5 “Representations of S and P atomic orbitals.” (Source: Sven, CC-BY-SA 3.0.)

The valence bond theory states that atoms in a covalent bond share electron density through the overlapping of their valence atomic orbitals. This creates an area of electron pair density between the two atoms. Since these electrons are simultaneously attracted to both nuclei, the electron pair holds the two atoms together.

Let’s examine the simplest case of atomic overlap resulting in a covalent bond, the formation of H_2 from two hydrogen atoms (Figure 9.6 “A diagram showing the overlap of *s* orbitals of two hydrogen atoms to form H_2”). The 1*s* orbitals of the two hydrogens approach each other and overlap to form a bond that has cylindrical symmetry known as a **sigma bond (σ bond)**. Repulsion forces between the two nuclei and between the two electrons are also present. The optimal distance between atoms, which maximizes the attractive forces and minimizes the repulsive forces, gives the H-H sigma bond a length of 74 pm.

Figure 9.6. A diagram showing the overlap of s orbitals of two hydrogen atoms to form H_2.

For molecules that contain double or triple bonds, one of these bonds is a sigma bond, and the remaining multiple bonds are a different type of bond known as a **pi bond (π bond)**. Pi bonds result from the sideways overlap of *p* orbitals, placing electron density on opposite sides of the internuclear axis (Figure 9.7 “Pi bond diagram showing sideways overlapping of *p* orbitals”).

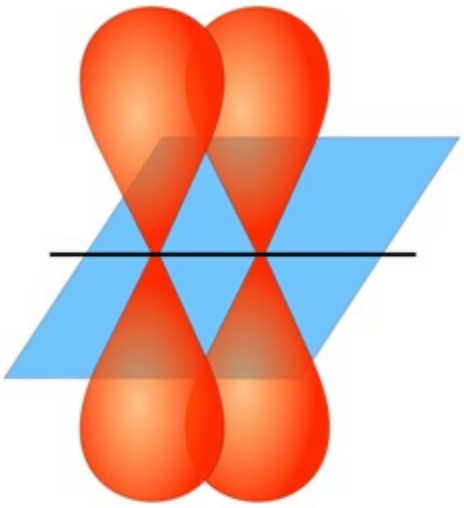


Figure 9.7 “Pi bond diagram showing sideways overlap of p orbitals.” (Source: Adapted from Pi-bond.jpg by JoJan under a CC-BY-SA-3.0.)

Hybrid Orbitals

sp^3 hybridization

A problem arises when we apply the valence bond theory method of orbital overlap to even simple molecules like methane (CH_4) (Figure 9.8 “Methane”). Carbon ($1s^2\ 2s^2\ 2p^2$) only has two unpaired valence electrons that are available to be shared through orbital overlap, yet CH_4 has four C-H σ bonds!

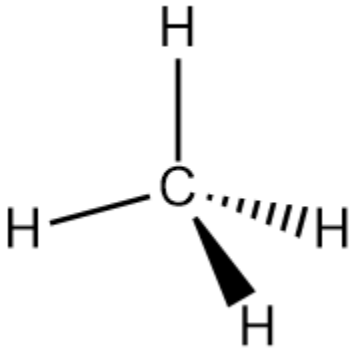


Figure 9.8 "Methane."

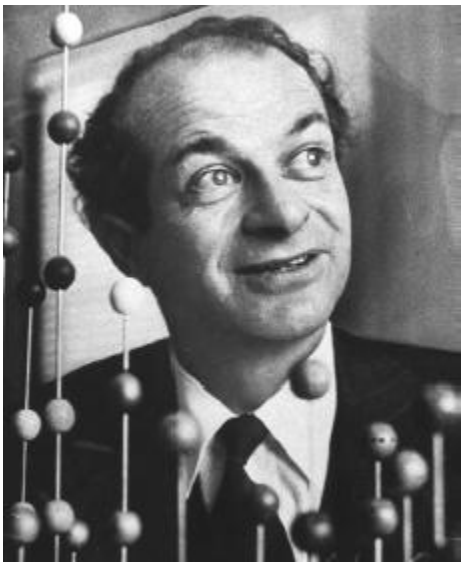


Figure 9.9 "Nobel laureate Linus Pauling." (Source: L. Pauling is in the public domain.)

In 1931, Linus Pauling (Figure 9.9) proposed a mathematical mixing of atomic orbitals known as **hybridization**. The 2*s* and *three* 2*p* orbitals are averaged mathematically through hybridization to produce *four* degenerate sp^3 hybrid orbitals (Figure 9.10 "Hybridization of carbon to generate sp^3 orbitals"). Note that in hybridization, the number of atomic orbitals hybridized is equal to the number of hybrid orbitals generated.

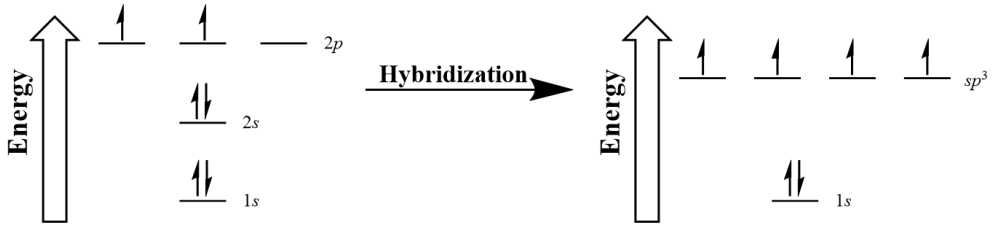


Figure 9.10 "Hybridization of carbon to generate sp^3 orbitals."

The sp^3 orbitals, being a combination of a spherical *s* orbital and propeller- (or peanut-) shaped *p* orbital, give an unsymmetrical propeller shape where one lobe of the orbital is larger (fatter) than the

other (Figure 9.11 “An sp^3 hybridized atomic orbital”). This larger lobe is typically used for orbital overlap in covalent bonding.

Figure 9.11 “An sp^3 hybridized atomic orbital.”

According to VSEPR theory, the four degenerate orbitals will arrange as far apart from each other as possible, giving a tetrahedral geometry with each orbital 109.5° apart (Figure 9.12 “A carbon atom’s four tetrahedral sp^3 hybridized orbitals”).

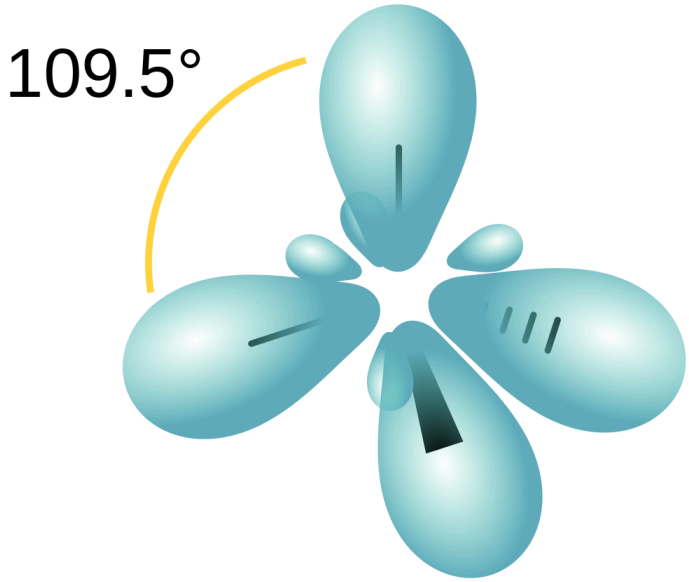


Figure 9.12 “A carbon atom’s four tetrahedral sp3 hybridized orbitals.” (Source: Adapted from AE4h by Jfmelero, used under a CC-BY-SA-3.0.)

sp^2 hybridization

Let’s examine another simple molecule, ethene (C_2H_4) (Figure 9.13 “Ethene”). Each carbon of ethene is bonded to two hydrogens and a carbon. There is also a double bond between the two carbons.

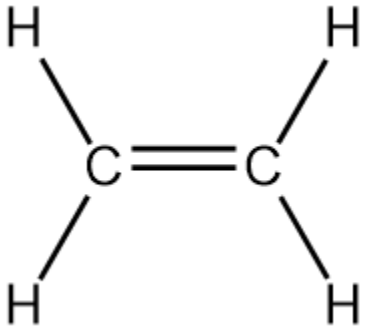


Figure 9.13 "Ethene."

Both the unhybridized atomic orbitals of carbon and the sp^3 hybridization we just examined do not explain the bonding observed in ethene. In this case, only the 2*s* and *two* of the 2*p* orbitals hybridize to give three new sp^2 hybridized orbitals capable of forming the three σ bonds of each carbon in ethene (Figure 9.14 "Hybridization of carbon to generate sp^2 orbitals").

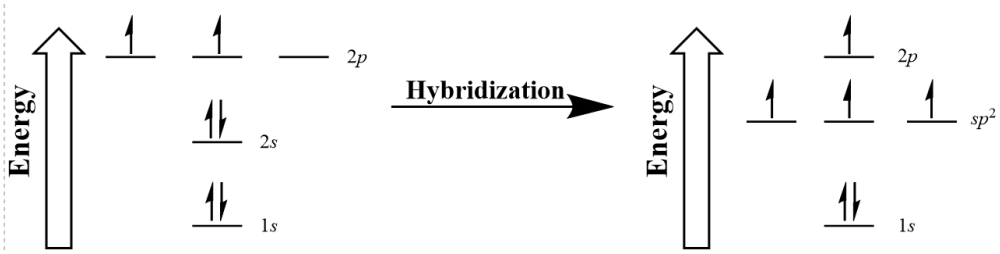


Figure 9.14 "Hybridization of carbon to generate sp^2 orbitals."

The three hybridized orbitals arrange in a trigonal planar structure with a bond angle of 120° following VSEPR (Figure 9.15 "A carbon atom's trigonal planar sp^2 hybridized orbitals").

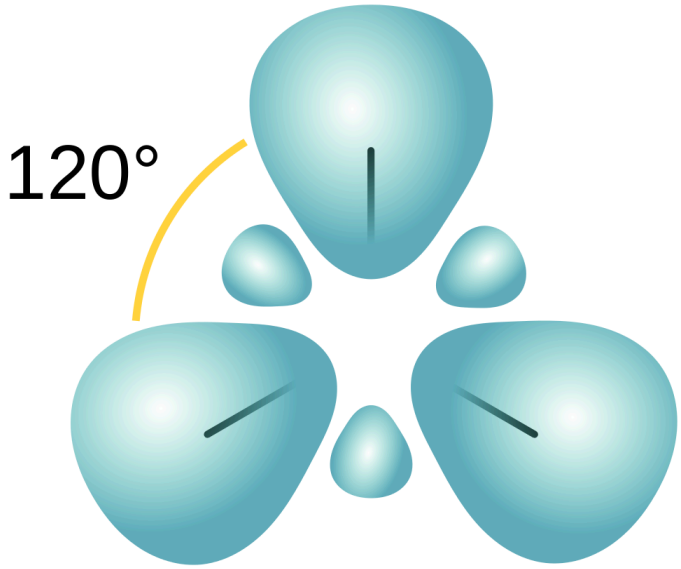


Figure 9.15 "A carbon atom's trigonal planar sp2 hybridized orbitals." (Source: Adapted from AE3h by Jfmelero, used under a CC BY-SA 3.0.)

The unhybridized 2*p* orbital in both carbons are left available to form the double bond's π bond.

sp hybridization

The final example of hybridization we will examine is the molecule ethyne (C_2H_2) (Figure 9.16 "Ethyne").

Figure 9.16 "Ethyne."

The carbons in ethyne are each sigma bonded to a single hydrogen, but triple bonded to each other. Again, the models of hybridization we have looked at so far are insufficient to explain the bonding pattern observed. In ethyne, only the 2*s* and *one* of the 2*p* orbitals hybridize to give two new *sp* hybridized orbitals capable of forming the two σ bonds of each carbon in ethyne (Figure 9.17 "Hybridization of carbon to generate *sp* orbitals").

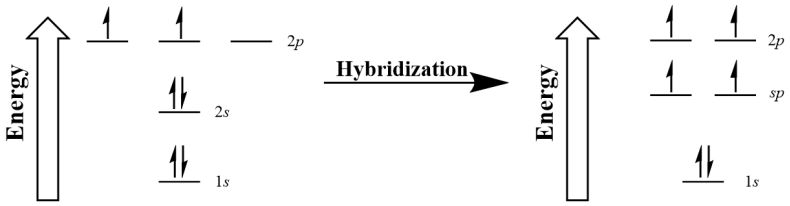


Figure 9.17 "Hybridization of carbon to generate sp orbitals."

The two hybridized *sp* orbitals arrange linearly with a bond angle of 180° following VSEPR (Figure 9.18 "A carbon atom's linear *sp* hybridized orbitals").

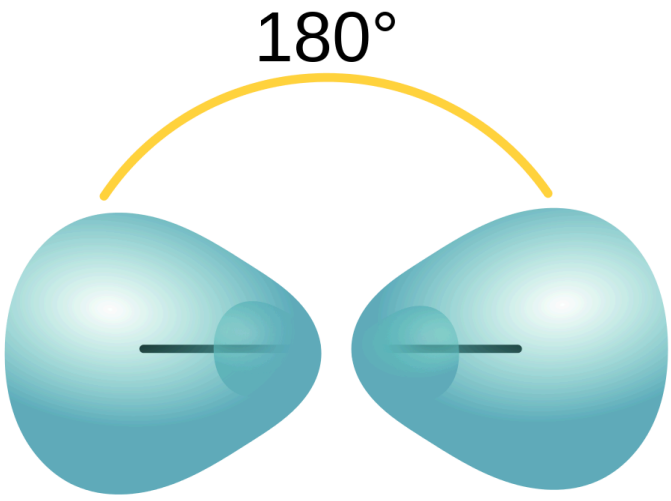


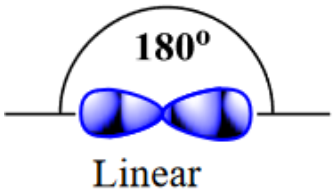
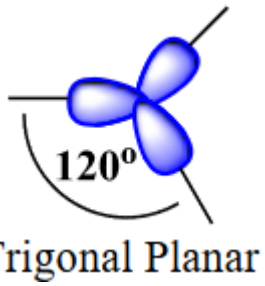
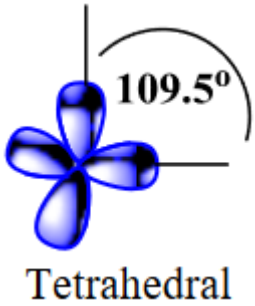
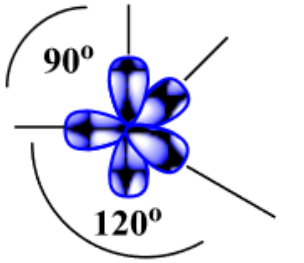
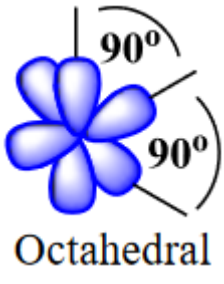
Figure 9.18 "A carbon atom's linear sp hybridized orbitals."(Source: Adapted from AE2h by Jfmelero, used under a CC BY-SA 3.0.)

The two remaining unhybridized 2*p* orbitals in both carbons are left available to form the triple bond's two π bonds.

Other hybridizations

Other hybridizations are possible, allowing us to apply valence bond theory to explain the bonding patterns observed in most real molecules. Some additional hybridizations are summarized in Table 9.5 “Hybrid Orbitals and Geometry.”

Table 9.5 Hybrid Orbitals and Geometry[1]

Atomic Orbitals Used	Hybrid Orbitals Formed	Geometry	Example Compound
s,p	Two *sp* orbitals		CO_2
s,p,p	Three sp^2 orbitals		SO_3
s,p,p,p	Four sp^3 orbitals		$GeCl_4$
s,p,p,p,d	Five dsp^3 orbitals		PCl_5
s,p,p,p,d,d	Six d^2sp^3 orbitals		$Mo(CO)_6$

1. Hybrid orbital and geometries by Chem507f10grp4 is in the public domain.

Key Takeaways

- Valence bond theory explains bonding through the overlap of atomic orbitals.
- Atomic orbitals can be hybridized mathematically to better explain actual bonding patterns.

Molecular Orbitals

Jessie A. Key

Learning Objectives

1. Gain an understanding of molecular orbital theory.
2. Learn to calculate bond orders.
3. Learn to draw molecular orbital electron configuration energy diagrams.

Valence bond theory is able to explain many aspects of bonding, but not all. To complement this theory, we use another called the **molecular orbital (MO) theory**. Molecular orbital theory is a more sophisticated model for understanding the nature of chemical bonding.

MO theory takes the idea of atomic orbitals overlapping to a new level, where new molecular orbitals are generated using a mathematical process called *linear combination of atomic orbitals* (LCAO).

Molecular orbitals share many similarities with atomic orbitals:

- They are filled from lowest energy to highest energy (Aufbau principle).
- They can hold a maximum of two electrons of opposite spin per orbital (Pauli exclusion principle).

The major difference between atomic and molecular orbitals is that atomic orbitals represent electron density in space associated with a particular atom. Molecular orbitals are associated with the entire molecule, meaning the electron density is delocalized (spread out) over more than one atom.

The Molecular Orbitals of the Hydrogen Molecule

Combining the 1*s* orbitals of each hydrogen atom using LCAO, two molecular orbitals are generated σ_{1s} (pronounced sigma one *s*) and σ^*_{1s} (pronounced sigma star one *s*).

The σ_{1s} orbital is generated by a constructive combination (or interference), where the two atomic orbitals wave functions reinforce (add to) each other. This is the lower energy of the two molecular orbitals and is known as the **bonding molecular orbital**. Notice in Figure 9.19 “Hydrogen molecular orbital combination diagram” that the electron density of this orbital is concentrated between the two nuclei. These electrons are stabilized by attractions to both nuclei, and they hold the atoms together with a covalent bond.

The σ^*_{1s} orbital is generated by a destructive combination (or interference), where the wave functions

of the two atomic orbitals cancel each other. This type of combination results in an area of zero electron density between the two nuclei, known as a **nodal plane (or node)**. This node of zero electron density is destabilizing toward the bond, making it higher energy, and subsequently this type of orbital is known as an **antibonding molecular orbital** (denoted by the asterisk in the orbital name).

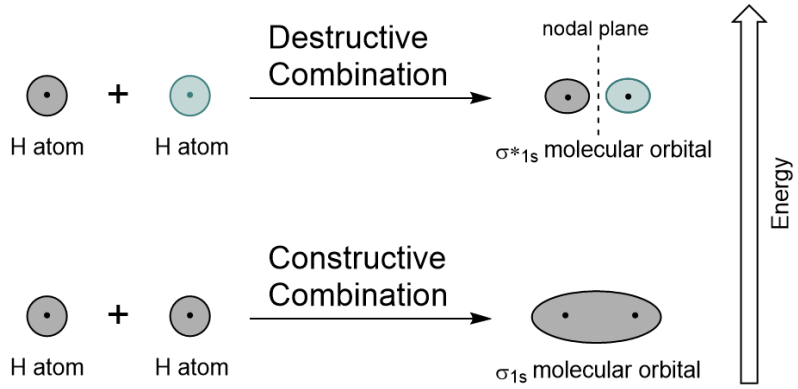


Figure 9.19 "Hydrogen molecular orbital combination diagram."

Similar to atomic orbitals, we can write electron configuration energy diagrams for molecular orbitals (Figure 9.20 "Hydrogen molecular orbital electron configuration energy diagram"). Notice that the atomic orbitals of each atom are written on either side, and the newly formed molecular orbitals are written in the centre of the diagram. The bonding molecular orbital is filled and is relatively lower in energy than the contributing atomic orbitals, supporting the fact that hydrogen molecules (H_2) are more stable than lone hydrogen atoms.

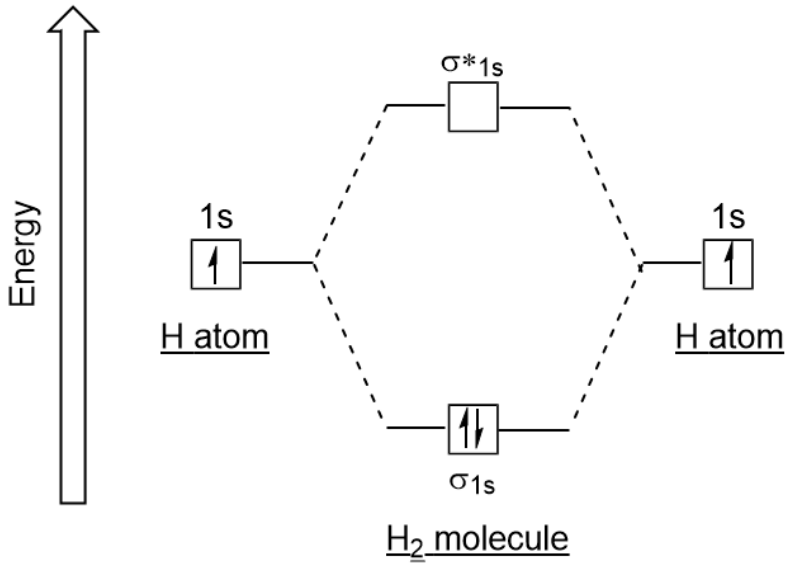


Figure 9.20 "Hydrogen molecular orbital electron configuration energy diagram."

Bond Order

We have just seen that the bonding molecular orbital is lower energy and promotes the formation of a

covalent bond, while the antibonding molecular orbital is higher energy with a node of zero electron density between the atoms that destabilizes the formation of a covalent bond. We can evaluate the strength of a covalent bond by determining its **bond order**.

$$\text{Bond order} = \tfrac{1}{2}\,(\#\text{ of electrons in bonding MOs} \;-\; \#\text{ of electrons in antibonding MOs})$$

Bond-order values can be whole numbers, fractions, or zero. These values correspond to the valence bond model, so a bond order of 1 is equal to a single bond, and 2 is equal to a double bond. A value of zero means that there is no bond present, and the atoms exist separately.

Example 9.11

Determine the bond order of the hydrogen molecule.

Solution

$$\begin{aligned}\text{Bond order} &= \frac{1}{2}(\#\text{ of electrons in bonding MOs} \\ &\qquad - \;\#\text{ of electrons in antibonding MOs}) \\ &= \frac{1}{2}(2-0) = 1\end{aligned}$$

Therefore there is a single bond in the hydrogen molecule.

Molecular Orbitals of Li_2

Generating molecular orbitals of molecules more complex than hydrogen using the LCAO method requires following a few additional guidelines:

- The number of MOs generated is equal to the number of atomic orbitals combined.
- Combined atomic orbitals should be of similar energy levels.
- The effectiveness of atomic orbital combination depends on the amount of orbital overlap. Increased overlap lowers the energy of the bonding molecular orbital further, and raises the energy of the antibonding molecular orbital.

Let’s follow these guidelines and generate a molecular orbital electron configuration diagram for Li_2 (Figure 9.21 “Molecular orbital electron configuration energy diagram for dilithium”):

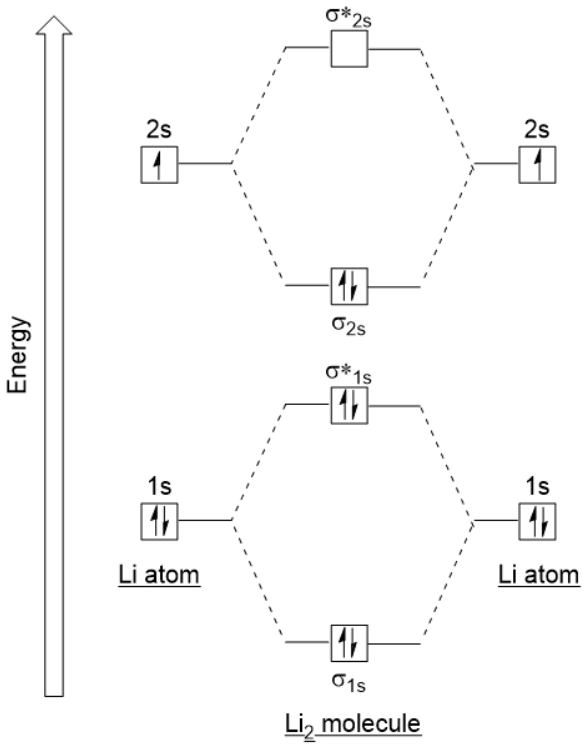


Figure 9.21 "Molecular orbital electron configuration energy diagram for dilithium."

Notice that we have combined the 1*s* atomic orbitals, as before in the H_2 example, to generate bonding and antibonding molecular orbitals that are completely filled by both atoms' 1*s* electrons. Similarly 2*s* atomic orbitals combine, giving a bonding orbital and an antibonding orbital, which are filled with the remaining valence electrons starting from the bottom up. The atomic orbitals that combine are of similar energy levels; a 1s orbital *does not* combine with one of the 2*s* orbitals.

The bond order can be determined for this molecule to be:

$$\text{Bond order} = \tfrac{1}{2}(4-2) = 1$$

Therefore Li_2 would have a single bond.

Molecular Orbitals from *p* Atomic Orbitals

To determine the molecular orbitals of many other molecules, we need to examine how *p* orbitals combine to give molecular orbitals. The *p* orbitals can overlap in two ways: head-to-head or sideways. Head-to-head overlap of *p* atomic orbitals results in a bonding and antibonding molecular orbital, where the electron density is centred along the internuclear axis, making them σ orbitals (Figure 9.22 "Head-to-head overlap of *p* orbitals").

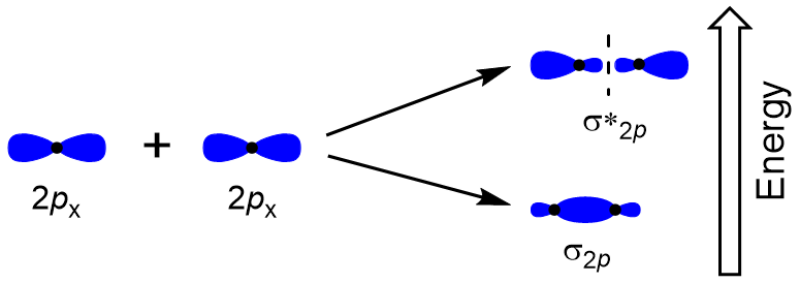


Figure 9.22 "Head-to-head overlap of p orbitals."

Sideways overlap of the remaining four *p* atomic orbitals can occur along the two other axes, generating four π molecular orbitals having electron density on opposite sides of the internuclear axis (Figure 9.23 "Sideways overlap of *p* orbitals").

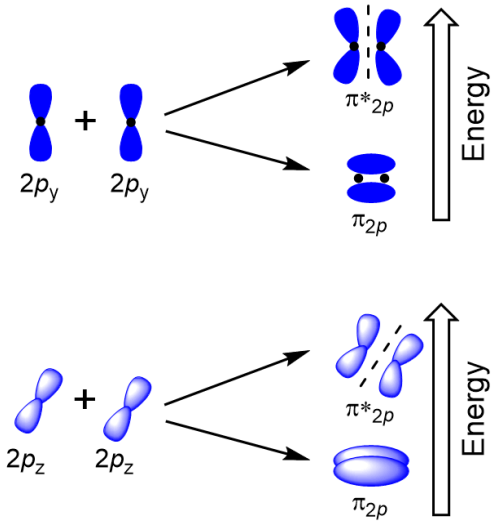


Figure 9.23 "Sideways overlap of p orbitals."

The head-to-head overlap giving σ molecular orbitals results in greater overlap, making its bonding molecular orbital the most stable and lowest energy, while the σ* antibonding is least stable and has the highest energy (Figure 9.24 "Molecular orbital energy diagram for homonuclear diatomic molecules made from atoms of atomic number 8-10"). Sideways overlap gives four π molecular orbitals, two lower-energy degenerate-bonding molecular orbitals, and two higher-energy antibonding orbitals.

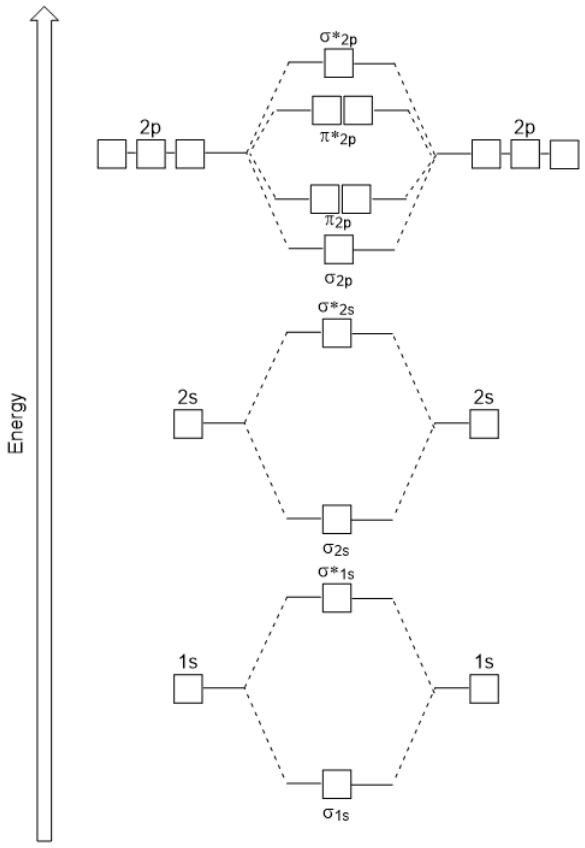


Figure 9.24 "Molecular orbital energy diagram for homonuclear diatomic molecules made from atoms of atomic number 8-10."

The energy diagram we have just generated fits experimentally with O_2, F_2, and Ne_2, but does not fit for B_2, C_2, and N_2. In the latter, homonuclear diatomic molecules (B_2, C_2, and N_2), interactions take place between the 2*s* and 2*p* atomic orbitals that are strong enough to swap the ordering of the σ_{2p} and π_{2p} molecular orbitals (Figure 9.25).

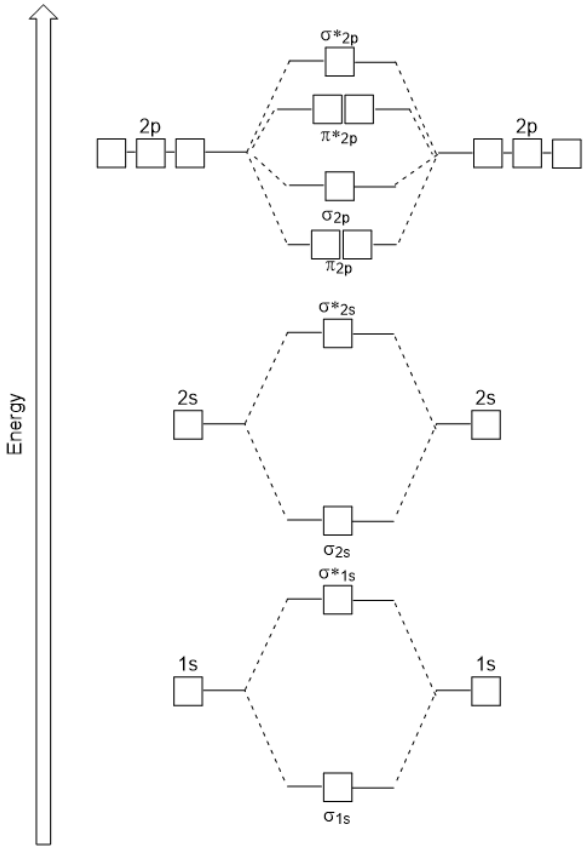


Figure 9.25 "Molecular orbital energy diagram for homonuclear diatomic molecules made from atoms of atomic number 5-7."

Heteronuclear Diatomic Molecules

In heteronuclear diatomic molecules, where two different molecules are bonded, the energy levels of the individual atoms' atomic orbitals may differ. However, the molecular orbital diagram we see in Figure 9.25 ("Molecular orbital energy diagram for homonuclear diatomic molecules made from atoms of atomic number 5-7") can be used to estimate the electron configuration and bond order.

Frontier Molecular Orbitals

We can focus further on two very important types of molecular orbitals: the **highest occupied molecular orbital (HOMO)** and the **lowest unoccupied molecular orbital (LUMO)**, also referred to collectively as the **frontier molecular orbitals** (Figure 9.26 "Frontier molecular orbitals HOMO and LUMO"). As their names imply, the HOMO is the molecular orbital that has the highest energy and contains electrons, while the LUMO is the lowest energy molecular orbital that does not contain electrons.

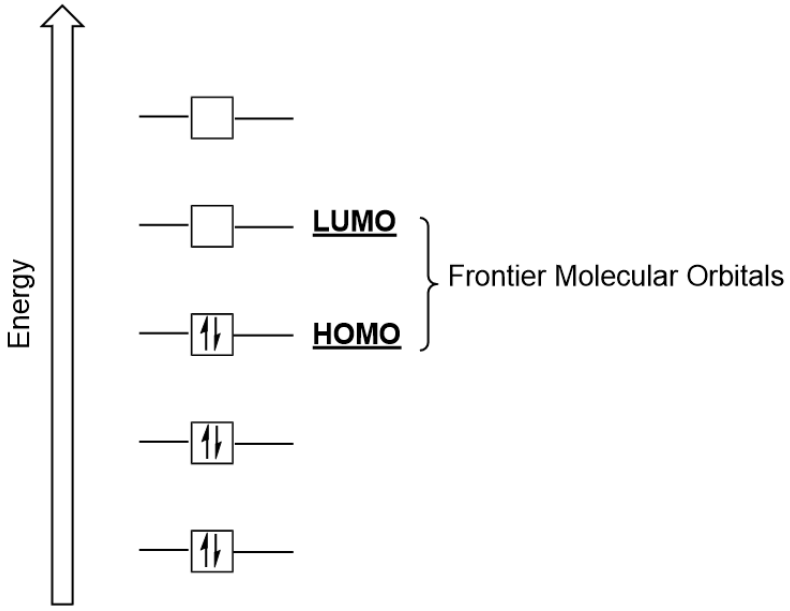


Figure 9.26 "Frontier molecular orbitals HOMO and LUMO."

When molecules absorb energy, it is typical for a HOMO electron to use this energy to transition from the ground HOMO orbital to the LUMO excited-state orbital. This type of transition can be observed in ultraviolet-visible (UV-Vis) radiation spectroscopy experiments. As well, in many chemical reactions, one reactant molecule may donate HOMO electrons to the LUMO of another reactant (Figure 9.27 "Formation of a new bonding molecular orbital by combining reactant HOMO and LUMO"). Therefore, understanding frontier molecular orbital energy levels can provide chemists with a great deal of insight in the areas of molecular spectroscopy and reactivity.

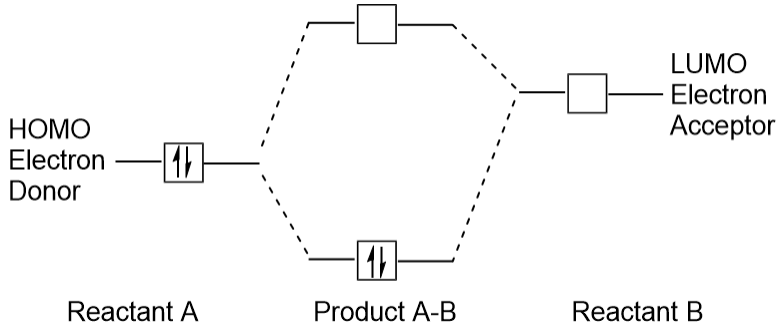


Figure 9.27 "Formation of a new bonding molecular orbital by combining reactant HOMO and LUMO."

Key Takeaways

- Atomic orbitals can combine to make bonding and antibonding molecular orbitals.
- Bonding orbitals are lower in energy than antibonding orbitals.
- Molecular orbitals are filled using similar principles to atomic orbitals.

- Bond order can be used to evaluate bond strength.
- Frontier molecular orbitals are of particular importance in molecular spectroscopy and reactivity.

End-of-Chapter Material

Additional Exercises

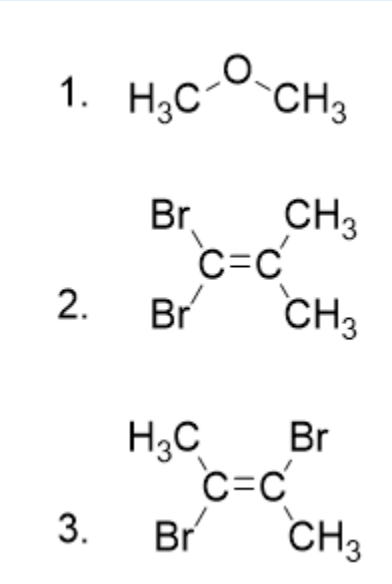
1. Explain why iron and copper have the same Lewis electron dot diagram when they have different numbers of electrons.
2. Name two ions with the same Lewis electron dot diagram as the Cl^- ion.
3. Based on the known trends, what ionic compound from the first column of the periodic table and the next-to-last column of the periodic table should have the highest lattice energy?
4. Based on the known trends, what ionic compound from the first column of the periodic table and the next-to-last column of the periodic table should have the lowest lattice energy?
5. P_2 is not a stable form of phosphorus, but if it were, what would be its likely Lewis electron dot diagram?
6. Se_2 is not a stable form of selenium, but if it were, what would be its likely Lewis electron dot diagram?
7. What are the Lewis electron dot diagrams of SO_2, SO_3, and SO_4^{2-}?
8. What are the Lewis electron dot diagrams of PO_3^{3-} and PO_4^{3-}?
9. Which bond do you expect to be more polar: an O–H bond or an N–H bond?
10. Which bond do you expect to be more polar: an O–F bond or an S–O bond?
11. Use bond energies to estimate the energy change of this reaction.

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

12. Use bond energies to estimate the energy change of this reaction.

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

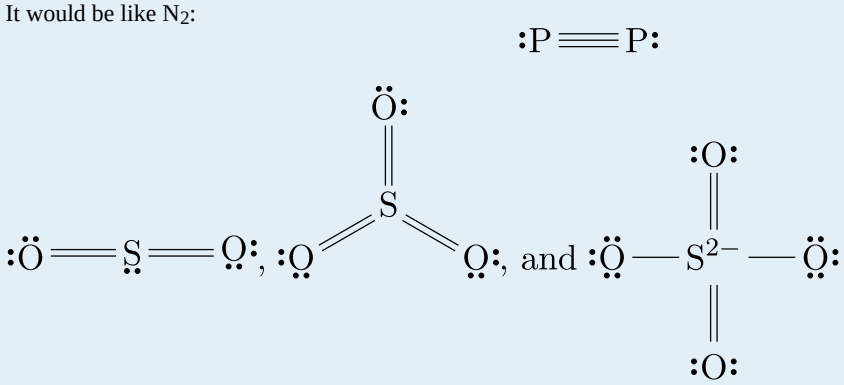
13. Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule.
14. Hydrogen peroxide (H_2O_2) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule.
15. Determine the molecular dipole moments for the following molecules:



16. What is the hybridization in the central atom of:
    a. HCN
    b. NH_4
    c. $TeBr_2$
17. Draw the molecular orbital electron configuration energy diagram of He_2 and determine the bond order.
18. Draw the molecular orbital electron configuration energy diagram of O_2 and determine the bond order.

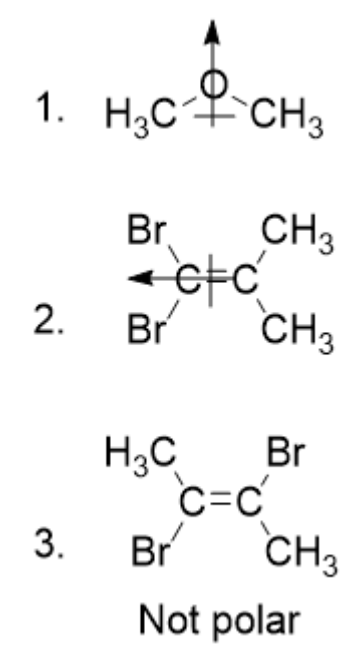
Answers

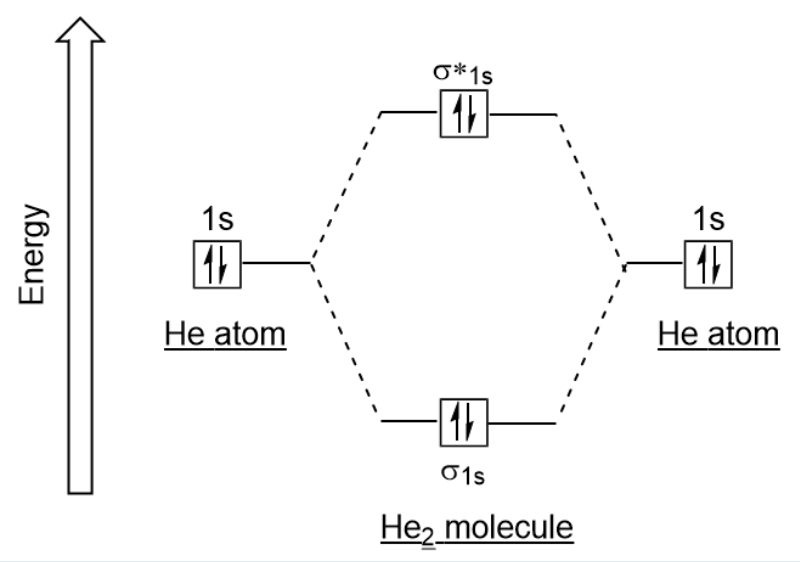
1. Iron has *d* electrons that typically are not shown on Lewis electron dot diagrams.
3. LiF
5. It would be like N_2:



7.
9. an O–H bond
11. −2,000 kJ

13. trigonal planar about both central C atoms

15. 

17. 

bond order = 0

Chapter 10. Solids and Liquids

There is an urban legend that glass is an extremely thick liquid rather than a solid, even at room temperature. Proponents claim that old windows are thicker at the bottom than at the top, suggesting that the glass flowed down over time. Unfortunately, the proponents of this idea have no credible evidence that this is true, as old windows were likely not subject to the stricter manufacturing standards that exist today. Also, when mounting a piece of glass that has an obviously variable thickness, it makes structural sense to put the thicker part at the bottom, where it will support the object better.

Liquids flow when a small force is placed on them, even if only very slowly. Solids, however, may deform under a small force, but they return to their original shape when the force is relaxed. This is how glass behaves: it goes back to its original shape (unless it breaks under the applied force). Observers also point out that telescopes with glass lenses to focus light still do so even decades after manufacture — a circumstance that would not be so if the lens were liquid and flowed.

Glass is a solid at room temperature. Don’t let anyone tell you otherwise!

Figure 10.0 “Cleaning Window.” Is he cleaning a solid or a liquid? Contrary to some claims, glass is a solid, not a very thick liquid.

In the chapter “Gases”, we discussed the properties of gases. Here, we consider some properties of liquids and solids. As a review, Table 10.1 “Properties of the Three Phases of Matter” lists some general properties of the three phases of matter.

Table 10.1 Properties of the Three Phases of Matter

Phase	Shape	Density	Compressibility
Gas	fills entire container	low	high
Liquid	fills a container from bottom to top	high	low
Solid	rigid	high	low

Media Attributions

- "Cleaning Window" by newlivinghouston © CC BY (Attribution)

Properties of Liquids

Learning Objectives

1. Define the vapour pressure of liquids.
2. Explain the origin of both surface tension and capillary action.

There are some properties that all liquids have. The liquid that we are most familiar with is probably water, and it has these properties. Other liquids have them as well, which is something to keep in mind.

All liquids have a certain portion of their particles having enough energy to enter the gas phase, and if these particles are at the surface of the liquid, they do so (see Figure 10.1 “Evaporation”). The formation of a gas from a liquid at temperatures below the boiling point is called **evaporation**. At these temperatures, the material in the gas phase is called **vapour**, rather than gas; the term *gas* is reserved for when the gas phase is the stable phase.

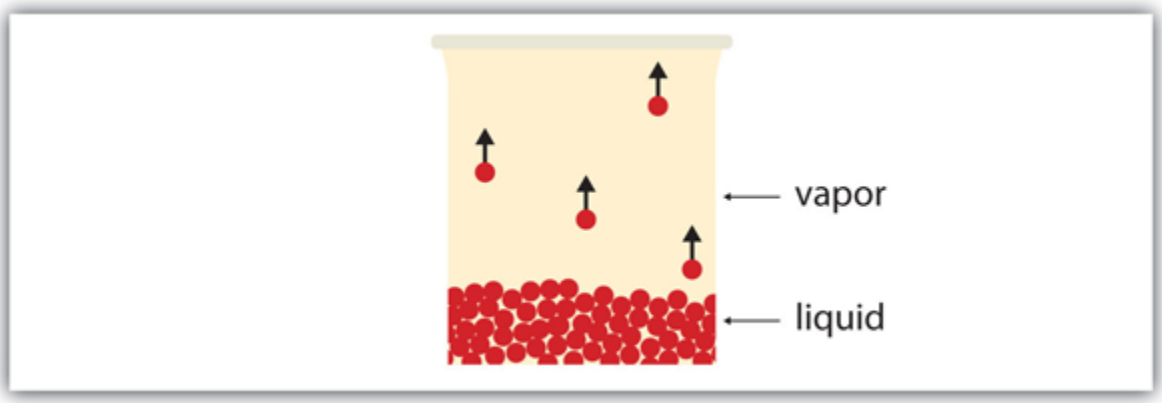


Figure 10.1 “Evaporation.” Some particles of a liquid have enough energy to escape the liquid phase to become a vapour.

If the available volume is large enough, eventually all the liquid will become vapour. But if the available volume is not enough, eventually some of the vapour particles will reenter the liquid phase (see Figure 10.2 “Equilibrium”). At some point, the number of particles entering the vapour phase will equal the number of particles leaving the vapour phase, so there is no net change in the amount of vapour in the system. We say that the system is *at equilibrium*. The partial pressure of the vapour at equilibrium is called the *vapour pressure of the liquid*.

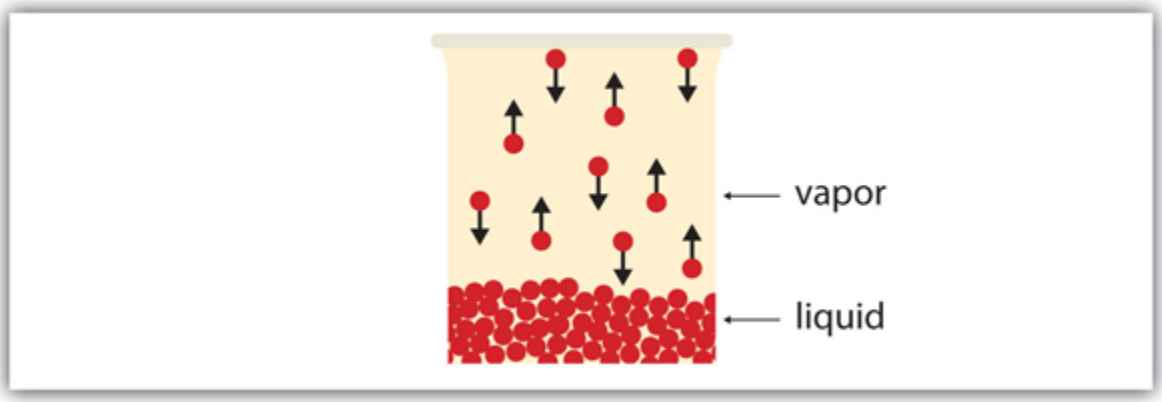


Figure 10.2 "Equilibrium." At some point, the number of particles entering the vapour phase will be balanced by the number of particles returning to the liquid. This point is called equilibrium.

Understand that the liquid has not stopped evaporating. The reverse process — condensation — is occurring as fast as evaporation is, so there is no net change in the amount of vapour in the system. The term **dynamic equilibrium** represents a situation in which a process still occurs, but the opposite process also occurs at the same rate so that there is no net change in the system.

The vapour pressure for a substance is dependent on the temperature of the substance; as the temperature increases, so does the vapour pressure. Figure 10.3 "Plots of Vapour Pressure versus Temperature for Several Liquids" is a plot of vapour pressure versus temperature for several liquids. Having defined vapour pressure, we can also redefine the *boiling point* of a liquid: the temperature at which the vapour pressure of a liquid equals the surrounding environmental pressure. The normal vapour pressure, then, is the temperature at which the vapour pressure is 760 torr, or exactly 1 atm. Thus boiling points vary with surrounding pressure, a fact that can have large implications on cooking foods at lower- or higher-than-normal elevations. Atmospheric pressure varies significantly with altitude.

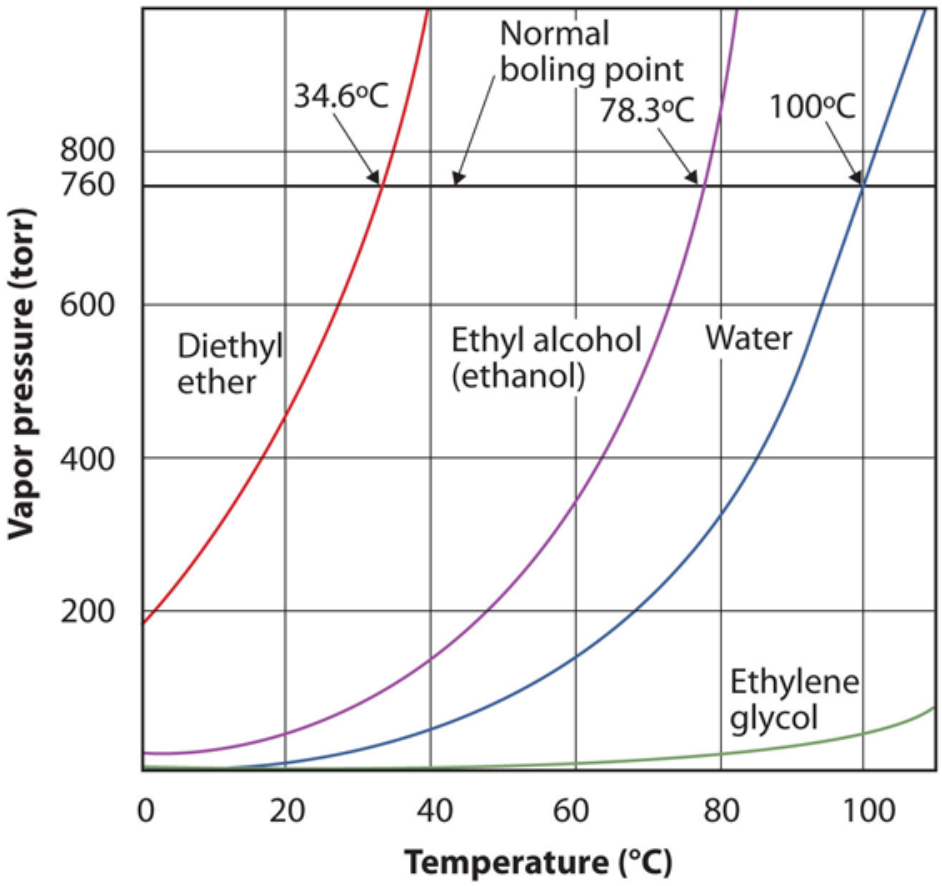


Figure 10.3 "Plots of Vapour Pressure versus Temperature for Several Liquids." The vapour pressure of a liquid depends on the identity of the liquid and the temperature, as this plot shows.

Example 10.1

Use Figure 10.3 "Plots of Vapour Pressure versus Temperature for Several Liquids" to estimate the boiling point of water at 500 torr, which is the approximate atmospheric pressure at the top of Mount Everest.

Solution

See the accompanying figure. Five hundred torr is between 400 and 600, so we extend a line from that point on the *y*-axis across to the curve for water and then drop it down to the *x*-axis to read the associated temperature. It looks like the point on the water vapour pressure curve corresponds to a temperature of about 90°C, so we conclude that the boiling point of water at 500 torr is 90°C.

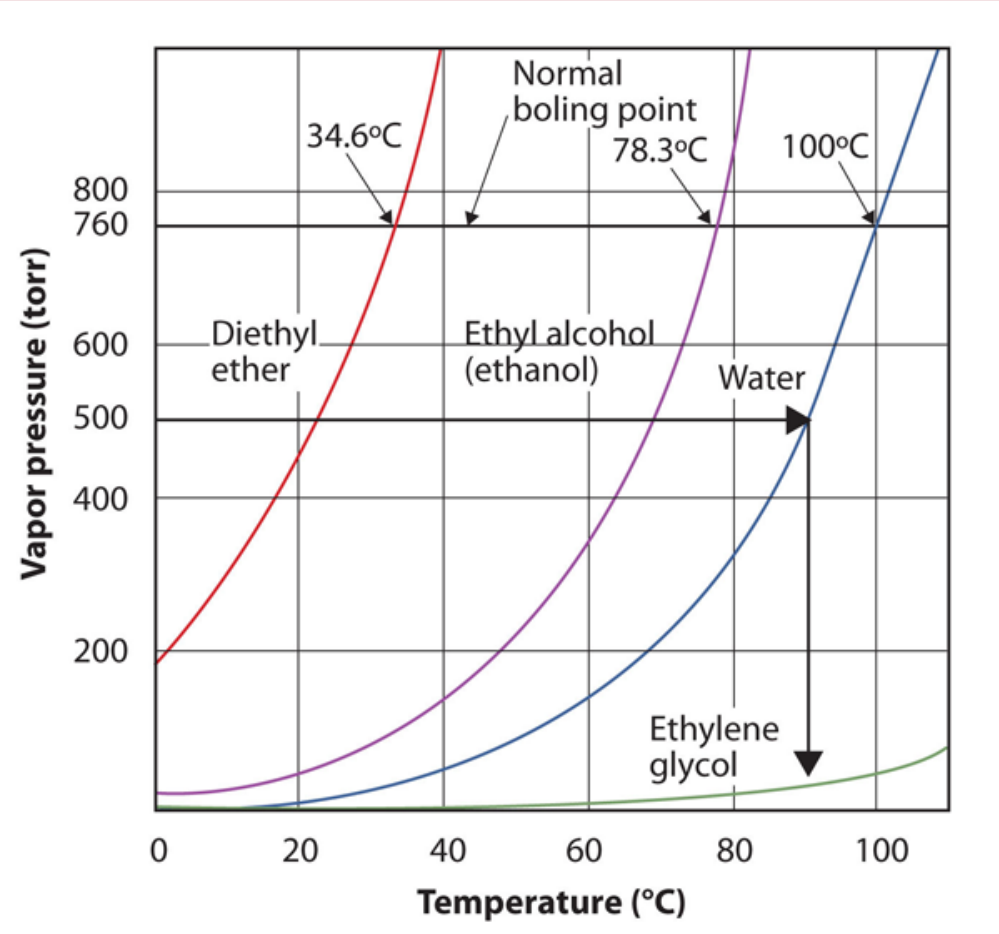


Figure 10.4 Using Figure 10.3 "Plots of Vapour Pressure versus Temperature for Several Liquids" to Answer Example 10.1

By reading the graph properly, you can estimate the boiling point of a liquid at different temperatures.

Test Yourself

Use Figure 10.3 "Plots of Vapour Pressure versus Temperature for Several Liquids" to estimate the boiling point of ethanol at 400 torr.

Answer

About 65°C.

The vapour pressure curve for water is not exactly zero at the melting point — 0°C. Even ice has a vapour pressure; that is why it sublimes over time. However, the vapour pressures of solids are typically much lower than that of liquids. At −1°C, the vapour pressure of ice is 4.2 torr. At a freezer temperature of 0°F (−17°C), the vapour pressure of ice is only 1.0 torr; so-called deep freezers can get down to −23°C, where the vapour pressure of ice is only 0.6 torr.

Phase Diagrams

A phase diagram is a graphical representation of the equilibrium relationships that exist between the phases of a substance under specified pressures and temperatures (see Figure 10.5 "A generic phase

diagram"). The phase diagram is a combination of three curves: the vapour pressure curve, the melting curve and the sublimation curve. We have previously seen that vapour pressure curves represent the equilibrium between the liquid and gas phase, and the point at which the pressure equals 1 atm is the normal boiling point. One additional feature of this curve in the phase diagram (green), is that it ends at the **critical point**. The critical point is the point at the highest temperature and pressure at which liquids and gases remain distinguishable. At temperatures and pressure beyond this point the matter exists in a phase with properties of both liquids and gases known as a **supercritical fluid**.

The melting curve (orange) represents the equilibrium between solid and liquid, and the point at which the pressure equals 1 atm is the normal melting point. The sublimation curve (blue) represents the equilibrium which exists between solid and gas. Finally, the point where all three curves meet is known as the triple point. At this point, three phases (solid, liquid and gas) all exist at equilibrium.

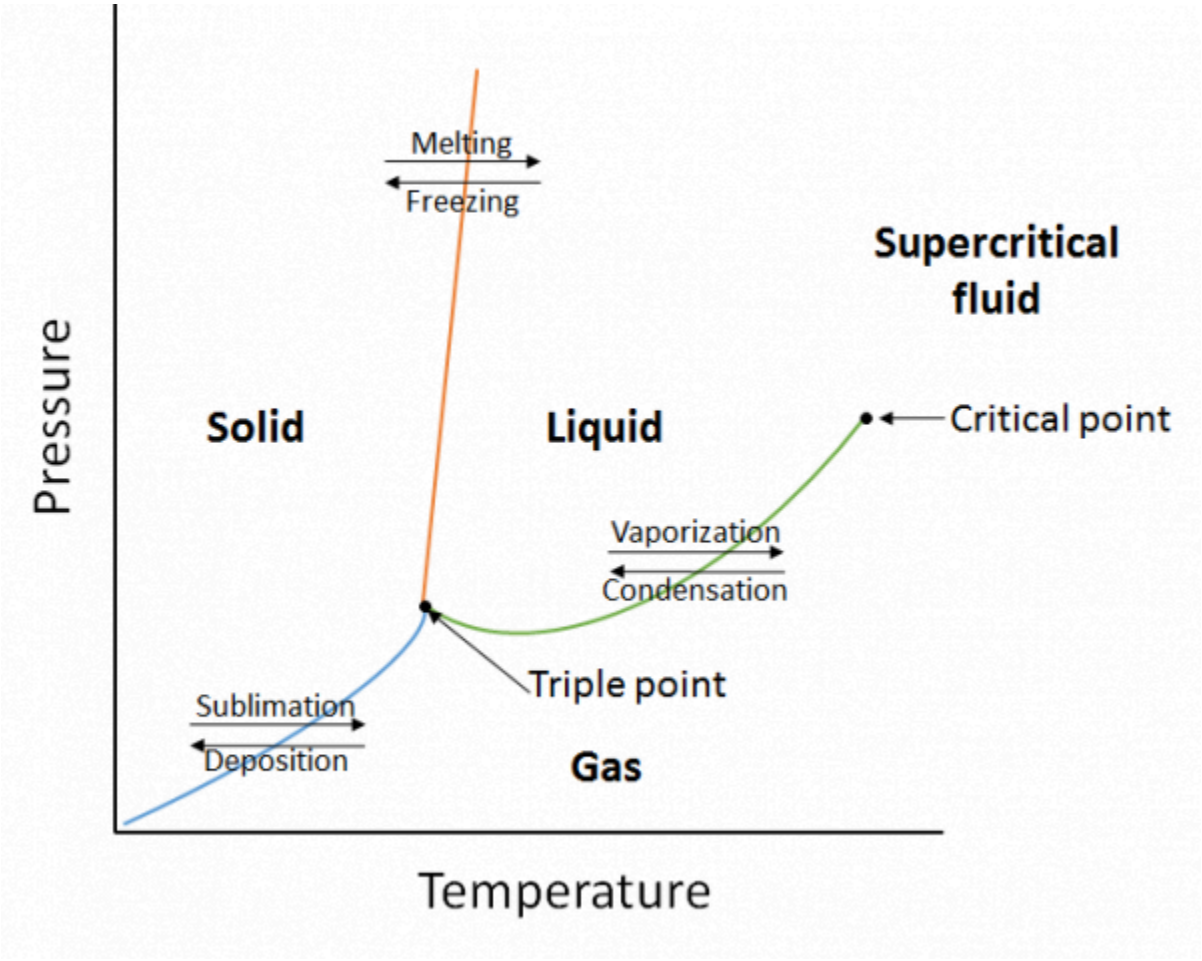


Figure 10.5 "A generic phase diagram."

Example 10.2

Using the following phase diagram, determine what would happen if:

1. The temperature is increased for matter at point 1.

2. The pressure is increased for matter at point 3.

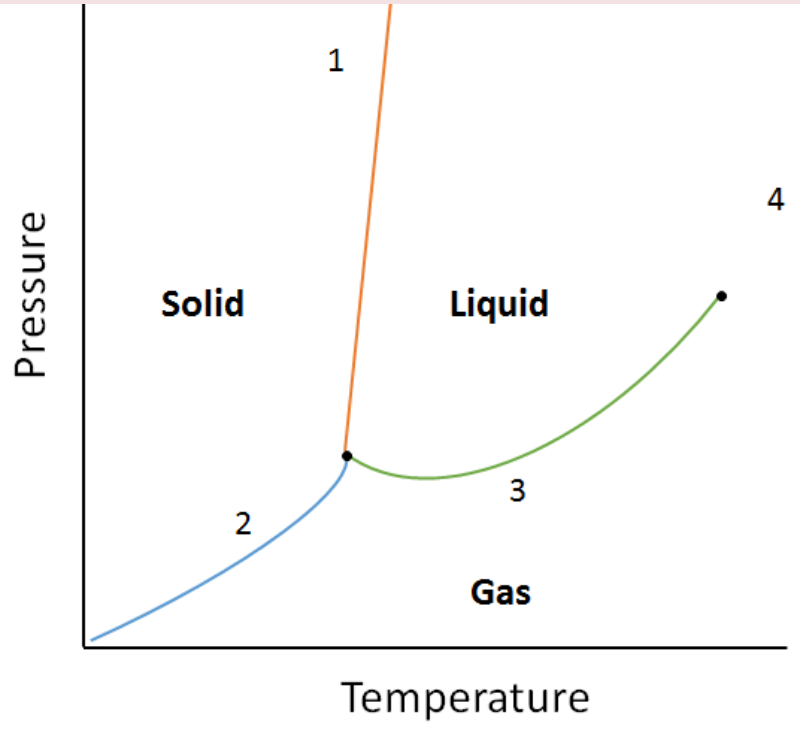


Figure 10.6 "Example phase diagram."

Solution

1. Matter at point 1 will melt (change phase from solid to liquid) if the temperature is increased.
2. Matter at point 3 will condense (change phase from gas to liquid) if the temperature is increased.

Surface Tension and Capillary Action

All liquids share some other properties as well. **Surface tension** is an effect caused by an imbalance of forces on the atoms at the surface of a liquid, as shown in Figure 10.7 "Surface Tension". The blue particle in the bulk of the liquid experiences intermolecular forces from all around, as illustrated by the arrows. However, the yellow particle on the surface does not experience any forces above it because there are no particles above it. This leads to an imbalance of forces that we call surface tension.

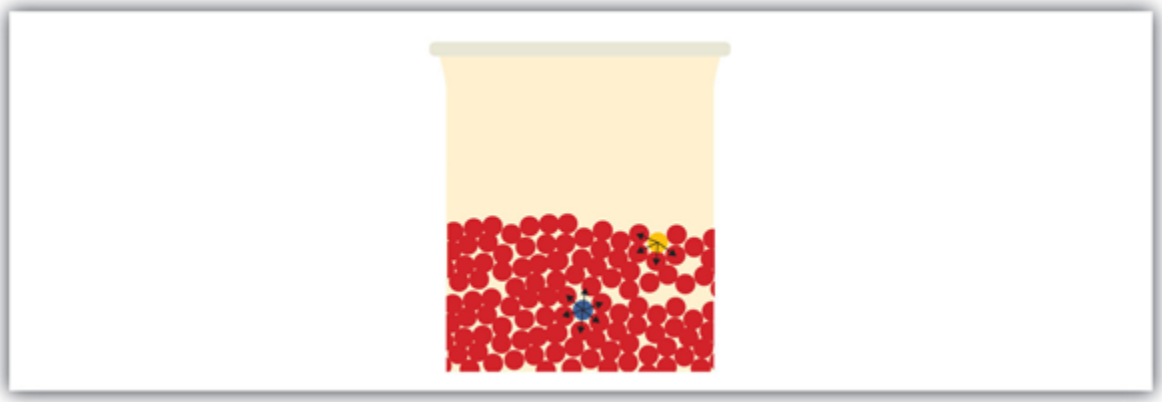


Figure 10.7 "Surface Tension." Surface tension comes from the fact that particles at the surface of a liquid do not experience interactions from all directions, leading to an imbalance of forces on the surface.

Figure 10.8 "Effects of Surface Tension." Water on the surface of this apple beads up due to the effect of surface tension.

Surface tension is responsible for several well-known behaviours of liquids, including water. Liquids with high surface tension tend to bead up when present in small amounts (Figure 10.8 "Effects of Surface Tension"). Surface tension causes liquids to form spheres in free fall or zero gravity (see Figure 10.16 "Liquids and Gravity": the "floating" water isn't in the shape of a sphere by accident; it is the result of surface tension). Surface tension is also responsible for the fact that small insects can "walk" on water. Because of surface tension, it takes energy to break the surface of a liquid, and if an object (such as an insect) is light enough, there is not enough force due to gravity for the object to break through the surface, so the object stays on top of the water (Figure 10.9 "Walking on Water"). Carefully done, this phenomenon can also be illustrated with a thin razor blade or a paper clip.

Figure 10.9 "Walking on Water." Small insects can actually walk on top of water because of surface tension effects.

The fact that small droplets of water bead up on surfaces does not mean that water — or any other liquid — does not interact with other substances. Sometimes the attraction can be very strong. **Adhesion** is the tendency of a substance to interact with other substances because of intermolecular forces, while **cohesion** is the tendency of a substance to interact with itself. If cohesive forces within a liquid are stronger than adhesive forces between a liquid and another substance, then the liquid tends to keep to itself; it will bead up. However, if adhesive forces between a liquid and another substance are stronger than cohesive forces, then the liquid will spread out over the other substance, trying to maximize the interface between the other substance and the liquid. We say that the liquid *wets* the other substance.

Adhesion and cohesion are important for other phenomena as well. In particular, if adhesive forces are strong, then when a liquid is introduced to a small-diameter tube of another substance, the liquid moves up or down in the tube, as if ignoring gravity. Because tiny tubes are called capillaries, this phenomenon is called **capillary action**. For example, one type of capillary action — *capillary rise* — is seen when water or water-based liquids rise up in thin glass tubes (like the capillaries sometimes used in blood tests), forming an upwardly curved surface called a **meniscus**. Capillary action is also responsible for the "wicking" effect that towels and sponges use to dry wet objects; the matting of fibres forms tiny capillaries that have good adhesion with water. Cotton is a good material for this; polyester and other synthetic fabrics do not display similar capillary action, which is why you seldom find rayon bath towels. A similar effect is observed with liquid fuels or melted wax and their wicks. Capillary action is thought to be at least partially responsible for transporting water from the roots to the tops of trees, even tall ones.

On the other hand, some liquids have stronger cohesive forces than adhesive forces. In this case, in the presence of a capillary, the liquid is forced down from its surface; this is an example of a type of capillary action called *capillary depression*. In this case, the meniscus curves downward. Mercury has very strong cohesive forces; when a capillary is placed in a pool of mercury, the surface of the mercury liquid is depressed (Figure 10.10 "Capillary Action").

Figure 10.10 "Capillary Action." (a) Capillary rise is seen when adhesion is strong, such as with water in a thin glass tube. (b) Capillary depression is seen when cohesive forces are stronger than adhesive forces, such as with mercury and thin glass tubes.

Chemistry Is Everywhere: Waxing a Car

Responsible car owners are encouraged to wax their cars regularly. In addition to making the car look nicer, it also helps protect the surface, especially if the surface is metal. Why?

The answer has to do with cohesion and adhesion (and, to a lesser extent, rust). Water is an important factor in the rusting of iron, sometimes used extensively in outer car bodies. Keeping water away from the metal is one way to minimize rusting. A coat of paint helps with this. However, dirty or scratched paint can attract water, and adhesive forces will allow the water to wet the surface, maximizing its contact with the metal and promoting rust.

Wax is composed of long hydrocarbon molecules that do not interact well with water. (Hydrocarbons are compounds with C and H atoms; for more information on hydrocarbons, see Chapter 16 "Organic Chemistry".) That is, a thin layer of wax will not be wetted by water. A freshly waxed car has low adhesive forces with water, so water beads up on the surface, as a consequence of its cohesion and surface tension. This minimizes the contact between water and metal, thus minimizing rust.

Figure 10.11 Droplets of water on a freshly waxed car do not wet the car well because of low adhesion between water and the waxed surface. This helps protect the car from rust.

Key Takeaways

- All liquids evaporate.
- If volume is limited, evaporation eventually reaches a dynamic equilibrium, and a constant vapour pressure is maintained.
- All liquids experience surface tension, an imbalance of forces at the surface of the liquid.
- All liquids experience capillary action, demonstrating either capillary rise or capillary depression in the presence of other substances.

Exercises

Questions

1. What is the difference between evaporation and boiling?
2. What is the difference between a gas and vapour?
3. Define *normal boiling point* in terms of vapour pressure.
4. Is the boiling point higher or lower at higher environmental pressures? Explain your answer.
5. Referring to Figure 10.3 “Plots of Vapour Pressure versus Temperature for Several Liquids”, if the pressure is 400 torr, which liquid boils at the lowest temperature?
6. Referring to Figure 10.3, if the pressure is 100 torr, which liquid boils at the highest temperature?
7. Referring to Figure 10.3, estimate the boiling point of ethanol at 200 torr.

8. Referring to Figure 10.3, at approximately what pressure is the boiling point of water 40°C?
9. Explain how surface tension works.
10. From what you know of intermolecular forces, which substance do you think might have a higher surface tension — ethyl alcohol or mercury? Why?
11. Under what conditions would a liquid demonstrate a capillary rise?
12. Under what conditions would a liquid demonstrate a capillary depression?
13. Using the phase diagram from the example question earlier in this section, what state of matter is depicted by point 4? How could you change matter at point 2 to the gas phase?

Answers

1. Evaporation occurs when a liquid becomes a gas at temperatures below that liquid's boiling point, whereas boiling is the conversion of a liquid to a gas at the liquid's boiling point.

3. the temperature at which the vapour pressure of a liquid is 760 torr

5. diethyl ether

7. 48°C

9. Surface tension is an imbalance of attractive forces between liquid molecules at the surface of a liquid.

11. Adhesion must be greater than cohesion.

13. Point 4 represents the supercritical fluid state. Matter at point 2 could be changed to the gas phase by either decreasing the pressure, or increasing the temperature.

Media Attributions

Solids

Learning Objectives

1. Describe the general properties of a solid.
2. Describe the six different types of solids.

A solid is like a liquid in that particles are in contact with each other. Solids are unlike liquids in that the intermolecular forces are strong enough to hold the particles in place. At low enough temperatures, all substances are solids (helium is the lone exception), but the temperature at which the solid state becomes the stable phase varies widely among substances, from 20 K (−253°C) for hydrogen to over 3,900 K (3,600°C) for carbon.

The solid phase has several characteristics. First, solids maintain their shape. They do not fill their entire containers like gases do, and they do not adopt the shape of their containers like liquids do. They cannot be easily compressed like gases can, and they have relatively high densities.

Solids may also demonstrate a variety of properties. For example, many metals can be beaten into thin sheets or drawn into wires, while compounds such as NaCl will shatter if they are struck. Some metals, such as sodium and potassium, are rather soft, while others, such as diamond, are very hard and can easily scratch other substances. Appearances differ as well: most metals are shiny and silvery, but sulfur (a nonmetal) is yellow, and ionic compounds can take on a rainbow of colours. Solid metals conduct electricity and heat, while ionic solids do not. Many solids are opaque, but some are transparent. Some dissolve in water, but some do not. Figure 10.12 “Properties of Solids” shows two solids that exemplify the similar and dissimilar properties of solids.

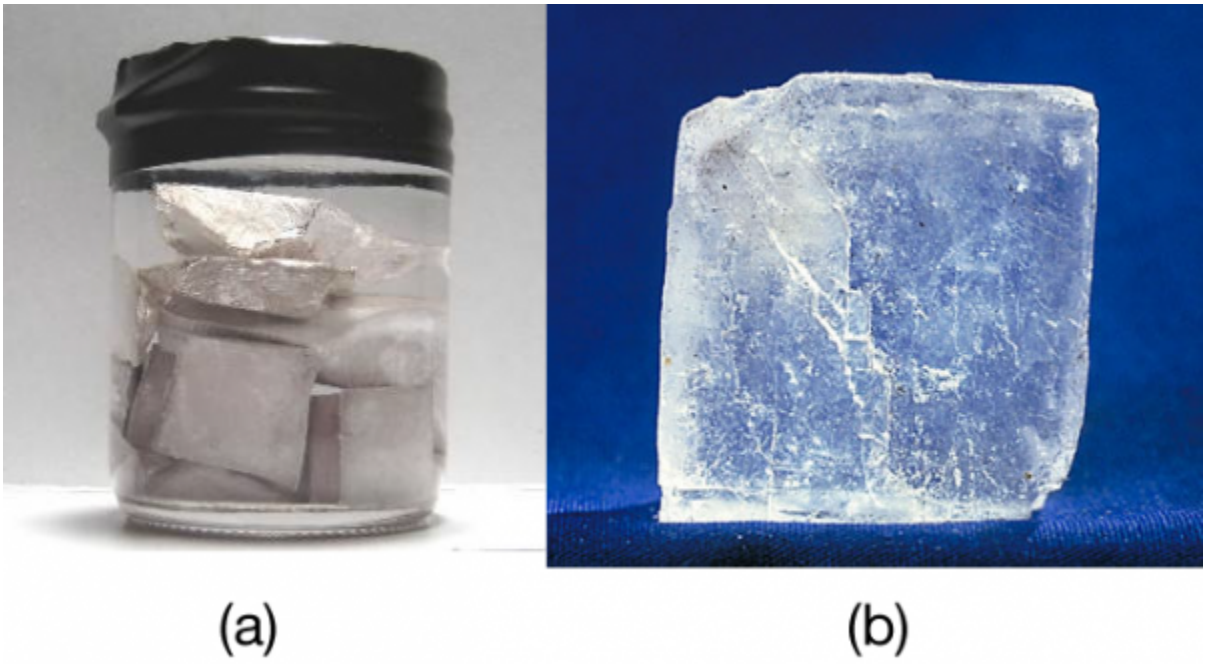


Figure 10.12 "Properties of Solids." (a) Sodium metal is silvery, soft, and opaque and conducts electricity and heat well. (b) NaCl is transparent, hard, and colourless and does not conduct electricity or heat well in the solid state. These two substances illustrate the range of properties that solids can have.

Solids can have a wide variety of physical properties because there are different types of solids. Here we will review the different types of solids and the bonding that gives them their properties.

First, we must distinguish between two general types of solids. An **amorphous solid** is a solid with no long-term structure or repetition. Examples include glass and many plastics, both of which are composed of long chains of molecules with no order from one molecule to the next. A **crystalline solid** is a solid that has a regular, repeating three-dimensional structure. A crystal of NaCl (see Figure 10.12 "Properties of Solids") is one example: at the atomic level, NaCl is composed of a regular three-dimensional array of Na^+ ions and Cl^- ions.

There is only one type of amorphous solid. However, there are several different types of crystalline solids, depending on the identity of the units that compose the crystal.

An **ionic solid** is a crystalline solid composed of ions (even if the ions are polyatomic). NaCl is an example of an ionic solid (see Figure 10.13 "An Ionic Solid"). The Na^+ ions and Cl^- ions alternate in three dimensions, repeating a pattern that goes on throughout the sample. The ions are held together by the attraction of opposite charges — a very strong force. Hence most ionic solids have relatively high melting points; for example, the melting point of NaCl is 801°C. Ionic solids are typically very brittle. To break them, the very strong ionic attractions need to be broken; a displacement of only about 1×10^{-10} m will move ions next to ions of the same charge, which results in repulsion. Ionic solids do not conduct electricity in their solid state; however, in the liquid state and when dissolved in some solvent, they do conduct electricity. This fact originally promoted the idea that some substances exist as ionic particles.

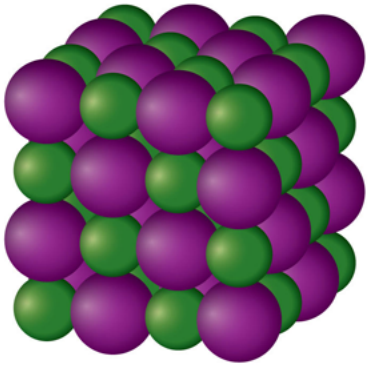


Figure 10.13 "An Ionic Solid." NaCl is a solid composed of a three-dimensional array of alternating Na^+ ions (green) and Cl^- ions (purple) held together by the attraction of opposite charges.

A **molecular solid** is a crystalline solid whose components are covalently bonded molecules. Many molecular substances, especially when carefully solidified from the liquid state, form solids where the molecules line up with a regular fashion similar to an ionic crystal, but they are composed of molecules instead of ions. Because the intermolecular forces between molecules are typically less strong than in ionic solids, molecular solids typically melt at lower temperatures and are softer than ionic solids. Ice is an example of a molecular solid. In the solid state, the molecules line up in a regular pattern (see Figure 10.14 "Molecular Solids"). Some very large molecules, such as biological molecules, will form crystals only if they are very carefully solidified from the liquid state or, more usually, from a dissolved state; otherwise, they will form amorphous solids.

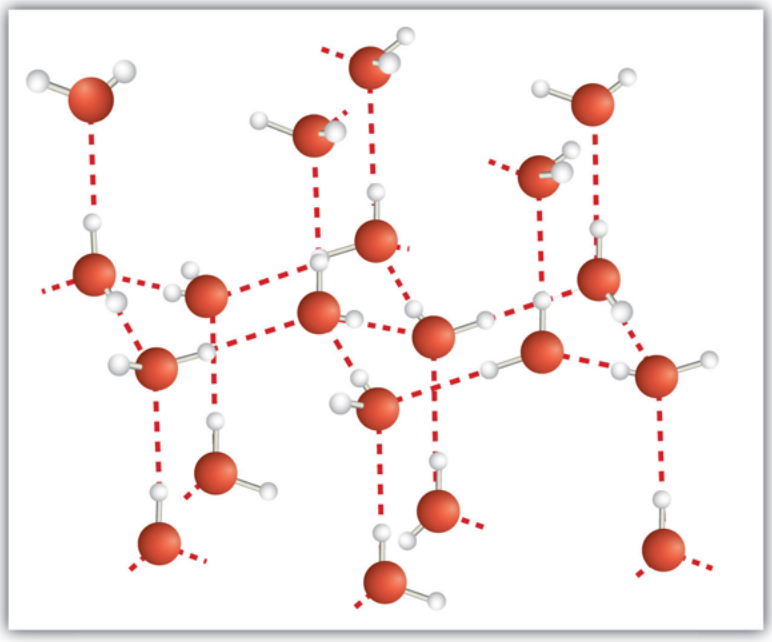


Figure 10.14 "Molecular Solids." Water molecules line up in a regular pattern to form molecular solids. The dotted lines show how the polar O–H covalent bonds in one molecule engage in hydrogen bonding with other molecules. The O atoms are red, and the H atoms are white.

Some solids are composed of atoms of one or more elements that are covalently bonded together in a seemingly never-ending fashion. Such solids are called **covalent network solids**. Each piece of the substance is essentially one huge molecule, as the covalent bonding in the crystal extends throughout the entire crystal. The two most commonly known covalent network solids are carbon in its diamond form and silicon dioxide (SiO_2). Figure 10.15 “Covalent Network Solids” shows the bonding in a covalent network solid. Generally, covalent network solids are poor conductors of electricity, although their ability to conduct heat is variable: diamond is one of the most thermally conductive substances known, while SiO_2 is about 100 times less thermally conductive. Most covalent network solids are very hard, as exemplified by diamond, which is the hardest known substance. Covalent network solids have high melting points by virtue of their network of covalent bonds, all of which would have to be broken for them to transform into a liquid. Indeed, covalent network solids are among the highest-melting substances known: the melting point of diamond is over 3,500°C, while the melting point of SiO_2 is around 1,650°C. These characteristics are explained by the network of covalent bonds throughout the sample.

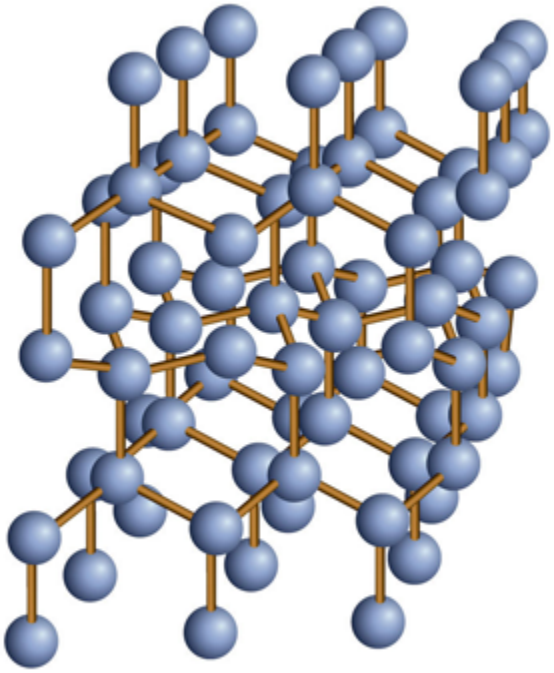


Figure 10.15 “Covalent Network Solids.” Diamond is a covalent network solid, with each C atom making four covalent bonds to four other C atoms. A diamond is essentially one huge molecule.

A **metallic solid** is a solid with the characteristic properties of a metal: shiny and silvery in colour and a good conductor of heat and electricity. A metallic solid can also be hammered into sheets and pulled into wires. A metallic solid exhibits metallic bonding, a type of intermolecular interaction caused by the sharing of the *s* valence electrons by all atoms in the sample. It is the sharing of these valence electrons that explains the ability of metals to conduct electricity and heat well. It is also relatively easy for metals to lose these valence electrons, which explains why metallic elements usually form cations when they make compounds.

Example 10.3

Predict the type of crystal exhibited by each solid.

1. MgO
2. Ag
3. CO_2

Solution

1. A combination of a metal and a nonmetal makes an ionic compound, so MgO would exist as ionic crystals in the solid state.
2. Silver is a metal, so it would exist as a metallic solid in the solid state.
3. CO_2 is a covalently bonded molecular compound. In the solid state, it would form molecular crystals. (You can actually see the crystals in dry ice with the naked eye.)

Test Yourself

Predict the type of crystal exhibited by each solid.

1. I_2
2. $Ca(NO_3)_2$

Answers

1. molecular crystals
2. ionic crystals

Food and Drink App: The Rocks We Eat

The foods and beverages we eat and drink all have different phases: solid, liquid, and gas. (How do we ingest gases? Carbonated beverages have gas, which sometimes cause a person to belch.) However, among the solids we eat, three in particular are, or are produced from, rocks. Yes, rocks!

The first one is NaCl, or common salt. Salt is the only solid that we ingest that is actually mined as a rock (hence the term *rock salt*; it really is a rock). Salt provides both Na^+ ions and Cl^- ions, both of which are necessary for good health. Salt preserves food, a function that was much more important before the days of modern food preparation and storage. The fact that saltiness is one of the major tastes the tongue can detect suggests a strong evolutionary link between ingesting salt and survival. There is some concern today that there is too much salt in the diet; it is estimated that the average person consumes at least three times as much salt daily than is necessary for proper bodily function.

The other two rocks we eat are related: sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3). However, we do not mine these substances directly from the ground; we mine trona, whose chemical formula is $Na_3H(CO_3)_2$. This substance is dissolved in water and treated with CO_2 gas to make either Na_2CO_3 or $NaHCO_3$. Another process, called the Solvay process, is also used to make Na_2CO_3. In the Solvay process, NH_3 and CO_2 are added to solutions of NaCl to make $NaHCO_3$ and NH_4Cl; the $NaHCO_3$ precipitates and is heated to produce Na_2CO_3. Either way, we get these two products from the ground (i.e., rocks).

$NaHCO_3$ is also known as baking soda, which is used in many baked goods. Na_2CO_3 is used in foods to regulate the acid balance. It is also used in laundry (where it is called washing soda) to interact with other ions in water that tend to reduce detergent efficiency.

Key Takeaways

- Solids can be divided into amorphous solids and crystalline solids.
- Crystalline solids can be ionic, molecular, covalent network, or metallic.

Exercises

Questions

1. What is the difference between a crystalline solid and an amorphous solid?
2. What two properties do solids have in common? What two properties of solids can vary?
3. Explain how the bonding in an ionic solid explains some of the properties of these solids.
4. Explain how the bonding in a molecular solid explains some of the properties of these solids.
5. Explain how the bonding in a covalent network solid explains some of the properties of these solids.
6. Explain how the bonding in a metallic solid explains some of the properties of these solids.
7. Which type(s) of solid has/have high melting points?
8. Which type(s) of solid conduct(s) electricity in their solid state? In their liquid state?
9. Which type of solid(s) is/are considered relatively soft?
10. Which type of solid(s) is/are considered very hard?
11. Predict the type of solid exhibited by each substance.
    a. Hg
    b. PH_3
    c. CaF_2
12. Predict the type of solid exhibited by each substance.
    a. $(CH_2)_n$ (polyethylene, a form of plastic)
    b. PCl_3
    c. NH_4Cl
13. Predict the type of solid exhibited by each substance.
    a. SO_3
    b. Br_2
    c. Na_2SO_3
14. Predict the type of solid exhibited by each substance.
    a. BN (boron nitride, a diamond-like compound)
    b. B_2O_3
    c. $NaBF_4$
15. Predict the type of solid exhibited by each substance.

a. H_2S
b. Si
c. CsF

16. Predict the type of solid exhibited by each substance.

a. Co
b. CO
c. CaCO3

Answers

1. At the atomic level, a crystalline solid has a regular arrangement of atoms, whereas an amorphous solid has a random arrangement of atoms.
3. The oppositely charged ions are very strongly held together, so ionic crystals have high melting points. Ionic crystals are also brittle because any distortion of the crystal moves same-charged ions closer to each other, so they repel.
5. The covalent network solid is essentially one molecule, making it very hard and giving it a very high melting point.
7. ionic solids, covalent network solids
9. molecular solids
11. a. metallic
    b. molecular solid
    c. ionic crystal
13. a. molecular solid
    b. molecular solid
    c. ionic crystal
15. a. molecular solid
    b. molecular solid
    c. ionic crystal

Media Attributions

Phase Transitions: Melting, Boiling, and Subliming

Learning Objectives

1. Describe what happens during a phase change.
2. Calculate the energy change needed for a phase change.

Substances can change phase — often because of a temperature change. At low temperatures, most substances are solid; as the temperature increases, they become liquid; at higher temperatures still, they become gaseous.

The process of a solid becoming a liquid is called **melting** (an older term that you may see sometimes is *fusion*). The opposite process, a liquid becoming a solid, is called **solidification**. For any pure substance, the temperature at which melting occurs — known as the **melting point** — is a characteristic of that substance. It requires energy for a solid to melt into a liquid. Every pure substance has a certain amount of energy it needs to change from a solid to a liquid. This amount is called the **enthalpy of fusion (or heat of fusion)** of the substance, represented as ΔH_{fus}. Some ΔH_{fus} values are listed in Table 10.2 “Enthalpies of Fusion for Various Substances”; it is assumed that these values are for the melting point of the substance. Note that the unit of ΔH_{fus} is kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{fus} is always tabulated as a positive number. However, it can be used for both the melting and the solidification processes as long as you keep in mind that melting is always endothermic (so ΔH will be positive), while solidification is always exothermic (so ΔH will be negative).

Table 10.2 Enthalpies of Fusion for Various Substances

Substance (Melting Point)	**ΔH_{fus} (kJ/mol)**
Water (0°C)	6.01
Aluminum (660°C)	10.7
Benzene (5.5°C)	9.95
Ethanol (−114.3°C)	5.02
Mercury (−38.8°C)	2.29

Example 10.4

What is the energy change when 45.7 g of H_2O melt at 0°C?

Solution

The ΔH_{fus} of H_2O is 6.01 kJ/mol. However, our quantity is given in units of grams, not moles, so the first step is to convert grams to moles using the molar mass of H_2O, which is 18.0 g/mol. Then we can use ΔH_{fus} as a conversion factor. Because the substance is melting, the process is endothermic, so the energy change will have a positive sign.

$$45.7 \text{ g } H_2O \times \left(\frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} \right) \times \left(\frac{6.01 \text{ kJ}}{1 \text{ mol } H_2O} \right) = 15.3 \text{ kJ}$$

Without a sign, the number is assumed to be positive.

Test Yourself

What is the energy change when 108 g of C_6H_6 freeze at 5.5°C?

Answer

−13.8 kJ

During melting, energy goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. Hence melting is an **isothermal** process because a substance stays at the same temperature. Only when all of a substance is melted does any additional energy go to changing its temperature.

What happens when a solid becomes a liquid? In a solid, individual particles are stuck in place because the intermolecular forces cannot be overcome by the energy of the particles. When more energy is supplied (e.g., by raising the temperature), there comes a point at which the particles have enough energy to move around but not enough energy to separate. This is the liquid phase: particles are still in contact but are able to move around each other. This explains why liquids can assume the shape of their containers: the particles move around and, under the influence of gravity, fill the lowest volume possible (unless the liquid is in a zero-gravity environment — see Figure 10.16 “Liquids and Gravity”).

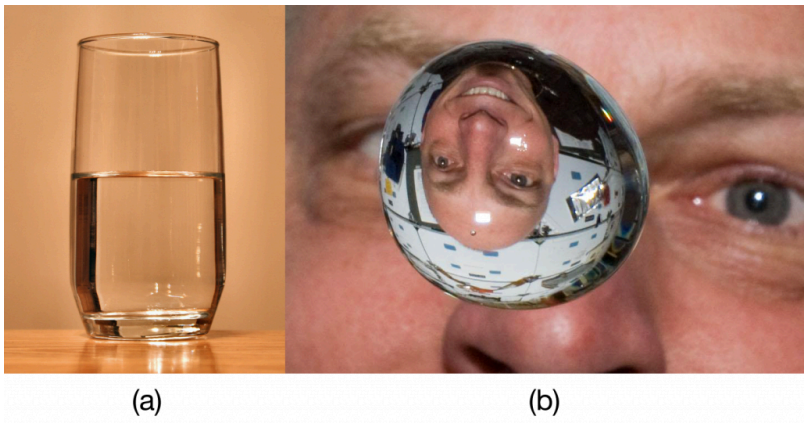


Figure 10.16 “Liquids and Gravity.” (a) A liquid fills the bottom of its container as it is drawn downward by gravity and the particles slide over each other. (b) A liquid floats in a zero- gravity environment. The particles still slide over each other because they are in the liquid phase, but now there is no gravity to pull them down.

The phase change between a liquid and a gas has some similarities to the phase change between a solid and a liquid. At a certain temperature, the particles in a liquid have enough energy to become a gas. The process of a liquid becoming a gas is called **boiling (or vapourization)**, while the process of a gas becoming a liquid is called **condensation**. However, unlike the solid/liquid conversion process, the liquid/gas conversion process is noticeably affected by the surrounding pressure on the liquid because gases are strongly affected by pressure. This means that the temperature at which a liquid becomes a gas, the **boiling point**, can change with surrounding pressure. Therefore, we define the **normal boiling point** as the temperature at which a liquid changes to a gas when the surrounding pressure is exactly 1 atm, or 760 torr. Unless otherwise specified, it is assumed that a boiling point is for 1 atm of pressure.

Like the solid/liquid phase change, the liquid/gas phase change involves energy. The amount of energy required to convert a liquid to a gas is called the **enthalpy of vaporization** (or heat of vaporization), represented as ΔH_{vap}. Some ΔH_{vap} values are listed in Table 10.3 “Enthalpies of Vaporization for Various Substances”; it is assumed that these values are for the normal boiling point temperature of the substance, which is also given in the table. The unit for ΔH_{vap} is also kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{vap} is also always tabulated as a positive number. It can be used for both the boiling and the condensation processes as long as you keep in mind that boiling is always endothermic (so ΔH will be positive), while condensation is always exothermic (so ΔH will be negative).

Table 10.3 Enthalpies of Vaporization for Various Substances

Substance (Normal Boiling Point)	**ΔH_{vap} (kJ/mol)**
Water (100°C)	40.68
Bromine (59.5°C)	15.4
Benzene (80.1°C)	30.8
Ethanol (78.3°C)	38.6
Mercury (357°C)	59.23

Example 10.5

What is the energy change when 66.7 g of $Br_2(g)$ condense to a liquid at 59.5°C?

Solution

The ΔH_{vap} of Br_2 is 15.4 kJ/mol. Even though this is a condensation process, we can still use the numerical value of ΔH_{vap} as long as we realize that we must take energy out, so the ΔH value will be negative. To determine the magnitude of the energy change, we must first convert the amount of Br_2 to moles. Then we can use ΔH_{vap} as a conversion factor.

$$66.7 \text{ g } Br_2 \times \left(\frac{1 \text{ mol } Br_2}{159.8 \text{ g } Br_2} \right) \times \left(\frac{15.4 \text{ kJ}}{1 \text{ mol } Br_2} \right) = 6.43 \text{ kJ}$$

Because the process is exothermic, the actual value will be negative: $\Delta H = -6.43$ kJ.

Test Yourself

What is the energy change when 822 g of $C_2H_5OH(\ell)$ boil at its normal boiling point of 78.3°C?

Answer

689 kJ

As with melting, the energy in boiling goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. So boiling is also an isothermal process. Only when all of a substance has boiled does any additional energy go to changing its temperature.

What happens when a liquid becomes a gas? We have already established that a liquid is composed of particles in contact with each other. When a liquid becomes a gas, the particles separate from each other, with each particle going its own way in space. This is how gases tend to fill their containers. Indeed, in the gas phase most of the volume is empty space; only about one one-thousandth of the volume is actually taken up by matter (see Figure 10.17 “Liquids and Gases”). It is this property of gases that explains why they can be compressed, a fact that is considered in Chapter 6 “Gases”.

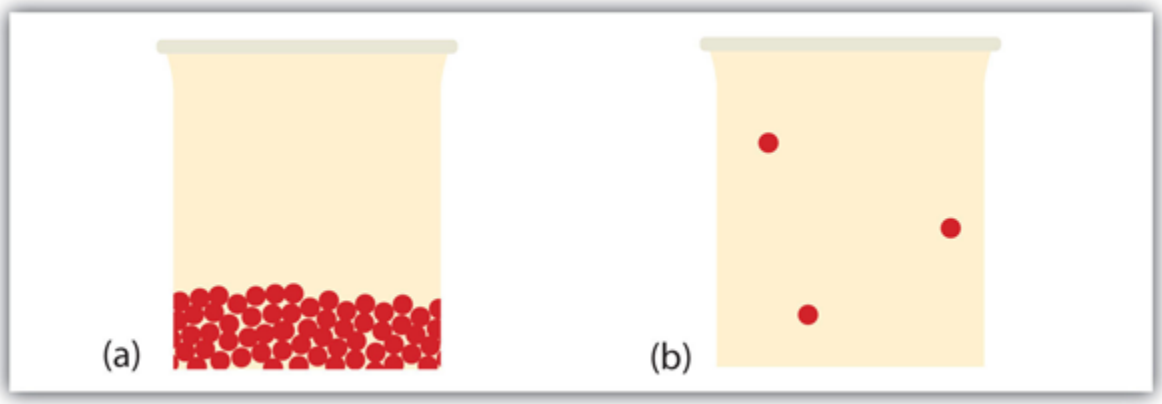


Figure 10.17 Liquids and Gases. In (a), the particles are a liquid; the particles are in contact but are also able to move around each other. In (b), the particles are a gas, and most of the volume is actually empty space. The particles are not to scale; in reality, the dots representing the particles would be about one one-thousandth the size as depicted.

Under some circumstances, the solid phase can transition directly to the gas phase without going through a liquid phase, and a gas can directly become a solid. The solid-to-gas change is called **sublimation**, while the reverse process is called **deposition**. Sublimation is isothermal, like the other phase changes. There is a measurable energy change during sublimation; this energy change is called the **enthalpy of sublimation**, represented as ΔH_{sub}. The relationship between the ΔH_{sub} and the other enthalpy changes is as follows:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

As such, ΔH_{sub} is not always tabulated because it can be simply calculated from ΔH_{fus} and ΔH_{vap}.

There are several common examples of sublimation. A well-known product — dry ice — is actually solid CO_2. Dry ice is dry because it sublimes, with the solid bypassing the liquid phase and going straight to the gas phase. The sublimation occurs at temperature of −77°C, so it must be handled with caution. If you have ever noticed that ice cubes in a freezer tend to get smaller over time, it is because the solid water is very slowly subliming. “Freezer burn” isn’t actually a burn; it occurs when certain

foods, such as meats, slowly lose solid water content because of sublimation. The food is still good but looks unappetizing. Reducing the temperature of a freezer will slow the sublimation of solid water.

Chemical equations can be used to represent a phase change. In such cases, it is crucial to use phase labels on the substances. For example, the chemical equation for the melting of ice to make liquid water is as follows:

$$H_2O(s) \rightarrow H_2O(\ell)$$

No chemical change is taking place; however, a physical change is taking place.

Heating Curves

A plot of the temperature versus the amount of heat added is known as a **heating curve** (see Figure 10.18). These are commonly used to visually show the relationship between phase changes and enthalpy for a given substance.

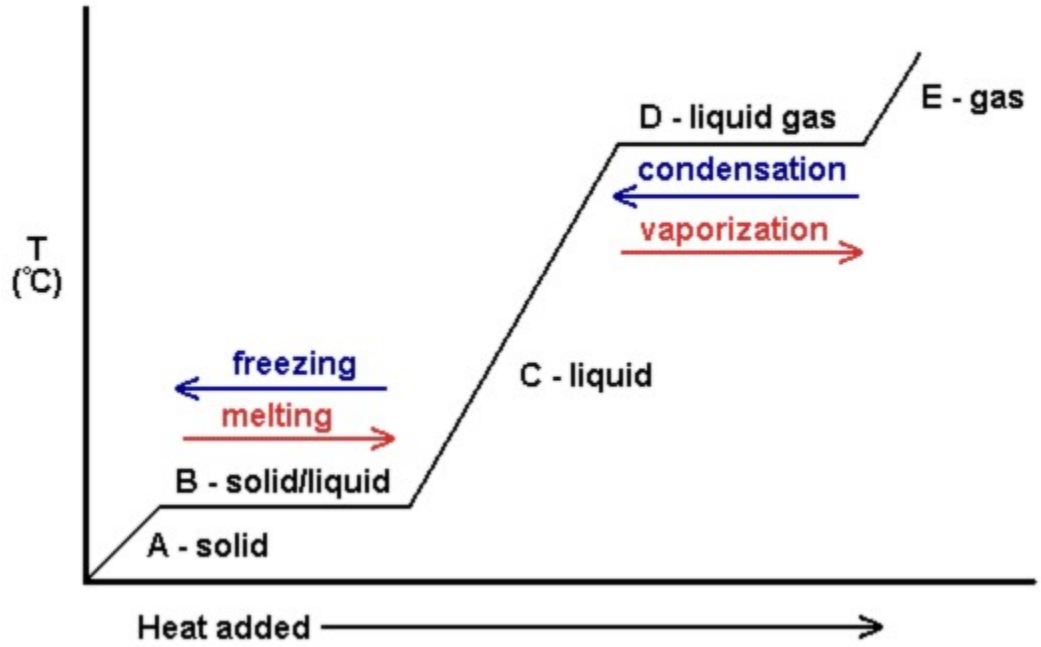


Figure 10.18 "Generic heating curve diagram."

In Figure 10.18[1], the solid gains kinetic energy and consequently rises in temperature as heat is added. At the melting point, the heat added is used to break the attractive intermolecular forces of the solid instead of increasing kinetic energy, and therefore the temperature remains constant. After all the solid has melted, once again, the heat added goes to increasing the kinetic energy (and temperature) of the liquid molecules until the boiling point. At the boiling point, once again, the heat added is used to break the attractive intermolecular forces instead of supplying kinetic energy, and the temperature remains constant until all liquid has been turned to gas.

1. Courtesy UC Davis Chemwiki\CC-BY-NC-SA-3.0

Key Takeaways

- Phase changes can occur between any two phases of matter.
- All phase changes occur with a simultaneous change in energy.
- All phase changes are isothermal.

Exercises

Questions

1. What is the difference between *melting* and *solidification*?
2. What is the difference between *boiling* and *condensation*?
3. Describe the molecular changes when a solid becomes a liquid.
4. Describe the molecular changes when a liquid becomes a gas.
5. What is the energy change when 78.0 g of Hg melt at −38.8°C?
6. What is the energy change when 30.8 g of Al solidify at 660°C?
7. What is the energy change when 111 g of Br_2 boil at 59.5°C?
8. What is the energy change when 98.6 g of H_2O condense at 100°C?
9. Each of the following statements is incorrect. Rewrite them so they are correct.
    a. Temperature changes during a phase change.
    b. The process of a liquid becoming a gas is called sublimation.
10. Each of the following statements is incorrect. Rewrite them so they are correct.
    a. The volume of a gas contains only about 10% matter, with the rest being empty space.
    b. ΔH_{sub} is equal to ΔH_{vap}.
11. Write the chemical equation for the melting of elemental sodium.
12. Write the chemical equation for the solidification of benzene (C_6H_6).
13. Write the chemical equation for the sublimation of CO_2.
14. Write the chemical equation for the boiling of propanol (C_3H_7OH).
15. What is the ΔH_{sub} of H_2O? (Hint: see Table 10.2 “Enthalpies of Fusion for Various Substances” and Table 10.3 “Enthalpies of Vaporization for Various Substances”.)
16. The ΔH_{sub} of I_2 is 60.46 kJ/mol, while its ΔH_{vap} is 41.71 kJ/mol. What is the ΔH_{fus} of I_2?

Answers

1. Melting is the phase change from a solid to a liquid, whereas solidification is the phase change from a liquid to a solid.
3. The molecules have enough energy to move about each other but not enough to completely separate from each other.
5. 890 J

7. 10.7 kJ

    a. Temperature does not change during a phase change.
    b. The process of a liquid becoming a gas is called boiling; the process of a solid becoming a gas is called sublimation.

11. $Na(s) \rightarrow Na(\ell)$

13. $CO_2(s) \rightarrow CO_2(g)$

15. 46.69 kJ/mol

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Intermolecular Forces

Learning Objectives

1. Relate phase to intermolecular forces.

Why does a substance have the phase it does? The preferred phase of a substance at a given set of conditions is a balance between the energy of the particles and intermolecular forces (or intermolecular interactions) between the particles. If the forces between particles are strong enough, the substance is a liquid or, if stronger, a solid. If the forces between particles are weak and sufficient energy is present, the particles separate from each other, so the gas phase is the preferred phase. The energy of the particles is mostly determined by temperature, so temperature is the main variable that determines what phase is stable at any given point.

What forces define intermolecular interactions? There are several. A force present in all substances with electrons is the **dispersion force** (sometimes called the *London dispersion force*, after the physicist Fritz London, who first described this force in the early 1900s). This interaction is caused by the instantaneous position of an electron in a molecule, which temporarily makes that point of the molecule negatively charged and the rest of the molecule positively charged. In an instant, the electron is now somewhere else, but the fleeting imbalance of electric charge in the molecule allows molecules to interact with each other. As you might expect, the greater the number of electrons in a species, the stronger the dispersion force; this partially explains why smaller molecules are gases and larger molecules are liquids and solids at the same temperature. (Mass is a factor as well.)

Molecules with a permanent dipole moment experience **dipole-dipole interactions**, which are generally stronger than dispersion forces if all other things are equal. The oppositely charged ends of a polar molecule, which have partial charges on them, attract each other (see Figure 10.19 “Dipole-Dipole Interactions”). Thus a polar molecule such CH_2Cl_2 has a significantly higher boiling point (313 K, or 40°C) than a nonpolar molecule like CF_4 (145 K, or −128°C), even though it has a lower molar mass (85 g/mol vs. 88 g/mol).

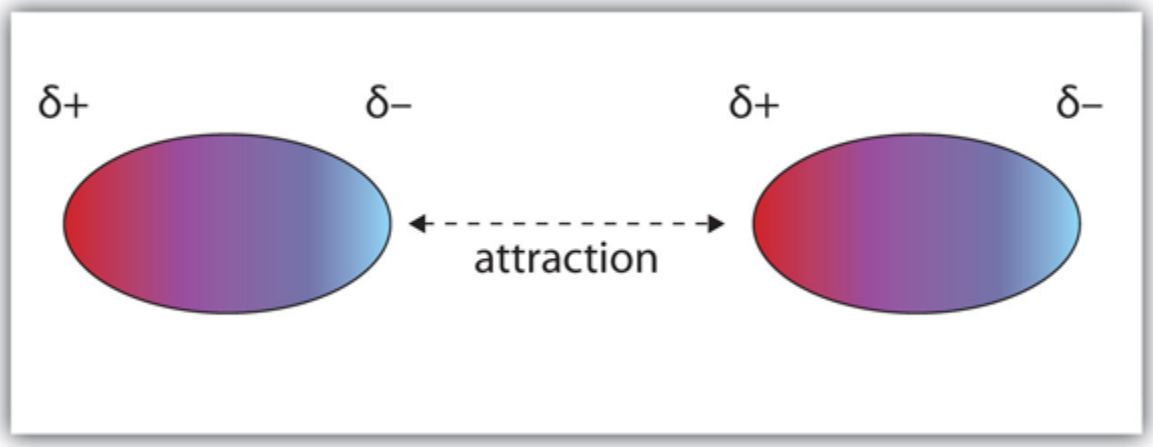


Figure 10.19 "Dipole-Dipole Interactions." Oppositely charged ends of polar molecules attract each other.

An unusually strong form of dipole-dipole interaction is called **hydrogen bonding**. Hydrogen bonding is found in molecules with an H atom bonded to an N atom, an O atom, or an F atom. Such covalent bonds are very polar, and the dipole-dipole interaction between these bonds in two or more molecules is strong enough to create a new category of intermolecular force. Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), H_2O has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, H_2S, is 233 K (−60°C). This is because H_2O molecules experience hydrogen bonding, while H_2S molecules do not. This strong attraction between H_2O molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected. Hydrogen bonding is also responsible for water's ability as a solvent, its high heat capacity, and its ability to expand when freezing; the molecules line up in such a way that there is extra space between the molecules, increasing its volume in the solid state (see Figure 10.20 "Hydrogen Bonding").

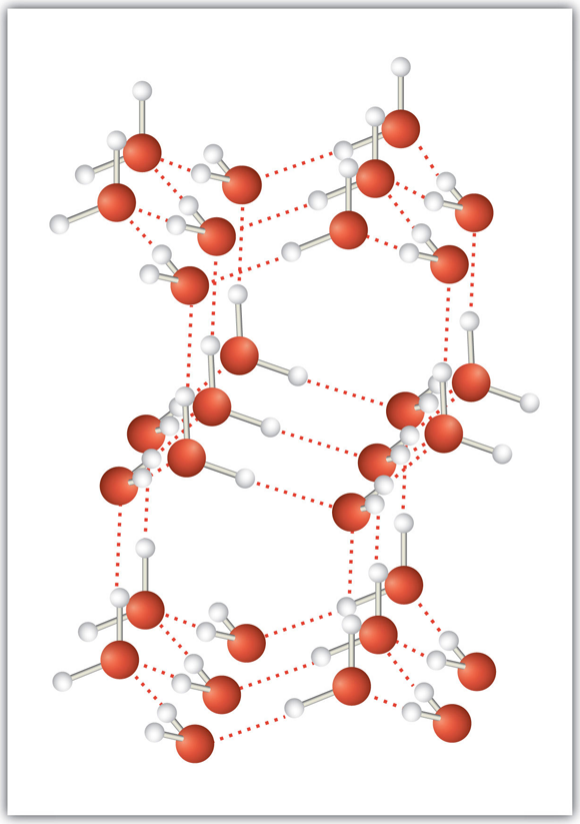


Figure 10.20 "Hydrogen Bonding." When water solidifies, hydrogen bonding between the molecules forces the molecules to line up in a way that creates empty space between the molecules, increasing the overall volume of the solid. This is why ice is less dense than liquid water.

Example 10.6

Identify the most significant intermolecular force in each substance.

1. C_3H_8
2. CH_3OH
3. H_2S

Solution

1. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
2. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
3. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Test Yourself

Identify the most significant intermolecular force in each substance.

1. HF
2. HCl

Answers

1. hydrogen bonding
2. dipole-dipole interactions

The preferred phase a substance adopts can change with temperature. At low temperatures, most substances are solids (only helium is predicted to be a liquid at absolute zero). As the temperature increases, those substances with very weak intermolecular forces become gases directly (in a process called *sublimation*, which is discussed in the section "Phase Transitions: Melting, Boiling, and Subliming"). Substances with weak interactions can become liquids as the temperature increases. As the temperature increases even more, the individual particles will have so much energy that the intermolecular forces are overcome, so the particles separate from each other, and the substance becomes a gas (assuming that their chemical bonds are not so weak that the compound decomposes from the high temperature). Although is it difficult to predict the temperature ranges for which solid, liquid, or gas is the preferred phase for any random substance, all substances progress from solid to liquid to gas in that order as temperature increases.

Key Takeaways

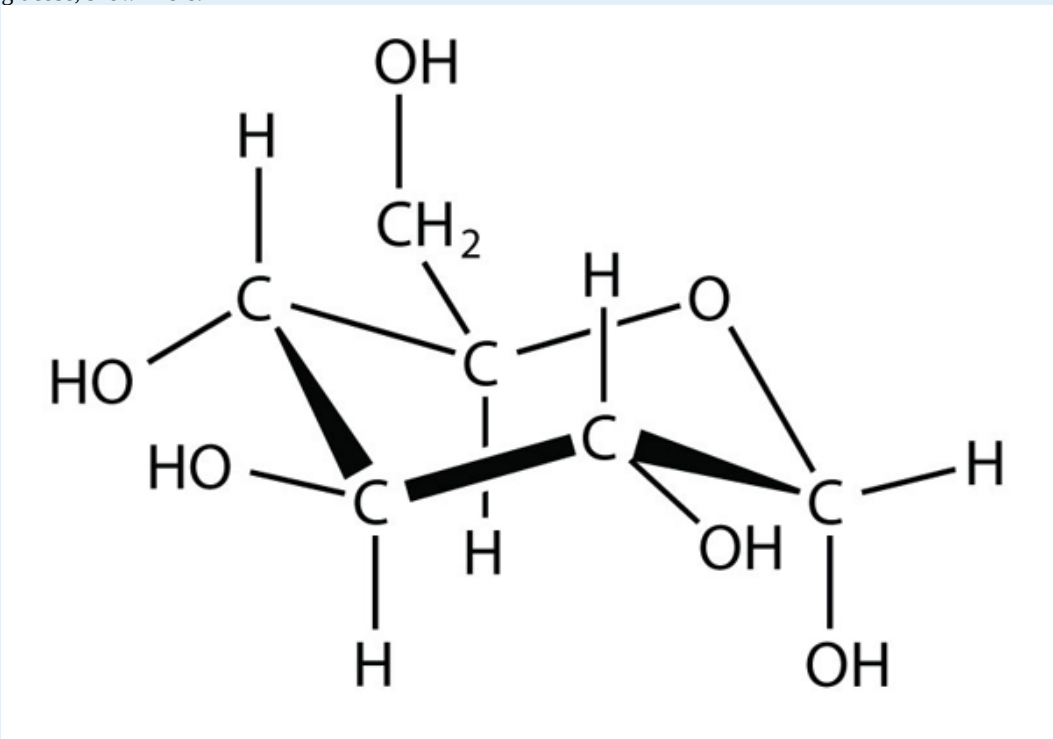
- All substances experience dispersion forces between their particles.
- Substances that are polar experience dipole-dipole interactions.
- Substances with covalent bonds between an H atom and N, O, or F atoms experience hydrogen bonding.
- The preferred phase of a substance depends on the strength of the intermolecular force and the energy of the particles.

Exercises

Questions

1. What type of intermolecular force do all substances have?
2. What is necessary for a molecule to experience dipole-dipole interactions?
3. What is necessary for a molecule to experience hydrogen bonding?
4. How does varying the temperature change the preferred phase of a substance?
5. Identify the strongest intermolecular force present in each substance.
    a. He
    b. $CHCl_3$
    c. HOF

6. Identify the strongest intermolecular force present in each substance.
    a. CH_3OH
    b. $(CH_3)_2CO$
    c. N_2
7. Identify the strongest intermolecular force present in each substance.
    a. HBr
    b. $C_6H_5NH_2$
    c. CH_4
8. Identify the strongest intermolecular force present in each substance.
    a. $C_{10}H_{22}$
    b. HF
    c. glucose, shown here:



Answers

1. dispersion force
3. An H atom must be bonded to an N, O, or F atom.
5. a. dispersion forces
    b. dipole-dipole interactions
    c. hydrogen bonding
7. a. dipole-dipole interactions
    b. hydrogen bonding

c. dispersion forces

End-of-Chapter Material

Additional Exercises

1. All other things being equal, rank the intermolecular forces in order of increasing strength.
2. Which subatomic particles (protons, neutrons, electrons) are most responsible for intermolecular forces? Explain your answer.
3. Can a molecule experience more than one intermolecular force at the same time? Why or why not?
4. Of the properties boiling point, structure of the solid phase, and molar mass, which are influenced by hydrogen bonding? Explain your answer.
5. How many grams of solid water can be melted with 1.55 kJ of energy?
6. How many grams of Hg can be vapourized using 29,330 J of energy?
7. Another way to minimize freezer burn is to wrap food tightly before freezing. Why would this minimize freezer burn?
8. The ΔH_{sub} of naphthalene ($C_{10}H_8$) is 72.6 kJ/mol. What energy is needed to sublime 100.0 g of $C_{10}H_8$?
9. Which do you think would have a higher surface tension — liquid neon or liquid krypton? Explain your answer.
10. Under what condition would a liquid not show either capillary rise or capillary depression?

Answers

1. dispersion forces < dipole-dipole interactions < hydrogen bonding < ionic bonding
3. Yes, but one intermolecular force usually dominates.
5. 4.64 g
7. Water in the vapour phase has no space to evaporate into.
9. Liquid krypton, because it would have stronger dispersion forces.

Chapter 11. Solutions

More than 70% of the earth's surface is covered by a very important solution — seawater. It is likely that without seawater, no life would exist on Earth.

At its simplest, seawater is mostly H_2O. But about 3.5% of seawater is dissolved solids, mostly NaCl but other ions as well. Table 11.1 "Percentage by Mass of Ions in Seawater and Blood" lists the percentage by mass of the various ions in seawater.

Because it is highly likely that life on Earth originated in the oceans, it should not be surprising that many bodily fluids resemble seawater — especially blood. Table 11.1 also lists the percentage by mass of ions in a typical sample of blood.

Table 11.1 Percentage by Mass of Ions in Seawater and Blood

Ion	Percentage in Seawater	Percentage in Blood
Na^+	2.36	0.322
Cl^-	1.94	0.366
Mg^{2+}	0.13	0.002
SO_4^{2-}	0.09	—
K^+	0.04	0.016
Ca^{2+}	0.04	0.0096
HCO_3^-	0.002	0.165
HPO_4^{2-}, $H_2PO_4^-$	—	0.01

Most ions are more abundant in seawater than they are in blood, with some notable exceptions. There is far more hydrogen carbonate ion (HCO_3^-) in blood than in seawater; indeed, it is the third most common ion in blood. This difference is significant because the HCO_3^- ion and some related species [CO_3^{2-}, $CO_2(aq)$] have an important role in controlling the acid-base properties of blood. Although there is a negligible amount of the two hydrogen phosphate ions (HPO_4^{2-} and $H_2PO_4^-$) in seawater, there is a small amount in blood, where these ions affect acid-base properties. Another notable difference is that blood has a negligible amount of the sulfate ion (SO_4^{2-}), but this ion is present in seawater.

Gold is present in seawater — but only a tiny amount. A current estimate of the amount of gold is about 1 part per every 1×10^{13} parts of seawater, which makes the extraction of gold from seawater unfeasible. However, it does mean that there are about 1.4×10^{14} g of gold in the world's oceans!

Figure 11.1 "Ocean." There are approximately 1.4 × 10^{14} g of gold in the oceans, but extracting it effectively is beyond current technologies.

A solution is a *homogeneous mixture* — a mixture of two or more substances that are so intimately mixed that the mixture behaves in many ways like a single substance. Many chemical reactions occur when the reactants are dissolved in solution. In this chapter, we will introduce concepts that are applicable to solutions and the chemical reactions that occur in them.

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Colligative Properties of Solutions

Learning Objectives

1. Name the four colligative properties.
2. Calculate changes in vapour pressure, melting point, and boiling point of solutions.
3. Calculate the osmotic pressure of solutions.

The properties of solutions are very similar to the properties of their respective pure solvents. This makes sense because the majority of the solution *is* the solvent. However, some of the properties of solutions differ from pure solvents in measurable and predictable ways. The differences are proportional to the fraction that the solute particles occupy in the solution. These properties are called **colligative properties**; the word *colligative* comes from the Greek word meaning "related to the number," implying that these properties are related to the number of solute particles, not their identities.

Before we introduce the first colligative property, we need to introduce a new concentration unit. The **mole fraction** of the *i*th component in a solution, χ_i, is the number of moles of that component divided by the total number of moles in the sample:

$$\chi_i = \frac{\text{moles of } i\text{th component}}{\text{total moles}}$$

(χ is the lowercase Greek letter chi.) The mole fraction is always a number between 0 and 1 (inclusive) and has no units; it is just a number.

Example 11.1

A solution is made by mixing 12.0 g of $C_{10}H_8$ in 45.0 g of C_6H_6. What is the mole fraction of $C_{10}H_8$ in the solution?

Solution

We need to determine the number of moles of each substance, add them together to get the total number of moles, and then divide to determine the mole fraction of $C_{10}H_8$. The number of moles of $C_{10}H_8$ is as follows:

$$12.0 \text{ g } \cancel{\text{C}_{10}\text{H}_8} \times \frac{1 \text{ mol } \text{C}_{10}\text{H}_8}{128.18 \text{ g } \cancel{\text{C}_{10}\text{H}_8}} = 0.0936 \text{ mol } \text{C}_{10}\text{H}_8$$

The number of moles of C_6H_6 is as follows:

$$45.0 \text{ g } \cancel{\text{C}_6\text{H}_6} \times \frac{1 \text{ mol } \text{C}_6\text{H}_6}{78.12 \text{ g } \cancel{\text{C}_6\text{H}_6}} = 0.576 \text{ mol } \text{C}_6\text{H}_6$$

The total number of moles is:

$$0.0936 \text{ mol} + 0.576 \text{ mol} = 0.670 \text{ mol}$$

Now we can calculate the mole fraction of $C_{10}H_8$:

$$\chi_{C_{10}H_8} = \frac{0.0936 \text{ mol}}{0.670 \text{ mol}} = 0.140$$

The mole fraction is a number between 0 and 1 and is unitless.

Test Yourself

A solution is made by mixing 33.8 g of CH_3OH in 50.0 g of H_2O. What is the mole fraction of CH_3OH in the solution?

Answer

0.275

A useful thing to note is that the sum of the mole fractions of all substances in a mixture equals 1. Thus the mole fraction of C_6H_6 in Example 11.1 could be calculated by evaluating the definition of mole fraction a second time, or — because there are only two substances in this particular mixture — we can subtract the mole fraction of the $C_{10}H_8$ from 1 to get the mole fraction of C_6H_6.

Now that this new concentration unit has been introduced, the first colligative property can be considered. As was mentioned in Chapter 10 "Solids and Liquids", all pure liquids have a characteristic vapour pressure in equilibrium with the liquid phase, the partial pressure of which is dependent on temperature. Solutions, however, have a lower vapour pressure than the pure solvent has, and the amount of lowering is dependent on the fraction of solute particles, as long as the solute itself does not have a significant vapour pressure (the term *nonvolatile* is used to describe such solutes). This colligative property is called **vapour pressure depression** (or *lowering*). The actual vapour pressure of the solution can be calculated as follows:

$$P_{\text{soln}} = \chi_{\text{solv}} P^*_{\text{solv}}$$

where P_{soln} is the vapour pressure of the solution, χ_{solv} is the mole fraction of the solvent particles, and P^*_{solv} is the vapour pressure of the pure solvent at that temperature (which is data that must be provided). This equation is known as **Raoult's law** (the approximate pronunciation is *rah-OOLT*). Vapour pressure depression is rationalized by presuming that solute particles take positions at the surface in place of solvent particles, so not as many solvent particles can evaporate.

Example 11.2

A solution is made by mixing 12.0 g of $C_{10}H_8$ in 45.0 g of C_6H_6. If the vapour pressure of pure C_6H_6 is 95.3 torr, what is the vapour pressure of the solution?

Solution

This is the same solution that was in Example 11.1, but here we need the mole fraction of C_6H_6. The number of moles of $C_{10}H_8$ is as follows:

$$12.0 \cancel{\text{ g } C_{10}H_8} \times \frac{1 \text{ mol } C_{10}H_8}{128.18 \cancel{\text{ g } C_{10}H_8}} = 0.0936 \text{ mol } C_{10}H_8$$

The number of moles of C_6H_6 is as follows:

$$45.0 \text{ g } \cancel{\text{C}_6\text{H}_6} \times \frac{1 \text{ mol } \text{C}_6\text{H}_6}{78.12 \text{ g } \cancel{\text{C}_6\text{H}_6}} = 0.576 \text{ mol } \text{C}_6\text{H}_6$$

So the total number of moles is:

$$0.0936 \text{ mol} + 0.576 \text{ mol} = 0.670 \text{ mol}$$

Now we can calculate the mole fraction of C_6H_6:

$$\chi_{\text{C}_6\text{H}_6} = \frac{0.576 \text{ mol}}{0.670 \text{ mol}} = 0.860$$

(The mole fraction of $C_{10}H_8$ calculated in Example 11.1 plus the mole fraction of C_6H_6 equals 1, which is mathematically required by the definition of mole fraction.) Now we can use Raoult's law to determine the vapour pressure in equilibrium with the solution:

$$P_{\text{soln}} = (0.860)(95.3 \text{ torr}) = 82.0 \text{ torr}$$

The solution has a lower vapour pressure than the pure solvent.

Test Yourself

A solution is made by mixing 33.8 g of $C_6H_{12}O_6$ in 50.0 g of H_2O. If the vapour pressure of pure water is 25.7 torr, what is the vapour pressure of the solution?

Answer
24.1 torr

Two colligative properties are related to solution concentration as expressed in molality. As a review, recall the definition of molality:

$$\text{molality} = \frac{\text{moles solute}}{\text{kilograms solvent}}$$

Because the vapour pressure of a solution with a nonvolatile solute is depressed compared to that of the pure solvent, it requires a higher temperature for the solution's vapour pressure to reach 1.00 atm (760 torr). Recall that this is the definition of the normal boiling point: the temperature at which the vapour pressure of the liquid equals 1.00 atm. As such, the normal boiling point of the solution is higher than that of the pure solvent. This property is called **boiling point elevation**.

The change in boiling point (ΔT_b) is easily calculated:

$$\Delta T_b = mK_b$$

where m is the molality of the solution and K_b is called the **boiling point elevation constant**, which is a characteristic of the solvent. Several boiling point elevation constants (as well as boiling point temperatures) are listed in Table 11.2 "Boiling Point Data for Various Liquids".

Table 11.2 Boiling Point Data for Various Liquids

Liquid	Boiling Point (°C)	K_b (°C/*m*)
$HC_2H_3O_2$	117.90	3.07
C_6H_6	80.10	2.53
CCl_4	76.8	4.95
H_2O	100.00	0.512

Remember that what is initially calculated is the *change* in boiling point temperature, not the new boiling point temperature. Once the change in boiling point temperature is calculated, it must be added to the boiling point of the pure solvent — because boiling points are always elevated — to get the boiling point of the solution.

Example 11.3

What is the boiling point of a 2.50 *m* solution of $C_6H_4Cl_2$ in CCl_4? Assume that $C_6H_4Cl_2$ is not volatile.

Solution

Using the equation for the boiling point elevation:

$$\Delta T_\text{b} = (2.50 \cancel{m}) \left(\frac{4.95^\circ \text{ C}}{\cancel{m}} \right) = 12.4^\circ \text{ C}$$

Note how the molality units have cancelled. However, we are not finished. We have calculated the change in the boiling point temperature, not the final boiling point temperature. If the boiling point goes up by 12.4°C, we need to add this to the normal boiling point of CCl_4 to get the new boiling point of the solution:

$$T_\text{BP} = 76.8^\circ\text{C} + 12.4^\circ\text{C} = 89.2^\circ\text{C}$$

The boiling point of the solution is predicted to be 89.2°C.

Test Yourself

What is the boiling point of a 6.95 *m* solution of $C_{12}H_{22}O_{11}$ in H_2O?

Answer
103.6°C

The boiling point of a solution is higher than the boiling point of the pure solvent, but the opposite occurs with the freezing point. The freezing point of a solution is lower than the freezing point of the pure solvent. Think of this by assuming that solute particles interfere with solvent particles coming together to make a solid, so it takes a lower temperature to get the solvent particles to solidify. This is called **freezing point depression**.

The equation to calculate the change in the freezing point for a solution is similar to the equation for the boiling point elevation:

$$\Delta T_\text{f} = mK_\text{f}$$

where *m* is the molality of the solution and K_f is called the **freezing point depression constant**, which

is also a characteristic of the solvent. Several freezing point depression constants (as well as freezing point temperatures) are listed in Table 11.3 “Freezing Point Data for Various Liquids”.

Table 11.3 Freezing Point Data for Various Liquids

Liquid	Freezing Point (°C)	K_f (°C/*m*)
$HC_2H_3O_2$	16.60	3.90
C_6H_6	5.51	4.90
C_6H_{12}	6.4	20.2
$C_{10}H_8$	80.2	6.8
H_2O	0.00	1.86

Remember that this equation calculates the change in the freezing point, not the new freezing point. What is calculated needs to be subtracted from the normal freezing point of the solvent because freezing points always go down.

Example 11.4

What is the freezing point of a 1.77 *m* solution of CBr_4 in C_6H_6?

Solution

We use the equation to calculate the change in the freezing point and then subtract this number from the normal freezing point of C_6H_6 to get the freezing point of the solution:

$$\Delta T_f = (1.77 \cancel{m}) \left(\frac{4.90^\circ\text{C}}{\cancel{m}} \right) = 8.67^\circ\text{C}$$

Now we subtract this number from the normal freezing point of C_6H_6, which is 5.51°C:

$$5.51^\circ\text{C} - 8.67^\circ\text{C} = -3.16^\circ\text{C}$$

The freezing point of the solution is −3.16°C.

Test Yourself

What is the freezing point of a 3.05 *m* solution of CBr_4 in $C_{10}H_8$?

Answer
59.5°C

Freezing point depression is one colligative property we use in everyday life. Many antifreezes used in automobile radiators use solutions that have a lower freezing point than normal so that automobile engines can operate at subfreezing temperatures. We also take advantage of freezing point depression when we sprinkle various compounds on ice to thaw it in the winter for safety (see Figure 11.2 “Salt and Safety”). The compounds make solutions that have a lower freezing point, so rather than forming slippery ice, any ice is liquefied and runs off, leaving a safer pavement behind.

Figure 11.2 “Salt and Safety.” Salt or other compounds take advantage of the freezing point depression to minimize the formation of ice on sidewalks and roads, thus increasing safety.

Before we introduce the final colligative property, we need to present a new concept. A **semipermeable membrane** is a thin membrane that will pass certain small molecules but not others. A thin sheet of cellophane, for example, acts as a semipermeable membrane.

Consider the system in part (a) of Figure 11.3 “Osmosis.” A semipermeable membrane separates two solutions having the different concentrations marked. Curiously, this situation is not stable; there is a tendency for water molecules to move from the dilute side (on the left) to the concentrated side (on the right) until the concentrations are equalized, as in part (b) of Figure 11.3. This tendency is called **osmosis**. In osmosis, the solute remains in its original side of the system; only solvent molecules move through the semipermeable membrane. In the end, the two sides of the system will have different volumes. Because a column of liquid exerts a pressure, there is a pressure difference Π on the two sides of the system that is proportional to the height of the taller column. This pressure difference is called the **osmotic pressure**, which is a colligative property.

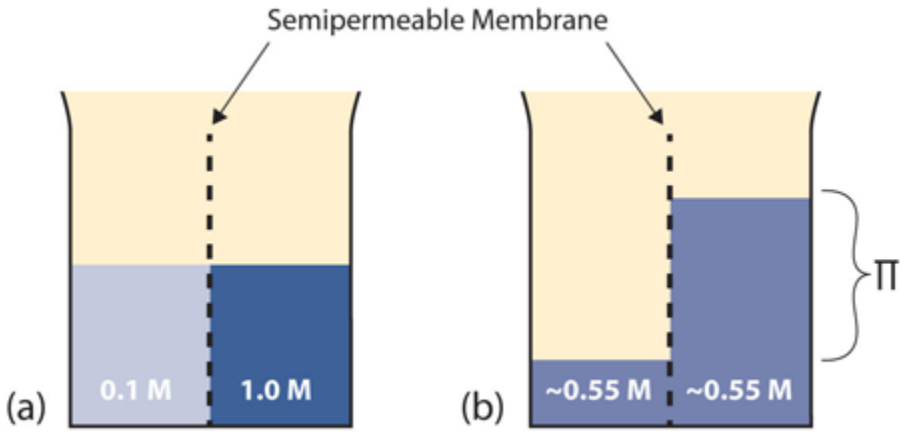

Figure 11.3 Osmosis. (a) Two solutions of differing concentrations are placed on either side of a semipermeable membrane. (b) When osmosis occurs, solvent molecules selectively pass through the membrane from the dilute solution to the concentrated solution, diluting it until the two concentrations are the same. The pressure exerted by the different height of the solution on the right is called the osmotic pressure.

The osmotic pressure of a solution is easy to calculate:

$$\Pi = MRT$$

where Π is the osmotic pressure of a solution, *M* is the molarity of the solution, *R* is the ideal gas law constant, and *T* is the absolute temperature. This equation is reminiscent of the ideal gas law we considered in Chapter 6 “Gases”.

Example 11.5

What is the osmotic pressure of a 0.333 M solution of $C_6H_{12}O_6$ at 25°C?

Solution

First we need to convert our temperature to kelvins:

$$T = 25 + 273 = 298 \text{ K}$$

Now we can substitute into the equation for osmotic pressure, recalling the value for *R*:

$$\Pi = (0.333 \text{ M}) \left(0.08205 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (298 \text{ K})$$

The units may not make sense until we realize that molarity is defined as moles per litre:

$$\Pi = (0.333 \frac{\cancel{\text{mol}}}{\cancel{\text{L}}}) \left(0.08205 \frac{\cancel{\text{L}} \cdot \text{atm}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}}\right) (298 \cancel{\text{K}})$$

Now we see that the moles, litres, and kelvins cancel, leaving atmospheres, which is a unit of pressure. Solving, we get:

$$\Pi = 8.14 \text{ atm}$$

This is a substantial pressure! It is the equivalent of a column of water 84 m tall.

Test Yourself

What is the osmotic pressure of a 0.0522 M solution of $C_{12}H_{22}O_{11}$ at 55°C?

Answer
1.40 atm

Osmotic pressure is important in biological systems because cell walls are semipermeable membranes. In particular, when a person is receiving intravenous (IV) fluids, the osmotic pressure of the fluid needs to be approximately the same as blood serum; otherwise bad things can happen. Figure 11.4 “Osmotic Pressure and Red Blood Cells” shows three red blood cells: (a) a healthy red blood cell; (b) a red blood cell that has been exposed to a lower concentration than normal blood serum (a so-called *hypotonic* solution) so that the cell has plumped up as solvent moves into the cell to dilute the solutes inside; and (c) a red blood cell exposed to a higher concentration than normal blood serum (*hypertonic*) such that water leaves the red blood cell and it collapses onto itself. Only when the solutions inside and outside the cell are the same (*isotonic*) will the red blood cell be able to do its job.

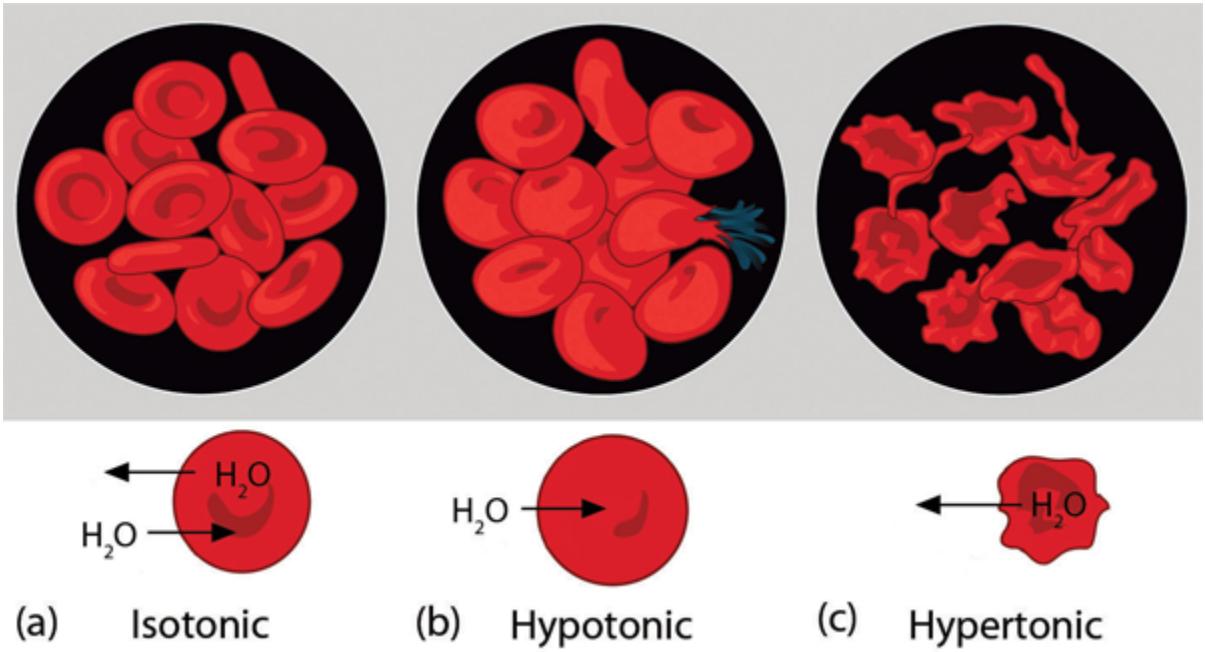

Figure 11.4 “Osmotic Pressure and Red Blood Cells.” (a) This is what a normal red blood cell looks like. (b) When a red blood cell is exposed to a hypotonic solution, solvent goes through the cell membrane and dilutes the inside of the cell. (c) When a red blood cell is exposed to a hypertonic solution, solvent goes from the cell to the surrounding solution, diluting the hypertonic solution and collapsing the cell. Neither of these last two cases is desirable, so IV solutions must be isotonic with blood serum to not cause deleterious effects.

Osmotic pressure is also the reason you should not drink seawater if you’re stranded in a lifeboat on an ocean; seawater has a higher osmotic pressure than most of the fluids in your body. You *can* drink the water, but ingesting it will pull water out of your cells as osmosis works to dilute the seawater. Ironically, your cells will die of thirst, and you will also die. (It is OK to drink the water if you are stranded on a body of freshwater, at least from an osmotic pressure perspective.) Osmotic pressure is also thought to be important — in addition to capillary action — in getting water to the tops of tall trees.

Key Takeaways

- Colligative properties depend only on the number of dissolved particles (that is, the concentration), not their identity.
- Raoult's law is concerned with the vapour pressure depression of solutions.
- The boiling points of solutions are always higher, and the freezing points of solutions are always lower, than those of the pure solvent.
- Osmotic pressure is caused by concentration differences between solutions separated by a semipermeable membrane and is an important biological issue.

Exercises

Questions

1. What are the three colligative properties that involve phase changes?
2. Which colligative property does not involve a phase change? Give an example of its importance.
3. If 45.0 g of C_6H_6 and 60.0 g of $C_6H_5CH_3$ are mixed together, what is the mole fraction of each component?
4. If 125 g of N_2 are mixed with 175 g of O_2, what is the mole fraction of each component?
5. If 36.5 g of NaCl are mixed with 63.5 g of H_2O, what is the mole fraction of each component?
6. An alloy of stainless steel is prepared from 75.4 g of Fe, 12.6 g of Cr, and 10.8 g of C. What is the mole fraction of each component?
7. A solution is made by mixing 12.0 g of $C_{10}H_8$ in 45.0 g of C_6H_6. If the vapour pressure of pure C_6H_6 is 76.5 torr at a particular temperature, what is the vapour pressure of the solution at the same temperature?
8. A solution is made by mixing 43.9 g of $C_6H_{12}C_6$ in 100.0 g of H_2O. If the vapour pressure of pure water is 26.5 torr at a particular temperature, what is the vapour pressure of the solution at the same temperature?
9. At 300°C, the vapour pressure of Hg is 32.97 torr. If 0.775 g of Au were dissolved into 3.77 g of Hg, what would be the vapour pressure of the solution?
10. At 300°C, the vapour pressure of Hg is 32.97 torr. What mass of Au would have to be dissolved in 5.00 g of Hg to lower its vapour pressure to 25.00 torr?
11. If 25.0 g of $C_6H_{12}O_6$ are dissolved in 100.0 g of H_2O, what is the boiling point of this solution?
12. If 123 g of $C_{10}H_{16}O$ are dissolved in 355 g of C_6H_6, what is the boiling point of this solution?
13. If 1 mol of solid CBr_4 is mixed with 2 mol of CCl_4, what is the boiling point of this solution?
14. A solution of $C_2H_2O_4$ in CH_3COOH has a boiling point of 123.40°C. What is the molality of the solution?
15. If 123 g of $C_{10}H_{16}O$ are dissolved in 355 g of C_6H_6, what is the freezing point of this solution?
16. If 25.0 g of $C_6H_{12}O_6$ are dissolved in 100.0 g of H_2O, what is the freezing point of this solution?
17. $C_8H_{17}OH$ is a nonvolatile solid that dissolves in C_6H_{12}. If 7.22 g of $C_8H_{17}OH$ is dissolved in 45.3 g of C_6H_{12}, what is the freezing point of this solution?
18. A solution of $C_2H_2O_4$ in CH_3COOH has a freezing point of 10.00°C. What is the molality of the solution?
19. If 25.0 g of $C_6H_{12}O_6$ are dissolved in H_2O to make 0.100 L of solution, what is the osmotic pressure of this solution at 25°C?
20. If 2.33 g of $C_{27}H_{46}O$ are dissolved in liquid CS_2 to make 50.00 mL of solution, what is the osmotic pressure of this solution at 298 K?

21. At 298 K, what concentration of solution is needed to have an osmotic pressure of 1.00 atm?
22. The osmotic pressure of blood is about 7.65 atm at 37°C. What is the approximate concentration of dissolved solutes in blood? (There are many different solutes in blood, so the answer is indeed an approximation.)

Answers

1. boiling point elevation, freezing point depression, vapour pressure depression
3. mole fraction C_6H_6: 0.469; mole fraction $C_6H_5CH_3$: 0.531
5. mole fraction NaCl: 0.157; mole fraction H_2O: 0.843
7. 65.8 torr
9. 27.26 torr
11. 100.71°C
13. 92.9°C
15. −5.65°C
17. −18.3°C
19. 33.9 atm
21. 0.0409 M

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Concentrations as Conversion Factors

Learning Objectives

1. Apply concentration units as conversion factors.

Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition. For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

$$0.108 \cancel{\text{ L NaCl}} \times \frac{0.887 \text{ mol NaCl}}{1 \cancel{\text{ L NaCl}}} = 0.0958 \text{ mol NaCl}$$

(There is an understood 1 in the denominator of the conversion factor.) If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Example 11.6

Using concentration as a conversion factor, how many litres of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:

$$4.88 \cancel{\text{ mol CuSO}_4} \times \frac{1 \text{ L}}{2.35 \cancel{\text{ mol CuSO}_4}} = 2.08 \text{ L of solution}$$

Test Yourself

Using concentration as a conversion factor, how many litres of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer

1.74 L

Of course, once quantities in moles are available, another conversion can give the mass of the substance, using molar mass as a conversion factor.

Example 11.7

What mass of solute is present in 0.765 L of 1.93 M NaOH?

Solution

This is a two-step conversion, first using concentration as a conversion factor to determine the number of moles and then the molar mass of NaOH (40.0 g/mol) to convert to mass:

$$0.765 \cancel{\text{L}} \times \frac{1.93 \cancel{\text{ mol NaOH}}}{\cancel{\text{L}} \text{ solution}} \times \frac{40.0 \text{ g NaOH}}{1 \cancel{\text{ mol NaOH}}} = 59.1 \text{ g NaOH}$$

Test Yourself

What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?

Answer

6.12 g

More complex stoichiometry problems using balanced chemical reactions can also use concentrations as conversion factors. For example, suppose the following equation represents a chemical reaction:

$$2AgNO_3(aq) + CaCl_2(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$$

If we wanted to know what volume of 0.555 M $CaCl_2$ would react with 1.25 mol of $AgNO_3$, we first use the balanced chemical equation to determine the number of moles of $CaCl_2$ that would react and then use concentration to convert to litres of solution:

$$1.25 \cancel{\text{ mol AgNO}_3} \times \frac{1 \cancel{\text{ mol CaCl}_2}}{2 \cancel{\text{ mol AgNO}_3}} \times \frac{1 \text{ L solution}}{0.555 \cancel{\text{ mol CaCl}_2}} = 1.13 \text{ L CaCl}_2$$

This can be extended by starting with the mass of one reactant, instead of moles of a reactant.

Example 11.8

What volume of 0.0995 M $Al(NO_3)_3$ will react with 3.66 g of Ag according to the following chemical equation?

$$3Ag(s) + Al(NO_3)_3(aq) \rightarrow 3AgNO_3 + Al(s)$$

Solution

Here, we first must convert the mass of Ag to moles before using the balanced chemical equation and then the definition of molarity as a conversion factor:

$$3.66 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.97 \text{ g Ag}} \times \frac{1 \text{ mol Al(NO}_3)_3}{3 \text{ mol Ag}} \times \frac{1 \text{ L solution}}{0.0995 \text{ mol Al(NO}_3)_3}$$

$$= 0.114 \text{ L}$$

Test Yourself
What volume of 0.512 M NaOH will react with 17.9 g of $H_2C_2O_4$(s) according to the following chemical equation?

$$H_2C_2O_4(s) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(\ell)$$

Answer
0.777 L

We can extend our skills even further by recognizing that we can relate quantities of one solution to quantities of another solution. Knowing the volume and concentration of a solution containing one reactant, we can determine how much of another solution of another reactant will be needed using the balanced chemical equation.

Example 11.9

A student takes a precisely measured sample, called an *aliquot*, of 10.00 mL of a solution of $FeCl_3$. The student carefully adds 0.1074 M $Na_2C_2O_4$ until all the Fe^{3+}(aq) has precipitated as $Fe_2(C_2O_4)_3$(s). Using a precisely measured tube called a burette, the student finds that 9.04 mL of the $Na_2C_2O_4$ solution was added to completely precipitate the Fe^{3+}(aq). What was the concentration of the $FeCl_3$ in the original solution? (A precisely measured experiment like this, which is meant to determine the amount of a substance in a sample, is called a *titration*.) The balanced chemical equation is as follows:

$$2FeCl_3(aq) + 3Na_2C_2O_4(aq) \rightarrow Fe_2(C_2O_4)_3(s) + 6NaCl(aq)$$

Solution
First we need to determine the number of moles of $Na_2C_2O_4$ that reacted. We will convert the volume to litres and then use the concentration of the solution as a conversion factor:

$$9.04 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1074 \text{ mol } Na_2C_2O_4}{\text{L}} = 0.000971 \text{ mol } Na_2C_2O_4$$

Now we will use the balanced chemical equation to determine the number of moles of Fe^{3+}(aq) that were present in the initial aliquot:

$$0.000971 \text{ mol } Na_2C_2O_4 \times \frac{2 \text{ mol } FeCl_3}{3 \text{ mol } Na_2C_2O_4} = 0.000647 \text{ mol } FeCl_3$$

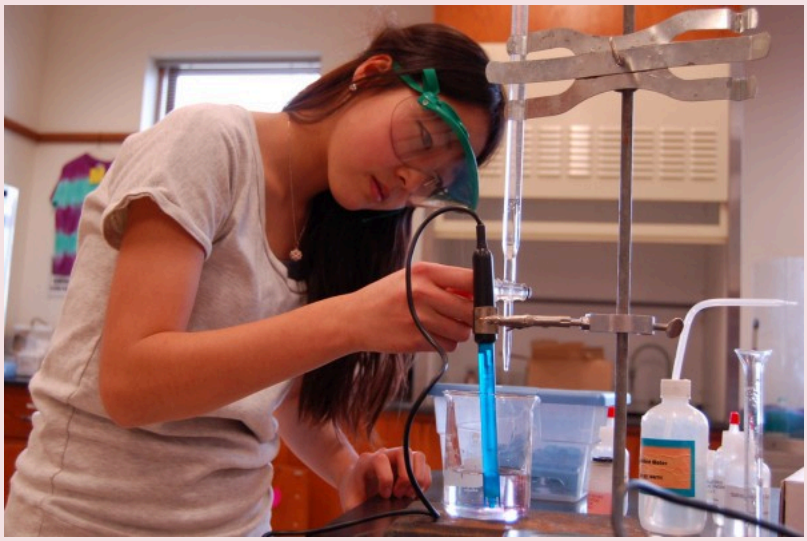
Then we determine the concentration of $FeCl_3$ in the original solution. Converting 10.00 mL into litres (0.01000 L), we use the definition of molarity directly:

$$\text{M} = \frac{\text{mol}}{\text{L}} = \frac{0.000647 \text{ mol } FeCl_3}{0.01000 \text{ L}} = 0.0647 \text{ M } FeCl_3$$

Test Yourself
A student titrates 25.00 mL of H_3PO_4 with 0.0987 M KOH. She uses 54.06 mL to complete the chemical reaction. What is the concentration of H_3PO_4?

$$H_3PO_4(aq) + 3KOH(aq) \rightarrow K_3PO_4(aq) + 3H_2O$$

Answer
0.0711 M



When a student performs a titration, a measured amount of one solution is added to another reactant.

We have used molarity exclusively as the concentration of interest, but that will not always be the case. The next example shows a different concentration unit being used.

Example 11.10

H_2O_2 is used to determine the amount of Mn according to this balanced chemical equation:

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(\ell)$$

What mass of 3.00% m/m H_2O_2 solution is needed to react with 0.355 mol of $MnO_4^-(aq)$?

Solution
Because we are given an initial amount in moles, all we need to do is use the balanced chemical equation to determine the number of moles of H_2O_2 and then convert to find the mass of H_2O_2. Knowing that the H_2O_2 solution is 3.00% by mass, we can determine the mass of solution needed:

$$0.355 \cancel{\text{ mol } MnO_4^-} \times \frac{5 \cancel{\text{ mol } H_2O_2}}{2 \cancel{\text{ mol } MnO_4^-}} \times \frac{34.02 \cancel{\text{ g } H_2O_2}}{1 \cancel{\text{ mol } H_2O_2}} \times \frac{100 \text{ g solution}}{3 \cancel{\text{ g } H_2O_2}}$$

$$= 1006 \text{ g solution}$$

The first conversion factor comes from the balanced chemical equation, the second conversion factor is the molar mass of H_2O_2, and the third conversion factor comes from the definition of percentage concentration by mass.

Test Yourself
Use the balanced chemical reaction for MnO_4^- and H_2O_2 to determine what mass of O_2 is produced if 258 g of 3.00% m/m H_2O_2 is reacted with MnO_4^-.

Answer
7.28 g

Key Takeaways

- Know how to apply concentration units as conversion factors.

Exercises

Questions

1. Using concentration as a conversion factor, how many moles of solute are in 3.44 L of 0.753 M $CaCl_2$?
2. Using concentration as a conversion factor, how many moles of solute are in 844 mL of 2.09 M $MgSO_4$?
3. Using concentration as a conversion factor, how many litres are needed to provide 0.822 mol of NaBr from a 0.665 M solution?
4. Using concentration as a conversion factor, how many litres are needed to provide 2.500 mol of $(NH_2)_2CO$ from a 1.087 M solution?
5. What is the mass of solute in 24.5 mL of 0.755 M $CoCl_2$?
6. What is the mass of solute in 3.81 L of 0.0232 M $Zn(NO_3)_2$?
7. What volume of solution is needed to provide 9.04 g of NiF_2 from a 0.332 M solution?
8. What volume of solution is needed to provide 0.229 g of CH_2O from a 0.00560 M solution?
9. What volume of 3.44 M HCl will react with 5.33 mol of $CaCO_3$?
$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$$
10. What volume of 0.779 M NaCl will react with 40.8 mol of $Pb(NO_3)_2$?
$$Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2 + 2NaNO_3$$
11. What volume of 0.905 M H_2SO_4 will react with 26.7 mL of 0.554 M NaOH?
$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$
12. What volume of 1.000 M Na_2CO_3 will react with 342 mL of 0.733 M H_3PO_4?
$$3Na_2CO_3 + 2H_3PO_4 \rightarrow 2Na_3PO_4 + 3H_2O + 3CO_2$$
13. It takes 23.77 mL of 0.1505 M HCl to titrate with 15.00 mL of $Ca(OH)_2$. What is the concentration of $Ca(OH)_2$? You will need to write the balanced chemical equation first.
14. It takes 97.62 mL of 0.0546 M NaOH to titrate a 25.00 mL sample of H_2SO_4. What is the concentration of H_2SO_4? You will need to write the balanced chemical equation first.
15. It takes 4.667 mL of 0.0997 M HNO_3 to dissolve some solid Cu. What mass of Cu can be dissolved?
$$Cu + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2 + 2H_2O$$
16. It takes 49.08 mL of 0.877 M NH_3 to dissolve some solid AgCl. What mass of AgCl can be dissolved?
$$AgCl(s) + 4NH_3(aq) \rightarrow Ag(NH_3)_4Cl(aq)$$
17. What mass of 3.00% H_2O_2 is needed to produce 66.3 g of $O_2(g)$?
$$2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$$
18. A 0.75% solution of Na_2CO_3 is used to precipitate Ca^{2+} ions from solution. What mass of solution is needed to precipitate 40.7 L of solution with a concentration of 0.0225 M $Ca^{2+}(aq)$?
$$Na_2CO_3(aq) + Ca^{2+}(aq) \rightarrow CaCO_3(s) + 2Na^+(aq)$$

Answers

1. 2.59 mol
3. 1.24 L
5. 2.40 g
7. 0.282 L
9. 3.10 L
11. 8.17 mL
13. 0.1192 M
15. 7.39 mg
17. 4.70 kg

Media Attributions

Quantitative Units of Concentration

Learning Objectives

1. Learn to determine specific concentrations with several common units.

Rather than qualitative terms (see the later section "Some Definitions"), we need quantitative ways to express the amount of solute in a solution; that is, we need specific units of concentration. In this section, we will introduce several common and useful units of concentration.

Molarity (M) is defined as the number of moles of solute divided by the number of litres of solution:

$$\text{molarity} = \frac{\text{moles of solute}}{\text{litres of solution}}$$

which can be simplified as

$$\text{M} = \frac{\text{mol}}{\text{L}}, \text{ or mol/L}$$

As with any mathematical equation, if you know any two quantities, you can calculate the third, unknown, quantity.

For example, suppose you have 0.500 L of solution that has 0.24 mol of NaOH dissolved in it. The concentration of the solution can be calculated as follows:

$$\text{molarity} = \frac{0.24 \text{ mol NaOH}}{0.500 \text{ L}} = 0.48 \text{ M NaOH}$$

The concentration of the solution is 0.48 M, which is spoken as "zero point forty-eight molarity" or "zero point forty-eight molar." If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L? First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4 \text{ g } \cancel{\text{HCl}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g } \cancel{\text{HCl}}} = 0.614 \text{ mol HCl}$$

Now we can use the definition of molarity to determine a concentration:

$$\text{M} = \frac{0.614 \text{ mol HCl}}{1.56 \text{ L}} = 0.394 \text{ M}$$

Example 11.11

What is the molarity of a solution made when 32.7 g of NaOH are dissolved to make 445 mL of solution?

Solution
To use the definition of molarity, both quantities must be converted to the proper units. First, convert the volume units from millilitres to litres:

$$445 \cancel{\text{mL}} \times \frac{1 \text{ L}}{1000 \cancel{\text{mL}}} = 0.445 \text{ L}$$

Now we convert the amount of solute to moles, using the molar mass of NaOH, which is 40.0 g/mol:

$$32.7 \cancel{\text{ g NaOH}} \times \frac{1 \text{ mol NaOH}}{40.0 \cancel{\text{ g NaOH}}} = 0.818 \text{ mol NaOH}$$

Now we can use the definition of molarity to determine the molar concentration:

$$\text{M} = \frac{0.818 \text{ mol NaOH}}{0.445 \text{ L}} = 1.84 \text{ M NaOH}$$

Test Yourself
What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer
1.57 M

The definition of molarity can be used to determine the amount of solute or the volume of solution, if the other information is given. Example 11.12 illustrates this situation.

Example 11.12

How many moles of solute are present in 0.108 L of a 0.887 M NaCl solution?

Solution

We know the volume and the molarity; we can use the definition of molarity to mathematically solve for the amount in moles. Substituting the quantities into the definition of molarity:

$$0.887 \text{ M} = \frac{1 \text{ mol NaCl}}{0.108 \text{ L}}$$

We multiply the 0.108 L over to the other side of the equation and multiply the units together; “molarity × litres” equals moles, according to the definition of molarity. So:

$$1 \text{ mol NaCl} = (0.887 \text{ M})(0.108 \text{ L}) = 0.0958 \text{ mol}$$

Test Yourself
How many moles of solute are present in 225 mL of a 1.44 M $CaCl_2$ solution?

Answer
0.324 mol

If you need to determine volume, remember the rule that the unknown quantity must be by itself and in the numerator to determine the correct answer. Thus rearrangement of the definition of molarity is required.

Example 11.13

What volume of a 2.33 M $NaNO_3$ solution is needed to obtain 0.222 mol of solute?

Solution

Using the definition of molarity, we have:

$$2.33\ \text{M} = \frac{0.222\ \text{mol}}{\text{L}}$$

To solve for the number of litres, we bring the 2.33 M over to the right into the denominator, and the number of litres over to the left in the numerator. We now have:

$$\text{L} = \frac{0.222\ \text{mol}}{2.33\ \text{M}}$$

Dividing, the volume is 0.0953 L = 95.3 mL.

Test Yourself

What volume of a 0.570 M K_2SO_4 solution is needed to obtain 0.872 mol of solute?

Answer
1.53 L

A similar unit of concentration is **molality** (*m*), which is defined as the number of moles of solute per kilogram of solvent, not per litre of solution:

$$\text{molality} = \frac{\text{moles solute}}{\text{kilograms solvent}}$$

Mathematical manipulation of molality is the same as with molarity.

Another way to specify an amount is **percentage composition by mass** (or *mass percentage*, % m/m). It is defined as follows:

$$\%\ \text{m/m} = \frac{\text{mass of solute}}{\text{mass of entire sample}} \times 100\%$$

It is not uncommon to see this unit used on commercial products.

Example 11.14

What is the mass percentage of Fe in a piece of metal with 87.9 g of Fe in a 113 g sample?

Solution
Using the definition of mass percentage, we have:

$$\%\ \text{m/m} = \frac{87.9\ \text{g Fe}}{113\ \text{g sample}} \times 100\% = 77.8\%\ \text{Fe}$$

Test Yourself
What is the mass percentage of H_2O_2 in a solution with 1.67 g of H_2O_2 in a 55.5 g sample?

Answer
3.01%

Related concentration units are **parts per thousand (ppth)**, **parts per million (ppm)**, and **parts per billion (ppb)**. Parts per thousand is defined as follows:

$$\text{ppth} = \frac{\text{mass of solute}}{\text{mass of sample}} \times 1,000$$

There are similar definitions for parts per million and parts per billion:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of sample}} \times 1,000,000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of sample}} \times 1,000,000,000$$

Each unit is used for progressively lower and lower concentrations. The two masses must be expressed in the same unit of mass, so conversions may be necessary.

Example 11.15

If there is 0.6 g of Pb present in 277 g of solution, what is the Pb concentration in parts per thousand?

Solution
Use the definition of parts per thousand to determine the concentration. Substituting:

$$\frac{0.6 \text{ g Pb}}{277 \text{ g solution}} \times 1000 = 2.17 \text{ ppth}$$

Test Yourself
If there is 0.551 mg of As in 348 g of solution, what is the As concentration in ppm?

Answer
1.58 ppm

As with molarity and molality, algebraic rearrangements may be necessary to answer certain questions.

Example 11.16

The concentration of Cl^- ion in a sample of H_2O is 15.0 ppm. What mass of Cl^- ion is present in 240.0 mL of H_2O, which has a density of 1.00 g/mL?

Solution
First, use the density of H_2O to determine the mass of the sample:

$$240.0 \cancel{\text{mL}} \times \frac{1.00 \text{ g}}{\cancel{\text{mL}}} = 240.0 \text{ g}$$

Now we can use the definition of ppm:

$$15.0 \text{ ppm} = \frac{\text{mass solute}}{240.0 \text{ g solution}} \times 1,000,000$$

Rearranging to solve for the mass of solute:

$$\text{mass solute} = \frac{(15.0 \text{ ppm})(240.0 \text{ g solution})}{1,000,000} = 0.0036 \text{ g} = 3.6 \text{ mg}$$

Test Yourself
The concentration of Fe^{3+} ion in a sample of H_2O is 335.0 ppm. What mass of Fe^{3+} ion is present in 3,450 mL of H_2O, which has a density of 1.00 g/mL?

Answer
1.16 g

For ionic solutions, we need to differentiate between the concentration of the salt versus the concentration of each individual ion. Because the ions in ionic compounds go their own way when a compound is dissolved in a solution, the resulting concentration of the ion may be different from the concentration of the complete salt. For example, if 1 M NaCl were prepared, the solution could also be described as a solution of 1 M Na^+(aq) and 1 M Cl^-(aq) because there is one Na^+ ion and one Cl^- ion per formula unit of the salt. However, if the solution were 1 M $CaCl_2$, there are two Cl^-(aq) ions for every formula unit dissolved, so the concentration of Cl^-(aq) would be 2 M, not 1 M.

In addition, the total ion concentration is the sum of the individual ion concentrations. Thus for the 1 M NaCl, the total ion concentration is 2 M; for the 1 M $CaCl_2$, the total ion concentration is 3 M.

Key Takeaways

- Quantitative units of concentration include molarity, molality, mass percentage, parts per thousand, parts per million, and parts per billion.

Exercises

Questions

1. Differentiate between molarity and molality.
2. Differentiate between mass percentage and parts per thousand.
3. What is the molarity of a solution made by dissolving 13.4 g of $NaNO_3$ in 345 mL of solution?
4. What is the molarity of a solution made by dissolving 332 g of $C_6H_{12}O_6$ in 4.66 L of solution?
5. How many moles of $MgCl_2$ are present in 0.0331 L of a 2.55 M solution?

6. How many moles of NH_4Br are present in 88.9 mL of a 0.228 M solution?
7. What volume of 0.556 M NaCl is needed to obtain 0.882 mol of NaCl?
8. What volume of 3.99 M H_2SO_4 is needed to obtain 4.61 mol of H_2SO_4?
9. What volume of 0.333 M $Al(NO_3)_3$ is needed to obtain 26.7 g of $Al(NO_3)_3$?
10. What volume of 1.772 M $BaCl_2$ is needed to obtain 123 g of $BaCl_2$?
11. What are the individual ion concentrations and the total ion concentration in 0.66 M $Mg(NO_3)_2$?
12. What are the individual ion concentrations and the total ion concentration in 1.04 M $Al_2(SO_4)_3$?
13. If the $C_2H_3O_2^-$ ion concentration in a solution is 0.554 M, what is the concentration of $Ca(C_2H_3O_2)_2$?
14. If the Cl^- ion concentration in a solution is 2.61 M, what is the concentration of $FeCl_3$?

Answers

1. Molarity is moles per litre, whereas molality is moles per kilogram of solvent.
3. 0.457 M
5. 0.0844 mol
7. 1.59 L
9. 0.376 L
11. Mg^{2+} = 0.66 M; NO_3^- = 1.32 M; total: 1.98 M
13. 0.277 M

Colligative Properties of Ionic Solutes

Learning Objectives

1. Determine the colligative properties of solutions of ionic solutes.

In the section "Colligative Properties of Solutions", we considered the colligative properties of solutions with molecular solutes. What about solutions with ionic solutes? Do they exhibit colligative properties?

There is a complicating factor: ionic solutes separate into ions when they dissolve. This increases the total number of particles dissolved in solution and *increases the impact on the resulting colligative property*. Historically, this greater-than-expected impact on colligative properties was one main piece of evidence for ionic compounds separating into ions (increased electrical conductivity was another piece of evidence).

For example, when NaCl dissolves, it separates into two ions:

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

This means that a 1 M solution of NaCl actually has a net particle concentration of 2 M. The observed colligative property will then be twice as large as expected for a 1 M solution.

It is easy to incorporate this concept into our equations to calculate the respective colligative property. We define the **van't Hoff factor** (i) as the number of particles each solute formula unit breaks apart into when it dissolves. Previously, we have always tacitly assumed that the van't Hoff factor is simply 1. But for some ionic compounds, i is not 1, as shown in Table 11.4 "Ideal van't Hoff Factors for Ionic Compounds".

Table 11.4 Ideal van't Hoff Factors for Ionic Compounds

Compound	***i***
NaCl	2
KBr	2
$LiNO_3$	2
$CaCl_2$	3
$Mg(C_2H_3O_2)_2$	3
$FeCl_3$	4
$Al_2(SO_4)_3$	5

The ideal van't Hoff factor is equal to the number of ions that form when an ionic compound dissolves.

Example 11.17

Predict the van't Hoff factor for $Sr(OH)_2$.

Solution
When $Sr(OH)_2$ dissolves, it separates into one Sr^{2+} ion and two OH^- ions:

$$Sr(OH)_2 \rightarrow Sr^{2+}(aq) + 2OH^-(aq)$$

Because it breaks up into three ions, its van't Hoff factor is 3.

Test Yourself
What is the van't Hoff factor for $Fe(NO_3)_3$?

Answer
4

It is the "ideal" van't Hoff factor because this is what we expect from the ionic formula. However, this factor is usually correct only for dilute solutions (solutions less than 0.001 M). At concentrations greater than 0.001 M, there are enough interactions between ions of opposite charge that the net concentration of the ions is less than expected—sometimes significantly. The actual van't Hoff factor is thus less than the ideal one. Here, we will use ideal van't Hoff factors.

Revised equations to calculate the effect of ionization are then easily produced:

$$\begin{aligned} \Delta T_\mathrm{b} &= imK_\mathrm{b} \\ \Delta T_\mathrm{f} &= imK_\mathrm{g} \\ \Pi &= iMRT \end{aligned}$$

where all variables have been previously defined. To calculate vapour pressure depression according to Raoult's law, the mole fraction of solvent particles must be recalculated to take into account the increased number of particles formed on ionization.

Example 11.18

Determine the freezing point of a 1.77 *m* solution of NaCl in H_2O.

Solution
For NaCl, we need to remember to include the van't Hoff factor, which is 2. Otherwise, the calculation of the freezing point is straightforward:

$$\Delta T_f = (2)(1.77\cancel{m})\left(\frac{1.86^\circ\text{C}}{\cancel{m}}\right) = 6.58^\circ\text{C}$$

This represents the change in the freezing point, which is decreasing. So we have to subtract this change from the normal freezing point of water, 0.00°C:

$$0.00^\circ\text{C} - 6.58^\circ\text{C} = -6.58^\circ\text{C}$$

Test Yourself
Determine the boiling point of a 0.887 *m* solution of $CaCl_2$ in H_2O.

Answer
101.36°C

Food and Drink App: Salting Pasta Cooking Water

When cooking dried pasta, many recipes call for salting the water before cooking the pasta. Some argue — with colligative properties on their side — that adding salt to the water raises the boiling point, thus cooking the pasta faster. Is there any truth to this?

To judge the veracity of this claim, we can calculate how much salt should be added to the water to raise the boiling temperature by 1.0°C, with the presumption that dried pasta cooks noticeably faster at 101°C than at 100°C (although a 1° difference may make only a negligible change in cooking times). We can calculate the molality that the water should have:

$$1.0^\circ\text{C} = m\,(0.512^\circ\text{C}/m)$$

$$m = 1.95$$

We have ignored the van't Hoff factor in our estimation because this obviously is not a dilute solution. Let us further assume that we are using 4 L of water (which is very close to 4 qt, which in turn equals 1 gal). Because 4 L of water is about 4 kg (it is actually slightly less at 100°C), we can determine how much salt (NaCl) to add:

$$\cancel{4\text{ kg }H_2O} \times \frac{1.95\ \cancel{\text{mol NaCl}}}{\cancel{1\text{ kg }H_2O}} \times \frac{58.5\text{ g NaCl}}{1\ \cancel{\text{mol NaCl}}} = 456.3\text{ g NaCl}$$

This is just over 1 lb of salt and is equivalent to nearly 1 cup in the kitchen. In your experience, do you add almost a cup of salt to a pot of water to make pasta? Certainly not! A few pinches, perhaps one-fourth of a teaspoon, but not almost a cup! It is obvious that the little amount of salt that most people add to their pasta water is not going to significantly raise the boiling point of the water.

So why do people add some salt to boiling water? There are several possible reasons, the most obvious of which is taste: adding salt adds a little bit of salt flavour to the pasta. It cannot be much because most of the salt remains in the water, not in the cooked pasta. However, it may be enough to detect with our taste buds. The other obvious reason is habit; recipes tell us to add salt, so we do, even if there is little scientific or culinary reason to do so.

Key Takeaways

- For ionic solutes, the calculation of colligative properties must include the fact that the solutes separate into multiple particles when they dissolve.
- The equations for calculating colligative properties of solutions of ionic solvents include the van't Hoff factor, *i*.

Exercises

Questions

1. Explain why we need to consider a van't Hoff factor for ionic solutes but not for molecular solutes.
2. NaCl is often used in winter to melt ice on roads and sidewalks, but calcium chloride ($CaCl_2$) is also used. Which would be better (on a mole-by-mole basis), and why?
3. Calculate the boiling point of an aqueous solution of $NaNO_3$ made by mixing 15.6 g of $NaNO_3$ with 100.0 g of H_2O. Assume an ideal van't Hoff factor.
4. Many labs use a cleaning solution of KOH dissolved in C_2H_5OH. If 34.7 g of KOH were dissolved in 88.0 g of C_2H_5OH, what is the boiling point of this solution? The normal boiling point of C_2H_5OH is 78.4°C and its K_b = 1.19°C/*m*. Assume an ideal van't Hoff factor.
5. What is the freezing point of a solution made by dissolving 345 g of $CaCl_2$ in 1,550 g of H_2O? Assume an ideal van't Hoff factor.
6. A classic homemade ice cream can be made by freezing the ice cream mixture using a solution of 250 g of NaCl dissolved in 1.25 kg of ice water. What is the temperature of this ice water? Assume an ideal van't Hoff factor.
7. Seawater can be approximated as a 3.5% NaCl solution by mass; that is, 3.5 g of NaCl are combined with 96.5 g H_2O. What is the osmotic pressure of seawater? Assume an ideal van't Hoff factor.
8. The osmotic pressure of blood is 7.65 atm at 37°C. If blood were considered a solution of NaCl, what is the molar concentration of NaCl in blood? Assume an ideal van't Hoff factor.
9. What is the vapour pressure of an aqueous solution of 36.4 g of KBr in 199.5 g of H_2O if the vapour pressure of H_2O at the same temperature is 32.55 torr? What other solute(s) would give a solution with the same vapour pressure? Assume an ideal van't Hoff factor.
10. Assuming an ideal van't Hoff factor, what mole fraction is required for a solution of $Mg(NO_3)_2$ to have a vapour pressure of 20.00 torr at 25.0°C? The vapour pressure of the solvent is 23.61 torr at this temperature.

Answers

1. Ionic solutes separate into more than one particle when they dissolve, whereas molecular solutes do not.
3. 101.9°C
5. −7.5°C
7. 30.3 atm
9. 30.86 torr; any two-ion salt should have the same effect.

Some Definitions

Learning Objectives

1. Learn some terminology involving solutions.
2. Recognize which terminology is qualitative and which terminology is quantitative.
3. Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent**. The minor component of a solution is called the **solute**. By major and minor we mean whichever component has the greater presence by mass or by moles. Sometimes this becomes confusing, especially with substances with very different molar masses. However, here we will confine the discussion to solutions for which the major component and the minor component are obvious.

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water; soda water is a solution of gaseous CO_2 in liquid water, while air is a solution of a gaseous solute (O_2) in a gaseous solvent (N_2). In all cases, however, the overall phase of the solution is the same phase as the solvent.

Example 11.19

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution
Either by mass or by moles, the obvious minor component is sucrose, so it is the solute. Water — the majority component — is the solvent. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Test Yourself

A solution is made by dissolving 3.33 g of HCl(g) in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer
The solute is HCl(g); the solvent is CH_3OH.

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. This concept is called **concentration**. Various words are used to describe the relative amounts of solute. **Dilute** describes a solution that has very little solute, while **concentrated** describes a solution that has a lot of solute. One problem is that these terms are qualitative; they describe more or less but not exactly how much.

In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent.

This maximum amount is called the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. Table 11.5 “Solubilities of Some Ionic Compounds” lists the solubilities of some simple ionic compounds. These solubilities vary widely: NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

Table 11.5 Solubilities of Some Ionic Compounds

Solute	Solubility (g per 100 g of H_2O at 25°C)
AgCl	0.00019
$CaCO_3$	0.0006
KBr	70.7
NaCl	36.1
$NaNO_3$	94.6

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is **saturated** with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is **unsaturated**. These terms are also qualitative terms because each solute has its own solubility. A solution of 0.00019 g of AgCl per 100 g of H_2O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H_2O is also saturated but rather concentrated. Ideally, we need more precise ways of specifying the amount of solute in a solution. We introduced such ways in the section “Quantitative Units of Concentration”.

In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called **supersaturated** solutions and are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.

It should be obvious that some solutes dissolve in certain solvents but not others. NaCl, for example, dissolves in water but not in vegetable oil. Beeswax dissolves in liquid hexane but not water. What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in Chapter 10 “Solids and Liquids”). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl — a very polar substance because it is composed of ions — dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane but not in polar water. This concept leads to the general rule that “like dissolves like” for predicting whether a solute is soluble in a given solvent. However, this is a general rule, not an absolute statement, so it must be applied with care.

Example 11.20

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution
I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

Test Yourself
Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer
H_2O, because both experience hydrogen bonding.

Key Takeaways

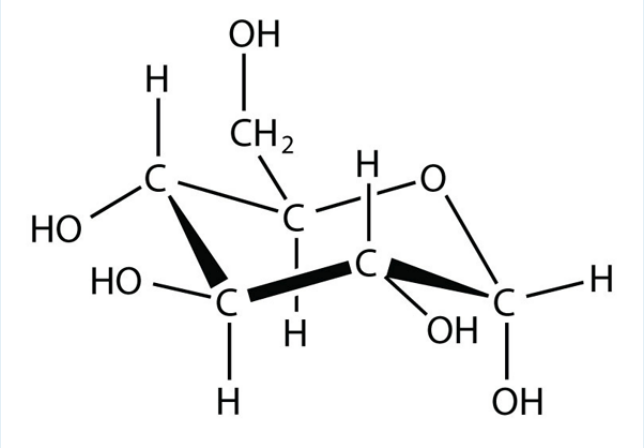
- Solutions are composed of a solvent (major component) and a solute (minor component).
- Concentration is the expression of the amount of solute in a given amount of solvent and can be described by several qualitative terms.
- Solubility is a specific amount of solute that can dissolve in a given amount of solvent.
- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

Exercises

Questions

1. Define *solute* and *solvent*.
2. Define *saturated*, *unsaturated*, and *supersaturated*.
3. A solution is prepared by combining 2.09 g of CO_2 and 35.5 g of H_2O. Identify the solute and solvent.
4. A solution is prepared by combining 10.3 g of Hg(ℓ) and 45.0 g of Ag(s). Identify the solute and solvent.
5. Use Table 11.5 "Solubilities of Some Ionic Compounds" to decide if a solution containing 45.0 g of NaCl per 100 g of H_2O is unsaturated, saturated, or supersaturated.
6. Use Table 11.5 to decide if a solution containing 0.000092 g of AgCl per 100 g of H_2O is unsaturated, saturated, or supersaturated.
7. Would the solution in Exercise 5 be described as dilute or concentrated? Explain your answer.
8. Would the solution in Exercise 6 be described as dilute or concentrated? Explain your answer.
9. Identify a solute from Table 11.5 whose saturated solution can be described as dilute.
10. Identify a solute from Table 11.5 whose saturated solution can be described as concentrated.
11. Which solvent is Br_2 more likely soluble in — CH_3OH or C_6H_6?
12. Which solvent is NaOH more likely soluble in — CH_3OH or C_6H_6?
13. Compounds with the formula $C_nH_{2n+1}OH$ are soluble in H2O when n is small but not when n is large. Suggest an explanation for this phenomenon.

14. Glucose has the following structure:



What parts of the molecule indicate that this substance is soluble in water?

Answers

1. The solvent is the majority component of a solution, whereas the solute is the minority component of a solution.
3. solute: CO_2; solvent: H_2O
5. supersaturated
7. concentrated, because there is a lot of solute
9. AgCl or $CaCO_3$
11. C_6H_6
13. The nonpolar end dominates intermolecular forces when *n* is large.

Dilutions and Concentrations

Learning Objectives

1. Learn how to dilute and concentrate solutions.

Often, a worker will need to change the concentration of a solution by changing the amount of solvent. **Dilution** is the addition of solvent, which decreases the concentration of the solute in the solution. **Concentration** is the removal of solvent, which increases the concentration of the solute in the solution. (Do not confuse the two uses of the word *concentration* here!)

In both dilution and concentration, the amount of solute stays the same. This gives us a way to calculate what the new solution volume must be for the desired concentration of solute. From the definition of molarity, which is:

$$\text{molarity} = \frac{\text{moles of solute}}{\text{litres of solution}}$$

we can solve for the number of moles of solute:

$$\text{moles of solute} = (\text{molarity})(\text{litres of solution})$$

A simpler way of writing this is to use *M* to represent molarity and *V* to represent volume. So the equation becomes:

$$\text{moles of solute} = MV$$

Because this quantity does not change before and after the change in concentration, the product *MV* must be the same before and after the concentration change. Using numbers to represent the initial and final conditions, we have:

$$M_1V_1 = M_2V_2$$

as the **dilution equation**. The volumes must be expressed in the same units. Note that this equation gives only the initial and final conditions, not the amount of the change. The amount of change is determined by subtraction.

Example 11.21

If 25.0 mL of a 2.19 M solution are diluted to 72.8 mL, what is the final concentration?

Solution
It does not matter which set of conditions is labelled 1 or 2, as long as the conditions are paired together properly. Using the dilution equation, we have:

$$(2.19\ \text{M})(25.0\ \text{mL}) = M_2(72.8\ \text{mL})$$

Solving for the second concentration (noting that the millilitre units cancel):

$$M_2 = 0.752\ \text{M}$$

The concentration of the solution has decreased. In going from 25.0 mL to 72.8 mL, 72.8 − 25.0 = 47.8 mL of solvent must be added.

Test Yourself
A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

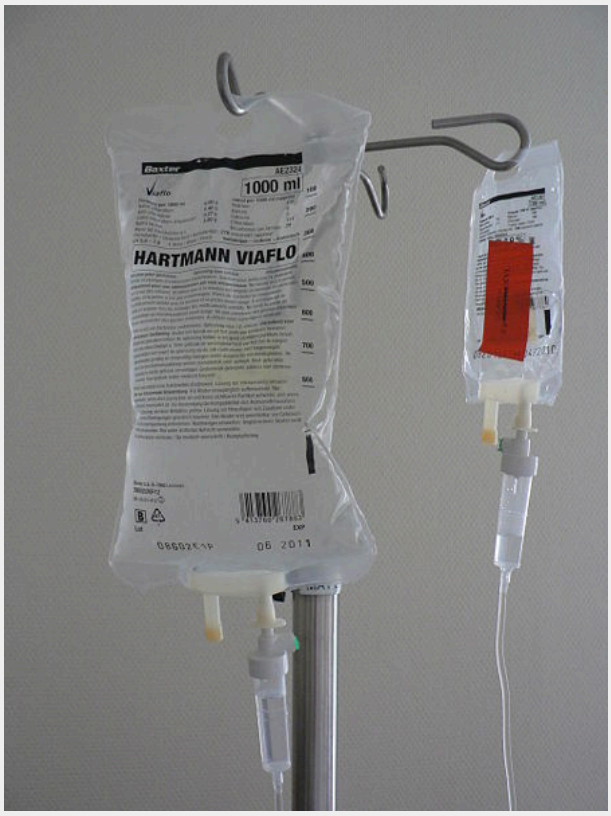
Answer
135.4 mL

Concentrating solutions involves removing solvent. Usually this is done by evaporating or boiling, assuming that the heat of boiling does not affect the solute. The dilution equation is used in these circumstances as well.

Chemistry Is Everywhere: Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Medical personnel commonly must perform dilutions for IV solutions.

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is an easy calculation to determine how much stock solution to use:

$$\begin{aligned}(10\%)V_1 &= (0.50\%)(100\text{ mL}) \\ V_1 &= 5\text{ mL}\end{aligned}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Key Takeaways

- Calculate the new concentration or volume for a dilution or concentration of a solution.

Exercises

Questions

1. What is the difference between dilution and concentration?
2. What quantity remains constant when you dilute a solution?
3. A 1.88 M solution of NaCl has an initial volume of 34.5 mL. What is the final concentration of the solution if it is diluted to 134 mL?
4. A 0.664 M solution of NaCl has an initial volume of 2.55 L. What is the final concentration of the solution if it is diluted to 3.88 L?
5. If 1.00 mL of a 2.25 M H_2SO_4 solution needs to be diluted to 1.00 M, what will be its final volume?
6. If 12.00 L of a 6.00 M HNO_3 solution needs to be diluted to 0.750 M, what will be its final volume?
7. If 665 mL of a 0.875 M KBr solution are boiled gently to concentrate the solute to 1.45 M, what will be its final volume?
8. If 1.00 L of an LiOH solution is boiled down to 164 mL and its initial concentration is 0.00555 M, what is its final concentration?
9. How much water must be added to 75.0 mL of 0.332 M $FeCl_3(aq)$ to reduce its concentration to 0.250 M?
10. How much water must be added to 1.55 L of 1.65 M $Sc(NO_3)_3(aq)$ to reduce its concentration to 1.00 M?

Answers

1. Dilution is a decrease in a solution's concentration, whereas concentration is an increase in a solution's concentration.
3. 0.484 M
5. 2.25 mL
7. 401 mL
9. 24.6 mL

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End-of-Chapter Material

Additional Exercises

1. One brand of ethyl alcohol (Everclear) is 95% ethyl alcohol, with the remaining 5% being water. What is the solvent and what is the solute of this solution?
2. Give an example of each type of solution from your own experience.
    a. A solution composed of a gas solute in a liquid solvent.
    b. A solution composed of a solid solute in a liquid solvent.
    c. A solution composed of a liquid solute in a liquid solvent.
    d. A solution composed of a solid solute in a solid solvent. (Hint: usually such solutions are made as liquids and then solidified.)
3. Differentiate between the terms *saturated* and *concentrated*.
4. Differentiate between the terms *unsaturated* and *dilute*.
5. What mass of $FeCl_2$ is present in 445 mL of 0.0812 M $FeCl_2$ solution?
6. What mass of SO_2 is present in 26.8 L of 1.22 M SO_2 solution?
7. What volume of 0.225 M $Ca(OH)_2$ solution is needed to deliver 100.0 g of $Ca(OH)_2$?
8. What volume of 12.0 M HCl solution is needed to obtain exactly 1.000 kg of HCl?
9. The World Health Organization recommends that the maximum fluoride ion concentration in drinking water is 1.0 ppm. Assuming water has the maximum concentration, if an average person drinks 1,920 mL of water per day, how many milligrams of fluoride ion are being ingested?
10. For sanitary reasons, water in pools should be chlorinated to a maximum level of 3.0 ppm. In a typical 5,000 gal pool that contains 21,200 kg of water, what mass of chlorine must be added to obtain this concentration?
11. Given its notoriety, you might think that uranium is very rare, but it is present at about 2–4 ppm of the earth's crust, which is more abundant than silver or mercury. If the earth's crust is estimated to have a mass of 8.50×10^{20} kg, what range of mass is thought to be uranium in the crust?
12. Chromium is thought to be an ultratrace element, with about 8.9 ng present in a human body. If the average body mass is 75.0 kg, what is the concentration of chromium in the body in pptr?
13. What mass of 3.00% H_2O_2 solution is needed to produce 35.7 g of $O_2(g)$ at 295 K at 1.05 atm pressure?
$$2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$$
14. What volume of pool water is needed to generate 1.000 L of $Cl_2(g)$ at standard temperature and pressure if the pool contains 4.0 ppm HOCl and the water is slightly acidic? The chemical reaction is as follows:
$$HOCl(aq) + HCl(aq) \rightarrow H_2O(\ell) + Cl_2(g)$$
Assume the pool water has a density of 1.00 g/mL.
15. A 0.500 m solution of $MgCl_2$ has a freezing point of −2.60°C. What is the true van't Hoff factor of this ionic compound? Why is it less than the ideal value?
16. The osmotic pressure of a 0.050 M LiCl solution at 25.0°C is 2.26 atm. What is the true van't Hoff factor of this ionic compound? Why is it less than the ideal value?
17. Order these solutions in order of increasing boiling point, assuming an ideal van't Hoff factor for each: 0.10 *m* $C_6H_{12}O_6$, 0.06 *m* NaCl, 0.4 *m* $Au(NO_3)_3$, and 0.4 *m* $Al_2(SO_4)_3$.
18. Order these solutions in order of decreasing osmotic pressure, assuming an ideal van't Hoff factor: 0.1 M HCl, 0.1 M $CaCl_2$, 0.05 M $MgBr_2$, and 0.07 M $Ga(C_2H_3O_2)_3$

Answers

1. solvent: ethyl alcohol; solute: water
3. Saturated means all the possible solute that can dissolve is dissolved, whereas concentrated implies that a lot of solute is dissolved.
5. 4.58 g
7. 6.00 L
9. 1.92 mg
11. 1.7×10^{15} to 3.4×10^{15} kg
13. 2,530 g
15. 2.80; it is less than 3 because not all ions behave as independent particles.
17. 0.10 *m* $C_6H_{12}O_6$ < 0.06 *m* NaCl < 0.4 *m* $Au(NO_3)_3$ < 0.4 *m* $Al_2(SO_4)_3$

Chapter 12. Acids and Bases

Formerly there were rather campy science-fiction television shows in which the hero was always being threatened with death by being plunged into a vat of boiling acid: “Mwa ha ha, Buck Rogers [or whatever the hero’s name was], prepare to meet your doom by being dropped into a vat of boiling acid!” (The hero always escapes, of course.) This may have been interesting drama but not very good chemistry. If the villain knew their science, the hero would have been dropped into a vat of boiling base.

Recall that the active component of a classic acid is the H^+ ion, while the active part of a classic base is the OH^- ion. Both ions are related to water in that all H^+ ion needs to become a water molecule is an OH^- ion, while all an OH^- ion needs to become water is an H^+ ion. Consider the relative masses involved: an ion of mass 1 needs an ion of mass 17 to make water, while an ion of mass 17 needs an ion of mass 1 to make water. Which process do you think will be easier?

In fact, bases are more potentially dangerous than acids because it is much easier for an OH^- ion to rip off an H^+ ion from surrounding matter than it is for an H^+ ion to rip off an OH^- ion. Certain household chemicals, such as some brands of cleanser, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home; if spilled on the skin, the strong caustic compound can immediately remove H^+ ions from the flesh, resulting in chemical burns. Compare that to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine — all of which contain acids. (Of course, some parts of the body, such as the eyes, are extremely sensitive to acids as well as bases.) It seems that our bodies are more capable of dealing with acids than with bases.

Figure 12.0 “Acids and Bases.” On the left is a common acid, and on the right is a common base. Which one is more potentially hazardous?

So a note to all the villains out there: get your chemistry right if you want to be successful!

Acids and bases are important classes of chemical compounds. They are part of the foods and beverages we ingest, they are present in medicines and other consumer products, and they are prevalent in the world around us. In this chapter, we will focus on acids and bases and their chemistry.

Media Attributions

Acid-Base Titrations

Learning Objectives

1. Describe a titration experiment.
2. Explain what an indicator does.
3. Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because so many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Figure 12.1 “Equipment for Titrations”). The burette has markings to determine how much volume of solution has been added to the analyte. When the reaction is complete, it is said to be at the **equivalence point**; the number of moles of titrant can be calculated from the concentration and the volume, and the balanced chemical equation can be used to determine the number of moles (and then concentration or mass) of the unknown reactant.

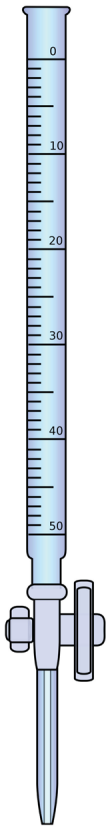


Figure 12.1 "Equipment for Titrations." A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\#\text{ mol HCl} = (0.02566\text{ L})(0.1078\text{ M}) = 0.002766\text{ mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$\text{HCl + NaOH} \rightarrow \text{NaCl + H}_2\text{O}$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\ \cancel{\text{mol HCl}} \times \frac{1\text{ mol NaOH}}{1\ \cancel{\text{mol HCl}}} = 0.002766\text{ mol NaOH}$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\ \cancel{\text{mol NaOH}} \times \frac{40.00\text{ g NaOH}}{1\ \cancel{\text{mol NaOH}}} = 0.1106\text{ g NaOH}$$

This is type of calculation is performed as part of a titration.

Example 12.1

What mass of $Ca(OH)_2$ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO_3? The balanced chemical equation is as follows:

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

Solution
In litres, the volume is 0.04402 L. We calculate the number of moles of titrant:

$$\# \text{ moles } HNO_3 = (0.04402 \text{ L})(0.0885 \text{ M}) = 0.00390 \text{ mol } HNO_3$$

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390 \cancel{\text{ mol } HNO_3} \times \frac{1 \text{ mol } Ca(OH)_2}{2 \cancel{\text{ mol } HNO_3}} = 0.00195 \text{ mol } Ca(OH)_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195 \cancel{\text{ mol } Ca(OH)_2} \times \frac{74.1 \text{ g } Ca(OH)_2}{1 \cancel{\text{ mol } Ca(OH)_2}} = 0.144 \text{ g } Ca(OH)_2$$

Test Yourself

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

Answer
0.182 g

How does one know if a reaction is at its equivalence point? Usually, the person performing the titration adds a small amount of an **indicator**, a substance that changes colour depending on the acidity or basicity of the solution. Because different indicators change colours at different levels of acidity, choosing the correct one is important in performing an accurate titration.

For more information, watch this video: "Titration" by Jessie Key.

Key Takeaways

- A titration is the quantitative reaction of an acid and a base.
- Indicators are used to show that all the analyte has reacted with the titrant.

Exercises

Questions

1. Define *titration*.
2. What is the difference between the titrant and the analyte?
3. True or false: An acid is always the titrant. Explain your answer.
4. True or false: An analyte is always dissolved before reaction. Explain your answer.
5. If 55.60 mL of 0.2221 M HCl was needed to titrate a sample of NaOH to its equivalence point, what mass of NaOH was present?
6. If 16.33 mL of 0.6664 M KOH was needed to titrate a sample of $HC_2H_3O_2$ to its equivalence point, what mass of $HC_2H_3O_2$ was present?
7. It takes 45.66 mL of 0.1126 M HBr to titrate 25.00 mL of $Ca(OH)_2$ to its equivalence point. What is the original concentration of the $Ca(OH)_2$ solution?
8. It takes 9.77 mL of 0.883 M H_2SO_4 to titrate 15.00 mL of KOH to its equivalence point. What is the original concentration of the KOH solution?

Answers

1. A chemical reaction performed in a quantitative fashion.

3. False; a base can be a titrant, or the reaction being performed may not even be an acid-base reaction.

5. 0.494 g

7. 0.1028 M

Strong and Weak Acids and Bases and Their Salts

Learning Objectives

1. Define a strong and a weak acid and base.
2. Recognize an acid or a base as strong or weak.
3. Determine if a salt produces an acidic or a basic solution.

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(aq). When HCl is dissolved in H_2O, it completely dissociates into $H^+(aq)$ and $Cl^-(aq)$ ions; all the HCl molecules become ions:

$$HCl \rightarrow H^+(aq) + Cl^-(aq) \text{ (100\%)}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \rightarrow H^+(aq) + C_2H_3O_2^-(aq) \text{ (~5\%)}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as an equilibrium:

$$HC_2H_3O_2 \rightleftarrows H^+(aq) + C_2H_3O_2^-(aq)$$

As it turns out, there are very few strong acids, which are given in Table 12.1 “Strong Acids and Bases”. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (see Table 12.1); any base not listed is a weak base. All strong bases are OH^- compounds. So a base based on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.

Table 12.1 Strong Acids and Bases

Acids	**Bases**
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

Example 12.2

Identify each acid or base as strong or weak.

1. HCl
2. $Mg(OH)_2$
3. C_5H_5N

Solution

1. Because HCl is listed in Table 12.1, it is a strong acid.
2. Because $Mg(OH)_2$ is listed in Table 12.1, it is a strong base.
3. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Test Yourself
Identify each acid or base as strong or weak.

1. RbOH
2. HNO_2

Answers

1. strong base
2. weak acid

Example 12.3

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution
This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

$$Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

Because $Ca(OH)_2$ is listed in Table 12.1, this reaction proceeds 100% to products.

Test Yourself
Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer
The reaction is as follows:

$$HN_3 \rightarrow H^+(aq) + N_3^-(aq)$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Certain salts will also affect the acidity or basicity of aqueous solutions because some of the ions will undergo hydrolysis, just like NH_3 does to make a basic solution. The general rule is that salts with ions that are part of strong acids or bases will not hydrolyze, while salts with ions that are part of weak acids or bases will hydrolyze.

Consider NaCl. When it dissolves in an aqueous solution, it separates into Na^+ ions and Cl^- ions:

$$NaCl \rightarrow Na^+(aq) + Cl^-(aq)$$

Will the $Na^+(aq)$ ion hydrolyze? If it does, it will interact with the OH^- ion to make NaOH:

$$Na^+(aq) + H_2O \rightarrow NaOH + H^+(aq)$$

However, NaOH is a strong base, which means that it is 100% ionized in solution:

$$NaOH \rightarrow Na^+(aq) + OH^-(aq)$$

The free $OH^-(aq)$ ion reacts with the $H^+(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Na^+(aq)$ ion. What about the Cl^- ion? Will it hydrolyze? If it does, it will take an H^+ ion from a water molecule:

$$Cl^-(aq) + H_2O \rightarrow HCl + OH^-$$

However, HCl is a strong acid, which means that it is 100% ionized in solution:

$$HCl \rightarrow H^+(aq) + Cl^-(aq)$$

The free $H^+(aq)$ ion reacts with the $OH^-(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Cl^-(aq)$ ion. Because neither ion in NaCl affects the acidity or basicity of the solution, NaCl is an example of a **neutral salt**.

Things change, however, when we consider a salt like $NaC_2H_3O_2$. We already know that the Na^+ ion won't affect the acidity of the solution. What about the acetate ion? If it hydrolyzes, it will take an H^+ from a water molecule:

$$C_2H_3O_2^-(aq) + H_2O \rightarrow HC_2H_3O_2 + OH^-(aq)$$

Does this happen? Yes, it does. Why? *Because $HC_2H_3O_2$ is a weak acid.* Any chance a weak acid has to form, it will (the same with a weak base). As some $C_2H_3O_2^-$ ions hydrolyze with H_2O to make the molecular weak acid, OH^- ions are produced. OH^- ions make solutions basic. Thus $NaC_2H_3O_2$ solutions are slightly basic, so such a salt is called a **basic salt**.

There are also salts whose aqueous solutions are slightly acidic. NH_4Cl is an example. When NH_4Cl is dissolved in H_2O, it separates into NH_4^+ ions and Cl^- ions. We have already seen that the Cl^- ion does not hydrolyze. However, the NH_4^+ ion will:

$$NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$$

Recall from the section "Arrhenius Acids and Bases" that H_3O^+ ion is the hydronium ion, the more chemically proper way to represent the H^+ ion. This is the classic acid species in solution, so a solution of $NH_4^+(aq)$ ions is slightly acidic. NH_4Cl is an example of an **acid salt**. The molecule NH_3 is a weak base, and it will form when it can, just like a weak acid will form when it can.

So there are two general rules:

1. If an ion derives from a strong acid or base, it will not affect the acidity of the solution.
2. If an ion derives from a weak acid, it will make the solution basic; if an ion derives from a weak base, it will make the solution acidic.

Example 12.4

Identify each salt as acidic, basic, or neutral.

1. KCl
2. KNO_2
3. NH_4Br

Solution

1. The ions from KCl derive from a strong acid (HCl) and a strong base (KOH). Therefore, neither ion will affect the acidity of the solution, so KCl is a neutral salt.
2. Although the K^+ ion derives from a strong base (KOH), the NO_2^- ion derives from a weak acid (HNO_2). Therefore the

solution will be basic, and KNO_2 is a basic salt.

3. Although the Br^- ions derive from a strong acid (HBr), the NH_4^+ ion derives from a weak base (NH_3), so the solution will be acidic, and NH_4Br is an acidic salt.

Test Yourself
Identify each salt as acidic, basic, or neutral.

1. $(C_5H_5NH)Cl$
2. Na_2SO_3

Answers

1. acidic
2. basic

Some salts are composed of ions that come from both weak acids and weak bases. The overall effect on an aqueous solution depends on which ion exerts more influence on the overall acidity. We will not consider such salts here.

Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.
- Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

Exercises

Questions

1. Differentiate between a strong acid and a weak acid.
2. Differentiate between a strong base and a weak base.
3. Identify each as a strong acid or a weak acid. Assume aqueous solutions.
    a. HF
    b. HCl
    c. HC_2O_4
4. Identify each as a strong base or a weak base. Assume aqueous solutions.
    a. NaOH
    b. $Al(OH)_3$
    c. $C_4H_9NH_2$
5. Write a chemical equation for the ionization of each acid and indicate whether it proceeds 100% to products or not.

a. HNO_3
b. HNO_2
c. HI_3

6. Write a chemical equation for the ionization of each base and indicate whether it proceeds 100% to products or not.

a. NH_3
b. $(CH_3)_3N$
c. $Mg(OH)_2$

7. Write the balanced chemical equation for the reaction of each acid and base pair.

a. $HCl + C_5H_5N$
b. $H_2C_2O_4 + NH_3$
c. $HNO_2 + C_7H_9N$

8. Write the balanced chemical equation for the reaction of each acid and base pair.

a. $H_3C_5H_5O_7 + Mg(OH)_2$
b. $HC_3H_3O_3 + (CH_3)_3N$
c. $HBr + Fe(OH)_3$

9. Identify each salt as neutral, acidic, or basic.

a. NaBr
b. $Fe(NO_3)_2$
c. $Fe(NO_3)_3$

10. Identify each salt as neutral, acidic, or basic.

a. NH_4I
b. $C_2H_5NH_3Cl$
c. KI

11. Identify each salt as neutral, acidic, or basic.

a. $NaNO_2$
b. $NaNO_3$
c. NH_4NO_3

12. Identify each salt as neutral, acidic, or basic.

a. $KC_2H_3O_2$
b. $KHSO_4$
c. $KClO_3$

13. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.

a. K_2SO_3
b. KI
c. NH_4ClO_3

14. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.

a. $NaNO_3$
b. CaC_2O_4

c. C_5H_5NHCl

15. When NH_4NO_2 dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?
16. When pyridinium acetate ($C_5H_5NHC_2H_3O_2$) dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?
17. A lab technician mixes a solution of 0.015 M $Mg(OH)_2$. Is the resulting OH^- concentration greater than, equal to, or less than 0.015 M? Explain your answer.
18. A lab technician mixes a solution of 0.55 M HNO_3. Is the resulting H^+ concentration greater than, equal to, or less than 0.55 M? Explain your answer.

Answers

1. A strong acid is 100% ionized in aqueous solution, whereas a weak acid is not 100% ionized.

3. a. weak acid
   b. strong acid
   c. weak acid

5. a. $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$; proceeds 100%
   b. $HNO_2(aq) \rightarrow H^+(aq) + NO_2^-(aq)$; does not proceed 100%
   c. $HI_3(aq) \rightarrow H^+(aq) + I_3^-(aq)$; does not proceed 100%

7. a. $HCl + C_5H_5N \rightarrow Cl^- + C_5H_5NH^+$
   b. $H_2C_2O_4 + 2NH_3 \rightarrow C_2O_4^{2-} + 2NH_4^+$
   c. $HNO_2 + C_7H_9N \rightarrow NO_2^- + C_7H_9NH^+$

9. a. neutral
   b. acidic
   c. acidic

11. a. basic
    b. neutral
    c. acidic

13. a. $SO_3^{2-} + H_2O \rightarrow HSO_3^- + OH^-$
    b. no reaction
    c. $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$

15. $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$; $NO_2^- + H_2O \rightarrow HNO_2 + OH^-$; it is not possible to determine whether the solution will be acidic or basic.

17. Greater than 0.015 M, because there are two OH^- ions per formula unit of $Mg(OH)_2$.

Brønsted-Lowry Acids and Bases

Learning Objectives

1. Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
2. Identify conjugate acid-base pairs in an acid-base reaction.

The Arrhenius definition of acid and base is limited to aqueous (that is, water) solutions. Although this is useful because water is a common solvent, it is limited to the relationship between the H^+ ion and the OH^- ion. What would be useful is a more general definition that would be more applicable to other chemical reactions and, importantly, independent of H_2O.

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor (PD), while a Brønsted-Lowry base is a proton acceptor (PA).

It is easy to see that the Brønsted-Lowry definition covers the Arrhenius definition of acids and bases. Consider the prototypical Arrhenius acid-base reaction:

$$\underset{(\text{acid})}{\mathrm{H^+(aq)}} + \underset{(\text{base})}{\mathrm{OH^-(aq)}} \rightarrow \mathrm{H_2O(\ell)}$$

The acid species and base species are marked. The proton, however, is (by definition) a proton donor (labelled PD), while the OH^- ion is acting as the proton acceptor (labelled PA):

$$\underset{(\text{PD})}{\mathrm{H^+(aq)}} + \underset{(\text{PA})}{\mathrm{OH^-(aq)}} \rightarrow \mathrm{H_2O(\ell)}$$

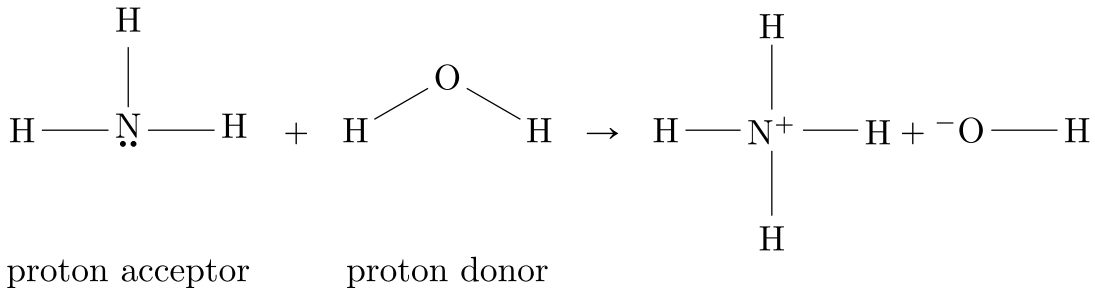
The proton donor is a Brønsted-Lowry acid, and the proton acceptor is the Brønsted-Lowry base:

$$\underset{(\text{BL acid})}{\mathrm{H^+(aq)}} + \underset{(\text{BL base})}{\mathrm{OH^-(aq)}} \rightarrow \mathrm{H_2O(\ell)}$$

Thus H^+ is an acid by both definitions, and OH^- is a base by both definitions.

Ammonia (NH_3) is a base even though it does not contain OH^- ions in its formula. Instead, it generates

OH^- ions as the product of a proton-transfer reaction with H_2O molecules; NH_3 acts like a Brønsted-Lowry base, and H_2O acts like a Brønsted-Lowry acid:



A reaction with water is called **hydrolysis**; we say that NH_3 hydrolyzes to make NH_4^+ ions and OH^- ions.

Even the dissolving of an Arrhenius acid in water can be considered a Brønsted-Lowry acid-base reaction. Consider the process of dissolving HCl(g) in water to make an aqueous solution of hydrochloric acid. The process can be written as follows:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while H_2O is the proton acceptor and a Brønsted-Lowry base. These two examples show that H_2O can act as both a proton donor and a proton acceptor, depending on what other substance is in the chemical reaction. A substance that can act as a proton donor or a proton acceptor is called **amphiprotic**. Water is probably the most common amphiprotic substance we will encounter, but other substances are also amphiprotic.

Example 12.5

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$C_6H_5OH + NH_2^- \rightarrow C_6H_5O^- + NH_3$$

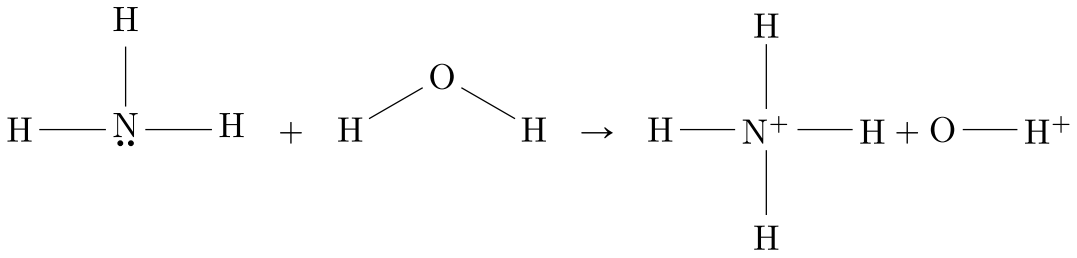
Solution
The C_6H_5OH molecule is losing an H^+; it is the proton donor and the Brønsted-Lowry acid. The NH_2^- ion (called the amide ion) is accepting the H^+ ion to become NH_3, so it is the Brønsted-Lowry base.

Test Yourself
Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

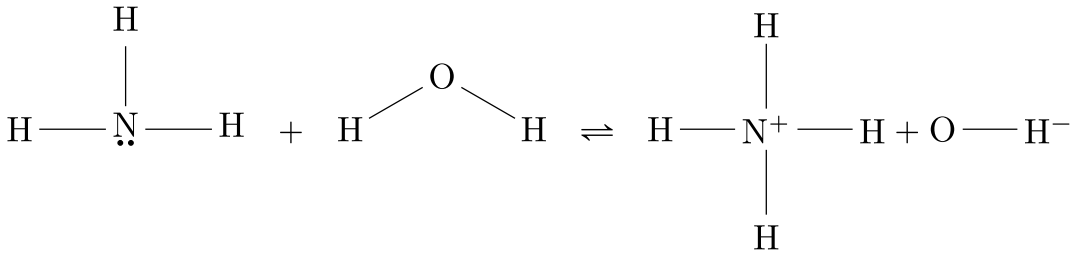
$$Al(H_2O)_6^{3+} + H_2O \rightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+$$

Answer
Brønsted-Lowry acid: $Al(H_2O)_6^{3+}$; Brønsted-Lowry base: H_2O

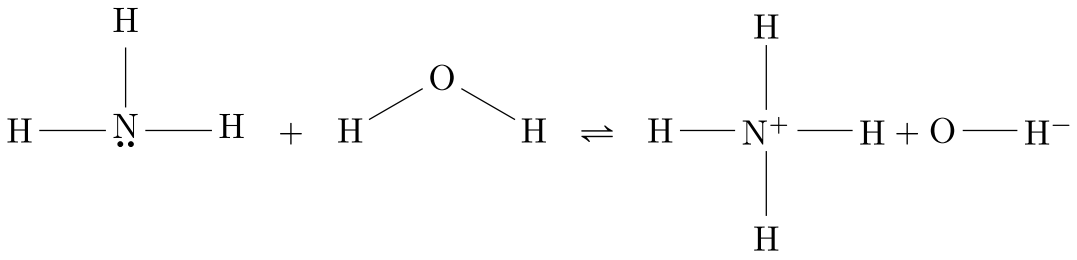
Observe the reaction between NH_3 and H_2O:



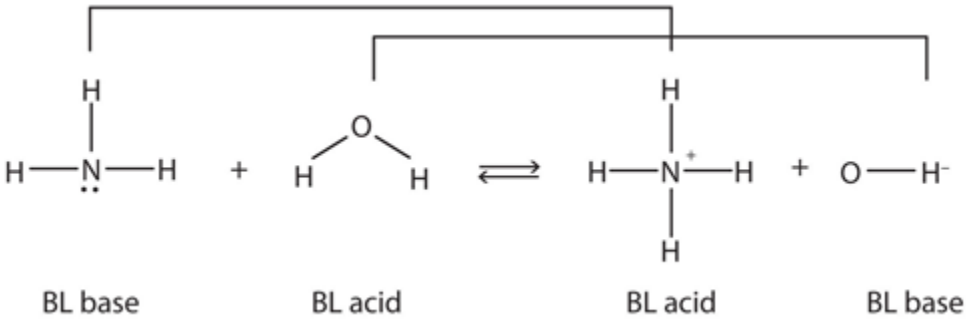
The chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change by the other process; it is a *dynamic*, rather than a *static*, equilibrium. Because both reactions are occurring, it makes sense to use a double arrow instead of a single arrow:



What do you notice about the reverse reaction? The NH_4^+ ion is donating a proton to the OH^- ion, which is accepting it. This means that the NH_4^+ ion is acting as the proton donor, or Brønsted-Lowry acid, while OH^- ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:



This means that both reactions are acid-base reactions by the Brønsted-Lowry definition. If you consider the species in this chemical reaction, two sets of similar species exist on both sides. Within each set, the two species differ by a proton in their formulas, and one member of the set is a Brønsted-Lowry acid, while the other member is a Brønsted-Lowry base. These sets are marked here:



The two sets — NH_3/NH_4^+ and H_2O/OH^- — are called **conjugate acid-base pairs**. We say that NH_4^+ is the conjugate acid of NH_3, OH^- is the conjugate base of H_2O, and so forth. Every Brønsted-Lowry acid-base reaction can be labelled with two conjugate acid-base pairs.

Example 12.6

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftarrows (CH_3)_3NH+ + OH^-$$

Solution
One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base. The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Test Yourself
Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftarrows NH_3 + OH^-$$

Answer
H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

Chemistry Is Everywhere: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for HCl(aq). In Chapter 4 "Chemical Reactions and Equations", in the section "Neutralization Reactions", vinegar was mentioned as a dilute solution of acetic acid [$HC_2H_3O_2$(aq)]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is NH_3, which is found in numerous cleaning products. NH_3 is a base because it increases the OH^- ion concentration by reacting with H_2O:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from H_2O and forming excess OH^- ions. This is one explanation for why soap solutions are slippery.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for NaOH, although it is also used as a synonym for KOH. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and clog a water pipe. Unfortunately, lye can also attack body tissues and other substances in our bodies. Thus when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner

or spill the water it was poured into. Safer, nonlye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.

Key Takeaways

- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- Acid-base reactions include two sets of conjugate acid-base pairs.

Exercises

Questions

1. Define *Brønsted-Lowry acid*. How does it differ from an Arrhenius acid?
2. Define *Brønsted-Lowry base*. How does it differ from an Arrhenius base?
3. Write the dissociation of hydrogen bromide in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
4. Write the dissociation of nitric acid in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
5. Pyridine (C_5H_5N) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for pyridine and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
6. The methoxide ion (CH_3O^-) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for the methoxide ion and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
7. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$

8. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

$$H_2C_2O_4 + 2F^- \rightarrow 2HF + C_2O_4^{2-}$$

9. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

$$HC_2H_3O_2 + C_5H_5N \rightarrow ?$$

10. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

$$(C_2H_5)_3N + H_2O \rightarrow ?$$

11. What is the conjugate acid of H_2O? NH_3?
12. What is the conjugate acid of $H_2PO_4^-$? NO_3^-?
13. What is the conjugate base of HSO_4^-? H_2O?
14. What is the conjugate base of H_3O^+? H_2SO_4?
15. Identify the conjugate acid-base pairs in this reaction.

$$HSO_4^- + PO_4^{3-} \rightarrow SO_4^{2-} + HPO_4^{2-}$$

16. Identify the conjugate acid-base pairs in this reaction.

$$HClO_3 + (C_2H_5)_3N \rightarrow ClO_3^- + (C_2H_5)_3NH^+$$

17. Identify the conjugate acid-base pairs in this reaction.

$$NH_3 + C_6H_5O^- \rightarrow C_6H_5OH + NH_2^-$$

18. Identify the conjugate acid-base pairs in this reaction.

$$C_5H_5NH^+ + C_2O_4^{2-} \rightarrow C_5H_5N + HC_2O_4^-$$

Answers

1. A Brønsted-Lowry acid is a proton donor. It does not necessarily increase the H^+ concentration in water.
3. $HBr + H_2O \rightarrow H_3O^+ + Br^-$; PD: HBr; PA: H_2O
5. $C_5H_5N + H_2O \rightarrow C_5H_5NH^+ + OH^-$; PD: H_2O; PA: C_5H_5N
7. BL acid: H_3PO_4; BL base: OH^-
9. $C_2H_3O_2^-$ and $C_5H_5NH^+$
11. H_3O^+; NH_4^+
13. SO_4^{2-}; OH^-
15. HSO_4^- and SO_4^{2-}; PO_4^{3-} and HPO_4^{2-}
17. NH_3 and NH_2^-; $C_6H_5O^-$ and C_6H_5OH

Arrhenius Acids and Bases

Learning Objectives

1. Identify an Arrhenius acid and an Arrhenius base.
2. Write the chemical reaction between an Arrhenius acid and an Arrhenius base.

Historically, the first chemical definition of an acid and a base was put forward by Svante Arrhenius, a Swedish chemist, in 1884. An **Arrhenius acid** is a compound that increases the H^+ ion concentration in aqueous solution. The H^+ ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the **hydronium ion** (H_3O^+) as the actual chemical species that represents an H^+ ion. H^+ ions and H_3O^+ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional H_2O). Classic Arrhenius acids can be considered ionic compounds in which H^+ is the cation. Table 12.2 “Some Arrhenius Acids” lists some Arrhenius acids and their names.

Table 12.2 Some Arrhenius Acids

Formula	Name
$HC_2H_3O_2$ (also written CH_3COOH)	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid

An **Arrhenius base** is a compound that increases the OH^- ion concentration in aqueous solution. Ionic compounds of the OH^- ion are classic Arrhenius bases.

Example 12.7

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. HNO_3
2. CH_3OH
3. $Mg(OH)_2$

Solution

1. This compound is an ionic compound between H^+ ions and NO_3^- ions, so it is an Arrhenius acid.
2. Although this formula has an OH in it, we do not recognize the remaining part of the molecule as a cation. It is neither an acid nor a base. (In fact, it is the formula for methanol, an organic compound.)
3. This formula also has an OH in it, but this time we recognize that the magnesium is present as Mg^{2+} cations. As such, this is an ionic compound of the OH^- ion and is an Arrhenius base.

Test Yourself
Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH
2. H_2SO_4
3. C_2H_6

Answer

1. Arrhenius base
2. Arrhenius acid
3. neither

Acids have some properties in common. They turn litmus, a plant extract, red. They react with some metals to give off H_2 gas. They react with carbonate and hydrogen carbonate salts to give off CO_2 gas. Acids that are ingested typically have a sour, sharp taste. (The name *acid* comes from the Latin word *acidus*, meaning “sour.”) Bases also have some properties in common. They are slippery to the touch, turn litmus blue, and have a bitter flavour if ingested.

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as follows:

$$\text{acid} + \text{base} \rightarrow H_2O + \text{salt}$$

The stoichiometry of the balanced chemical equation depends on the number of H^+ ions in the acid and the number of OH^- ions in the base.

Example 12.8

Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and KOH. What is the name of the salt that is formed?

Solution
The general reaction is as follows:

$$H_2SO_4 + KOH \rightarrow H_2O + \text{salt}$$

Because the acid has two H^+ ions in its formula, we need two OH^- ions to react with it, making two H_2O molecules as product. The remaining ions, K^+ and SO_4^{2-}, make the salt potassium sulfate (K_2SO_4). The balanced chemical reaction is as follows:

$$H_2SO_4 + 2KOH \rightarrow 2H_2O + K_2SO_4$$

Test Yourself
Write the balanced chemical equation for the neutralization reaction between HCl and $Mg(OH)_2$. What is the name of the salt that is formed?

Answer
$2HCl + Mg(OH)_2 \rightarrow 2\ H_2O + MgCl_2$; magnesium chloride

Key Takeaways

- An Arrhenius acid is a compound that increases the H^+ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

Exercises

Questions

1. Define *Arrhenius acid*.
2. Define *Arrhenius base*.
3. What are some general properties of Arrhenius acids?
4. What are some general properties of Arrhenius bases?
5. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
    a. NaOH
    b. C_2H_5OH
    c. H_3PO_4
6. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
    a. $C_6H_{12}O_6$
    b. HNO_2

c. $Ba(OH)_2$

7. Write the balanced chemical equation for the neutralization reaction between KOH and $H_2C_2O_4$. What is the salt?
8. Write the balanced chemical equation for the neutralization reaction between $Sr(OH)_2$ and H_3PO_4. What is the salt?
9. Write the balanced chemical equation for the neutralization reaction between HCl and $Fe(OH)_3$. What is the salt?
10. Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and $Cr(OH)_3$. What is the salt?
11. $CaCl_2$ would be the product of the reaction of what acid and what base?
12. $Zn(NO_3)_2$ would be product of the reaction of what acid and what base?
13. $BaSO_4$ would be product of the reaction of what acid and what base?
14. Na_3PO_4 would be product of the reaction of what acid and what base?

Answers

1. A compound that increases the H^+ concentration in water.
3. Sour taste, react with metals, and turn litmus red
    a. Arrhenius base
    b. neither
    c. Arrhenius acid
7. $2KOH + H_2C_2O_4 \rightarrow 2H_2O + K_2C_2O_4$; $K_2C_2O_4$
9. $3HCl + Fe(OH)_3 \rightarrow 3H_2O + FeCl_3$; $FeCl_3$
11. HCl and $Ca(OH)_2$
13. H_2SO_4 and $Ba(OH)_2$

Autoionization of Water

Learning Objectives

1. Describe the autoionization of water.
2. Calculate the concentrations of H^+ and OH^- in solutions, knowing the other concentration.

We have already seen that H_2O can act as an acid or a base:

$$\begin{array}{lcll} NH_3 + H_2O & \rightarrow & NH_4{}^+ + OH^- & H_2O \text{ acts as an acid} \\ HCl + H_2O & \rightarrow & H_3O^+ + Cl^- & H_2O \text{ acts as a base} \end{array}$$

It may not surprise you to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both H^+(aq) and OH^-(aq) in a sample of pure H_2O is about 1.0×10^{-7} M. If we use square brackets around a dissolved species to imply the molar concentration of that species, we have:

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water, because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In acids, the concentration of H^+(aq) — written as $[H^+]$ — is greater than 1.0×10^{-7} M, while for bases the concentration of OH^-(aq) — $[OH^-]$ — is greater than 1.0×10^{-7} M. However, the *product* of the two concentrations — $[H^+][OH^-]$ — is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_w:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$ has to be for the product

to equal 1.0×10^{-14}, or if you know $[OH^-]$, you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

Example 12.9

What is $[OH^-]$ of an aqueous solution if $[H^+]$ is 1.0×10^{-4} M?

Solution
Using the expression and known value for K_w:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[OH^-]$$

We solve by dividing both sides of the equation by 1.0×10^{-4}:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10}\ \text{M}$$

It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M.

Test Yourself
What is $[H^+]$ of an aqueous solution if $[OH^-]$ is 1.0×10^{-9} M?

Answer
1.0×10^{-5} M

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H^+ or OH^- ions in the formula unit because $[H^+]$ or $[OH^-]$ may not be the same as the concentration of the acid or base itself.

Example 12.10

What is $[H^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

Solution
We begin by determining $[OH^-]$.

The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two OH^- ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this, or 2×0.0044 M = 0.0088 M.

Now we can use the K_w expression:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088\ \text{M})$$

Dividing both sides by 0.0088:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.0088} = 1.1 \times 10^{-12}\ \text{M}$$

$[H^+]$ has decreased significantly in this basic solution.

Test Yourself
What is $[OH^-]$ in a 0.00032 M solution of H_2SO_4? (Hint: assume both H^+ ions ionize.)

Answer
1.6×10^{-11} M

For strong acids and bases, $[H^+]$ and $[OH^-]$ can be determined directly from the concentration of the

acid or base itself because these ions are 100% ionized by definition. However, for weak acids and bases, this is not so. The degree, or percentage, of ionization would need to be known before we can determine $[H^+]$ and $[OH^-]$.

Example 12.11

A 0.0788 M solution of $HC_2H_3O_2$ is 3.0% ionized into H^+ ions and $C_2H_3O_2^-$ ions. What are $[H^+]$ and $[OH^-]$ for this solution?

Solution
Because the acid is only 3.0% ionized, we can determine $[H^+]$ from the concentration of the acid. Recall that 3.0% is 0.030 in decimal form:

$$[H^+] = 0.030 \times 0.0788 = 0.00236 \text{ M}$$

With this $[H^+]$, then $[OH^-]$ can be calculated as follows:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} \text{ M}$$

This is about 30 times higher than would be expected for a strong acid of the same concentration.

Test Yourself
A 0.0222 M solution of pyridine (C_5H_5N) is 0.44% ionized into pyridinium ions ($C_5H_5NH^+$) and OH^- ions. What are $[OH^-]$ and $[H^+]$ for this solution?

Answer
$[OH^-] = 9.77 \times 10^{-5}$ M; $[H^+] = 1.02 \times 10^{-10}$ M

Key Takeaways

- In any aqueous solution, the product of $[H^+]$ and $[OH^-]$ equals 1.0×10^{-14}.

Exercises

Questions

1. Does $[H^+]$ remain constant in all aqueous solutions? Why or why not?
2. Does $[OH^-]$ remain constant in all aqueous solutions? Why or why not?
3. What is the relationship between $[H^+]$ and K_w? Write a mathematical expression that relates them.
4. What is the relationship between $[OH^-]$ and K_w? Write a mathematical expression that relates them.
5. Write the chemical equation for the autoionization of water and label the conjugate acid-base pairs.
6. Write the reverse of the reaction for the autoionization of water. It is still an acid-base reaction? If so, label the acid and base.
7. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-3}$ M, what is $[OH^-]$?
8. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-9}$ M, what is $[OH^-]$?

9. For a given aqueous solution, if $[H^+] = 7.92 \times 10^{-5}$ M, what is $[OH^-]$?
10. For a given aqueous solution, if $[H^+] = 2.07 \times 10^{-11}$ M, what is $[H^+]$?
11. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-5}$ M, what is $[H^+]$?
12. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-12}$ M, what is $[H^+]$?
13. For a given aqueous solution, if $[OH^-] = 3.77 \times 10^{-4}$ M, what is $[H^+]$?
14. For a given aqueous solution, if $[OH^-] = 7.11 \times 10^{-10}$ M, what is $[H^+]$?
15. What are $[H^+]$ and $[OH^-]$ in a 0.344 M solution of HNO_3?
16. What are $[H^+]$ and $[OH^-]$ in a 2.86 M solution of HBr?
17. What are $[H^+]$ and $[OH^-]$ in a 0.00338 M solution of KOH?
18. What are $[H^+]$ and $[OH^-]$ in a 6.02×10^{-4} M solution of $Ca(OH)_2$?
19. If HNO_2 is dissociated only to an extent of 0.445%, what are $[H^+]$ and $[OH^-]$ in a 0.307 M solution of HNO_2?
20. If $(C_2H_5)_2NH$ is dissociated only to an extent of 0.077%, what are $[H^+]$ and $[OH^-]$ in a 0.0955 M solution of $(C_2H_5)_2NH$?

Answers

1. $[H^+]$ varies with the amount of acid or base in a solution.
3. $[H^+] = K_w[OH^-]$
5. $H_2O + H_2O \rightarrow H_3O^+ + OH^-$; H_2O/H_3O^+ and H_2O/OH^-
7. 1.0×10^{-11} M
9. 1.26×10^{-10} M
11. 1.0×10^{-9} M
13. 2.65×10^{-11} M
15. $[H^+] = 0.344$ M; $[OH^-] = 2.91 \times 10^{-14}$ M
17. $[OH^-] = 0.00338$ M; $[H^+] = 2.96 \times 10^{-12}$ M
19. $[H^+] = 0.00137$ M; $[OH^-] = 7.32 \times 10^{-12}$ M

Buffers

Learning Objectives

1. Define *buffer*.
2. Correctly identify the two components of a buffer.

As indicated in the section "Strong and Weak Acids and Bases and Their Salts", weak acids are relatively common, even in the foods we eat. But we occasionally encounter a strong acid or base, such as stomach acid, which has a strongly acidic pH of 1.7. By definition, strong acids and bases can produce a relatively large amount of H^+ or OH^- ions and consequently have marked chemical activities. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [approximated as 0.1 M HCl(aq)] were added to the bloodstream and no correcting mechanism were present, the pH of the blood would decrease from about 7.4 to about 4.7 — a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved $HC_2H_3O_2$ (a weak acid) and $NaC_2H_3O_2$ (the salt derived from that weak acid). Another example of a buffer is a solution containing NH_3 (a weak base) and NH_4Cl (a salt derived from that weak base).

Let us use an $HC_2H_3O_2/NaC_2H_3O_2$ buffer to demonstrate how buffers work. If a strong base — a source of $OH^-(aq)$ ions — is added to the buffer solution, those OH^- ions will react with the $HC_2H_3O_2$ in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(\ell) + {C_2H_3O_2}^-(aq)$$

Rather than changing the pH dramatically by making the solution basic, the added OH^- ions react to make H_2O, so the pH does not change much.

If a strong acid — a source of H^+ ions — is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of H^+ ions and ${C_2H_3O_2}^-$ ions are present in the same solution, they will come together to make $HC_2H_3O_2$:

$$H^+(aq) + {C_2H_3O_2}^-(aq) \rightarrow HC_2H_3O_2(aq)$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to

make molecules of a weak acid. Figure 12.2 “The Actions of Buffers” illustrates both actions of a buffer.

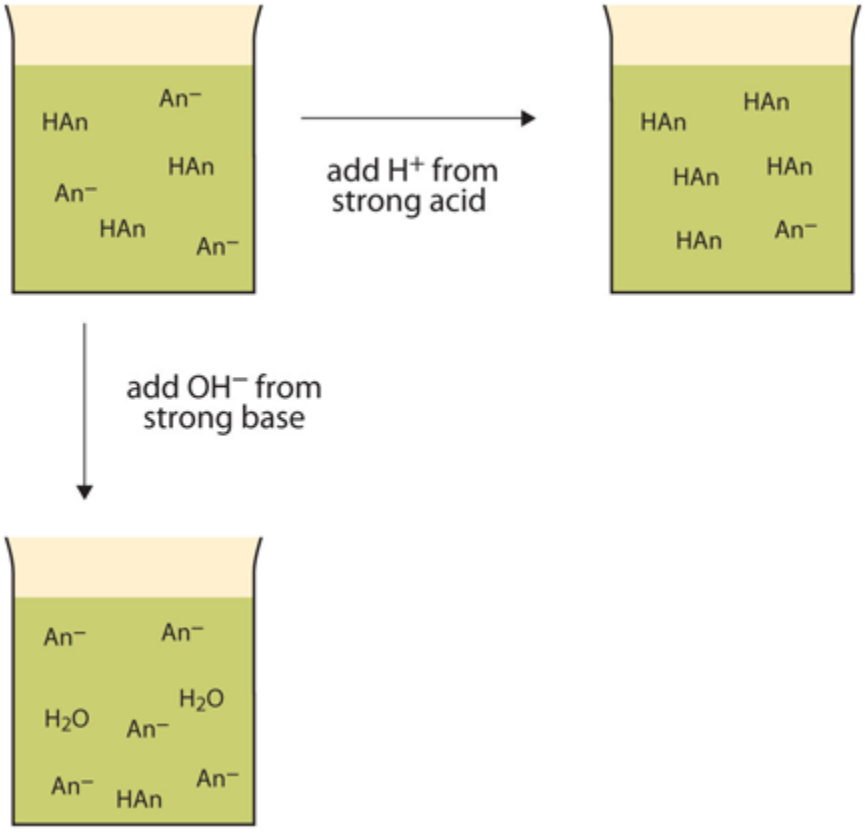


Figure 12.2 “The Actions of Buffers.” Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, NH_3 molecules can react with any excess H^+ ions introduced by strong acids:

$$\mathrm{NH_3(aq) + H^+(aq) \rightarrow NH_4{}^+(aq)}$$

while the $NH_4{}^+$(aq) ion can react with any OH^- ions introduced by strong bases:

$$\mathrm{NH_4{}^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell)}$$

Example 12.12

Which combinations of compounds can make a buffer solution?

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. CH_3NH_2 and CH_3NH_3Cl
4. NH_3 and NaOH

Solution

1. $HCHO_2$ is formic acid, a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid (the formate ion [CHO_2^-]). The combination of these two solutes would make a buffer solution.
2. HCl is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
3. CH_3NH_2 is methylamine, which is like NH_3 with one of its H atoms substituted with a CH_3 group. Because it is not listed in Table 12.1 “Strong Acids and Bases”, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. NH_3 is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Test Yourself
Which combinations of compounds can make a buffer solution?

1. $NaHCO_3$ and NaCl
2. H_3PO_4 and NaH_2PO_4
3. NH_3 and $(NH_4)_3PO_4$
4. NaOH and NaCl

Answers

1. no
2. yes
3. yes
4. no

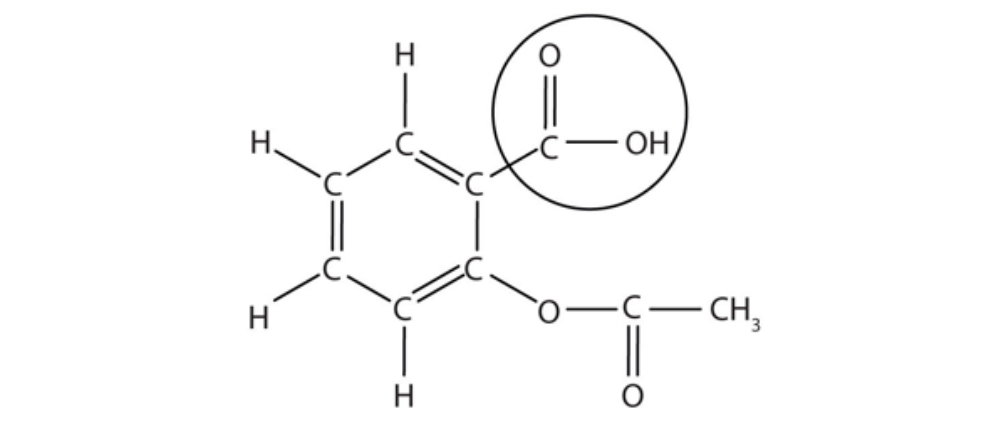
Buffers work well only for limited amounts of added strong acid or base. Once either solute is completely reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [the second compound is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body’s cells, there is a buffering system based on phosphate ions.

Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly “food and drink,” we do ingest them, so let’s take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 12.1 “Strong Acids and Bases”, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach’s defenses against its own stomach acid.



Because the acid properties of aspirin may be problematic, many aspirin brands offer a “buffered aspirin” form of the medicine. In these cases, the aspirin also contains a buffering agent — usually MgO — that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn’t formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects — gastrointestinal bleeding, ringing in the ears, Reye’s syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

Key Takeaways

- A buffer is a solution that resists sudden changes in pH.

Exercises

Questions

1. Define *buffer*. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which combinations of compounds can make a buffer? Assume aqueous solutions.
    a. HCl and NaCl
    b. HNO_2 and $NaNO_2$
    c. NH_4NO_3 and HNO_3
    d. NH_4NO_3 and NH_3
4. Which combinations of compounds can make a buffer? Assume aqueous solutions.
    a. H_3PO_4 and Na_3PO_4
    b. $NaHCO_3$ and Na_2CO_3
    c. $NaNO_3$ and $Ca(NO_3)_2$
    d. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Two solutions are made containing the same concentrations of solutes. One solution is composed of H_3PO_4 and Na_3PO_4, while the other is composed of HCN and NaCN. Which solution should have the larger capacity as a buffer?
10. Two solutions are made containing the same concentrations of solutes. One solution is composed of NH_3 and NH_4NO_3, while the other is composed of H_2SO_4 and Na_2SO_4. Which solution should have the larger capacity as a buffer?

Answers

1. A buffer is the combination of a weak acid or base and a salt of that weak acid or base.

3. a. no
    b. yes
    c. no
    d. yes

5. b. strong acid: $NO_2^- + H^+ \rightarrow HNO_2$; strong base: $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$
    d. strong base: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$; strong acid: $NH_3 + H^+ \rightarrow NH_4^+$

7. Buffers can be made from three combinations: (1) H_3PO_4 and $H_2PO_4^-$; (2) $H_2PO_4^-$ and HPO_4^{2-}; and (3) HPO_4^{2-} and PO_4^{3-}. (Technically, a buffer can be made from any two components.)

9. The phosphate buffer should have the larger capacity.

The pH Scale

Learning Objectives

1. Define *pH*.
2. Determine the pH of acidic and basic solutions.

As we have seen, $[H^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a logarithmic function of $[H^+]$:

$$\text{pH} = -\log[\text{H}^+]$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the **pH scale**. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral.

Example 12.13

Label each solution as acidic, basic, or neutral based only on the stated pH.

1. milk of magnesia, pH = 10.5
2. pure water, pH = 7
3. wine, pH = 3.0

Solution

1. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
2. Pure water, with a pH of 7, is neutral.
3. With a pH of less than 7, wine is acidic.

Test Yourself
Identify each substance as acidic, basic, or neutral based only on the stated pH.

1. human blood, pH = 7.4
2. household ammonia, pH = 11.0
3. cherries, pH = 3.6

Answers

1. basic
2. basic
3. acidic

Table 12.3 “Typical pH Values of Various Substances” gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

Table 12.3 Typical pH Values of Various Substances[1]

Substance	pH
stomach acid	1.7
lemon juice	2.2
vinegar	2.9
soda	3.0
wine	3.5
coffee, black	5.0
milk	6.9
pure water	7.0
blood	7.4
seawater	8.5
milk of magnesia	10.5
ammonia solution	12.5
1.0 M NaOH	14.0

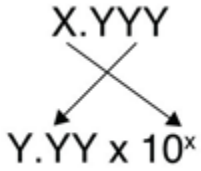
pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the $[H^+]$ as a solution with a pH of 2.0, which in turn has 10 times the $[H^+]$ as a solution with a pH of 3.0 and so forth.

Using the definition of pH, it is also possible to calculate $[H^+]$ (and $[OH^-]$) from pH and vice versa. The general formula for determining $[H^+]$ from pH is as follows:

$$[H^+] = 10^{-pH}$$

You need to determine how to evaluate the above expression on your calculator. Ask your instructor if you have any questions.

The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer:



1. Actual values may vary depending on conditions.

Example 12.14

What are $[H^+]$ and $[OH^-]$ for an aqueous solution whose pH is 4.88?

Solution
We need to evaluate the following expression:

$$[H^+] = 10^{-4.88}$$

Depending on the calculator you use, the method for solving this problem will vary. In some cases, the "−4.88" is entered and a "10^x" key is pressed; for other calculators, the sequence of keystrokes is reversed. In any case, the correct numerical answer is as follows:

$$[H^+] = 1.3 \times 10^{-5}\ \text{M}$$

Because 4.88 has two digits after the decimal point, $[H^+]$ is limited to two significant figures. From this, $[OH^-]$ can be determined:

$$[OH^-] = \frac{1 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}\ \text{M}$$

Test Yourself
What are $[H^+]$ and $[OH^-]$ for an aqueous solution whose pH is 10.36?

Answer
$[H^+] = 4.4 \times 10^{-11}$ M; $[OH^-] = 2.3 \times 10^{-4}$ M

There is an easier way to relate $[H^+]$ and $[OH^-]$. We can also define **pOH** similar to pH:

$$\text{pOH} = -\log[OH^-]$$

(In fact, p"anything" is defined as the negative logarithm of that anything.) This also implies that:

$$[OH^-] = 10^{-\text{pOH}}$$

A simple and useful relationship is that, for any aqueous solution:

$$\text{pH} + \text{pOH} = 14$$

This relationship makes it simple to determine pH from pOH or pOH from pH and then calculate the resulting ion concentration.

Example 12.15

The pH of a solution is 8.22. What are pOH, $[H^+]$, and $[OH^-]$?

Solution
Because the sum of pH and pOH equals 14, we have:

$$8.22 + \text{pOH} = 14$$

Subtracting 8.22 from 14, we get:

$$\text{pOH} = 5.78$$

Now we evaluate the following two expressions:

$$\left[\mathrm{H}^+\right] = 10^{-8.22}$$

$$\left[\mathrm{OH}^-\right] = 10^{-5.78}$$

So:

$$\left[\mathrm{H}^+\right] = 6.0 \times 10^{-9}\ \mathrm{M}$$

$$\left[\mathrm{OH}^-\right] = 1.7 \times 10^{-6}\ \mathrm{M}$$

Test Yourself
The pOH of a solution is 12.04. What are pH, $[H^+]$, and $[OH^-]$?

Answer
pH = 1.96; $[H^+] = 1.1 \times 10^{-2}$ M; $[OH^-] = 9.1 \times 10^{-13}$ M

Key Takeaways

- pH is a logarithmic function of $[H^+]$.
- $[H^+]$ can be calculated directly from pH.
- pOH is related to pH and can be easily calculated from pH.

Exercises

Questions

1. Define *pH*. How is it related to pOH?
2. Define *pOH*. How is it related to pH?
3. What is the pH range for an acidic solution?
4. What is the pH range for a basic solution?
5. What is $[H^+]$ for a neutral solution?
6. What is $[OH^-]$ for a neutral solution? Compare your answer to Exercise 5. Does this make sense?
7. Which substances in Table 12.3 “Typical pH Values of Various Substances” are acidic?
8. Which substances in Table 12.3 are basic?
9. What is the pH of a solution when $[H^+]$ is 3.44×10^{-4} M?
10. What is the pH of a solution when $[H^+]$ is 9.04×10^{-13} M?
11. What is the pH of a solution when $[OH^-]$ is 6.22×10^{-7} M?
12. What is the pH of a solution when $[OH^-]$ is 0.0222 M?
13. What is the pOH of a solution when $[H^+]$ is 3.44×10^{-4} M?
14. What is the pOH of a solution when $[H^+]$ is 9.04×10^{-13} M?
15. What is the pOH of a solution when $[OH^-]$ is 6.22×10^{-7} M?

16. What is the pOH of a solution when $[OH^-]$ is 0.0222 M?
17. If a solution has a pH of 0.77, what is its pOH, $[H^+]$, and $[OH^-]$?
18. If a solution has a pOH of 13.09, what is its pH, $[H^+]$, and $[OH^-]$?

Answers

1. pH is the negative logarithm of $[H^+]$ and is equal to 14 − pOH.
3. pH < 7
5. 1.0×10^{-7} M
7. Every entry above pure water is acidic.
9. pH of 3.46
11. pH of 7.79
13. pOH of 10.54
15. pOH of 6.21
17. pOH = 13.23; $[H^+] = 1.70 \times 10^{-1}$ M; $[OH^-] = 5.89 \times 10^{-14}$ M

End-of-Chapter Material

Additional Exercises

1. Write the balanced chemical equation between Zn metal and HCl(aq). The other product is $ZnCl_2$.
2. Write the neutralization reaction in which $ZnCl_2$, also found in Exercise 1, is the salt product.
3. Why isn't an oxide compound like CaO considered a salt? (Hint: what acid-base combination would be needed to make it if it were a salt?)
4. Metal oxides are considered basic because they react with H_2O to form OH compounds. Write the chemical equation for a reaction that forms a base when CaO is combined with H_2O.
5. Write the balanced chemical equation between aluminum hydroxide and sulfuric acid.
6. Write the balanced chemical equation between phosphoric acid and barium hydroxide.
7. Write the equation for the chemical reaction that occurs when caffeine ($C_8H_{10}N_4O_2$) acts as a Brønsted-Lowry base.
8. Citric acid ($C_6H_8O_7$) is the acid found in citrus fruits. It can lose a maximum of three H^+ ions in the presence of a base. Write the chemical equations for citric acid acting stepwise as a Brønsted-Lowry acid.
9. Can an amphiprotic substance be a strong acid and a strong base at the same time? Explain your answer.
10. Can an amphiprotic substance be a weak acid and a weak base at the same time? If so, explain why and give an example.
11. Under what conditions will the equivalence point of a titration be slightly acidic?
12. Under what conditions will the equivalence point of a titration be slightly basic?
13. Write the chemical equation for the autoionization of NH_3.
14. Write the chemical equation for the autoionization of HF.
15. What is the pOH range for an acidic solution?
16. What is the pOH range for a basic solution?
17. The concentration of commercial HCl is about 12 M. What is its pH and pOH?
18. The concentration of concentrated H_2SO_4 is about 18 M. Assuming only one H^+ comes off the H_2SO_4 molecule, what is its pH and pOH? What would the pH and pOH be if the second H^+ were also ionized?

Answers

1. $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
3. The O^{2-} ion would come from H_2O, which is not considered a classic acid in the Arrhenius sense.
5. $2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$
7. $C_8H_{10}N_4O_2 + H_2O \rightarrow C_8H_{10}N_4O_2H^+ + OH^-$; the H^+ ion attaches to one of the N atoms in the caffeine molecule.
9. As a strong acid or base, an amphiprotic substance reacts 100% as an acid or a base, so it cannot be a base or an acid at the same time.
11. if the salt produced is an acidic salt

13. $NH_3 + NH_3 \rightarrow NH_4^+ + NH_2^-$

15. pOH > 7

17. pH = −1.08; pOH = 15.08

Chapter 13. Chemical Equilibrium

Imagine you are stranded in a rowboat in the middle of the ocean. Suddenly, your boat springs a small leak, and you need to bail out water. You grab a bucket and begin to bail. After a few minutes, your efforts against the leak keep the water to only about half an inch, but any further bailing doesn't change the water level; the leak brings in as much water as you bail out.

You are at *equilibrium*. Two opposing processes have reached the same speed, and there is no more overall change in the process.

Chemical reactions are like that as well. Most of them come to an equilibrium. The actual position of the equilibrium — whether it favours the reactants or the products — is characteristic of a chemical reaction; it is difficult to see just by looking at the balanced chemical equation. But chemistry has tools to help you understand the equilibrium of chemical reactions — the focus of our study in this chapter.

So far in this text, when we present a chemical reaction, we have implicitly assumed that the reaction goes to completion. Indeed, our stoichiometric calculations were based on this; when we asked how much of a product is produced when so much of a reactant reacts, we are assuming that *all* of a reactant reacts. However, this is usually not the case; many reactions do not go to completion, and many chemists have to deal with that. In this chapter, we will study this phenomenon and see ways in which we can affect the extent of chemical reactions.

Chemical Equilibrium

Learning Objectives

1. Define *chemical equilibrium*.
2. Recognize chemical equilibrium as a dynamic process.

Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$H_2 + I_2 \rightarrow 2HI$$

This is simply the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the H_2 and the I_2 react to make HI.

However, this is not the case. The reverse chemical reaction is also taking place:

$$2HI \rightarrow H_2 + I_2$$

It acts to undo what the first reaction does. Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, any continued overall reaction stops: the reaction has reached **chemical equilibrium** (sometimes just spoken as *equilibrium*; plural *equilibria*), the point at which the forward and reverse processes balance each other's progress.

Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \rightleftarrows 2HI$$

The double arrow implies that the reaction is going in both directions. Note that the reaction must still be balanced.

Example 13.1

Write the equilibrium equation that exists between calcium carbonate as a reactant and calcium oxide and carbon dioxide as products.

Solution
As this is an equilibrium situation, a double arrow is used. The equilibrium equation is written as follows:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

Test Yourself
Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer
$2H_2 + O_2 \rightleftarrows 2H_2O$

One thing to note about equilibrium is that the reactions do not stop; both the forward reaction and the reverse reaction continue to occur. They both occur at the same rate, so any overall change by one reaction is cancelled by the reverse reaction. We say that chemical equilibrium is *dynamic*, rather than static. Also, because both reactions are occurring simultaneously, the equilibrium can be written backward. For example, representing an equilibrium as

$$H_2 + I_2 \rightleftarrows 2HI$$

is the same thing as representing the same equilibrium as

$$2HI \rightleftarrows H_2 + I_2$$

The reaction must be at equilibrium for this to be the case, however.

Key Takeaways

- Chemical reactions eventually reach equilibrium, a point at which forward and reverse reactions balance each other's progress.
- Chemical equilibria are dynamic: the chemical reactions are always occurring; they just cancel each other's progress.

Exercises

Questions

1. Define *chemical equilibrium*. Give an example.
2. Explain what is meant when it is said that chemical equilibrium is dynamic.
3. Write the equilibrium equation between elemental hydrogen and elemental chlorine as reactants and hydrochloric acid as

the product.

4. Write the equilibrium equation between iron(III) sulfate as the reactant and iron(III) oxide and sulfur trioxide as the products.
5. Graphite and diamond are two forms of elemental carbon. Write the equilibrium equation between these two forms in two different ways.
6. At 1,500 K, iodine molecules break apart into iodine atoms. Write the equilibrium equation between these two species in two different ways.

Answers

1. The situation when the forward and reverse chemical reactions occur, leading to no additional net change in the reaction position; H_2+ I_2 ⇄ 2HI (answers will vary)

3. H_2 + Cl_2 ⇄ 2HCl

5. C (gra) ⇄ C (dia); C (dia) ⇄ C (gra)

The Equilibrium Constant

Learning Objectives

1. Explain the importance of the equilibrium constant.
2. Construct an equilibrium constant expression for a chemical reaction.

In the mid 1860s, Norwegian scientists C. M. Guldberg and P. Waage noted a peculiar relationship between the amounts of reactants and products in an equilibrium. No matter how many reactants they started with, a certain ratio of reactants and products was achieved at equilibrium. Today, we call this observation the **law of mass action**. It relates the amounts of reactants and products at equilibrium for a chemical reaction. For a general chemical reaction occurring in solution,

$$\mathrm{aA + bB \rightleftarrows cC + dD}$$

the **equilibrium constant**, also known as K_{eq}, is defined by the following expression:

$$K_{\mathrm{eq}} = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}^a][\mathrm{B}]^b}$$

where [A] is the molar concentration of species A at equilibrium, and so forth. The coefficients *a*, *b*, *c*, and *d* in the chemical equation become exponents in the expression for K_{eq}. The K_{eq} is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic K_{eq}. The concentration of each reactant and product in a chemical reaction at equilibrium is *related*; the concentrations cannot be random values, but they depend on each other. The numerator of the expression for K_{eq} has the concentrations of every product (however many products there are), while the denominator of the expression for K_{eq} has the concentrations of every reactant, leading to the common *products over reactants* definition for the K_{eq}.

Let us consider a simple example. Suppose we have this equilibrium:

$$\mathrm{A \rightleftarrows B}$$

There is one reactant, one product, and the coefficients on each are just 1 (assumed, not written). The K_{eq} expression for this equilibrium is

$$K_{\mathrm{eq}} = \frac{[\mathrm{B}]}{[\mathrm{A}]}$$

(Exponents of 1 on each concentration are understood.)

Suppose the numerical value of K_{eq} for this chemical reaction is 2.0. If [B] = 4.0 M, then [A] must equal 2.0 M so that the value of the fraction equals 2.0:

$$K_{eq} = \frac{[B]}{[A]} = \frac{4.0}{2.0} = 2.0$$

By convention, the units are understood to be M and are omitted from the K_{eq} expression. Suppose [B] were 6.0 M. For the K_{eq} value to remain constant (it is, after all, called the equilibrium *constant*), then [A] would have to be 3.0 M at equilibrium:

$$K_{eq} = \frac{[B]}{[A]} = \frac{6.0}{3.0} = 2.0$$

If [A] were *not* equal to 3.0 M, the reaction would not be at equilibrium, and a net reaction would occur until that ratio was indeed 2.0. At that point, the reaction is at equilibrium, and any net change would cease. (Recall, however, that the forward and reverse reactions do not stop because chemical equilibrium is dynamic.)

The issue is the same with more complex expressions for the K_{eq}; only the mathematics becomes more complex. Generally speaking, given a value for the K_{eq} and all but one concentration at equilibrium, the missing concentration can be calculated.

Example 13.2

Given the following reaction:

$$H_2 + I_2 \rightleftarrows 2HI$$

If the equilibrium [HI] is 0.75 M and the equilibrium [H_2] is 0.20 M, what is the equilibrium [I_2] if the K_{eq} is 0.40?

Solution
We start by writing the K_{eq} expression. Using the *products over reactants* approach, the K_{eq} expression is as follows:

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Note that [HI] is squared because of the coefficient 2 in the balanced chemical equation. Substituting for the equilibrium [H_2] and [HI] and for the given value of K_{eq}:

$$0.40 = \frac{(0.75)^2}{(0.20)[I_2]}$$

To solve for [I_2], we have to do some algebraic rearrangement: divide the 0.40 into both sides of the equation and multiply both sides of the equation by [I_2]. This brings [I_2] into the numerator of the left side and the 0.40 into the denominator of the right side:

$$[I_2] = \frac{(0.75)^2}{(0.20)(0.40)}$$

Solving,

$$[I_2] = 7.0 \text{ M}$$

The concentration unit is assumed to be molarity. This value for [I_2] can be easily verified by substituting 0.75, 0.20, and 7.0 into the expression for K_{eq} and evaluating: you should get 0.40, the numerical value of K_{eq} (and you do).

Test Yourself
Given the following reaction:

$$H_2 + I_2 \rightleftarrows 2HI$$

If the equilibrium [HI] is 0.060 M and the equilibrium [I_2] is 0.90 M, what is the equilibrium [H_2] if the K_{eq} is 0.40?

Answer
0.010 M

In some types of equilibrium problems, square roots, cube roots, or even higher roots need to be analyzed to determine a final answer. Make sure you know how to perform such operations on your calculator; if you do not know, ask your instructor for assistance.

Example 13.3

The following reaction is at equilibrium:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N_2] is 1.88 M and the equilibrium [NH_3] is 6.62 M, what is the equilibrium [H_2]?

Solution
We start by writing the K_{eq} expression from the balanced chemical equation:

$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Substituting for the known equilibrium concentrations and the K_{eq}, this becomes

$$13.7 = \frac{(6.62)^2}{(1.88)[\text{H}_2]^3}$$

Rearranging algebraically and then evaluating the numerical expression, we get

$$[\text{H}_2]^3 = \frac{(6.22)^2}{(1.88)(13.7)} = 1.502112129$$

To solve for $[\text{H}_2]$, we need to take the cube root of the equation. Performing this operation, we get

$$[\text{H}_2] = 1.15 \text{ M}$$

You should verify that this is correct using your own calculator to confirm that you know how to do a cube root correctly.

Test Yourself
The following reaction is at equilibrium:

$$\text{N}_2 + 3\text{H}_2 \rightleftarrows 2\text{NH}_3$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium $[\text{N}_2]$ is 0.055 M and the equilibrium $[\text{H}_2]$ is 1.62 M, what is the equilibrium $[\text{NH}_3]$?

Answer
1.79 M

The K_{eq} was defined earlier in terms of concentrations. For gas-phase reactions, the K_{eq} can also be defined in terms of the partial pressures of the reactants and products, P_i. For the gas-phase reaction

$$\text{aA(g)} + \text{bB(g)} \rightleftarrows \text{cC(g)} + \text{dD(g)}$$

the pressure-based equilibrium constant, K_{P}, is defined as follows:

$$K_{\text{P}} = \frac{P_{\text{C}}^c P_{\text{D}}^d}{P_{\text{A}}^a P_{\text{B}}^b}$$

where P_{A} is the partial pressure of substance A at equilibrium in atmospheres, and so forth. As with the concentration-based equilibrium constant, the units are omitted when substituting into the expression for K_{P}.

Example 13.4

What is the K_{P} for this reaction, given the equilibrium partial pressures of 0.664 atm for NO_2 and 1.09 for N_2O_4?

$$2\text{NO}_2\text{(g)} \rightleftarrows \text{N}_2\text{O}_4\text{(g)}$$

Solution
Write the K_{P} expression for this reaction:

$$K_{\text{P}} = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$$

Then substitute the equilibrium partial pressures into the expression and evaluate:

$$K_\text{P} = \frac{(1.09)}{(0.664)^2} = 2.47$$

Test Yourself
What is the K_P for this reaction, given the equilibrium partial pressures of 0.44 atm for H_2, 0.22 atm for Cl_2, and 2.98 atm for HCl?

$$H_2 + Cl_2 \rightleftarrows 2HCl$$

Answer
91.7

There is a simple relationship between K_eq (based on concentration units) and K_P (based on pressure units):

$$K_\text{P} = K_\text{eq} \cdot (RT)^{\Delta n}$$

where R is the ideal gas law constant (in units of L·atm/mol·K), T is the absolute temperature, and Δn is the change in the number of moles of gas in the balanced chemical equation, defined as $n_\text{gas,prods} - n_\text{gas,rcts}$.

Note that this equation implies that if the number of moles of gas are the same in reactants and products, $K_\text{eq} = K_\text{P}$.

Example 13.5

What is the K_P at 25°C for this reaction if the K_eq is 4.2×10^{-2}?

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

Solution
Before we use the relevant equation, we need to do two things: convert the temperature to kelvins and determine Δn. Converting the temperature is easy:

$$T = 25 + 273 = 298 \text{ K}$$

To determine the change in the number of moles of gas, take the number of moles of gaseous products and subtract the number of moles of gaseous reactants. There are 2 mol of gas as product and 4 mol of gas of reactant:

$$\Delta n = 2 - 4 = -2 \text{ mol}$$

Note that Δn is negative. Now we can substitute into our equation, using R = 0.08205 L·atm/mol·K. The units are omitted for clarity:

$$K_\text{P} = (4.2 \times 10^{-2})(0.08205)(298)^{-2}$$

Solving,

$$K_\text{P} = 7.0 \times 10^{-5}$$

Test Yourself
What is the K_P at 25°C for this reaction if the K_eq is 98.3?

$$I_2(g) \rightleftarrows 2I(g)$$

Answer
2.40×10^3

Finally, we recognize that many chemical reactions involve substances in the solid or liquid phases. For example, a particular chemical reaction is represented as follows:

$$2NaHCO_3(s) \rightleftarrows Na_2CO_3(s) + CO_2(g) + H_2O(\ell)$$

This chemical equation includes all three phases of matter. This kind of equilibrium is called a **heterogeneous equilibrium** because there is more than one phase present.

The rule for heterogeneous equilibria is as follows: *Do not include the concentrations of pure solids and pure liquids in K_{eq} expressions.* Only partial pressures for gas-phase substances or concentrations in solutions are included in the expressions of equilibrium constants. As such, the equilibrium constant expression for this reaction would simply be

$$K_P = P_{CO_2}$$

because the two solids and one liquid would not appear in the expression.

Key Takeaways

- Every chemical equilibrium can be characterized by an equilibrium constant, known as K_{eq}.
- The K_{eq} and K_P expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation.
- Solids and liquids do not appear in the expression for the equilibrium constant.

Exercises

Questions

1. Define the *law of mass action*.
2. What is an equilibrium constant for a chemical reaction? How is it constructed?
3. Write the K_{eq} expression for each reaction.
    a. $H_2 + Cl_2 \rightleftarrows 2HCl$
    b. $NO + NO_2 \rightleftarrows N_2O_3$
4. Write the K_{eq} expression for each reaction.
    a. $C_2H_5OH + NaI \rightleftarrows C_2H_5I + NaOH$
    b. $PCl_3 + Cl_2 \rightleftarrows PCl_5$
5. Write the K_P expression for each reaction.
    a. $2H_2(g) + O_2(g) \rightleftarrows 2H_2O(g)$
    b. $2H_2O_2(g) \rightleftarrows 2H_2O(g) + O_2(g)$
6. Write the K_P expression for each reaction.

a. $CH_4(g) + 2O_2(g) \rightleftarrows CO_2(g) + 2H_2O(g)$

b. $CH_4(g) + 4Cl_2(g) \rightleftarrows CCl_4(g) + 4HCl(g)$

7. The following reaction is at equilibrium:

$$PBr_3 + Br_2 \rightleftarrows PBr_5$$

The equilibrium $[Br_2]$ and $[PBr_5]$ are 2.05 M and 0.55 M, respectively. If the K_{eq} is 1.65, what is the equilibrium $[PBr_3]$?

8. The following reaction is at equilibrium:

$$CO + Cl_2 \rightleftarrows CoCl_2$$

The equilibrium [CO] and $[Cl_2]$ are 0.088 M and 0.103 M, respectively. If the K_{eq} is 0.225, what is the equilibrium $[COCl_2]$?

9. The following reaction is at equilibrium:

$$CH_4 + 2Cl_2 \rightleftarrows CH_2Cl_2 + 2HCl$$

If $[CH_4]$ is 0.250 M, $[Cl_2]$ is 0.150 M, and $[CH_2Cl_2]$ is 0.175 M at equilibrium, what is [HCl] at equilibrium if the K_{eq} is 2.30?

10. The following reaction is at equilibrium:

$$4HBr + O_2 \rightleftarrows 2H_2O + 2Br_2$$

If [HBr] is 0.100 M, $[O_2]$ is 0.250 M, and $[H_2O]$ is 0.0500 M at equilibrium, what is $[Br_2]$ at equilibrium if the K_{eq} is 0.770?

11. Write the K_P expression for the following gas-phase reaction:

$$4NO_2(g) + O_2(g) \rightleftarrows 2N_2O_5(g)$$

12. Write the K_P expression for the following gas-phase reaction:

$$ClO(g) + O_3(g) \rightleftarrows ClO_2(g) + O_2(g)$$

13. What is the equilibrium partial pressure of $COBr_2$ if the equilibrium partial pressures of CO and Br_2 are 0.666 atm and 0.235 atm and the K_P for this equilibrium is 4.08?

$$CO(g) + Br_2(g) \rightleftarrows COBr_2(g)$$

14. What is the equilibrium partial pressure of O_3 if the equilibrium partial pressure of O_2 is 0.0044 atm and K_P for this equilibrium is 0.00755?

$$3O_2(g) \rightleftarrows 2O_3(g)$$

15. Calculate the K_P for this reaction at 298 K if the $K_{eq} = 1.76 \times 10^{-3}$.

$$3O_2(g) \rightleftarrows 2O_3(g)$$

16. Calculate the K_P for this reaction at 310 K if the $K_{eq} = 6.22 \times 10^{3}$.

$$4NO_2(g) + O_2(g) \rightleftarrows 2N_2O_5(g)$$

17. Calculate the K_{eq} for this reaction if the $K_P = 5.205 \times 10^{-3}$ at 660°C.

$$CO(g) + F_2(g) \rightleftarrows COF_2(g)$$

18. Calculate the K_{eq} for this reaction if the $K_P = 78.3$ at 100°C.

$$4HCl(g) + O_2(g) \rightleftarrows 2H_2O(g) + 2Cl_2(g)$$

19. Write the correct K_{eq} expression for this reaction.

$$NaOH(aq) + HCl(aq) \rightleftarrows NaCl(aq) + H_2O(\ell)$$

20. Write the correct K_{eq} expression for this reaction.

$$AgNO_3(aq) + NaCl(aq) \rightleftarrows AgCl(s) + NaNO_3(aq)$$

21. Write the correct K_P expression for this reaction.

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

22. Write the correct K_P expression for this reaction.

$$C_2H_2(g) + 2I_2(s) \rightleftarrows C_2H_2I_4(g)$$

Answers

1. The relationship between the concentrations of reactants and products of a chemical reaction at equilibrium

3. a. $K_{\text{eq}} = \dfrac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]}$

   b. $K_{\text{eq}} = \dfrac{[\text{N}_2\text{O}_3]}{[\text{NO}][\text{NO}_2]}$

5. a. $K_{\text{P}} = \dfrac{P^2_{\text{H}_2\text{O}}}{P^2_{\text{H}_2} P_{\text{O}_2}}$

   b. $K_{\text{P}} = \dfrac{P^2_{\text{H}_2\text{O}} P_{\text{O}_2}}{P^2_{\text{H}_2\text{O}_2}}$

7. 0.163 M

9. 0.272 M

11. $K_{\text{P}} = \dfrac{P^2_{\text{N}_2\text{O}_5}}{P^4_{\text{NO}_2} P_{\text{O}_2}}$

13. 0.639 atm

15. 7.20×10^{-5}

17. $K_{\text{eq}} = 3.98 \times 10^{-1}$

19. $K_{\text{eq}} = \dfrac{[\text{NaCl}]}{[\text{NaOH}][\text{HCl}]}$

21. $K_{\text{P}} = P_{\text{CO}_2}$

Shifting Equilibria: Le Chatelier's Principle

Learning Objectives

1. Define *Le Chatelier's principle*.
2. Predict the direction of shift for an equilibrium under stress.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Chatelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

Example 13.6

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

In which direction — toward reactants or toward products — does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Test Yourself
Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftarrows COBr_2(g)$$

In which direction — toward reactants or toward products — does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants
2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the K_{eq} does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

How does an equilibrium react to a change in pressure? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Example 13.7

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

Test Yourself
What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftarrows 2O_3(g)$$

Answer
Reaction shifts toward reactants.

What is the effect of temperature changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

$$\begin{aligned} \text{endothermic:} \quad & \text{energy} + \text{reactants} \rightarrow \text{products} \\ \text{exothermic:} \quad & \text{reactants} \rightarrow \text{products} + \text{energy} \end{aligned}$$

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

Example 13.8

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftarrows PCl_5 + 60\ kJ$$

Solution
Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

Test Yourself
Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57\ kJ \rightleftarrows 2NO_2$$

Answer
Equilibrium shifts toward reactants.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

Chemistry Is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different coloured flowers like this?

Figure 13.1 "Garden Equilibria." This species of hydrangea has flowers that can be either red or blue. Why the colour difference?

Interestingly, the colour of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the colour of the flowers. However, it is not the H^+ or OH^- ions that affect the colour of the flowers. Rather, it is the presence of aluminum that causes the colour change.

The solubility of aluminum in soil — and thus the ability of plants to absorb it — is dependent on the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the colour of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the colour of the flowers.

Key Takeaways

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

Exercises

Questions

1. Define *Le Chatelier's principle*.

2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53\ kJ \rightleftarrows 2HI(g)$$

   a. decreased temperature
   b. increased pressure
   c. removal of HI

4. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftarrows 2HF(g) + 546\ kJ$$

   a. increased temperature
   b. addition of H_2
   c. decreased pressure

5. Given this equilibrium, predict the direction of shift for each stress.

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g) + 196\ kJ$$

   a. removal of SO_3
   b. addition of O_2
   c. decreased temperature

6. Given this equilibrium, predict the direction of shift for each stress listed.

$$CO_2(g) + C(s) + 171\ kJ \rightleftarrows 2CO(g)$$

   a. addition of CO
   b. increased pressure
   c. addition of a catalyst

7. The synthesis of NH_3 uses this chemical reaction.

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) + 92\ kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.

8. The synthesis of $CaCO_3$ uses this chemical reaction.

$$CaO(s) + CO_2(g) \rightleftarrows CaCO_3(s) + 180\ kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

Answers

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.

3.
   a. toward reactants
   b. toward reactants
   c. toward products

5.
   a. toward products
   b. toward products
   c. toward products

7. increased pressure, decreased temperature, removal of NH_3

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Calculating Equilibrium Constant Values

Learning Objectives

1. Calculate equilibrium concentrations from the values of the initial amounts and the K_{eq}.

There are some circumstances in which, given some initial amounts and the K_{eq}, you will have to determine the concentrations of all species when equilibrium is achieved. Such calculations are not difficult to do, especially if a consistent approach is applied. We will consider such an approach here.

Suppose we have this simple equilibrium. Its associated K_{eq} is 4.0, and the initial concentration of each reactant is 1.0 M:

$$\begin{array}{ccccc} \mathrm{H_2(g)} & + & \mathrm{Cl_2(g)} & \rightleftharpoons & 2\,\mathrm{HCl(g)} \\ 1.0\ \mathrm{M} & & 1.0\ \mathrm{M} & & \end{array} \qquad K_{\text{eq}} = 4.0$$

Because we have concentrations for the reactants but not the products, we presume that the reaction will proceed in the forward direction to make products. But by how much will it proceed? We don't know, so let us assign it a variable. Let us assume that x M H_2 reacts as the reaction goes to equilibrium. This means that at equilibrium, we have (1.0 − x) M H_2 left over.

According to the balanced chemical equation, H_2 and Cl_2 react in a 1:1 ratio. How do we know that? The coefficients of these two species in the balanced chemical equation are 1 (unwritten, of course). This means that if x M H_2 reacts, x M Cl_2 reacts as well. If we start with 1.0 M Cl_2 at the beginning and we react x M, we have (1.0 − x) M Cl_2 left at equilibrium.

How much HCl is made? We start with zero, but we also see that 2 mol of HCl are made for every mole of H_2 (or Cl_2) that reacts (from the coefficients in the balanced chemical equation), so if we lose x M H_2, we gain 2x M HCl. So now we know the equilibrium concentrations of our species:

$$\begin{array}{ccccc} \mathrm{H_2(g)} & + & \mathrm{Cl_2(g)} & \rightleftharpoons & 2\,\mathrm{HCl(g)} \\ (1.0-x)\mathrm{M} & & (1.0-x)\mathrm{M} & & 2x\mathrm{M} \end{array} \qquad K_{\text{eq}} = 4.0$$

We can substitute these concentrations into the K_{eq} expression for this reaction and combine it with the known value of K_{eq}:

$$K_{\text{eq}} = \frac{[\mathrm{HCl}]^2}{[\mathrm{H_2}][\mathrm{Cl_2}]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$

This is an equation in one variable, so we should be able to solve for the unknown value. This expression may look formidable, but first we can simplify the denominator and write it as a perfect square as well:

$$\frac{(2x)^2}{(1-x)^2} = 4.0$$

The fraction is a perfect square, as is the 4.0 on the right. So we can take the square root of both sides:

$$\frac{2x}{1-x} = 2.0$$

Now we rearrange and solve (be sure you can follow each step):

$$\begin{array}{rcrcr} 2x & = & 2.0 & - & 2x \\ +2x & & & + & 2x \\ \hline 4x & = & 2.0 & & \end{array}$$

$$\frac{4x}{4} = \frac{2.0}{4}$$

$$x = 0.50$$

Now we have to remind ourselves what *x* is — the amount of H_2 and Cl_2 that reacted — and 2*x* is the equilibrium [HCl]. To determine the equilibrium concentrations, we need to go back and evaluate the expressions 1 − *x* and 2*x* to get the equilibrium concentrations of our species:

$$\begin{array}{rcccccl} 1.0 - x & = & 1.0 - 0.50 & = & 0.50\ \text{M} & = & [\text{H}_2] = [\text{Cl}_2] \\ 2x & = & 2(0.50) & = & 1.0\ \text{M} & = & [\text{HCl}] \end{array}$$

The units are assumed to be molarity. To check, we simply substitute these concentrations and verify that we get the numerical value of the K_{eq}, in this case 4.0:

$$\frac{(1.0)^2}{(0.50)(0.50)} = 4.0$$

We formalize this process by introducing the ICE chart, where ICE stands for initial, change, and equilibrium.

The initial values go in the first row of the chart. The change values, usually algebraic expressions because we do not yet know their exact numerical values, go in the next row. However, the change values *must* be in the proper stoichiometric ratio as indicated by the balanced chemical equation. Finally, the equilibrium expressions in the last row are a combination of the initial value and the change value for each species. The expressions in the equilibrium row are substituted into the K_{eq} expression, which yields an algebraic equation that we try to solve.

The ICE chart for the above example would look like this:

	$H_2(g)$	+	$Cl_2(g)$	⇄	$2HCl(g)$	$K_{eq} = 4.0$
I	1.0		1.0		0	
C	$-x$		$-x$		$+2x$	
E	$1.0 - x$		$1.0 - x$		$+2x$	

Substituting the last row into the expression for the K_{eq} yields

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$

which, of course, is the same expression we have already solved and yields the same answers for the equilibrium concentrations. The ICE chart is a more formalized way to do these types of problems. The + sign is included explicitly in the change row of the ICE chart to avoid any confusion.

Sometimes when an ICE chart is set up and the K_{eq} expression is constructed, a more complex algebraic equation will result. One of the more common equations has an x^2 term in it and is called a *quadratic equation*. There will be two values possible for the unknown x, and for a quadratic equation with the general formula $ax^2 + bx + c = 0$ (where a, b, and c are the *coefficients* of the quadratic equation), the two possible values are as follows:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

One value of x is the + sign used in the numerator, and the other value of x is the − sign used in the numerator. In this case, one value of x typically makes no sense as an answer and can be discarded as physically impossible, leaving only one possible value and the resulting set of concentrations. Example 13.9 illustrates this.

Example 13.9

Set up an ICE chart and solve for the equilibrium concentrations in this chemical reaction.

$$\underset{0.55\ \text{M}}{\text{COI}_2(\text{g})} \rightleftharpoons \underset{0}{\text{CO}(\text{g})} + \underset{0}{\text{I}_2(\text{g})} \qquad K_{eq} = 0.00088$$

Solution

The ICE chart is set up like this. First, the initial values:

	$COI_2(g)$	⇄	$CO(g)$	+	$I_2(g)$
I	0.55		0		0
C					
E					

Some of the COI_2 will be lost, but how much? We don't know, so we represent it by the variable *x*. So *x* M COI_2 will be lost, and for each COI_2 that is lost, *x* M CO and *x* M I_2 will be produced. These expressions go into the change row:

	COI_2(g)	⇄	**CO(g)**	+	**I_2(g)**
I	0.55		0		0
C	$-x$		$+x$		$+x$
E					

At equilibrium, the resulting concentrations will be a combination of the initial amount and the changes:

	COI_2(g)	⇄	**CO(g)**	+	**I_2(g)**
I	0.55		0		0
C	$-x$		$+x$		$+x$
E	$0.55 - x$		$+x$		$+x$

The expressions in the equilibrium row go into the K_{eq} expression:

$$K_{\text{eq}} = \frac{[\text{CO}][\text{I}_2]}{\text{COI}_2} = 0.00088 = \frac{(x)(x)}{(0.55 - x)}$$

We rearrange this into a quadratic equation that equals 0:

$$(0.55 - x)0.00088 = \frac{(x)(x)}{\cancel{(0.55 - x)}} \times \cancel{(0.55 - x)}$$

$$\begin{aligned} 0.000484 - 0.00088x &= x^2 \\ x^2 + 0.00088x - 0.000484 &= 0 \end{aligned}$$

Now we use the quadratic equation to solve for the two possible values of *x*:

$$x = \frac{-0.00088 \pm \sqrt{(0.00088)^2 - 4(1)(-0.000484)}}{2(1)}$$

Evaluate for both signs in the numerator — first the + sign and then the − sign:

$$x = 0.0216 \text{ or } x = -0.0224$$

Because *x* is the final concentration of both CO and I_2, it cannot be negative, so we discount the second numerical answer as impossible. Thus *x* = 0.0216.

Going back to determine the final concentrations using the expressions in the E row of our ICE chart, we have:

$$[\text{COI}_2] = 0.55 - x = 0.55 - 0.0216 = 0.53 \text{ M}$$
$$[\text{CO}] = x = 0.0216 \text{ M}$$
$$[\text{I}_2] = x = 0.0216 \text{ M}$$

You can verify that these numbers are correct by substituting them into the K_{eq} expression and evaluating and comparing to the known K_{eq} value.

Test Yourself
Set up an ICE chart and solve for the equilibrium concentrations in this chemical reaction.

$$\begin{array}{ccccc} \text{N}_2\text{H}_2(\text{g}) & \leftrightharpoons & \text{N}_2(\text{g}) & + & \text{H}_2(\text{g}) \\ 0.075 \text{ M} & & 0 & & 0 \end{array} \qquad K_{\text{eq}} = 0.052$$

Answer
The completed ICE chart is as follows:

	$N_2H_2(g)$	⇄	$N_2(g)$	+	$H_2(g)$
I	0.075		0		0
C	$-x$		$+x$		$+x$
E	$0.075 - x$		$+x$		$+x$

Solving for x gives the equilibrium concentrations as $[N_2H_2] = 0.033$ M; $[N_2] = 0.042$ M; and $[H_2] = 0.042$ M

Key Takeaways

- An ICE chart is a convenient way to determine equilibrium concentrations from starting amounts.

Exercises

Questions

1. Describe the three parts of an ICE chart.
2. What is the relationship between the equilibrium row in an ICE chart and the other two rows?
3. Set up (but do not solve) an ICE chart for this reaction, given the initial conditions.

$$\underset{0.075\ \text{M}}{3\,\text{O}_2(\text{g})} \rightleftharpoons 2\,\text{O}_3(\text{g})$$

4. Set up (but do not solve) an ICE chart for this reaction, given the initial conditions.

$$\underset{0.750\ \text{M}}{\text{CH}_4(\text{g})} + \underset{0.450\ \text{M}}{2\,\text{O}_2(\text{g})} \rightleftharpoons \text{CO}_2(\text{g}) + 2\,\text{H}_2\text{O}(\text{g})$$

5. Given that pure solids and liquids do not appear in K_{eq} expressions, set up the ICE chart for this reaction, given the initial conditions.

$$\underset{0.0060\ \text{M}}{\text{CH}_4(\text{g})} + \underset{0.055\ \text{M}}{2\,\text{O}_2(\text{g})} \rightleftharpoons \text{CO}_2(\text{g}) + 2\,\text{H}_2\text{O}(\ell)$$

6. Given that pure solids and liquids do not appear in K_{eq} expressions, set up the ICE chart for this reaction, given the initial conditions.

$$\underset{2.33\ \text{M}}{\text{N}_2\text{H}_4(\ell)} + \underset{1.09\ \text{M}}{\text{O}_2(\text{g})} \rightleftharpoons \text{N}_2(\text{g}) + 2\,\text{H}_2\text{O}(\ell)$$

7. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$$\underset{2.00\ \text{M}}{\text{HCN}(\text{g})} \rightleftharpoons \text{HNC}(\text{g}) \qquad K_{\text{eq}} = 4.50$$

8. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$$\underset{1.0\ \text{M}}{\text{IF}_3(\text{g})} + \underset{0.50\ \text{M}}{\text{F}_2(\text{g})} \leftrightharpoons \text{IF}_5(\text{g}) \qquad K_{\text{eq}} = 7.59$$

9. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$$\underset{0.0663\ \text{M}}{\text{N}_2\text{O}_3(\text{g})} \leftrightharpoons \text{NO}(\text{g}) + \text{NO}_2(\text{g}) \qquad K_{\text{eq}} = 2.50$$

10. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$$\underset{0.750\ \text{M}}{\text{CO}(\text{g})} + \underset{0.750\ \text{M}}{\text{H}_2\text{O}(\text{g})} \leftrightharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \qquad K_{\text{eq}} = 16.0$$

11. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$$\underset{0.882\ \text{M}}{\text{H}_2\text{S}(\text{g})} \leftrightharpoons \text{H}_2(\text{g}) + \text{S}(\text{s}) \qquad K_{\text{eq}} = 0.055$$

12. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$$\text{AgCl}_2(\text{s}) + \underset{1.99\ \text{M}}{\text{F}_2(\text{g})} \leftrightharpoons 2\,\text{AgF}(\text{s}) + \text{Cl}_2(\text{g}) \qquad K_{\text{eq}} = 1.2 \times 10^2$$

Answers

1. I = initial concentrations; C = change in concentrations; E = equilibrium concentrations

3.

	$3O_2$	⇄	**$2O_3$**
I	0.075		0
C	−3*x*		+2*x*
E	0.075 − 3*x*		+2*x*

5.

	CH_4	+	**$2O_2$**	⇄	**CO_2**	+	**$2H_2O$**
I	0.0060		0.055		0		0
C	−*x*		−2*x*		+*x*		—
E	0.0060 − *x*		0.055 − 2*x*		+*x*		—

7. [HCN] = 0.364 M; [HNC] = 1.64 M

9. [N_2O_3] = 0.0017 M; [NO] = [NO_2] = 0.0646 M

11. [H_2S] = 0.836 M; [H_2] = 0.046 M

Some Special Types of Equilibria

Learning Objectives

1. Identify several special chemical equilibria and construct their K_a expressions.

In one sense, all chemical equilibria are treated the same. However, there are several classes of reactions that are noteworthy because of either the identities of the reactants and products or the form of the K_{eq} expression.

Weak Acids and Bases

In Chapter 12 “Acids and Bases”, we noted how some acids and bases are strong and some are weak. If an acid or base is strong, it is ionized 100% in H_2O. HCl(aq) is an example of a strong acid:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)\ (100\%)$$

However, if an acid or base is weak, it may dissolve in H_2O but does not ionize completely. This means that there is an equilibrium between the unionized acid or base and the ionized form. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2\ (aq) \rightleftarrows H^+(aq) + C_2H_3O_2^-(aq)$$

$HC_2H_3O_2$ is soluble in H_2O (in fact, it is the acid in vinegar), so the reactant concentration will appear in the equilibrium constant expression. But not all the molecules separate into ions. This is the case for all weak acids and bases.

An **acid dissociation constant**, K_a, is the equilibrium constant for the dissociation of a weak acid into ions. Note the *a* subscript on the *K*; it implies that the substance is acting as an acid. The larger K_a is, the stronger the acid is. Table 13.1 “Acid Dissociation Constants for Some Weak Acids” lists several acid dissociation constants. Keep in mind that they are just equilibrium constants.

Table 13.1 Acid Dissociation Constants for Some Weak Acids

Acid	K_a
$HC_2H_3O_2$	1.8×10^{-5}
$HClO_2$	1.1×10^{-2}
$H_2PO_4^-$	6.2×10^{-8}
HCN	6.2×10^{-10}
HF	6.3×10^{-4}
HNO_2	5.6×10^{-4}
H_3PO_4	7.5×10^{-3}

Note also that the acid dissociation constant refers to *one* H^+ ion coming off the initial reactant. Thus the acid dissociation constant for H_3PO_4 refers to this equilibrium:

$$H_3PO_4(aq) \rightleftarrows H^+(aq) + H_2PO_4^-(aq) \quad K_a = 7.5\times10^{-3}$$

The $H_2PO_4^-$ ion, called the dihydrogen phosphate ion, is also a weak acid with its own acid dissociation constant:

$$H_2PO_4^-(aq) \rightleftarrows H^+(aq) + HPO_4^{2-}(aq) \quad K_a = 6.2\times10^{-8}$$

Thus for so-called *polyprotic* acids, each H^+ ion comes off in sequence, and each H^+ ion that ionizes does so with its own characteristic K_a.

Example 13.10

Write the equilibrium equation and the K_a expression for HSO_4^- acting as a weak acid.

Solution
HSO_4^- acts as a weak acid by separating into an H^+ ion and an SO_4^{2-} ion:

$$HSO_4^-(aq) \rightleftarrows H^+(aq) + SO_4^{2-}(aq)$$

The K_a is written just like any other equilibrium constant, in terms of the concentrations of products divided by concentrations of reactants:

$$K_a = [H^+][SO_4^{2-}][HSO_4^-]$$

Test Yourself
Write the equilibrium equation and the K_a expression for HPO_4^{2-} acting as a weak acid.

Answer
$HPO_4^{2-}(aq) \rightleftarrows H^+(aq) + PO_4^{3-}(aq)$ $\quad K_a = [H^+][PO_4^{3-}][HPO_4^{2-}]$

The K_a is used in equilibrium constant problems just like other equilibrium constants are. However, in some cases, we can simplify the mathematics if the numerical value of the K_a is small, much smaller than the concentration of the acid itself. Example 13.11 illustrates this.

Example 13.11

What is the pH of a 1.00 M solution of $HC_2H_3O_2$? The K_a of $HC_2H_3O_2$ is 1.8×10^{-5}.

Solution
This is a two-part problem. We need to determine $[H^+]$ and then use the definition of pH to determine the pH of the solution. For the first part, we can use an ICE chart:

	$HC_2H_3O_2(aq)$	⇄	$H^+(g)$	+	$C_2H_3O_2^-(g)$
I	1.00		0		0
C	$-x$		$+x$		$+x$
E	$1.00 - x$		$+x$		$+x$

We now construct the K_a expression, substituting the concentrations from the equilibrium row in the ICE chart:

$$K_a = \frac{([H^+][C_2H_3O_2^-])}{[HC_2H_3O_2]} = \frac{(x)(x)}{(1.00 - x)} = 1.8 \times 10^{-5}$$

Here is where a useful approximation comes in: at 1.8×10^{-5}, $HC_2H_3O_2$ will not ionize very much, so we expect that the value of x will be small. It should be so small that in the denominator of the fraction, the term $(1.00 - x)$ will likely be very close to 1.00. As such, we would introduce very little error if we simply neglect the x in that term, making it equal to 1.00:

$$(1.00 - x) \approx 1.00 \text{ for small values of } x$$

This simplifies the mathematical expression we need to solve:

$$\frac{(x)(x)}{1.00} = 1.8 \times 10^{-5}$$

This is much easier to solve than a more complete quadratic equation. The new equation to solve becomes:

$$x^2 = 1.8 \times 10^{-5}$$

Taking the square root of both sides:

$$x = 4.2 \times 10^{-3}$$

Because x is the equilibrium concentrations of H^+ and $C_2H_3O_2^-$, we thus have:

$$[H^+] = 4.2 \times 10^{-3} \text{ M}$$

Notice that we are justified by neglecting the x in the denominator; it truly is small compared to 1.00. Now we can determine the pH of the solution:

$$\text{pH} = -\log[H^+] = -\log(4.2 \times 10^{-3}) = 2.38$$

Test Yourself
What is the pH of a 0.500 M solution of HCN? The K_a of HCN is 6.2×10^{-10}.

Answer
4.75

Weak bases also have dissociation constants, labelled K_b (the *b* subscript stands for base). However, values of K_b are rarely tabulated because there is a simple relationship between the K_b of a base and the K_a of its conjugate acid:

$$K_a \times K_b = 1.0 \times 10^{-14}$$

Thus it is simple to calculate the K_b of a base from the K_a of its conjugate acid.

Example 13.12

What is the value of K_b for $C_2H_3O_2^-$, which can accept a proton and act as a base?

Solution
To determine the K_b for $C_2H_3O_2^-$, we need to know the K_a of its conjugate acid. The conjugate acid of $C_2H_3O_2^-$ is $HC_2H_3O_2$. The K_a for $HC_2H_3O_2$ is in Table 13.1 "Acid Dissociation Constants for Some Weak Acids" and is 1.8×10^{-5}. Using the mathematical relationship between K_a and K_b:

$$(1.8 \times 10^{-5})K_b = 1.0 \times 10^{-14}$$

Solving,

$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Test Yourself
What is the value of K_b for PO_4^{3-}, which can accept a proton and act as a base? The K_a for HPO_4^{2-} is 2.2×10^{-13}.

Answer
4.5×10^{-2}

Autoionization of Water

In Chapter 12 “Acids and Bases”, we introduced the autoionization of water — the idea that water can act as a proton donor and proton acceptor simultaneously. Because water is not a strong acid (Table 12.1 “Strong Acids and Bases”), it must be a weak acid, which means that its behaviour as an acid must be described as an equilibrium. That equilibrium is as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

The equilibrium constant includes $[H_3O^+]$ and $[OH^-]$ but not $[H_2O(\ell)]$ because it is a pure liquid. Hence the expression *does not have any terms in its denominator*:

$$K = [H_3O^+][OH^-] \equiv K_w = 1.0 \times 10^{-14}$$

This is the same K_w that was introduced in Chapter 12 and the same 1.0×10^{-14} that appears in the relationship between the K_a and the K_b of a conjugate acid-base pair. In fact, we can rewrite this relationship as follows:

$$K_a \times K_b = K_w$$

Insoluble Compounds

In Chapter 4 “Chemical Reactions and Equations”, in section “Types of Chemical Reactions: Single- and Double-Displacement Reactions”, on chemical reactions, the concept of soluble and insoluble compounds was introduced. Solubility rules were presented that allow a person to predict whether certain simple ionic compounds will or will not dissolve.

Describing a substance as soluble or insoluble is a bit misleading because virtually all substances are soluble; they are just soluble to different extents. In particular for ionic compounds, what we typically describe as an *insoluble* compound can actually be ever so slightly soluble; an equilibrium is quickly established between the solid compound and the ions that do form in solution. Thus the hypothetical compound MX does in fact dissolve but only very slightly. That means we can write an equilibrium for it:

$$MX(s) \rightleftarrows M^+(aq) + X^-(aq)$$

The equilibrium constant for a compound normally considered insoluble is called a **solubility product constant**. The equilibrium constant for a compound normally considered insoluble. and is labelled K_{sp} (with the subscript *sp*, meaning “solubility product”). Because the reactant is a solid, its concentration does not appear in the K_{sp} expression, so like K_w, expressions for K_{sp} do not have denominators. For example, the chemical equation and the expression for the K_{sp} for AgCl, normally considered insoluble, are as follows:

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq) \quad K_{sp} = [Ag^+][Cl^-]$$