Table 13.2 “Solubility Product Constants for Slightly Soluble Ionic Compounds” lists some values of the K_{sp} for slightly soluble ionic compounds.

Table 13.2 Solubility Product Constants for Slightly Soluble Ionic Compounds

Compound	K_{sp}
$BaSO_4$	1.1×10^{-10}
$Ca(OH)_2$	5.0×10^{-6}
$Ca_3(PO_4)_2$	2.1×10^{-33}
$Mg(OH)_2$	5.6×10^{-12}
HgI_2	2.9×10^{-29}
AgCl	1.8×10^{-10}
AgI	8.5×10^{-17}
Ag_2SO_4	1.5×10^{-5}

Example 13.13

Write the K_{sp} expression for $Ca_3(PO_4)_2$.

Solution
Recall that when an ionic compound dissolves, it separates into its individual ions. For $Ca_3(PO_4)_2$, the ionization reaction is as follows:

$$Ca_3(PO_4)_2(s) \rightleftarrows 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Hence the K_{sp} expression is

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

Test Yourself
Write the K_{sp} expression Ag_2SO_4.

Answer
$K_{sp} = [Ag^+]^2[SO_4^{2-}]$

Equilibrium problems involving the K_{sp} can also be done, and they are usually more straightforward than other equilibrium problems because there is no denominator in the K_{sp} expression. Care must be taken, however, in completing the ICE chart and evaluating exponential expressions.

Example 13.14

What are $[Ag^+]$ and $[Cl^-]$ in a saturated solution of AgCl? The K_{sp} of AgCl is 1.8×10^{-10}.

Solution
The chemical equation for the dissolving of AgCl is

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$$

The K_{sp} expression is as follows:

$$K_{sp} = [Ag^+][Cl^-]$$

So the ICE chart for the equilibrium is as follows:

	AgCl(s)	⇄	**Ag^+(aq)**	+	**Cl^-(aq)**
I			0		0
C	$-x$		$+x$		$+x$
E			$+x$		$+x$

Notice that we have little in the column under AgCl except the stoichiometry of the change; we do not need to know its initial or equilibrium concentrations because its concentration does not appear in the K_{sp} expression. Substituting the equilibrium values into the expression:

$$(x)(x) = 1.8 \times 10^{-10}$$

Solving,

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.3 \times 10^{-5}$$

Thus $[Ag^+]$ and $[Cl^-]$ are both 1.3×10^{-5} M.

Test Yourself
What are $[Ba^{2+}]$ and $[SO_4^{2-}]$ in a saturated solution of $BaSO_4$? The K_{sp} of $BaSO_4$ is 1.1×10^{-10}.

Answer
1.0×10^{-5} M

Example 13.15

What are $[Ca^{2+}]$ and $[PO_4^{3-}]$ in a saturated solution of $Ca_3(PO_4)_2$? The K_{sp} of $Ca_3(PO_4)_2$ is 2.1×10^{-33}.

Solution
This is similar to Example 13.14, but the ICE chart is much different because of the number of ions formed.

	$Ca_3(PO_4)_2(s)$	⇄	$3Ca^{2+}(aq)$	+	$2PO_4^{3-}(aq)$
I			0		0
C	$-x$		$+3x$		$+2x$
E			$+3x$		$+2x$

For every unit of $Ca_3(PO_4)_2$ that dissolves, three Ca^{2+} ions and two PO_4^{3-} ions are formed. The expression for the K_{sp} is also different:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = 2.1 \times 10^{-33}$$

Now when we substitute the unknown concentrations into the expression, we get:

$$(3x)^3(2x)^2 = 2.1 \times 10^{-33}$$

When we raise each expression inside parentheses to the proper power, remember that the power affects everything inside the parentheses, including the number. So:

$$(27x^3)(4x^2) = 2.1 \times 10^{-33}$$

Simplifying:

$$108x^5 = 2.1 \times 10^{-33}$$

Dividing both sides of the equation by 108, we get:

$$x^5 = 1.9 \times 10^{-35}$$

Now we take the fifth root of both sides of the equation (be sure you know how to do this on your calculator):

$$x = 1.1 \times 10^{-7}$$

We are not done yet. We still need to determine the concentrations of the ions. According to the ICE chart, $[Ca^{2+}]$ is $3x$, not x. So

$$[Ca_2{}^{+}] = 3x = 3 \times 1.1 \times 10^{-7} = 3.3 \times 10^{-7}\ \text{M}$$

$$[PO_4{}^{3-}] = 2x = 2 \times 1.1 \times 10^{-7} = 2.2 \times 10^{-7}\ \text{M}$$

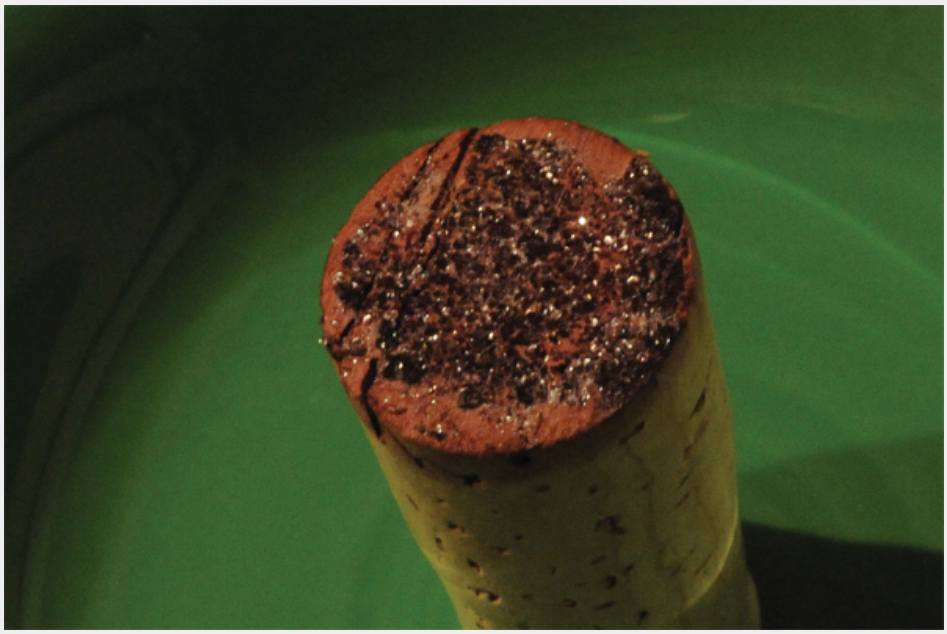
Test Yourself
What are $[Mg^{2+}]$ and $[OH^-]$ in a saturated solution of $Mg(OH)_2$? The K_{sp} of $Mg(OH)_2$ is 5.6×10^{-12}.

Answer
$[Mg^{2+}] = 1.1 \times 10^{-4}$ M; $[OH^-] = 2.2 \times 10^{-4}$ M

Food and Drink App: Solids in Your Wine Bottle

People who drink wine from bottles (as opposed to boxes) will occasionally notice some insoluble materials in the wine,

either crusting the bottle, stuck to the cork, or suspended in the liquid wine itself. The accompanying figure shows a cork encrusted with coloured crystals. What are these crystals?



The red crystals on the top of the wine cork are from insoluble compounds that are not soluble in the wine.

One of the acids in wine is tartaric acid ($H_2C_4H_4O_6$). Like the other acids in wine (citric and malic acids, among others), tartaric acid imparts a slight tartness to the wine. Tartaric acid is rather soluble in H_2O, dissolving over 130 g of the acid in only 100 g of H_2O. However, the potassium salt of singly ionized tartaric acid, potassium hydrogen tartrate ($KHC_4H_4O_6$; also known as potassium bitartrate and better known in the kitchen as cream of tartar), has a solubility of only 6 g per 100 g of H_2O. Thus, over time, wine stored at cool temperatures will slowly precipitate potassium hydrogen tartrate. The crystals precipitate in the wine or grow on the insides of the wine bottle and, if the bottle is stored on its side, on the bottom of the cork. The colour of the crystals comes from pigments in the wine; pure potassium hydrogen tartrate is clear in its crystalline form, but in powder form it is white.

The crystals are harmless to ingest; indeed, cream of tartar is used as an ingredient in cooking. However, most wine drinkers don't like to chew their wine, so if tartrate crystals are present in a wine, the wine is usually filtered or decanted to remove the crystals. Tartrate crystals are almost exclusively in red wines; white and rose wines do not have as much tartaric acid in them.

Key Takeaways

- Equilibrium constants exist for certain groups of equilibria, such as weak acids, weak bases, the autoionization of water, and slightly soluble salts.

Exercises

Questions

1. Explain the difference between the K_{eq} and the K_{sp}.
2. Explain the difference between the K_a and the K_b.
3. Write the balanced chemical equation that represents the equilibrium between HF(aq) as reactants and H^+(aq) and F^-(aq) as products.
4. Write the balanced chemical equation that represents the equilibrium between CaF_2(s) as reactants and Ca^{2+}(aq) and F^-(aq) as products.
5. Assuming that all species are dissolved in solution, write the Keq expression for the chemical equation in Exercise 3.
6. Noting the phase labels, write the K_{sp} expression for the chemical equation in Exercise 4.
7. Determine the concentrations of all species in the ionization of 0.100 M $HClO_2$ in H_2O. The Ka for $HClO_2$ is 1.1×10^{-2}.
8. Determine the concentrations of all species in the ionization of 0.0800 M HCN in H_2O. The Ka for HCN is 6.2×10^{-10}.
9. Determine the pH of a 1.00 M solution of HNO_2. The Ka for HNO_2 is 5.6×10^{-4}.
10. Determine the pH of a 3.35 M solution of $HC_2H_3O_2$. The Ka for $HC_2H_3O_2$ is 1.8×10^{-5}.
11. Write the chemical equations and Ka expressions for the stepwise dissociation of H_3PO_4.
12. Write the chemical equations and Ka expressions for the stepwise dissociation of $H_3C_6H_5O_7$.
13. If the Ka for HNO_2 is 5.6×10^{-4}, what is the Kb for NO_2^-(aq)?
14. If the Ka for HCN is 6.2×10^{-10}, what is the Kb for CN^-(aq)?
15. What is $[OH^-]$ in a solution whose $[H^+]$ is 3.23×10^{-6} M?
16. What is $[OH^-]$ in a solution whose $[H^+]$ is 9.44×10^{-11} M?
17. What is $[H^+]$ in a solution whose $[OH^-]$ is 2.09×10^{-2} M?
18. What is $[H^+]$ in a solution whose $[OH^-]$ is 4.07×10^{-7} M?
19. Write the balanced chemical equation and the K_{sp} expression for the slight solubility of $Mg(OH)_2$(s).
20. Write the balanced chemical equation and the K_{sp} expression for the slight solubility of $Fe_2(SO_4)_3$(s).
21. What are $[Sr^{2+}]$ and $[SO_4^{2-}]$ in a saturated solution of $SrSO_4$(s)? The K_{sp} of $SrSO_4$(s) is 3.8×10^{-4}.
22. What are $[Ba^{2+}]$ and $[F^-]$ in a saturated solution of BaF_2(s)? The K_{sp} of BaF_2(s) is 1.8×10^{-7}.
23. What are $[Ca^{2+}]$ and $[OH^-]$ in a saturated solution of $Ca(OH)_2$(s)? The K_{sp} of $Ca(OH)_2$(s) is 5.0×10^{-6}.
24. What are $[Pb^{2+}]$ and $[I^-]$ in a saturated solution of PbI_2? The K_{sp} for PbI_2 is 9.8×10^{-9}.

Answers

1. The K_{sp} is a special type of the K_{eq} and applies to compounds that are only slightly soluble.

3. $HF(aq) \rightleftarrows H^+(aq) + F^-(aq)$

5. $K_{eq} = [H^+][F^-][HF]$

7. $[HClO_2] = 0.0719$ M; $[H^+] = [ClO_2^-] = 0.0281$ M

9. 1.63

11.
    1. $H_3PO_4(aq) \rightleftarrows H^+(aq) + H_2PO_4^-(aq)$; $Ka = [H^+][H_2PO_4^-][H_3PO_4]$
    2. $H_2PO_4^-(aq) \rightleftarrows H^+(aq) + HPO_4^{2-}(aq)$; $Ka = [H^+][HPO_4^{2-}][H_2PO_4^-]$

3. $HPO_4^{2-}(aq) \rightleftarrows H^+(aq) + PO_4^{3-}(aq)$; $Ka = [H^+][PO_4^{3-}][HPO_4^{2-}]$

13. 1.8×10^{-11}

15. 3.10×10^{-9} M

17. 4.78×10^{-13} M

19. $Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2OH^-(aq)$; $K_{sp} = [Mg^{2+}][OH^-]^2$

21. $[Sr^{2+}] = [SO_4^{2-}] = 1.9 \times 10^{-2}$ M

23. $[Ca^{2+}] = 0.011$ M; $[OH^-] = 0.022$ M

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End-of-Chapter Material

Additional Exercises

1. What is the relationship between the K_{sp} expressions for a chemical reaction and its reverse chemical reaction?
2. What is the relationship between the K_w value for H_2O and its reverse chemical reaction?
3. For the equilibrium

$$PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g) + 60\ kJ$$

list four stresses that serve to increase the amount of PCl_5.

4. For the equilibrium

$$N_2O_4 + 57\ kJ \rightleftarrows 2NO_2$$

list four stresses that serve to increase the amount of NO_2.

5. Does a very large K_{eq} favour the reactants or the products? Explain your answer.
6. Is the K_{eq} for reactions that favour reactants large or small? Explain your answer.
7. Show that $K_a \times K_b = K_w$ by determining the expressions for these two reactions and multiplying them together.

$$HX(aq) \rightleftarrows H^+(aq) + X^-(aq)$$
$$X^-(aq) + H_2O(\ell) \rightleftarrows HX(aq) + OH^-(aq)$$

8. Is the conjugate base of a strong acid weak or strong? Explain your answer.
9. What is the solubility in moles per litre of AgCl? Use data from Table 13.2 “Solubility Product Constants for Slightly Soluble Ionic Compounds”.
10. What is the solubility in moles per litre of $Ca(OH)_2$? Use data from Table 13.2.
11. Under what conditions is $K_{eq} = K_P$?
12. Under what conditions is $K_{eq} > K_P$ when the temperature is 298 K?
13. What is the pH of a saturated solution of $Mg(OH)_2$? Use data from Table 13.2.
14. What are the pH and the pOH of a saturated solution of $Fe(OH)_3$? The K_{sp} of $Fe(OH)_3$ is 2.8×10^{-39}.
15. For a salt that has the general formula MX, an ICE chart shows that the K_{sp} is equal to x^2, where x is the concentration of the cation. What is the appropriate formula for the K_{sp} of a salt that has a general formula of MX_2?
16. Referring to Exercise 15, what is the appropriate formula for the K_{sp} of a salt that has a general formula of M_2X_3 if the concentration of the cation is defined as $2x$, rather than x?
17. Consider a saturated solution of $PbBr_2(s)$. If $[Pb^{2+}]$ is 1.33×10^{-5} M, find each of the following.
    a. $[Br-]$
    b. the K_{sp} of $PbBr_2(s)$
18. Consider a saturated solution of $Pb_3(PO_4)_2(s)$. If $[Pb^{2+}]$ is 7.34×10^{-14} M, find each of the following.
    a. $[PO_4^{3-}]$
    b. the K_{sp} of $Pb_3(PO_4)_2(s)$

Answers

1. They are reciprocals of each other.
3. increase the pressure; decrease the temperature; add PCl_3; add Cl_2; remove PCl_5
5. favour products because the numerator of the ratio for the Keq is larger than the denominator
7. $$K_a \times K_b = \frac{[H^+]\cancel{[X^-]}}{\cancel{[HX]}} \times \frac{\cancel{[HX]}[OH^-]}{\cancel{[X^-]}} = [H^+][OH^-] = K_w$$
9. 1.3×10^{-5} mol/L
11. $K_{eq} = K_P$ when the number of moles of gas on both sides of the reaction is the same.
13. 10.35
15. $4x^3$
17. a. 2.66×10^{-5} M
    b. 9.41×10^{-15}

Chapter 14. Oxidation and Reduction

Most of us are familiar with rusty iron: metal that has a dark red-brown scale that falls off an object, ultimately weakening it. Although we usually attribute rusting exclusively to iron, this process occurs with many materials. The more formal term for rusting is *corrosion*.

Figure 14.0 "Rust." These support beams on a bridge are obviously rusted. If the rusting becomes too bad, it will compromise the integrity of the bridge, requiring replacement.

Corrosion is defined as the disintegration of a material due to chemical reactions with other substances in the environment. In many cases, oxygen in the air causes the disintegration. Corrosion is not uniformly destructive. Although the corrosion of iron is generally considered bad, the corrosion of aluminum and copper forms a protective barrier on the surface of the metal, protecting it from further reaction with the environment.

Having said that, it has been estimated that as much as 5% of expenditures in the United States apply to fixing problems caused by corrosion. The replacement of structures built with iron, steel, aluminum, and concrete must be performed regularly to keep these structures safe. As an example of what might happen, consider the story of the Silver Bridge on US Interstate 35, connecting West Virginia and Ohio. On December 15, 1967, the 39-year-old bridge collapsed, killing 46 people. The ultimate cause of the collapse was determined to be corrosion of a suspension chain on the Ohio side of the bridge.

Corrosion is an example of the type of chemical reaction discussed in this chapter. Although we usually think of corrosion as bad, the reaction it typifies can actually be put to good use.

One important type of chemical reaction is the oxidation-reduction reaction, also known as the redox

reaction. Although we introduced redox reactions in Chapter 4 “Chemical Reactions and Equations”, section “Oxidation-Reduction Reactions”, it is worth reviewing some basic concepts.

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Oxidation-Reduction Reactions

Learning Objectives

1. Define *oxidation* and *reduction*.
2. Assign oxidation numbers to atoms in simple compounds.
3. Recognize a reaction as an oxidation-reduction reaction.

Consider this chemical reaction:

$$\mathrm{Mg(s) + Cl_2(g) \rightarrow MgCl_2}$$

The reactants are two electrically neutral elements; they have the same number of electrons as protons. The product, however, is ionic; it is composed of $\mathrm{Mg^{2+}}$ and $\mathrm{Cl^-}$ ions. Somehow, the individual Mg atoms lose two electrons to make the $\mathrm{Mg^{2+}}$ ion, while the Cl atoms gain an electron to become $\mathrm{Cl^-}$ ions. This reaction involves the *transfer of electrons* between atoms.

The process of losing and gaining electrons occurs simultaneously. However, mentally we can separate the two processes. **Oxidation** is defined as the loss of one or more electrons by an atom. **Reduction** is defined as the gain of one or more electrons by an atom. So oxidation and reduction always occur together; it is only mentally that we can separate them. Chemical reactions that involve the transfer of electrons are called **oxidation-reduction (or redox) reactions**.

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.
2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.
3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number [except in peroxide compounds (where it is −1) and in binary compounds with fluorine (where it is positive)]; and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion ($\mathrm{H^-}$), in which case rule 2 prevails].
4. In compounds, all other atoms are assigned an oxidation number so that the sum of the

oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).

Here are some examples for practice. In H_2, both H atoms have an oxidation number of 0 by rule 1. In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1 by rule 2. In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1. We can use rule 4 to determine oxidation numbers for the atoms in SO_2. Each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 14.1

Assign oxidation numbers to the atoms in each substance.

1. Cl_2
2. GeO_2
3. $Ca(NO_3)_2$

Solution

1. Cl_2 is the elemental form of chlorine. Rule 1 states each atom has an oxidation number of 0.
2. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
3. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation:
$$x + 3(-2) = -1$$
where *x* is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for *x*:
$$\begin{aligned} x + (-6) &= -1 \\ x &= 5 \end{aligned}$$
Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Test Yourself
Assign oxidation numbers to the atoms in H_3PO_4.

Answer
H: +1; O: −2; P: +5

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Thus oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$\underset{}{6\,H^+(aq)} + \underset{(+7)}{2\,MnO_4^-(aq)} + \underset{(-1)}{5\,H_2O_2(\ell)} \rightarrow \underset{(+2)}{2\,Mn^{2+}(aq)} + \underset{(0)}{5\,O_2(g)} + \underset{}{8\,H_2O(\ell)}$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

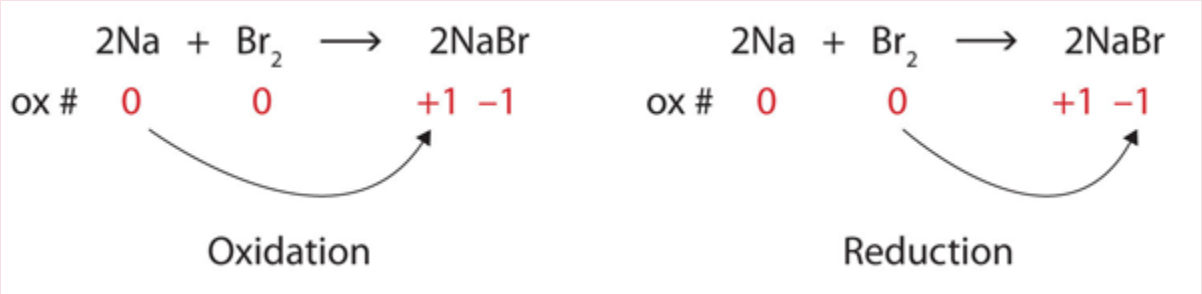
Example 14.2

Identify what is being oxidized and reduced in this redox reaction.

$$2Na + Br_2 \rightarrow 2NaBr$$

Solution
Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Test Yourself
Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \rightarrow CO_2$$

Answer
C is being oxidized from 0 to +4; O is being reduced from 0 to −2.

Food and Drink App: Fortifying Food with Iron

Iron is an essential mineral in our diet; iron-containing compounds like the heme protein in hemoglobin could not function without it. Most biological iron has the form of the Fe^{2+} ion; iron with other oxidation numbers is almost inconsequential in human biology (although the body does contain an enzyme to reduce Fe^{3+} to Fe^{2+}, so Fe^{3+} must have some biological significance, albeit minor). To ensure that we ingest enough iron, many foods are enriched with iron. Although Fe^{2+}

compounds are the most logical substances to use, some foods — bread and breakfast cereals are the most well-known examples — use “reduced iron” as an ingredient. Reduced iron is simply iron metal; iron is added as a fine metallic powder. The metallic iron is oxidized to Fe^{2+} in the digestive system and then absorbed by the body, but the question remains: Why are we ingesting metallic iron? Why not just use Fe^{2+} salts as an additive?

Many prepared foods list reduced iron in their ingredients list.

Although it is difficult to establish conclusive reasons, a search of scientific and medical literature suggests a few reasons. One reason is that fine iron filings do not affect the taste of the product. The size of the iron powder (several dozen micrometers) is not noticeable when chewing iron-supplemented foods, and the tongue does not detect any changes in flavour that can be detected when using Fe^{2+} salts. Fe^{2+} compounds can affect other properties of foodstuffs during preparation and cooking, like dough pliability, yeast growth, and colour. Finally, of the common iron substances that might be used, metallic iron is the least expensive. These factors appear to be among the reasons why metallic iron is the supplement of choice in some foods.

Key Takeaways

- Oxidation-reduction (redox) reactions involve the transfer of electrons from one atom to another.
- Oxidation numbers are used to keep track of electrons in atoms.
- There are rules for assigning oxidation numbers to atoms.
- Oxidation is an increase in oxidation number (loss of electrons); reduction is a decrease in oxidation number (gain of electrons).

Exercises

Questions

1. Is this reaction a redox reaction? Explain your answer.

$$2K(s) + Br_2(\ell) \rightarrow 2KBr(s)$$

2. Is this reaction a redox reaction? Explain your answer.

$$2NaCl(aq) + Pb(NO_3)_2(aq) \rightarrow 2NaNO_3(aq) + PbCl_2(s)$$

3. Which substance loses electrons and which substance gains electrons in this reaction?

$$2Mg(s) + O_2(g) \rightarrow 2MgO$$

4. Which substance loses electrons and which substance gains electrons in this reaction?

$$16Fe(s) + 3S_8(s) \rightarrow 8Fe_2S_3(s)$$

5. Which substance is oxidized and which substance is reduced in this reaction?

$$2Li(s) + O_2(g) \rightarrow Li_2O_2(s)$$

6. Which substance is oxidized and which substance is reduced in this reaction?

$$2Fe(s) + 3I_2(s) \rightarrow 2FeI_3(s)$$

7. What are two different definitions of oxidation?
8. What are two different definitions of reduction?
9. Assign oxidation numbers to the atoms in each substance.
    a. P_4
    b. SO_3
    c. SO_3^{2-}
    d. $Ca_3(PO_3)_2$
10. Assign oxidation numbers to the atoms in each substance.
    a. PCl_5
    b. $(NH_4)_2Se$
    c. Ag
    d. Li_2O_2
11. Assign oxidation numbers to the atoms in each substance.
    a. NO
    b. NO_2
    c. $CrCl_2$
    d. $CrCl_3$
12. Assign oxidation numbers to the atoms in each substance.
    a. NaH
    b. N_2O_3
    c. NO_2^-

d. $CuNO_3$

13. Assign oxidation numbers to the atoms in each substance.

    a. CH_2O
    b. NH_3
    c. Rb_2SO_4
    d. $Zn(C_2H_3O_2)_2$

14. Assign oxidation numbers to the atoms in each substance.

    a. C_6H_6
    b. $B(OH)_3$
    c. Li_2S
    d. Au

15. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms.

$$2NO + Cl_2 \rightarrow 2NOCl$$

16. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms.

$$Sr + SO_3 \rightarrow SrSO_3$$

17. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms.

$$2KrF_2 + 2H_2O \rightarrow 2Kr + 4HF + O_2$$

18. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms.

$$SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$$

19. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms.

$$2Rb + MgCl_2 \rightarrow 2RbCl + Mg$$

20. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms.

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

Answers

1. Yes, because oxidation numbers are changing.
3. lose: Mg; gain: O
5. oxidized: Li; reduced: O
7. increase in oxidation number; loss of electrons
9. a. P: 0
   b. S: +6; O: −2
   c. S: +4; O: −2
   d. Ca: +2; P: +3; O: −2
11. a. N: +2; O: −2
    b. N: +4; O: −2
    c. Cr: +2; Cl: −1
    d. Cr: +3; Cl: −1

13.
a. C: 0; H: +1; O: −2
b. N: −3; H: +1
c. Rb: +1; S: +6; O: −2
d. Zn: +2; C: 0; H: +1; O: −2

15. oxidized: N; reduced: Cl

17. oxidized: O; reduced: Kr

19. oxidized: Rb; reduced: Mg

Balancing Redox Reactions

Learning Objectives

1. Learn to balanced simple redox reactions by inspection.
2. Learn to balance complex redox reactions by the half reaction method.
3. Use the solvent, or parts of it, as a reactant or a product in balancing a redox reaction.

Balancing simple redox reactions can be a straightforward matter of going back and forth between products and reactants. For example, in the redox reaction of Na and Cl_2:

$$Na + Cl_2 \rightarrow NaCl$$

it should be immediately clear that the Cl atoms are not balanced. We can fix this by putting the coefficient 2 in front of the product:

$$Na + Cl_2 \rightarrow 2NaCl$$

However, now the sodium is unbalanced. This can be fixed by including the coefficient 2 in front of the Na reactant:

$$2Na + Cl_2 \rightarrow 2NaCl$$

This reaction is now balanced. That was fairly straightforward; we say that we are able to balance the reaction *by inspection*. Many simple redox reactions can be balanced by inspection.

Example 14.3

Balance this redox reaction by inspection.

$$SO_2 + O_2 \rightarrow SO_3$$

Solution

There is one S atom on both sides of the equation, so the sulfur is balanced. However, the reactant side has four O atoms while the product side has three. Clearly we need more O atoms on the product side, so let us start by including the coefficient 2 on the SO_3:

$$SO_2 + O_2 \rightarrow 2SO_3$$

This now gives us six O atoms on the product side, and it also imbalances the S atoms. We can balance both the elements by adding coefficient 2 on the SO_2 on the reactant side:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

This gives us two S atoms on both sides and a total of six O atoms on both sides of the chemical equation. This redox reaction is now balanced.

Test Yourself
Balance this redox reaction by inspection.

$$Al + O_2 \rightarrow Al_2O_3$$

Answer
$4Al + 3\ O_2 \rightarrow 2Al_2O_3$

The first thing you should do when encountering an unbalanced redox reaction is to try to balance it by inspection.

Some redox reactions are not easily balanced by inspection. Consider this redox reaction:

$$Al + Ag^+ \rightarrow Al^{3+} + Ag$$

At first glance, this equation seems balanced: there is one Ag atom on both sides and one Al atom on both sides. However, if you look at the total charge on each side, there is a charge imbalance: the reactant side has a total charge of 1+, while the product side has a total charge of 3+. Something is amiss with this chemical equation; despite the equal number of atoms on each side, it is not balanced.

A fundamental point about redox reactions that has not arisen previously is that *the total number of electrons being lost must equal the total number of electrons being gained* for a redox reaction to be balanced. This is not the case for the aluminum and silver reaction: the Al atom loses three electrons to become the Al^{3+} ion, while the Ag^+ ion gains only one electron to become elemental silver.

To balance this, we will write each oxidation and reduction reaction separately, listing the number of electrons explicitly in each. Individually, the oxidation and reduction reactions are called **half reactions**. We will then take multiples of each reaction until the number of electrons on each side cancels completely and combine the half reactions into an overall reaction, which should then be balanced. This method of balancing redox reactions is called the **half reaction method**. (There are other ways of balancing redox reactions, but this is the only one that will be used in this text. The reason for this will be seen in the section “Applications of Redox Reactions: Voltaic Cells”.)

The oxidation half reaction involves aluminum, which is being oxidized:

$$Al \rightarrow Al^{3+}$$

This half reaction is not completely balanced because the overall charges on each side are not equal. When an Al atom is oxidized to Al^{3+}, it loses three electrons. We can write these electrons explicitly as products:

$$Al \rightarrow Al^{3+} + 3e^-$$

Now this half reaction is balanced — in terms of both atoms and charges.

The reduction half reaction involves silver:

$$Ag^+ \rightarrow Ag$$

The overall charge is not balanced on both sides. But we can fix this by adding one electron to the reactant side because the Ag^+ ion must accept one electron to become the neutral Ag atom:

$$Ag^+ + e^- \rightarrow Ag$$

This half reaction is now also balanced.

When combining the two half reactions into a balanced chemical equation, the key is that *the total number of electrons must cancel*, so the number of electrons lost by atoms are equal to the number of electrons gained by other atoms. This may require we multiply one or both half reaction(s) by an integer to make the number of electrons on each side equal. With three electrons as products and one as reactant, the least common multiple of these two numbers is three: we can use a single aluminum reaction but must take three times the silver reaction:

$$\begin{aligned} Al &\rightarrow Al^{3+} + 3e^- \\ 3 \times [Ag^+ + e^- &\rightarrow Ag] \end{aligned}$$

The 3 on the second reaction is distributed to all species in the reaction:

$$\begin{aligned} Al &\rightarrow Al^{3+} + 3e^- \\ 3\,Ag^+ + 3e^- &\rightarrow 3\,Ag \end{aligned}$$

Now the two half reactions can be combined just like two algebraic equations, with the arrow serving as the equals sign. The same species on opposite sides of the arrow can be cancelled:

$$Al + 3\,Ag^+ + 3e^- \rightarrow Al^{3+} + 3\,Ag + 3e^-$$

The net balanced redox reaction is as follows:

$$Al + 3\,Ag^+ \rightarrow Al^{3+} + 3\,Ag$$

There is still only one Al atom on each side of the chemical equation, but there are now three Ag atoms, and the total charge on each side of the equation is the same (3+ for both sides). This redox reaction is balanced. It took more effort to use the half reaction method than by inspection, but the correct balanced redox reaction was obtained.

Example 14.4

Balance this redox reaction by using the half reaction method.

$$Fe^{2+} + Cr \rightarrow Fe + Cr^{3+}$$

Solution

We start by writing the two half reactions. Chromium is being oxidized, and iron is being reduced:

$$\begin{array}{rcll} \mathrm{Cr} & \rightarrow & \mathrm{Cr^{3+}} & \text{oxidation} \\ \mathrm{Fe^{2+}} & \rightarrow & \mathrm{Fe} & \text{reduction} \end{array}$$

Then we include the appropriate number of electrons on the proper side to balance the charges for each reaction:

$$\begin{array}{rcll} \mathrm{Cr} & \rightarrow & \mathrm{Cr^{3+}} + 3e^- \\ \mathrm{Fe^{2+}} + 2e^- & \rightarrow & \mathrm{Fe} \end{array}$$

The first reaction involves three electrons, while the second reaction involves two electrons. The least common multiple of these two numbers is six, so to get six electrons in each reaction we need to double the first reaction and triple the second one:

$$\begin{array}{rcrcl} 2 & \times & [\mathrm{Cr} \rightarrow \mathrm{Cr^{3+}} + 3e^-] & = & 2\,\mathrm{Cr} \rightarrow 2\,\mathrm{Cr^{3+}} + 6e^- \\ 3 & \times & [\mathrm{Fe^{2+}} + 2e^- \rightarrow \mathrm{Fe}] & = & 3\,\mathrm{Fe^{2+}} + 6e^- \rightarrow 3\,\mathrm{Fe} \end{array}$$

We can combine the two final reactions, noting that the electrons cancel:

$$2\,\mathrm{Cr} + 3\,\mathrm{Fe^{2+}} + 6e^- \rightarrow 2\,\mathrm{Cr^{3+}} + 3\,\mathrm{Fe} + 6e^-$$

The overall, balanced redox reaction is:

$$2\,\mathrm{Cr} + 3\,\mathrm{Fe^{2+}} \rightarrow 2\,\mathrm{Cr^{3+}} + 3\,\mathrm{Fe}$$

Test Yourself
Balance this redox reaction by using the half reaction method.

$$\mathrm{O^{2-}} + \mathrm{F_2} \rightarrow \mathrm{O_2} + \mathrm{F^-}$$

Answer
$2\,\mathrm{O^{2-}} + 2\,\mathrm{F_2} \rightarrow \mathrm{O_2} + 4\,\mathrm{F^-}$

Many redox reactions occur in aqueous solution — in water. Because of this, in many cases H_2O or a fragment of an H_2O molecule (H^+ or OH^-, in particular) can participate in the redox reaction. As such, we need to learn how to incorporate the solvent into a balanced redox equation.

Consider the following oxidation half reaction in aqueous solution, which has one Cr atom on each side:

$$Cr^{3+} \rightarrow CrO_4^-$$

Here, the Cr atom is going from the +3 to the +7 oxidation state. To do this, the Cr atom must lose four electrons. Let us start by listing the four electrons as products:

$$Cr^{3+} \rightarrow CrO_4^- + 4e^-$$

But where do the O atoms come from? They come from water molecules or a common fragment of a water molecule that contains an O atom: the OH^- ion. When we balance this half reaction, we should feel free to include either of these species in the reaction to balance the elements. Let us use H_2O to balance the O atoms; we need to include four water molecules to balance the four O atoms in the products:

$$4H_2O + Cr^{3+} \rightarrow CrO_4^- + 4e^-$$

This balances the O atoms, but now introduces hydrogen to the reaction. We can balance the H atoms by adding an H^+ ion, which is another fragment of the water molecule. We need to add eight H^+ ions to the product side:

$$4H_2O + Cr^{3+} \rightarrow CrO_4^- + 4e^- + 8H^+$$

The Cr atoms are balanced, the O atoms are balanced, and the H atoms are balanced; if we check the total charge on both sides of the chemical equation, they are the same (3+, in this case). This half reaction is now balanced, using water molecules and parts of water molecules as reactants and products.

Reduction reactions can be balanced in a similar fashion. When oxidation and reduction half reactions are individually balanced, they can be combined in the same fashion as before: by taking multiples of each half reaction as necessary to cancel all electrons. Other species, such as H^+, OH^-, and H_2O, may also have to be cancelled in the final balanced reaction.

Unless otherwise noted, it does not matter if you add H_2O or OH^- as a source of O atoms, although a reaction may specify *acidic solution* or *basic solution* as a hint of what species to use or what species to avoid. OH^- ions are not very common in acidic solutions, so they should be avoided in those circumstances.

Example 14.5

Balance this redox reaction. Assume a basic solution.

$$MnO_2 + CrO_3^- \rightarrow Mn + CrO_4^-$$

Solution

We start by separating the oxidation and reduction processes so we can balance each half reaction separately. The oxidation reaction is as follows:

$$CrO_3^- \rightarrow CrO_4^-$$

The Cr atom is going from a +5 to a +7 oxidation state and loses two electrons in the process. We add those two electrons to the product side:

$$CrO_3^- \rightarrow CrO_4^- + 2e^-$$

Now we must balance the O atoms. Because the solution is basic, we should use OH^- rather than H_2O:

$$OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^-$$

We have introduced H atoms as part of the reactants; we can balance them by adding H^+ as products:

$$OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^- + H^+$$

If we check the atoms and the overall charge on both sides, we see that this reaction is balanced. However, if the reaction is occurring in a basic solution, it is unlikely that H^+ ions will be present in quantity. The way to address this is to add an additional OH^- ion to each side of the equation:

$$OH^- + CrO_3^- + OH^- \rightarrow CrO_4^- + 2e^- + H^+ + OH^-$$

The two OH^- ions on the left side can be grouped together as $2OH^-$. On the right side, the H^+ and OH^- ions can be grouped into an H_2O molecule:

$$2OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^- + H_2O$$

This is a more appropriate form for a basic solution.

Now we balance the reduction reaction:

$$MnO_2 \rightarrow Mn$$

The Mn atom is going from +4 to 0 in oxidation number, which requires a gain of four electrons:

$$4e^- + MnO_2 \rightarrow Mn$$

Then we balance the O atoms and then the H atoms:

$$4e^- + MnO_2 \rightarrow Mn + 2\ OH^-$$
$$2\ H^+ + 4e^- + MnO_2 \rightarrow Mn + 2\ OH^-$$

We add two OH^- ions to each side to eliminate the H^+ ion in the reactants; the reactant species combine to make two water molecules, and the number of OH^- ions in the product increases to four:

$$2\ H_2O + 4e^- + MnO_2 \rightarrow Mn + 4\ OH^-$$

This reaction is balanced for a basic solution.

Now we combine the two balanced half reactions. The oxidation reaction has two electrons, while the reduction reaction has four. The least common multiple of these two numbers is four, so we multiply the oxidation reaction by 2 so that the electrons are balanced:

$$2 \times [2OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^- + H_2O]$$
$$2H_2O + 4e^- + MnO_2 \rightarrow Mn + 4\ OH^-$$

Combining these two equations results in the following equation:

$$4\ OH^- + 2CrO_3^- + 2H_2O + 4e^- + MnO_2 \rightarrow 2CrO_4^- + 4e^- + 2H_2O + Mn + 4OH^-$$

The four electrons cancel. So do the two H_2O molecules and the four OH^- ions. What remains is

$$2CrO_3^- + MnO_2 \rightarrow 2CrO_4^- + Mn$$

which is our final balanced redox reaction.

Test Yourself
Balance this redox reaction. Assume a basic solution.

$$Cl^- + MnO_4^- \rightarrow MnO_2 + ClO_3^-$$

Answer
$H_2O + Cl^- + 2MnO_4^- \rightarrow 2MnO_2 + ClO_3^- + 2OH^-$

Key Takeaways

- Redox reactions can be balanced by inspection or by the half reaction method.
- A solvent may participate in redox reactions; in aqueous solutions, H_2O, H^+, and OH^- may be reactants or products.

Exercises

Questions

1. Balance these redox reactions by inspection.
    a. $Na + F_2 \rightarrow NaF$
    b. $Al_2O_3 + H_2 \rightarrow Al + H_2O$
2. Balance these redox reactions by inspection.
    a. $Fe_2S_3 + O_2 \rightarrow Fe_2O_3 + S$
    b. $Cu_2O + H_2 \rightarrow Cu + H_2O$
3. Balance these redox reactions by inspection.

a. $CH_4 + O_2 \rightarrow CO_2 + H_2O$

b. $P_2O_5 + Cl_2 \rightarrow PCl_3 + O_2$

4. Balance these redox reactions by inspection.

a. $PbCl_2 + FeCl_3 \rightarrow PbCl_4 + FeCl_2$

b. $SO_2 + F_2 \rightarrow SF_4 + OF_2$

5. Balance these redox reactions by the half reaction method.

a. $Ca + H^+ \rightarrow Ca^{2+} + H_2$

b. $Sn^{2+} \rightarrow Sn + Sn^{4+}$ (Hint: both half reactions will start with the same reactant.)

6. Balance these redox reactions by the half reaction method.

a. $Fe^{3+} + Sn^{2+} \rightarrow Fe + Sn^{4+}$

b. $Pb^{2+} \rightarrow Pb + Pb^{4+}$ (Hint: both half reactions will start with the same reactant.)

7. Balance these redox reactions by the half reaction method.

a. $Na + Hg_2Cl_2 \rightarrow NaCl + Hg$

b. $Al_2O_3 + C \rightarrow Al + CO_2$

8. Balance these redox reactions by the half reaction method.

a. $Br^- + I_2 \rightarrow I^- + Br_2$

b. $CrCl_3 + F_2 \rightarrow CrF_3 + Cl_2$

9. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.

a. $Cu + NO_3^- \rightarrow Cu^{2+} + NO_2$

b. $Fe + MnO_4^- \rightarrow Fe^{3+} + Mn$

10. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.

a. $CrO_3 + Ni^{2+} \rightarrow Cr^{3+} + Ni^{3+}$

b. $OsO_4 + C_2H_4 \rightarrow Os + CO_2$

11. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.

a. $ClO^- + Ti^{2+} \rightarrow Ti^{4+} + Cl^-$

b. $BrO_3^- + Ag \rightarrow Ag^+ + BrO_2$

12. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.

a. $H_2O_2 + NO \rightarrow N_2O_3 + H_2O$

b. $VO_2^+ + NO \rightarrow V^{3+} + NO_2$

13. Explain why this chemical equation is not balanced and balance it if it can be balanced.

$$Cr^{2+} + Cl_2 \rightarrow Cr^{3+} + 2Cl^-$$

14. Explain why this equation is not balanced and balance it if it can be balanced.

$$O_2 + 2H_2O + Br_2 \rightarrow 4OH^- + 2Br^-$$

Answers

1. a. $2Na + F_2 \rightarrow 2NaF$
   b. $Al_2O_3 + 3H_2 \rightarrow 2Al + 3H_2O$

3. a. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
   b. $2P_2O_5 + 6Cl_2 \rightarrow 4PCl_3 + 5O_2$

5. a. $Ca + 2H^+ \rightarrow Ca^{2+} + H_2$
   b. $2Sn^{2+} \rightarrow Sn + Sn^{4+}$

7. a. $2Na + Hg_2Cl_2 \rightarrow 2NaCl + 2Hg$
   b. $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

9. a. $4H^+ + Cu + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$ in acidic solution; $2H_2O + Cu + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 4OH^-$ in basic solution
   b. $24H^+ + 3MnO_4^- + 7Fe \rightarrow 7Fe^{3+} + 3Mn + 12H_2O$ in acidic solution; $12H_2O + 3MnO_4^- + 7Fe \rightarrow 7Fe^{3+} + 3Mn + 24OH^-$ in basic solution

11. a. $2H^+ + ClO^- + Ti^{2+} \rightarrow Cl^- + H_2O + Ti^{4+}$ in acidic solution; $H_2O + ClO^- + Ti^{2+} \rightarrow Cl^- + Ti^{4+} + 2OH^-$ in basic solution
    b. $2H^+ + BrO_3^- + Ag \rightarrow BrO_2 + H_2O + Ag^+$ in acidic solution; $H_2O + BrO_3^- + Ag \rightarrow BrO_2 + Ag^+ + 2OH^-$ in basic solution

13. The charges are not properly balanced. The correct balanced equation is $2Cr^{2+} + Cl_2 \rightarrow 2Cr^{3+} + 2Cl^-$.

Applications of Redox Reactions: Voltaic Cells

Learning Objectives

1. Learn the parts of a voltaic cell.
2. Combine half reactions to determine the voltage of a voltaic cell.
3. Understand how voltaic cells are used as batteries.

Consider this redox reaction:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

If you were to mix zinc metal and copper ions in a container, this reaction would proceed by itself; we say that this reaction is *spontaneous*.

Suppose, however, we set up this reaction in a way depicted in Figure 14.1 “A Redox Reaction in Which the Two Half Reactions Are Physically Separated”. Zinc and zinc ions are on one side of the system, while copper and copper ions are on the other side of the system. The two parts are connected with a wire.

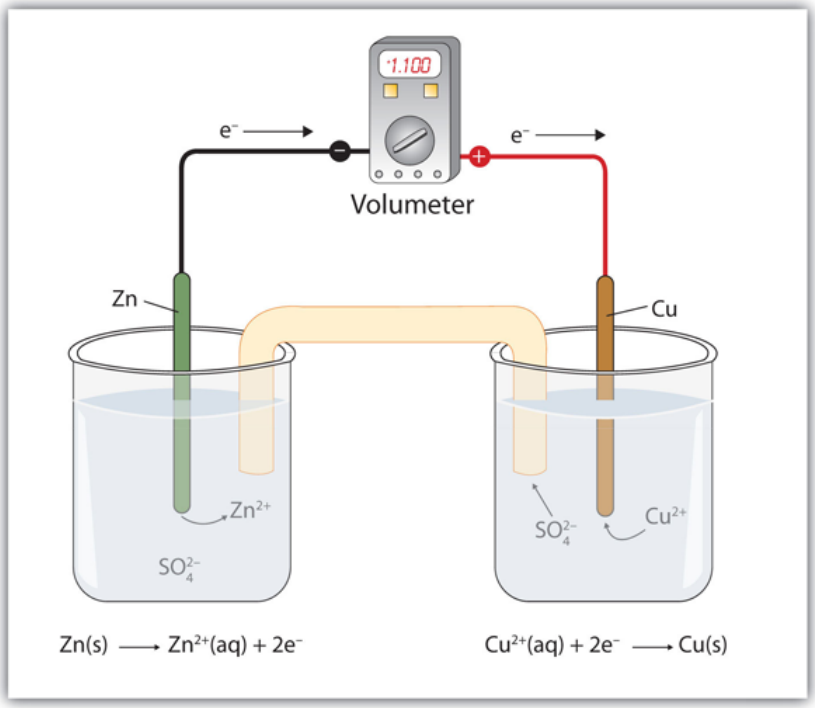


Figure 14.1 "A Redox Reaction in Which the Two Half Reactions Are Physically Separated." One application of redox reactions requires that they be physically separated.

Even though the two half reactions are physically separated, a spontaneous redox reaction still occurs. However, in this case, the electrons transfer through the wire connecting the two half reactions; that is, this setup becomes a source of electricity. Useful work can be extracted from the electrons as they transfer from one side to the other — for example, a light bulb can be lit, or a motor can be operated. The apparatus as a whole, which allows useful electrical work to be extracted from a redox reaction, is called a **voltaic (galvanic) cell**.

Each individual system that contains a half reaction is called a **half cell**. The half cell that contains the oxidation reaction is called the **anode**, while the half cell that contains the reduction reaction is called the **cathode**. The cathode and anode collectively are the **electrodes** of the voltaic cell. Because electrons are coming from the anode, the anode is considered the *negative* electrode of the cell, while the cathode is considered the *positive* electrode of the cell. Finally, because electrons are moving from one half cell to the other, a charge imbalance builds up as the reaction proceeds. To counter that, a **salt bridge** is used; the salt bridge contains a solution of some ionic compound whose ions migrate to either side of the voltaic cell to maintain the charge balance.

The tendency for electrons to go from one half cell to another is called the **voltage**. The tendency for electrons to go from one half cell to another. of the voltaic cell, represented by *E*. Sometimes the term *potential* is used to represent the voltage of a cell. Voltage is expressed in volts (V). The voltage of a voltaic cell is determined by the *difference* in the tendencies of the individual half cells and is characteristic of a given redox reaction when concentrations are specific (1.0 M for dissolved species and 1.0 atm for gases). Because the voltage of a redox reaction is determined by the difference of the tendencies of the individual half reactions, absolute voltages are unnecessary; only relative voltages of

each half reaction are needed. The relative voltage of each half cell is represented as $E_{½}$ and is based on the standard that the $E_{½}$ for the reaction

$$H^+ + e^- \rightarrow ½H_2$$

is assigned to be exactly 0.000 V under standard conditions of pressure and concentration. Table 14.1 “Standard Reduction Potentials of Half Reactions” lists some relative $E_{½}$ values for some half reactions. Note that all half reactions are listed as reduction reactions, so these values are called the **standard reduction potentials**. The voltage of a reduction half reaction relative to the hydrogen half reaction. of each half reaction.

Table 14.1 Standard Reduction Potentials of Half Reactions

Reduction Half Reaction	$E_{½}$ (V)
$F_2 + 2e^- \rightarrow 2\ F^-$	2.87
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.61
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	1.06
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96
$Ag^+ + e^- \rightarrow Ag$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	0.222
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.91
$Ba^{2+} + 2e^- \rightarrow Ba$	−1.57
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Na^+ + e^- \rightarrow Na$	−2.714
$Li^+ + e^- \rightarrow Li$	−3.045

Table 14.1 lists only reduction reactions, but a redox reaction has a reduction *and* an oxidation. To make the oxidation reaction, simply reverse the reduction reaction in Table 14.1 “Standard Reduction

Potentials of Half Reactions” and change the sign on the $E_{½}$ value. If the reduction potential is negative, make the voltage for the oxidation positive; if the reduction potential is positive, make the voltage for the oxidation negative.

Example 14.6

What is the value of $E_{½}$ for this half reaction?

$$Ag + Cl^- \rightarrow AgCl + e^-$$

Solution
The given reaction is the reverse of this reaction:

$$AgCl + e^- \rightarrow Ag + Cl^- \quad E_{½} = 0.222 \text{ V}$$

Therefore, the $E_{½}$ of the given reaction is −0.222 V.

Test Yourself
What is the value of $E_{½}$ for this half reaction?

$$Na \rightarrow Na^+ + e^-$$

Answer
2.714 V

To determine the overall voltage of a particular voltaic cell, simply combine the voltages of the oxidation and reduction half reactions. Even if you need to take a multiple of a half reaction for the electrons to cancel, do not take the multiple of the $E_{½}$. Use the values directly as is from Table 14.1 “Standard Reduction Potentials of Half Reactions”.

Spontaneous redox reactions have positive overall voltages. If the voltage of the reaction as written is negative, it is not spontaneous in that direction. Rather, the reverse reaction is the spontaneous redox reaction.

Example 14.7

What is the voltage of a voltaic cell based on this reaction? Is the reaction spontaneous as written?

$$2NO_3^- + 8H^+ + 3Cu \rightarrow 2NO + 4H_2O + 3Cu^{2+}$$

Solution
The overall redox reaction is formed from these two half reactions:

$$\mathrm{NO_3^-} + 4\,\mathrm{H^+} + 3e^- \rightarrow \mathrm{NO} + 2\,\mathrm{H_2O} \qquad E_{\frac{1}{2}} = 0.96 \text{ V}$$

$$\mathrm{Cu^{2+}} + 2e^- \rightarrow \mathrm{Cu} \qquad E_{\frac{1}{2}} = 0.34 \text{ V}$$

The second reaction is reversed in the overall redox reaction, so its voltage changes sign from the reduction reaction:

$$Cu \rightarrow Cu^{2+} + 2e^- \; E_{½} = -0.34 \text{ V}$$

To obtain the voltage of the voltaic cell based on the overall reaction, we simply combine the two voltages of the half reactions:

$$E = 0.96 + (-0.34) = 0.62 \text{ V}$$

Because the overall voltage is positive, the reaction is spontaneous as written.

Test Yourself
What is the voltage of a voltaic cell based on this reaction? Is the reaction spontaneous as written?

$$5Ni + 2\ MnO_4^- + 16H^+ \rightarrow 3Mn^{2+} + 8H_2O + 5Ni^{2+}$$

Answer
1.76 V; spontaneous

Technically, any redox reaction can be set up to make a voltaic cell. In modern society, however, only certain redox reactions are put to practical use. A portable voltaic cell that generates electricity to power devices for our convenience is called a **battery**. All batteries are based on redox reactions.

The first battery (called a “voltaic pile”) was constructed by the Italian scientist Alessandro Volta in 1800 and was based on the copper/zinc reaction depicted in Figure 14.1 “A Redox Reaction in Which the Two Half Reactions Are Physically Separated”. Unfortunately, it was messy, requiring quantities of copper and zinc salts dissolved in water. In 1866, the French scientist Georges Leclanché invented the **dry cell**, a precursor to today’s modern battery. A schematic of a dry cell is shown in Figure 14.2 “Dry Cells”. The zinc case and the central carbon rod serve as the anode and cathode, respectively. The other reactants are combined into a moist paste that minimizes free liquid, so the battery is less messy (hence the name *dry cell*). The actual redox reaction is complex but can be represented by the following redox reaction:

$$Zn + 2MnO_2 + 2NH_4^+ \rightarrow Zn^{2+} + Mn_2O_3 + 2NH_3 + H_2O$$

A dry cell has a voltage of about 1.56 V. While common and useful, dry cells have relatively short lifetimes and contain acidic components. They also cannot be recharged, so they are one-use only. Batteries that can be used only once are called **primary batteries**.

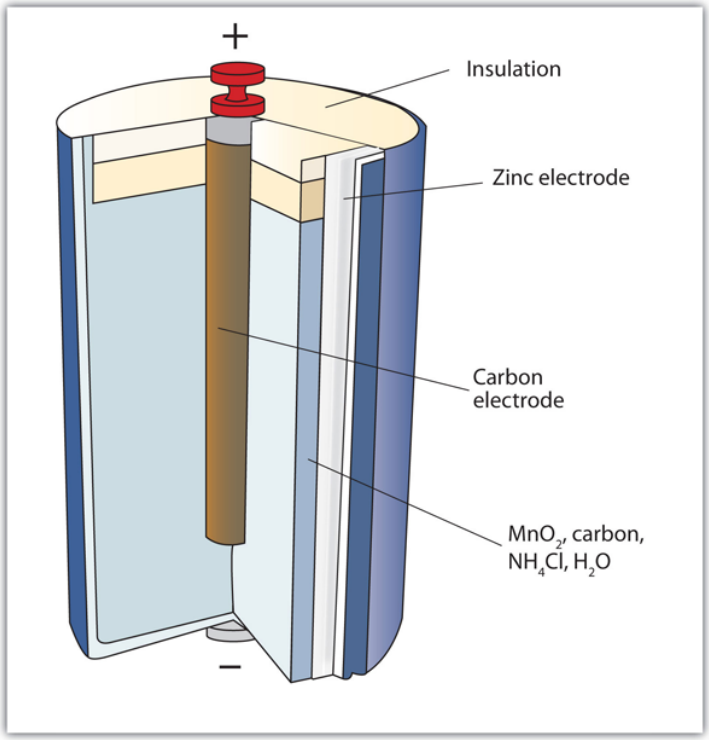


Figure 14.2 "Dry Cells." The Leclanché dry cell is a common type of battery.

In the late 1950s, Lewis Urry of the Eveready Battery Company in Ohio invented the **alkaline battery** (still marketed today under the trade name *Energizer*). Alkaline batteries are similar to dry cells, but they use a basic moist paste rather than an acidic one. Moreover, the net amount of base does not change during the course of the redox reaction. The overall redox reaction is as follows:

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$$

Alkaline batteries have the advantage of being longer lasting and holding their voltage better—about 1.54 V — throughout their lifetime.

A common type of battery, especially with the increased popularity of personal electronic devices, is the button battery (Figure 14.3 "Button Batteries"). A button battery is a small battery that can power small electronic devices; the batteries can be as small as 5 mm across. Two popular redox reactions used for button batteries are the alkaline dry-cell reaction and a silver oxide-based reaction:

$$Zn + Ag_2O \rightarrow ZnO + 2Ag$$

Some button batteries use a lithium-based redox reaction, typified by this anode reaction:

$$Li \rightarrow Li^+ + e^- E_{½} = 3.045 \text{ V}$$

The actual redox reaction depends on the composition of the cathode and is variable depending on voltage. Lithium batteries can also be used for applications that require more energy, such as portable computers and electric vehicles. Some lithium-based batteries are rechargeable and can be used over and over again; such batteries are called **secondary batteries**.

Figure 14.3 "Button Batteries." Button batteries like those seen here can be used for a variety of portable electronics, from watches and hearing aids to handheld gaming devices.

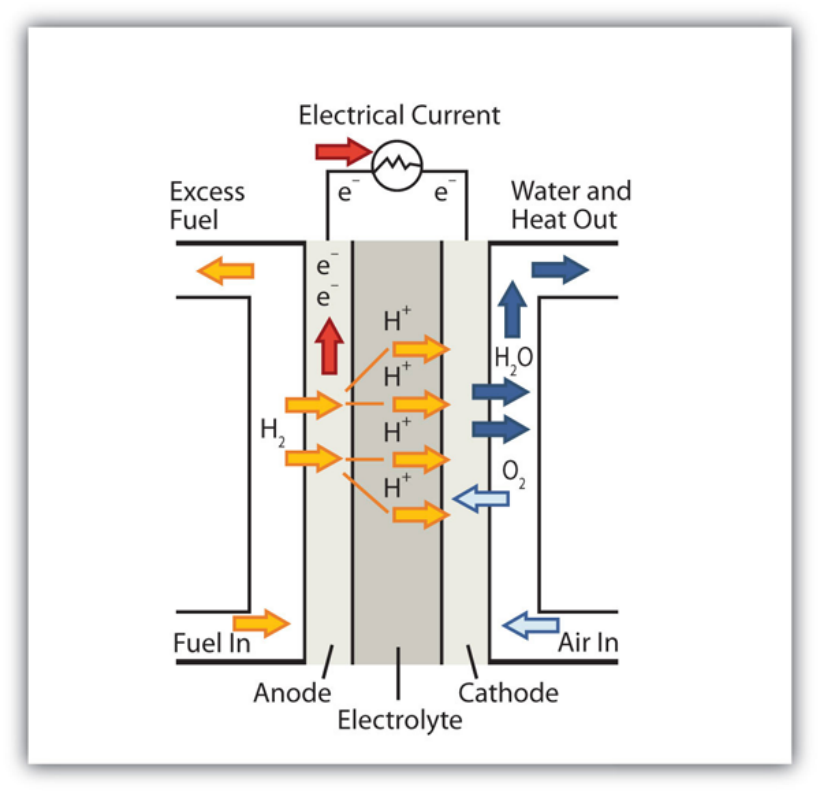
An important secondary battery is the lead storage battery. The lead storage battery is based on this redox reaction:

$$Pb + PbO_2 + 4\ H^+ + SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$$

The redox reaction produces about 2 V, but it is typical to tie several individual batteries together to generate a larger voltage. The lead storage battery has the distinction that the product of both half reactions is $PbSO_4$, which as a solid accumulates on the many plates within each cell. The lead storage battery is a secondary battery, as it can be recharged and reused many times. Because it is based on lead, these batteries are rather heavy. They should also be recycled when replaced so that potentially dangerous lead does not escape into the environment. Because of their characteristics, lead storage batteries are used to start large engines in automobiles, boats, and airplanes.

Chemistry Is Everywhere: Fuel Cells

A *fuel cell* is a type of battery in which reactants flow continuously into a specialized reaction chamber, and products flow out continuously while electrons are extracted from the reaction. Because all reactions in a fuel cell consist of a fuel and an oxidizer undergoing a redox reaction, an introduction of fuel cells is at home in a discussion of redox chemistry.



This fuel cell uses H_2 as the fuel and O_2 as the oxidizer.

By far the most common fuel cell reaction is based on hydrogen and oxygen:

$$2H_2 + O_2 \rightarrow 2H_2O \quad E = 1.23 \text{ V under standard conditions}$$

However, fuel cells typically do not work under standard nor even optimal conditions, so they typically generate about 0.6–0.7 V. In this fuel cell, the only two products are water and electricity, so the fuel cell not only does not create pollution but also makes a by-product that in some environments is a valuable commodity (water). Other fuels can be used besides hydrogen; fuel cells have been developed that work on methane, methyl alcohol, ethyl alcohol, carbon-rich materials, and even magnesium metal.

Hydrogen-based fuel cells were and are used to provide electricity for manned space vehicles, partly because their only chemical product is water, which could be used for drinking. However, there has been a recent resurgence in interest in fuel cells because of their potential use in electric cars. Most electric cars run on conventional batteries, which can be very heavy and expensive to replace. It is thought that fuel cells, rather than conventional batteries, might be better sources of electricity for automobiles.

Several current barriers to fuel cell use in electric cars include capacity, cost, and overall energy efficiency. The 2008 Honda FCX, the first production model of a vehicle powered with a fuel cell, can hold 4.1 kg (just under 9 lb) of highly pressured H_2 gas and has a range of 450 km (280 mi). It costs about $120,000–$140,000 to build, making the vehicle beyond the ability of most people to own. Finally, it always requires more energy to produce elemental hydrogen as a fuel than can be extracted from hydrogen as a fuel. As such, hydrogen is described as an energy carrier (like electricity) rather than an energy source (like oil and gas). This distinction points out a fundamental argument against fuel cells as a “better” power source.

The 2008 Honda FCX was the first production car to use a fuel cell as a power source. Nonetheless, the car is in very limited service because of its need for relatively large quantities of elemental hydrogen as fuel.

The limitations notwithstanding, there is a lot of interest in fuel cell research. If ways can be found to circumvent their current limitations, fuel cells may become more and more common as power sources.

Key Takeaways

- A voltaic cell produces electricity as a redox reaction occurs.
- The voltage of a voltaic cell can be determined by the reduction potentials of the half reactions.
- Voltaic cells are fashioned into batteries, which are a convenient source of electricity.

Exercises

Questions

1. Draw the voltaic cell represented by this reaction and label the cathode, the anode, the salt bridge, the oxidation half cell, the reduction half cell, the positive electrode, and the negative electrode. Use Figure 14.1 “A Redox Reaction in Which the Two Half Reactions Are Physically Separated” as a guide.

$$Zn + 2Ag^{+} \rightarrow Zn^{2+} + 2Ag$$

2. Draw the voltaic cell represented by this reaction and label the cathode, the anode, the salt bridge, the oxidation half cell, the reduction half cell, the positive electrode, and the negative electrode. Use Figure 14.1 as a guide.

$$3Mg + 2Cr^{3+} \rightarrow 3Mg^{2+} + 2Cr$$

3. What is the voltage of this half reaction?

$$2F^{-} \rightarrow F_2 + 2e^{-}$$

4. What is the voltage of this half reaction?

$$Na \rightarrow Na^{+} + e^{-}$$

5. What is the voltage of the voltaic cell in Exercise 1? Consult Table 14.1 “Standard Reduction Potentials of Half Reactions” for data.
6. What is the voltage of the voltaic cell in Exercise 2? Consult Table 14.1 for data.
7. Balance this redox reaction and determine its voltage. Is it spontaneous?

$$Li^{+} + Al \rightarrow Li + Al^{3+}$$

8. Balance this redox reaction and determine its voltage. Is it spontaneous?

$$Pb^{2+} + Ni \rightarrow Pb + Ni^{2+}$$

9. Balance this redox reaction and determine its voltage. Is it spontaneous?

$$Cu^{2+} + Ag + Cl^{-} \rightarrow Cu + AgCl$$

10. Balance this redox reaction and determine its voltage. Is it spontaneous?

$$Mn^{2+} + Br_2 \rightarrow MnO_4^{-} + Br^{-}$$

11. Which reaction represents the cathode reaction in Exercise 7? The anode reaction?
12. Which reaction represents the cathode reaction in Exercise 8? The anode reaction?
13. Which reaction represents the cathode reaction in Exercise 9? The anode reaction?
14. Which reaction represents the cathode reaction in Exercise 10? The anode reaction?
15. A voltaic cell is based on this reaction:

$$Ni + 2Au^{+} \rightarrow Ni^{2+} + 2Au$$

If the voltage of the cell is 0.33 V, what is the standard reduction potential of the $Au^{+} + e^{-} \rightarrow Au$ half reaction?

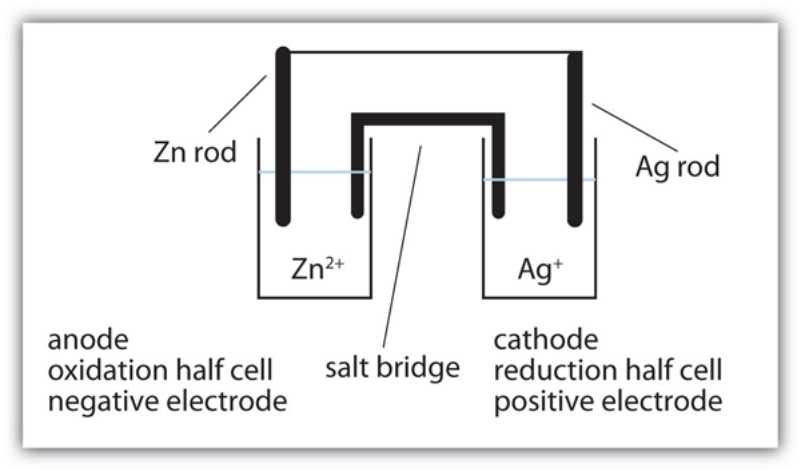
16. A voltaic cell is based on this reaction:

$$3Pb + 2V^{3+} \rightarrow 3Pb^{2+} + 2V$$

If the voltage of the cell is −0.72 V, what is the standard reduction potential of the $V^{3+} + 3e^{-} \rightarrow V$ half reaction?

17. What species is being oxidized and what species is being reduced in a dry cell?
18. What species is being oxidized and what species is being reduced in an alkaline battery?
19. What species is being oxidized and what species is being reduced in a silver oxide button battery?
20. What species is being oxidized and what species is being reduced in a lead storage battery?
21. Based on the data in Table 14.1, what is the highest voltage battery you can construct?
22. Based on the data in Table 14.1, what is the lowest voltage battery you can construct? (This may be more challenging to answer than Exercise 21.)

Answers

1. 

3. −2.87 V
5. 1.56 V
0. $3Li^{+} + Al \rightarrow 3Li + Al^{3+}$; −1.39 V; not spontaneous
9. $Cu^{2+} + 2Ag + 2Cl^{-} \rightarrow Cu + 2AgCl$; 0.12 V; spontaneous
11. cathode reaction: $Li^{+} + e^{-} \rightarrow Li$; anode reaction: $Al \rightarrow Al^{3+} + 3e^{-}$
13. cathode reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu$; anode reaction: $Ag + Cl^{-} \rightarrow AgCl + e^{-}$
15. 0.08 V
17. oxidized: Zn; reduced: Mn
19. oxidized: Zn; reduced: Ag
21. 5.92 V from the reaction of F_2 and Li

Media Attributions

Electrolysis

Learning Objectives

1. Describe electrolysis from a perspective of redox reactions.
2. Give examples of electrolysis applications.

Up to this point, we have considered redox reactions for processes that are spontaneous. When set up as a voltaic cell or battery, such reactions can be used as a source of electricity. However, it is possible to go in the other direction. By forcing electricity into a cell, we can make a redox reaction occur that normally would not be spontaneous. Under these circumstances, the cell is called an **electrolytic cell**, and the process that occurs in the cell is called **electrolysis** (Figure 14.4 “Electrolysis”).

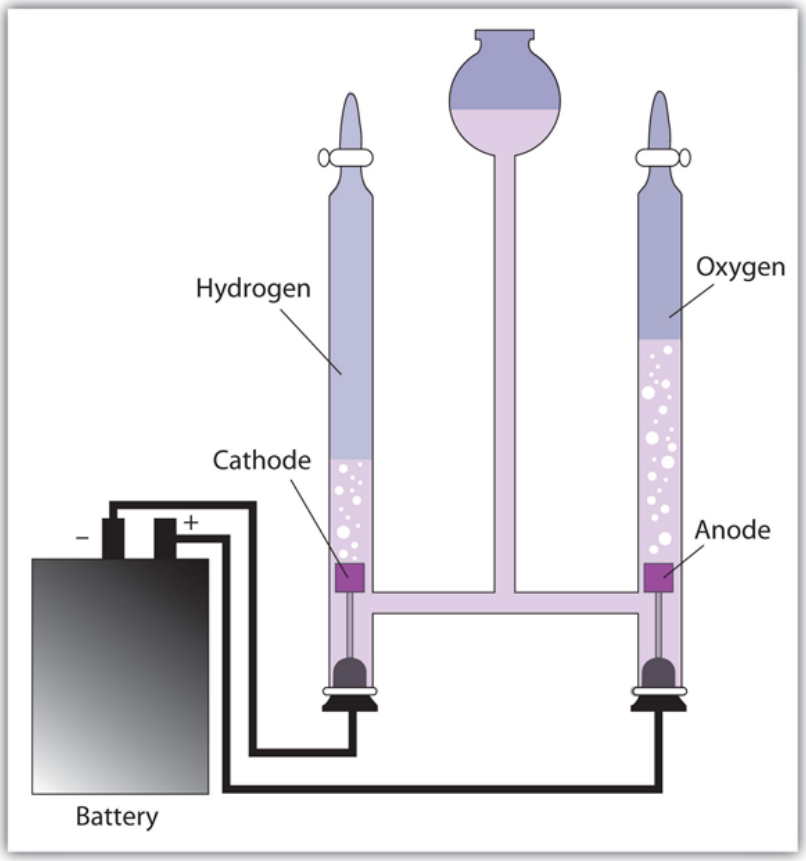


Figure 14.4 “Electrolysis.” In an electrolytic cell, electricity is forced through the cell to induce a nonspontaneous redox reaction. Here, the redox reaction $2\ H_2O \rightarrow 2\ H_2 + O_2$ is being caused by the introduction of electricity, which is supplied by the battery.

Electrolysis has many applications. For example, if NaCl is melted at about 800°C in an electrolytic cell and an electric current is passed through it, elemental sodium will appear at the cathode and elemental chlorine will appear at the anode as the following two reactions occur:

$$Na^+ + e^- \rightarrow Na$$
$$2\ Cl^- \rightarrow Cl_2 + 2e^-$$

Normally we expect elemental sodium and chlorine to react spontaneously to make NaCl. However, by using an input of electricity, we can force the opposite reaction to occur and generate the elements. Lithium, potassium, and magnesium can also be isolated from compounds by electrolysis.

Another element that is isolated by electrolysis is aluminum. Aluminum formerly was a difficult metal to isolate in its elemental form; in fact, the top of the Washington Monument has a 2.8 kg cap of aluminum metal, which at the time — 1884 — was the largest piece of elemental aluminum ever isolated. However, in 1886 the American Charles Hall and the Frenchman Paul Héroult almost simultaneously worked out an electrolytic process for isolating aluminum from bauxite, an ore of aluminum whose chemical formula is $AlO_x(OH)_{3-2x}$. The basic reactions are as follows:

$$Al^{3+} + 3e^- \rightarrow Al$$
$$2O^{2-} \rightarrow O_2 + 4e^-$$

With the development of the Hall-Héroult process, the price of aluminum dropped by a factor of over 200, and aluminum metal became common. So much elemental aluminum is produced in the United States each year that it has been estimated that the electrolysis of aluminum uses 5% of all the electricity in the country. (Recycling aluminum requires about 1/70th the energy of refining aluminum from ore, which illustrates the tremendous energy savings that recycling provides.)

Another application of electrolysis is **electroplating**, which is the deposition of a thin layer of metal on an object for protective or decorative purposes (see Figure 14.5). Essentially, a metal object is connected to the cathode of an electrolytic cell and immersed in a solution of a particular metal cation. When the electrolytic cell is operated, a thin coating of the metal cation is reduced to the elemental metal on the surface of the object; the thickness of the coating can be as little as a few micrometers (10^{-6} m). Jewellery, eating utensils, electrical contacts, and car parts like bumpers are common items that are electroplated. Gold, silver, nickel, copper, and chromium are common metals used in electroplating.

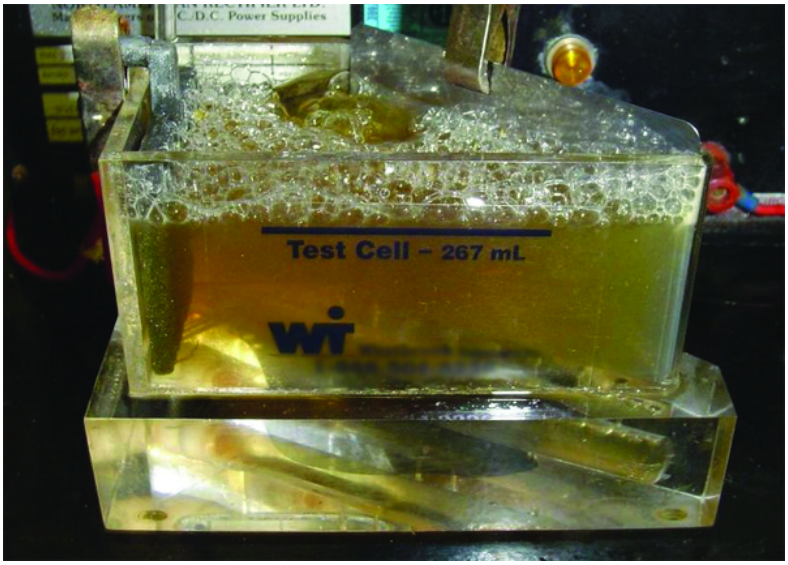


Figure 14.5 "Electroplating." Electroplating on a test cell.

Key Takeaways

- Electrolysis is the forcing of a nonspontaneous redox reaction to occur by the introduction of electricity into a cell from an outside source.
- Electrolysis is used to isolate elements and electroplate objects.

Exercises

Questions

1. Define *electrolytic cell*.
2. How does the operation of an electrolytic cell differ from a voltaic cell?
3. List at least three elements that are produced by electrolysis.
4. Write the half reactions for the electrolysis of the elements listed in Exercise 3.
5. Based on Table 14.1 "Standard Reduction Potentials of Half Reactions", what voltage must be applied to an electrolytic cell to electroplate copper from Cu^{2+}?
6. Based on Table 14.1, what voltage must be applied to an electrolytic cell to electroplate aluminum from Al^{3+}?

Answers

1. An electrochemical cell in which charge is forced through and a nonspontaneous reaction occurs.

3. Any three of the following: Al, K, Li, Na, Cl2, or Mg

5. 0.34 V

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End-of-Chapter Material

Additional Exercises

1. Oxidation was once defined as chemically adding oxygen to a substance. Use this reaction to argue that this definition is consistent with the modern definition of oxidation.

$$2Mg + O_2 \rightarrow 2MgO$$

2. Reduction was once defined as chemically adding hydrogen to a substance. Use this reaction to argue that this definition is consistent with the modern definition of reduction.

$$C_2H_2 + 2H_2 \rightarrow C_2H_6$$

3. Assign oxidation numbers to the atoms in each substance.
    a. Kr (krypton)
    b. krypton tetrafluoride (KrF_4)
    c. dioxygen difluoride (O_2F_2)
4. Assign oxidation numbers to the atoms in each substance.
    a. lithium hydride (LiH)
    b. potassium peroxide (K_2O_2)
    c. potassium fluoride (KF)
5. N atoms can have a wide range of oxidation numbers. Assign oxidation numbers for the N atom in each compound, all of which are known compounds.
    a. N_2O_5
    b. N_2O_4
    c. NO_2
    d. NO
    e. N_2H_4
    f. NH_3
6. Cr atoms can have a wide range of oxidation numbers. Assign oxidation numbers for the Cr atom in each compound, all of which are known compounds.
    a. Na_2CrO_4
    b. $Na_2Cr_2O_7$
    c. CrF_5
    d. $CrCl_3$
    e. $CrCl_2$
7. Balance this redox reaction by inspection.

$$S_8 + O_2 \rightarrow SO_2$$

8. Balance this redox reaction by inspection.

$$C_{18}H_{38} + O_2 \rightarrow CO_2 + H_2O$$

9. Balance this redox reaction by the half reaction method by assuming an acidic solution.

$$Cr_2O_7^{2-} + Fe \rightarrow Cr^{3+} + Fe^{3+}$$

10. Balance the redox reaction in Exercise 9 by the half reaction method by assuming a basic solution.
11. The uranyl ion (UO_2^{2+}) is a fairly stable ion of uranium that requires strong reducers to reduce the oxidation number of uranium further. Balance this redox reaction using the half reaction method by assuming an acidic solution.

$$UO_2^{2+} + HN_3 \rightarrow U + N_2$$

12. Balance the redox reaction in Exercise 11 by the half reaction method by assuming a basic solution.
13. Zinc metal can be dissolved by acid, which contains H^+ ions. Demonstrate that this is consistent with the fact that this reaction has a spontaneous voltage:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

14. Copper metal cannot be dissolved by acid, which contains H^+ ions. Demonstrate that this is consistent with the fact that this reaction has a nonspontaneous voltage:

$$Cu + 2H^+ \rightarrow Cu^{2+} + H_2$$

15. A disproportionation reaction occurs when a single reactant is both oxidized and reduced. Balance and determine the voltage of this disproportionation reaction. Use the data in Table 14.1 “Standard Reduction Potentials of Half Reactions”.

$$Cr^{2+} \rightarrow Cr + Cr^{3+}$$

16. A disproportionation reaction occurs when a single reactant is both oxidized and reduced. Balance and determine the voltage of this disproportionation reaction. Use the data in Table 14.1.

$$Fe^{2+} \rightarrow Fe + Fe^{3+}$$

17. What would be overall reaction for a fuel cell that uses CH_4 as the fuel?
18. What would be overall reaction for a fuel cell that uses gasoline (general formula C_8H_{18}) as the fuel?
19. When NaCl undergoes electrolysis, sodium appears at the cathode. Is the definition of cathode the same for an electrolytic cell as it is for a voltaic cell?
20. When NaCl undergoes electrolysis, chlorine appears at the anode. Is the definition of anode the same for an electrolytic cell as it is for a voltaic cell?
21. An award is being plated with pure gold before it is presented to a recipient. If the area of the award is 55.0 cm^2 and will be plated with 3.00 µm of Au, what mass of Au will be plated on the award? The density of Au is 19.3 g/cm^3.
22. The unit of electrical charge is called the coulomb (C). It takes 96,500 coulombs of charge to reduce 27.0 g of Al from Al^{3+} to Al metal. At 1,040 cm^3, how many coulombs of charge were needed to reduce the aluminum in the cap of the Washington monument, assuming the cap is pure Al? The density of Al is 2.70 g/cm^3.

Answers

1. As oxygen is added to magnesium, it is being oxidized. In modern terms, the Mg atoms are losing electrons and being oxidized, while the electrons are going to the O atoms.

3.
   a. Kr: 0
   b. Kr: +4; F: −1
   c. O: +1; F: −1

5.
   a. +5
   b. +4
   c. +4

d. +2
e. −2
f. −3

7. $S_8 + 8\ O_2 \rightarrow 8SO_2$
9. $14H^+ + Cr_2O_7^{2-} + 2Fe \rightarrow 2Cr^{3+} + 7H_2O + 2Fe^{3+}$
11. $6HN_3 + UO_2^{2+} \rightarrow U + 2H_2O + 9N_2 + 2H^+$
13. The voltage of the reaction is +0.76 V, which implies a spontaneous reaction.
15. $3Cr^{2+} \rightarrow Cr + 2Cr^{3+}$; −0.50 V
17. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
19. Yes, because reduction occurs at the cathode.
21. 0.318 g

Chapter 15. Nuclear Chemistry

Most of us have at least one device in our homes that guards our safety and, at the same time, depends on radioactivity to operate properly. This device is a smoke detector.

A typical smoke detector contains an electric circuit that includes two metal plates about 1 cm apart. A battery in the circuit creates a voltage between the plates. Next to the plates is a small disk containing a tiny amount (∼0.0002 g) of the radioactive element americium. The radioactivity of americium ionizes the air between the plates, causing a tiny current to constantly flow between them. (This constant drain on the battery explains why the batteries in smoke detectors should be replaced regularly, whether the alarm has been triggered or not.)

When particles of smoke from a fire enter the smoke detector, they interfere with the ions between the metal plates, interrupting the flow of current. When the current drops beneath a set value, another circuit triggers a loud alarm, warning of the possible presence of fire.

Although radioactive, the americium in a smoke detector is embedded in plastic and is not harmful unless the plastic package is taken apart, which is unlikely. Although many people have an unfounded fear of radioactivity, smoke detectors save thousands of lives every year.

Figure 15.0 “Smoke Detector.” Many people think of nuclear chemistry in connection with the nuclear power industry and atomic bombs but do not realize that most smoke detectors rely on nuclear chemistry and save countless lives every year. The applications of nuclear chemistry may be more widespread than you think.

Most chemists pay little attention to the nucleus of an atom except to consider the number of protons it

contains because that determines an element's identity. However, in nuclear chemistry, the composition of the nucleus and the changes that occur there are very important.

Applications of nuclear chemistry may be more widespread than you realize. Many people are aware of nuclear power plants and nuclear bombs, but nuclear chemistry also has applications ranging from smoke detectors to medicine, from the sterilization of food to the analysis of ancient artifacts. In this chapter, we will examine some of the basic concepts of nuclear chemistry and some of the nuclear reactions that are important in our everyday lives.

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Units of Radioactivity

Learning Objectives

1. Express amounts of radioactivity in a variety of units.

Later in this chapter, in the section "Half-Life", we use mass to indicate the amount of radioactive substance present. This is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation.

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one **becquerel (Bq)**. Even in a small mass of radioactive material, however, there are thousands upon thousands of decays or disintegrations per second. The unit **curie (Ci)**, now defined as 3.7×10^{10} decays/s, was originally defined as the number of decays per second in 1 g of radium. Many radioactive samples have activities that are on the order of microcuries (µCi) or more. Both the becquerel and the curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 µCi. (The curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena in the early 1900s; the becquerel is named after Henri Becquerel, who discovered radioactivity in 1896.)

Example 15.1

A sample of radium has an activity of 16.0 mCi (millicuries). If the half-life of radium is 1,600 y, how long before the sample's activity is 1.0 mCi?

Solution
The following table shows the activity of the radium sample over multiple half-lives:

Time in Years	Activity
0	16.0 mCi
1,600	8.0 mCi
3,200	4.0 mCi
4,800	2.0 mCi
6,400	1.0 mCi

Over a period of 4 half-lives, the activity of the radium will be halved four times, at which point its activity will be 1.0 mCi. Thus it takes 4 half-lives, or 4 × 1,600 y = 6,400 y, for the activity to decrease to 1.0 mCi.

Test Yourself
A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 3,750 Bq?

Answer
60 h

Example 15.2

A sample of radium has an activity of 16.0 mCi. If the half-life of radium is 1,600 y, how long before the sample's activity is 5.6 mCi?

Solution
In this case, we do not have an exact number of half-lives, so we need to use the more complicated equation (seen later in this chapter, in the section "Half-Life") and solve for time. If the initial amount is represented by 16.0 mCi and the final amount is 5.6 mCi, we have:

$$5.6 \text{ mCi} = (16.0 \text{ mCi}) e^{\frac{-0.693t}{1{,}600 \text{ y}}}$$

To solve, we divide both sides of the equation by 16.0 mCi to cancel the millicurie units:

$$\frac{5.6}{16.0} = e^{\frac{-0.693t}{1{,}600 \text{ y}}}$$

By taking the natural logarithm of both sides; the natural logarithm cancels the exponential function. The natural logarithm of 5.6/16.0 is −1.050. So:

$$-1.050 = \frac{-0.693t}{1{,}600 \text{ y}}$$

The negative sign cancels, and we solve for *t*. Thus:

$$t = 2{,}420 \text{ y}$$

It makes sense that the time is greater than one half-life (1,600 y) because we have less than one-half of the original activity left.

Test Yourself
A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 10,000 Bq?

Answer
38.8 h

Other measures of radioactivity are based on the effects it has on living tissue. Radioactivity can transfer energy to tissues in two ways: through the kinetic energy of the particles hitting the tissue and through the electromagnetic energy of the gamma rays being absorbed by the tissue. Either way, the transferred energy — like the thermal energy from boiling water — can damage the tissue.

The **rad** (an acronym for radiation absorbed dose) is a unit equivalent to 1 g of tissue absorbing 0.01 J:

$$1 \text{ rad} = 0.01 \text{ J/g}$$

Another unit of radiation absorption is the gray (Gy):

$$1 \text{ Gy} = 100 \text{ rad}$$

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of water (approximately the same mass as a 150 lb person) would

increase the temperature of the water by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

Predicting the effects of radiation is complicated by the fact that different types of emissions affect various tissues differently. To quantify these effects, the unit **rem** (an acronym for röntgen equivalent man) is defined as:

$$\text{rem} = \text{rad} \times \text{factor}$$

where factor is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, the factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X-ray is about 20 mrem. A sievert (Sv) is a related unit and is defined as 100 rem.

What is a person's annual exposure to radioactivity and radiation? Table 15.1 "Average Annual Radiation Exposure (Approximate)" lists the sources and annual amounts of radiation exposure. It may surprise you to learn that fully 82% of the radioactivity and radiation exposure we receive is from natural sources — sources we cannot avoid. Fully 10% of the exposure comes from our own bodies — largely from carbon-14 and potassium-40.

Table 15.1 Average Annual Radiation Exposure (Approximate)

Source	**Amount (mrem)**
radon gas	200
medical sources	53
radioactive atoms in the body naturally	39
terrestrial sources	28
cosmic sources	28[1]
consumer products	10
nuclear energy	0.05
Total	358

The actual effects of radioactivity and radiation exposure on a person's health depend on the type of radioactivity, the length of exposure, and the tissues exposed. Table 15.2 "Effects of Short-Term Exposure to Radioactivity and Radiation" lists the potential threats to health at various amounts of exposure over short periods of time (hours or days).

1. Flying from New York City to San Francisco adds 5 mrem to your overall radiation exposure because the plane flies above much of the atmosphere, which protects us from cosmic radiation.

Table 15.2 Effects of Short-Term Exposure to Radioactivity and Radiation

Exposure (rem)	Effect
1 (over a full year)	no detectable effect
~20	increased risk of some cancers
~100	damage to bone marrow and other tissues; possible internal bleeding; decrease in white blood cell count
200–300	visible “burns” in skin, nausea, vomiting, fatigue
>300	loss of white blood cells; hair loss
~600	death

One of the simplest ways of detecting radioactivity is by using a piece of photographic film embedded in a badge or a pen. On a regular basis, the film is developed and checked for exposure. Comparing the exposure level of the film with a set of standard exposures indicates the amount of radiation a person was exposed to.

Another means of detecting radioactivity is an electrical device called a **Geiger counter** (Figure 15.1 “Detecting Radioactivity”). It contains a gas-filled chamber with a thin membrane on one end that allows radiation emitted from radioactive nuclei to enter the chamber and knock electrons off atoms of gas (usually argon). The presence of electrons and positively charged ions causes a small current, which is detected by the Geiger counter and converted to a signal on a meter or, commonly, an audio circuit to produce an audible “click.”

Figure 15.1 “Detecting Radioactivity.” A Geiger counter is a common instrument used to detect radioactivity.

Key Takeaways

- Radioactivity can be expressed in a variety of units, including rems, rads, and curies.

Exercises

Questions

1. Define *rad*.
2. Define *rem*.
3. How does a becquerel differ from a curie?
4. Define *curie*.
5. A sample of radon gas has an activity of 140.0 mCi. If the half-life of radon is 1,500 y, how long before the activity of the sample is 8.75 mCi?
6. A sample of curium has an activity of 1,600 Bq. If the half-life of curium is 24.0 s, how long before its activity is 25.0 Bq?
7. If a radioactive sample has an activity of 65 µCi, how many disintegrations per second are occurring?
8. If a radioactive sample has an activity of 7.55×10^5 Bq, how many disintegrations per second are occurring?
9. A sample of fluorine-20 has an activity of 2.44 mCi. If its half-life is 11.0 s, what is its activity after 50.0 s?
10. Strontium-90 has a half-life of 28.1 y. If 66.7 Bq of pure strontium-90 were allowed to decay for 15.0 y, what would the activity of the remaining strontium-90 be?
11. How long does it take 100.0 mCi of fluorine-20 to decay to 10.0 mCi if its half-life is 11.0 s?
12. Technetium-99 is used in medicine as a source of radiation. A typical dose is 25 mCi. How long does it take for the activity to reduce to 0.100 mCi? The half-life of ^{99}Tc is 210,000 y.
13. Describe how a radiation exposure in rems is determined.
14. Which contributes more to the rems of exposure — alpha or beta particles? Why?
15. Use Table 15.2 “Effects of Short-Term Exposure to Radioactivity and Radiation” to determine which sources of radiation exposure are inescapable and which can be avoided. What percentage of radiation is unavoidable?
16. Name two isotopes that contribute to the radioactivity in our bodies.
17. Explain how a film badge works to detect radiation.
18. Explain how a Geiger counter works to detect radiation.

Answers

1. A unit of radioactive exposure equal to 0.01 J of energy per gram of tissue.
3. A becquerel is 1 decay/s, whereas a curie is 3.7×10^{10} decays/s.
5. 6.0×10^3 y
7. 2.41×10^6 disintegrations per second
9. 0.104 mCi

11. 36.5 s
13. By using a film badge, which is exposed by the radiation, or a Geiger counter.
15. Radioactive atoms in the body, most terrestrial sources, cosmic sources, and nuclear energy sources are likely unavoidable, which is about 27% of the total exposure. If exposure to radon gas is added, the total unavoidable exposure increases to 82%.
17. Film is exposed by the radiation. The more radiation film is subjected to, the more exposed it becomes.

Media Attributions

Uses of Radioactive Isotopes

Learning Objectives

1. Learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful because either we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A **tracer** is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium is a radioactive isotope of hydrogen.)

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of carbon-14 to determine the steps involved in photosynthesis in plants. We know these steps because researchers followed the progress of carbon-14 throughout the process.

Radioactive Dating

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, so the isotope acts like an internal clock. For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about 4.5×10^9 y. Many analyses like this, using a wide variety of isotopes, have indicated that age of the earth itself is over 4×10^9 y. In another interesting example of radioactive dating, hydrogen-3 dating has been used to verify the stated vintages of some old fine wines.

One isotope, carbon-14, is particularly useful in determining the age of once-living artifacts. A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant, albeit very low, level. Once a living thing dies, it no longer acquires carbon-14; as time passes the carbon-14 that was in the tissues decays. (The half-life of carbon-14 is 5,370 y.) If a once-living artifact is discovered and analyzed many years after its death and the remaining carbon-14 is compared to the known constant level, an approximate age of the artifact can be determined. Using such methods, scientists determined that the age of the Shroud of Turin (Figure 15.2 “Shroud of Turin”; purported by some to be the burial cloth of Jesus

Christ and composed of flax fibres, a type of plant) is about 600–700 y, not 2,000 y as claimed by some. Scientists were also able to use radiocarbon dating to show that the age of a mummified body found in the ice of the Alps was 5,300 y.

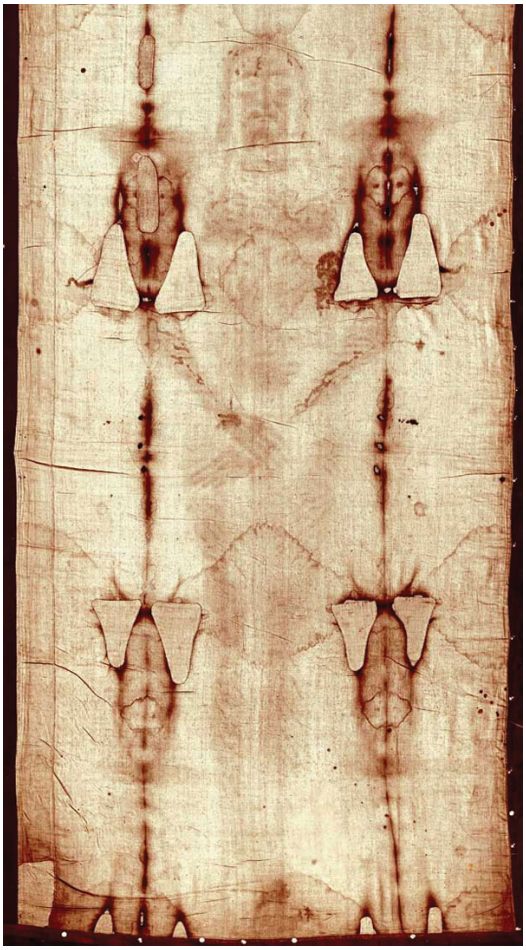


Figure 15.2 "Shroud of Turin." In 1989, several groups of scientists used carbon-14 dating to demonstrate that the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.

Irradiation of Food

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, extending the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from cobalt-60 or cesium-137. This exposure kills a lot of the bacteria that cause spoilage, so the produce stays fresh longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.

Medical Applications

Radioactive isotopes have numerous medical applications—diagnosing and treating illness and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure 15.3 “Medical Diagnostics”). The thyroid gland in the neck is one of the few places in the body with a significant concentration of iodine. To evaluate thyroid activity, a measured dose of ^{131}I is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing trained physicians to diagnose both hyperthyroidism and hypothyroidism. Iodine-131 has a half-life of only 8 d, so the potential for damage due to exposure is minimal. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

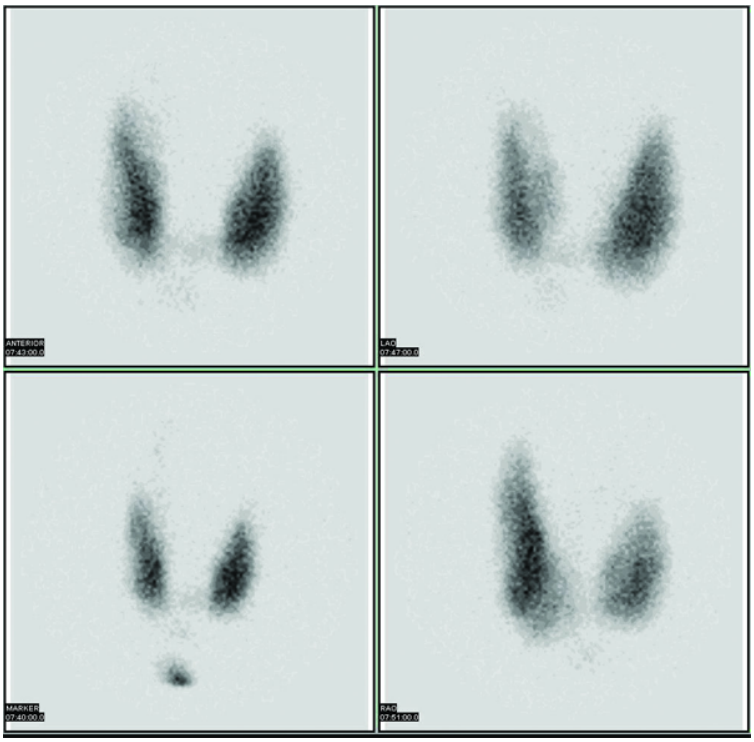


Figure 15.3 “Medical Diagnostics.” Radioactive iodine can be used to image the thyroid gland for diagnostic purposes.

Very little radioactive material is needed in these diagnostic techniques because the radiation emitted is so easy to detect. However, therapeutic applications usually require much larger doses because their purpose is to preferentially kill diseased tissues. For example, if a thyroid tumour were detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less than 40 rem) of iodine-131 could help destroy the tumour cells. Similarly, radioactive strontium is used to not only detect but also ease the pain of bone cancers. Table 15.3 “Some Radioactive Isotopes with Medical Applications” lists several radioactive isotopes and their medical uses.

Table 15.3 Some Radioactive Isotopes with Medical Applications

Isotope	Use
^{32}P	cancer detection and treatment, especially in eyes and skin
^{59}Fe	anemia diagnosis
^{60}Co	gamma ray irradiation of tumours
^{99m}Tc[1]	brain, thyroid, liver, bone marrow, lung, heart, and intestinal scanning; blood volume determination
^{131}I	diagnosis and treatment of thyroid function
^{133}Xe	lung imaging
^{198}Au	liver disease diagnosis

In addition to the direct application of radioactive isotopes to diseased tissue, the gamma ray emissions of some isotopes can be directed toward the tissue to be destroyed. Cobalt-60 is a useful isotope for this kind of procedure.

Food and Drink App: Radioactivity in Wines

Wine lovers put some stock in *vintages*, or the years in which the wine grapes were grown before they were turned into wine. Wine can differ in quality depending on the vintage. Some wine lovers willingly pay much more for a bottle of wine with a certain vintage. But how does one verify that a bottle of wine was in fact part of a certain vintage? Is the label a fake? Is that stash of wine found in the basement of a French chateau really from the 1940s, or was it made in 2009?

1. The “m” means that it is a metastable form of this isotope of technetium.

This wine label from a bottle of wine claims a vintage of 1991. Is the wine really from this vintage, or is it a fake? Radioactivity can help determine the answer.

Cesium-137 is a radioactive isotope that has a half-life of 30.1 y. It was introduced into the atmosphere in the 1940s and 1950s by the atmospheric testing of nuclear weapons by several countries after World War II. A significant amount of cesium-137 was released during the Chernobyl nuclear disaster in 1986. As a result of this atmospheric contamination, scientists have precise measurements of the amount of cesium-137 available in the environment since 1950. Some of the isotope of cesium is taken up by living plants, including grape vines. Using known vintages, oenologists (wine scientists) can construct a detailed analysis of the cesium-137 of various wines through the years.

The verification of a wine's vintage requires the measurement of the activity of cesium-137 in the wine. By measuring the current activity of cesium-137 in a sample of wine (the gamma rays from the radioactive decay pass through glass wine bottles easily, so there's no need to open the bottle), comparing it to the known amount of cesium-137 from the vintage, and taking into account the passage of time, researchers can collect evidence for or against a claimed wine vintage.

Before about 1950, the amount of cesium-137 in the environment was negligible, so if a wine dated before 1950 shows any measurable cesium-137 activity, it is almost surely a fake, so don't shell out lots of money for it! It may be a good wine, but it is almost definitely not over 60 years old.

Key Takeaways

- Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and preservation of food.

Exercises

Questions

1. Define *tracer* and give an example of how tracers work.
2. Name two isotopes that have been used as tracers.
3. Explain how radioactive dating works.
4. Name two isotopes that have been used in radioactive dating.
5. The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archaeological excavation is found to have a carbon-14 disintegration rate of 3.5 Bq. If the half-life of carbon-14 is 5,730 y, approximately how old is the wood sample?
6. A small asteroid crashes to Earth. After chemical analysis, it is found to contain 1 g of technetium-99 to every 3 g of ruthenium-99, its daughter isotope. If the half-life of technetium-99 is 210,000 y, approximately how old is the asteroid?
7. What is a positive aspect of the irradiation of food?
8. What is a negative aspect of the irradiation of food?
9. Describe how iodine-131 is used to both diagnose and treat thyroid problems.
10. List at least five organs that can be imaged using radioactive isotopes.
11. Which radioactive emissions can be used therapeutically?
12. Which isotope is used in therapeutics primarily for its gamma ray emissions?

Answers

1. A tracer is a radioactive isotope that can be detected far from its original source to trace the path of certain chemicals. Hydrogen-3 can be used to trace the path of water underground.

3. If the initial amount of a radioactive isotope is known, then by measuring the amount of the isotope remaining, a person can calculate how old that object is since it took up the isotope.

5. 11,500 y

7. increased shelf life (answers will vary)

9. The thyroid gland absorbs most of the iodine, allowing it to be imaged for diagnostic purposes or preferentially irradiated for treatment purposes.

11. gamma rays

Media Attributions

Half-Life

Learning Objectives

1. Define *half-life*.
2. Determine the amount of radioactive substance remaining after a given number of half-lives.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half-life**, which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Consider the following example. Suppose we have 100.0 g of tritium (a radioactive isotope of hydrogen). It has a half-life of 12.3 y. After 12.3 y, half of the sample will have decayed from hydrogen-3 to helium-3 by emitting a beta particle, so that only 50.0 g of the original tritium remains. After another 12.3 y — making a total of 24.6 y — another half of the remaining tritium will have decayed, leaving 25.0 g of tritium. After another 12.3 y — now a total of 36.9 y — another half of the remaining tritium will have decayed, leaving 12.5 g. This sequence of events is illustrated in Figure 15.4 “Radioactive Decay”.

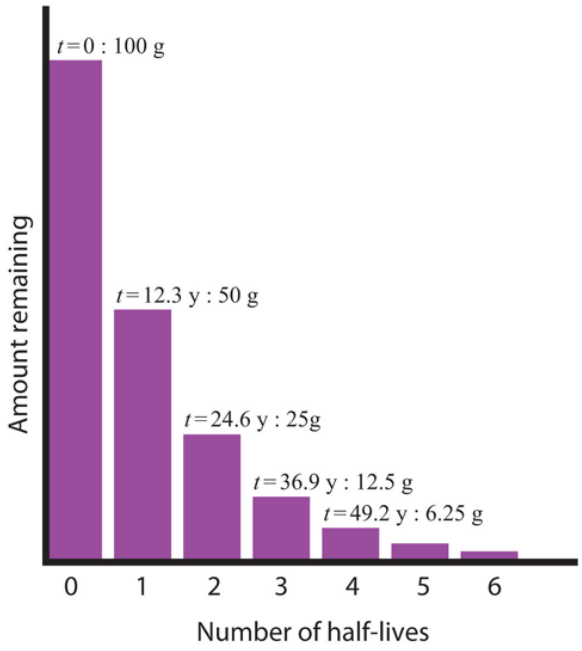


Figure 15.4 "Radioactive Decay." During each successive half-life, half of the initial amount will radioactively decay.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n}$$

where *n* is the number of half-lives. This expression works best when the number of half-lives is a whole number.

Example 15.3

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, $n = 4$. Substituting and solving results in the following:

$$\begin{aligned} \text{amount remaining} &= 5.00\ \text{g} \times \left(\frac{1}{2}\right)^{4} \\ &= 5.00\ \text{g} \times \frac{1}{16} \\ &= 0.313\ \text{g} \end{aligned}$$

Less than one-third of a gram of fluorine-20 remains.

Test Yourself
The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer
0.0375 g

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 15.4 “Half-Lives of Various Isotopes” lists the half-lives of some isotopes.

Table 15.4 Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5730 y
^{40}K	1.26×10^{9} y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^{8} y
^{238}U	4.47×10^{9} y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Chemistry Is Everywhere: Radioactive Elements in the Body

You may not think of yourself as radioactive, but you are. A small portion of certain elements in the human body are radioactive and constantly undergo decay. The following table summarizes radioactivity in the normal human body.

Radioactive Isotope	Half-Life (y)	Isotope Mass in the Body (g)	Activity in the Body (decays/s)
^{40}K	1.26×10^{9}	0.0164	4,340
^{14}C	5,730	1.6×10^{-8}	3,080
^{87}Rb	4.9×10^{10}	0.19	600
^{210}Pb	22.3	5.4×10^{-10}	15
^{3}H	12.3	2×10^{-14}	7
^{238}U	4.47×10^{9}	1×10^{-4}	5
^{228}Ra	5.76	4.6×10^{-14}	5
^{226}Ra	1,620	3.6×10^{-11}	3

The average human body experiences about 8,000 radioactive decays/s.

Most of the radioactivity in the human body comes from potassium-40 and carbon-14. Potassium and carbon are two elements that we absolutely cannot live without, so unless we can remove all the radioactive isotopes of these elements, there is no way to escape at least some radioactivity. There is debate about which radioactive element is more problematic. There is more potassium-40 in the body than carbon-14, and it has a much longer half-life. Potassium-40 also decays with about 10 times more energy than carbon-14, making each decay potentially more problematic. However, carbon is the element that makes up the backbone of most living molecules, making carbon-14 more likely to be present around important molecules, such as proteins and DNA molecules. Most experts agree that while it is foolhardy to expect absolutely no exposure to radioactivity, we can and should minimize exposure to excess radioactivity.

What if the elapsed time is not an exact number of half-lives? We can still calculate the amount of material we have left, but the equation is more complicated. The equation is:

$$\text{amount remaining} = (\text{amount initially}) \times e^{\frac{-0.693t}{t_{\frac{1}{2}}}}$$

where e is the base of natural logarithms (2.71828182…), t is the elapsed time, and $t_{½}$ is the half-life of the radioactive isotope. The variables t and $t_{½}$ should have the same units of time, and you may need to make sure you know how to evaluate natural-logarithm powers on your calculator (for many calculators, there is an “inverse logarithm” function that you can use; consult your instructor if you are not sure how to use your calculator). Although this is a more complicated formula, the length of time t need not be an exact multiple of half-lives.

Example 15.4

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 60.0 s?

Solution
Although similar to Example 15.3, the amount of time is not an exact multiple of a half-life. Here we identify the initial amount as 5.00 g, t = 60.0 s, and $t_{½}$ = 11.0 s. Substituting into the equation:

$$\text{amount remaining} = (5.00\ \text{g}) \times e^{\frac{(-0.693)(60.0\ \text{s})}{11.0\ \text{s}}}$$

Evaluating the exponent (and noting that the *s* units cancel), we get:

$$\text{amount remaining} = 5.00\ \text{g} \times e^{-3.78}$$

Solving, the amount remaining is 0.114 g. (You may want to verify this answer to confirm that you are using your calculator properly.)

Test Yourself
The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 100.0 y?

Answer
0.189 g

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

Exercises

Questions

1. Do all isotopes have a half-life? Explain your answer.
2. Which is more radioactive — an isotope with a long half-life or an isotope with a short half-life?
3. How long does it take for 1.00 g of palladium-103 to decay to 0.125 g if its half-life is 17.0 d?
4. How long does it take for 2.00 g of niobium-94 to decay to 0.0625 g if its half-life is 20,000 y?
5. It took 75 y for 10.0 g of a radioactive isotope to decay to 1.25 g. What is the half-life of this isotope?
6. It took 49.2 s for 3.000 g of a radioactive isotope to decay to 0.1875 g. What is the half-life of this isotope?
7. The half-live of americium-241 is 432 y. If 0.0002 g of americium-241 is present in a smoke detector at the date of manufacture, what mass of americium-241 is present after 100.0 y? After 1,000.0 y?
8. If the half-life of tritium (hydrogen-3) is 12.3 y, how much of a 0.00444 g sample of tritium is present after 5.0 y? After 250.0 y?
9. Explain why the amount left after 1,000.0 y in Exercise 7 is not one-tenth of the amount present after 100.0 y, despite the fact that the amount of time elapsed is 10 times as long.
10. Explain why the amount left after 250.0 y in Exercise 8 is not one-fiftieth of the amount present after 5.0 y, despite the fact that the amount of time elapsed is 50 times as long.
11. An artifact containing carbon-14 contains 8.4×10^{-9} g of carbon-14 in it. If the age of the artifact is 10,670 y, how much carbon-14 did it have originally? The half-life of carbon-14 is 5,730 y.
12. Carbon-11 is a radioactive isotope used in positron emission tomography (PET) scans for medical diagnosis. Positron emission is another, though rare, type of radioactivity. The half-life of carbon-11 is 20.3 min. If 4.23×10^{-6} g of carbon-11 is left in the body after 4.00 h, what mass of carbon-11 was present initially?

Answers

1. Only radioactive isotopes have a half-life.
3. 51.0 d
5. 25 y
7. 0.000170 g; 0.0000402 g
9. Radioactive decay is an exponential process, not a linear process.
11. 3.1×10^{-8} g

Radioactivity

Learning Objectives

1. Define and give examples of the major types of radioactivity.

We saw in Chapter 3 “Atoms, Molecules, and Ions” that atoms are composed of subatomic particles — protons, neutrons, and electrons. Protons and neutrons are located in the nucleus and provide most of the mass of an atom, while electrons circle the nucleus in shells and subshells and account for an atom’s size.

We also introduced in Chapter 3 the notation for succinctly representing an isotope of a particular atom:

$$^{12}_{6}\mathrm{C}$$

The element in this example, represented by the symbol C, is carbon. Its atomic number, 6, is the subscript next to the symbol and is the number of protons in the atom. The mass number, the superscript next to the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 12, which means that the number of neutrons in the atom is 12 − 6 = 6 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neurons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen — ^{2}H and ^{3}H — are given their own names and symbols: deuterium (D) and tritium (T), respectively.

Atomic theory in the nineteenth century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source being the atomic nucleus. These emanations were ultimately called, collectively, **radioactivity**.

There are three main forms of radioactive emissions. The first is called an **alpha particle**, which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons and is the same as a helium nucleus. (We often use $^{4}_{2}\mathrm{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom’s atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a chemical equation—for example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th}$$

Rather than calling this equation a chemical equation, we call it a **nuclear equation** to emphasize that the change occurs in an atomic nucleus. How do we know that a product of this reaction is $^{231}_{90}\mathrm{Th}$? We use the law of conservation of matter, which says that matter cannot be created or destroyed. This means we must have the same number of protons and neutrons on both sides of the nuclear equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose four nuclear particles of the original 235, there are 231 remaining. Thus we use subtraction to identify the isotope of the Th atom — in this case, $^{231}_{90}\mathrm{Th}$.

Chemists often use the names **parent isotope** and **daughter isotope** to represent the original atom and the product other than the alpha particle. In the previous example, $^{235}_{92}\mathrm{U}$ is the parent isotope, and $^{231}_{90}\mathrm{Th}$ is the daughter isotope. When one element changes into another in this manner, it undergoes **radioactive decay**.

Example 15.5

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\mathrm{Rn}$. We represent the alpha particle as $^{4}_{2}\mathrm{He}$ and use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as polonium:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{218}_{84}\mathrm{Po}$$

Test Yourself

Write the nuclear equation that represents radioactive decay of polonium-208 by alpha particle emission and identify the daughter isotope.

Answer

$^{208}_{84}\mathrm{Po} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{204}_{82}\mathrm{Pb}$; daughter isotope: $^{204}_{82}\mathrm{Pb}$

The second major type of radioactive emission is called a **beta particle**, symbolized by the Greek letter β. A beta particle is an electron ejected from the nucleus (not from the shells of electrons about the nucleus) and has a 1− charge. We can also represent a beta particle as $^{0}_{-1}\mathrm{e}$. The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

Again, the sum of the atomic numbers is the same on both sides of the equation, as is the sum of the mass numbers. (Note that the electron is assigned an “atomic number” of –1, equal to its charge.)

The third major type of radioactive emission is not a particle but rather a very energetic form of electromagnetic radiation called **gamma rays**, symbolized by the Greek letter γ. Gamma rays themselves do not carry an overall electrical charge, but they may knock electrons out of atoms in a sample of matter and make it electrically charged (for which gamma rays are termed *ionizing radiation*). For example, in the radioactive decay of radon-222, both alpha and gamma radiation are emitted, with the latter having an energy of 8.2×10^{-14} J per nucleus decayed:

$$^{222}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{218}_{84}\text{Po} + \gamma$$

This may not seem like much energy, but if 1 mol of Rn atoms were to decay, the gamma ray energy would be 4.9×10^7 kJ!

Example 15.6

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is $^{12}_{5}\text{B}$, while one of the products is $^{0}_{-1}\text{e}$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus the complete nuclear equation is as follows:

$$^{12}_{5}\text{B} \rightarrow {}^{12}_{6}\text{C} + {}^{0}_{-1}\text{e} + \gamma$$

The daughter isotope is carbon-12.

Test Yourself

Write the nuclear equation that represents the radioactive decay of technetium-133 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer

$^{133}_{43}\text{Tc} \rightarrow {}^{133}_{44}\text{Ru} + {}^{0}_{-1}\text{e} + \gamma$; daughter isotope: ruthenium-133

Alpha, beta, and gamma emissions have different abilities to penetrate matter. The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimetres at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter. Table 15.5 “The Three Main Forms of Radioactive Emissions” summarizes the properties of the three main types of radioactive emissions.

Table 15.5 The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, $^{4}_{2}\text{He}$	β, $^{0}_{-1}\text{e}$	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1−	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Occasionally, an atomic nucleus breaks apart into smaller pieces in a radioactive process called **spontaneous fission (or fission)**. Typically, the daughter isotopes produced by fission are a varied mix

of products, rather than a specific isotope as with alpha and beta particle emission. Often, fission produces excess neutrons that will sometimes be captured by other nuclei, possibly inducing additional radioactive events. Uranium-235 undergoes spontaneous fission to a small extent. One typical reaction is:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{139}_{56}\mathrm{Ba} + {}^{94}_{36}\mathrm{Kr} + 2{}^{1}_{0}\mathrm{n}$$

where $^{1}_{0}\mathrm{n}$ is a neutron. As with any nuclear process, the sums of the atomic numbers and mass numbers must be the same on both sides of the equation. Spontaneous fission is found only in large nuclei. The smallest nucleus that exhibits spontaneous fission is lead-208. (Fission is the radioactive process used in nuclear power plants and one type of nuclear bomb.)

Key Takeaways

- The major types of radioactivity include alpha particles, beta particles, and gamma rays.
- Fission is a type of radioactivity in which large nuclei spontaneously break apart into smaller nuclei.

Exercises

Questions

1. Define *radioactivity*.
2. Give an example of a radioactive element. How do you know if it is radioactive?
3. How many protons and neutrons are in each isotope?
    a. $^{11}_{5}\mathrm{B}$
    b. $^{27}_{13}\mathrm{Al}$
    c. $^{56}\mathrm{Fe}$
    d. $^{224}\mathrm{Rn}$
4. How many protons and neutrons are in each isotope?
    a. $^{2}_{1}\mathrm{H}$
    b. $^{112}_{48}\mathrm{Cd}$
    c. $^{252}\mathrm{Es}$
    d. $^{40}\mathrm{K}$
5. Describe an alpha particle. What nucleus is it equivalent to?
6. Describe a beta particle. What subatomic particle is it equivalent to?
7. What are gamma rays?
8. Why is it inappropriate to refer to gamma rays as “gamma particles”?

9. Plutonium has an atomic number of 94. Write the nuclear equation for the alpha particle emission of plutonium-244. What is the daughter isotope?
10. Francium has an atomic number of 87. Write the nuclear equation for the alpha particle emission of francium-212. What is the daughter isotope?
11. Tin has an atomic number of 50. Write the nuclear equation for the beta particle emission of tin-121. What is the daughter isotope?
12. Technetium has an atomic number of 43. Write the nuclear equation for the beta particle emission of technetium-99. What is the daughter isotope?
13. Energies of gamma rays are typically expressed in units of megaelectron volts (MeV), where 1 MeV = 1.602×10^{-13} J. Using the data provided in the text, calculate the energy in megaelectron volts of the gamma ray emitted when radon-222 decays.
14. The gamma ray emitted when oxygen-19 gives off a beta particle is 0.197 MeV. What is its energy in joules? (See Exercise 13 for the definition of a megaelectron volt.)
15. Which penetrates matter more deeply — alpha particles or beta particles? Suggest ways to protect yourself against both particles.
16. Which penetrates matter more deeply — alpha particles or gamma rays? Suggest ways to protect yourself against both emissions.
17. Define *nuclear fission*.
18. What general characteristic is typically necessary for a nucleus to undergo spontaneous fission?

Answers

1. Radioactivity is the spontaneous emission of particles and electromagnetic radiation from nuclei of unstable atoms.

3. a. 5 protons; 6 neutrons
   b. 13 protons; 14 neutrons
   c. 26 protons; 30 neutrons
   d. 86 protons; 138 neutrons

5. An alpha particle is a collection of two protons and two neutrons and is equivalent to a helium nucleus.

7. Gamma rays are high-energy electromagnetic radiation given off in radioactive decay.

9. ${}^{244}_{94}\mathrm{Pu} \rightarrow {}^{240}_{92}\mathrm{U} + {}^{4}_{2}\mathrm{He}$; daughter isotope: ${}^{240}\mathrm{U}$

11. ${}^{121}_{50}\mathrm{Sn} \rightarrow {}^{121}_{51}\mathrm{Sb} + {}^{0}_{-1}\mathrm{e}$; daughter isotope: ${}^{121}\mathrm{Sb}$

13. 0.51 MeV

15. Beta particles penetrate more. A thick wall of inert matter is sufficient to block both particles.

17. Nuclear fission is the breaking down of large nuclei into smaller nuclei, usually with the release of excess neutrons.

Nuclear Energy

Learning Objectives

1. Explain where nuclear energy comes from.
2. Describe the difference between fission and fusion.

Nuclear changes occur with a simultaneous release of energy. Where does this energy come from? If we could precisely measure the masses of the reactants and products of a nuclear reaction, we would notice that the amount of mass drops slightly in the conversion from reactants to products. Consider the following nuclear equation, in which the molar mass of each species is indicated to four decimal places:

$$\underset{235.0439}{^{235}\mathrm{U}} \rightarrow \underset{138.9088}{^{139}\mathrm{Ba}} + \underset{93.9343}{^{94}\mathrm{Kr}} + \underset{2\times1.0087}{2\,^{1}\mathrm{n}}$$

If we compare the mass of the reactant (235.0439) to the masses of the products (sum = 234.8605), we notice a mass difference of −0.1834 g, or −0.0001834 kg. Where did this mass go?

According to Albert Einstein's theory of relativity, energy (*E*) and mass (*m*) are related by the following equation:

$$E = mc^2$$

where *c* is the speed of light, or 3.00×10^8 m/s. In the course of the chemical reaction for uranium, the mass difference is converted to energy, which is given off by the reaction:

$$\begin{aligned} E &= (-0.0001834\ \mathrm{kg})(3.00 \times 10^8\ \mathrm{m/s})^2 \\ &= -1.65 \times 10^{13}\ \mathrm{J} \\ &= -1.65 \times 10^{10}\ \mathrm{kJ} \end{aligned}$$

(For the units to work out, mass must be expressed in units of kilograms.) That is, 16.5 billion kJ of energy is given off every time 1 mol of uranium-235 undergoes this nuclear reaction. This is an extraordinary amount of energy. Compare it to combustion reactions of hydrocarbons, which give off about 650 kJ/mol of energy for every CH_2 unit in the hydrocarbon — on the order of *hundreds* of kilojoules per mole. Nuclear reactions give off *billions* of kilojoules per mole.

If this energy could be properly harvested, it would be a significant source of energy for our society. **Nuclear energy** involves the controlled harvesting of energy from fission reactions. The reaction can

be controlled because the fission of uranium-235 (and a few other isotopes, such as plutonium-239) can be artificially initiated by injecting a neutron into a uranium nucleus. The overall nuclear equation, with energy included as a product, is then as follows:

$$^{235}\mathrm{U} + {}^{1}\mathrm{n} \rightarrow {}^{139}\mathrm{Ba} + {}^{94}\mathrm{Kr} + 3\,{}^{1}\mathrm{n} + \text{energy}$$

Thus by the careful addition of extra neutrons into a sample of uranium, we can control the fission process and obtain energy that can be used for other purposes. (Artificial or induced radioactivity, in which neutrons are injected into a sample of matter that subsequently cause fission, was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-in-law of Marie Curie.)

Example 15.7

Plutonium-239 can absorb a neutron and undergo a fission reaction to make an atom of gold-204 and an atom of phosphorus-31. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Solution
Using the data given, we can write the following initial equation:

$$^{1}_{0}\mathrm{n} + {}^{239}_{94}\mathrm{Pu} \rightarrow {}^{204}_{79}\mathrm{Au} + {}^{31}_{15}\mathrm{P} + ?\,{}^{1}_{0}\mathrm{n}$$

In balanced nuclear equations, the sums of the subscripts on each side of the equation are the same, as are the sums of the superscripts. The subscripts are already balanced: 0 + 94 = 94 and 79 + 15 = 94. The superscripts on the left equal 240 (1 + 239) but equal 235 (204 + 31) on the right. We need five more mass number units on the right. Five neutrons should be products of the process for the mass numbers to balance. (Because the atomic number of a neutron is zero, including five neutrons on the right does not change the overall sum of the subscripts.) Thus the balanced nuclear equation is as follows:

$$^{1}_{0}\mathrm{n} + {}^{239}_{94}\mathrm{Pu} \rightarrow {}^{204}_{79}\mathrm{Au} + {}^{31}_{15}\mathrm{P} + 5\,{}^{1}_{0}\mathrm{n}$$

We predict that the overall process will give off five neutrons.

Test Yourself
Uranium-238 can absorb a neutron and undergo a fission reaction to produce an atom of cesium-135 and an atom of rubidium-96. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Answer
$^{1}_{0}\mathrm{n} + {}^{238}_{92}\mathrm{U} \rightarrow {}^{96}_{37}\mathrm{Rb} + {}^{135}_{55}\mathrm{Cs} + 8\,{}^{1}_{0}\mathrm{n}$; eight neutrons

Example 15.8

One balanced nuclear reaction for the fission of plutonium-239 is as follows:

$$\underset{1.0087}{^{1}_{0}\mathrm{n}} + \underset{239.0522}{^{239}_{94}\mathrm{Pu}} \rightarrow \underset{203.9777}{^{204}_{79}\mathrm{Au}} + \underset{30.9738}{^{31}_{15}\mathrm{P}} + \underset{5\times1.0087}{5\,{}^{1}_{0}\mathrm{n}}$$

The molar mass in grams of each species is given for each particle. What is the energy change of this fission reaction?

Solution
We start by adding the masses of all species on each side of the nuclear equation. Then we determine the difference in mass as the reaction proceeds and convert this to an equivalent amount of energy. The total mass of the reactants is as follows:

$$1.0087 + 239.0522 = 240.0609 \text{ g}$$

The total mass of the products is as follows:

$$203.9777 + 30.9738 + (5 \times 1.0087) = 239.9950 \text{ g}$$

The change is mass is determined by subtracting the mass of the reactants from the mass of the products:

$$\text{change in mass} = 239.9950 - 240.0609 = -0.0659 \text{ g}$$

This mass change must be converted into kilogram units:

$$-0.0659 \text{ g} \times \frac{1 \text{ kg}}{1,000 \text{ g}} = -0.0000659 \text{ kg}$$

Now we can use Einstein's equation to determine the energy change of the nuclear reaction:

$$E = (-0.0000659 \text{ kg})(3.00 \times 10^8 \text{ m/s})^2 = -5.93 \times 10^{12} \text{ J}$$

This is almost 6 *trillion* joules given off.

Test Yourself

The nuclear equation for the fission of uranium-238 is as follows:

$$\underset{1.0087}{{}^{1}_{0}\text{n}} + \underset{238.0508}{{}^{238}_{92}\text{U}} \rightarrow \underset{95.9342}{{}^{96}_{37}\text{Rb}} + \underset{134.9060}{{}^{135}_{55}\text{Cs}} + \underset{8\times1.0087}{8\,{}^{1}_{0}\text{n}}$$

The molar mass in grams of each species is given for each particle. What is the energy change of this fission reaction?

Answer

-1.35×10^{13} J

A **nuclear reactor**: An apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes. is an apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes. Figure 15.5 "A Diagram of a Nuclear Power Plant for Generating Electricity" shows a simplified diagram of a nuclear reactor. The energy from the controlled nuclear reaction converts water into high-pressure steam, which is used to run turbines that generate electricity.

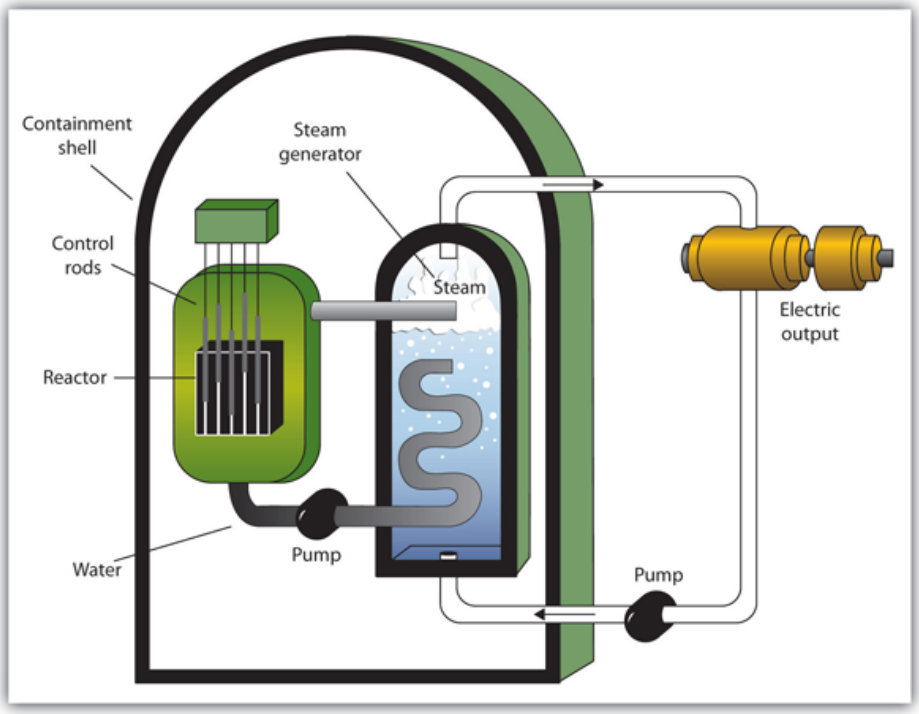


Figure 15.5 "A Diagram of a Nuclear Power Plant for Generating Electricity." The two main components of the power plant are the nuclear reactor itself and the steam-driven turbine and electricity generator.

Although the fission of large nuclei can produce different products, on average the fission of uranium produces two more free neutrons than were present to begin with. These neutrons can themselves stimulate other uranium nuclei to undergo fission, releasing yet more energy and even more neutrons, which can in turn induce even more uranium fission. A single neutron can thus begin a process that grows exponentially in a phenomenon called a **chain reaction**. An exponential growth in a phenomenon.:

$$1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow 64 \rightarrow 128 \rightarrow 256 \rightarrow 512 \rightarrow 1{,}024 \rightarrow 2{,}048 \rightarrow 4{,}096 \rightarrow 8{,}192 \rightarrow 16{,}384 \rightarrow \ldots$$

Because energy is produced with each fission event, energy is also produced exponentially and in an uncontrolled fashion. The quick production of energy creates an explosion. This is the mechanism behind the **atomic bomb**. A weapon that depends on a nuclear chain reaction to generate immense forces.. (The first controlled chain reaction was achieved on December 2, 1942, in an experiment supervised by Enrico Fermi in a laboratory underneath the football stadium at the University of Chicago.)

Although fairly simple in theory, an atomic bomb is difficult to produce, in part because uranium-235, the isotope that undergoes fission, makes up only 0.7% of natural uranium; the rest is mostly uranium-238, which does not undergo fission. (Remember that the radioactive process that a nucleus undergoes is characteristic of the isotope.) To make uranium useful for nuclear reactors, the uranium in uranium-235 must be *enriched* to about 3%. The enrichment of uranium is a laborious and costly series of physical and chemical separations. To be useful in an atomic bomb, uranium must be enriched to

70% or more. At lesser concentrations, the chain reaction cannot sustain itself, so no explosion is produced.

Fusion: A nuclear process in which small nuclei are combined into larger nuclei, releasing energy. is another nuclear process that can be used to produce energy. In this process, smaller nuclei are combined to make larger nuclei, with an accompanying release of energy. One example is hydrogen fusion, which makes helium:

$$4\,^{1}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + 2.58 \times 10^{12}\ \mathrm{J}$$

Notice that the amount of energy given off per mole of reactant is only one-tenth of the amount given off by the fission of 1 mol of uranium-235. On a mass (per gram) basis, however, hydrogen fusion gives off 10 times more energy than fission does. In addition, the product of fission is helium gas, not a wide range of isotopes (some of which are also radioactive) produced by fission.

Fusion occurs in nature: The sun and other stars use fusion as their ultimate energy source. Fusion is also the basis of very destructive weapons that have been developed by several countries around the world. However, one current goal is to develop a source of *controlled* fusion for use as an energy source. The practical problem is that to perform fusion, extremely high pressures and temperatures are necessary. Currently, the only known stable systems undergoing fusion are the interiors of stars. The conditions necessary for fusion can be created using an atomic bomb, but the resulting fusion is uncontrollable (and the basis for another type of bomb, a hydrogen bomb). Currently, researchers are looking for safe, controlled ways for producing useful energy using fusion.

Key Takeaways

- Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur.
- In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.

Exercises

Questions

1. According to Einstein’s equation, the conversion of 1.00 g of matter into energy generates how much energy?
2. How much matter needs to be converted to energy to supply 400 kJ of energy, the approximate energy of 1 mol of C–H bonds? What conclusion does this suggest about energy changes of chemical reactions?
3. In the spontaneous fission of lead-208, the following reaction occurs:

   $$^{208}\mathrm{Pb} \rightarrow {}^{129}\mathrm{I} + {}^{76}\mathrm{Cu} + 3\,^{1}\mathrm{n}$$

   For every mole of lead-208 that decays, 0.1002 g of mass is lost. How much energy is given off per mole of lead-208 reacted?
4. In the spontaneous fission of radium-226, the following reaction occurs:

$$^{226}\mathrm{Ra} \rightarrow {}^{156}\mathrm{Pm} + {}^{68}\mathrm{Co} + 2\,{}^{1}\mathrm{n}$$

For every mole of radium-226 that decays, 0.1330 g of mass is lost. How much energy is given off per mole of radium-226 reacted?

5. Recalculate the amount of energy from Exercise 3 in terms of the number of grams of lead-208 reacted.
6. Recalculate the amount of energy from Exercise 4 in terms of the number of grams of radium-226 reacted.
7. What is the energy change of this fission reaction? Masses in grams are provided.

$$\underset{241.0569}{{}^{241}\mathrm{Pu}} \rightarrow \underset{139.9106}{{}^{140}\mathrm{Ba}} + \underset{89.9077}{{}^{90}\mathrm{Sr}} + \underset{11\times1.0087}{11\,{}^{1}\mathrm{n}}$$

8. What is the energy change of this fission reaction? Masses in grams are provided.

$$\underset{247.0704}{{}^{247}\mathrm{Cm}} \rightarrow \underset{106.9099}{{}^{107}\mathrm{Ru}} + \underset{130.9085}{{}^{131}\mathrm{Te}} + \underset{9\times1.0087}{9\,{}^{1}\mathrm{n}}$$

9. The two rarer isotopes of hydrogen — deuterium and tritium — can also be fused to make helium by the following reaction:

$$^{2}\mathrm{H} + {}^{3}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + {}^{1}\mathrm{n}$$

In the course of this reaction, 0.01888 g of mass is lost. How much energy is given off in the reaction of 1 mol of deuterium and tritium?

10. A process called *helium burning* is thought to occur inside older stars, forming carbon:

$$3\,{}^{4}\mathrm{He} \rightarrow {}^{12}\mathrm{C}$$

If the reaction proceeds with 0.00781 g of mass lost on a molar basis, how much energy is given off?

11. Briefly describe how a nuclear reactor generates electricity.
12. Briefly describe the difference between how a nuclear reactor works and how a nuclear bomb works.
13. What is a chain reaction?
14. Why must uranium be enriched to supply nuclear energy?

Answers

1. 9.00×10^{13} J
3. 9.02×10^{12} J
5. 4.34×10^{10} J/g
7. -1.28×10^{13} J
9. 1.70×10^{12} J
11. A nuclear reactor controls a nuclear reaction to produce energy in usable amounts. The energy produced generates steam, which is used to turn a turbine that generates electricity for general use.
13. A process that generates more reaction pathways for each previous reaction.

End-of-Chapter Material

Additional Exercises

1. Given that many elements are metals, suggest why it would be unsafe to have radioactive materials in contact with acids.
2. Many alpha-emitting radioactive substances are relatively safe to handle, but inhaling radioactive dust can be very dangerous. Why?
3. Uranium can be separated from its daughter isotope thorium by dissolving a sample in acid and adding sodium iodide, which precipitates thorium(III) iodide:

   $$Th^{3+}(aq) + 3I^{-}(aq) \rightarrow ThI_3(s)$$

   If 0.567 g of Th^{3+} were dissolved in solution, how many millilitres of 0.500 M NaI(aq) would have to be added to precipitate all the thorium?
4. Thorium oxide can be dissolved in acidic solution:

   $$ThO_2(s) + 4H^{+} \rightarrow Th^{4+}(aq) + 2H_2O(\ell)$$

   How many millilitres of 1.55 M HCl(aq) are needed to dissolve 10.65 g of ThO_2?
5. Radioactive strontium is dangerous because it can chemically replace calcium in the human body. The bones are particularly susceptible to radiation damage. Write the nuclear equation for the beta emission of strontium-90.
6. Write the nuclear equation for the beta emission of iodine-131, the isotope used to diagnose and treat thyroid problems.
7. A common uranium compound is uranyl nitrate hexahydrate $[UO_2(NO_3)_2 \cdot 6H_2O]$. What is the formula mass of this compound?
8. Plutonium forms three oxides: PuO, PuO_2, and Pu_2O_3. What are the formula masses of these three compounds?
9. A banana contains 600 mg of potassium, 0.0117% of which is radioactive potassium-40. If 1 g of potassium-40 has an activity of 2.626×10^5 Bq, what is the activity of a banana?
10. Smoke detectors typically contain about 0.25 mg of americium-241 as part of the smoke detection mechanism. If the activity of 1 g of americium-241 is 1.26×10^{11} Bq, what is the activity of americium-241 in the smoke detector?
11. Uranium hexafluoride (UF_6) reacts with water to make uranyl fluoride (UO_2F_2) and HF. Balance the following reaction:

    $$UF_6 + H_2O \rightarrow UO_2F_2 + HF$$
12. The cyclopentadienyl anion ($C_5H_5^{-}$) is an organic ion that can make ionic compounds with positive ions of radioactive elements, such as Np^{3+}. Balance the following reaction:

    $$NpCl_3 + Be(C_5H_5)_2 \rightarrow Np(C_5H_5)_3 + BeCl_2$$
13. If the half-life of hydrogen-3 is 12.3 y, how much time does it take for 99.0% of a sample of hydrogen-3 to decay?
14. If the half-life of carbon-14 is 5,730 y, how long does it take for 10.0% of a sample of carbon-14 to decay?
15. Although bismuth is generally considered stable, its only natural isotope, bismuth-209, is estimated to have a half-life of 1.9×10^{19} y. If the universe is estimated to have a lifetime of 1.38×10^{10} y, what percentage of bismuth-209 has decayed over the lifetime of the universe? (Hint: Be prepared to use a lot of decimal places.)
16. The most common isotope of uranium (uranium-238) has a half-life of 4.5×10^9 y. If the universe is estimated to have a lifetime of 1.38×10^{10} y, what percentage of uranium-238 has decayed over the lifetime of the universe?
17. Refer to Table 15.1 “Average Annual Radiation Exposure (Approximate)” and separate the sources of radioactive exposure into voluntary and involuntary sources. What percentage of radioactive exposure is involuntary?
18. With reference to Table 15.1 and Exercise 17, suggest ways that a practical person can minimize exposure to radioactivity.

Answers

1. Acids can dissolve many metals; a spilled acid can lead to contamination.
3. 14.7 mL
5. $^{90}_{38}\mathrm{Sr} \rightarrow {}^{90}_{39}\mathrm{Y} + {}^{0}_{-1}\mathrm{e}$
7. 502.15 g/mol
9. about 18 Bq
11. $UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$
13. 81.7 y
15. about 0.000000005%
17. Radioactive atoms in the body, terrestrial sources, and cosmic sources are truly involuntary, which is about 27% of the total. Radon exposure, medical sources, consumer products, and even nuclear energy sources can be avoided.

Chapter 16. Organic Chemistry

All life on earth is ultimately based on photosynthesis — the process by which plants absorb CO_2 and H_2O from their environment and, in the presence of sunlight, convert those substances into a simple sugar (glucose) and ultimately into starches and other building blocks of life. The net photosynthesis chemical reaction is as follows:

$$6\,CO_2 + 6\,H_2O \xrightarrow{\text{light}} +C_6H_{12}O_6 + 6\,O_2$$

Oxygen is also a product of photosynthesis. Most forms of animal life (including people) depend on oxygen to breathe, which makes plants indispensable. Virtually all food sources come from plants, eaten either directly (as fruits, vegetables, or grains) or indirectly (as meat from animals that eat plants such as cattle, poultry, pigs, sheep, and goats). Plants are absolutely necessary for life to exist.

The net reaction for photosynthesis is misleadingly simple. A series of reactions, called *light-dependent reactions*, start by the absorption of light by pigments (not just chlorophyll, as commonly misunderstood) in plant cells. This is followed by a series of *light-independent reactions*, so named not because they happen in the dark but because they do not directly involve light. However, they involve the products of reactions stimulated by light, so they ultimately depend on light. The whole series of reactions involves many chemicals and enzymes, the breaking and making of chemical bonds, the transfer of electrons and H^+ ions, and other chemical processes. The elucidation of the actual steps of photosynthesis — a process still unduplicated artificially — is a major achievement of modern chemistry.

Figure 16.0 "Photosynthesis." In the presence of the sun, plants perform photosynthesis, the chemical reactions that convert CO_2 and H_2O to glucose. The reaction also produces O_2, which is necessary for animal life. Virtually all life on earth depends on photosynthesis.

Organic chemistry is the study of the chemistry of carbon compounds. Why focus on carbon? Carbon has properties that give its chemistry unparalleled complexity. It forms four covalent bonds, which give

it great flexibility in bonding. It makes fairly strong bonds with itself (a characteristic called *catenation*), allowing for the formation of large molecules; it also forms fairly strong bonds with other elements, allowing for the possibility of a wide variety of substances. No other element demonstrates the versatility of carbon when it comes to making compounds. So an entire field of chemistry is devoted to the study of the compounds and reactivity of one element.

Because of the potential for complexity, chemists have defined a rather rigorous system to describe the chemistry of carbon. We will introduce some of that system in this chapter. Should you continue your study of chemistry beyond this text, you will find a much larger world of organic chemistry than we can cover in a single chapter.

Media Attributions

Hydrocarbons

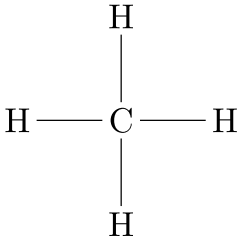
Learning Objectives

1. Identify alkanes, alkenes, alkynes, and aromatic compounds.
2. List some properties of hydrocarbons.

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons. **Aliphatic hydrocarbons** are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are aliphatic hydrocarbons that contain at least one C–C double bond, and **alkynes** are aliphatic hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called **cycloalkanes** (or cycloalkenes or cycloalkynes).

Aromatic hydrocarbons, such as benzene, are flat-ring systems that contain continuously overlapping *p* orbitals. Electrons in the benzene ring have special energetic properties that give benzene physical and chemical properties that are markedly different from alkanes. Originally, the term **aromatic** was used to describe this class of compounds because they were particularly fragrant. However, in modern chemistry the term aromatic denotes the presence of a very stable ring that imparts different and unique properties to a molecule.

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal alkanes*. They are named according to the number of C atoms in the chain. The smallest alkane is methane:



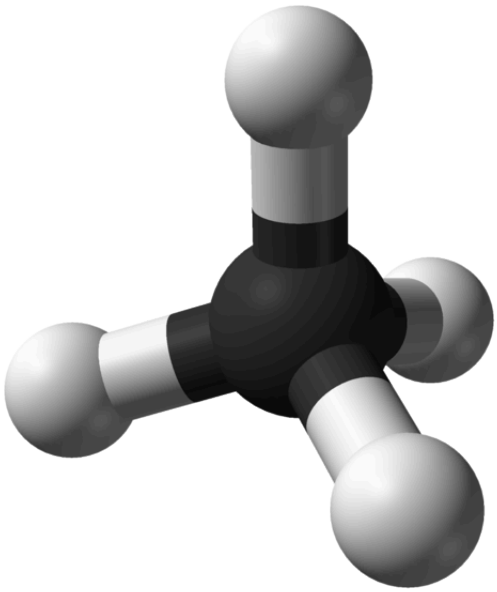
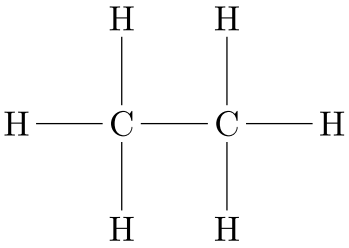


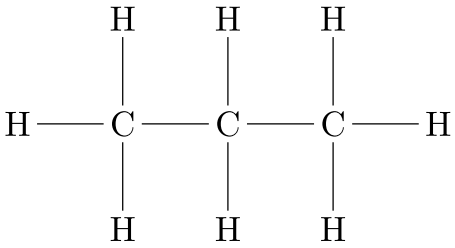
Figure 16.1 "Three-Dimensional Representation of Methane." The methane molecule is three-dimensional, with the H atoms in the positions of the four corners of a tetrahedron.

To make four covalent bonds, the C atom bonds to four H atoms, making the molecular formula for methane CH_4. The two-dimensional diagram for methane is misleading, however; the four covalent bonds that the C atom makes are oriented three-dimensionally toward the corners of a tetrahedron. A better representation of the methane molecule is shown in Figure 16.1 "Three-Dimensional Representation of Methane."

The next-largest alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule, whose formula is C_2H_6, is ethane:



Propane has a backbone of three C atoms surrounded by H atoms. You should be able to verify that the molecular formula for propane is C_3H_8:



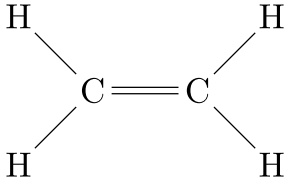
The diagrams we have seen so far representing alkanes are fairly simple Lewis structures. However, as molecules get larger, the Lewis structures become more and more complex. One way around this is to use a **condensed structure,** which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structure for ethane is CH_3CH_3, while it is $CH_3CH_2CH_3$ for propane. Table 16.1 “The First 10 Alkanes” gives the molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes.

Table 16.1 The First 10 Alkanes

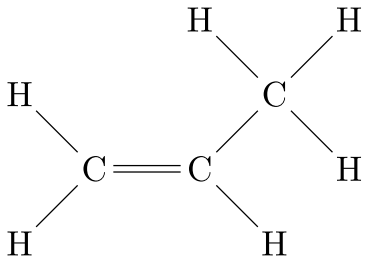
Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane

Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Alkenes have a C–C double bond. Because they have less than the maximum number of H atoms possible, they are called **unsaturated hydrocarbons**. The smallest alkene — ethene — has two C atoms and is also known by its common name, ethylene:

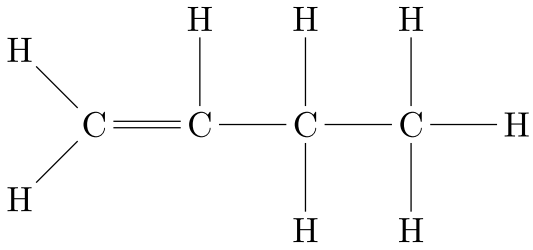


The next largest alkene — propene — has three C atoms with a C–C double bond between two of the C atoms. It is also known as propylene:

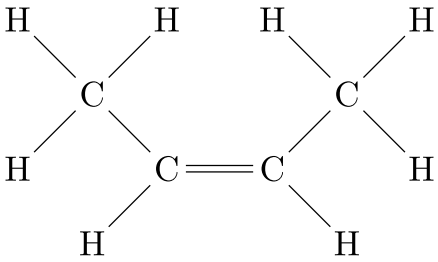


What do you notice about the names of alkanes and alkenes? The names of alkenes are the same as their corresponding alkanes except that the suffix (ending) is *–ene*, rather than *–ane*. Using a stem known as the *parent chain* to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry, as we shall see.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: choices. With four C atoms, the C–C double bond can go between the first and second C atoms, like so:



Or, the double bond can go between the second and third C atoms, like so:



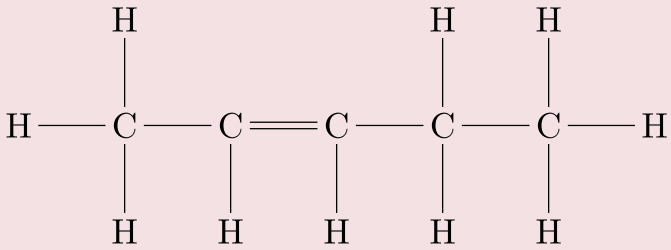
(A double bond between the third and fourth C atoms is the same as having it between the first and second C atoms, only flipped over.)

The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number between the parent-chain name and suffix is known as a **locant**, and indicates on which carbon the double bond originates. The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule *3-butene* would be incorrect. Numbers are common parts of organic chemical names because they indicate which C atom in a chain contains a distinguishing feature. When the double bond (or other functional group) is located on the first carbon, it is common practice for some authors to leave out the locant. For example, if butene were written without a locant, you should assume it refers to *1-butene*, not *2-butene*.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula — C_4H_8. Different molecules with the same molecular formula are called **isomers**. Isomers are common in organic chemistry and contribute to its complexity.

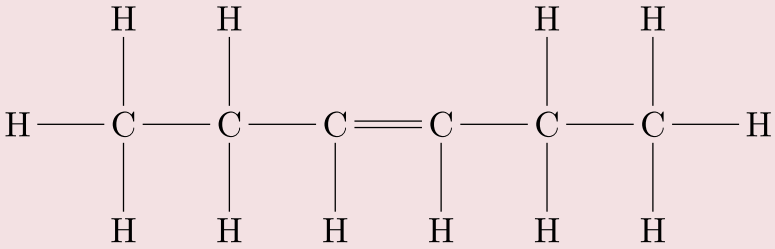
Example 16.1

Based on the names for the butene molecules, propose a name for this molecule.



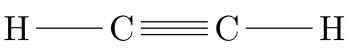
Solution
With five C atoms, we will use the *pent–* parent name, and with a C–C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number *2* because it is the lower possible label. So this molecule is named 2-pentene.

Test Yourself
Based on the names for the butene molecules, propose a name for this molecule.

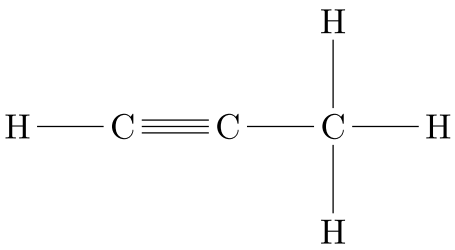


Answer
3-hexene

Alkynes, with a C–C triple bond, are named similarly to alkenes except their names end in *–yne*. The smallest alkyne is ethyne, which is also known as acetylene:

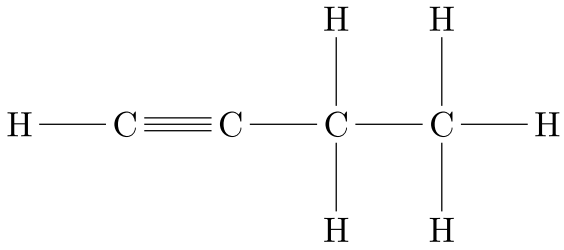


Propyne has this structure:

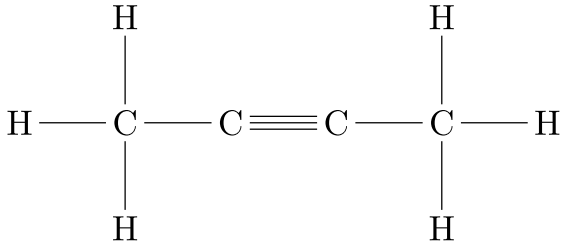


With butyne, we need to start numbering the position of the triple bond, just as we did with alkenes.

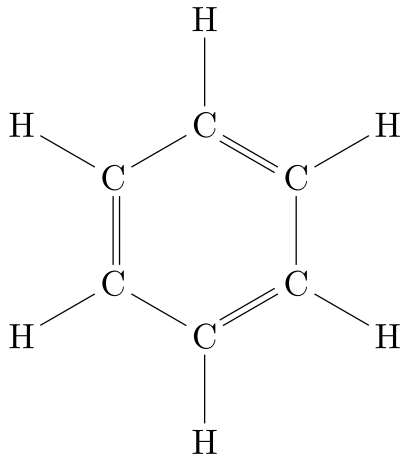
This is 1-butyne:



And this is 2-butyne:



Benzene is an aromatic compound composed of six C atoms in a ring, with alternating single and double C–C bonds:



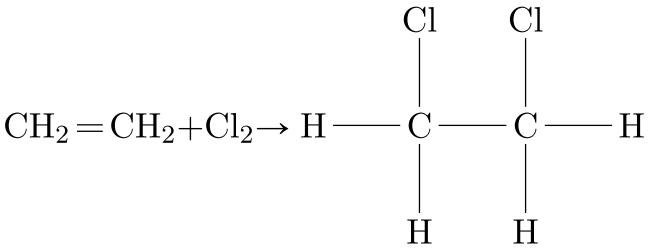
The alternating single and double C–C bonds give the benzene ring a special stability, and it does not react like an alkene as might be expected.

As fundamental as hydrocarbons are to organic chemistry, their properties and chemical reactions are rather mundane. Most hydrocarbons are nonpolar because of the close electronegativities of C and H atoms. As such, they dissolve only sparingly in H_2O and other polar solvents. Small hydrocarbons, such as methane and ethane, are gases at room temperature, while larger hydrocarbons, such as hexane and octane, are liquids. Even larger hydrocarbons, like hentriacontane ($C_{31}H_{64}$), are solids at room temperature and have a soft, waxy consistency.

Hydrocarbons are rather unreactive, but they do participate in some classic chemical reactions. One common reaction is substitution with a halogen atom by combining a hydrocarbon with an elemental halogen. Light is sometimes used to promote the reaction, such as this one between methane and chlorine:

$$\mathrm{CH_4 + Cl_2 \xrightarrow{light} CH_3Cl + HCl}$$

Halogens can also react with alkenes and alkynes, but the reaction is different. In these cases, the halogen molecules react with the C–C double or triple bond and attach onto each C atom involved in the multiple bonds. This reaction is called an **addition reaction**. One example is:



The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed at a reasonable pace:

$$\mathrm{CH_2{=}CH_2{+}H_2 \xrightarrow{metal\ catalyst} CH_3CH_3}$$

By far the most common reaction of hydrocarbons is combustion, which is the combination of a hydrocarbon with O_2 to make CO_2 and H_2O. The combustion of hydrocarbons is accompanied by a release of energy and is a primary source of energy production in our society (Figure 16.2 “Combustion”). The combustion reaction for gasoline, for example, which can be represented by C_8H_{18}, is as follows:

$$\mathrm{2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O + \sim 5060\ kJ}$$

Figure 16.2 "Combustion." The combustion of hydrocarbons is a primary source of energy in our society. This image depicts the first gas from the Oselvar module on the Ula platform in Norway on April 14, 2012.

Key Takeaways

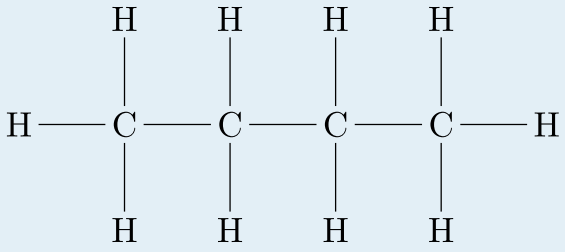
- The simplest organic compounds are hydrocarbons, which are composed of carbon and hydrogen.
- Hydrocarbons can be aliphatic or aromatic; aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes.
- The combustion of hydrocarbons is a primary source of energy for our society.

Exercises

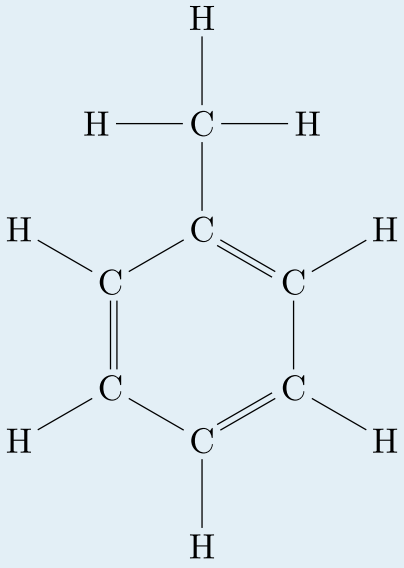
Questions

1. Define *hydrocarbon*. What are the two general types of hydrocarbons?
2. What are the three different types of aliphatic hydrocarbons? How are they defined?
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon. If it is aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

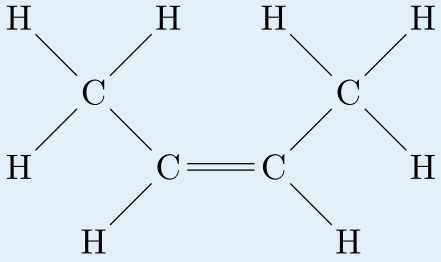
a.



b.

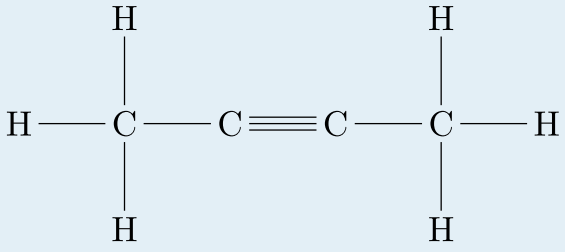


c.

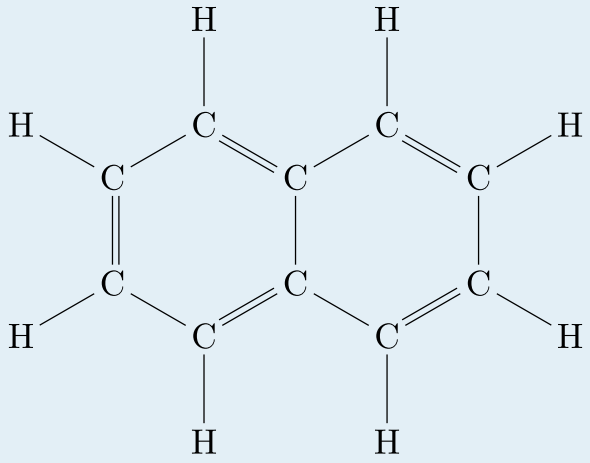


4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon. If it is aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

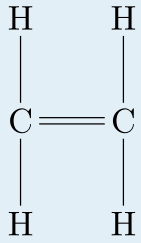
a.



b.

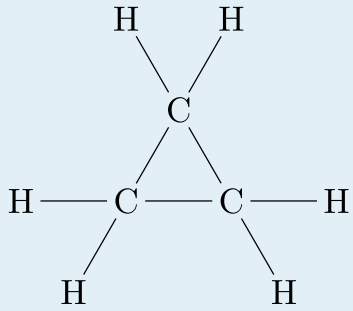


c.

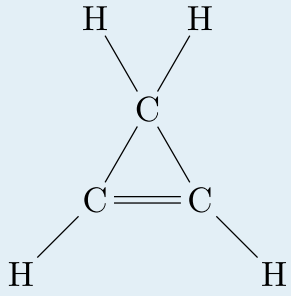


5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon. If it is aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

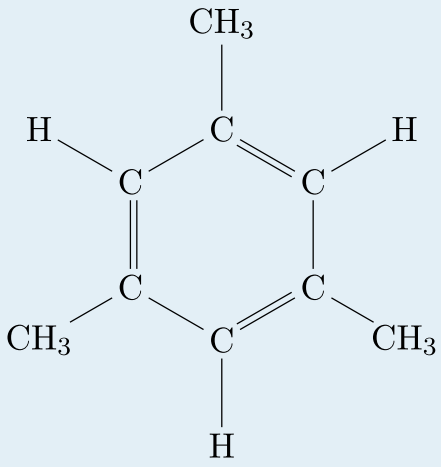
a.



b.

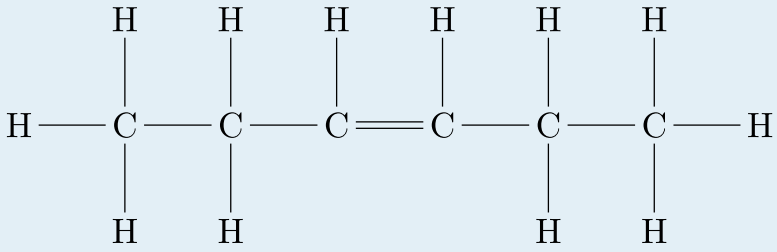


c.

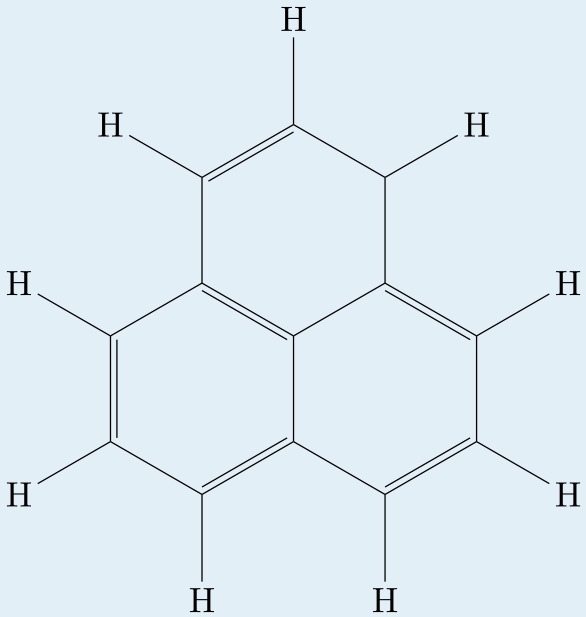


6. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon. If it is aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

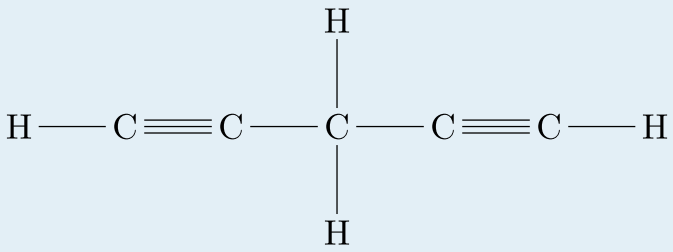
a.



b.



c.



7. Name and draw the structural formulas for the four smallest alkanes.
8. Name and draw the structural formulas for the four smallest alkenes.
9. What does the term *aromatic* imply about an organic molecule?
10. What does the term *normal* imply when used for alkanes?
11. Explain why you may see 1-propene written just as “propene.”
12. Explain why the name 3-butene is incorrect. What is the proper name for this molecule?
13. Name and draw the structural formula of each isomer of pentene.
14. Name and draw the structural formula of each isomer of hexyne.
15. Write a chemical equation for the reaction between methane and bromine.
16. Write a chemical equation for the reaction between ethane and chlorine.
17. Draw the structure of the product of the reaction of bromine with propene.
18. Draw the structure of the product of the reaction of chlorine with 2-butene.
19. Draw the structure of the product of the reaction of hydrogen with 1-butene.
20. Draw the structure of the product of the reaction of hydrogen with 2-pentene.
21. Write the balanced chemical equation for the combustion of heptane.
22. Write the balanced chemical equation for the combustion of nonane.

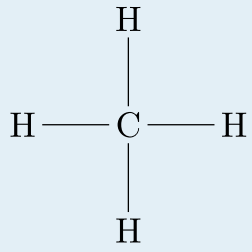
Answers

1. An organic compound composed of only carbon and hydrogen; aliphatic hydrocarbons and aromatic hydrocarbons

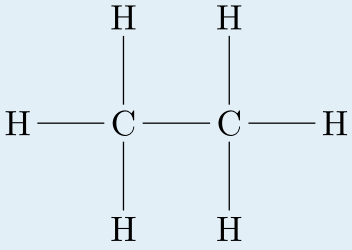
3. a. aliphatic; alkane
   b. aromatic
   c. aliphatic; alkene

5. a. aliphatic; alkane
   b. aliphatic; alkene
   c. aromatic

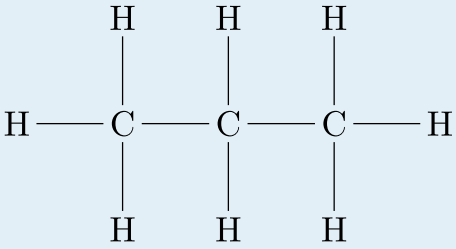
7.



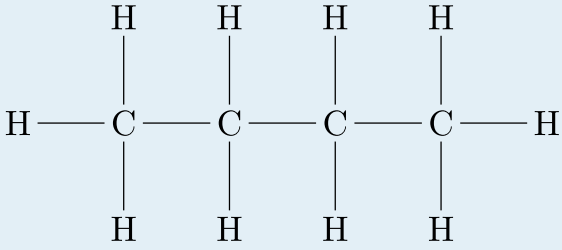
Methane



Ethane



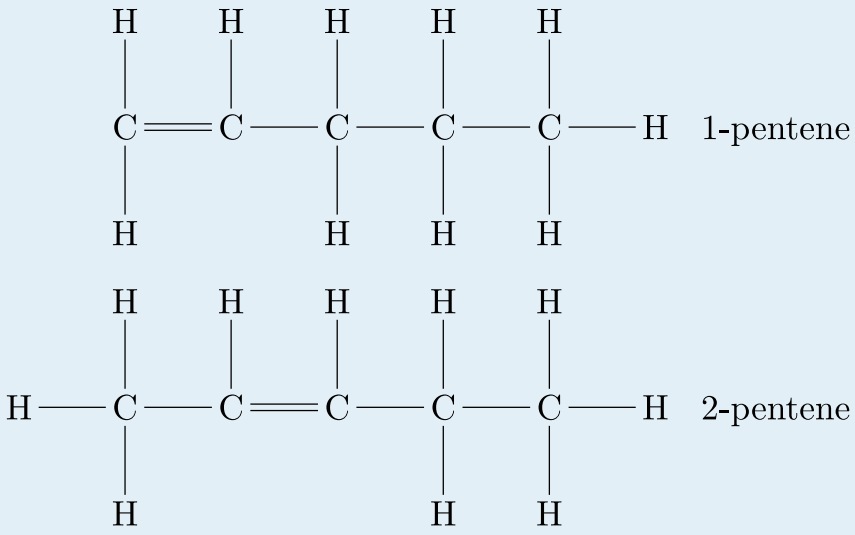
Propane



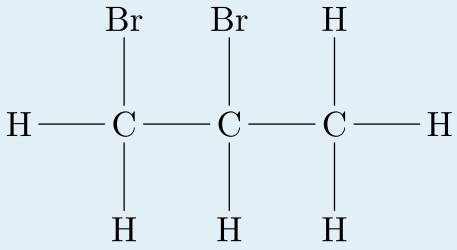
Butane

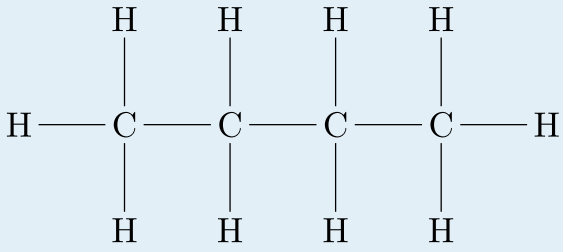
9. Aromatic means the molecule has a flat ring system with continuous *p* orbitals (e.g., benzene).

11. The 1 is not necessary, since the double bond is on the first carbon.

13. 

15. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$

17. 

19. 

21. $C_7H_{16} + 11\,O_2 \rightarrow 7\,CO_2 + 8\,H_2O$

Media Attributions

- "Methane-CRC-MW-3D-balls" © 2009 by Ben Mills is licensed under a Public Domain license
- "First gas from the Oselvar module on the Ula platform on April 14th, 2012" © 2012 by Varodrig is licensed under a CC BY-SA (Attribution-ShareAlike) license

Branched Hydrocarbons

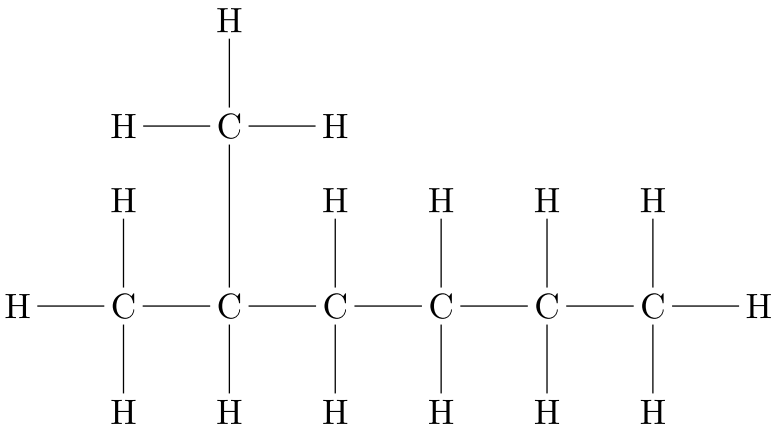
Learning Objectives

1. Name a branched hydrocarbon from its structure.
2. Draw the structural formula of a branched hydrocarbon from its name.

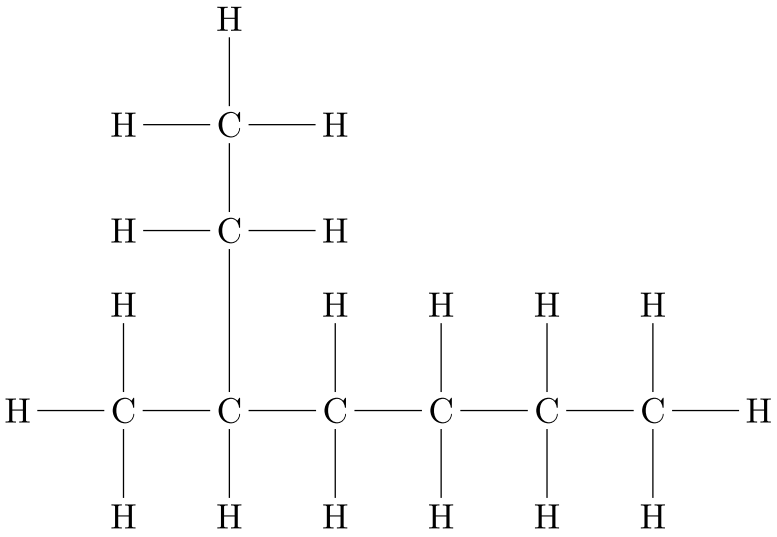
Not all hydrocarbons are straight chains. Many hydrocarbons have branches of C atoms attached to a chain; they are called **branched hydrocarbons**. These branched alkanes are isomers of straight-chain alkanes having the same number of C atoms. However, they are different compounds with different physical and chemical properties. As such, they need different names. How do we name **branched hydrocarbons**?

There are a series of rules for naming branched alkanes (and, ultimately, for all organic compounds). These rules make up the system of **nomenclature** for naming organic molecules. Worldwide, the International Union of Pure and Applied Chemistry (IUPAC) has developed the system of nomenclature for organic compounds, so these rules are sometimes called the IUPAC rules of nomenclature. By learning and applying these rules, you can name any organic compound when given its structure or determine the unique structure of a molecule from its name. You have already learned the basics of nomenclature — the names of the first 10 normal hydrocarbons. Here, we will add some steps to the procedure so you can name branched hydrocarbons.

First, given the structure of an alkane, identify the longest continuous chain of C atoms; this is known as the *parent chain*. Note that the longest chain may not be drawn in a straight line. The longest chain determines the parent name of the hydrocarbon. For example, in the molecule shown below, the longest chain of carbons has six C atoms. Therefore, it will be named as a hexane:



However, in this molecule, the longest chain of C atoms is not six, but seven, as shown. So this molecule will be named as a heptane:

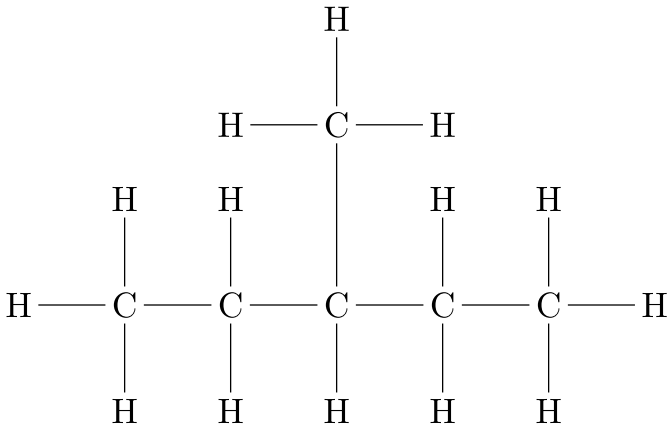


The next step is to identify the branches, or **substituents**, on the main chain. The names of the substituents, or *alkyl groups*, are derived from the names of the parent hydrocarbons; however, rather than having the ending *–ane*, the substituent name has the ending *–yl* (Table 16.2 “Substituent Names for the Five Smallest Substituents.”).

Table 16.2 Substituent Names for the Five Smallest Substituents

Substituent Formula	Number of C Atoms	Name of Substituent
CH_3	1	*methyl–*
CH_3CH_2	2	*ethyl–*
$CH_3CH_2CH_2$	3	*propyl–*
$CH_3CH_2CH_2CH_2$	4	*butyl–*
$CH_3CH_2CH_2CH_2CH_2$	5	*pentyl–*

To name a branched hydrocarbon, the name of the substituent is combined with the parent name of the hydrocarbon without spaces. However, there is likely one more step. The longest chain of the hydrocarbon must be numbered, and the **locant** (numerical position of the substituent) must be included to account for possible isomers. As with double and triple bonds, the main chain is numbered to give the substituent the lowest possible number. For example, in the alkane shown here, the longest chain is five C atoms long, so it is a pentane:



There is a one-carbon substituent on the third C atom, so there is a methyl group at position 3. We indicate the position using the number, which is followed by a hyphen, the substituent name, and the parent hydrocarbon name—in this case, 3-methylpentane. That name is specific to that particular hydrocarbon and no other molecule. Organic chemistry nomenclature is very specific following the general format shown in Figure 16.3 “IUPAC Nomenclature Guide.”

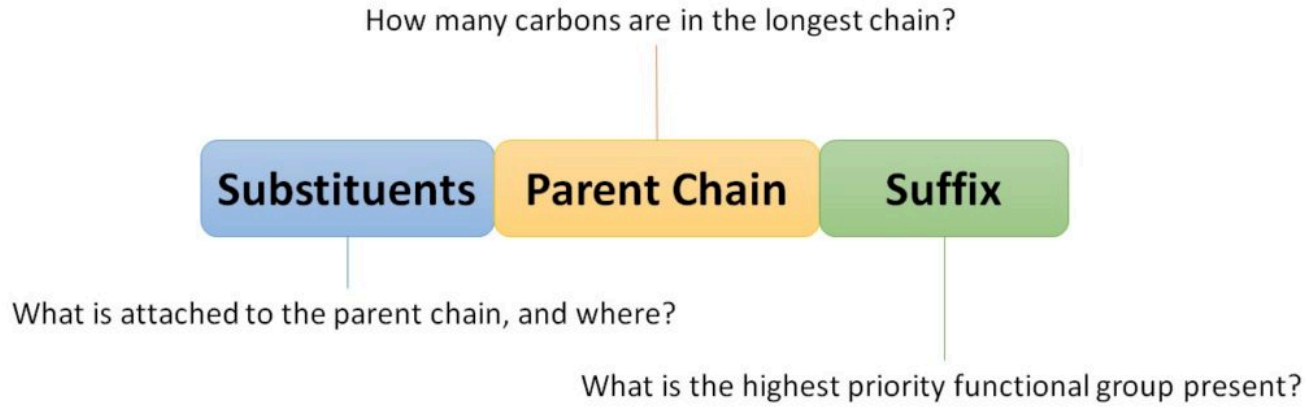
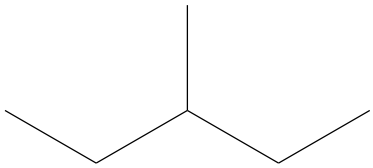


Figure 16.3 “IUPAC Nomenclature Guide.” Organic chemistry names are composed of a molecule’s substituents (what is attached to the parent chain, and where?), parent chain (how many carbons are in the longest chain?), and suffix (what is the highest priority functional group present?).

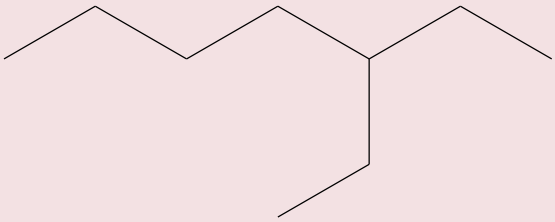
It is common to represent organic molecules using bond-line structures, where hydrogens are omitted for clarity, and carbons are represented by a corner or “kink” in the line. For example, 3-methylpentane can be written as:



It is understood that any unwritten covalent bonds are bonds with H atoms. With this understanding, we recognize that the structural formula for 3-methylpentane refers to a molecule with the formula C_6H_{14}.

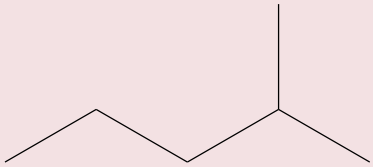
Example 16.2

Name this molecule.



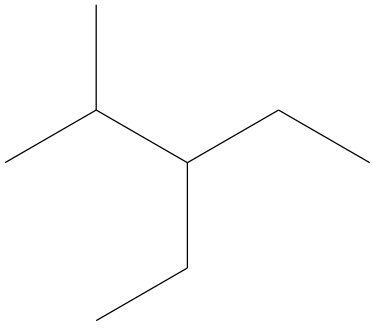
Solution
The longest continuous carbon chain has seven C atoms, so this molecule is named as a heptane. There is a two-carbon substituent on the main chain, which is an ethyl group. To give the substituent the lowest numbering, we number the chain from the *right* side and see that the substituent is on the third C atom. So this hydrocarbon is 3-ethylheptane.

Test Yourself
Name this molecule.



Answer
2-methylpentane

Branched hydrocarbons may have more than one substituent. If the substituents are different, give each substituent a number (using the smallest possible numbers) and list the substituents in alphabetical order, with the numbers separated by hyphens and no spaces in the name. So the molecule shown here is 3-ethyl-2-methylpentane:

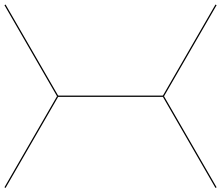


If the substituents are the same, use the name of the substituent only once, but use more than one number, separated by a comma. Also, put a numerical prefix before the substituent name that indicates the number of substituents of that type. The numerical prefixes are listed in Table 16.3 “Numerical Prefixes to Use for Multiple Substituents.” The number of the position values must agree with the numerical prefix before the substituent.

Table 16.3 Numerical Prefixes to Use for Multiple Substituents

Number of Same Substituent	Numerical Prefix
2	*di–*
3	*tri-*
4	*tetra–*
5	*penta–*
and so forth	and so forth

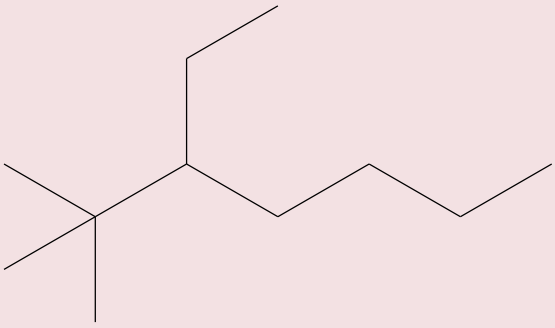
Consider this molecule:



The longest chain has four C atoms, so it is a butane. There are two substituents, each of which consists of a single C atom; they are methyl groups. The methyl groups are on the second and third C atoms in the chain (no matter which end the numbering starts from), so we would name this molecule 2,3-dimethylbutane. Note the comma between the numbers, the hyphen between the numbers and the substituent name, and the presence of the prefix *di–* before the *methyl*. Other molecules — even with larger numbers of substituents — can be named similarly.

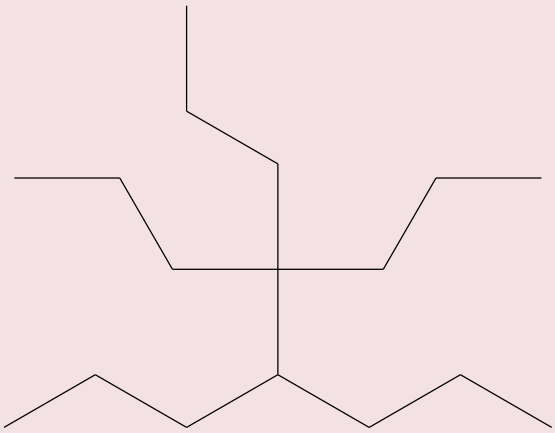
Example 16.3

Name this molecule.



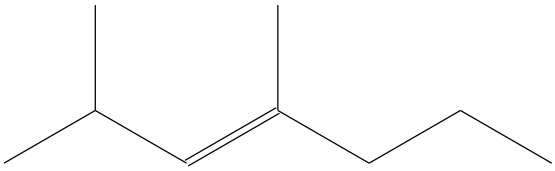
Solution
The longest chain has seven C atoms, so we name this molecule as a heptane. We find two one-carbon substituents on the second C atom and a two-carbon substituent on the third C atom. So this molecule is named 3-ethyl-2,2-dimethylheptane.

Test Yourself
Name this molecule.



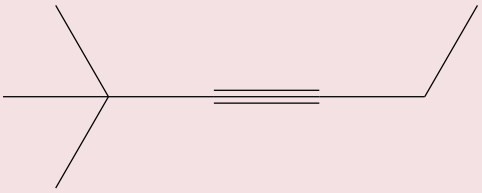
Answer
4,4,5-tripropyloctane

Alkenes and alkynes are named in a similar fashion. The biggest difference is that when identifying the longest carbon chain, it *must* contain the C–C double or triple bond. Furthermore, when numbering the main chain, the double or triple bond gets the lowest possible number. This means that there may be longer or higher-numbered substituents than would be allowed if the molecule were an alkane. For example, this molecule is 2,4-dimethyl-3-heptene (note the number and the hyphens that indicate the position of the double bond).



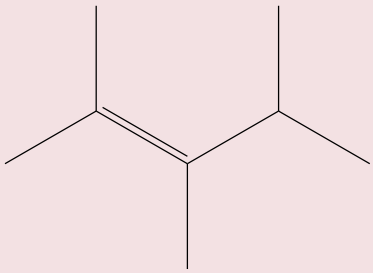
Example 16.4

Name this molecule.



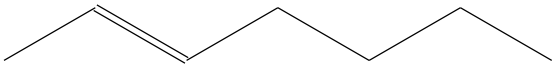
Solution
The longest chain that contains the C–C triple bond has six C atoms, so this is a hexyne molecule. The triple bond starts at the third C atom, so this is a 3-hexyne. Finally, there are two methyl groups on the chain; to give them the lowest possible number, we number the chain from the left side, giving the methyl groups the second position. So the name of this molecule is 2,2-dimethyl-3-hexyne.

Test Yourself
Name this molecule.

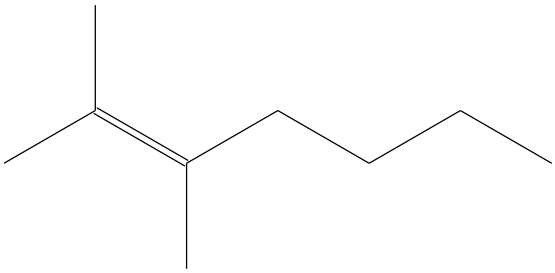


Answer
2,3,4-trimethyl-2-pentene

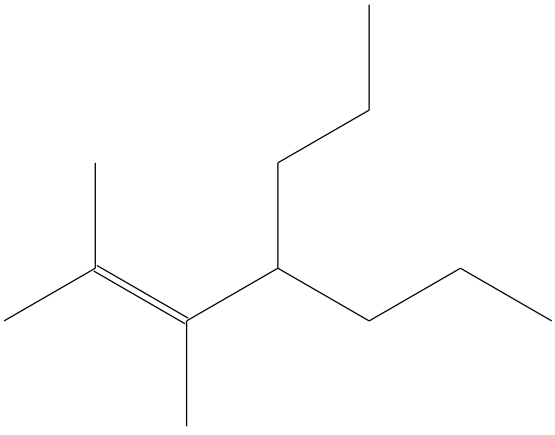
Once you master naming hydrocarbons from their given structures, it is rather easy to draw a structure from a given name. Just draw the parent chain with the correct number of C atoms (putting the double or triple bond in the right position, as necessary) and add the substituents in the proper positions. If you start by drawing the C atom backbone, you can go back and complete the structure by adding H atoms to give each C atom four covalent bonds. From the name 2,3-dimethyl-4-propyl-2-heptene, we start by drawing the seven-carbon parent chain with a double bond starting at the third carbon:



We add to this structure two one-carbon substituents on the second and third C atoms:



We finish the carbon backbone by adding a three-carbon propyl group to the fourth C atom in the parent chain:



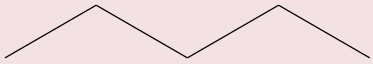
If we so choose, we can add H atoms to each C atom to give each carbon four covalent bonds, being

careful to note that the C atoms in the double bond already have an additional covalent bond. (How many H atoms do you think are required?[1])

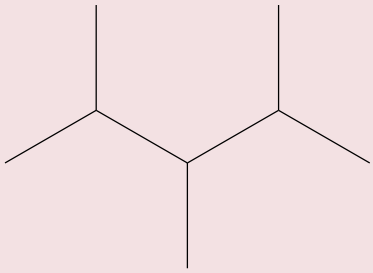
Example 16.5

Draw the carbon backbone for 2,3,4-trimethylpentane.

Solution
First, we draw the five-carbon backbone that represents the pentane chain:

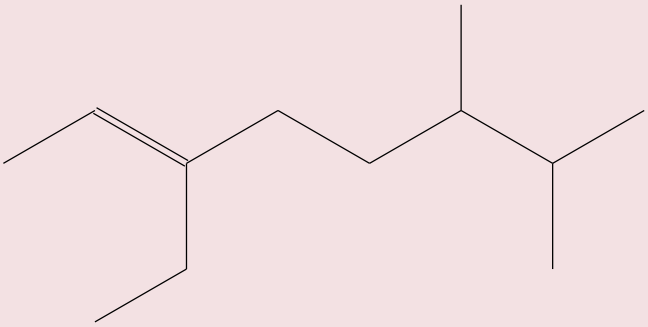


According to the name, there are three one-carbon methyl groups attached to the second, third, and fourth C atoms in the chain. We finish the carbon backbone by putting the three methyl groups on the pentane main chain:



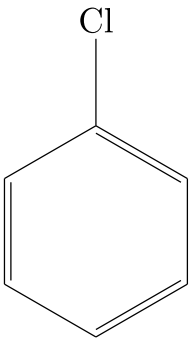
Test Yourself
Draw the carbon backbone for 3-ethyl-6,7-dimethyl-2-octene.

Answer

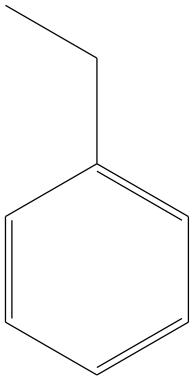


Naming substituted benzene molecules is straightforward. If there is only one substituent, the substituent is named as a side chain on a benzene molecule, like this:

1. There will need to be 24 H atoms to complete the molecule.

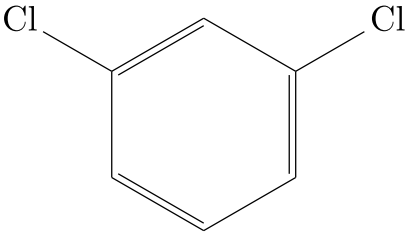


chlorobenzene

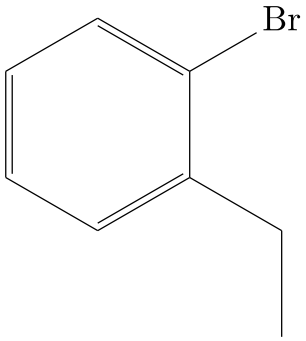


ethylbenzene

If there are two or more substituents on a benzene molecule, the relative positions must be numbered, just as an aliphatic chain of C atoms is numbered. The substituent that is first alphabetically is assigned position 1, and the ring is numbered in a circle to give the other substituents the lowest possible number(s).

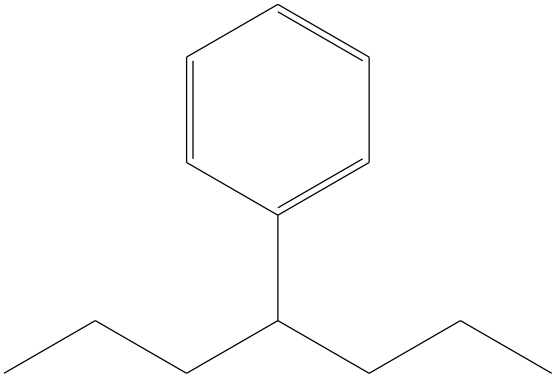


1,3-dichlorobenzene



1-bromo-2-ethylbenzene

If an aliphatic chain attached to a benzene ring has more carbons, the benzene ring is treated as a substituent and is given the name *phenyl-*. This molecule is 4-phenylheptane:



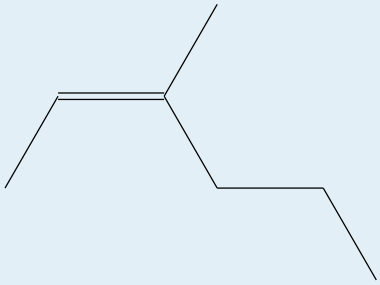
Key Takeaways

- A unique name can be given to branched hydrocarbons using IUPAC nomenclature rules.
- A unique structure can be drawn for the name of a given hydrocarbon.
- Bond-line diagrams are commonly used to represent organic molecules and simplify the structure by not showing C–H bonds or carbon atoms.

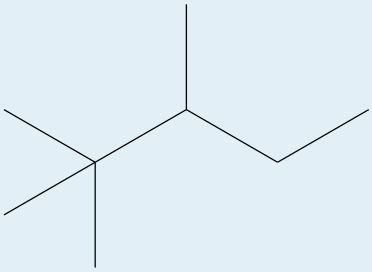
Exercises

Questions

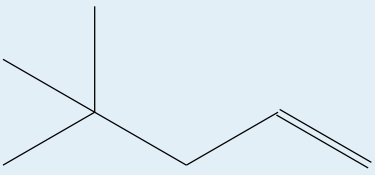
1. How does a branched hydrocarbon differ from a normal hydrocarbon?
2. How does a substituent get its unique name?
3. Name this molecule:



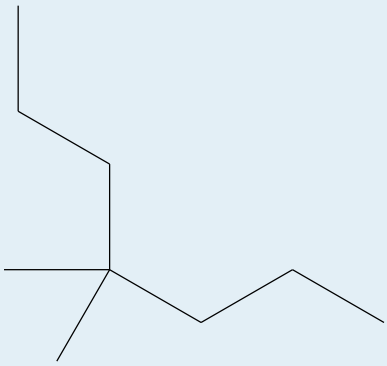
4. Name this molecule:



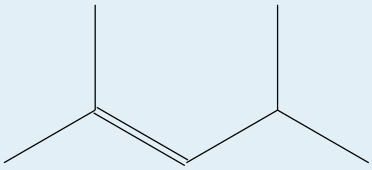
5. Name this molecule:



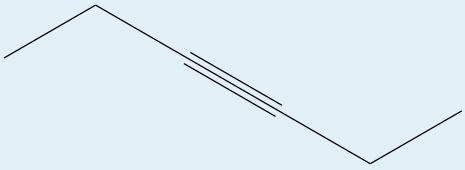
6. Name this molecule:



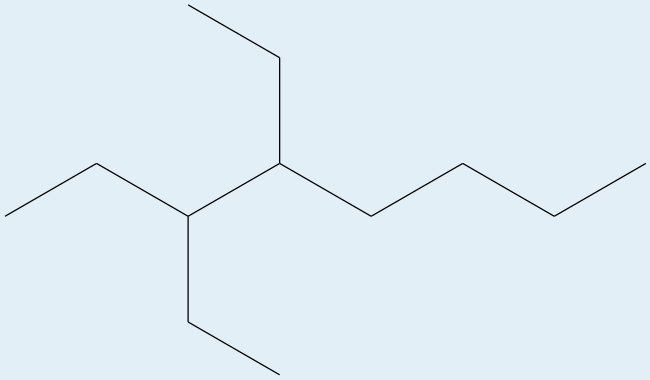
7. Name this molecule:



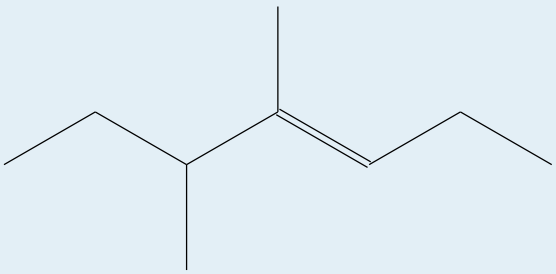
8. Name this molecule:



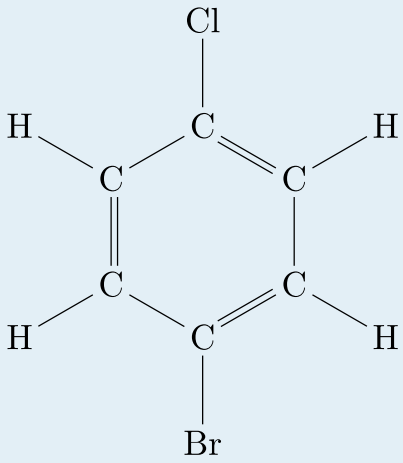
9. Name this molecule:



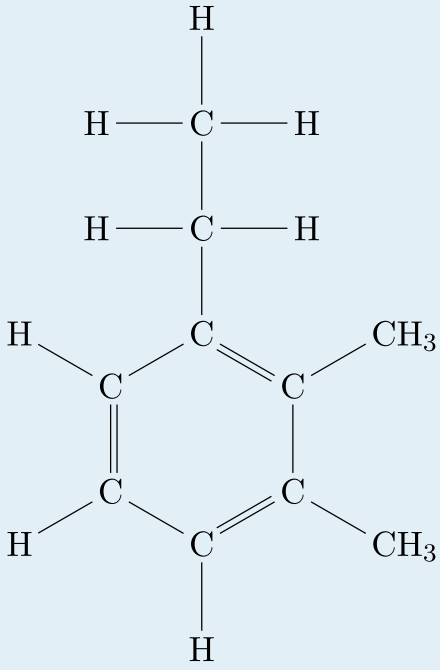
10. Name this molecule:



11. Name this molecule:



12. Name this molecule:



13. Draw the carbon backbone for each molecule.
    a. 3,4-diethyloctane
    b. 2,2-dimethyl-4-propylnonane
14. Draw the carbon backbone for each molecule.
    a. 3-ethyl-4-methyl-3-heptene
    b. 3,3-diethyl-1-pentyne
15. Draw the carbon backbone for each molecule.
    a. 4-ethyl-4-propyl-2-octyne
    b. 5-butyl-2,2-dimethyldecane
16. Draw the carbon backbone for each molecule.
    a. 3,4-diethylhexyne

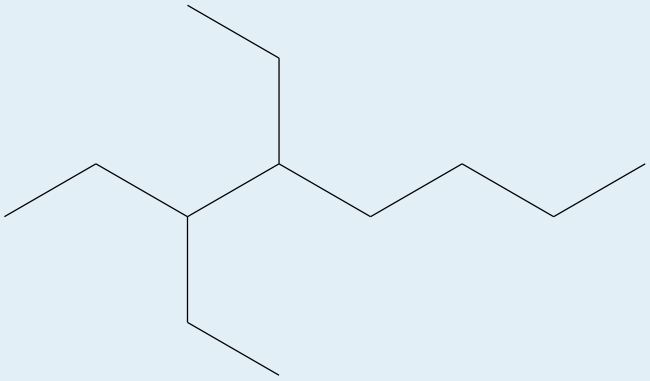
b. 4-propyl-3-ethyl-2-methyloctane

17. The name 2-ethylhexane is incorrect. Draw the carbon backbone and write the correct name for this molecule.
18. The name 3-butyl-7-methyloctane is incorrect. Draw the carbon backbone and write the correct name for this molecule.

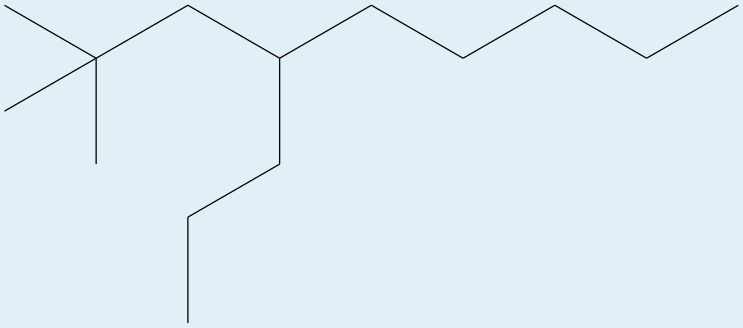
Answers

1. A branched hydrocarbon does not have all of its C atoms in a single row.
3. 3-methyl-2-hexene
5. 4,4-dimethyl-1-pentene
7. 2,4-dimethyl-2-pentene
9. 3,4-diethyloctane
11. 1-bromo-4-chlorobenzene

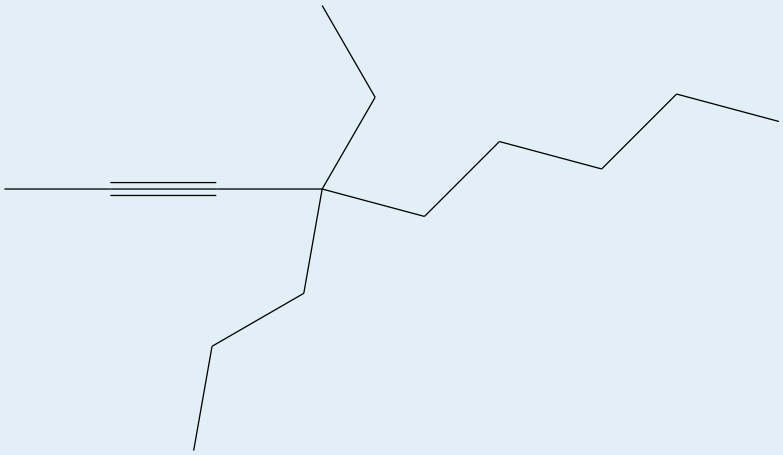
a.



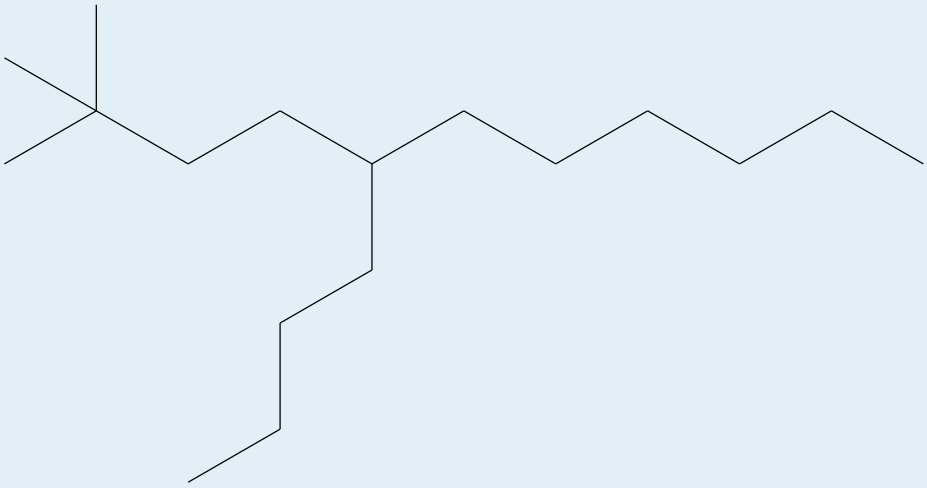
b.

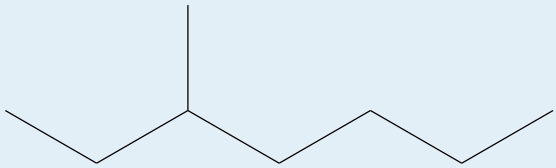


a.



b.





17. 3-methylheptane

Alkyl Halides and Alcohols

Learning Objectives

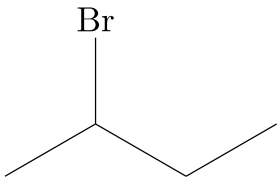
1. Define *functional group*.
2. Identify and name a simple alkyl halide.
3. Identify and name a simple alcohol.
4. Predict the product(s) of an elimination reaction of an alkyl halide or an alcohol.

A **functional group** is any collection of atoms and/or bonds with certain characteristic chemical reactions. We have already seen two functional groups: the C–C double bond and the C–C triple bond. They undergo certain characteristic chemical reactions — for example, the addition of a halogen across the multiple bond.

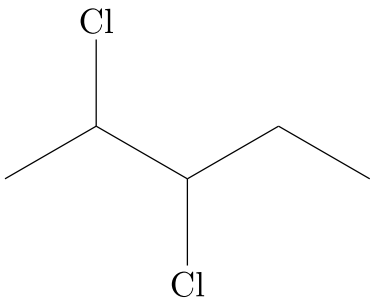
The presence of a halogen atom (F, Cl, Br, or I; X is used to represent any halogen atom) is one of the simplest functional groups. Organic compounds that contain a halogen atom are called **alkyl halides**. We have already seen some examples of alkyl halides when the addition of halogens across double and triple bonds was introduced in the section “Branched Hydrocarbons”; the products of these reactions were alkyl halides.

A simple alkyl halide can be named like an ionic salt, first by stating the name of the parent alkane as a substituent group (with the *–yl* suffix) and then the name of the halogen as if it were the anion. So CH_3Cl has the common name of methyl chloride, while CH_3CH_2Br is ethyl bromide and $CH_3CH_2CH_2I$ is propyl iodide. However, this system is not ideal for more complicated alkyl halides.

The systematic way of naming alkyl halides is to name the halogen as a substituent, just like an alkyl group, and use numbers to indicate the position of the halogen atom on the main chain. The name of the halogen as a substituent comes from the stem of the element’s name plus the ending *–o*, so the substituent names are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. If there is more than one of a certain halogen, we use numerical prefixes to indicate the number of each kind, just as with alkyl groups. For example, this molecule is 2-bromobutane.



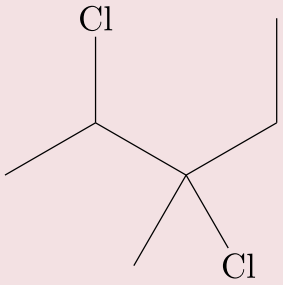
And this molecule is 2,3-dichloropentane:



If alkyl groups are present, the substituents are listed alphabetically. Numerical prefixes are ignored when determining the alphabetical ordering of substituent groups.

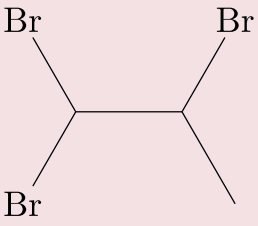
Example 16.6

Name this molecule.



Solution
The longest carbon chain has five C atoms, so the molecule is a pentane. There are two chlorine substituents located on the second and third C atoms, with a one-carbon methyl group on the third C atom as well. The correct name for this molecule is 2,3-dichloro-3-methylpentane.

Test Yourself
Name this molecule.



Answer
1,1,2-tribromopropane

Another simple functional group is the covalently bonded OH group. This is the **alcohol** functional group. It is not the hydroxide ion; in organic chemistry, rather than being present as a negatively charged species, it is a covalently bonded functional group.

Like alkyl halides, alcohols have a common naming system and a more formal system. The common system is similar to that of alkyl halides: name the alkyl group attached to the OH group, ending with the suffix *–yl*, and add the word *alcohol* as a second word. So CH_3OH is methyl alcohol, CH_3CH_2OH is ethyl alcohol, and $CH_3CH_2CH_2OH$ is propyl alcohol.

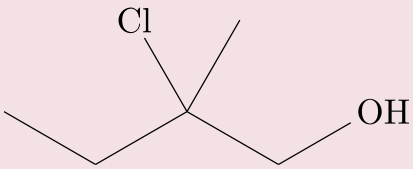
As with alkyl halides, though, this system is limited (although for smaller alcohols, it is very common in everyday usage). The formal system of naming uses the name of the hydrocarbon containing the OH group and having the correct number of C atoms, dropping the final *–e* of the name and appending the suffix *–ol*. Thus CH_3OH is methanol and CH_3CH_2OH is ethanol. For larger alcohol molecules, we use a number to indicate the position of the OH group on the longest carbon chain, similar to the number needed for alkenes and alkynes. Again, the carbon chain is numbered to give the OH group the lowest number, no matter how large the other numbers are. So $CH_3CH_2CH_2OH$ is 1-propanol, while $CH_3CHOHCH_3$ is 2-propanol.

Figure 16.4 "Isopropyl Alcohol." What you find labelled "isopropyl alcohol" in a medicine cabinet is more formally called "2-propanol."

Another acceptable way of naming an alcohol — especially a more complicated molecule — is to name the OH group as the hydroxy substituent and give it a numerical position like an alkyl group or a halogen atom. Thus 2-propanol would be called 2-hydroxypropane by this convention.

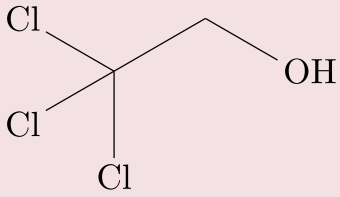
Example 16.7

Name this molecule as an alcohol and as a substituted alkane.



Solution
The longest carbon chain containing the OH group has four C atoms, so the parent hydrocarbon is butane. Because the OH group is on the first C atom, it is 1-butanol. There is a methyl group on the second C atom, as well as a Cl atom, so the formal name for this alcohol is 2-chloro-2-methyl-1-butanol. If naming the alcohol group as a substituent, it would be 2-chloro-1-hydroxy-2-methylbutane.

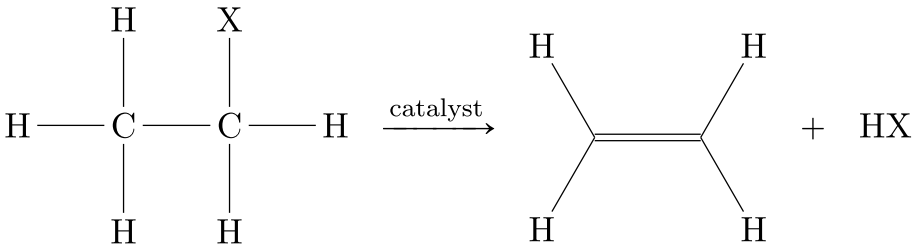
Test Yourself
Name this molecule as an alcohol and as a substituted alkane.



Answer
2,2,2-trichloroethanol

Most alkyl halides are insoluble in H_2O. Smaller alcohols, however, are very soluble in H_2O because these molecules can engage in hydrogen bonding with H_2O molecules. For larger molecules, however, the polar OH group is overwhelmed by the nonpolar alkyl part of the molecule. While methanol is soluble in H_2O in all proportions, only about 2.6 g of pentanol will dissolve in 100 g of H_2O. Larger alcohols have an even lower solubility in H_2O.

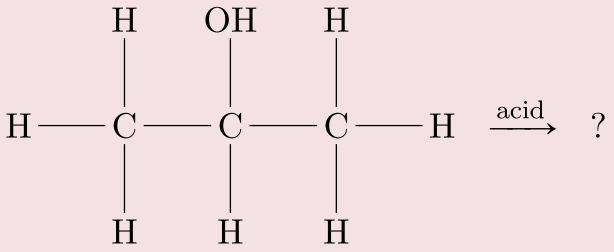
One reaction common to alcohols and alkyl halides is the **elimination reaction**, which is the removal of the functional group (either X or OH) and an H atom from an adjacent carbon. The general reaction can be written this way:



where X can represent either the X or the OH group. The biggest difference between elimination in alkyl halides and elimination in alcohols is the identity of the catalyst: for alkyl halides, the catalyst is a strong base; for alcohols, the catalyst is a strong acid. For compounds in which there are H atoms on more than one adjacent carbon, a mixture of products results.

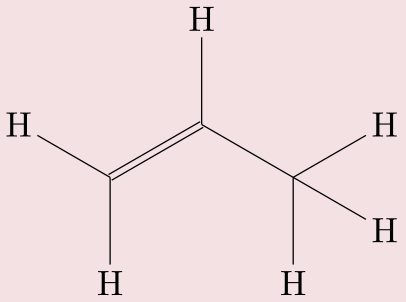
Example 16.8

Predict the organic product(s) of this reaction.



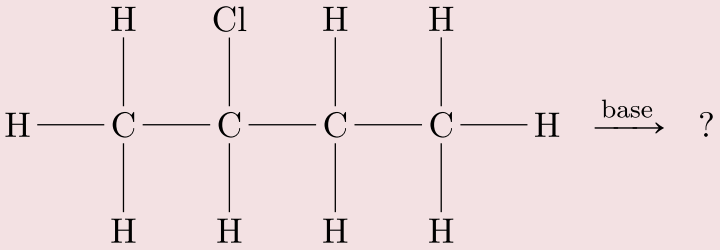
Solution

Under these conditions, an HOH (otherwise known as H_2O) molecule is eliminated, and an alkene forms. It does not matter which adjacent carbon loses the H atom; in either case the product will be propene:



Test Yourself

Predict the organic product(s) of this reaction.



Answer

1-butene and 2-butene

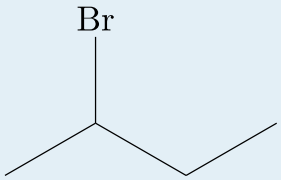
Key Takeaways

- Alkyl halides have a halogen atom as a functional group.
- Alcohols have an OH group as a functional group.
- Nomenclature rules allow us to name alkyl halides and alcohols.
- In an elimination reaction, a double bond is formed as an HX or an HOH molecule is removed.

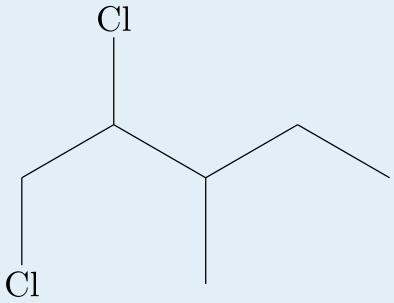
Exercises

Questions

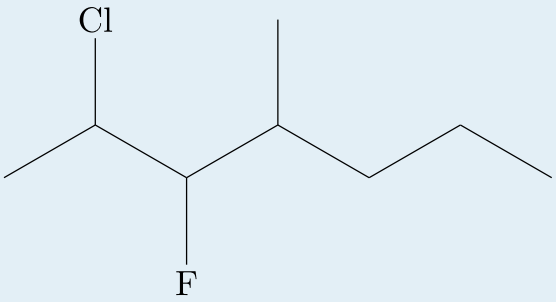
1. Define *functional group* and give two examples.
2. What is elimination? How does it differ for alkyl halides and alcohols?
3. Name this molecule.



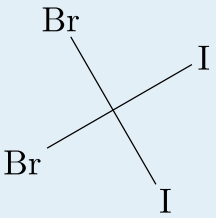
4. Name this molecule.



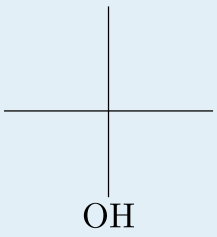
5. Name this molecule.



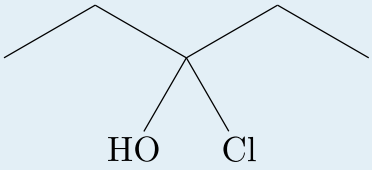
6. Name this molecule.



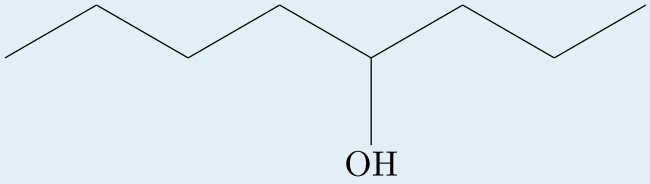
7. Name this molecule.



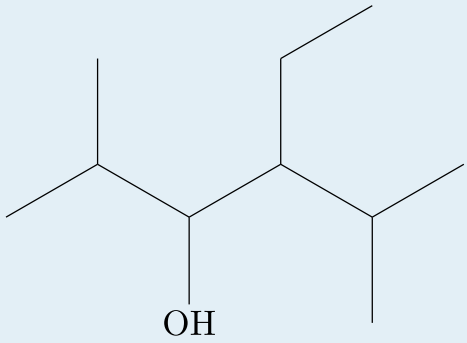
8. Name this molecule.



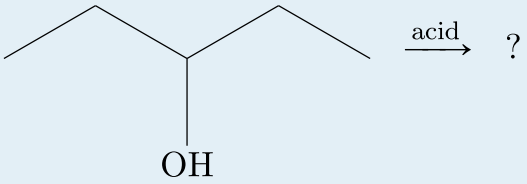
9. Name this molecule.



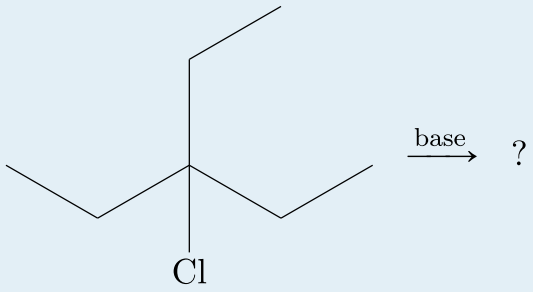
10. Name this molecule.



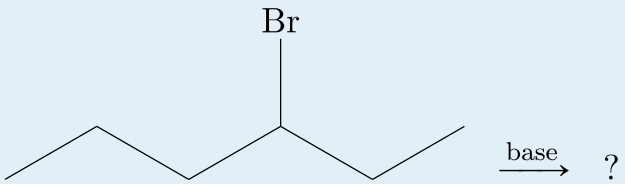
11. Predict the product(s) of this elimination reaction.



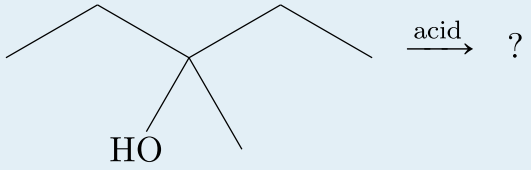
12. Predict the product(s) of this elimination reaction.



13. Predict the product(s) of this elimination reaction.



14. Predict the product(s) of this elimination reaction.



Answers

1. A group of atoms with a certain reactivity; halogen atoms and alcohol groups (answers will vary).
3. 2-bromobutane
5. 2-chloro-3-fluoro-4-methylheptane
7. 2-methyl-2-propanol
9. 4-octanol
11. 2-pentene
13. 2-hexene and 3-hexene

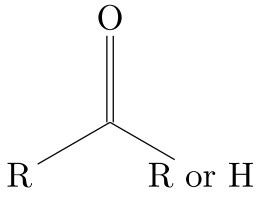
Media Attributions

Other Oxygen-Containing Functional Groups

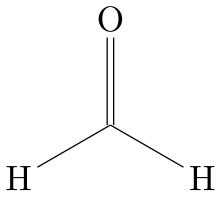
Learning Objectives

1. Identify the aldehyde, ketone, acid, ester, and ether functional groups.
2. Use proper naming conventions for aldehyde, ketone, carboxylic acid, and ester- and ether-containing molecules.

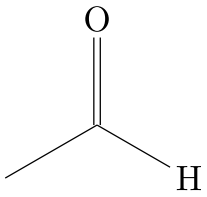
There are other functional groups that contain oxygen atoms. A **carbonyl group** is formed when an O atom and a C atom are joined by a double bond. In this diagram, the R group represents any hydrocarbon chain:



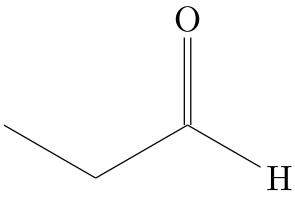
If one bond of the carbonyl group is made to a hydrogen atom, then the molecule is further classified as an **aldehyde**. When naming aldehydes, the main chain of C atoms must include the carbon in the carbonyl group, which is numbered as position 1 in the carbon chain. The parent name of the hydrocarbon is used, but the suffix *–al* is appended. (Do not confuse *–al* with *–ol*, which is the suffix used for alcohols.) So we have:



methanal



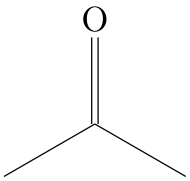
ethanal



propanal

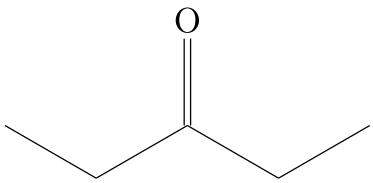
Methanal has a common name with which you may be familiar: formaldehyde. The main thing to note about aldehydes is that the carbonyl group is at the *end* of a carbon chain.

A carbonyl group in the middle of a carbon chain implies that both remaining bonds of the carbonyl group are made to C atoms. This type of molecule is called a **ketone**. Despite the fact that aldehydes and ketones have the same carbonyl group, they have different chemical and physical properties and are properly grouped as two different types of compounds. The smallest ketone has three C atoms in it. When naming a ketone, we take the name of the parent hydrocarbon and change the suffix to *–one*:



propanone

The common name for propanone is acetone. With larger ketones, we must use a locant number to indicate the position of the carbonyl group just before the suffix, as we did with alkenes and alkynes:



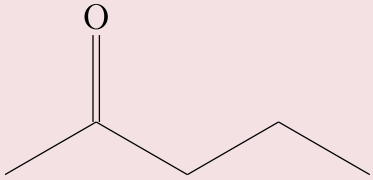
3-pentanone

There is a non-IUPAC way to name ketones that is commonly used as well: name the alkyl groups that are attached to the carbonyl group and add the word *ketone* to the name. So propanone can also be called dimethyl ketone, while butan-2-one is called methyl ethyl ketone.

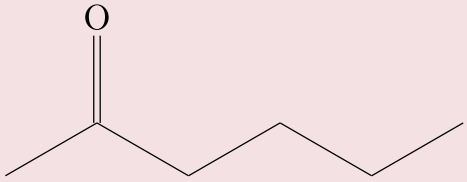
Example 16.9

Draw the structure of 2-pentanone.

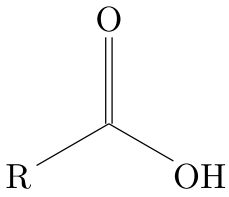
Solution
This molecule has five C atoms in a chain, with the carbonyl group on the second C atom. Its structure is:



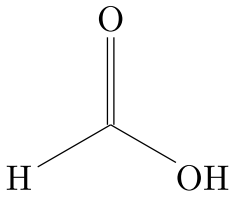
Test Yourself
Draw the structure of methyl butyl ketone.
Answer



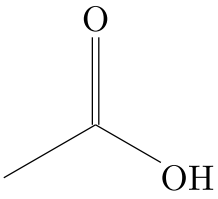
The combination of a carbonyl functional group and a hydroxyl group makes the **carboxyl group**.



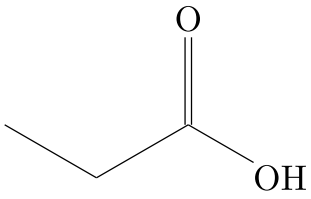
Molecules with a carboxyl group are called **carboxylic acids**. As with aldehydes, the functional group in carboxylic acids is at the end of a carbon chain. Also as with aldehydes, the C atom in the functional group is counted as one of the C atoms that defines the parent hydrocarbon name. To name carboxylic acids, the parent name of the hydrocarbon is used, but the suffix *–oic acid* is added:



methanoic acid



ethanoic acid

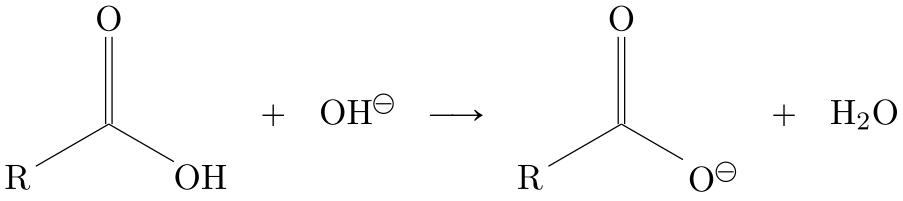


propanoic acid

Methanoic acid and ethanoic acid are also called formic acid and acetic acid, respectively. Formic acid is the compound that makes certain ant bites sting, while acetic acid is the active substance in vinegar.

How acidic are carboxylic acids? It turns out that they are not very acidic. No carboxylic acid is on the list of strong acids (Table 12.1 “Strong Acids and Bases”). (For more information about strong acids, see the section “Strong and Weak Acids and Bases and Their Salts.”) This means that all carboxylic acids are weak acids. A 1 M solution of formic acid is only about 1.3% dissociated into H^+ ions and formate ions, while a similar solution of acetic acid is ionized by about only 0.4%. Some carboxylic acids are stronger — for example, trichloroacetic acid is about 45% dissociated in aqueous solution. But no carboxylic acid approaches the 100% dissociation amount required by the definition of a strong acid.

As their name suggests, however, carboxylic acids do act like acids in the presence of bases. The H atom in the carboxyl group comes off as the H^+ ion, leaving a **carboxylate** ion:

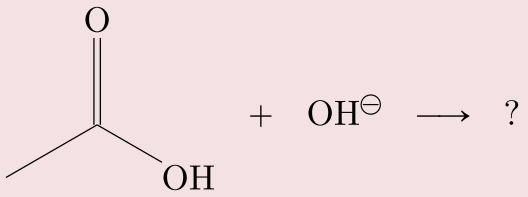


carboxylate ion

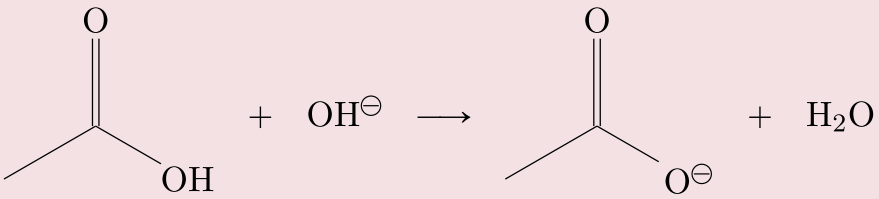
Carboxylate ions are named from the acid name: the *–oic acid* is replaced with *–oate* to name the ion.

Example 16.10

Complete the chemical reaction. Can you name the carboxylate ion formed?

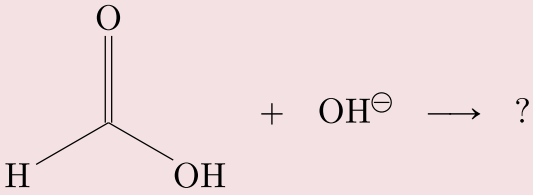


Solution
The OH^- ion removes the H atom that is part of the carboxyl group:

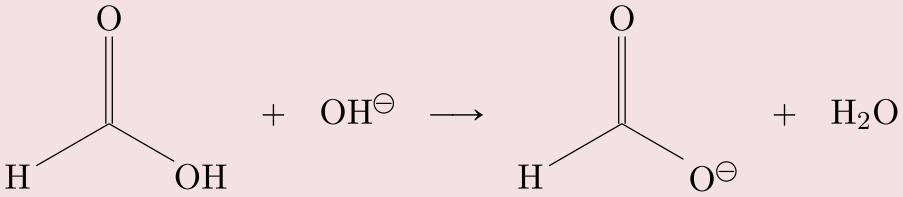


The carboxylate ion, which has the condensed structural formula $CH_3CO_2^-$, is the ethanoate ion, but it is commonly called the acetate ion.

Test Yourself
Complete the chemical reaction. Can you name the carboxylate ion formed?

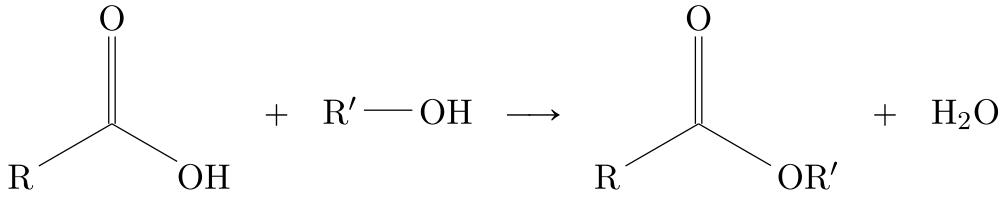


Answer



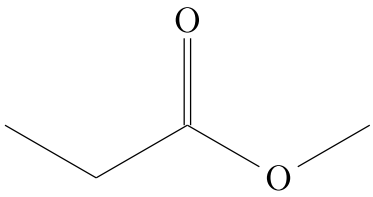
The ion is the methanoate ion, which is commonly called the formate ion.

One reaction to consider is that of a carboxylic acid and an alcohol. When combined under the proper conditions, a water molecule will be removed, and the remaining pieces will combine to form a new functional group — the **ester** group:



ester

Note how the acid molecule contributes one alkyl side (represented by R), while the alcohol contributes the other side (represented by R′). Esters are named using the alkyl group name from the alcohol plus the carboxylate name from the acid—for example, this molecule is called methyl propanoate:



methyl propanoate

Chemistry Is Everywhere: Esters, Fragrances, and Flavourings

Esters are very interesting compounds, in part because many have pleasant odours and flavours. (Remember, never taste anything in the chemistry lab!) Many esters occur naturally and contribute to the fragrance of flowers and the taste of fruits. Other esters are synthesized industrially and are added to food products to improve their smell or taste. It is likely that if you eat a product whose ingredients include artificial flavourings, those flavourings are esters. Here are some esters and their uses, thanks to their odours, flavours, or both:

Ester	**Tastes/Smells Like**
allyl hexanoate	pineapple
benzyl acetate	pear
butyl butanoate	pineapple
ethyl butanoate	banana
ethyl hexanoate	pineapple
ethyl heptanoate	apricot
ethyl pentanoate	apple
isobutyl formate	raspberry
isobutyl acetate	pear
methyl phenylacetate	honey
nonyl caprylate	orange
pentyl acetate	apple
propyl ethanoate	pear
propyl isobutyrate	rum

Finally, the **ether** functional group is an O atom that is bonded to two organic groups:

$$\mathrm{R{-\!\!-}O{-\!\!-}R'}$$

The two R groups may be the same or different. Naming ethers is like the alternate way of naming ketones. In this case, the R groups are named sequentially, and the word *ether* is appended. The molecule CH_3OCH_3 is dimethyl ether, while $CH_3OCH_2CH_3$ is methyl ethyl ether. Diethyl ether, another ether, was once used as an anaesthetic, but its flammability

and toxicity caused it to fall out of favor. Smaller ether molecules that are liquids at room temperature are common solvents for organic chemical reactions.

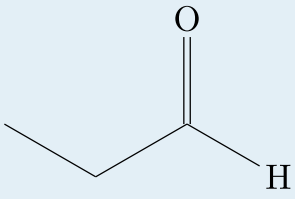
Key Takeaways

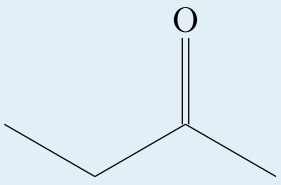
- Aldehydes, ketones, carboxylic acids, esters, and ethers have oxygen-containing functional groups.
- IUPAC naming can be used for aldehyde, ketone, carboxylic acid, and ester- and ether-containing molecules.

Exercises

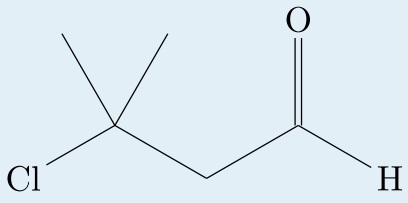
Questions

1. Name a similarity between the functional groups found in aldehydes and ketones. Can you name a difference between them?
2. Explain how a carboxylic acid is used to make an ester.
3. Name each molecule.

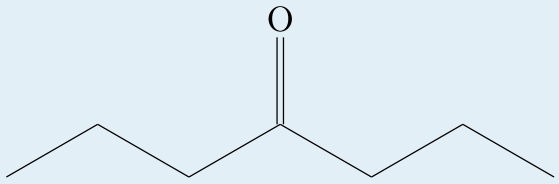
a. 

b. 

4. Name each molecule.

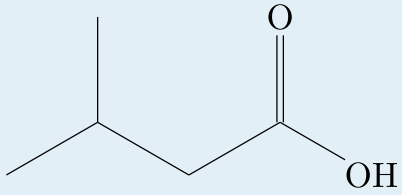
a. 

b.

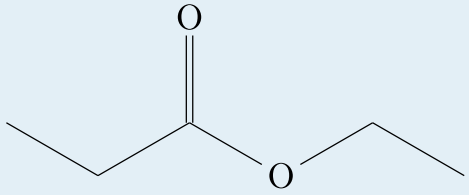


5. Name each molecule.

a.

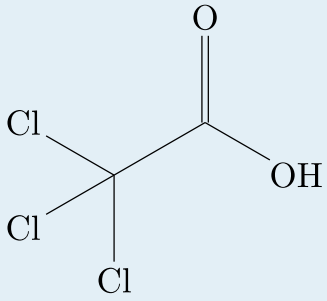


b.

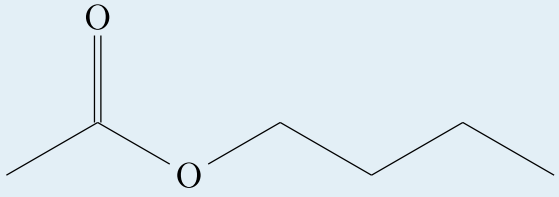


6. Name each molecule.

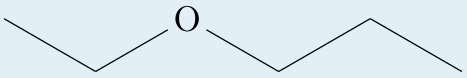
a.



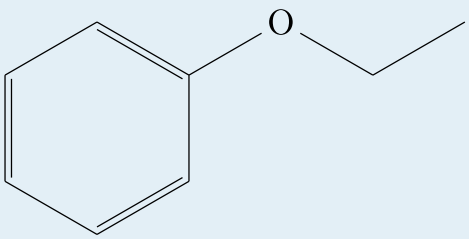
b.



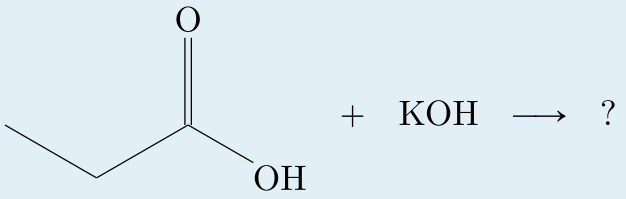
7. Name this molecule:



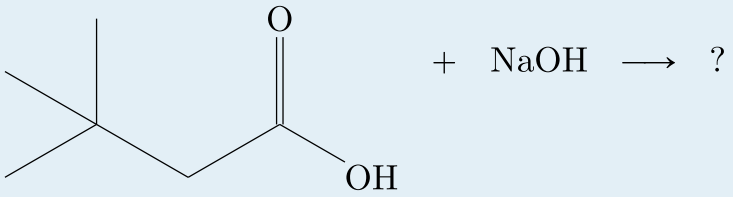
8. Name this molecule:



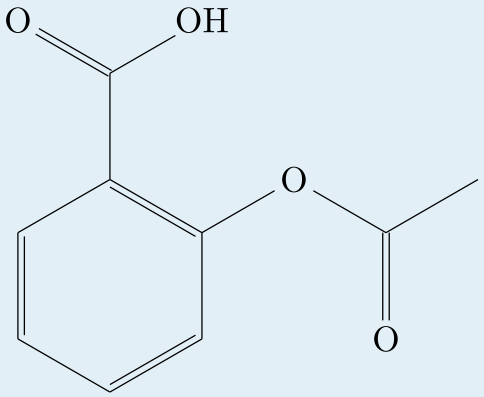
9. Give an alternate but acceptable name to the molecule in Exercise 3b.
10. Give an alternate but acceptable name to the molecule in Exercise 4b.
11. Complete this chemical reaction:



12. Complete this chemical reaction:

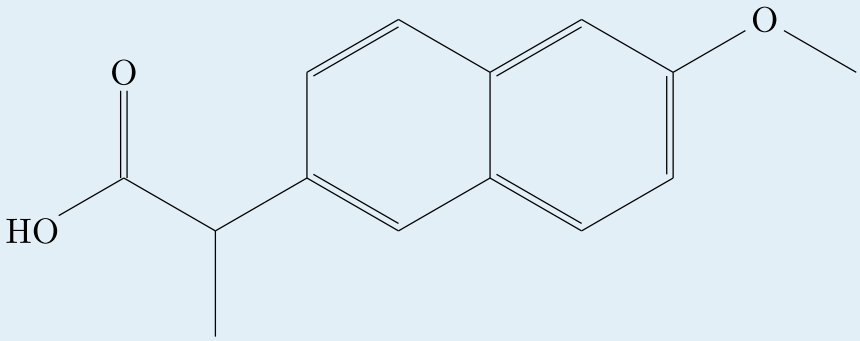


13. The drug known as aspirin has this molecular structure:



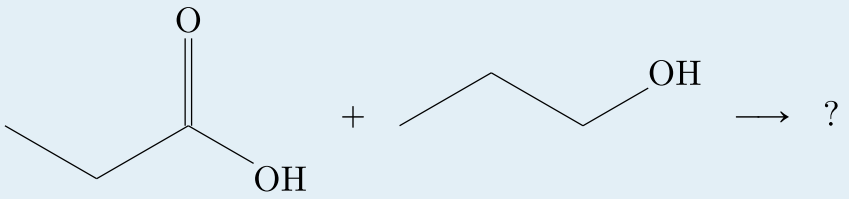
Identify the functional group(s) in this molecule.

14. The drug known as naproxen sodium is the sodium salt of this molecule:

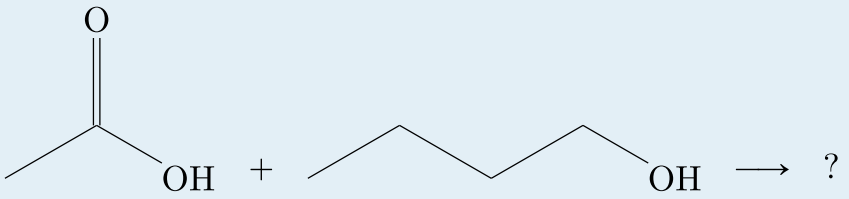


Identify the functional group(s) in this molecule.

15. Identify the ester made by reacting these molecules:



16. Identify the ester made by reacting these molecules:



Answers

1. They both have a carbonyl group, but an aldehyde has the carbonyl group at the end of a carbon chain, and a ketone's carbonyl carbon is surrounded by two other carbons.

3. a. propanal
   b. 2-butanone

5. a. 3-methylbutanoic acid
   b. ethyl propionate

7. ethyl propyl ether

9. ethyl methyl ketone

11. $H_2O + KCH_3CH_2CO_2$

13. acid, ester, and aromatic (benzene ring)

15. propyl propionate

Other Functional Groups

Learning Objectives

1. Identify the amine, amide, and thiol functional groups.

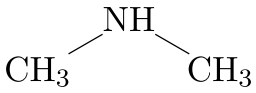
There are some common — and important — functional groups that contain elements other than oxygen. In this section, we will consider three of them.

Nitrogen-Containing Compounds

An **amine** is an organic derivative of ammonia (NH_3). In amines, one or more of the H atoms in NH_3 is substituted with an organic group. A *primary* amine has one H atom substituted with an R group:

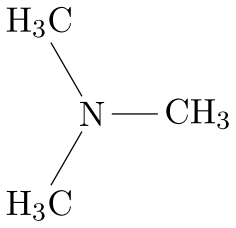
methylamine

A *secondary* amine has two H atoms substituted with R groups:



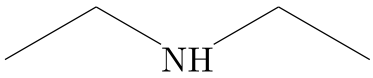
dimethylamine

A *tertiary* amine has all three H atoms substituted with R groups:

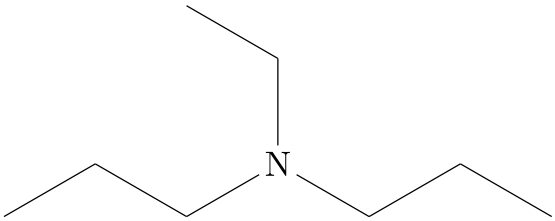


trimethylamine

Naming simple amines is straightforward: name the R groups as substituents and then add the suffix *–amine*, using numerical suffixes on the substituent names as necessary. This amine is diethylamine:

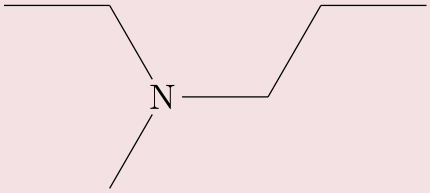


This amine is ethyldipropylamine:



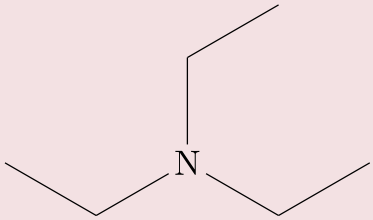
Example 16.11

Name this amine.



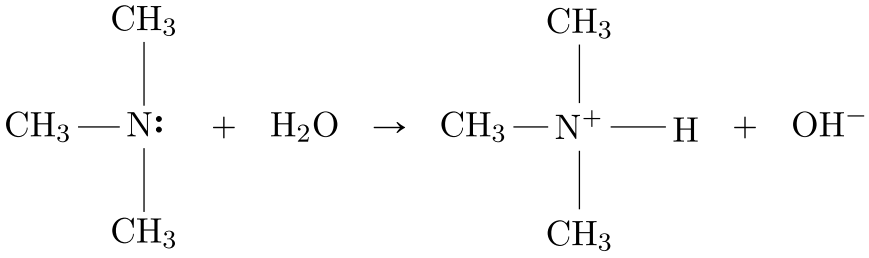
Solution
This amine has a methyl group, an ethyl group, and a propyl group. Listing the names in alphabetical order, this amine is ethylmethylpropylamine.

Test Yourself
Name this amine.



Answer
triethylamine

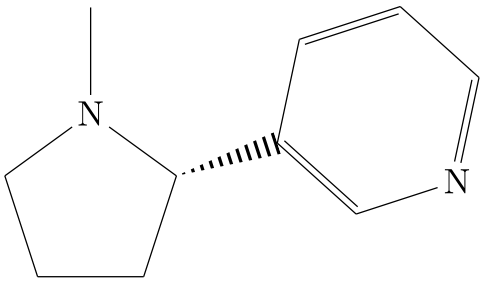
As with NH_3, the N atom in amines can accept a proton onto the lone electron pair on the N atom. That is, amines act as Brønsted-Lowry bases (i.e., proton acceptors):



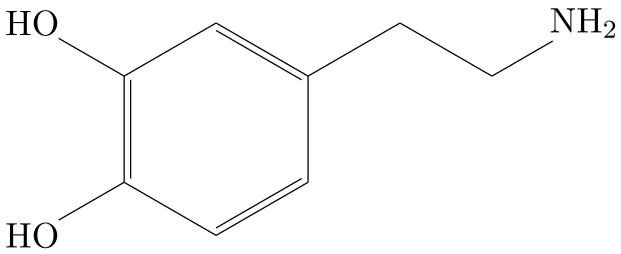
(For more information on Brønsted-Lowry bases, see the section "Brønsted-Lowry Acids and Bases".) The amine becomes an ion, the organic counterpart of the ammonium (NH_4^+) ion.

Because no amine is presented in Table 12.1 "Strong Acids and Bases," all amines are weak bases. The

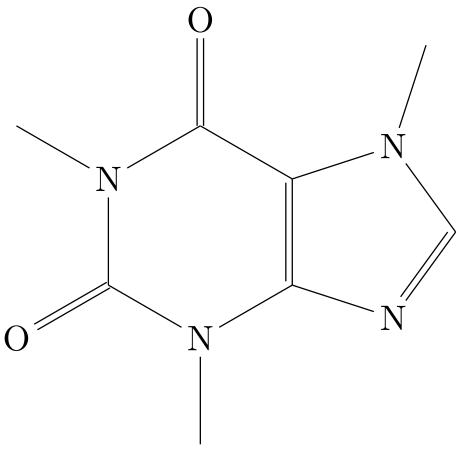
weakness of amines is about the same as that of carboxylic acids. N-containing organic compounds are very common in nature, and they all act as weak bases. Some of these compounds have rather complicated structures. Below are some N-containing substances that you may recognize.



Nicotine (Compound found in tobacco)

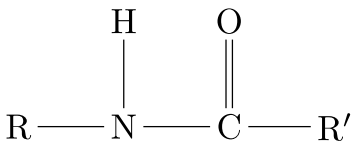


Dopamine (Associated with motor skills and emotions)



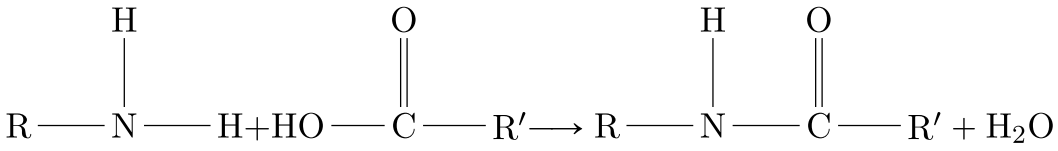
Caffeine (Stimulant found in coffee and tea)

An **amide** functional group is a combination of an amine group and a carbonyl group:



amide

Amides are actually formed by bringing together an amine-containing molecule and a carboxylic acid-containing molecule. A molecule of H_2O is lost, much like when an ester forms:

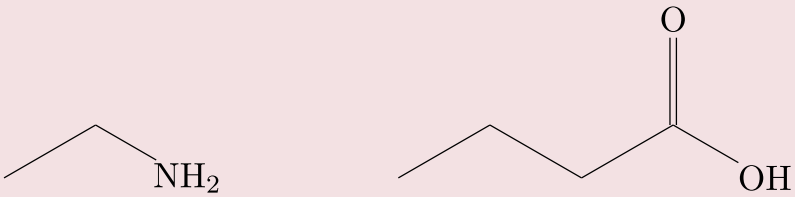


The bond between the N of the amine group and the C of the carbonyl group is called an **amide bond**. Amide bonds are particularly important in biological molecules called *proteins*, which are composed of strings of amino acids — molecules that have an amine group and a carboxylic acid group in them. The amine group on one amino acid reacts with the carboxylic acid group of another amino acid, making a chain held together by amide bonds. We will consider proteins later in this chapter.

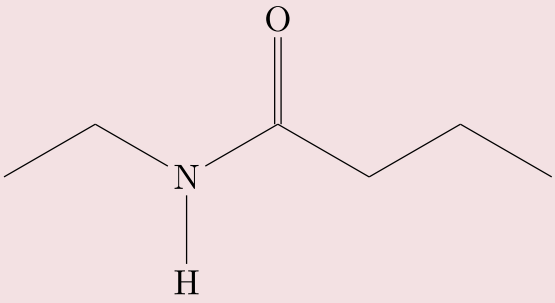
Example 16.12

Draw the structure of the amide formed by the combination of ethylamine and butanoic acid.

Solution
The structures of ethylamine and butanoic acid are:

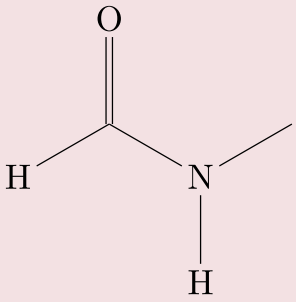


When they come together to make an amide, an H_2O molecule is lost, and the N of the amine group bonds to the C of the carboxyl group. The resulting molecule is:



Test Yourself
Draw the structure of the amide formed by the combination of methylamine and formic acid.

Answer



Sulfur-Containing Compounds

Sulfur is below oxygen on the periodic table, and it occasionally shows some similar chemistry. One similarity is that an S atom can take the place of an O atom in an alcohol, to make a molecule that looks like this:

$$R\text{——}SH$$

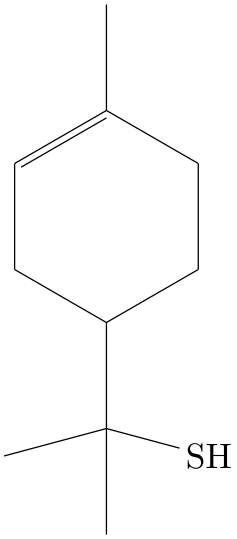
The sulfur analog of an alcohol is called a **thiol**. The formal way of naming a thiol is similar to that of alcohols, except that instead of using the suffix *–ol*, you use the suffix *–thiol*. The following illustrates thiol nomenclature:

$CH_3\text{—}SH$	$C_2H_5\text{—}SH$	$C_3H_7\text{—}SH$
Methanethiol	Ethanethiol	Propanethiol

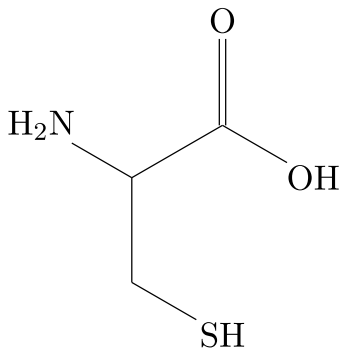
An older system uses the word *mercaptan* in naming simple thiols, much like the word *alcohol* is used with small alcohols. These thiols can also be named like this:

$CH_3\text{—}SH$	$C_2H_5\text{—}SH$	$C_3H_7\text{—}SH$
Methyl mercaptan	Ethyl mercaptan	Propyl mercaptan

Many thiols have strong, objectionable odours; indeed, the spray from skunks is composed of thiols and is detectable by the human nose at concentrations of less than 10 ppb. Because natural gas is odourless, thiols are intentionally added — at very low levels, of course — so that gas leaks can be more easily detected. Not all thiols have objectionable odours; this thiol, grapefruit mercaptan, is responsible for the odour of grapefruit:



Cysteine is an amino acid that is a thiol:



Cysteine plays an important role in protein structure. If two cysteine amino acids in a protein chain approach each other, they can be oxidized, and an S–S bond (also known as a *disulfide bond*) is formed:

$$\mathrm{R{-}SH + HS{-}R \longrightarrow R{-}S{-}S{-}R}$$

where the R group is the rest of the cysteine molecule. The disulfide bond is strong enough to fix the position of the two cysteine groups, thus imposing a structure on the protein. Hair is composed of about 5% cysteine, and the breaking and remaking of disulfide bonds between cysteine units is the primary mechanism behind straightening and curling hair (hair "perms").

Food and Drink App: Amino Acids — Essential and Otherwise

The description of cysteine mentioned that it is an amino acid. Amino acids are the fundamental building blocks of proteins, a major biological component. Proteins are a necessary part of the diet; meat, eggs, and certain vegetables such as beans and soy are good sources of protein and amino acids.

All life on earth — from the lowliest single-celled organism to humans to blue whales — relies on proteins for life, so all life on earth is dependent on amino acids. The human body contains 20 different amino acids (curiously, other organisms may have a different number of amino acids). However, not all of them must be obtained from the diet. The body can synthesize 12 amino acids. The other 8 *must* be obtained from the diet. These 8 amino acids are called the *essential amino acids*. Daily requirements range from 4 mg per kilogram of body weight for tryptophan to 40 mg per kilogram of body weight for leucine. Infants and children need a greater mass per kg of body weight to support their growing bodies; also, the number of amino acids that are considered essential for infants and children is greater than for adults due to the greater protein synthesis associated with growth.

Because of the existence of essential amino acids, a diet that is properly balanced in protein is necessary. Rice and beans, a very popular food dish in Latin cuisines, actually provides all the essential amino acids in one dish; without one component, the dish would be nutritionally incomplete. Corn (maize) is the most-grown grain crop in the world, but an overreliance on it as a primary food source deprives people of lysine and tryptophan, which are two essential amino acids. People on restricted diets — whether out of necessity or by choice (e.g., vegetarians) — may be missing the proper amount of an essential amino acid, so it is important to vary the diet when possible to ensure ingestion of a wide range of protein sources.

Key Takeaways

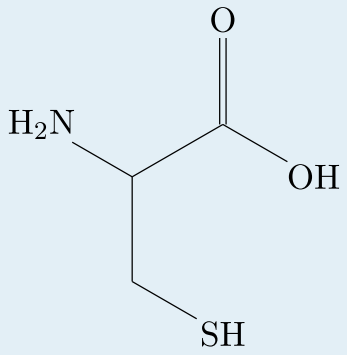
- Other functional groups include amine, amide, and thiol functional groups.

Exercises

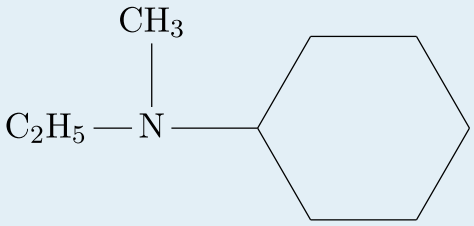
Questions

1. What are the structure and name of the smallest amine?
2. What are the structure and name of the smallest thiol?
3. Identify each compound as a primary, secondary, or tertiary amine.

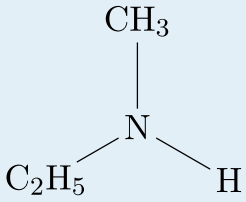
a.



b.

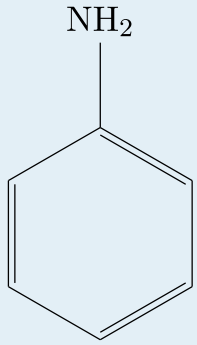


c.

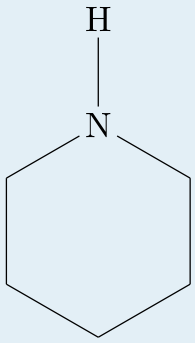


4. Identify each compound as a primary, secondary, or tertiary amine.

a.

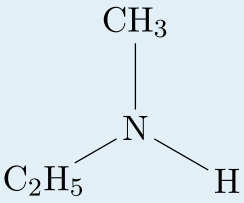


b.

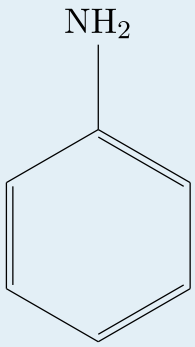


5. Write the chemical reaction between each amine in Exercise 3 and HCl.
6. Write the chemical reaction between each amine in Exercise 4 and HNO_3.
7. Name each amine.

a.

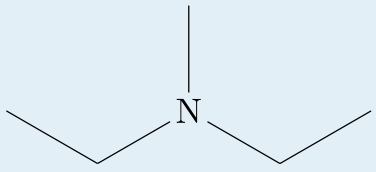


b.

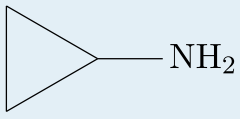


8. Name each amine.

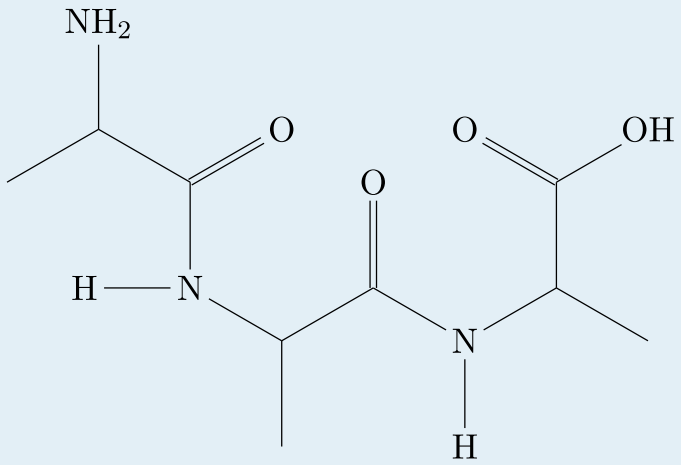
a.



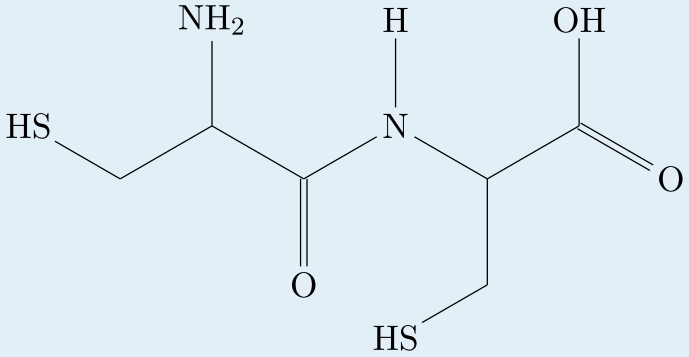
b.



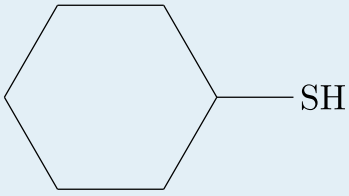
9. A *peptide* is a short chain of amino acids connected by amide bonds. How many amide bonds are present in this peptide?



10. How many amide bonds are present in this peptide? (See Exercise 9 for the definition of a peptide.)



11. Draw the backbone structure of the amide formed by reacting propylamine with propanoic acid.
12. Draw the backbone structure of the amide formed by reacting hexylamine with ethanoic acid.
13. Name each thiol using the *–thiol* suffix.

a. 

b. C_4H_9-SH

14. Name each thiol in Exercise 13 with the mercaptan label.
15. One component of skunk spray is 3-methylbutane-1-thiol. Draw its structure. (The 1 indicates the position of the S atom.)
16. An S–S bond can be fairly easily broken into proteins, yielding two lone cysteine units in a protein chain. Is this process an oxidation or a reduction? Explain your answer.

Answers

1. CH_3NH_2; methylamine

3. a. primary
   b. tertiary

c. secondary

5. a. $C_3H_3CO_2HSHNH_2 + HCl \rightarrow C_3H_3CO_2HSHNH_3Cl$

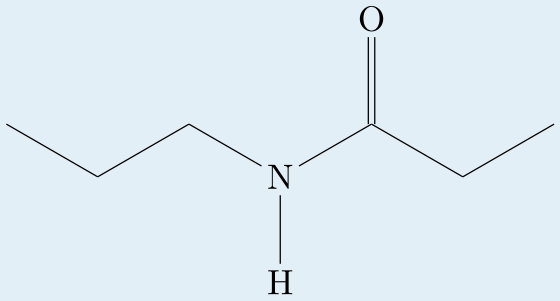
b. $(C_6H_{11})(C_2H_5)(CH_3)N + HCl \rightarrow (C_6H_{11})(C_2H_5)(CH_3)NHCl$

7. a. ethylmethylamine

b. phenylamine

9. two

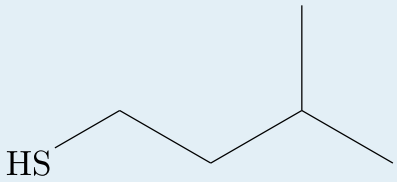
11.



a. cyclohexanethiol

b. butanethiol

15.



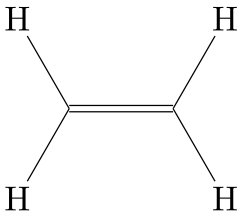
Polymers

Learning Objectives

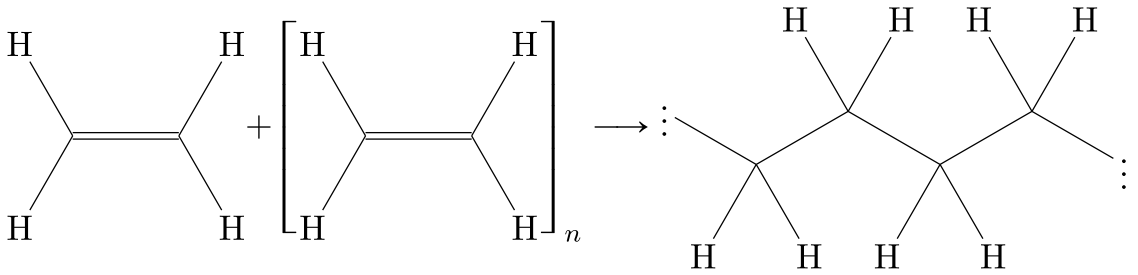
1. Define the terms *monomer* and *polymer*.
2. Draw the structure of a polymer from its monomer.

Among other applications, organic chemistry has had a huge impact on the development of modern materials called polymers. Many objects in daily life are composed of polymers; curiously, so are several important biological materials.

Consider a molecule with a double bond, such as ethylene:



The pi electrons of the double bond can be used to form a new sigma bond to join to other ethylene molecules. The end result is a long, virtually endless molecule:



This long, almost nonstop molecule is called a **polymer** (from the Greek meaning “many parts”). The original part — ethylene — is called the **monomer** (meaning “one part”). The process of making a polymer is called **polymerization**. A polymer is an example of a *macromolecule*, the name given to a large molecule.

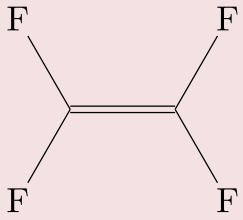
Simple polymers are named after their monomers; the ethylene polymer is formally called poly(ethylene), although in common use, the names are used without parentheses: polyethylene. Because adding one monomer to another forms this polymer, polyethylene is an example of a type of polymer called *addition polymers*. Table 16.4 “Some Monomers and Their Addition Polymers” lists some monomers and their addition polymers.

Table 16.4 Some Monomers and Their Addition Polymers[1]

Monomer	Polymer Name	Trade Name	Uses
$F_2C{=}CF_2$	polytetrafluoroethylene	Teflon	Non-stick coating for cooking utensils, chemically resistant specialty plastic parts, Gore-Tex
$H_2C{=}CCl_2$	polyvinylidene dichloride	Saran	Clinging food wrap
$H_2C{=}CH(CN)$	polyacrylonitrile	Orlon, Acrilan, Creslan	Fibres for textiles, carpets, upholstery
$H_2C{=}CH(OCOCH_3)$	polyvinyl acetate		Elmer's glue, Silly Putty demo
$H_2C{=}C(CH_3)COOCH_3$	polymethyl methacrylate	Plexiglass, Lucite	Stiff, clear, plastic sheets, blocks, tubing, and other shapes

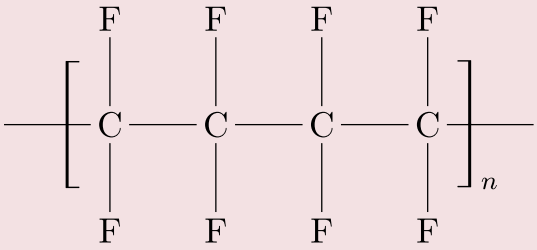
Example 16.13

Draw the polymer that results from the polymerization of tetrafluoroethylene.



Solution

In the case of this monomer, the double bond opens up and joins to other monomers, just as with ethylene. The polymer has this structure:

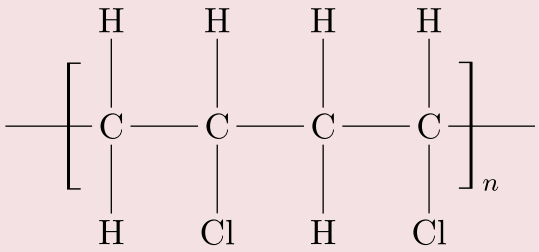


Test Yourself

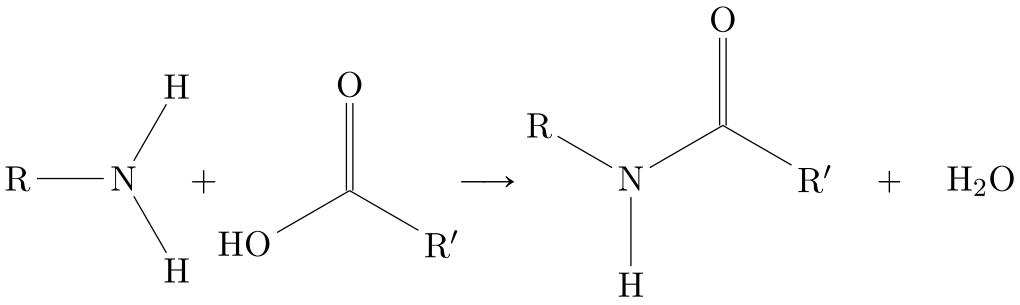
Draw the polymer that results from the polymerization of vinyl chloride.

1. Courtesy of UC Davis ChemWiki\CC-BY-NC-SA-3.0

Answer

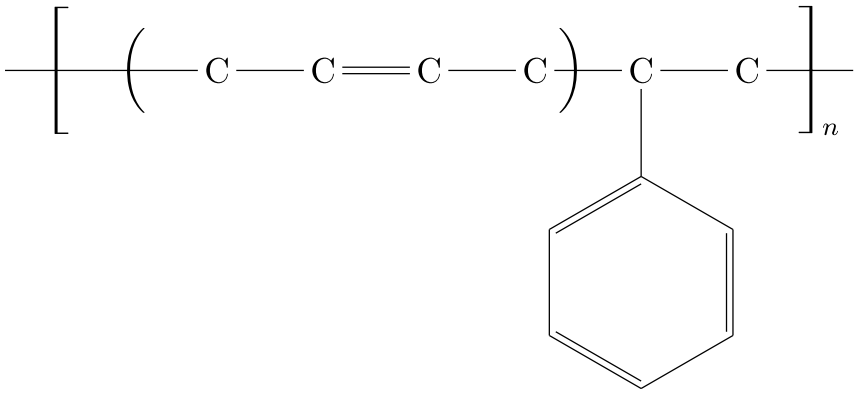


Another type of polymer is the *condensation polymer*, which is a polymer made when two different monomers react together and release some other small molecule as a product. We have already seen an example of this in the formation of an amide bond:



Here, H_2O is released when the ends of the molecules react to form a polymer.

Related to condensation polymers are the *copolymers*, polymers made from more than one type of monomer. For example, ethylene and propylene can be combined into a polymer that is a mixture of the two monomers. A common form of synthetic rubber called *styrene butadiene rubber(SBR)* is made from two monomers: styrene and butadiene:

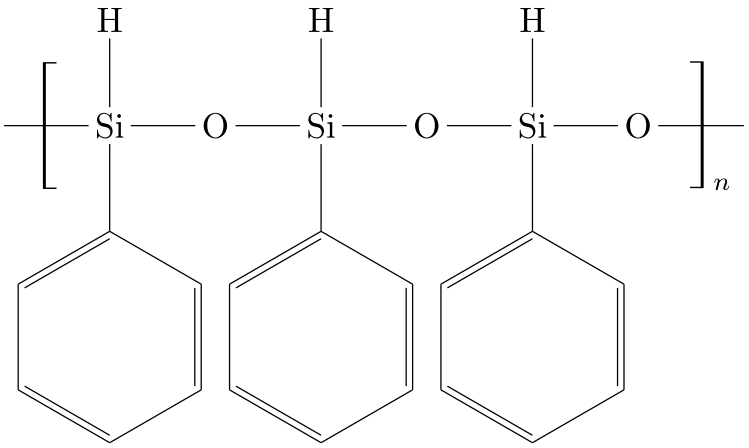


The physical and chemical properties of polymers vary widely, based on their monomers, structures,

and additives. Among the other properties that can be modified based on these factors include solubility in H_2O and other solvents, melting point, flammability, colour, hardness, transparency, film thickness, wetability, surface friction, moldability, and particle size — the list goes on.

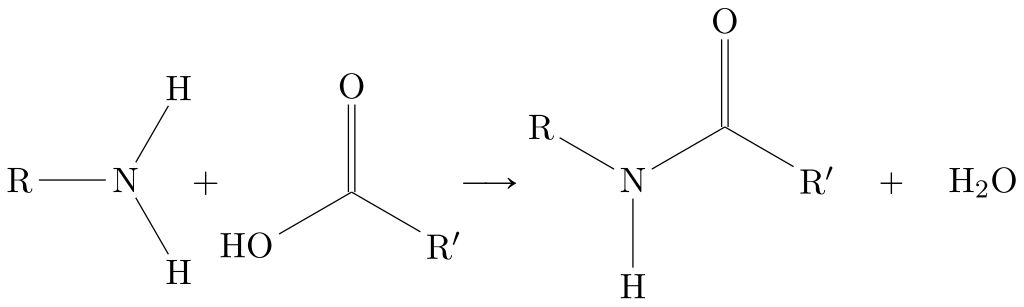
The uses of polymers are almost too numerous to consider. Anything that you might describe as "plastic" is likely a polymer. Polymers are used to make everything from toothbrushes to computer cases to automobile parts. Many epoxy-based adhesives are condensation polymers that adhere strongly to other surfaces. Polyurethane paints and coatings are polymers, as are the polyester fabrics used to make clothing. Nylon, Dacron, and Mylar are polymers (in fact, both Dacron and Mylar are forms of polyethylene terephthalate [PET]). The product known as Saran Wrap was originally constructed from Saran, a name for poly(vinylidene chloride), which was relatively impervious to oxygen and could be used as a barrier to help keep food fresh. (It has since been replaced with polyethylene, which is not as impervious to atmospheric oxygen.) Poly(vinyl chloride) is the third-most produced polymer [after poly(ethylene) and poly(propylene)] and is used to make everything from plastic tubing to automobile engine parts, water pipes to toys, flooring to waterbeds and pools.

All the polymers we have considered so far are based on a backbone of (largely) carbon. There is another class of polymers based on a backbone of Si and O atoms; these polymers are called **silicones**. The Si atoms have organic groups attached to them, so these polymers are still organic. One example of a silicone is as follows:



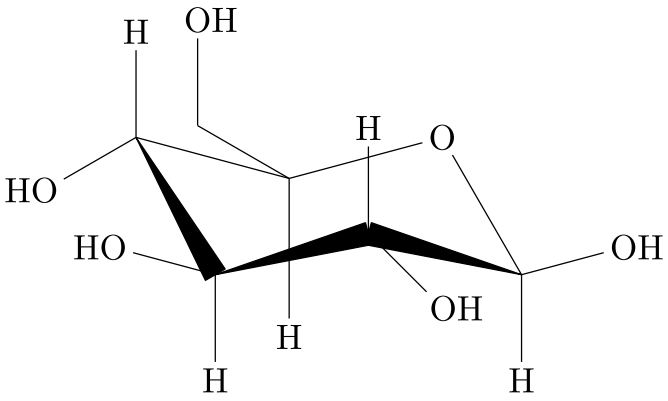
Silicones are used to make oils and lubricants. They are also used as sealants for glass objects (such as aquariums) and films for waterproofing objects. Solid silicones are heat resistant and rubbery and are used to make cookware and electrical insulation.

Some very important biological materials are polymers. Of the three major food groups, polymers are represented in two: proteins and carbohydrates. Proteins are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. These two groups react to make a condensation polymer, forming an amide bond:

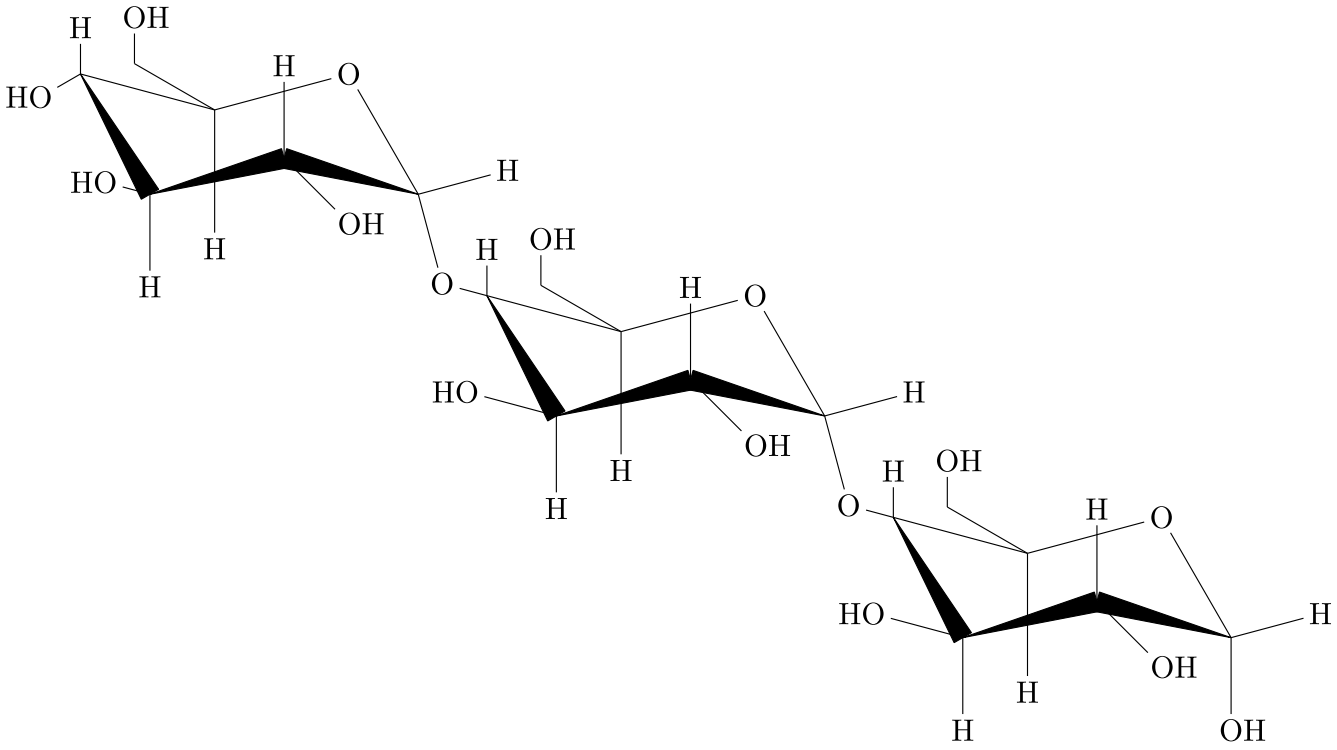


Proteins are formed when hundreds or even thousands of amino acids form amide bonds to make polymers. Proteins play a crucial role in living organisms.

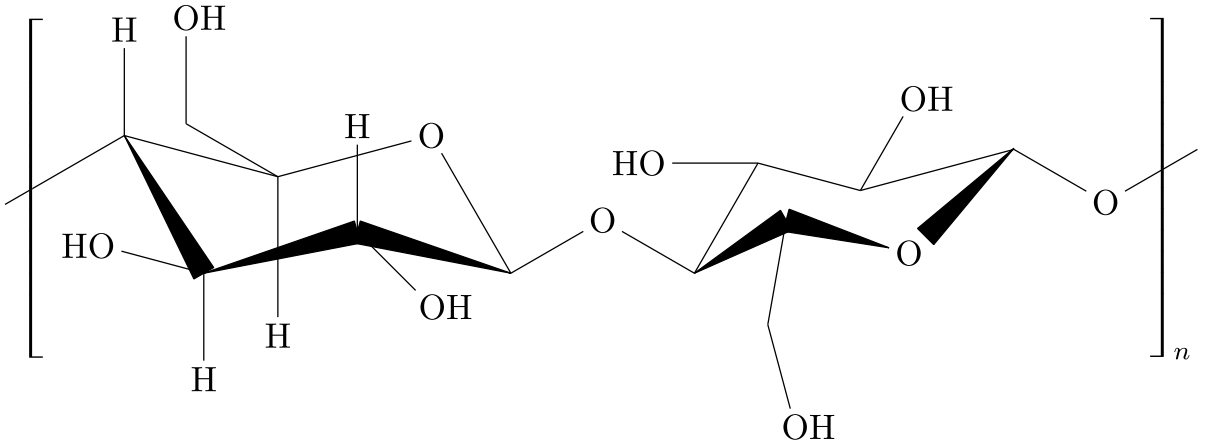
A *carbohydrate* is a compound that has the general formula $C_n(H_2O)_n$. Many carbohydrates are relatively small molecules, such as glucose:



Linking hundreds of glucose molecules together makes a relatively common material known as *starch*:



Starch is an important source of energy in the human diet. Note how individual glucose units are joined together. They can also be joined together in another way, like this:



This polymer is known as *cellulose*. Cellulose is a major component in the cell walls of plants. Curiously, despite the similarity in the building blocks, some animals (such as humans) cannot digest cellulose; those animals that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered *dietary fibre*.

Deoxyribonucleic acid (*DNA*) and *ribonucleic acid* (*RNA*) are also polymers, composed of long, three-part chains consisting of phosphate groups, sugars with five C atoms (ribose or deoxyribose), and N-containing rings referred to as *bases*. Each combination of the three parts is called a nucleotide; DNA

and RNA are essentially polymers of nucleotides that have rather complicated but intriguing structures (Figure 16.5 “Nucleotides”). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

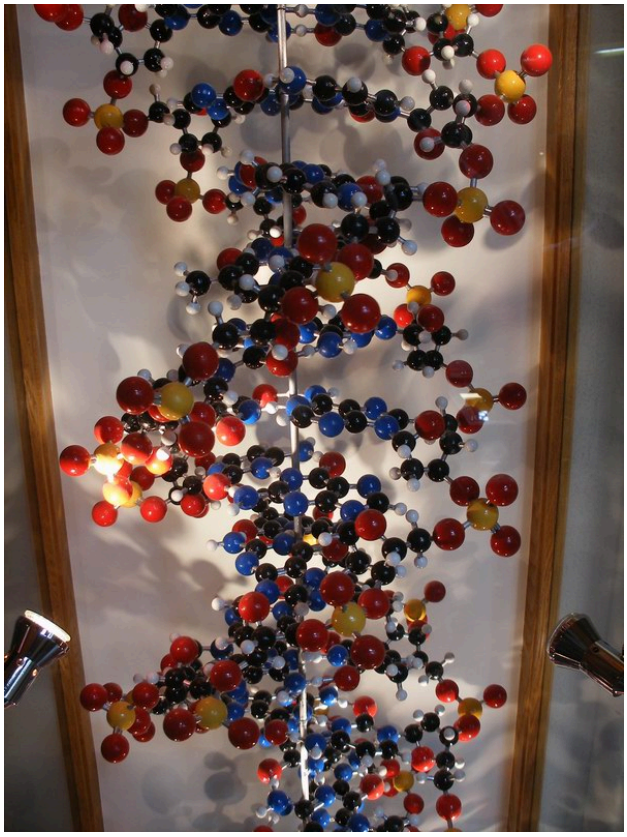


Figure 16.5 “Nucleotides.” The DNA in our cells is a polymer of nucleotides, each of which is composed of a phosphate group, a sugar, and a N-containing base.

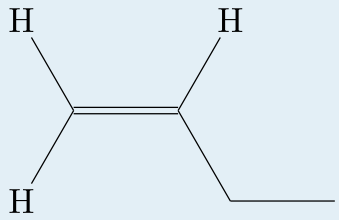
Key Takeaways

- Polymers are long molecules composed of chains of units called monomers.
- Several important biological polymers include proteins, starch, cellulose, and DNA.

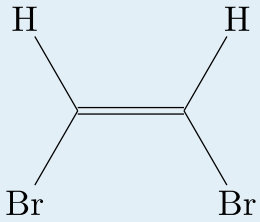
Exercises

Questions

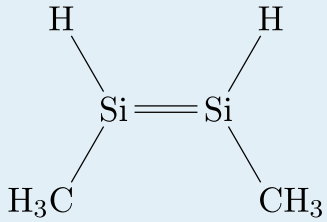
1. Explain the relationship between a monomer and a polymer.
2. Must a monomer have a double bond to make a polymer? Give an example to illustrate your answer.
3. Draw the polymer made from this monomer.



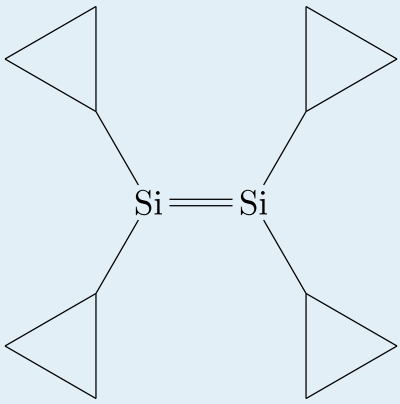
4. Draw the polymer made from this monomer.



5. What is the difference between an addition polymer and a condensation polymer?
6. What is the difference between a condensation polymer and a copolymer?
7. List three properties of polymers that vary widely with composition.
8. List three uses of polymers.
9. Draw the silicone made from this monomer.



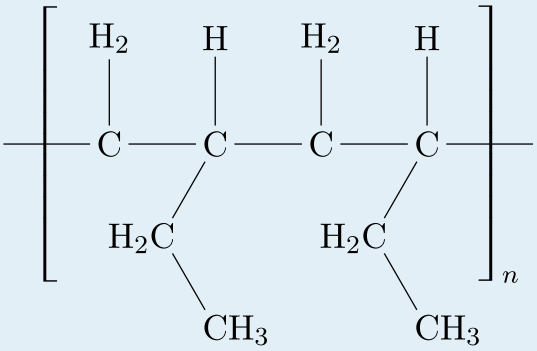
10. Draw the silicone made from this monomer.



11. Explain how starch is a polymer.
12. What is the difference between starch and cellulose?
13. Explain how protein is a polymer.
14. What are the parts that compose DNA?

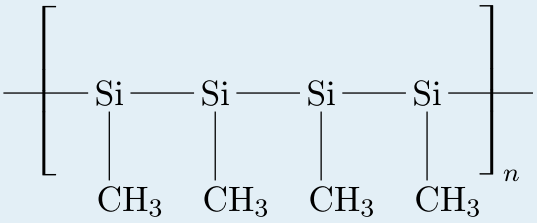
Answers

1. A polymer is many monomers bonded together.

3. 

5. In an addition polymer, no small molecule is given off as a product, whereas in a condensation polymer, small parts of each monomer come off as a small molecule.

7. solubility in H_2O and other solvents, melting point, flammability, colour, hardness, transparency, film thickness, wetability, surface friction, moldability, and particle size (answers will vary)

9. 

11. Starch is composed of many glucose monomer units.

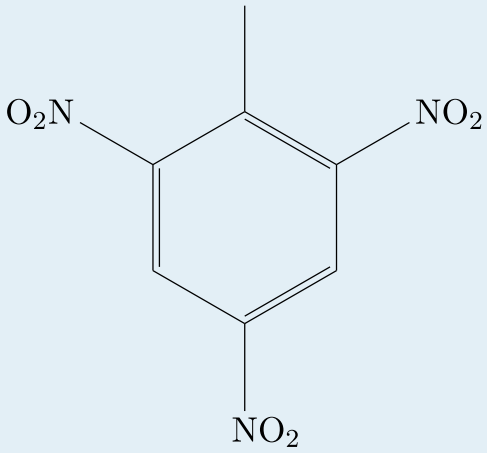
13. Proteins are polymers of amino acids, which act as the monomers.

Media Attributions

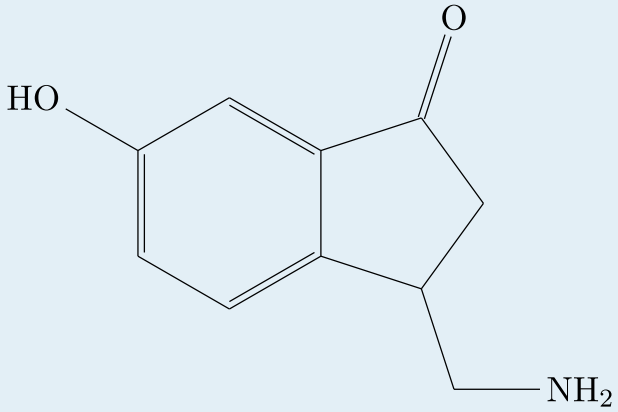
End-of-Chapter Material

Additional Exercises

1. Cycloalkanes are named based on the number of C atoms in them, just like regular alkanes, but with the prefix *cyclo–* on the name. What are the names of the three smallest cycloalkanes?
2. Cycloalkenes are named similarly to cycloalkanes (see Exercise 1). What are the names of the cycloalkenes with five, six, and seven C atoms?
3. Draw the bond-line structure of all noncyclic alkanes with only four C atoms.
4. Draw the bond-line structure of all noncyclic alkanes with only five C atoms.
5. Cyclic alkanes can also have substituent groups on the ring. Draw the bond-line structure of all cyclic alkanes with only four C atoms.
6. Cyclic alkanes can also have substituent groups on the ring. Draw the bond-line structure of all cyclic alkanes with only five C atoms.
7. Draw and name all possible isomers of pentene.
8. Draw and name all possible normal (that is, straight-chain) isomers of heptyne.
9. Polyunsaturated alkenes have more than one C–C double bond. Draw the carbon backbone of all possible noncyclic polyunsaturated alkenes with four C atoms and two double bonds. What are the complete molecular formulas for each possible molecule?
10. Draw the carbon backbone of all possible five-carbon cyclic alkenes with two double bonds, assuming no substituents on the ring.
11. If a hydrocarbon is combined with enough halogen, all the H atoms will eventually be substituted with that halogen atom. Write the balanced chemical reaction between ethane and excess chlorine.
12. If a hydrocarbon is combined with enough halogen, all the H atoms will eventually be substituted with that halogen atom. Write the balanced chemical reaction between butane and excess bromine.
13. Molecules with multiple double bonds can also participate in addition reactions. Draw the structure of the product when butadiene, CH_2=CH–CH=CH_2, reacts with chlorine.
14. Draw the structure of the product when allene, CH_2=C=CH_2, reacts with bromine.
15. What is the maximum number of methyl groups that can be on a propane backbone before the molecule cannot be named as a propane compound?
16. Explain why cycloethane cannot exist as a real molecule.
17. In the gasoline industry, what is called isooctane is actually 2,2,4-trimethylpentane. Draw the structure of isooctane.
18. Isooctane (see Exercise 17) is an isomer of what straight-chain alkane?
19. The actual name for the explosive TNT is 2,4,6-trinitrotoluene. If the structure of TNT is as shown below, propose the structure of the parent compound toluene.

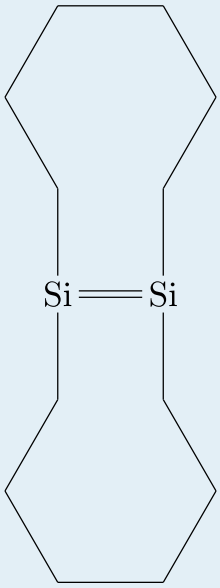


20. Phenol is hydroxybenzene, the simplest aromatic alcohol. Picric acid is an explosive derivative of phenol whose formal name is 2,4,6-trinitrophenol. With reference to Exercise 19, draw the structure of picric acid.
21. Draw the structures of all possible straight-chain isomers of bromopentane.
22. Draw the structures of all the possible isomers of butanol. Include branched isomers.
23. What is the final product of the *double* elimination of HCl from 1,1-dichloroethane?
24. Draw the structure of the final product of the *double* elimination of 1,3-dibromopropane.
25. Draw the structure of and name the alcohol whose double elimination would yield the same product as in Exercise 23. Name the molecule as a hydroxyl-substituted compound.
26. Draw the structure of and name the alcohol whose double elimination would yield the same product as in Exercise 24. Name the molecule as a hydroxyl-substituted compound.
27. Draw the smallest molecule that can have a separate aldehyde and carboxylic acid group.
28. Name the functional group(s) in the following structure:



29. Ethyl acetate is a common ingredient in nail-polish remover because it is a good solvent. Draw the structure of ethyl acetate.
30. A lactone is an ester that has its ester functional group in a ring. Draw the structure of the smallest possible lactone. (It is called acetolactone, which might give you a hint about its structure.)
31. Draw the structure of diethyl ether, once used as an anaesthetic.
32. The smallest cyclic ether is called an epoxide. Draw its structure.
33. Write the chemical reaction of HCl with trimethylamine.
34. Putrescine and cadaverine are molecules with two amine groups on the opposite ends of a butane backbone and a pentane backbone, respectively. They are both emitted by rotting corpses. Draw their structures and determine their molecular formulas.

35. With four monomers, draw two possible structures of a copolymer composed of ethylene and propylene.
36. With four monomers, draw two possible structures of a copolymer composed of ethylene and styrene.
37. Draw the silicone that can be made from this monomer:

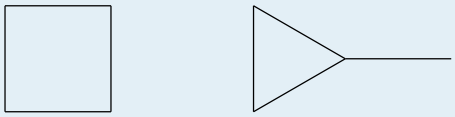


38. One of the ingredients in the original Silly Putty was a silicone polymer with two methyl groups on each Si atom. Draw this silicone.

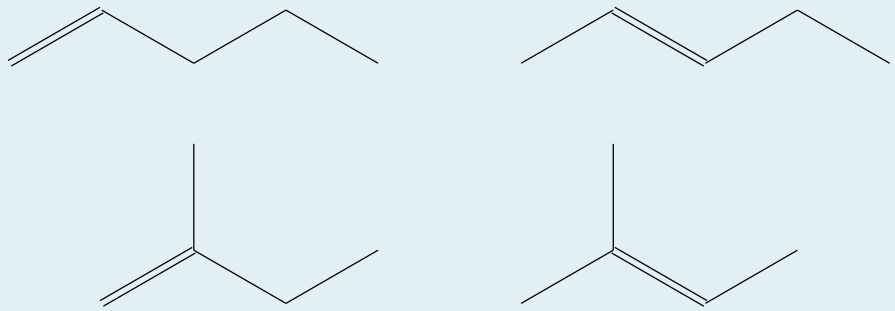
Answers

1. cyclopropane, cyclobutane, and cyclopentane
3. Bond-line structure of all noncyclic alkanes with only four C atoms:

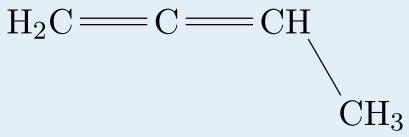
5. Bond-line structure of all cyclic alkanes with only four C atoms:

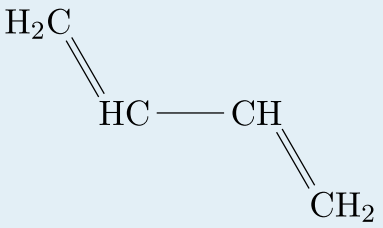


7. Isomers of pentene:



9. Carbon backbone of all possible noncyclic polyunsaturated alkenes with four C atoms and two double bonds:

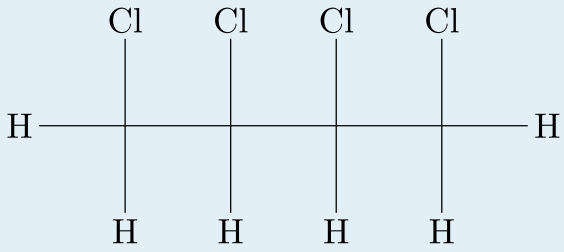




Both molecular formulas are C_4H_6.

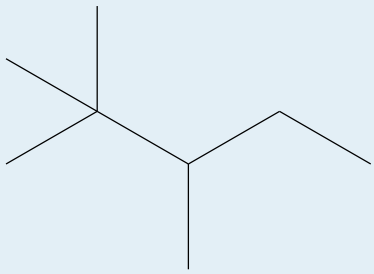
11. $C_2H_6 + 6Cl_2 \rightarrow C_2Cl_6 + 6HCl$

13. Structure of butadiene's reaction with chlorine:

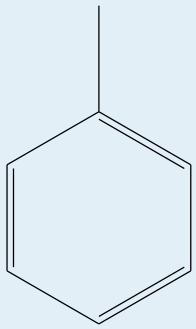


15. two

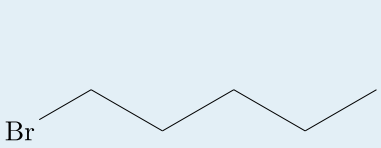
17. Structure of isooctane:

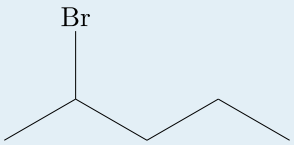


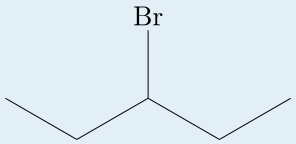
19. Structure of toluene:



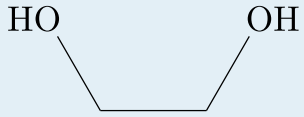
21. Straight-chain isomers of bromopentane:

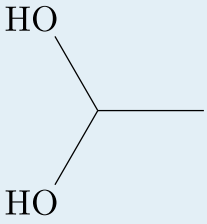






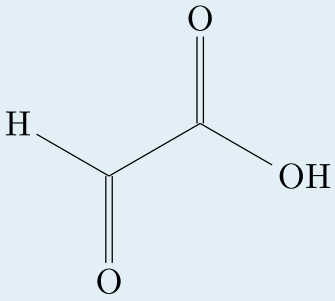
23. ethyne





25. The names are 1,2-dihydroxyethane and 1,1-dihydroxyethane, respectively.

27.



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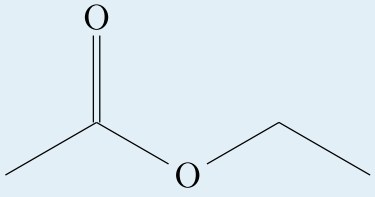
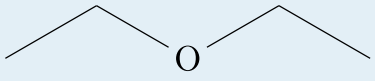
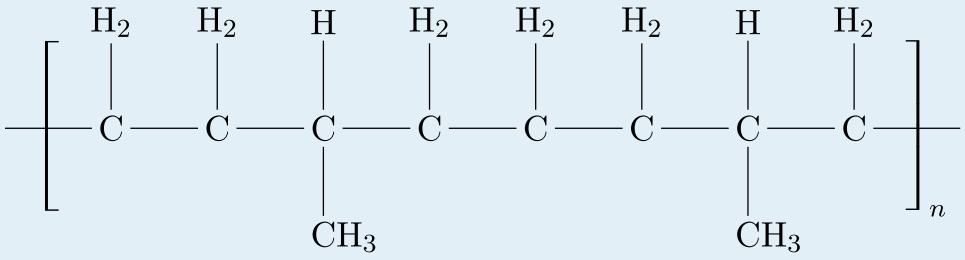


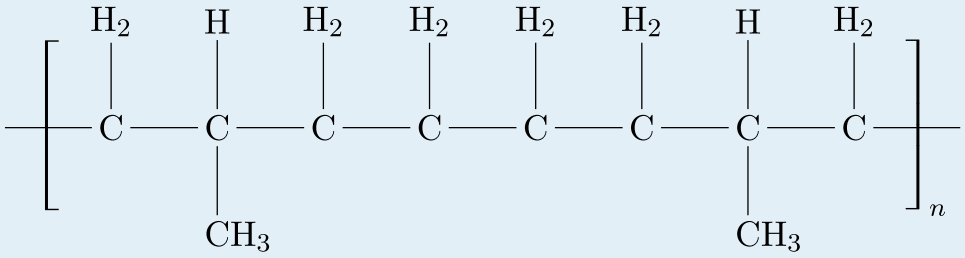
31.



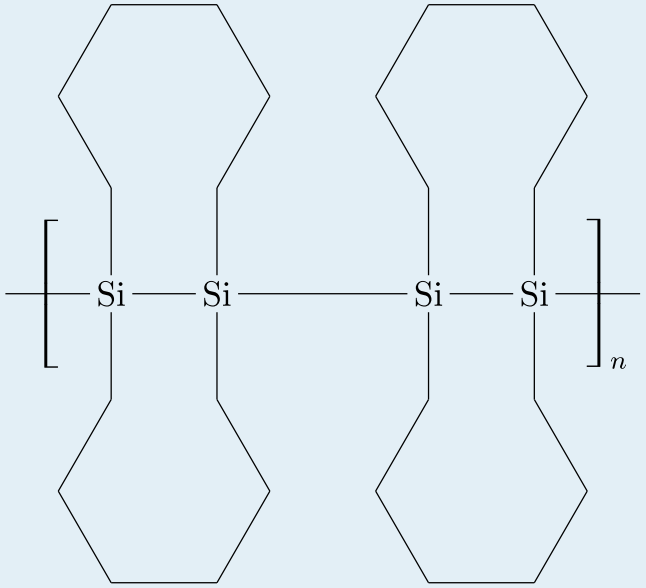
33. $(CH_3)_3N + HCl \rightarrow (CH_3)_3NHCl$

35. (answers will vary)





37.



Chapter 17. Kinetics

Speed plays an important role in many of the things we do in everyday life. If you sleep in and need to get to your chemistry lecture quickly, you may choose to drive instead of walk because driving is faster. You may use a favourite website for streaming video content online, because of its quick and reliable download speeds. Applying for a summer job, you may have had to include your typing speed on your resume to show your competency on computers. These examples emphasize that the speed of a process is an important consideration in our everyday lives.

Similarly, the speed of a chemical reaction is also a significant consideration and is called its **reaction rate**. Reaction rates vary dramatically, with some reactions occurring on a time scale of seconds, while other reactions take many thousands of years. Several factors can influence reaction rate, and the study of the interplay between these factors and the rate of a chemical reaction is called **kinetics**.

Factors that Affect the Rate of Reactions

Jessie A. Key

Learning Objectives

- To gain an understanding of collision theory.
- To gain an understanding of the four main factors that affect reaction rate.

Reaction kinetics is the study of the rate of chemical reactions, and reaction rates can vary greatly over a large range of time scales. Some reactions can proceed at explosively fast rates like the detonation of fireworks (Figure 17.1 “Fireworks at Night Over River”), while others can occur at a sluggish rate over many years like the rusting of barbed wire exposed to the elements (Figure 17.2 “Rusted Barbed Wire”).

Figure 17.1 “Fireworks at Night Over River.” The chemical reaction in fireworks happens at an explosive rate.

Figure 17.2 "Rusted Barbed Wire." The rusting of barbed wire occurs over many years.

Collision Theory

To understand the kinetics of chemical reactions, and the factors that affect kinetics, we should first examine what happens during a reaction on the molecular level. According to the **collision theory** of reactivity, reactions occur when reactant molecules "effectively collide." For an "effective collision" to occur, the reactant molecules must be oriented in space correctly to facilitate the breaking and forming of bonds and the rearrangement of atoms that result in the formation of product molecules (see Figure 17.3 "Collision Visualizations").

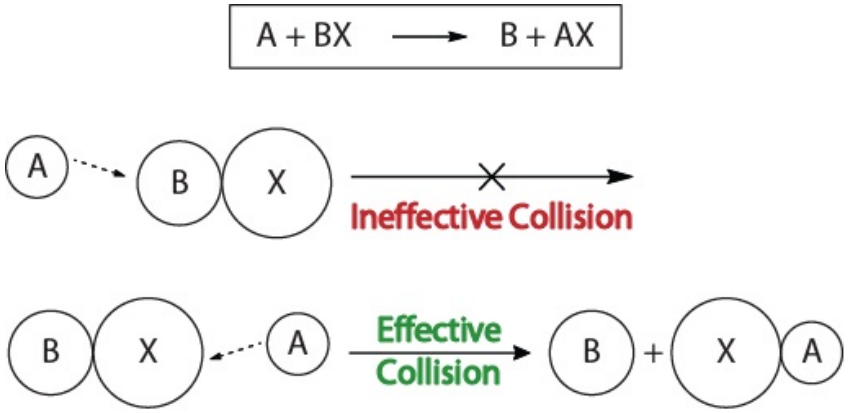


Figure 17.3 "Collision Visualizations." This visualization shows an ineffective and effective collision based on molecular orientation.

During a molecular collision, molecules must also possess a minimum amount of kinetic energy for an effective collision to occur. This energy varies for each reaction, and is known as the **activation energy (E_a)** (Figure 17.4 "Potential Energy and Activation Energy"). The rate of reaction therefore depends on the activation energy; a higher activation energy means that fewer molecules will have sufficient energy to undergo an effective collision.

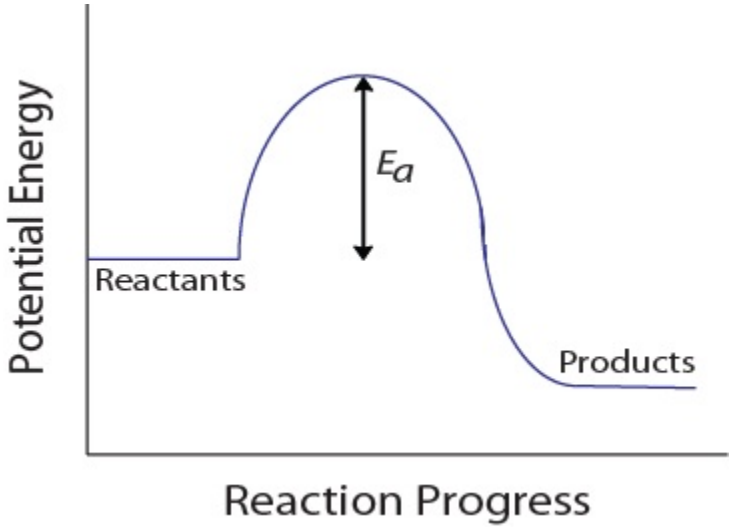


Figure 17.4 "Potential Energy and Activation Energy." This potential energy diagram shows the activation energy of a hypothetical reaction.

Factors That Affect Rate

There are four main factors that can affect the reaction rate of a chemical reaction:

1. **Reactant concentration.** Increasing the concentration of one or more reactants will often increase the rate of reaction. This occurs because a higher concentration of a reactant will lead to more collisions of that reactant in a specific time period.
2. **Physical state of the reactants and surface area.** If reactant molecules exist in different phases, as in a heterogeneous mixture, the rate of reaction will be limited by the surface area of the phases that are in contact. For example, if a solid metal reactant and gas reactant are mixed, only the molecules present on the surface of the metal are able to collide with the gas molecules. Therefore, increasing the surface area of the metal by pounding it flat or cutting it into many pieces will increase its reaction rate.
3. **Temperature**. An increase in temperature typically increases the rate of reaction. An increase in temperature will raise the average kinetic energy of the reactant molecules. Therefore, a greater proportion of molecules will have the minimum energy necessary for an effective collision (Figure. 17.5 "Temperature and Reaction Rate").

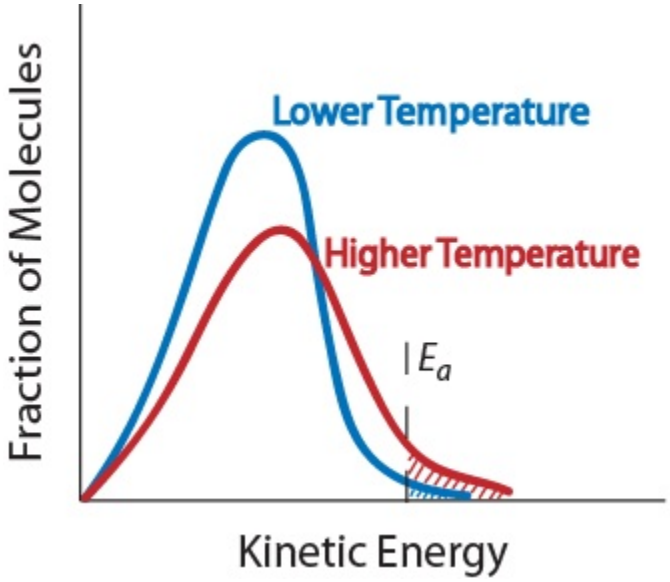


Figure 17.5 "Temperature and Reaction Rate." Effect of temperature on the kinetic energy distribution of molecules in a sample

4. **Presence of a catalyst**. A **catalyst** is a substance that accelerates a reaction by participating in it without being consumed. Catalysts provide an alternate reaction pathway to obtain products. They are critical to many biochemical reactions. They will be examined further in the section "Catalysis."

Key Takeaways

- Reactions occur when two reactant molecules effectively collide, each having minimum energy and correct orientation.
- Reactant concentration, the physical state of the reactants, and surface area, temperature, and the presence of a catalyst are the four main factors that affect reaction rate.

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Reaction Rates

Jessie A. Key

Learning Objectives

- To gain an understanding of relative reaction rates.
- To gain an understanding of instantaneous reaction rates and initial reaction rates.

We encounter rates or speeds often in daily life; for example, the rate at which this textbook was typed could be measured in words per minute. This rate is a measure of the *change* in words typed in the *time period* of a minute. Similarly, the rate of a chemical reaction is also a measure of change that occurs in a given time period:

$$\text{Rate of reaction} = \frac{\text{Change in Concentration}}{\text{Change in Time}}$$

For a chemical reaction, we can measure the change in concentration in terms of either the disappearance of starting material or the appearance of the product. For the hypothetical reaction: A + B → C, we can express the average rate of reaction as follows:

$$\text{Rate of reaction} = -\frac{\Delta\,[A]}{\Delta\,t} = -\frac{\Delta\,[B]}{\Delta\,t} = \frac{\Delta\,[C]}{\Delta\,t}$$

Notice that a negative sign is included when expressing reaction rates with respect to the disappearance of starting materials. Reaction rates are always positive, so the decrease in concentration must be corrected for.

When the stoichiometric relationships in the balanced equation are not 1:1, the coefficient for each species must also be corrected for. In the hypothetical reaction 2A + B → 3C, two molecules of A are consumed for every one molecule of B, this means *A is consumed twice as fast*. To correct for this and express the average rate of reaction for each species, we must divide each by its coefficient in the balanced equation:

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta\,[A]}{\Delta\,t} = -\frac{\Delta\,[B]}{\Delta\,t} = \frac{1}{3}\frac{\Delta\,[C]}{\Delta\,t}$$

Example 17.1

The decomposition of dinitrogen pentoxide $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ was performed in the lab and the rate of formation of NO_2 was found to be 0.53 M/s.

1. What was the rate of formation of $O_2(g)$?
2. What was the rate of consumption $N_2O_5(g)$?

Solution

1. First determine the rate relationship between $NO_2(g)$ and $O_2(g)$ using the coefficients of the balanced equation:

$$\text{Rate of reaction} = \frac{1}{4}\frac{\Delta\,[\text{NO}_2]}{\Delta\,t} = \frac{\Delta\,[\text{O}_2]}{\Delta\,t}$$

   Next substitute in the given values and solve for the rate of formation of $O_2(g)$:

   Rate of formation of $O_2(g)$ = (¼) (0.53 M/s) = 0.13 M/s

2. First determine the rate relationship between $NO_2(g)$ and $N_2O_5(g)$ using the coefficients of the balanced equation:

$$\text{Rate of reaction} = \frac{1}{4}\frac{\Delta\,[\text{NO}_2]}{\Delta\,t} = -\frac{1}{2}\frac{\Delta\,[\text{N}_2\text{O}_5]}{\Delta\,t}$$

   Next substitute the given values and solve for the rate of consumption of $N_2O_5(g)$:

   −(½) rate of consumption of $N_2O_5(g)$ = −(¼) rate of formation $NO_2(g)$

   Rate of consumption of $N_2O_5(g)$ = −½(0.53 M/s) = 0.27 M/s

Instantaneous Rate

For most chemical reactions, the rate of the reaction tends to decrease as time passes (Figure 17.6 “Reactant Concentration vs. Time”). As the reaction proceeds, more and more of the reactant molecules are consumed to become product, which lowers the concentration of reactant molecules. The reduction in reactant concentration results in fewer effective collisions.

The decrease in reaction rate over time means that average reaction rates do not accurately represent the actual rate of reaction at all time points. **Instantaneous reaction rates**, the rate of reaction at one instant in time, can be determined from the slope of the tangent at that point in the plot of concentration vs. time. The instantaneous rate at the start of the reaction, $t = 0$, is of particular interest in kinetics and is known as the **initial rate** of the reaction.

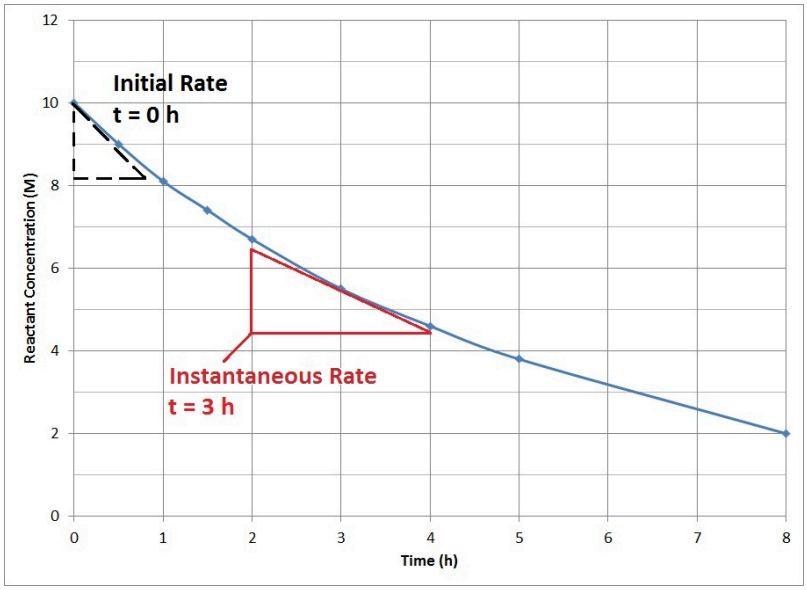


Figure 17.6 "Reactant Concentration vs. Time." A plot of reactant concentration vs. time for a hypothetical reaction.

Example 17.2

Use Figure 17.6 to determine the instantaneous rate at 3 h.

Solution

The slope of the tangent at 3 h can be determined by drawing a triangle such as the one shown in Figure 17.6, and comparing the ratio of the height of the rise to the run of the length.

$$\text{Slope} = \frac{\text{Rise}}{\text{Run}} = -\frac{\Delta\,[\text{Reactant}]}{\Delta\,t} = -\frac{4.5 - 6.5\ \text{M}}{4 - 2\ \text{h}} = -\frac{-2\ \text{M}}{2\ \text{h}} = 1\frac{\text{M}}{\text{h}}$$

Key Takeaways

- Reaction rates can be measured by the disappearance of starting material or the appearance of the product over time.
- Instantaneous reaction rates can be determined from the slope of the tangent at that point in the plot of concentration vs. time.
- The initial reaction rate is the instantaneous rate at the start of the reaction (at $t = 0$).

Rate Laws

Jessie A. Key

Learning Objectives

- To gain an understanding of rate laws and determine rate laws from initial rates.
- To gain an understanding of and the ability to determine reaction orders (including units).

The mathematical relationship of reaction rate with reactant concentrations is known as the **rate law**. This relationship may rely more heavily on the concentration of one particular reactant, and the resulting rate law may include some, all, or none of the reactant species involved in the reaction.

For the following hypothetical reaction

$$aA + bB \rightarrow cC$$

the rate law can be expressed as:

$$\text{rate} = k[A]^y[B]^z$$

The proportionality constant, *k*, is known as the **rate constant** and is specific for the reaction shown at a particular temperature. The rate constant changes with temperature, and its units depend on the sum of the concentration term exponents in the rate law. The exponents (*y* and *z*) must be experimentally determined and do not necessarily correspond to the coefficients in the balanced chemical equation.

Reaction Order

The sum of the concentration term exponents in a rate law equation is known as its **reaction order**. We can also refer to the relationship for each reactant in terms of its exponent as an order.

For the following reaction between nitrogen dioxide and carbon monoxide:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The rate law is experimentally determined to be: rate = $k[NO_2]^2$

Therefore, we would say that the overall reaction order for this reaction is second-order (the sum of all exponents in the rate law is 2), but zero-order for [CO] and second-order for [NO_2].

The reaction order is most often a whole number such as 0, 1, or 2; however, there are instances where the reaction order may be a fraction or even a negative value.

Earlier, it was mentioned that the units of the rate constant depend on the order of the reaction. Let's quickly examine why this occurs. A simplified rate law can be expressed generically in the following way:

$$\text{rate} = k[\text{reactant}]^y$$

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^y$$

$$\text{Units of rare constant} = \frac{\text{Units of rate}}{(\text{Units of concentration})^y}$$

$$= \frac{\text{M/s}}{\text{M}^y}$$

Therefore, the units of the rate constant should be:

Reaction Order	**Units of rate constant**
Zero-order	M s^{-1}
First-order	s^{-1}
Second-order	$\text{L mol}^{-1}\ \text{s}^{-1}$

Determining Rate Laws from Initial Rates

The rate law can be determined experimentally using the method of initial rates, where the instantaneous reaction rate is measured immediately on mixing the reactants. The process is repeated over several runs or trials, varying the concentration one reactant at a time. These runs can then be compared to elucidate how changing the concentration of each reactant affects the initial rate.

Example 17.3

The initial rate of reaction for the reaction E + F → G was measured at three different initial concentrations of reactants as shown in the table.

1. Determine the rate law of the reaction.
2. Determine the rate constant.

Trial	**Initial Rate (mol L^{-1} s^{-1})**	**[E] (mol L^{-1})**	**[F] (mol L^{-1})**
1	2.73×10^{-5}	0.100	0.100
2	5.47×10^{-5}	0.200	0.100
3	2.71×10^{-5}	0.100	0.200

Solution

1. Comparing trials 1 and 2, [E] is doubled, while [F] and the rate constant are held constant. This comparison will allow us to determine the order of reactant E:

$$\frac{\text{initial rate 2}}{\text{initial rate 1}} = \left(\frac{[\text{E}]_2}{[\text{E}]_1}\right)^y$$

$$\frac{5.47 \times 10^{-5}\text{M s}^{-1}}{2.73 \times 10^{-5}\text{ M s}^{-1}} = \left(\frac{0.200\text{ M}}{0.100\text{ M}}\right)^y$$

$$2.00 = 2.00^y$$

$$y = 1$$

Therefore, the reaction is first order with respect to [E].

Comparing trials 1 and 3, [F] is doubled, while [E] and the rate constant are held constant. This comparison will allow us to determine the order of reactant F:

$$\frac{\text{initial rate 3}}{\text{initial rate 1}} = \left(\frac{[\text{F}]_3}{[\text{F}]_1}\right)^z$$

$$\frac{2.71 \times 10^{-5}\ \text{M s}^{-1}}{2.73 \times 10^{-5}\ \text{M s}^{-1}} = \left(\frac{0.200\ \text{M}}{0.100\ \text{M}}\right)^z$$

$$0.993 = 2.00^z$$

$$z = 0$$

Therefore, the reaction is zero order with respect to [F].

The rate law can now be written as:

$$\text{rate} = k[\text{E}]^1$$

2. Using the rate law we have just determined, substitute in the initial concentration values and initial rate for any trial and solve for the rate constant:

$$\text{rate} = k[\text{E}]^1$$

Using Trial 1:

$$2.73 \times 10^{-5}\ \text{M s}^{-1} = k(0.100\ \text{M})$$

$$k = \frac{2.73 \times 10^{-5}\ \text{M s}^{-1}}{(0.100\ \text{M})}$$

$$k = 2.73 \times 10^{-4}\ \text{s}^{-1}$$

Key Takeaways

- The rate law is a mathematical relationship obtained by comparing reaction rates with reactant concentrations.

- The reaction order is the sum of the concentration term exponents in a rate law equation.
- A reaction's rate law may be determined by the initial rates method.

Concentration–Time Relationships: Integrated Rate Laws

Jessie A. Key

Learning Objectives

- To gain an understanding of graphical methods used to determine rate laws.
- To gain an understanding of half-life with respect to first-order reactions.

An alternate way to determine a rate law is to monitor the concentration of reactants or products in a single trial over a period of time and compare that to what is expected mathematically for a first-, second-, or zero-order reaction.

First-Order Reactions

We have seen earlier that the rate law of a generic first-order reaction where A → B can be expressed in terms of the reactant concentration:

$$\text{Rate of reaction} = -\frac{\Delta\ [A]}{\Delta\ t} = \text{k}[A]^1$$

This form of the rate law is sometimes referred to as the **differential rate law**. We can perform a mathematical procedure known as an **integration** to transform the rate law to another useful form known as **the integrated rate law**:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

where "ln" is the natural logarithm, $[A]_0$ is the initial concentration of *A*, and $[A]_t$ is the concentration of *A* at another time.

The process of integration is beyond the scope of this textbook, but is covered in most calculus textbooks and courses. The most useful aspect of the integrated rate law is that it can be rearranged to have the general form of a straight line ($y = mx + b$).

$$\ln[A]_t = -kt + \ln[A]_0$$
$$y = mx + b$$

Therefore, if we were to graph the natural logarithm of the concentration of a reactant (ln) versus time, a reaction that has a first-order rate law will yield a straight line, while a reaction with any other order

will not yield a straight line (Figure 17.7 “Concentration vs. Time, First-Order Reaction”). The slope of the straight line corresponds to the negative rate constant, –*k*, and the *y*-intercept corresponds to the natural logarithm of the initial concentration.

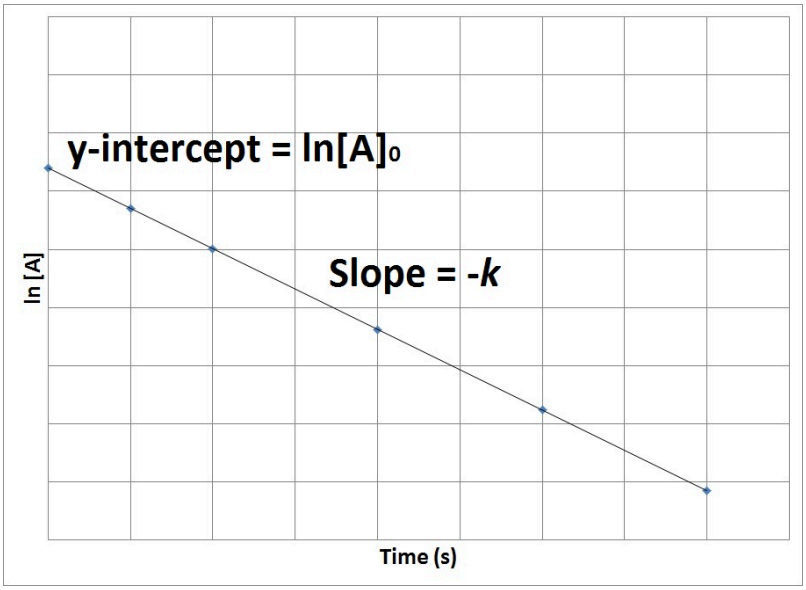


Figure 17.7. “Concentration vs. Time, First-Order Reaction.” This graph shows the plot of the natural logarithm of concentration versus time for a first-order reaction.

Example 17.4

The decomposition of a pollutant in water at 15°C occurs with a rate constant of 2.39 y^{-1}, following first-order kinetics. If a local factory spills 6,500 moles of this pollutant into a lake with a volume of 2,500 L, what will the concentration of pollutant be after two years, assuming the lake temperature remains constant at 15°C?

Solution

We are given the rate constant and time and can determine an initial concentration from the number of moles and volume given.

$$[\text{Pollutant}]_0 = \frac{6500 \text{ mol}}{2500 \text{ L}} = 2.6 \text{ M}$$

We can substitute this data into the integrated rate law of a first-order equation and solve for the concentration after 2.0 years:

$$\begin{aligned} \ln[\text{Pollutant}]_{2\ y} &= -kt + \ln[\text{Pollutant}]_0 \\ &= -(2.39y_{-1})(2.0y) + \ln(2.6 \text{ M}) \\ &= -4.78 + 0.955 = -3.82 \end{aligned}$$

$$[\text{Pollutant}]_{2\ y} = e^{-3.82} = 0.022 \text{ M}$$

Second-Order Reactions

The rate for second-order reactions depends either on two reactants raised to the first power or a single reactant raised to the second power. We will examine a reaction that is the latter type: C → D. The differential rate law can be written:

$$\text{Rate of reaction} = -\frac{\Delta\,[C]}{\Delta\,t} = k[C]^2$$

The integrated rate law can be written in the form of a straight line as:

$$\frac{1}{[C]_t} = kt + \frac{1}{[C]_0}$$

Therefore, if the reaction is second order, a plot of $\frac{1}{[C]_t}$ versus *t* will produce a straight line with a slope that corresponds to the rate constant, *k*, and a *y*-intercept that corresponds to the inverse of the initial concentration, $\frac{1}{[C]_0}$ (Figure 17.8 "$\frac{1}{[C]_t}$ vs. Time, Second-Order Reaction").

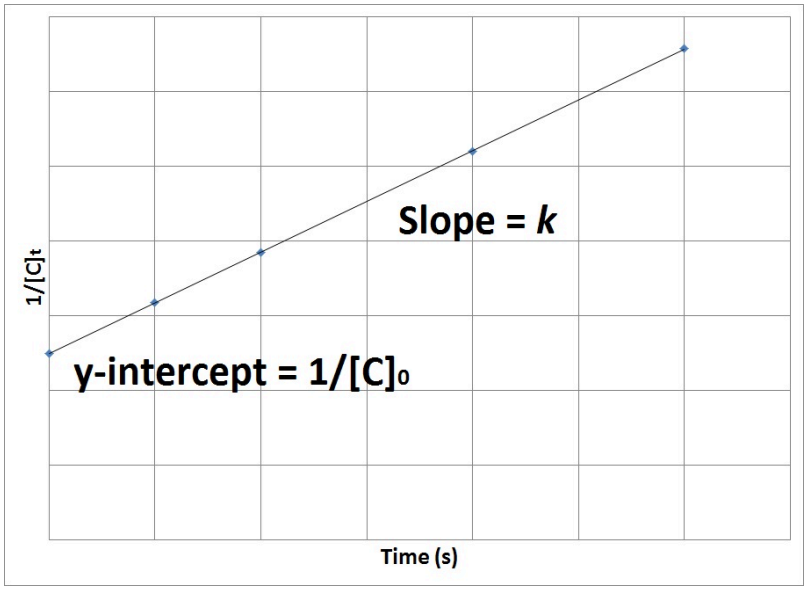


Figure 17.8 "$\frac{1}{[C]_t}$ vs. Time, Second-Order Reaction." The graph shows a plot of $\frac{1}{[C]_t}$ versus time for a second-order reaction.

Zero-Order Reactions

Zero-order reaction rates occur when the rate of reactant disappearance is independent of reactant concentrations. The differential rate law for the hypothetical zero-order reaction E → F could be written as:

$$\text{Rate of reaction} = -\frac{\Delta\,[E]}{\Delta\,t} = k$$

The integrated rate law can be written in the form of a straight line as:

$$[E]_t = -kt + [E]_0$$

Therefore, if the reaction is zero order, a plot of [*E*] versus *t* will produce a straight line with a slope that corresponds to the negative of the product of the rate constant and time, −*kt*, and a *y*-intercept that corresponds to the initial concentration, $[E]_0$ (Figure 17.9 “Concentration vs. Time, Zero-Order Reaction”).

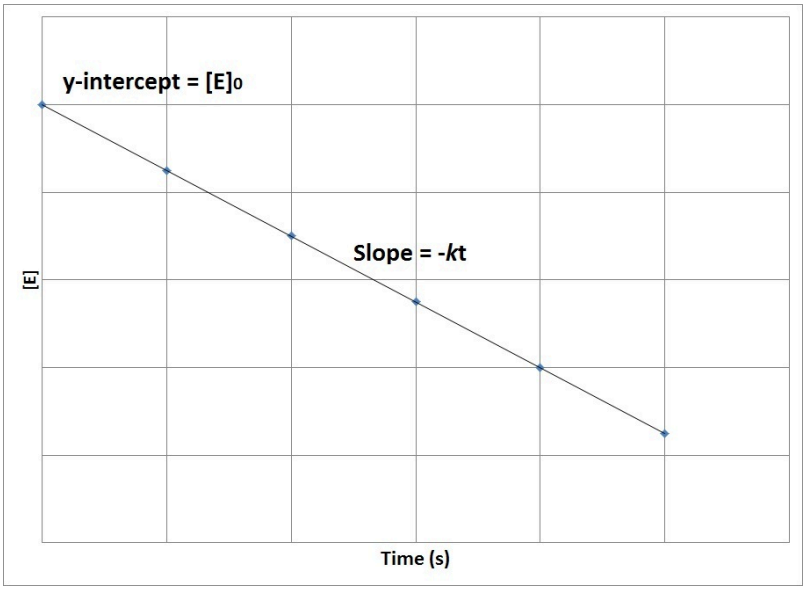


Figure 17.9 “Concentration vs. Time, Zero-Order Reaction.” The graph shows the plot of concentration versus time for a zero-order reaction.

Graphical Methods for Determining Reaction Order—A Summary

We have just seen that first-, second-, and zero-order reactions all have unique, integrated rate-law equations that allow us to plot them as a straight line (*y* = *mx* + *b*) (Table 17.1 “Integrated Rate Law Summary”). When presented with experimental concentration–time data, we can determine the order by simply plotting the data in different ways to obtain a straight line.

Table 17.1 Integrated Rate Law Summary

Reaction Order	Integrated Rate Law	Characteristic Kinetic Plot	Slope of Kinetic Plot	Units of Rate Constant
Zero	$[E]_t = -kt + [E]_0$	[*E*] vs. *t*	−*kt*	mol $L^{-1}s^{-1}$
First	$\ln [A]_t = -kt + \ln [A]_0$	ln [*A*] vs. *t*	−*k*	s^{-1}
Second	$\frac{1}{[C]_t} = kt + \frac{1}{[C]_0}$	$\frac{1}{[C]}$ vs. *t*	*k*	L $mol^{-1}s^{-1}$

Example 17.5

The following data were obtained for the reaction 3A → 2B:

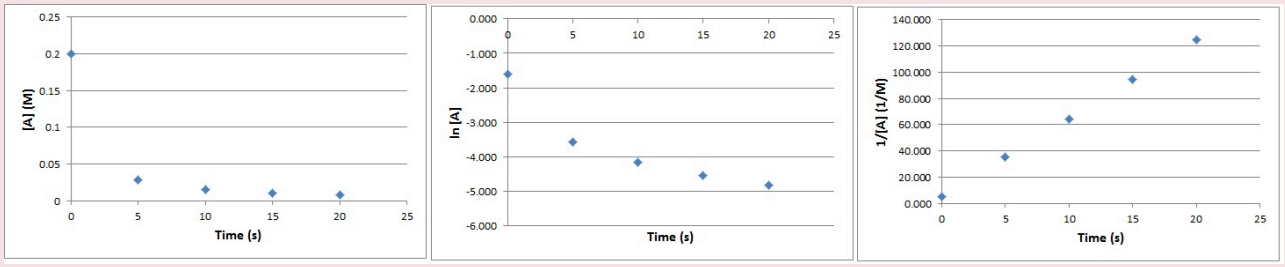
Time, s	0	5	10	15	20
[*A*], M	0.200	0.0282	0.0156	0.0106	0.008

Determine the order of the reaction.

Solution

We can plot the characteristic kinetic plots of zero-, first-, and second-order reactions to determine which will give a straight line.

Time, s	**[A], mol L^{-1}**	**ln [*A*]**	**$\frac{1}{[A]}$, L mol^{-1}**
0	0.200	−1.61	5.00
5	0.0282	−3.57	35.5
10	0.0156	−4.16	64.1
15	0.0106	−4.55	94.3
20	0.008	−4.83	125



Example Kinetics Plots

The reaction is second order since $\frac{1}{[A]_t}$ versus *t* gives a straight line.

Half-Life

The **half-life** of a reaction, $t_{\frac{1}{2}}$, is the duration of time required for the concentration of a reactant to drop to one-half of its initial concentration.

$$[A]_{t_{\frac{1}{2}}} = \frac{1}{2}[A]_0$$

Half-life is typically used to describe first-order reactions and serves as a metric to discuss the relative speeds of reactions. A slower reaction will have a longer half-life, while a faster reaction will have a shorter half-life.

To determine the half-life of a first-order reaction, we can manipulate the integrated rate law by substituting $t_{\frac{1}{2}}$ for *t* and $[A]_{t_{\frac{1}{2}}} = [A]_0$ for $[A]_t$, then solve for $t_{\frac{1}{2}}$:

$$\ln = -kt + \ln \qquad \text{(integrated rate law for a first-order reaction)}$$

$$\ln \frac{1}{2}[A]_0 = -kt_{\frac{1}{2}} + \ln[A]_0$$

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{\frac{1}{2}}$$

$$\ln \frac{1}{2} = -kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = -\frac{\ln \frac{1}{2}}{k} = \frac{0.693}{k}$$

Since the half-life equation of a first-order reaction does not include a reactant concentration term, it does not rely on the concentration of reactant present. In other words, a half-life is independent of concentration and remains constant throughout the duration of the reaction. Consequently, plots of kinetic data for first-order reactions exhibit a series of regularly spaced $t_{\frac{1}{2}}$ intervals (Figure 17.10 “Generic First-Order Reaction Kinetics Plot”).

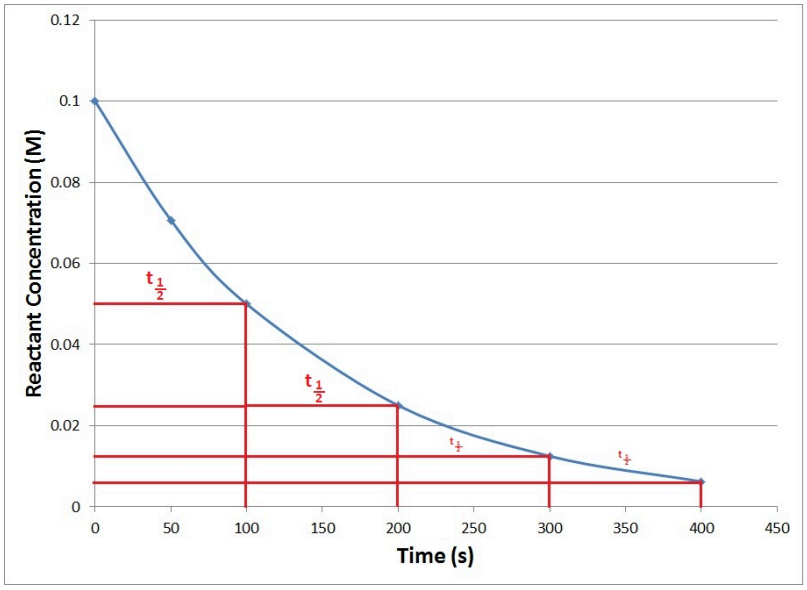


Figure 17.10 "Generic First-Order Reaction Kinetics Plot." This graph shows repeating half-lives on a kinetics plot of a generic first-order reaction.

Example 17.6

A reaction having a first-order rate has a rate constant of $4.00 \times 10^{-3}\ \text{s}^{-1}$.

1. Determine the half-life.
2. How long will it take for a sample of reactant at 1.0 M to decrease to 0.25 M?
3. What concentration of the 1.0 M sample of reactant would you expect to be present after it has reacted for 500 s?

Solution

1. $$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{4.00 \times 10^{-3}\ \text{s}^{-1}} = 173\ \text{s}$$
2. A simple way to calculate this is to determine how many half-lives it will take to go from 1.00 M to 0.250 M and use the half-life calculated in part 1.

   $$1\ \text{half-life} = 0.500\ \text{M}$$
   $$2\ \text{half-lives} = 0.250\ \text{M}$$

   Therefore, it will take 2 × 173 s = 346 s.
3. We can use the rate-constant value in the integrated rate law to determine the concentration remaining.

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{[A]_t}{1.0\ \text{M}} = -(4.00 \times 10^{-3}\ \text{s}^{-1})(500\ \text{s})$$

$$\ln \frac{[A]_t}{1.0\ \text{M}} = -2$$

$$\frac{[A]_t}{1.0\ \text{M}} = e^{-2} = 0.135$$

$$[A]_t = 0.14\ \text{M}$$

Key Takeaways

- The reaction rate may be determined by monitoring the concentration of reactants or products in a single trial over a period of time and comparing it to what is expected mathematically for a first-, second-, or zero-order reaction.
- The half-life of a reaction is the duration of time required for the concentration of a reactant to drop to one-half of its initial concentration.

Activation Energy and the Arrhenius Equation

Jessie A. Key

Learning Objectives

- To gain an understanding of activation energy.
- To determine activation energy graphically or algebraically.

Figure 17.11 "Svante Arrhenius." Swedish scientist Svante Arrhenius (1859–1927).

Earlier in the chapter, reactions were discussed in terms of effective collision frequency and molecule energy levels. In 1889, a Swedish scientist named Svante Arrhenius proposed an equation that relates these concepts with the rate constant:

$$k = Ae^{\frac{-E_a}{RT}}$$

where *k* represents the rate constant, E_a is the activation energy, *R* is the gas constant $\left(\frac{8.3145\ \text{J}}{\text{K mol}}\right)$, and *T* is the temperature expressed in Kelvin. *A* is known as the **frequency factor**, having units of L mol^{-1} s^{-1}, and takes into account the frequency of reactions and likelihood of correct molecular orientation.

The Arrhenius equation allows us to calculate activation energies if the rate constant is known, or vice

versa. As well, it mathematically expresses the relationships we established earlier: as activation energy term E_a increases, the rate constant *k* decreases and therefore the rate of reaction decreases.

Determining the Activation Energy

Graphically

We can graphically determine the activation energy by manipulating the Arrhenius equation to put it into the form of a straight line. Taking the natural logarithm of both sides gives us:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

A slight rearrangement of this equation then gives us a straight line plot (*y* = *mx* + *b*) for ln *k* versus $\frac{1}{T}$, where the slope is $-\frac{E_a}{R}$:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{t}\right) + \ln A$$

Example 17.7

Using the data from the following table, determine the activation energy of the reaction:

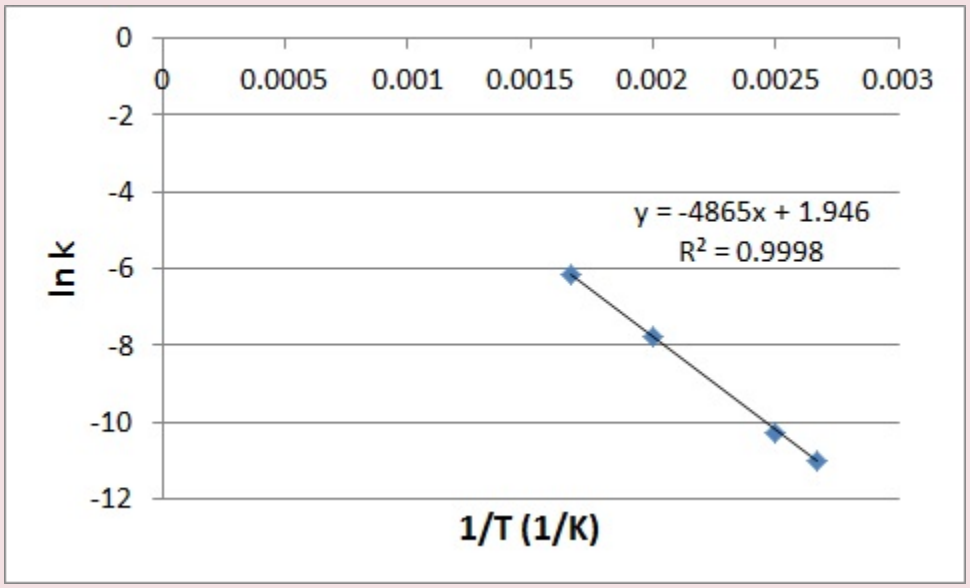
Temperature (K)	**Rate Constant, *k* (s^{-1})**
375	1.68×10^{-5}
400	3.5×10^{-5}
500	4.2×10^{-4}
600	2.11×10^{-3}

Solution

We can obtain the activation energy by plotting ln *k* versus $\frac{1}{T}$, knowing that the slope will be equal to $-\frac{E_a}{R}$.

First determine the values of ln *k* and $\frac{1}{T}$, and plot them in a graph:

$\frac{1}{T}$	**ln *k***
0.002667	−10.9941
0.0025	−10.2602
0.002	−7.77526
0.001667	−6.16107



Graphical determination of E_a example plot

$$\text{Slope} = -\frac{E_a}{R}$$

$$-4865\ \text{K} = -\frac{E_a}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

$$E_a = 4.0 \times 10^4\ \text{J/mol}$$

Algebraically

The activation energy can also be calculated algebraically if *k* is known at two different temperatures:

$$\text{At temperature 1: } \ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

$$\text{At temperature 2: } \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

We can subtract one of these equations from the other:

$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

This equation can then be further simplified to:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example 17.8

Determine the value of E_a given the following values of k at the temperatures indicated:

$600\ \text{K}$: $k = 2.75 \times 10^{-8}\ \text{L mol}^{-1}\text{s}^{-1}$

$800\ \text{K}$: $k = 1.95 \times 10^{-7}\ \text{L mol}^{-1}\text{s}^{-1}$

Solution

Substitute the values stated into the algebraic method equation:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{2.75 \times 10^{-8}\ \text{L mol}^{-1}\text{s}^{-1}}{1.95 \times 10^{-7}\ \text{L mol}^{-1}\text{s}^{-1}} = \frac{E_a}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{800\ \text{K}} - \frac{1}{600\ \text{K}}\right)$$

$$1.96 = \frac{E_a}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\left(-4.16 \times 10^{-4}\ \text{K}^{-1}\right)$$

$$4.704 \times 10^{-3}\ \text{K}^{-1} = \frac{E_a}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}$$

$$E_a = 3.92 \times 10^{4}\ \text{J/mol}$$

Key Takeaways

- The activation energy can be graphically determined by manipulating the Arrhenius equation.
- The activation energy can also be calculated algebraically if *k* is known at two different temperatures.

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Reaction Mechanisms

Jessie A. Key

Learning Objectives

- To gain an understanding of reaction mechanisms, including the concepts of elementary steps and molecularity.
- To become familiar with reaction potential energy diagrams.
- To gain an understanding of rate-determining steps in multi-step reactions.

For us to truly understand a chemical reaction, including its rate, it would be ideal to see the exact bond-making and bond-breaking steps that occur at the molecular level — the **reaction mechanism**. Unfortunately, we cannot watch reactions occurring at the molecular level, but we can infer these events using kinetics and other chemical methods.

Elementary Steps

Each event that occurs in a chemical reaction as a result of an effective collision is known as an **elementary step**. The total number of molecules that participate in the effective collision of an elementary step is known as its **molecularity**. Molecularity can be used to classify elementary steps into three categories:

- Unimolecular: Only one molecule participates
- Bimolecular: Two molecules participate
- Termolecular: Three molecules participate

There are only three main categories of molecularity because it is rare that more than three molecules participate simultaneously in an effective collision.

Elementary Steps and Rate Laws

A complete chemical reaction may occur in one or more elementary steps, each having its own rate law. The rate of a single elementary step can be derived directly from its stoichiometric equation, since it is an individual effective collision describing a single bond-breaking or bond-forming event. This explains why the rate law of an overall reaction, potentially involving several steps, does not necessarily correlate to the stoichiometry of its balanced chemical equation. For example:

$$5\,\mathrm{Br^-(aq)} + \mathrm{BrO_3{}^-(aq)} + 6\,\mathrm{H^+(aq)} \rightarrow 3\,\mathrm{Br_2}(\ell) + 3\,\mathrm{H_2O}(\ell)$$

$$\text{Rate} = k[\text{Br}^-][\text{BrO}_3{}^-][\text{H}^+]^2$$

However, the rate law for an elementary step is determined from its molecularity: the number of molecules involved in the single effective collision (Table 17.2 “Elementary Steps and Their Rate Laws”). For the following elementary step:

$$A \rightarrow B$$
$$\text{Rate} = k[A]$$

This is a unimolecular step, and as the concentration of reactant A molecules increases, the number of effective collisions also increases.

Table 17.2 Elementary Steps and Their Rate Laws

Elementary Step	Molecularity	Rate Law
A → B	Unimolecular	Rate = *k*[A]
2A → C	Bimolecular	Rate = $k[A]^2$
2A + D → E	Termolecular	Rate = $k[A]^2[D]$

Multi-step Mechanisms

The overall reaction process often corresponds to a series of two or more elementary steps, which must always add up to give the overall balanced chemical equation. For example, in the following elimination reaction (a type of reaction typically discussed in introductory organic chemistry courses):

$$\text{C}_4\text{H}_9\text{Br} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_8 + \text{H}_3\text{O}^+ + \text{Br}^-$$

This reaction process proceeds in two elementary steps and would therefore be called a two-step mechanism. In the first step, bromide leaves from the starting material to give the cation $C_4H_9{}^+$. In the second step, $C_4H_9{}^+$ reacts with water to generate the product C_4H_8 and H_3O^+.

$$\text{Step 1: } \text{C}_4\text{H}_9\text{Br} \leftrightarrow \text{C}_4\text{H}_9{}^+ + \text{Br}^- \qquad \text{(slow)}$$
$$\text{Step 2: } \text{C}_4\text{H}_9{}^+ + \text{H}_2\text{O} \leftrightarrow \text{C}_4\text{H}_8 + \text{H}_3\text{O}^+$$
$$\text{Net: } \text{C}_4\text{H}_9\text{Br} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_8 + \text{H}_3\text{O}^+ + \text{Br}^-$$

The cation $C_4H_9{}^+$ is called an **intermediate**, since it does not appear in the overall balanced equation and is generated in one elementary step but used up in a subsequent step. A potential energy diagram for this multi-step reaction can be drawn as shown in Figure 17.12 “Multi-step Reaction Potential Energy Diagram.” Notice each step has its own activation energy, and **transition state** (or **activated complex**), which is the highest-energy transitional point in the elementary step. Transition states are very unstable (high energy) as bonds are in the process of breaking or forming, and therefore transition

states cannot be isolated. Intermediates are more stable than transition states and can sometimes be isolated and characterized by certain techniques.

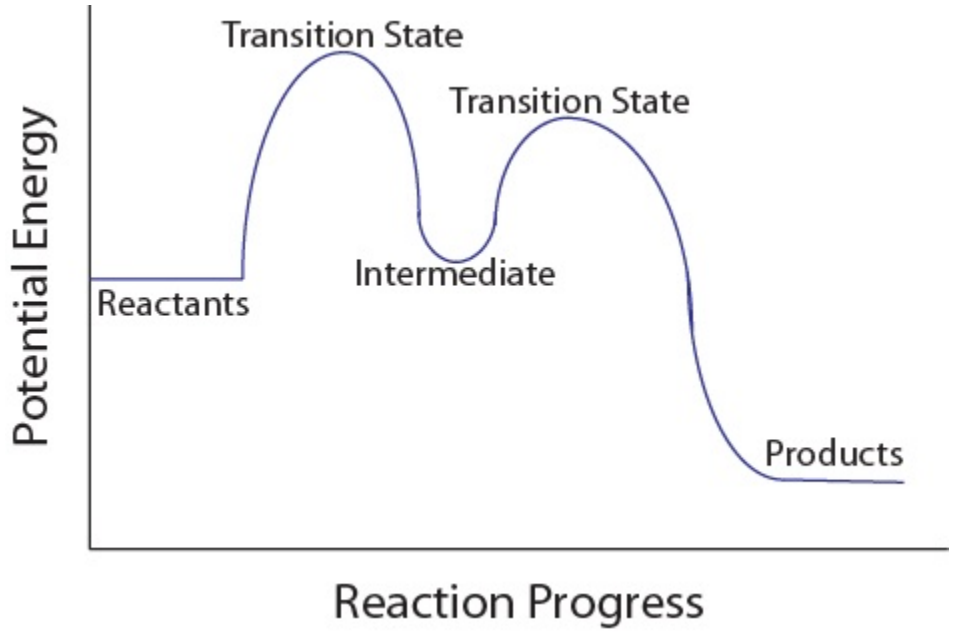


Figure 17.12 "Multi-step Reaction Potential Energy Diagram." Multi-step reaction potential energy diagram showing the intermediate.

The Rate-Determining Step

For multi-step mechanisms, there is often one step that is significantly slower than the other steps. This slowest step is referred to as the **rate-determining step**, as it limits the rate of the entire reaction. An analogy that illustrates this concept is an hourglass having two different sized openings. The rate of the sand falling to the bottom-most chamber is determined by the smaller of the two openings (see Figure 17.13 "Rate-Determining Point in an Hourglass"). Similarly, the rate law of the overall reaction is determined from its rate-determining slowest step.

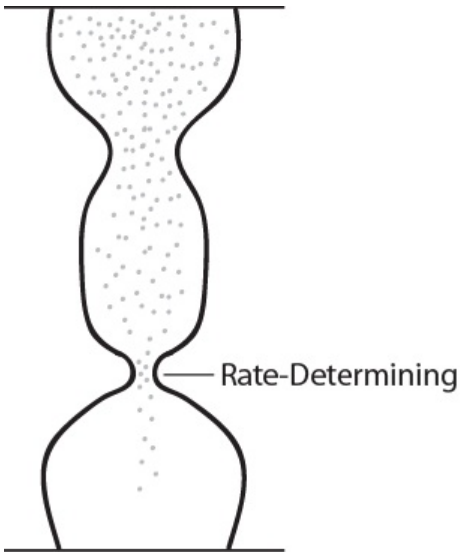


Figure 17.13 "Rate-Determining Point in an Hourglass." Double hourglass with one opening smaller than the other, which determines rate.

Example 17.9

The following reaction occurs in a two-step mechanism:

$$\begin{aligned} \mathrm{A} &\rightarrow \mathrm{B} + \mathrm{C} && \text{slow} \\ \mathrm{A} + \mathrm{C} &\rightarrow \mathrm{B} + \mathrm{D} && \text{fast} \end{aligned}$$

1. Determine the overall reaction equation.
2. Write the rate law for the overall reaction.

Solution

1. Add the two elementary steps together and cancel out any intermediates to give the overall reaction:

$$2\mathrm{A} \rightarrow 2\mathrm{B} + \mathrm{D}$$

2. Rate = $k[\mathrm{A}]^2$

Key Takeaways

- The overall reaction process often corresponds to a series of more than one elementary step, which must always add up to give the overall balanced chemical equation.
- Each step has its own activation energy and transition state.
- The slowest step of a multi-step reaction is the rate-determining step.

Catalysis

Jessie A. Key

Learning Objectives

- To gain an understanding of homogeneous, heterogeneous, and biological catalysts.

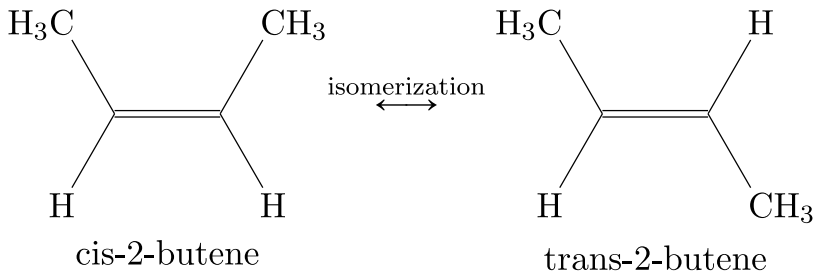
Catalysts are substances that lower the activation energy of a specific reaction by providing an alternate reaction pathway. Catalysts participate in a reaction, but are not permanently changed in the process, as they are regenerated to their original state. Many scientists classify catalysts into one of three categories: homogeneous catalysts, heterogeneous catalysts, and biological catalysts (enzymes).

Homogeneous Catalysts

A **homogeneous catalyst** is any catalyst that is present in the same phase as the reactant molecules. There are numerous examples of homogeneous catalysts, and we will examine one that is commonly used in textbooks.

The alkene 2-butene can exist as one of two isomers: *cis* where the methyl groups are located on the same side of the double bond, and *trans* where the methyl groups are located on opposite sides of the double bond (Figure 17.14 “Isomerization of 2-Butene”). To convert (isomerize) between the two structures, the carbon-carbon double bond must be broken and the molecule must rotate. This process has a relatively high activation energy of approximately 264 kJ/mol and is therefore fairly slow to occur at room temperature.

2-butene can exist as one of two isomers. This diagram shows the isomerization of 2-butene:



A catalyst like iodine can be used to provide an alternate pathway for the reaction with a much lower activation energy of approximately 118 kJ/mol (see Figure 17.14 “Catalyzed and Uncatalyzed Reaction Pathways”).

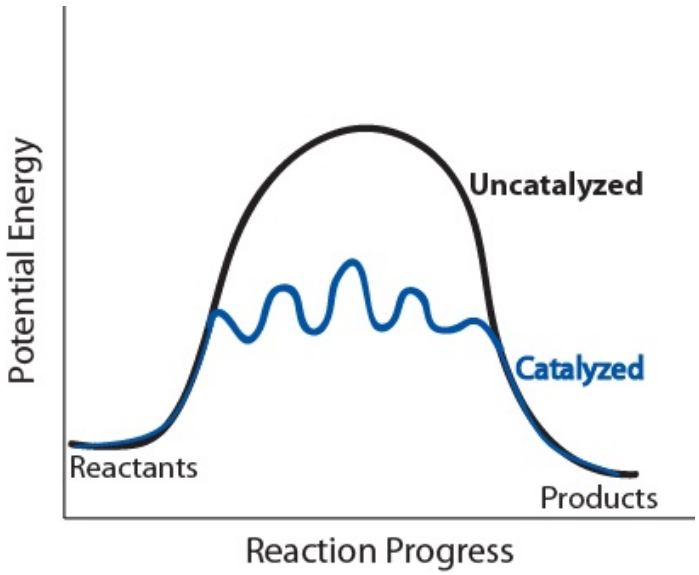


Figure 17.14 "Catalyzed and Uncatalyzed Reaction Pathways." Potential energy diagrams of catalyzed and uncatalyzed reaction pathways.

In the catalyzed pathway, an iodine atom is generated that reacts with cis-2-butene to produce a reaction intermediate that has broken its carbon-carbon double bond and formed a new C-I bond and a radical (see Figure 17.15 "2-Butene Catalyzed Isomerization Steps"). The molecule can rotate more easily and the C-I breaks to reform the double bond.

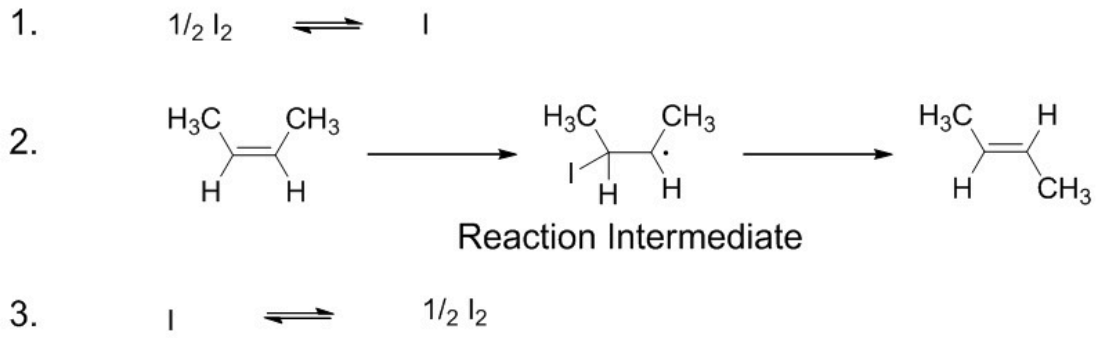


Figure 17.15 "2-Butene Catalyzed Isomerization Steps." 2-butene catalyzed isomerization steps using iodine as the catalyst.

Heterogeneous Catalysts

Heterogeneous catalysts are those that are in a different phase from one or more of the reactants. Commonly solid metals and metal oxides are used to catalyze the reactions of gaseous or liquid reactants. Solid catalysts often serve as a surface on which reactions can occur, where one or more reactants will **adsorb** (bind to the surface) to the solid.

A common example of heterogeneous catalysis is the hydrogenation reaction of simple alkenes. The conversion of ethene (C_2H_4) to ethane (C_2H_6) can be performed with hydrogen gas in the presence of a

metal catalyst such as palladium (Figure 17.16 “Conversion of Ethene to Ethane with Hydrogen and a Metal Catalyst”).

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

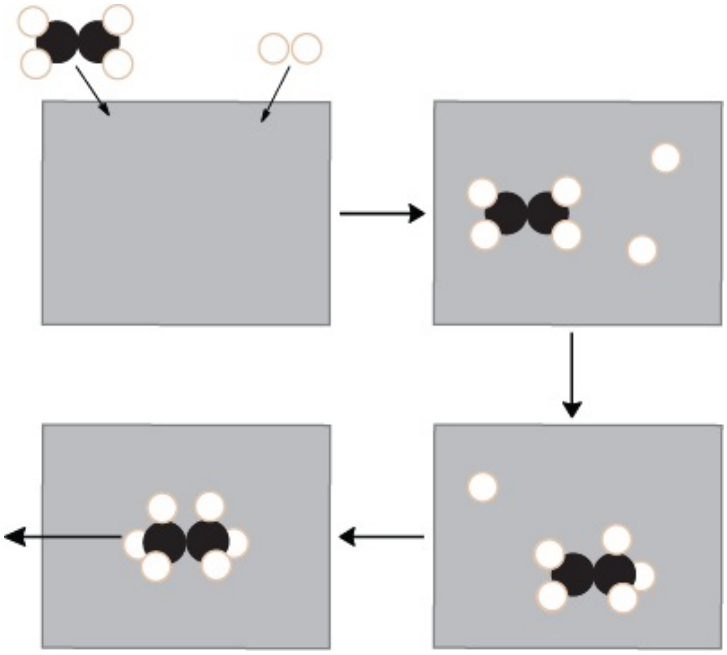


Figure 17.16 “Conversion of Ethene to Ethane with Hydrogen and a Metal Catalyst.” Heterogeneous catalysis mechanisms of reaction for ethene with hydrogen on a catalytic metal surface

Ethene and hydrogen adsorb onto the metal surface, where the H_2 breaks into two individual hydrogen atoms bonded to the metal surface. A reaction occurs between adjacent ethene and hydrogen atoms on the metal surface, first to generate a C_2H_5 intermediate, then to generate ethane, C_2H_6, which desorbs from the surface.

Biological Catalysts

Catalysts within living things facilitate the vast and intricate system of chemical reactions required for life. There are two main types of naturally occurring catalytic biomolecules: ribozymes and enzymes.

Ribozymes are ribonucleic acid (RNA) molecules capable of catalyzing certain chemical reactions. Ribozymes are a relatively recent discovery, first reported in 1982, but their importance was demonstrated by the awarding of the 1989 Nobel Prize to the discoverers Sidney Altman and Thomas Cech. Research is ongoing to better understand these catalysts and develop new therapeutics and medicines using them.

Enzymes are protein molecules that catalyze biochemical reactions. They are remarkably specific for the reactants they can use, known as **substrates**, and many dramatically increase reaction rate by factors of 10^7 to 10^{14}. A simple model often used to describe enzyme activity is known as the lock-and-key model (see Figure 17.17 “Lock-and-Key Model of Enzymatic Catalysis”). In this model, enzymes accelerate reactions by providing a tight-fitting area, known as the **active site**, where substrate

molecules can react. Hydrophobicity and intermolecular forces such as hydrogen bonding, London-dispersion forces, and dipole-dipole interactions facilitate the binding of substrate molecules to the active site, forming an **enzyme-substrate complex**. When the reaction is completed at the active site, the product is released.

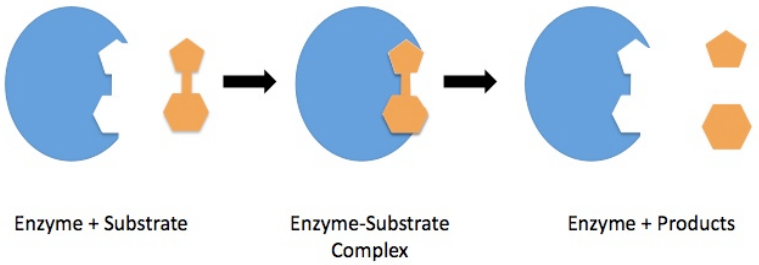


Figure 17.17 "Lock-and-Key Model of Enzymatic Catalysis." Lock-and-key model of enzymatic catalysis showing the tight-fitting area where substrate molecules react.

Key Takeaways

- Catalysts provide an alternate, lower-energy reaction pathway.
- A homogeneous catalyst is any catalyst that is present in the same phase as the reactant molecules.
- Heterogeneous catalysts are in a different phase from one or more of the reactants, and often act as a surface on which the reaction can occur.
- According to the lock-and-key model, enzymes accelerate reactions by providing a tight-fitting area, where substrate molecules can react.

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End-of-Chapter Material

Jessie A. Key

Additional Exercises

1. What factors affect the rate of a reaction?
2. How does a decrease in temperature affect the reaction rate? Explain the outcome by describing changes that occur at the molecular level.
3. For which of the following two reactions would you expect the orientation of the molecules to be more important?
    a. $AB + C \rightarrow AC + B$
    b. $D + E \rightarrow F$
4. Determine the relative rates of disappearance of reactants and formation of products for the following reactions:
    a. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
    b. $2A + 3B \rightarrow 4C$
    c. $2N_2O_5 \rightarrow 4\ NO_2 + O_2$
5. Methanol reacts with hydrochloric acid to produce methyl chloride and water by the following reaction:

$$CH_3OH(aq) + HCl(aq) \rightarrow CH_3Cl(aq) + H_2O(\ell)$$

The following data were obtained for this reaction at a particular temperature:

Time (min)	[CH3OH] (M)
0.0	1.95
60.0	1.50
120.0	1.24
180.0	1.04
240.0	0.85
300.0	0.70

    a. Calculate the average reaction rate between 0 and 60 minutes and 180 and 240 minutes. Which is faster? Explain using your knowledge of factors that can affect rate.
    b. Determine the instantaneous rate at 200 minutes.
6. For the following reaction: $3\ E + 2\ F \rightarrow 2\ G$, the rate law is Rate = $k[F]^2$.
    a. How does the rate change if [E] is doubled?
    b. How does the rate change is [F] is doubled?
    c. What is the overall reaction order?
    d. What are the units for the rate constant for this reaction?
7. The rate of oxidation of bromide ions by bromate in an acidic aqueous solution is

$$6\,H^+ + BrO_3^- + 5Br^- \rightarrow 3Br_2 + 3H_2O$$

and is found to follow the rate law

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

What happens to the rate if, in separate experiments:

a. $[BrO_3^-]$ is doubled?
b. the pH is increased by one unit?
c. the solution is diluted to twice its volume, with the pH kept constant by use of a buffer?[1]

8. The following data was obtained using the initial rate method:

$$A + B \rightarrow C + D$$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	2.0×10^{-3}	2.0×10^{-3}	1.45×10^{-4}
2	4.0×10^{-3}	2.0×10^{-3}	2.90×10^{-4}
3	2.0×10^{-3}	4.0×10^{-3}	2.90×10^{-4}

a. Determine the rate law for this equation.
b. Calculate the rate constant, including units.
c. Determine the rate when [A] = 0.250 M and [B] = 0.100 M.

9. A study of the gas-phase reduction of nitric oxide by hydrogen

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

yielded the following initial-rate data (all pressures in torr):

Experiment	*P*(NO)	*P*(H_2)	Initial Rate (torr s^{-1})
1	359	300	1.50
2	300	300	1.03
3	152	300	0.25
4	300	289	1.00
5	300	205	0.71
6	200	147	0.51

Find the order of the reaction with respect to each component.[2]

10. What should be plotted on the *x*– and *y*-axis to obtain a straight line for:

a. a first-order reaction?
b. a zero-order reaction?

11. What does the slope represent for:

a. a second-order reaction kinetic plot?
b. a first-order reaction kinetic plot?

12. Common sugar, sucrose $C_{12}H_{22}O_{11}$, reacts in dilute acidic solutions to produce glucose and fructose, both having the

1. Question and solution from Chem1 Virtual Textbook, Stephen Lower/CC-BY-SA-3.0
2. Question and solution from Chem1 Virtual Textbook, Stephen Lower/CC-BY-SA-3.0

molecular formula $C_6H_{12}O_6$.

$$C_{12}H_{22}O_{11}(aq) + H_2O(\ell) \rightarrow 2C_6H_{12}O_6(aq)$$

During an experiment, the following data were obtained:

Time (hours)	[Sucrose] (mM)
0.00	316
0.65	274
1.33	238
2.33	190
3.50	146

a. What is the order of the reaction?

b. Determine the rate law and the rate constant.

c. Calculate the expected concentration of sucrose after 100 min.

13. The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant in reciprocal seconds?[3]

14. The mass-241 isotope of americium, widely used as an ionizing source in smoke detectors, has a half-life of 432 years.

a. What fraction of the Am^{241} in a smoke detector will have decayed after 50 years?

b. How long will it take for the activity to decline to 80% of its initial value?

c. What would be the "seventh-life" of Am^{241}?[4]

15. A widely used "rule of thumb" for the temperature dependence of a reaction rate is that a 10°C rise in the temperature approximately doubles the rate. (This is obviously not generally true, especially when a strong covalent bond must be broken.) For a reaction that shows this behaviour, what would the activation energy be?[5]

16. The temperature dependence of the rate constant, *k*, for a reaction was found to be:

Temperature (K)	k ($M^{-1}s^{-1}$)
500	0.025
600	0.300
700	1.500
800	7.000
900	28.000

Calculate the activation energy (E_a) and *A*.

17. State the molecularity and rate law for each of the following elementary steps:

a. $Cl(g) + CCl_3(g) \rightarrow CCl_4(\ell)$

b. $Br_2 \rightarrow 2Br$

c. $2A \rightarrow B$

18. A reaction is believed to occur by the following two elementary steps:

$$2NO_2 \rightarrow NO_3 + NO$$

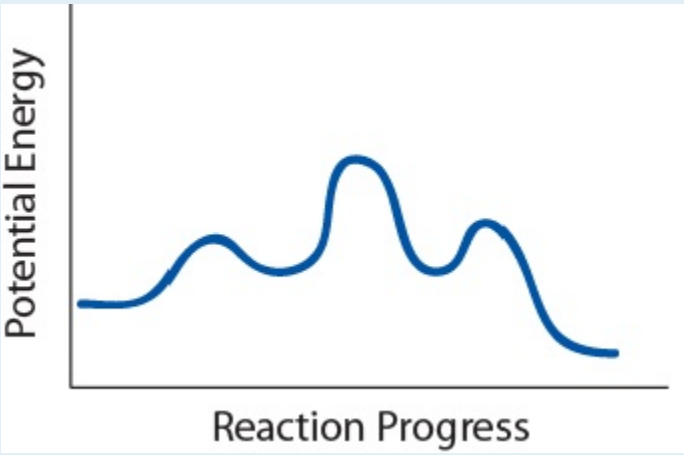
3. Question and solution from Chem1 Virtual Textbook, Stephen Lower/CC-BY-SA-3.0
4. Question and solution from Chem1 Virtual Textbook, Stephen Lower/CC-BY-SA-3.0
5. Question and solution from Chem1 Virtual Textbook, Stephen Lower/CC-BY-SA-3.0

$$NO_3 \rightarrow NO + O_2$$

With this in mind:

a. Write the balanced overall equation of this reaction.
b. Identify any intermediates in the mechanism.
c. If the first step is much slower than the second, what would you expect the rate law for the overall reaction to be?

19. Use the following potential energy diagram to answer questions 19a to 19c:



Potential energy plot of a given reaction mechanism.

a. How many steps are in this mechanism?
b. How many intermediates are there in this reaction?
c. What is the slowest step?

20. What is a catalyst? Explain how a catalyst affects reaction rates.
21. Many solid catalysts are commercially sold as fine powders or small spherical beads. Explain why this might be beneficial.

Answers

1. temperature, reactant concentrations, physical state (surface area of solids), presence of a catalyst

3. $AB + C \rightarrow AC + B$

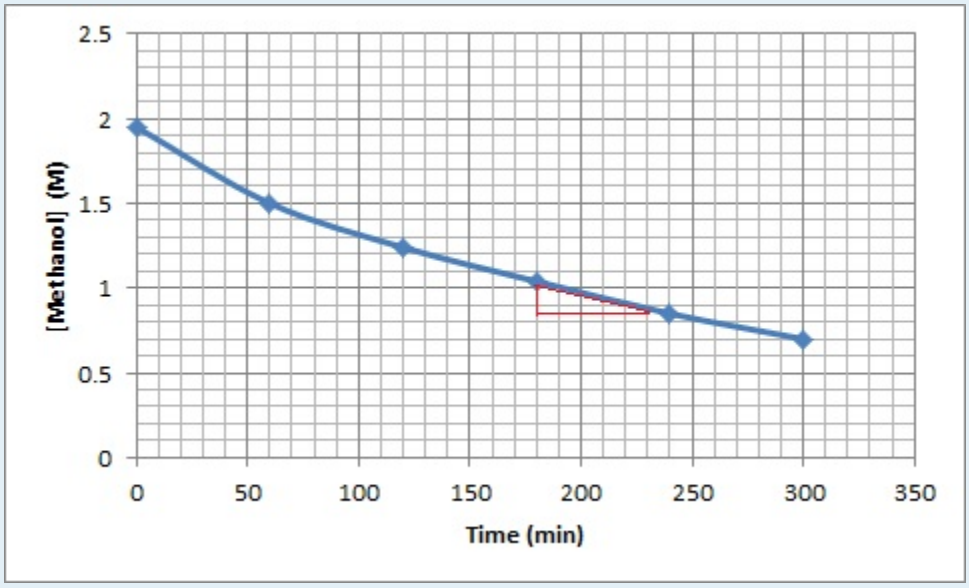
5. a. average reaction rate 0–60 minutes:

$$-\frac{[CH_3OH]_{60} - [CH_3OH]_0}{60.0 \text{ min} - 0.0 \text{ min}} = \frac{1.50 \text{ M} - 19.5 \text{ M}}{60.0 \text{ min}} = 7.50 \times 10^{-3} \text{ M/min}$$

average reaction rate 180–240 minutes:

$$-\frac{[CH_3OH]_{240} - [CH_3OH]_{180}}{240.0 \text{ min} - 180.0 \text{ min}} = \frac{0.85 \text{ M} - 1.04 \text{ M}}{60.0 \text{ min}} = 3.17 \times 10^{-3} \text{ M/min}$$

Therefore the average reaction rate between 0–60 minutes is faster. This is because, as the reaction proceeds, the reactant gets consumed to make product, lowering the concentration of reactants.



b.

Instantaneous rate at 200 minutes:

$$-\frac{\text{Rise}}{\text{Run}} = \frac{1.0\text{ M} - 0.84\text{ M}}{230\text{ min} - 180\text{ min}} = \frac{0.16\text{ M}}{50\text{ min}} = 3.2 \times 10^{-3}\text{ M/min}$$

7. a. Since the rate is first-order in bromate, doubling its concentration will double the reaction rate.

b. Increasing the pH by one unit will *decrease* the $[H^+]$ by a factor of 10. Since the reaction is second-order in $[H^+]$, this will decrease the rate by a factor of 100.

c. Dilution reduces the concentrations of both Br_2 and BrO_3^- to half their original values. Doing this to each concentration alone would reduce the rate by a factor of 2, so reducing both concentrations will reduce the rate by a factor of 4, to (½) × (½) = ¼ of its initial value.

9. a. **Experiments 2 and 3**: Reduction of the initial partial pressure of NO by a factor of about 2 $\left(\frac{300}{152}\right)$ results in a reduction of the initial rate by a factor of about 4, so the reaction is second-order in nitric oxide.

b. **Experiments 4 and 6**: Reducing the initial partial pressure of hydrogen by a factor of approximately 2 $\left(\frac{289}{147}\right)$ causes a similar reduction in the initial rate, so the reaction is first-order in hydrogen.

c. **The rate law is**: rate = $k[NO]^2[H_2]$.

11. a. k

b. $-k$

13. From the above equation, $k = \frac{-0.693}{600\text{ s}} = 0.00115\text{ s}^{-1}$

15. We will centre our ten-degree interval at 300 K. Substituting into the above expression yields:

$$E_a = \frac{8.314 \ln \frac{2}{1}}{\frac{1}{295} - \frac{1}{305}}$$

$$= \frac{(8.314)(0.693)}{0.00339 - 0.00328}$$

$$= \frac{5.76 \text{ J mol}^{-1} \text{ K}^{-1}}{0.00011 \text{ K}^{-1}}$$

$$= 52,400 \text{ J mol}^{-1} = 52.4 \text{ kJ mol}^{-1}$$

17.
a. bimolecular, rate = k[Cl] [CCl_3]
b. unimolecular, rate = k[Br_2]
c. bimolecular 2A, rate = k[A]^2

19.
a. 3 steps
b. 2 intermediates
c. The second step is the slowest step

21. Finely divided powders and spherical beads have larger surface areas than big solid chunks, allowing for more sites for reactions to occur, which further speeds up the reaction.

Chapter 18. Chemical Thermodynamics

You have previously learned about energy and its relationship to chemical processes (enthalpy). There are some processes that require the input of heat (endothermic) while others release heat (exothermic), but how do we know if any of these processes will proceed under certain conditions? Enthalpy is only part of the answer, so we must delve further into chemical thermodynamics.

In this chapter, we will examine the concept of spontaneity: whether a process will occur without external influences. As well, we will focus on the thermodynamic state function known as *entropy*, a measure of "randomness" or the amount of energy dispersal in molecules. Finally, we will discuss Gibbs free energy, a thermodynamic quantity used to predict spontaneity, which incorporates both enthalpy and entropy.

Spontaneous Change

Jessie A. Key

Learning Objectives

- Gain an understanding of what is meant by the term *spontaneous*.

Generally speaking, a **spontaneous process** is one that occurs without the influence of external forces. A common example that is used to portray the difference between a spontaneous and nonspontaneous processes is the dropping of a breakable object like a beaker. The beaker will fall and break unless outside forces are used to stop it. However, the opposite process, a broken beaker being reformed into its original condition and defying gravity to lift into the air, is **nonspontaneous**. The beaker cannot simply reform and lift into the air on its own, it requires a skilled glassworker to fix a broken beaker and someone to lift it in the air.

Chemically, when we use the term **spontaneous**, we are referring to any change that moves a system toward equilibrium. The term spontaneous does not imply anything about the speed or rate; this is the domain of kinetics. Spontaneity simply provides information on the *direction* of a reaction.

Key Takeaways

- A spontaneous reaction or process is one that moves a system toward equilibrium.

Entropy and the Second Law of Thermodynamics

Jessie A. Key

Learning Objectives

- To gain an understanding of the term *entropy*.
- To gain an understanding of the Boltzmann equation and the term *microstates*.
- To be able to estimate change in entropy qualitatively.

To assess the spontaneity of a process we must use a thermodynamic quantity known as **entropy** (*S*). The second law of thermodynamics states that *a spontaneous process will increase the entropy of the universe*. But what exactly is entropy? Entropy is typically defined as either the level of randomness (or disorder) of a system or a measure of the energy dispersal of the molecules in the system. These definitions can seem a bit vague or unclear when you are first learning thermodynamics, but we will try to clear this up in the following subsections.

The Molecular Interpretation of Entropy

Consider the following system, where two flasks are sealed together and connected by a stopcock (see Figure 18.1 “Two-Atom, Double-Flask Diagram”). In this system, we have placed two atoms of gas, one green and one blue. At first, both atoms are contained in only the left flask. When the stopcock is opened, both atoms are free to move around randomly in both flasks. If we were to take snapshots over time, we would see that these atoms can have four possible arrangements. The likelihood of all atoms being found in their original flask, in this case, is only 1 in 4. If we increased the number of atoms, we would see that the probability of finding all of the atoms in the original flask would decrease dramatically following $(½)^n$, where *n* is the number of atoms.

Thus we can say that it is entropically favoured for the gas to spontaneously expand and distribute between the two flasks, because the resulting increase in the number of possible arrangements is an increase in the randomness/disorder of the system.

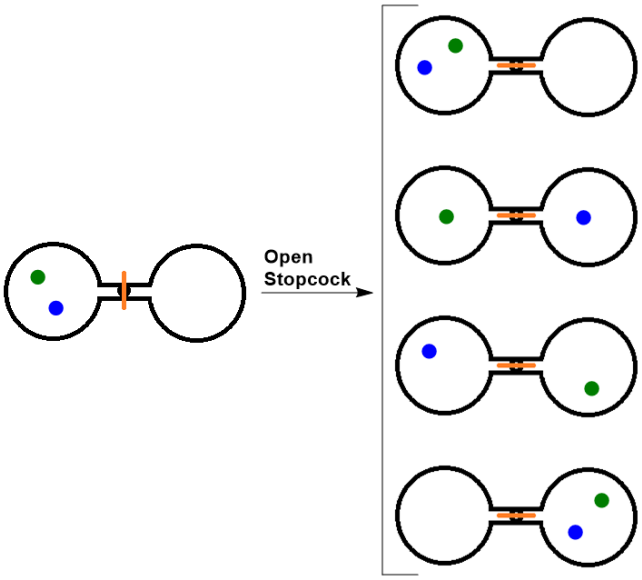


Figure 18.1 "Two-Atom, Double-Flask Diagram." When the stopcock is opened between the flasks, the two atoms can distribute in four possible ways.

The Boltzmann Equation

Figure 18.2 "Ludwig Boltzmann"

Ludwig Boltzmann (1844–1906) pioneered the concept that entropy could be calculated by examining the positions and energies of molecules. He developed an equation, known as the **Boltzmann equation**, which relates entropy to the number of **microstates (*W*)**:

$$S = k \ln W$$

where k is the Boltzmann constant (1.38×10^{-23} J/K), and W is the number of microstates.

Microstates is a term used to describe the number of different possible arrangements of molecular position and kinetic energy at a particular thermodynamic state. A process that gives an increase in the number of microstates therefore increases the entropy.

Qualitative Estimates of Entropy Change

We can estimate changes in entropy qualitatively for some simple processes using the definition of entropy discussed earlier and incorporating Boltzmann's concept of microstates.

As a substance is heated, it gains kinetic energy, resulting in increased molecular motion and a broader distribution of molecular speeds. This increases the number of microstates possible for the system. Increasing the number of molecules in a system also increases the number of microstates, as now there are more possible arrangements of the molecules. As well, increasing the volume of a substance increases the number of positions where each molecule could be, which increases the number of microstates. Therefore, any change that results in a higher temperature, more molecules, or a larger volume yields an increase in entropy.

Key Takeaways

- Entropy is the level of randomness (or disorder) of a system. It could also be thought of as a measure of the energy dispersal of the molecules in the system.
- Microstates are the number of different possible arrangements of molecular position and kinetic energy at a particular thermodynamic state.
- Any change that results in a higher temperature, more molecules, or a larger volume yields an increase in entropy.

Media Attributions

- "Portrait of Ludwig Boltzmann" © American Institute of Physics, Emilio Segrè Visual Archives, Segrè Collection is licensed under a Public Domain license

Measuring Entropy and Entropy Changes

Jessie A. Key

Learning Objectives

- To gain an understanding of methods of measuring entropy and entropy change.

As the temperature of a sample decreases, its kinetic energy decreases and, correspondingly, the number of microstates possible decreases. The third law of thermodynamics states: *at absolute zero (0 K), the entropy of a pure, perfect crystal is zero*. In other words, at absolute zero, there is only one microstate and according to Boltzmann's equation:

$$S = k \ln W = k \ln 1 = 0$$

Using this as a reference point, the entropy of a substance can be obtained by measuring the heat required to raise the temperature a given amount, using a reversible process. Reversible heating requires very slow and very small increases in heat.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Example 18.1

Determine the change in entropy (in J/K) of water when 425 kJ of heat is applied to it at 50°C. Assume the change is reversible and the temperature remains constant.

Solution

$$\Delta \text{S} = \frac{q_{\text{rev}}}{T} = \frac{425 \text{ kJ}}{323.15 \text{ K}} = \frac{4.25 \times 10^5 \text{ J}}{323.15 \text{ K}} = 1.32 \times 10^5 \text{ J/K}$$

Standard Molar Entropy, *S*°

The **standard molar entropy**, *S*°, is the entropy of 1 mole of a substance in its standard state, at 1 atm of pressure. These values have been tabulated, and selected substances are listed in Table 18.1a to c "Standard Molar Entropies of Selected Substances at 298 K".[1]

1. These tables are based on a table from UC Davis ChemWiki by University of California\CC-BY-SA-3.0

Table 18.1a Standard Molar Entropies of Selected Gases at 298 K

Gas	S°[J/(mol·K)]
He	126.2
H_2	130.7
Ne	146.3
Ar	154.8
Kr	164.1
Xe	169.7
H_2O	188.8
N_2	191.6
O_2	205.2
CO_2	213.8
I_2	260.7

Table 18.1b Standard Molar Entropies of Selected Liquids at 298 K

Liquid	S°[J/(mol·K)]
H_2O	70.0
CH_3OH	126.8
Br_2	152.2
CH_3CH_2OH	160.7
C_6H_6	173.4
CH_3COCl	200.8
C_6H_{12} (cyclohexane)	204.4
C_8H_{16} (isooctane)	329.3

Table 18.1c Standard Molar Entropies of Selected Solids at 298 K

Solid	S°[J/(mol·K)]
C (diamond)	2.4
C (graphite)	5.7
LiF	35.7
SiO_2 (quartz)	41.5
Ca	41.6
Na	51.3
MgF_2	57.2
K	64.7
NaCl	72.1
KCl	82.6
I_2	116.1

Several trends emerge from standard molar entropy data:

- Larger, more complex molecules have higher standard molar enthalpy values than smaller or simpler molecules. There are more possible arrangements of atoms in space for larger, more complex molecules, increasing the number of possible microstates.
- Gases tend to have much larger standard molar enthalpies than liquids, and liquids tend to have larger values than solids, when comparing the same or similar substances.
- The standard molar entropy of any substance increases as the temperature increases. This can be seen in Figure 18.3 “Entropy vs. Temperature of a Single Substance.” Large jumps in entropy occur at the phase changes: solid to liquid and liquid to gas. These large increases occur due to sudden increased molecular mobility and larger available volumes associated with the phase changes.

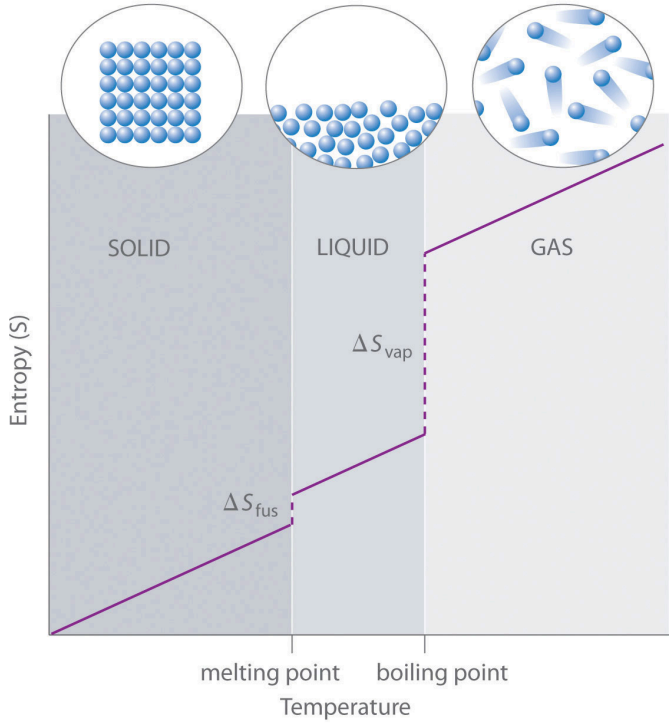


Figure 18.3 "Entropy vs. Temperature of a Single Substance." This is a generalized plot of entropy versus temperature for a single substance. (Source: UC Davis ChemWiki by University of California\CC-BY-SA-3.0)

Standard Entropy Change of a Reaction, ΔS°

The entropy change of a reaction where the reactants and products are in their standard state can be determined using the following equation:

$$\Delta S^\circ = \sum_{\text{products}} nS^\circ - \sum_{\text{reactants}} mS^\circ$$

where *n* and *m* are the coefficients found in the balanced chemical equation of the reaction.

Example 18.2

Determine the change in the standard entropy, ΔS°, for the synthesis of carbon dioxide from graphite and oxygen:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Solution

$$\begin{aligned}\Delta S^\circ &= \sum_{\text{products}} nS^\circ - \sum_{\text{reactants}} mS^\circ \\ &= (213.8\ \text{J/mol K}) - (205.2\ \text{J/mol K} + 5.7\ \text{J/mol K}) \\ &= +2.9\ \text{J/mol K}\end{aligned}$$

Entropy Changes in the Surroundings

The second law of thermodynamics states that a spontaneous reaction will result in an increase of entropy in the universe. The universe comprises both the system being examined and its surroundings.

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Standard entropy change can also be calculated by the following:

$$\Delta S^\circ_{\text{universe}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}}$$

The change in entropy of the surroundings is essentially just a measure of how much energy is being taken in or given off by the system. Under isothermal conditions, we can express the entropy change of the surroundings as:

$$\Delta \text{S}_{\text{surr}} = \frac{-q_{\text{sys}}}{T} \text{ or } \Delta \text{S}_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad \text{(at constant pressure)}$$

Example 18.3

For the previous example, the change in the standard entropy, Δ*S*°, for the synthesis of carbon dioxide from graphite and oxygen, use the previously calculated Δ*S*°$_{\text{sys}}$ and standard enthalpy of formation values to determine *S*°$_{\text{surr}}$ and Δ*S*°$_{\text{universe}}$.

Solution

First we should solve for the Δ*H*°$_{\text{sys}}$ using the standard enthalpies of formation values:

$$\begin{aligned}\Delta H^\circ_{\text{sys}} &= \Delta H^\circ_{\text{f}}[\text{CO}_2(\text{g})] - \Delta H^\circ_{\text{f}}[\text{C(s)} + \text{O}_2(\text{g})] \\ &= (-393.5\ \text{kJ/mol}) - (0\ \text{kJ/mol} + 0\ \text{kJ/mol}) \\ &= -393.5\ \text{kJ/mol}\end{aligned}$$

Now we can convert this to the Δ*S*°$_{\text{surr}}$:

$$\Delta S^\circ_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-393.5\ \text{kJ/mol}}{298\ \text{K}} = -1.32\ \text{kJ/mol K}$$

Finally, solve for Δ*S*°$_{\text{universe}}$:

$$\begin{aligned}\Delta S^\circ_{\text{universe}} &= \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}} \\ &= (+2.9\ \text{J/mol K}) + (-1.32 \times 10^3\ \text{J/mol K}) \\ &= -1.3 \times 10^3\ \text{J/mol K}\end{aligned}$$

Key Takeaways

- At absolute zero (0 K), the entropy of a pure, perfect crystal is zero.
- The entropy of a substance can be obtained by measuring the heat required to raise the temperature a given amount, using a reversible process.
- The standard molar entropy, S°, is the entropy of 1 mole of a substance in its standard state, at 1 atm of pressure.

Gibbs Free Energy

Jessie A. Key

Learning Objectives

- To gain an understanding of Gibbs free energy.
- To understand the relationship between the sign of Gibbs free energy change and the spontaneity of a process.
- To be able to determine Gibbs free energy using standard free energies of formation.

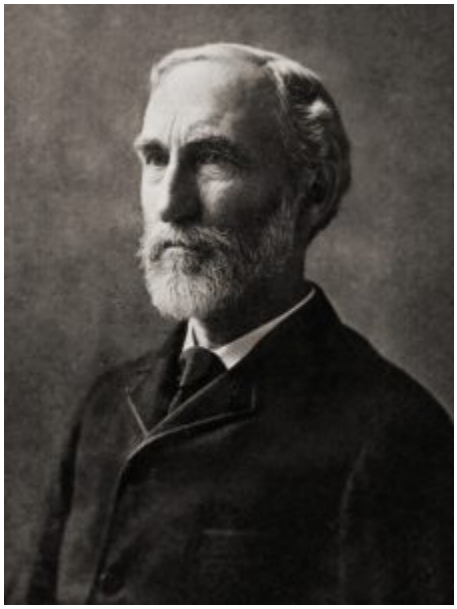


Figure 18.4 "J. Willard Gibbs."

J. Willard Gibbs (1839–1903) proposed a single state function to determine spontaneity:

$$G = H - TS$$

where *H* is the enthalpy of the system, *S* is the entropy of the system, and *G* is **Gibbs free energy**.

The change in Gibbs free energy, Δ*G*, is the maximum amount of free energy available to do useful work. For an isothermal process, it can be expressed as:

$$\Delta G = \Delta H - T\Delta S$$

or at standard conditions:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

This single term, Gibbs free energy (*G*), allows us to avoid calculating the entropy of the surroundings. It is really just a simplification of our previous method of estimating spontaneity:

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \frac{-\Delta H_{\text{sys}}}{T}$$

Multiply both sides of the equation by −*T*:

$$-T\left(\Delta S_{\text{universe}}\right) = \left(\Delta S_{\text{sys}} + \frac{-\Delta H_{\text{sys}}}{T}\right) - T$$

$$-T\Delta S_{\text{universe}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

Therefore, $\Delta G = -T\Delta S_{\text{universe}}$.

As a result of this relationship, the sign of Gibbs free energy provides information on the spontaneity of a given reaction:

If $\Delta G > 0$, the reaction is nonspontaneous in the direction written.
If $\Delta G = 0$, the reaction is in a state of equilibrium.
If $\Delta G < 0$, the reaction is spontaneous in the direction written.

The significance of the sign of a change in Gibbs free energy parallels the relationship of terms from the equilibrium chapter: the reaction quotient, *Q*, and the equilibrium constant, *K*.

If $Q > K$, the reaction is nonspontaneous in the direction written.
If $Q = K$, the reaction is in a state of equilibrium.
If $Q < K$, the reaction is spontaneous in the direction written.

Example 18.4

Calculate Δ*G*° for a reaction where Δ*H*° is equal to 36.2 kJ and Δ*S*° is equal to 123 J/K at 298 K. Is this a spontaneous reaction?

Solution

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 36.2\ \text{kJ} - (298\ \text{K} \times 123\ \text{J/K}) \\ &= -0.4\ \text{kJ}\end{aligned}$$

Therefore the reaction is spontaneous because $\Delta G°$ is negative.

Determining ΔG° from Standard Free Energy of Formation

The standard Gibbs free energy change, $\Delta G°$, for a reaction can be calculated from the standard free energies of formation, $\Delta G°_\text{f}$.

$$\Delta G^\circ_\text{f} = \sum_{\text{products}} n\Delta G^\circ_\text{f} - \sum_{\text{reactants}} m\Delta G^\circ_\text{f}$$

where *n* and *m* are the coefficients in the balanced chemical equation of the reaction.

Standard free energies of formation values are listed in the appendix, “Standard Thermodynamic Quantities for Chemical Substances at 25°C.”

Example 18.5

Calculate the standard free energy change for the following reaction, using standard free energies of formation:

$$5C(s) + 2SO_2(g) \rightarrow CS_2(g) + 4CO(g)$$

Is this a spontaneous reaction?

Solution

$$\begin{aligned}\Delta G^\circ &= \sum_{\text{products}} n\Delta G^\circ_\text{f} - \sum_{\text{reactants}} m\Delta G^\circ_\text{f} \\ &= [(4 \times -137.2\ \text{kJ/mol}) + (67.1\ \text{kJ/mol})] \\ &\quad - [(5 \times 0\ \text{kJ/mol}) + (2 \times -300.1\ \text{kJ/mol})] \\ &= (-481.7\ \text{kJ/mol}) - (-600.2\ \text{kJ/mol}) \\ &= 118.5\ \text{kJ/mol}\end{aligned}$$

$\Delta G°$ has a positive value, so this is not a spontaneous process.

Key Takeaways

- The change in Gibbs free energy (ΔG) is the maximum amount of free energy available to do useful work.
- If $\Delta G > 0$, the reaction is nonspontaneous in the direction written. If $\Delta G = 0$, the reaction is in a state of equilibrium. If $\Delta G < 0$, the reaction is spontaneous in the direction written.
- The standard Gibbs free energy change, $\Delta G°$, for a reaction can be calculated from the standard free energies of formation, $\Delta G°_f$.

Media Attributions

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Spontaneity: Free Energy and Temperature

Jessie A. Key

Learning Objectives

- To gain an understanding of the relationship between spontaneity, free energy, and temperature.
- To be able to calculate the temperature at which a process is at equilibrium under standard conditions.

In the Gibbs free energy change equation, the only part we as scientists can control is the temperature. We have seen how we can calculate the standard change in Gibbs free energy, $\Delta G°$, but not all reactions we are interested in occur at exactly 298 K. The temperature plays an important role in determining the Gibbs free energy and spontaneity of a reaction.

$$\Delta G = \Delta H - T\Delta S$$

If we examine the Gibbs free energy change equation, we can cluster the components to create two general terms, an enthalpy term, ΔH, and an entropy term, $-T\Delta S$. Depending on the sign and magnitude of each, the sum of these terms determines the sign of ΔG and therefore the spontaneity (Table 18.2 “Spontaneity and the Signs of Enthalpy and Entropy Terms”).

Table 18.2 Spontaneity and the Signs of Enthalpy and Entropy Terms

ΔH	ΔS	$-T\Delta S$	ΔG	Spontaneity
+	−	+	+	Nonspontaneous
−	+	−	−	Spontaneous
−	−	+	+ or −	• Low temp: Spontaneous • High temp: Nonspontaneous
+	+	−	+ or −	• Low temp: Nonspontaneous • High temp: Spontaneous

Since all temperature values are positive in the Kelvin scale, the temperature affects the magnitude of

the entropy term. As shown in Table 18.2 “Spontaneity and the Signs of Enthalpy and Entropy Terms,” the temperature can be the deciding factor in spontaneity when the enthalpy and entropy terms have opposite signs. If Δ*H* is negative, and –*T*Δ*S* positive, the reaction will be spontaneous at low temperatures (decreasing the magnitude of the entropy term). If Δ*H* is positive, and –*T*Δ*S* negative, the reaction will be spontaneous at high temperatures (increasing the magnitude of the entropy term).

Sometimes it can be helpful to determine the temperature when Δ*G*° = 0 and the process is at equilibrium. Knowing this value, we can adjust the temperature to drive the process to spontaneity or alternatively to prevent the process from occurring spontaneously. Remember that, at equilibrium:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

We can rearrange and solve for the temperature *T*:

$$T\Delta S^\circ = \Delta H^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Example 18.6

Using the appendix table of standard thermodynamic quantities, determine the temperature at which the following process is at equilibrium:

$$\mathrm{CHCl_3}(\ell) \leftrightharpoons \mathrm{CHCl_3}(\mathrm{g})$$

How does the value you calculated compare to the boiling point of chloroform given in the literature?

Solution

At equilibrium: $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$

We must estimate Δ*H*° and *S*° from their enthalpies of formation and standard molar entropies, respectively.

$$\Delta H^\circ = \sum_{\text{products}} n\Delta H^\circ_{\text{f}} - \sum_{\text{reactants}} m\Delta H^\circ_{\text{f}}$$

$$\Delta H^\circ = -102.7 \text{ kJ/mol} - (-134.1 \text{ kJ/mol})$$

$$\Delta H^\circ = +31.4 \text{ kJ/mol}$$

$$\Delta S^\circ = \sum_{\text{products}} n\Delta S^\circ - \sum_{\text{reactants}} m\Delta S^\circ$$

$$\Delta S^\circ = 295.7 \text{ J/mol K} - (201.7 \text{ J/mol K})$$

$$\Delta S^\circ = 94.0 \text{ J/mol K (or } 94.0 \times 10^{-3} \text{ kJ/mol K)}$$

Now we can use these values to solve for the temperature:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{31.4 \text{ kJ/mol}}{94.0 \times 10^{-3} \text{ kJ/mol K}}$$

$$T = 334 \text{ K} = 60.9^\circ\text{C}$$

The literature boiling point of chloroform is 61.2°C. The value we have calculated is very close but slightly lower due to the assumption that Δ*H*° and *S*° do not change with temperature when we estimate the Δ*H*° and *S*° from their enthalpies of formation and standard molar entropies.

Key Takeaways

- The temperature can be the deciding factor in spontaneity when the enthalpy and entropy terms have opposite signs:
  - If Δ*H* is negative, and –*T*Δ*S* positive, the reaction will be spontaneous at low temperatures (decreasing the magnitude of the entropy term).
  - If Δ*H* is positive, and –*T*Δ*S* negative, the reaction will be spontaneous at high temperatures (increasing the magnitude of the entropy term).

Free Energy under Nonstandard Conditions

Jessie A. Key

Learning Objectives

- To be able to determine free energy at nonstandard conditions using the standard change in Gibbs free energy, Δ*G*°.
- To understand and use the relationship between Δ*G*° and the equilibrium constant *K*.

Many reactions do not occur under standard conditions, and therefore we need some ways of determining the free energy under nonstandard conditions.

Using Standard Change in Gibbs Free Energy, ΔG°

The change in Gibbs free energy under nonstandard conditions, Δ*G*, can be determined from the standard change in Gibbs free energy, Δ*G*°:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where *R* is the ideal gas constant 8.314 J/mol K, *Q* is the reaction quotient, and *T* is the temperature in Kelvin.

Under standard conditions, the reactant and product solution concentrations are 1 M, or the pressure of gases is 1 bar, and *Q* is equal to 1. Taking the natural logarithm simplifies the equation to:

$$\Delta G = \Delta G^\circ \text{ (under standard conditions)}$$

Under nonstandard conditions, *Q* must be calculated (in a manner similar to the calculation for an equilibrium constant). For gases, the concentrations are expressed as partial pressures in the units of either atmospheres or bars, and solutes in the units of molarity.

For the reaction $aA + bB \leftrightharpoons cC + dD$:

$$Q_{\text{gases}} = \frac{(P_C)^c\,(P_D)^d}{(P_A)^a\,(P_B)^b} \qquad \text{or} \qquad Q_{\text{solutes}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Example 18.7

Consider the following reaction:

$4NH_3(g) + 5O_2(g) \rightleftharpoons 6H_2O(g) + 4NO(g)$

1. Use the thermodynamic data in the appendix to calculate $\Delta G°$ at 298 K.
2. Calculate ΔG at 298 K for a mixture of 2.0 bar $NH_3(g)$, 1.0 bar $O_2(g)$, 1.5 bar $H_2O(g)$, and 1.2 bar NO(g).

Solution

1.

$$\begin{aligned}\Delta G^\circ &= \sum_{\text{products}} n\Delta G^\circ_{\text{f}} - \sum_{\text{reactants}} m\Delta G^\circ_{\text{f}} \\ &= [(6 \times -228.6\ \text{kJ/mol}) + (4 \times 87.6\ \text{kJ/mol})] \\ &\quad - [(4 \times -16.4\ \text{kJ/mol}) + (5 \times 0.0\ \text{kJ/mol})] \\ &= (-1021.2\ \text{kJ/mol}) - (-65.6\ \text{kJ/mol}) \\ &= -955.6\ \text{kJ/mol} = -9.56 \times 10^5\ \text{J/mol}\end{aligned}$$

2.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$Q = \frac{(1.5\ \text{bar})^6 (1.2\ \text{bar})^4}{(2.0\ \text{bar})^4 (1.0\ \text{bar})^5} = 1.5$$

$$\begin{aligned}\Delta G &= (-9.56 \times 10^5\ \text{J/mol}) + (8.314\ \text{J/mol K})(298\ \text{K}) \ln(1.5) \\ &= (-9.56 \times 10^5\ \text{J/mol}) + (1.0 \times 10^3\ \text{J/mol}) \\ &= -9.6 \times 10^5\ \text{J/mol}\end{aligned}$$

The Relationship between ΔG° and *K*

There is a direct relationship between ΔG^0 and the equilibrium constant *K*. We can establish this relationship by substituting the equilibrium values ($\Delta G = 0$, and $K = Q$) into the equation for determining free energy change under nonstandard conditions:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ 0 &= \Delta G^\circ + RT \ln K \\ \Delta G^\circ &= -RT \ln K \end{aligned}$$

We now have a way of relating the equilibrium constant directly to changes in enthalpy and entropy. As well, we can now determine the equilibrium constant from thermochemical data tables or determine the standard free energy change from equilibrium constants.

Example 18.8

The K_{sp} for CuI(s) at 25°C is 1.27×10^{-12}. Determine $\Delta G°$ for the following:

$$Cu^+(aq) + I^-(aq) \rightarrow CuI(s)$$

Solution

$$\Delta G^\circ = -RT \ln K$$

The equation given is in the opposite direction to the definition of K_{sp}:

$$K = \frac{1}{K_{sp}} = \left(\frac{1}{1.27} \times 10^{-12} \right) = 7.87 \times 10^{11}$$

$$\begin{aligned} \Delta G^\circ &= -(8.314 \text{ J/mol K})(298 \text{ K}) \ln(7.87 \times 10^{11}) \\ &= -(8.314 \text{ J/mol K})(298 \text{ K})(27.4) \\ &= -6.79 \times 10^4 \text{ J/mol} = -67.9 \text{ kJ/mol} \end{aligned}$$

Key Takeaways

- The free energy at nonstandard conditions can be determined using $\Delta G = \Delta G° + RT \ln Q$.
- There is a direct relationship between $\Delta G°$ and the equilibrium constant K: $\Delta G° = -RT \ln K$.

End-of-Chapter Material

Jessie A. Key

Exercises

1. Classify each of the following as spontaneous or nonspontaneous processes:
    a. the browning of a cut apple slice on a snack tray over time
    b. the rolling of a ball uphill
    c. the formation of diamond from the graphite in your pencil
    d. the melting of ice cubes in a glass of water you are holding
2. State the second law of thermodynamics.
3. What sign would you expect for ΔS for the following processes?
    a. water freezing in a lake during a cold Alberta winter
    b. $AB(s) + CD(s) \rightarrow AC(g) + BD(g)$
    c. a balloon with a fixed amount of gas stretched to a larger volume
    d. the sublimation of dry ice
    e. $3E_2F_2(g) \rightarrow E_6F_6(g)$
4. Which of the following would you expect to have the higher standard molar entropy, $S°$?
    a. $Br_2(\ell)$ or $Br_2(g)$
    b. $NO_2(g)$ or $NO(g)$
    c. $C_2H_6(g)$ or $C_5H_{12}(g)$
5. Calculate the $\Delta S°$ of the following reactions using the values listed in the appendix.
    a. $4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$
    b. $2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$
    c. $3FeCl_2(s) + KNO_3(s) + 4HCl\ (aq) \rightarrow 3FeCl_3(s) + KCl(s) + NO(g) + 2H_2O(\ell)$
6. Draw a diagram showing the approximate entropy change of water from −100°C to 250°C.
7. A chemical reaction has $\Delta H° = -43.5$ kJ and $\Delta S° = -65.8$ J/K. Calculate $\Delta G°$ at 298 K. Is this a spontaneous process?
8. Using data from the appendix, determine $\Delta G°$ for all reactions listed in question 5.
9. Find the standard Gibbs energy change for the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$.
The $\Delta G_f°$ values for the three components of this reaction system are $CaCO_3(s)$: –1128 kJ mol^{-1}; CaO(s): –603.5 kJ/mol; $CO_2(g)$: –137.2 kJ/mol.[1]
10. Using the appendix data, determine the approximate temperature at which the following processes are at equilibrium:
    a. $CH_2Cl_2(\ell) \rightarrow CH_2Cl_2(g)$
    b. $CH_3OH(\ell) \rightarrow CH_3OH(g)$
11. Determine if the following reactions would be spontaneous at any temperature, nonspontaneous at any temperature, spontaneous at low temperature but not high temperature, or spontaneous at high temperature but not low temperature:

1. Question and solution from Chem1 Virtual Textbook, Stephen Lower/CC-BY-SA-3.0

a. $\Delta H° = -750$ kJ and $\Delta S° = 250$ J/K

b. $\Delta H° = -100$ kJ and $\Delta S° = -300$ J/K

c. $\Delta H° = 95$ kJ and $\Delta S° = -70$ J/K

d. $\Delta H° = 400$ kJ and $\Delta S° = 500$ J/K

12. The K_a for acetic acid, CH_3COOH, is 1.75×10^{-5} at 25°C.

    a. Using the K_a value, determine the $\Delta G°$ for the dissociation of acetic acid in aqueous solution.

    b. What is the value of ΔG when $[H^+]$ is 7.5×10^{-2} M, $[CH_3COO^-]$ is 2.5×10^{-2} M, and $[CH_3COOH]$ is 0.10 M?

13. Calculate the equilibrium constant for the reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ from the following data:

	$H^+(aq)$	$OH^-(aq)$	$H_2(\ell)$
$\Delta H°_f$, kJ mol^{-1}	0	–230.0	–285.8
$S°$, J K^{-1} mol^{-1}	0*	–10.9	70.0

*Note that the standard entropy of the hydrogen ion is zero by definition. This reflects the fact that it is impossible to carry out thermodynamic studies on a single-charged species. All ionic entropies are relative to that of $H^+(aq)$, which explains why some values (as for the aqueous hydroxide ion) are negative.[2]

14. Using data from the appendix, calculate the equilibrium constants at 298 K for all the reactions in question 5.

Answers

1. a. spontaneous
   b. nonspontaneous
   c. nonspontaneous
   d. spontaneous

3. a. $\Delta S = -$
   b. $\Delta S = +$
   c. $\Delta S = +$
   d. $\Delta S = +$
   e. $\Delta S = -$

5. a.

2. Question and solution from Chem1 Virtual Textbook, Stephen Lower/CC-BY-SA-3.0

$$\begin{aligned}\Delta S^\circ &= \sum_{\text{products}} nS^\circ - \sum_{\text{reactants}} mS^\circ \\ &= (6\ S^\circ\ \mathrm{H_2O(g)} + 4\ S^\circ\ \mathrm{NO(g)}) \\ &\quad - (4\ S^\circ\ \mathrm{NH_3(g)} + 5\ S^\circ\ \mathrm{O_2(g)}) \\ &= [(6 \times 188.8\ \text{J/mol K}) + (4 \times 210.8\ \text{J/mol K})] \\ &\quad - [(4 \times 192.8\ \text{J/mol K}) + (5 \times 205.2\ \text{J/mol K})] \\ &= 178.8\ \text{J/mol K}\end{aligned}$$

b.

$$\begin{aligned}\Delta S^\circ &= \sum_{\text{products}} nS^\circ - \sum_{\text{reactants}} mS^\circ \\ &= (2\ S^\circ\ \mathrm{Hg}(\ell) + S^\circ\ \mathrm{O_2(g)}) - (2\ S^\circ\ \mathrm{HgO}) \\ &= [(2 \times 75.9\ \text{J/mol K}) + (205.2\ \text{J/mol K})] \\ &\quad - (2 \times 70.3\ \text{J/mol K}) \\ &= 216.4\ \text{J/mol K}\end{aligned}$$

c.

$$\begin{aligned}\Delta S^\circ &= \sum_{\text{products}} nS^\circ - \sum_{\text{reactants}} mS^\circ \\ &= (3\ S^\circ\ \mathrm{FeCl_3(s)} + S^\circ\ \mathrm{KCl(s)} + S^\circ\ \mathrm{NO(g)} + 2\ S^\circ\ \mathrm{H_2O}(\ell)) \\ &\quad - (3\ S^\circ\ \mathrm{FeCl_2(s)} + \ S^\circ\ \mathrm{KNO_3(s)} + 4\ S^\circ\ \mathrm{HCl(aq)}) \\ &= [(3 \times 142.3\ \mathrm{J/mol\ K}) + (82.6\ \mathrm{J/mol\ K}) \\ &\quad + (210.8\ \mathrm{J/mol\ K}) + (2 \times 70.0\ \mathrm{J/mol\ K})] \\ &\quad - [(3 \times 118.0\ \mathrm{J/mol\ K}) + (133.1\ \mathrm{J/mol\ K}) \\ &\quad + (4 \times 56.5\ \mathrm{J/mol\ K})] \\ &= 147.2\ \mathrm{J/mol\ K}\end{aligned}$$

7.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -43.5\ \mathrm{kJ} - [(298\ \mathrm{K})(-65.8\ \mathrm{J/K})] \\ &= -23.9\ \mathrm{kJ}\end{aligned}$$

ΔG° is negative. Therefore, this is a spontaneous process.

9. ΔG° = (–603.5 – 137.2) – (–1128) kJ/mol = +130.9 kJ/mol, indicating that the process is not spontaneous under standard conditions (i.e., solid calcium carbonate will not form solid calcium oxide and CO_2 at 1 atm partial pressure at 25°C).

11.

a. spontaneous at all temperatures
b. spontaneous at low temperatures, nonspontaneous at high temperatures
c. nonspontaneous at all temperatures
d. spontaneous at high temperatures, nonspontaneous at low temperatures

13.

$$\begin{aligned}\Delta H^\circ &= \sum_{\text{products}} \Delta H^\circ{}_\text{f} - \sum_{\text{reactants}} \Delta H^\circ{}_\text{f} \\ &= (-285.8) - (-230) \\ &= -55.8 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum_{\text{products}} \Delta S^\circ - \sum_{\text{reactants}} \Delta S^\circ \\ &= (70.0) - (-10.9) \\ &= +80.8 \text{ J/mol K}\end{aligned}$$

The value of $\Delta G°$ at 298 K is:

$$\Delta H^\circ - T\Delta S^\circ = (-55,800) - (298)(80.8) = -79,900 \text{ J/mol}$$

$$K = \exp\left(\frac{-79,900}{8.314 \times 298}\right) = e^{-32.2} = 1.01 \times 10^{-14}$$

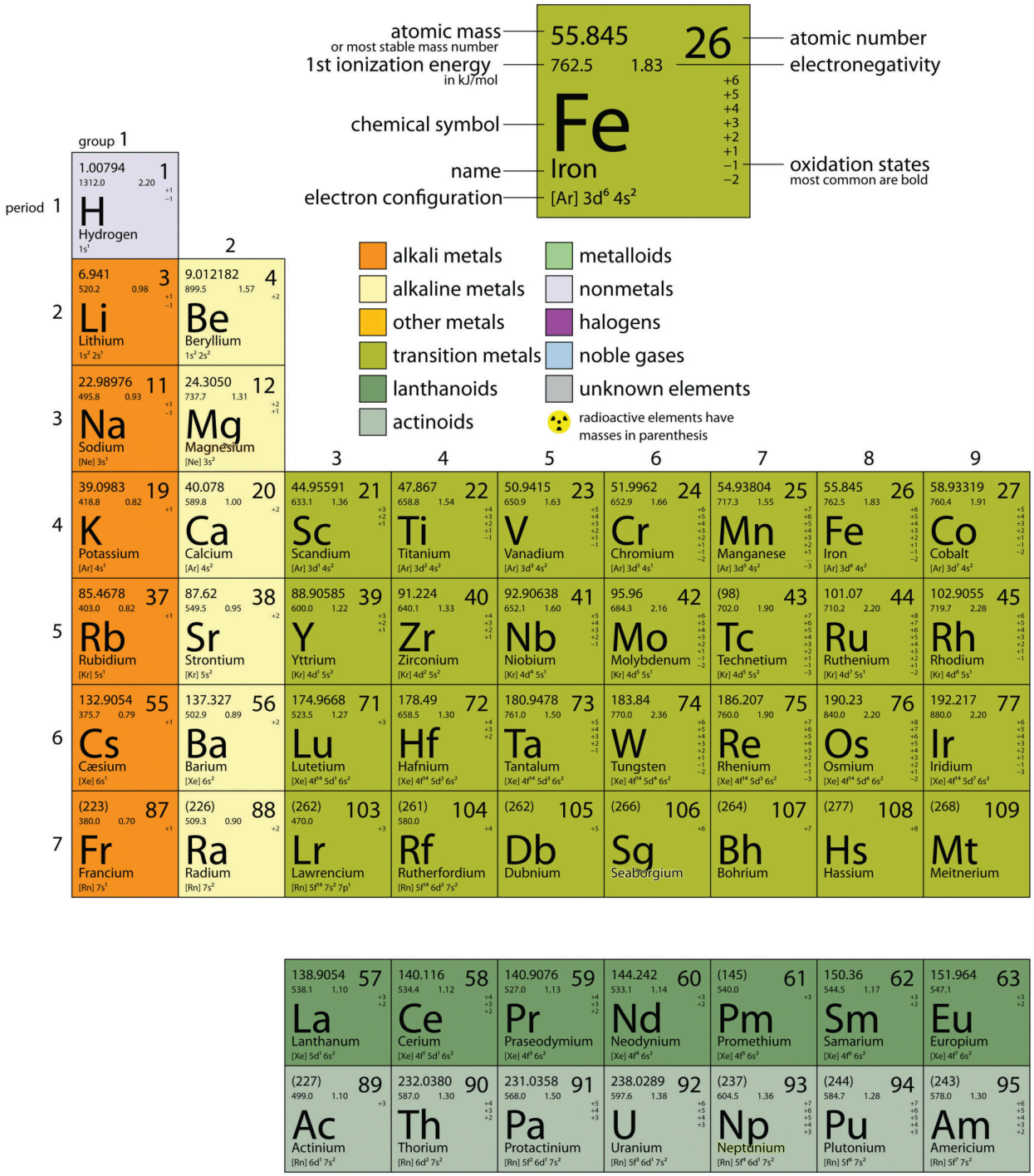
Appendix A: Periodic Table of the Elements

David W. Ball

In this appendix, we present some data on the chemical elements. The periodic table, introduced in Chapter 3 "Atoms, Molecules, and Ions," lists all the known chemical elements, arranged by atomic number (that is, the number of protons in the nucleus). The periodic table is arguably the best tool in all of science; no other branch of science can summarize its fundamental constituents in such a concise and useful way. Many of the physical and chemical properties of the elements are either known or understood based on their positions on the periodic table. Periodic tables are available with a variety of chemical and physical properties listed in each element's box. What follows here is a more complex version of the periodic table than what was presented in the chapter "Atoms, Molecules, and Ions." The internet is a great place to find periodic tables that contain additional information.

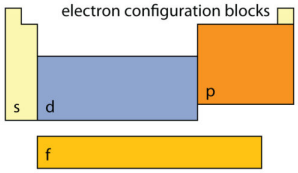
One item on most periodic tables is the atomic mass of each element. For many applications, only one or two decimal places are necessary for the atomic mass. However, some applications (especially nuclear chemistry; see Chapter 15 "Nuclear Chemistry") require more decimal places. The atomic masses in Table A.1 "The Basics of the Elements of the Periodic Table" represent the number of decimal places recognized by the International Union of Pure and Applied Chemistry, the worldwide body that develops standards for chemistry. The atomic masses of some elements are known very precisely, to a large number of decimal places. The atomic masses of other elements, especially radioactive elements, are not known as precisely. Some elements, such as lithium, can have varying atomic masses depending on how their isotopes are isolated.

The web offers many interactive periodic table resources. For example, see PTable and the Accessible Syngenta Periodic Table of Elements.



The properties listed in each box are introduced throughout the text. Atomic masses may vary by source.

by Robert Campion



notes

- as of yet, elements 112-118 have no official name designated by the IUPAC.
- 1 kJ/mol ≈ 96.485 eV.
- all elements are implied to have an oxidation state of zero.

10	11	12	13	14	15	16	17	18
								4.002602 2372.3 **2** **He** Helium $1s^2$
			10.811 800.6 2.04 **5** **B** Boron $1s^2\ 2s^2\ 2p^1$	12.0107 1086.5 2.55 **6** **C** Carbon $1s^2\ 2s^2\ 2p^2$	14.0067 1402.3 3.04 **7** **N** Nitrogen $1s^2\ 2s^2\ 2p^3$	15.9994 1313.9 3.44 **8** **O** Oxygen $1s^2\ 2s^2\ 2p^4$	18.998403 1681.0 3.98 **9** **F** Fluorine $1s^2\ 2s^2\ 2p^5$	20.1797 2080.7 **10** **Ne** Neon $1s^2\ 2s^2\ 2p^6$
			26.98153 577.5 1.61 **13** **Al** Aluminium [Ne] $3s^2\ 3p^1$	28.0855 786.5 1.90 **14** **Si** Silicon [Ne] $3s^2\ 3p^2$	30.97696 1011.8 2.19 **15** **P** Phosphorus [Ne] $3s^2\ 3p^3$	32.065 999.6 2.58 **16** **S** Sulfer [Ne] $3s^2\ 3p^4$	35.453 1251.2 3.16 **17** **Cl** Chlorine [Ne] $3s^2\ 3p^5$	39.948 1520.6 **18** **Ar** Argon [Ne] $3s^2\ 3p^6$
58.6934 737.1 1.88 **28** **Ni** Nickel [Ar] $3d^8\ 4s^2$	63.546 745.5 1.90 **29** **Cu** Copper [Ar] $3d^{10}\ 4s^1$	65.38 906.4 1.65 **30** **Zn** Zinc [Ar] $3d^{10}\ 4s^2$	69.723 578.8 1.81 **31** **Ga** Gallium [Ar] $3d^{10}\ 4s^2\ 4p^1$	72.64 762.0 2.01 **32** **Ge** Germanium [Ar] $3d^{10}\ 4s^2\ 4p^2$	74.92160 947.0 2.18 **33** **As** Arsenic [Ar] $3d^{10}\ 4s^2\ 4p^3$	78.96 941.0 2.55 **34** **Se** Selenium [Ar] $3d^{10}\ 4s^2\ 4p^4$	79.904 1139.9 2.96 **35** **Br** Bromine [Ar] $3d^{10}\ 4s^2\ 4p^5$	83.798 1350.8 3.00 **36** **Kr** Krypton [Ar] $3d^{10}\ 4s^2\ 4p^6$
106.42 804.4 2.20 **46** **Pd** Palladium [Kr] $4d^{10}$	107.8682 731.0 1.93 **47** **Ag** Silver [Kr] $4d^{10}\ 5s^1$	112.441 867.8 1.69 **48** **Cd** Cadmium [Kr] $4d^{10}\ 5s^2$	114.818 558.3 1.78 **49** **In** Indium [Kr] $4d^{10}\ 5s^2\ 5p^1$	118.710 708.6 1.96 **50** **Sn** Tin [Kr] $4d^{10}\ 5s^2\ 5p^2$	121.760 834.0 2.05 **51** **Sb** Antimony [Kr] $4d^{10}\ 5s^2\ 5p^3$	127.60 869.3 2.10 **52** **Te** Tellurium [Kr] $4d^{10}\ 5s^2\ 5p^4$	126.9044 1008.4 2.66 **53** **I** Iodine [Kr] $4d^{10}\ 5s^2\ 5p^5$	131.293 1170.4 2.60 **54** **Xe** Xenon [Kr] $4d^{10}\ 5s^2\ 5p^6$
195.084 870.0 2.28 **78** **Pt** Platinum [Xe] $4f^{14}\ 5d^9\ 6s^1$	196.9665 890.1 2.54 **79** **Au** Gold [Xe] $4f^{14}\ 5d^{10}\ 6s^1$	200.59 1007.1 2.00 **80** **Hg** Mercury [Xe] $4f^{14}\ 5d^{10}\ 6s^2$	204.3833 589.4 1.62 **81** **Tl** Thallium [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$	207.2 715.6 2.33 **82** **Pb** Lead [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$	208.9804 703.0 2.02 **83** **Bi** Bismuth [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$	(210) 812.1 2.00 **84** **Po** Polonium [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	(210) 890.0 2.20 **85** **At** Astatine [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$	(220) 1037.0 **86** **Rn** Radon [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$
(271) **110** **Ds** Darmstadium	(272) **111** **Rg** Roentgenium	(285) **112** **Cn** Copernicium	(284) **113** **Uut** Ununtrium	(289) **114** **Uuq** Ununquadium	(288) **115** **Uup** Ununpentium	(292) **116** **Uuh** Ununhexium	**117** **Uus** Ununseptium	(294) **118** **Uuo** Ununoctium

157.25 593.4 1.20 **64** **Gd** Gadolinium [Xe] $4f^7\ 5d^1\ 6s^2$	158.9253 565.8 **65** **Tb** Terbium [Xe] $4f^9\ 6s^2$	162.500 573.0 1.22 **66** **Dy** Dysprosium [Xe] $4f^{10}\ 6s^2$	164.9303 581.0 1.23 **67** **Ho** Holmium [Xe] $4f^{11}\ 6s^2$	167.259 589.3 1.24 **68** **Er** Erbium [Xe] $4f^{12}\ 6s^2$	168.9342 596.7 1.25 **69** **Tm** Thulium [Xe] $4f^{13}\ 6s^2$	173.054 603.4 **70** **Yb** Ytterbium [Xe] $4f^{14}\ 6s^2$
(247) 581.0 1.30 **96** **Cm** Curium [Rn] $5f^7\ 6d^1\ 7s^2$	(247) 601.0 1.30 **97** **Bk** Berkelium [Rn] $5f^9\ 7s^2$	(251) 608.0 1.30 **98** **Cf** Californium [Rn] $5f^{10}\ 7s^2$	(252) 619.0 1.30 **99** **Es** Einsteinium [Rn] $5f^{11}\ 6s^2$	(257) 627.0 1.30 **100** **Fm** Fermium [Rn] $5f^{12}\ 7s^2$	(258) 635.0 1.30 **101** **Md** Mendelevium [Rn] $5f^{13}\ 7s^2$	(259) 642.0 1.30 **102** **No** Nobelium [Rn] $5f^{14}\ 7s^2$

Table A.1 The Basics of the Elements of the Periodic Table

Name	Atomic Symbol	Atomic Number	Atomic Mass	Footnotes
actinium*	Ac	89		
aluminum	Al	13	26.9815386(8)	
americium*	Am	95		
antimony	Sb	51	121.760(1)	g
argon	Ar	18	39.948(1)	g, r
arsenic	As	33	74.92160(2)	
astatine*	At	85		
barium	Ba	56	137.327(7)	
berkelium*	Bk	97		
beryllium	Be	4	9.012182(3)	
bismuth	Bi	83	208.98040(1)	
bohrium*	Bh	107		
boron	B	5	10.811(7)	g, m, r
bromine	Br	35	79.904(1)	
cadmium	Cd	48	112.411(8)	g
caesium (cesium)	Cs	55	132.9054519(2)	
calcium	Ca	20	40.078(4)	g
californium*	Cf	98		
carbon	C	6	12.0107(8)	g, r
cerium	Ce	58	140.116(1)	g
chlorine	Cl	17	35.453(2)	g, m, r
chromium	Cr	24	51.9961(6)	
cobalt	Co	27	58.933195(5)	
copernicium*	Cn	112		
copper	Cu	29	63.546(3)	r
curium*	Cm	96		
darmstadtium*	Ds	110		
dubnium*	Db	105		

Name	Atomic Symbol	Atomic Number	Atomic Mass	Footnotes
dysprosium	Dy	66	162.500(1)	g
einsteinium*	Es	99		
erbium	Er	68	167.259(3)	g
europium	Eu	63	151.964(1)	g
fermium*	Fm	100		
fluorine	F	9	18.9984032(5)	
francium*	Fr	87		
gadolinium	Gd	64	157.25(3)	g
gallium	Ga	31	69.723(1)	
germanium	Ge	32	72.64(1)	
gold	Au	79	196.966569(4)	
hafnium	Hf	72	178.49(2)	
hassium*	Hs	108		
helium	He	2	4.002602(2)	g, r
holmium	Ho	67	164.93032(2)	
hydrogen	H	1	1.00794(7)	g, m, r
indium	In	49	114.818(3)	
iodine	I	53	126.90447(3)	
iridium	Ir	77	192.217(3)	
iron	Fe	26	55.845(2)	
krypton	Kr	36	83.798(2)	g, m
lanthanum	La	57	138.90547(7)	g
lawrencium*	Lr	103		
lead	Pb	82	207.2(1)	g, r
lithium	Li	3	[6.941(2)]†	g, m, r
lutetium	Lu	71	174.967(1)	g
magnesium	Mg	12	24.3050(6)	
manganese	Mn	25	54.938045(5)	
meitnerium*	Mt	109		

Name	Atomic Symbol	Atomic Number	Atomic Mass	Footnotes
mendelevium*	Md	101		
mercury	Hg	80	200.59(2)	
molybdenum	Mo	42	95.94(2)	g
neodymium	Nd	60	144.242(3)	g
neon	Ne	10	20.1797(6)	g, m
neptunium*	Np	93		
nickel	Ni	28	58.6934(2)	
niobium	Nb	41	92.90638(2)	
nitrogen	N	7	14.0067(2)	g, r
nobelium*	No	102		
osmium	Os	76	190.23(3)	g
oxygen	O	8	15.9994(3)	g, r
palladium	Pd	46	106.42(1)	g
phosphorus	P	15	30.973762(2)	
platinum	Pt	78	195.084(9)	
plutonium*	Pu	94		
polonium*	Po	84		
potassium	K	19	39.0983(1)	
praseodymium	Pr	59	140.90765(2)	
promethium*	Pm	61		
protactinium*	Pa	91	231.03588(2)	
radium*	Ra	88		
radon*	Rn	86		
roentgenium*	Rg	111		
rhenium	Re	75	186.207(1)	
rhodium	Rh	45	102.90550(2)	
rubidium	Rb	37	85.4678(3)	g
ruthenium	Ru	44	101.07(2)	g
rutherfordium*	Rf	104		

Name	Atomic Symbol	Atomic Number	Atomic Mass	Footnotes
samarium	Sm	62	150.36(2)	g
scandium	Sc	21	44.955912(6)	
seaborgium*	Sg	106		
selenium	Se	34	78.96(3)	r
silicon	Si	14	28.0855(3)	r
silver	Ag	47	107.8682(2)	g
sodium	Na	11	22.98976928(2)	
strontium	Sr	38	87.62(1)	g, r
sulfur	S	16	32.065(5)	g, r
tantalum	Ta	73	180.94788(2)	
technetium*	Tc	43		
tellurium	Te	52	127.60(3)	g
terbium	Tb	65	158.92535(2)	
thallium	Tl	81	204.3833(2)	
thorium*	Th	90	232.03806(2)	g
thulium	Tm	69	168.93421(2)	
tin	Sn	50	118.710(7)	g
titanium	Ti	22	47.867(1)	
tungsten	W	74	183.84(1)	
ununhexium*	Uuh	116		
ununoctium*	Uuo	118		
ununpentium*	Uup	115		
ununquadium*	Uuq	114		
ununtrium*	Uut	113		
uranium*	U	92	238.02891(3)	g, m
vanadium	V	23	50.9415(1)	
xenon	Xe	54	131.293(6)	g, m
ytterbium	Yb	70	173.04(3)	g
yttrium	Y	39	88.90585(2)	

Name	Atomic Symbol	Atomic Number	Atomic Mass	Footnotes
zinc	Zn	30	65.409(4)	
zirconium	Zr	40	91.224(2)	g
***Element has no stable nuclides. However, three such elements (Th, Pa, and U) have a characteristic terrestrial isotopic composition, and for these an atomic mass is tabulated.**				
†Commercially available Li materials have atomic weights that range between 6.939 and 6.996; if a more accurate value is required, it must be determined for the specific material.				
g Geological specimens are known in which the element has an isotopic composition outside the limits for normal material. The difference between the atomic mass of the element in such specimens and that given in the table may exceed the stated uncertainty.				
m Modified isotopic compositions may be found in commercially available material because it has been subjected to an undisclosed or inadvertent isotopic fractionation. Substantial deviations in the atomic mass of the element from that given in the table can occur.				
r Range in isotopic composition of normal terrestrial material prevents a more precise *A*r(E) being given; the tabulated *A*r(E) value and uncertainty should be applicable to normal material.				

Source: Adapted from *Pure and Applied Chemistry* 78, no. 11 (2005): 2051–66. © IUPAC (International Union of Pure and Applied Chemistry).

Appendix B: Selected Acid Dissociation Constants at 25°C

Selected Acid Dissociation Constants at 25°C

Name	Formula	K a1	pKa1	K a2	pKa2
Acetic acid	CH_3CO_2H	1.75×10^{-5}	4.756		
Arsenic acid	H_3AsO_4	5.5×10^{-3}	2.26	1.7×10^{-7}	6.76
Benzoic acid	$C_6H_5CO_2H$	6.25×10^{-5}	4.204		
Boric acid	H_3BO_3	5.4×10^{-10}*	9.27*	$>1 \times 10^{-14}$*	>14*
Bromoacetic acid	CH_2BrCO_2H	1.3×10^{-3}	2.90		
Carbonic acid	H_2CO_3	4.5×10^{-7}	6.35	4.7×10^{-11}	10.33
Chloroacetic acid	CH_2ClCO_2H	1.3×10^{-3}	2.87		
Chlorous acid	$HClO_2$	1.1×10^{-2}	1.94		
Chromic acid	H_2CrO_4	1.8×10^{-1}	0.74	3.2×10^{-7}	6.49
Citric acid	$C_6H_8O_7$	7.4×10^{-4}	3.13	1.7×10^{-5}	4.76
Cyanic acid	HCNO	3.5×10^{-4}	3.46		
Dichloroacetic acid	$CHCl_2CO_2H$	4.5×10^{-2}	1.35		
Fluoroacetic acid	CH_2FCO_2H	2.6×10^{-3}	2.59		
Formic acid	CH_2O_2	1.8×10^{-4}	3.75		
Hydrazoic acid	HN_3	2.5×10^{-5}	4.6		
Hydrocyanic acid	HCN	6.2×10^{-10}	9.21		
Hydrofluoric acid	HF	6.3×10^{-4}	3.20		
Hydrogen selenide	H_2Se	1.3×10^{-4}	3.89	1.0×10^{-11}	11.0
Hydrogen sulfide	H_2S	8.9×10^{-8}	7.05	1×10^{-19}	19
Hydrogen telluride	H_2Te	2.5×10^{-3}‡	2.6‡	1×10^{-11}	11
Hypobromous acid	HBrO	2.8×10^{-9}	8.55		
Hypochlorous acid	HClO	4.0×10^{-8}	7.40		
Hypoiodous acid	HIO	3.2×10^{-11}	10.5		
Iodic acid	HIO_3	1.7×10^{-1}	0.78		
Iodoacetic acid	CH_2ICO_2H	6.6×10^{-4}	3.18		
Nitrous acid	HNO_2	5.6×10^{-4}	3.25		
Oxalic acid	$C_2H_2O_4$	5.6×10^{-2}	1.25	1.5×10^{-4}	3.81
Periodic acid	HIO_4	2.3×10^{-2}	1.64		

Name	Formula	K a1	pKa1	K a2	pKa2
Phenol	C_6H_5OH	1.0×10^{-10}	9.99		
Phosphoric acid	H_3PO_4	6.9×10^{-3}	2.16	6.2×10^{-8}	7.21
Phosphorous acid	H_3PO_3	5.0×10^{-2}*	1.3*	2.0×10^{-7}*	6.70*
Pyrophosphoric acid	$H_4P_2O_7$	1.2×10^{-1}	0.91	7.9×10^{-3}	2.10
Resorcinol	$C_6H_4(OH)_2$	4.8×10^{-10}	9.32	7.9×10^{-12}	11.1
Selenic acid	H_2SeO_4	Strong	Strong	2.0×10^{-2}	1.7
Selenious acid	H_2SeO_3	2.4×10^{-3}	2.62	4.8×10^{-9}	8.32
Sulfuric acid	H_2SO_4	Strong	Strong	1.0×10^{-2}	1.99
Sulfurous acid	H_2SO_3	1.4×10^{-2}	1.85	6.3×10^{-8}	7.2
meso-Tartaric acid	$C_4H_6O_6$	6.8×10^{-4}	3.17	1.2×10^{-5}	4.91
Telluric acid	H_2TeO_4	2.1×10^{-8}‡	7.68‡	1.0×10^{-11}‡	11.0‡
Tellurous acid	H_2TeO_3	5.4×10^{-7}	6.27	3.7×10^{-9}	8.43
Trichloroacetic acid	CCl_3CO_2H	2.2×10^{-1}	0.66		
Trifluoroacetic acid	CF_3CO_2H	3.0×10^{-1}	0.52		

Original source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004).

Appendix C: Solubility Constants for Compounds at 25°C

Solubility Constants for Compounds at 25°C

Compound Name	Compound Formula	K sp
Aluminum phosphate	$AlPO_4$	9.84×10^{-21}
Barium bromate	$Ba(BrO_3)_2$	2.43×10^{-4}
Barium carbonate	$BaCO_3$	2.58×10^{-9}
Barium chromate	$BaCrO_4$	1.17×10^{-10}
Barium fluoride	BaF_2	1.84×10^{-7}
Barium iodate	$Ba(IO_3)_2$	4.01×10^{-9}
Barium nitrate	$Ba(NO_3)_2$	4.64×10^{-3}
Barium sulfate	$BaSO_4$	1.08×10^{-10}
Barium sulfite	$BaSO_3$	5.0×10^{-10}
Beryllium hydroxide	$Be(OH)_2$	6.92×10^{-22}
Bismuth arsenate	$BiAsO_4$	4.43×10^{-10}
Bismuth iodide	BiI_3	7.71×10^{-19}
Cadmium carbonate	$CdCO_3$	1.0×10^{-12}
Cadmium fluoride	CdF_2	6.44×10^{-3}
Cadmium hydroxide	$Cd(OH)_2$	7.2×10^{-15}
Cadmium iodate	$Cd(IO_3)_2$	2.5×10^{-8}
Cadmium phosphate	$Cd_3(PO_4)_2$	2.53×10^{-33}
Cadmium sulfide	CdS	8.0×10^{-27}
Calcium carbonate	$CaCO_3$	3.36×10^{-9}
Calcium fluoride	CaF_2	3.45×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}
Calcium iodate	$Ca(IO_3)_2$	6.47×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.07×10^{-33}
Calcium sulfate	$CaSO_4$	4.93×10^{-5}
Cesium perchlorate	$CsClO_4$	3.95×10^{-3}
Cesium periodate	$CsIO_4$	5.16×10^{-6}
Cobalt(II) arsenate	$Co_3(AsO_4)_2$	6.80×10^{-29}
Cobalt(II) hydroxide	$Co(OH)_2$	5.92×10^{-15}

Compound Name	**Compound Formula**	**K sp**
Cobalt(II) phosphate	$Co_3(PO_4)_2$	2.05×10^{-35}
Copper(I) bromide	CuBr	6.27×10^{-9}
Copper(I) chloride	CuCl	1.72×10^{-7}
Copper(I) cyanide	CuCN	3.47×10^{-20}
Copper(I) iodide	CuI	1.27×10^{-12}
Copper(I) thiocyanate	CuSCN	1.77×10^{-13}
Copper(II) arsenate	$Cu_3(AsO_4)_2$	7.95×10^{-36}
Copper(II) oxalate	CuC_2O_4	4.43×10^{-10}
Copper(II) phosphate	$Cu_3(PO_4)_2$	1.40×10^{-37}
Copper(II) sulfide	CuS	6.3×10^{-36}
Europium(III) hydroxide	$Eu(OH)_3$	9.38×10^{-27}
Gallium(III) hydroxide	$Ga(OH)_3$	7.28×10^{-36}
Iron(II) carbonate	$FeCO_3$	3.13×10^{-11}
Iron(II) fluoride	FeF_2	2.36×10^{-6}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}
Iron(III) hydroxide	$Fe(OH)_3$	2.79×10^{-39}
Iron(III) sulfide	FeS	6.3×10^{-18}
Lanthanum iodate	$La(IO_3)_3$	7.50×10^{-12}
Lead(II) bromide	$PbBr_2$	6.60×10^{-6}
Lead(II) carbonate	$PbCO_3$	7.40×10^{-14}
Lead(II) chloride	$PbCl_2$	1.70×10^{-5}
Lead(II) fluoride	PbF_2	3.3×10^{-8}
Lead(II) hydroxide	$Pb(OH)_2$	1.43×10^{-20}
Lead(II) iodate	$Pb(IO_3)_2$	3.69×10^{-13}
Lead(II) iodide	PbI_2	9.8×10^{-9}
Lead(II)selenite	$PbSeO_4$	1.37×10^{-7}
Lead(II) sulfate	$PbSO_4$	2.53×10^{-8}
Lead(II) sulfide	PbS	8.0×10^{-28}

Compound Name	**Compound Formula**	**K sp**
Lithium carbonate	Li_2CO_3	8.15×10^{-4}
Lithium fluoride	LiF	1.84×10^{-3}
Lithium phosphate	Li_3PO_4	2.37×10^{-11}
Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Magnesium fluoride	MgF_2	5.16×10^{-11}
Magnesium hydroxide	$Mg(OH)_2$	5.61×10^{-12}
Magnesium phosphate	$Mg_3(PO_4)_2$	1.04×10^{-24}
Manganese(II) carbonate	$MnCO_3$	2.24×10^{-11}
Manganese(II) iodate	$Mn(IO_3)_2$	4.37×10^{-7}
Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}
Mercury(I) fluoride	Hg_2F_2	3.10×10^{-6}
Mercury(I) iodide	Hg_2I_2	5.2×10^{-29}
Mercury(I) oxalate	$Hg_2C_2O_4$	1.75×10^{-13}
Mercury(I) sulfate	Hg_2SO_4	6.5×10^{-7}
Mercury(I) thiocyanate	$Hg_2(SCN)_2$	3.2×10^{-20}
Mercury(II) bromide	$HgBr_2$	6.2×10^{-20}
Mercury (II) iodide	HgI_2	2.9×10^{-29}
Mercury(II) sulfide (red)	HgS	4×10^{-53}
Mercury(II) sulfide (black)	HgS	1.6×10^{-52}
Neodymium carbonate	$Nd_2(CO_3)_3$	1.08×10^{-33}
Nickel(II) carbonate	$NiCO_3$	1.42×10^{-7}
Nickel(II) hydroxide	$Ni(OH)_2$	5.48×10^{-16}
Nickel(II) iodate	$Ni(IO_3)_2$	4.71×10^{-5}
Nickel(II) phosphate	$Ni_3(PO_4)_2$	4.74×10^{-32}
Palladium(II) thiocyanate	$Pd(SCN)_2$	4.39×10^{-23}
Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}

Compound Name	Compound Formula	K sp
Potassium perchlorate	$KClO_4$	1.05×10^{-2}
Potassium periodate	KIO_4	3.71×10^{-4}
Praseodymium hydroxide	$Pr(OH)_3$	3.39×10^{-24}
Rubidium perchlorate	$RbClO_4$	3.00×10^{-3}
Scandium fluoride	ScF_3	5.81×10^{-24}
Scandium hydroxide	$Sc(OH)_3$	2.22×10^{-31}
Silver(I) acetate	$AgCH_3CO_2$	1.94×10^{-3}
Silver(I) arsenate	Ag_3AsO_4	1.03×10^{-22}
Silver(I) bromate	$AgBrO_3$	5.38×10^{-5}
Silver(I) bromide	$AgBr$	5.35×10^{-13}
Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Silver(I) chloride	$AgCl$	1.77×10^{-10}
Silver(I) chromate	Ag_2CrO_4	1.12×10^{-12}
Silver(I) cyanide	$AgCN$	5.97×10^{-17}
Silver(I) iodate	$AgIO_3$	3.17×10^{-8}
Silver(I) iodide	AgI	8.52×10^{-17}
Silver(I) oxalate	$Ag_2C_2O_4$	5.40×10^{-12}
Silver(I) phosphate	Ag_3PO_4	8.89×10^{-17}
Silver(I) sulfate	Ag_2SO_4	1.20×10^{-5}
Silver(I) sulfide	Ag_2S	6.3×10^{-50}
Silver(I) sulfite	Ag_2SO_3	1.50×10^{-14}
Silver(I) thiocyanate	$AgSCN$	1.03×10^{-12}
Strontium arsenate	$Sr_3(AsO_4)_2$	4.29×10^{-19}
Strontium carbonate	$SrCO_3$	5.60×10^{-10}
Strontium fluoride	SrF_2	4.33×10^{-9}
Strontium iodate	$Sr(IO_3)_2$	1.14×10^{-7}
Strontium sulfate	$SrSO_4$	3.44×10^{-7}
Thallium(I) bromate	$TlBrO_3$	1.10×10^{-4}

Compound Name	Compound Formula	K sp
Thallium(I) bromide	TlBr	3.71×10^{-6}
Thallium(I) chloride	TlCl	1.86×10^{-4}
Thallium(I) chromate	Tl_2CrO_4	8.67×10^{-13}
Thallium(I) iodate	$TlIO_3$	3.12×10^{-6}
Thallium(I) iodide	TlI	5.54×10^{-8}
Thallium(I) thiocyanate	TlSCN	1.57×10^{-4}
Thallium(III) hydroxide	$Tl(OH)_3$	1.68×10^{-44}
Tin(II) hydroxide	$Sn(OH)_2$	5.45×10^{-27}
Tin(II) sulfide	SnS	1.0×10^{-25}
Yttrium carbonate	$Y_2(CO_3)_3$	1.03×10^{-31}
Yttrium fluoride	YF_3	8.62×10^{-21}
Yttrium hydroxide	$Y(OH)_3$	1.00×10^{-22}
Yttrium iodate	$Y(IO_3)_3$	1.12×10^{-10}
Zinc arsenate	$Zn_3(AsO_4)_2$	2.8×10^{-28}
Zinc carbonate	$ZnCO_3$	1.46×10^{-10}
Zinc fluoride	ZnF_2	3.04×10^{-2}
Zinc hydroxide	$Zn(OH)_2$	3×10^{-17}
Zinc selenide	ZnSe	3.6×10^{-26}
Zinc sulfide (wurtzite)	ZnS	1.6×10^{-24}
Zinc sulfide (sphalerite)	ZnS	2.5×10^{-22}

Original source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004); sulfide data from *Lange's Handbook of Chemistry*, 15th Edition (1999).

Appendix D: Standard Thermodynamic Quantities for Chemical Substances at 25°C

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Aluminum:			
Al(s)	0.0	0.0	28.3
Al(g)	330.0	289.4	164.6
$AlCl_3$(s)	−704.2	−628.8	109.3
Al_2O_3(s)	−1675.7	−1582.3	50.9
Barium:			
Ba(s)	0.0	0.0	62.5
Ba(g)	180.0	146.0	170.2
BaO(s)	−548.0	−520.3	72.1
$BaCO_3$(s)	−1213.0	−1134.4	112.1
$BaSO_4$(s)	−1473.2	−1362.2	132.2
Beryllium:			
Be(s)	0.0	0.0	9.5
Be(g)	324.0	286.6	136.3
$Be(OH)_2$(s)	−902.5	−815.0	45.5
BeO(s)	−609.4	−580.1	13.8
Bismuth:			
Bi(s)	0.0	0.0	56.7
Bi(g)	207.1	168.2	187.0
Bromine:			

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Br(g)	111.9	82.4	175.0
Br_2(l)	0.0	0.0	152.2
Br^-(aq)	−121.6	−104.0	82.4
Br_2(g)	30.9	3.1	245.5
HBr(g)	−36.3	−53.4	198.7
HBr(aq)	−121.6	−104.0	82.4
Cadmium:			
Cd(s)	0.0	0.0	51.8
Cd(g)	111.8	—	167.7
$CdCl_2$(s)	−391.5	−343.9	115.3
CdS(s)	−161.9	−156.5	64.9
Calcium:			
Ca(s)	0.0	0.0	41.6
Ca(g)	177.8	144.0	154.9
$CaCl_2$(s)	−795.4	−748.8	108.4
CaF_2(s)	−1228.0	−1175.6	68.5
$Ca(OH)_2$(s)	−985.2	−897.5	83.4
CaO(s)	−634.9	−603.3	38.1
$CaSO_4$(s)	−1434.5	−1322.0	106.5

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$CaCO_3$(s, calcite)	−1207.6	−1129.1	91.7
$CaCO_3$(s, aragonite)	−1207.8	−1128.2	88.0
Carbon:			
C(s, graphite)	0.0	0.0	5.7
C(s, diamond)	1.9	2.9	2.4
C(s, fullerene—C_{60})	2327.0	2302.0	426.0
C(s, fullerene—C_{70})	2555.0	2537.0	464.0
C(g)	716.7	671.3	158.1
C(g, fullerene—C_{60})	2502.0	2442.0	544.0
C(g, fullerene—C_{70})	2755.0	2692.0	614.0
CBr_4(s)	29.4	47.7	212.5
CBr_4(g)	83.9	67.0	358.1
CCl_2F_2(g)	−477.4	−439.4	300.8
CCl_2O(g)	−219.1	−204.9	283.5
CCl_4(l)	−128.2	−62.6	216.2
CCl_4(g)	−95.7	−53.6	309.9
CF_4(g)	−933.6	−888.3	261.6
$CHCl_3$(l)	−134.1	−73.7	201.7

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$CHCl_3(g)$	−102.7	6.0	295.7
$CH_2Cl_2(l)$	−124.2	—	177.8
$CH_2Cl_2(g)$	−95.4	−68.9	270.2
$CH_3Cl(g)$	−81.9	−58.5	234.6
$CH_4(g)$	−74.6	−50.5	186.3
$CH_3COOH(l)$	−484.3	−389.9	159.8
$CH_3OH(l)$	−239.2	−166.6	126.8
$CH_3OH(g)$	−201.0	−162.3	239.9
$CH_3NH_2(l)$	−47.3	35.7	150.2
$CH_3NH_2(g)$	−22.5	32.7	242.9
$CH_3CN(l)$	40.6	86.5	149.6
$CH_3CN(g)$	74.0	91.9	243.4
$CO(g)$	−110.5	−137.2	197.7
$CO_2(g)$	−393.5	−394.4	213.8
$CS_2(l)$	89.0	64.6	151.3
$CS_2(g)$	116.7	67.1	237.8
$C_2H_2(g)$	227.4	209.9	200.9
$C_2H_4(g)$	52.4	68.4	219.3

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$C_2H_6(g)$	−84.0	−32.0	229.2
$C_3H_8(g)$	−103.8	−23.4	270.3
$C_3H_6O_3(s)$ (lactic acid)	−694.1	−522.9	142.3
$C_6H_6(l)$	49.1	124.5	173.4
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_{12}O_6(s)$ (glucose)	−1273.3	−910.4	212.1
$C_2H_5OH(l)$	−277.6	−174.8	160.7
$C_2H_5OH(g)$	−234.8	−167.9	281.6
$(CH_3)_2O(l)$	−203.3	—	—
$(CH_3)_2O(g)$	−184.1	−112.6	266.4
$CH_3CO_2^-(aq)$	−486.0	−369.3	86.6
***n*-$C_{12}H_{26}(l)$ (dodecane)**	−350.9	28.1	490.6
Cesium:			
$Cs(s)$	0.0	0.0	85.2
$Cs(g)$	76.5	49.6	175.6
$CsCl(s)$	−443.0	−414.5	101.2
Chlorine:			
$Cl(g)$	121.3	105.3	165.2
$Cl_2(g)$	0.0	0.0	223.1

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$Cl^-(aq)$	−167.2	−131.2	56.5
HCl(g)	−92.3	−95.3	186.9
HCl(aq)	−167.2	−131.2	56.5
$ClF_3(g)$	−163.2	−123.0	281.6
Chromium:			
Cr(s)	0.0	0.0	23.8
Cr(g)	396.6	351.8	174.5
$CrCl_3(s)$	−556.5	−486.1	123.0
$CrO_3(g)$	−292.9	—	266.2
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
Cobalt:			
Co(s)	0.0	0.0	30.0
Co(g)	424.7	380.3	179.5
$CoCl_2(s)$	−312.5	−269.8	109.2
Copper:			
Cu(s)	0.0	0.0	33.2
Cu(g)	337.4	297.7	166.4
CuCl(s)	−137.2	−119.9	86.2
$CuCl_2(s)$	−220.1	−175.7	108.1

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
CuO(s)	−157.3	−129.7	42.6
Cu_2O(s)	−168.6	−146.0	93.1
CuS(s)	−53.1	−53.6	66.5
Cu_2S(s)	−79.5	−86.2	120.9
CuCN(s)	96.2	111.3	84.5
Fluorine:			
F(g)	79.4	62.3	158.8
F^-(aq)	−332.6	−278.8	−13.8
F_2(g)	0.0	0.0	202.8
HF(g)	−273.3	−275.4	173.8
HF(aq)	−332.6	−278.8	−13.8
Hydrogen:			
H(g)	218.0	203.3	114.7
H_2(g)	0.0	0.0	130.7
H^+(aq)	0.0	0.0	0.0
Iodine:			
I(g)	106.8	70.2	180.8
I^-(aq)	−55.2	−51.6	111.3
I_2(s)	0.0	0.0	116.1

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
I_2(g)	62.4	19.3	260.7
HI(g)	26.5	1.7	206.6
HI(aq)	−55.2	−51.6	111.3
Iron:			
Fe(s)	0.0	0.0	27.3
Fe(g)	416.3	370.7	180.5
Fe^{2+}(aq)	−89.1	−78.9	−137.7
Fe^{3+}(aq)	−48.5	−4.7	−315.9
$FeCl_2$(s)	−341.8	−302.3	118.0
$FeCl_3$(s)	−399.5	−334.0	142.3
FeO(s)	−272.0	−251.4	60.7
Fe_2O_3(s)	−824.2	−742.2	87.4
Fe_3O_4(s)	−1118.4	−1015.4	146.4
FeS_2(s)	−178.2	−166.9	52.9
$FeCO_3$(s)	−740.6	−666.7	92.9
Lead:			
Pb(s)	0.0	0.0	64.8
Pb(g)	195.2	162.2	175.4
PbO(s, red or litharge)	−219.0	−188.9	66.5

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
PbO(s, yellow or massicot)	−217.3	−187.9	68.7
PbO_2(s)	−277.4	−217.3	68.6
$PbCl_2$(s)	−359.4	−314.1	136.0
PbS(s)	−100.4	−98.7	91.2
$PbSO_4$(s)	−920.0	−813.0	148.5
$PbCO_3$(s)	−699.1	−625.5	131.0
$Pb(NO_3)_2$(s)	−451.9	—	—
$Pb(NO_3)_2$(aq)	−416.3	−246.9	303.3
Lithium:			
Li(s)	0.0	0.0	29.1
Li(g)	159.3	126.6	138.8
Li^+(aq)	−278.5	−293.3	13.4
LiCl(s)	−408.6	−384.4	59.3
Li_2O(s)	−597.9	−561.2	37.6
Magnesium:			
Mg(s)	0.0	0.0	32.7
Mg(g)	147.1	112.5	148.6
$MgCl_2$(s)	−641.3	−591.8	89.6

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
MgO(s)	−601.6	−569.3	27.0
$Mg(OH)_2$(s)	−924.5	−833.5	63.2
$MgSO_4$(s)	−1284.9	−1170.6	91.6
MgS(s)	−346.0	−341.8	50.3
Manganese:			
Mn(s)	0.0	0.0	32.0
Mn(g)	280.7	238.5	173.7
$MnCl_2$(s)	−481.3	−440.5	118.2
MnO(s)	−385.2	−362.9	59.7
MnO_2(s)	−520.0	−465.1	53.1
$KMnO_4$(s)	−837.2	−737.6	171.7
MnO_4^-(aq)	−541.4	−447.2	191.2
Mercury:			
Hg(l)	0.0	0.0	75.9
Hg(g)	61.4	31.8	175.0
$HgCl_2$(s)	−224.3	−178.6	146.0
Hg_2Cl_2(s)	−265.4	−210.7	191.6
HgO(s)	−90.8	−58.5	70.3
HgS(s, red)	−58.2	−50.6	82.4

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$Hg_2(g)$	108.8	68.2	288.1
Molybdenum:			
Mo(s)	0.0	0.0	28.7
Mo(g)	658.1	612.5	182.0
$MoO_2(s)$	−588.9	−533.0	46.3
$MoO_3(s)$	−745.1	−668.0	77.7
Nickel:			
Ni(s)	0.0	0.0	29.9
Ni(g)	429.7	384.5	182.2
$NiCl_2(s)$	−305.3	−259.0	97.7
$Ni(OH)_2(s)$	−529.7	−447.2	88.0
Nitrogen:			
N(g)	472.7	455.5	153.3
$N_2(g)$	0.0	0.0	191.6
$NH_3(g)$	−45.9	−16.4	192.8
$NH_4^+(aq)$	−132.5	−79.3	113.4
$N_2H_4(l)$	50.6	149.3	121.2
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4Cl(s)$	−314.4	−202.9	94.6

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$NH_4OH(l)$	−361.2	−254.0	165.6
$NH_4NO_3(s)$	−365.6	−183.9	151.1
$(NH_4)_2SO_4(s)$	−1180.9	−901.7	220.1
NO(g)	91.3	87.6	210.8
$NO_2(g)$	33.2	51.3	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_4(l)$	−19.5	97.5	209.2
$N_2O_4(g)$	11.1	99.8	304.4
$HNO_2(g)$	−79.5	−46.0	254.1
$HNO_3(l)$	−174.1	−80.7	155.6
$HNO_3(g)$	−133.9	−73.5	266.9
$HNO_3(aq)$	−207.4	−111.3	146.4
$NF_3(g)$	−132.1	−90.6	260.8
HCN(l)	108.9	125.0	112.8
HCN(g)	135.1	124.7	201.8
Osmium:			
Os(s)	0.0	0.0	32.6
Os(g)	791.0	745.0	192.6
$OsO_4(s)$	−394.1	−304.9	143.9

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$OsO_4(g)$	−337.2	−292.8	293.8
Oxygen:			
O(g)	249.2	231.7	161.1
$O_2(g)$	0.0	0.0	205.2
$O_3(g)$	142.7	163.2	238.9
$OH^-(aq)$	−230.0	−157.2	−10.8
$H_2O(l)$	−285.8	−237.1	70.0
$H_2O(g)$	−241.8	−228.6	188.8
$H_2O_2(l)$	−187.8	−120.4	109.6
$H_2O_2(g)$	−136.3	−105.6	232.7
Phosphorus:			
P(s, white)	0.0	0.0	41.1
P(s, red) −17.6	−17.6	−12.5	22.8
P(s, black)	−39.3	—	—
P(g, white)	316.5	280.1	163.2
$P_2(g)$	144.0	103.5	218.1
$P_4(g)$	58.9	24.4	280.0
$PCl_3(l)$	−319.7	−272.3	217.1
$PCl_3(g)$	−287.0	−267.8	311.8

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$POCl_3(l)$	−597.1	−520.8	222.5
$POCl_3(g)$	−558.5	−512.9	325.5
$PCl_5(g)$	−374.9	−305.0	364.6
$PH_3(g)$	5.4	13.5	210.2
$H_3PO_4(s)$	−1284.4	−1124.3	110.5
$H_3PO_4(l)$	−1271.7	−1123.6	150.8
Potassium:			
K(s)	0.0	0.0	64.7
K(g)	89.0	60.5	160.3
KBr(s)	−393.8	−380.7	95.9
KCl(s)	−436.5	−408.5	82.6
$KClO_3(s)$	−397.7	−296.3	143.1
$K_2O(s)$	−361.5	−322.1	94.1
$K_2O_2(s)$	−494.1	−425.1	102.1
$KNO_2(s)$	−369.8	−306.6	152.1
$KNO_3(s)$	−494.6	−394.9	133.1
KSCN(s)	−200.2	−178.3	124.3
$K_2CO_3(s)$	−1151.0	−1063.5	155.5
$K_2SO_4(s)$	−1437.8	−1321.4	175.6

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Rubidium:			
Rb(s)	0.0	0.0	76.8
Rb(g)	80.9	53.1	170.1
RbCl(s)	−435.4	−407.8	95.9
Selenium:			
Se(s, gray)	0.0	0.0	42.4
Se(g, gray)	227.1	187.0	176.7
H_2Se(g)	29.7	15.9	219.0
Silicon:			
Si(s)	0.0	0.0	18.8
Si(g)	450.0	405.5	168.0
$SiCl_4$(l)	−687.0	−619.8	239.7
$SiCl_4$(g)	−657.0	−617.0	330.7
SiH_4(g)	34.3	56.9	204.6
SiC(s, cubic)	−65.3	−62.8	16.6
SiC(s, hexagonal)	−62.8	−60.2	16.5
Silver:			
Ag(s)	0.0	0.0	42.6
Ag(g)	284.9	246.0	173.0
Ag^+(aq)	105.6	77.1	72.7

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
AgBr(s)	−100.4	−96.9	107.1
AgCl(s)	−127.0	−109.8	96.3
$AgNO_3$(s)	−124.4	−33.4	140.9
Ag_2O(s)	−31.1	−11.2	121.3
Ag_2S(s)	−32.6	−40.7	144.0
Sodium:			
Na(s)	0.0	0.0	51.3
Na(g)	107.5	77.0	153.7
Na^+(aq)	−240.1	−261.9	59.0
NaF(s)	−576.6	−546.3	51.1
NaF(aq)	−572.8	−540.7	45.2
NaCl(s)	−411.2	−384.1	72.1
NaCl(aq)	−407.3	−393.1	115.5
NaBr(s)	−361.1	−349.0	86.8
NaBr(g)	−143.1	−177.1	241.2
NaBr(aq)	−361.7	−365.8	141.4
NaO_2(s)	−260.2	−218.4	115.9
Na_2O(s)	−414.2	−375.5	75.1
Na_2O_2(s)	−510.9	−447.7	95.0

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
NaCN(s)	−87.5	−76.4	115.6
$NaNO_3$(aq)	−447.5	−373.2	205.4
$NaNO_3$(s)	−467.9	−367.0	116.5
NaN_3(s)	21.7	93.8	96.9
Na_2CO_3(s)	−1130.7	−1044.4	135.0
Na_2SO_4(s)	−1387.1	−1270.2	149.6
Sulfur:			
S(s, rhombic)	0.0	0.0	32.1
S(g, rhombic)	277.2	236.7	167.8
SO_2(g)	−296.8	−300.1	248.2
SO_3(g)	−395.7	−371.1	256.8
SO_4^{2-}(aq)	−909.3	−744.5	20.1
$SOCl_2$(g)	−212.5	−198.3	309.8
H_2S(g)	−20.6	−33.4	205.8
H_2SO_4(aq)	−909.3	−744.5	20.1
Tin:			
Sn(s, white)	0.0	0.0	51.2
Sn(s, gray)	−2.1	0.1	44.1
Sn(g, white)	301.2	266.2	168.5

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$SnCl_4(l)$	−511.3	−440.1	258.6
$SnCl_4(g)$	−471.5	−432.2	365.8
$SnO_2(s)$	−557.6	−515.8	49.0
Titanium:			
Ti(s)	0.0	0.0	30.7
Ti(g)	473.0	428.4	180.3
$TiCl_2(s)$	−513.8	−464.4	87.4
$TiCl_3(s)$	−720.9	−653.5	139.7
$TiCl_4(l)$	−804.2	−737.2	252.3
$TiCl_4(g)$	−763.2	−726.3	353.2
$TiO_2(s)$	−944.0	−888.8	50.6
Uranium:			
U(s)	0.0	0.0	50.2
U(g)	533.0	488.4	199.8
$UO_2(s)$	−1085.0	−1031.8	77.0
$UO_2(g)$	−465.7	−471.5	274.6
$UF_4(s)$	−1914.2	−1823.3	151.7
$UF_4(g)$	−1598.7	−1572.7	368.0
$UF_6(s)$	−2197.0	−2068.5	227.6

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
UF_6(g)	−2147.4	−2063.7	377.9
Vanadium:			
V(s)	0.0	0.0	28.9
V(g)	514.2	754.4	182.3
VCl_3(s)	−580.7	−511.2	131.0
VCl_4(l)	−569.4	−503.7	255.0
VCl_4(g)	−525.5	−492.0	362.4
V_2O_5(s)	−1550.6	−1419.5	131.0
Zinc:			
Zn(s)	0.0	0.0	41.6
Zn(g)	130.4	94.8	161.0
$ZnCl_2$(s)	−415.1	−369.4	111.5
$Zn(NO_3)_2$(s)	−483.7	—	—
ZnS(s, sphalerite)	−206.0	−201.3	57.7
$ZnSO_4$(s)	−982.8	−871.5	110.5
Zirconium:			
Zr(s)	0.0	0.0	39.0
Zr(g)	608.8	566.5	181.4
$ZrCl_2$(s)	−502.0	−386	110

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$ZrCl_4$(s)	−980.5	−889.9	181.6

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Original Source of data: CRC Handbook of Chemistry and Physics, 84th Edition (2004).

Appendix E: Standard Reduction Potentials by Value

Standard Cathode (Reduction) Half-Reaction	Standard Reduction Potential E° (volts)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.040
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	–2.92
$Rb^+ + e^- \rightleftharpoons Rb\ (s)$	-2.98
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Cs^+(aq) + e^- \rightleftharpoons Cs(s)$	-2.92
$Ba^{2+}(aq) + 2e\text{-} \rightleftharpoons Ba(s)$	-2.91
$Sr^{2+}(aq) + 2e\text{-} \rightleftharpoons Sr(s)$	-2.89
$Ca^{2+}(aq) + 2e\text{-} \rightleftharpoons Ca(s)$	–2.84
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.713
$Mg(OH)_2(s) + 2e^- \rightleftharpoons Mg(s) + 2OH^-$	–2.687
$La^{3+} + 3e^- \rightleftharpoons La(s)$	–2.38
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-2.356
$Ce^{3+} + 3e^- \rightleftharpoons Ce(s)$	–2.336
$Al(OH)_4^- + 3e^- \rightleftharpoons Al(s) + 4OH^-$	–2.310
$AlF_6^{3-} + 3e^- \rightleftharpoons Al(s) + 6F^-$	–2.07
$Be^{2+} + 2e^- \rightleftharpoons Be(s)$	–1.99
$B(OH)_4^- + 3e^- \rightleftharpoons B(s) + 4OH^-$	–1.811
$U^{3+} + 3e^- \rightleftharpoons U(s)$	–1.66

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.676
$SiF_6^{2-} + 4e^- \rightleftharpoons Si(s) + 6F^-$	–1.37
$Zn(CN)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4CN$	–1.34
$Zn(OH)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4OH^-$	–1.285
$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	–1.17
$V^{2+} + 2e^- \rightleftharpoons V(s)$	–1.13
$2SO_3^{2-} + 2H_2O(l) + 2e^- \rightleftharpoons S_2O_4^{2-} + 4OH^-$	–1.13
$Zn(NH_3)_4^{2+} + 2e^- \rightleftharpoons Zn(s) + 4NH_3$	–1.04
$O_2\ (aq) + e^- \rightleftharpoons O_2^-(aq)$	-1.0
$Cd(CN)_4^{2-} + 2e^- \rightleftharpoons Cd(s) + 4CN^-$	–0.943
$MoO_4^{2-} + 4H_2O(l) + 6e^- \rightleftharpoons Mo(s) + 8OH^-$	–0.913
$SiO_2(s) + 4H^+ + 4e^- \rightleftharpoons Si(s) + 2H_2O(l)$	–0.909
$SO_4^{2-} + H_2O(l) + 2e^- \rightleftharpoons SO_3^{2-} + 2OH^-$	–0.936
$Cr^{2+} + 2e^- \rightleftharpoons Cr(s)$	–0.90
$B(OH)_3 + 3H^+ + 3e^- \rightleftharpoons B(s) + 3H_2O(l)$	–0.890
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.828
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.7618
$Co(OH)_2(s) + 2e^- \rightleftharpoons Co(s) + 2OH^-$	–0.746
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.424

$Ni(OH)_2 + 2e^- \rightleftharpoons Ni(s) + 2OH^-$	–0.72
$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}$	–0.71
$Se(s) + 2e^- \rightleftharpoons Se^{2-}$	–0.67 in 1 M NaOH
$Cd(NH_3)_4^{2+} + 2e^- \rightleftharpoons Cd(s) + 4NH_3$	–0.622
$2SO_3^{2-} + 3H_2O(l) + 4e^- \rightleftharpoons S_2O_3^{2-} + 6OH^-$	–0.576 in 1 M NaOH
$U^{4+} + e^- \rightleftharpoons U^{3+}$	–0.52
$SiO_2(s) + 8H^+ + 8e^- \rightleftharpoons SiH_4(g) + 2H_2O(l)$	–0.516
$Sb + 3H^+ + 3e^- \rightleftharpoons SbH_3(g)$	–0.510
$H_3PO_3 + 2H^+ + 2e^- \rightleftharpoons H_3PO_2 + H_2O(l)$	-0.50
$Ni(NH_3)_6^{2+} + 2e^- \rightleftharpoons Ni(s) + 6NH_3$	–0.49
$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4$	–0.481
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.424
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$S(s) + 2e^- \rightleftharpoons S^{2-}$	–0.407
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	–0.4030
$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag(s) + 2NH_3$	–0.373
$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$	–0.37
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	–0.356
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	–0.277

$2SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons S_2O_6^{2-} + 2H_2O(l)$	–0.25
$N_2(g) + 5H^+ + 4e^- \rightleftharpoons N_2H_5^+$	–0.23
$H_3PO_4 + 2H^+ + 2e^- \rightleftharpoons H_3PO_3 + H_2O(l)$	-0.28
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.257
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.255
$As + 3H^+ + 3e^- \rightleftharpoons AsH_3(g)$	–0.225
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	–0.20
$Mo^{3+} + 3e^- \rightleftharpoons Mo(s)$	–0.2
$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	–0.19 in 1 M HCl
$Ti^{2+} + 2e^- \rightleftharpoons Ti(s)$	–0.163
$MoO_2(s) + 4H^+ + 4e^- \rightleftharpoons Mo(s) + 2H_2O(l)$	–0.152
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	–0.152
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.126
$CrO_4^{2-} + 4H_2O(l) + 3e^- \rightleftharpoons 2Cr(OH)_4^- + 4OH^-$	–0.13 in 1 M NaOH
$WO_2(s) + 4H^+ + 4e^- \rightleftharpoons W(s) + 2H_2O(l)$	–0.119
$Se(s) + 2H^+ + 2e^- \rightleftharpoons H_2Se(g)$	–0.115
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons CO(g) + H_2O(l)$	–0.106
$WO_3(s) + 6H^+ + 6e^- \rightleftharpoons W(s) + 3H_2O(l)$	–0.090

$Hg_2I_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2I^-$	–0.0405
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	-0.037
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$P(s,white) + 3H^+ + 3e^- \rightleftharpoons PH_3(g)$	0.06
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	0.071
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	0.080
$Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+}$	0.1
$Ru(NH_3)_6^{3+} + e^- \rightleftharpoons Ru(s) + Ru(NH_3)_6^{2+}$	0.10
$S(s) + 2H^+ + 2e^- \rightleftharpoons H_2S$	0.144
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.154
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.159
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	0.16
$Co(OH)_3(s) + e^- \rightleftharpoons Co(OH)_2(s) + OH^-$	0.17
$ClO_4^-(aq) + H_2O(l) + 2e- \rightleftharpoons ClO_3^-(aq) + 2OH^-(aq)$	0.17
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SO_3^{2-} + H_2O(l)$	0.172
$BiCl_4^- + 3e^- \rightleftharpoons Bi(s) + 4Cl^-$	0.199
$SbO^+ + 2H^+ + 3e^- \rightleftharpoons Sb(s) + H_2O(l)$	0.212
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	0.2223
$HCHO + 2H^+ + 2e^- \rightleftharpoons CH_3OH$	0.2323

$HAsO_2 + 3H^+ + 3e^- \rightleftharpoons As(s) + 2H_2O(l)$	0.240
$Ru^{3+} + e^- \rightleftharpoons Ru^{2+}$	0.249
$IO_3^- + 3H_2O(l) + 6e^- \rightleftharpoons I^- + 6OH^-$	0.257
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	0.2682
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.27
$Bi^{3+} + 3e^- \rightleftharpoons Bi(s)$	0.317
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.327
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O(l)$	0.337
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.3419
$ClO_3^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO_2^-(aq) + 2OH^-(aq)$	0.35
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.356
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-$	0.401
$ClO^- + H_2O(l) + e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + 2OH^-$	0.421 in 1 M NaOH
$Ag_2C_2O_4(s) + 2e^- \rightleftharpoons 2Ag(s) + C_2O_4^{2-}$	0.47
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.5355
$I_3^- + 2e^- \rightleftharpoons 3I^-$	0.536
$Ga^{3+} + 3e^- \rightleftharpoons Ga(s)$	-0.56
$Cu^{2+} + Cl^- + e^- \rightleftharpoons CuCl(s)$	0.559

$S_2O_6^{2-} + 4H^+ + 2e^- \rightleftharpoons 2H_2SO_3$	0.569
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O(l)$	0.560
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO^-(aq) + 2OH^-(aq)$	0.59
$MnO_4^- + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-$	0.60
$Sb_2O_5(s) + 6H^+ + 4e^- \rightleftharpoons 2SbO^+ + 3H_2O(l)$	0.605
$PtCl_6^{2-} + 2e^- \rightleftharpoons PtCl_4^{2-} + 2Cl^-$	0.68
$RuO_2(s) + 4H^+ + 4e^- \rightleftharpoons Ru(s) + 2H_2O(l)$	0.68
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.695
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4Cl^-$	0.73
$H_2SeO_3 + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O(l)$	0.74
$Tl^{3+} + 3e^- \rightleftharpoons Tl(s)$	0.742
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	0.771
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.7960
$Ag^+(aq) + e\text{-} \rightleftharpoons Ag(s)$	0.7996
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	0.8535
$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	0.86
$Ru(CN)_6^{3-} + e^- \rightleftharpoons Ru(s) + Ru(CN)_6^{4-}$	0.86
$ClO^- + H_2O(l) + 2e^- \rightleftharpoons Cl^- + 2OH^-$	0.890 in 1 M NaOH
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.911

$HgO(s) + 2H^+ + 2e^- \rightleftharpoons Hg(l) + H_2O(l)$	0.926
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O(l)$	0.94
$MnO_2(s) + 4H^+ + e^- \rightleftharpoons Mn^{3+}(aq) + H_2O(I)$	0.95
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$HIO + H^+ + 2e^- \rightleftharpoons I^- + H_2O(l)$	0.985
$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O(l)$	0.996
$VO_2^{2+} + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O(l)$	1.000
$AuCl_4^- + 3e^- \rightleftharpoons Au(s) + 4Cl^-$	1.002
$NO_2(g) + H^+(aq) + e^- \rightleftharpoons HNO_2(aq)$	1.07
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.087
$Fe(phen)_6^{3+} + e^- \rightleftharpoons Fe(phen)_6^{2+}$	1.147
$SeO_4^{3-} + 4H^+ + e^- \rightleftharpoons H_2SeO_3 + H_2O(l)$	1.151
$ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2(g) + H_2O$	1.175
$ClO_3^- + 3H^+ + 2e^- \rightleftharpoons HClO_2 + H_2O$	1.181
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O(l)$	1.195
$Pt^{2+} + 2e^- \rightleftharpoons Pt(s)$	1.2
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	1.201
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.229
$MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O(l)$	1.23

$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	0.77 in 1 M HCl
$2HNO_2 + 4H^+ + 4e^- \rightleftharpoons N_2O(g) + 3H_2O(l)$	1.297
$HOBr + H^+ + 2e^- \rightleftharpoons Br^- + H_2O(l)$	1.341
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O(l)$	1.36
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.396
$Au^{3+} + 2e^- \rightleftharpoons Au^+$	1.36
$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Br^-$	1.392
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	1.44
$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	1.46
$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$	1.478
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	1.5
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.51
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Br_2(l) + 3H_2O$	1.5
$Au^{3+} + 3e^- \rightleftharpoons Au(s)$	1.52
$2NO(g) + 2H^+ + 2e^- \rightleftharpoons N_2O(g) + H_2O(l)$	1.59
$HOBr + H^+ + e^- \rightleftharpoons \frac{1}{2}Br^- + H_2O(l)$	1.604
$HClO_2 + 2H^+ + 2e^- \rightleftharpoons HOCl + H_2O$	1.64
$PbO_2(s) + 4SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	1.690

$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	1.70
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.72
$N_2O(g) + 2H^+ + 2e^- \rightleftharpoons N_2(g) + H_2O(l)$	1.77
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.763
$Au^+ + e^- \rightleftharpoons Au(s)$	1.83
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	1.92
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	1.96
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	2.07
$BaO(s) + 2H^+ + 2e^- \rightleftharpoons Ba(s) + H_2O(l)$	2.365
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87
$F_2(g) + 2H^+ + 2e^- \rightleftharpoons 2HF$	3.053

Original source materials: Bard, A. J.; Parsons, B.; Jordon, J., eds. *Standard Potentials in Aqueous Solutions*, Dekker: New York, 1985; Milazzo, G.; Caroli, S.; Sharma, V. K. *Tables of Standard Electrode Potentials*, Wiley: London, 1978; Swift, E. H.; Butler, E. A. *Quantitative Measurements and Chemical Equilibria*, Freeman: New York, 1972.

Glossary

Jessie A. Key

Term	Definition	Section of Book
abbreviated electron configuration	An electron configuration that uses one of the noble gases to represent the core of electrons up to that element.	Organization of Electrons in Atoms
absolute zero	The minimum possible temperature, labeled 0 K (zero kelvins)	Other Units: Temperature and Density
acid	An ionic compound of the H+ cation dissolved in water	Acids
acid	A compound that increases the amount of H+ ions in an aqueous solution	Neutralization Reactions
acid dissociation constant (K_a)	The equilibrium constant for the dissociation of a weak acid into ions	Some Special Types of Equilibria
acid salt	An ionic compound whose aqueous solution is slightly acidic	Strong and Weak Acids and Bases and Their Salts
activated complex	See transition state	Reaction Mechanisms
activation energy (Ea)	The minimum amount of kinetic energy molecules must possess for an effective collision to occur	Factors that Affect the Rate of Reactions
active site	Area of enzymatic action where substrate molecules react	Catalysis
activity series	A list of elements that will replace elements below them in single-replacement reactions	Types of Chemical Reactions: Single- and Double-Displacement Reactions
actual yield	The amount that is actually produced in a chemical reaction	Yields
addition reaction	A reaction where atoms are added across a double or triple bond	Hydrocarbons
adhesion	The tendency of a substance to interact with other substances because of intermolecular forces	Properties of Liquids
adsorb	Bind to the surface of another substance	Catalysis
alcohol	An organic compound that contains an OH functional group	Alkyl halides and alcohols
aldehyde	A compound that has a carbonyl functional group at the end of a chain of C atoms	Other Oxygen-Containing Functional Groups
aliphatic hydrocarbons	A hydrocarbon based on chains of C atoms	Hydrocarbons
alkaline battery	A type of dry cell that contains an alkaline (i.e., basic) moist paste, rather than an acidic paste	Applications of Redox Reactions: Voltaic Cells
alkane	An aliphatic hydrocarbon with only single covalent bonds	Hydrocarbons

alkene	An aliphatic hydrocarbon that contains a C–C double bond	Hydrocarbons
alkyl halide	An organic compound that contains a halogen atom	Alkyl halides and alcohols
alkyne	An aliphatic hydrocarbon that contains a C–C triple bond	Hydrocarbons
alpha particle	A type of radioactive emission equivalent to a helium nucleus	Radioactivity
amide group	A functional group that is the combination of the amine and carbonyl functional groups	Other Functional Groups
amide bond	The bond between the N atom and the C atom in an amide.	Other Functional Groups
amine	An organic derivative of ammonia	Other Functional Groups
amorphous solid	A solid with no long-term structure or repetition	Solids
amphiprotic	A substance that can act as a proton donor or a proton acceptor	Brønsted-Lowry Acids and Bases
analyte	The reagent of unknown concentration	Acid-Base Titrations
angular momentum quantum number (ℓ)	An index that affects the energy and the spatial distribution of an electron in an atom.	Quantum Numbers for Electrons
anion	A species with an overall negative charge	Ions and Ionic Compounds
anode	The half cell that contains the oxidation reaction	Applications of Redox Reactions: Voltaic Cells
antibonding molecular orbital	A higher energy molecular orbital generated by destructive combination of atomic orbitals	Molecular Orbitals
aromatic hydrocarbons	Flat ring systems, which contain continuously overlapping p orbitals, such as benzene	Hydrocarbons
Arrhenius acid	A compound that increases the hydrogen ion concentration in aqueous solution	Arrhenius Acids and Bases
Arrhenius base	A compound that increases the hydroxide ion concentration in aqueous solution	Arrhenius Acids and Bases
atmosphere (atm)	A unit of pressure equal to the average atmospheric pressure at sea level; defined as exactly 760 mmHg	Pressure
atom	The smallest piece of an element that maintains the identity of that element	Atomic Theory
atomic mass	The sum of the number of protons and neutrons in a nucleus	Atomic Theory
atomic mass	The weighted average of the masses of the isotopes that compose an element	Masses of Atoms and Molecules

atomic mass unit	One-twelfth of the mass of a carbon-12 atom	Masses of Atoms and Molecules
atomic number	The number of protons in an atom	Atomic Theory
atomic radius	An indication of the size of an atom.	Periodic Trends
atomic symbol	A one- or two-letter representation of the name of an element	Atomic Theory
atomic theory	The concept that atoms play a fundamental role in chemistry	Atomic Theory
aufbau principle	The way that electrons fill the lowest energy orbitals first. From the German for “building up.”	Organization of Electrons in Atoms
autoionization constant of water (K_w)	The product of the hydrogen ion and hydroxide ion concentrations	Autoionization of Water
autoionization of water	Water molecules act as acids (proton donors) and bases (proton acceptors) with each other to a tiny extent in all aqueous solutions	Autoionization of Water
Avogadro’s law	A gas law that relates number of particles to volume	Other Gas Laws
balanced chemical equation	A condition when the reactants and products of a chemical equation have the same number of atoms of all elements present	The Chemical Equation
base	A compound that increases the amount of OH^- ions in an aqueous solution	Neutralization Reactions
basic salt	An ionic compound whose aqueous solution is slightly basic	Strong and Weak Acids and Bases and Their Salts
becquerel (Bq)	A unit of radioactivity equal to 1 decay per second	Units of Radioactivity
beta particle	A type of radioactive emission equivalent to an electron	Radioactivity
boiling (or vaporization)	The process of a liquid becoming a gas	Phase Transitions: Melting, Boiling and Subliming
boiling point	The characteristic temperature at which a liquid becomes a gas	Phase Transitions: Melting, Boiling and Subliming
boiling point elevation	The increase of a solution’s boiling point because of the presence of solute	Colligative Properties of Solutions
boiling point elevation constant (K_b)	The constant that relates the molality concentration of a solution and its boiling point change	Colligative Properties of Solutions
bond energy	The approximate amount of energy needed to break a covalent bond	Other Aspects of Covalent Bonding
bond order	A method of evaluating bond strength	Molecular Orbitals

bonding electron pair	A pair of electrons that makes a covalent bond	Covalent Bonds
bonding molecular orbital	The lower energy molecular orbital generated by constructive combination of atomic orbitals	Molecular Orbitals
Boyle's law	A gas law that relates pressure and volume at constant temperature and amount	Gas Laws
branched hydrocarbons	A carbon compound that is not a straight chain, having substituents appended to the longest chain	Branched Hydrocarbons
Brønsted-Lowry acid	Any species that can donate a proton to another molecule	Brønsted-Lowry Acids and Bases
Brønsted-Lowry base	Any species that can accept a proton from another molecule	Brønsted-Lowry Acids and Bases
buffer	A solution that resists dramatic changes in pH	Buffers
buffer capacity	The amount of strong acid or base a buffer can counteract	Buffers
burette or buret	A precisely calibrated volumetric delivery tube	Acid-Base Titrations
calorie	A unit of energy measurement originally defined in terms of warming up a given quantity of water. 1 cal = 4.184 J	Energy
calorimeter	A container used to measure the heat of a chemical reaction.	Enthalpy and Chemical Reactions
calorimetry	The process of measuring enthalpy changes in chemical reactions.	Enthalpy and Chemical Reactions
capillary action	The behavior of a liquid in narrow surfaces due to differences in adhesion and cohesion	Properties of Liquids
carbonyl group	A functional group where an O atom and a C atom are joined with a double bond	Other Oxygen-Containing Functional Groups
carboxyl group	A functional group composed of a carbonyl group and an OH group	Other Oxygen-Containing Functional Groups
carboxylate ion	A negatively charged ion derived from a carboxylic acid	Other Oxygen-Containing Functional Groups
carboxylic acid	A molecule with a carboxyl group	Other Oxygen-Containing Functional Groups
catalyst	A substance that increases the speed of a reaction	Shifting Equilibria: Le Chatelier's Principle
catalyst	A substance thaty accelerates a reaction by participating in it without being consumed	Factors that Affect the Rate of Reactions
catalyst	A substance that lowers the activation energy of a specific reaction by providing an alternate reaction pathway	Catalysis

cathode	The half cell that contains the reduction reaction	Applications of Redox Reactions: Voltaic Cells
cation	A species with an overall positive charge	Ions and Ionic Compounds
central atom	The atom in the center of a molecule	Covalent Bonds
Charles's law	A gas law that relates volume and temperature at constant pressure and amount	Gas Laws
chemical bond	The connection between two atoms in a molecule	Molecules an Chemical Nomenclature
chemical change	The process of demonstrating a chemical property	Some Basic Definitions
chemical equation	A concise way of representing a chemical reaction	The Chemical Equation
chemical equilibrium	The point at which forward and reverse chemical reactions balance each other's progress	Chemical Equilibrium
chemical nomenclature	A very specific system for naming compounds, in which unique substances get unique names	Molecules an Chemical Nomenclature
chemical property	A characteristic that describes how matter changes form in the presence of other matter	Some Basic Definitions
chemistry	The study of the interactions of matter with other matter and with energy	Introduction
coefficient	The part of a number in scientific notation that is multiplied by a power of 10	Expressing Numbers
coefficient	A number in a chemical equation indicating more than one molecule of the substance	The Chemical Equation
cohesion	The tendency of a substance to interact with itself	Properties of Liquids
colligative property	A property of solutions related to the fraction that the solute particles occupy in the solution, not their identity	Colligative Properties of Solutions
collision theory	The theory that reactions occur when reactant molecules "effectively collide"	Factors that Affect the Rate of Reactions
combined gas law	A gas law that combines pressure, volume, and temperature	Other Gas Laws
combustion reaction	A chemical reaction in which a reactant combines with oxygen to produce oxides of all other elements as products	Composition, Decomposition, and Combustion Reactions
complete ionic equation	A chemical equation in which the dissolved ionic compounds are written as separated ions	Ionic Equations: A Closer Look
composition reaction	A chemical reaction in which a single substance is produced from multiple reactants	Composition, Decomposition, and Combustion Reactions

compound	A combination of more than one element	Some Basic Definitions
compressibility factor	A measure of the extent of deviation from ideal gas behaviour.	Real Gases
concentrated solution	A solution with a lot of solute	Some Definitions
concentration	How much solute is dissolved in a given amount of solvent	Some Definitions
concentration (verb)	The removal of solvent, which increases the concentration of the solute in the solution	Dilutions and Concentrations
condensation	The process of a gas becoming a liquid	Phase Transitions: Melting, Boiling and Subliming
condensed structure	A listing of the atoms bonded to each C atom in a chain	Hydrocarbons
conjugate acid-base pair	Two species whose formulas differ by only a hydrogen ion	Brønsted-Lowry Acids and Bases
continuous spectrum	An image that contains all colours of light.	Quantum Numbers for Electrons
conversion factor	A fraction that can be used to convert a quantity from one unit to another	Converting Units
covalent bond	A chemical bond formed by two atoms sharing electrons.	Covalent Bonds
covalent network solids	A crystalline solid composed of atoms of one or more elements that are covalently bonded together in a seemingly never-ending fashion	Solids
critical point	The point at the highest temperature and pressure at which liquids and gases remain distinguishable	Properties of Liquids
crystalline solid	A solid with a regular, repeating three-dimensional structure	Solids
curie	A unit of radioactivity equal to 3.7×1010 decays/s	Units of Radioactivity
d block	The columns of the periodic table in which *d* subshells are being occupied.	Electronic Structure and the Periodic Table
Dalton’s law of partial pressures	The total pressure of a gas mixture, Ptot, is equal to the sum of the partial pressures of the components, Pi	Gas Mixtures
daughter isotope	The product left over from the parent isotope in a nuclear equation	Radioactivity
decomposition reaction	A chemical reaction in which a single substance becomes more than one substance	Composition, Decomposition, and Combustion Reactions

degrees	The unit of temperature scales	Other Units: Temperature and Density
density	A physical property defined as a substance's mass divided by its volume	Other Units: Temperature and Density
deposition	The process of a gas becoming a solid	Phase Transitions: Melting, Boiling and Subliming
derived unit	A unit that is a product or a quotient of a fundamental unit	Expressing Units
diatomic molecule	A molecule with only two atoms	Molecules an Chemical Nomenclature
diffusion	The movement of gas molecules through one or more additional types of gas via random molecular motion	Molecular Effusion and Diffusion
dilute	A solution with very little solute	Some Definitions
dilution	The addition of solvent, which decreases the concentration of the solute in the solution	Dilutions and Concentrations
dilution equation	The mathematical formula for calculating new concentrations or volumes when a solution is diluted or concentrated	Dilutions and Concentrations
dipole-dipole interactions	An intermolecular force caused by molecules with a permanent dipole	Intermolecular Forces
dispersion force (or London dispersion force)	An intermolecular force caused by the instantaneous position of an electron in a molecule	Intermolecular Forces
dissociation	The process of an ionic compound separating into ions when it dissolves	Ionic Equations: A Closer Look
double bond	A covalent bond composed of two pairs of bonding electrons	Covalent Bonds
double-replacement reaction	A chemical reaction in which parts of two ionic compounds are exchanged	Types of Chemical Reactions: Single- and Double-Displacement Reactions
dry cell	A modern battery that does not contain large amounts of aqueous solution	Applications of Redox Reactions: Voltaic Cells
dynamic equilibrium	When a process still occurs but the opposite process also occurs at the same rate so that there is no net change in the system.	Properties of Liquids
effective nuclear charge (Zeff)	The net nuclear charge felt by valence electrons.	Periodic Trends
effusion	The movement of gas molecules from one container to another via a tiny hole	Molecular Effusion and Diffusion

electrodes	The cathode or anode of a voltaic cell	Applications of Redox Reactions: Voltaic Cells
electrolysis	The process of making a nonspontaneous redox reaction occur by forcing electricity into a cell	Electrolysis
electrolytic cell	A cell into which electricity is forced to make a nonspontaneous reaction occur	Electrolysis
electromagnetic spectrum	The full span of the possible wavelengths, frequencies, and energies of light.	Light
electron	A tiny subatomic particle with a negative charge	Atomic Theory
electron affinity (EA)	The energy change when a gas-phase atom accepts an electron.	Periodic Trends
electron configuration	A listing of the shell and subshell labels.	Organization of Electrons in Atoms
electron deficient molecules	A molecule with less than eight electrons in the valence shell of an atom	Violations of the Octet Rule
electron group geometry	how electron groups (bonds and nonbonding electron pairs) are arranged	Molecular Shapes and Polarity
electron groups	A covalent bond of any type or a lone electron pair	Molecular Shapes and Polarity
electron shell	A term used to describe electrons with the same principal quantum number.	Quantum Numbers for Electrons
electronegativity	A scale for judging how much atoms of any element attract electrons	Other Aspects of Covalent Bonding
electroplating	The deposition of a thin layer of metal on an object for protective or decorative purposes	Electrolysis
element	A substance that cannot be broken down into simpler chemical substances by ordinary chemical means	Some Basic Definitions
elementary step	Each event that occurs in a chemical reaction as a result of an effective collision	Reaction Mechanisms
elimination reaction	The removal of a functional group (either X or OH) and a H atom from an adjacent carbon	Alkyl halides and alcohols
endothermic	A chemical reaction that has a positive change in enthalpy.	Enthalpy and Chemical Reactions
energy	The ability to do work.	Energy
enthalpy change	The heat of a process at constant pressure. Denoted as ΔH.	Enthalpy and Chemical Reactions
enthalpy of formation	The enthalpy change for a formation reaction; denoted as ΔHf.	Formation Reactions

enthalpy of fusion	The amount of energy needed to change from a solid to a liquid or from a liquid to a solid	Phase Transitions: Melting, Boiling and Subliming
enthalpy of sublimation	The amount of energy needed to change from a solid to a gas or from a gas to a solid	Phase Transitions: Melting, Boiling and Subliming
enthalpy of vaporization	The amount of energy needed to change from a liquid to a gas or from a gas to a liquid	Phase Transitions: Melting, Boiling and Subliming
entropy	The level of randomness (or disorder) of a system, or a measure of the energy dispersal of the molecules in the system	Entropy and the Second Law of Thermodynamics
enzyme	Protein molecules which serve to catalyze biochemical reactions	Catalysis
enzyme-substrate complex	The binding of substrate to the enzymatic active site	Catalysis
equilibrium constant (Keq)	A numerical value that relates to the ratio of products and reactants at equilibrium	The Equilibrium Constant
equivalence point	The point of the reaction when all the analyte has been reacted with the titrant	Acid-Base Titrations
ester group	A functional group made by combining a carboxylic acid with an alcohol	Other Oxygen-Containing Functional Groups
ether group	A functional group that has an O atom attached to two organic groups	Other Oxygen-Containing Functional Groups
evaporation	The formation of a gas phase from a liquid at temperatures below the boiling point	Properties of Liquids
exact number	A number from a defined relationship that technically has an infinite number of significant figures	Converting Units
exothermic	A chemical reaction that has a negative change in enthalpy.	Enthalpy and Chemical Reactions
expanded valence shell molecules	A molecule with more than eight electrons in the valence shell of an atom	Violations of the Octet Rule
experiment	A test of the natural universe to see if a guess (hypothesis) is correct	Chemistry as a Science
exponent	The raised number to the right of a 10 indicating the number of factors of 10 in the original number	Expressing Numbers
f block	The columns of the periodic table in which *f* subshells are being occupied.	Electronic Structure and the Periodic Table
fission	The breaking apart of an atomic nucleus into smaller nuclei	Radioactivity

formation reaction	A chemical reaction that forms one mole of a substance from its constituent elements in their standard states.	Formation Reactions
freezing point depression	The decrease of a solution's freezing point because of the presence of solute	Colligative Properties of Solutions
freezing point depression constant (Kf)	The constant that relates the molality concentration of a solution and its freezing point change	Colligative Properties of Solutions
frequency	The number of cycles of light that pass a given point in one second.	Light
frequency factor (*A*)	A factor that takes into account the frequency of reactions and the likelihood of correct molecular orientation	Activation Energy and the Arrhenius Equation
frontier molecular orbitals	A term which refers to the HOMO and LUMO, the most likely orbitals to be involved in chemical reactions or processes	Molecular Orbitals
functional group	A collection of atoms or bonds with certain characteristic reactions	Alkyl halides and alcohols
fundamental units	One of the seven basic units of SI used in science	Expressing Units
gamma ray	A type of radioactive emission that is a very energetic form of electromagnetic radiation	Radioactivity
gas law	A simple mathematical formula that allows one to model, or predict, the behaviour of a gas	Gas Laws
Gay-Lussac's law	A gas law that relates pressure with absolute temperature	Other Gas Laws
Geiger counter	An electrical device that detects radioactivity	Units of Radioactivity
Gibbs free energy (*G*)	A measure of spontaneity which incorporates both enthalpy and entropy	Gibbs Free Energy
Graham's law of effusion	A law that relates the rate of effusion of a gas to the inverse of the square root of its molar mass.	Molecular Effusion and Diffusion
gray (Gy)	A unit of radioactive exposure equal to 100 rad	Units of Radioactivity
half cell	A part of a voltaic cell that contains one half reaction	Applications of Redox Reactions: Voltaic Cells
half reaction	The individual oxidation or reduction reaction of a redox reaction	Balancing Redox Reactions
half reaction method	The method of balancing redox reactions by writing and balancing the individual half reactions	Balancing Redox Reactions
half-life	The amount of time it takes for one-half of a radioactive isotope to decay	Half-Life

half-life	The amount of time required for the concentration of a reactant to drop to one half of its initial concentration	Concentration-Time Relationships: Integrated Rate Laws
heat	The transfer of energy from one body to another due to a difference in temperature.	Work and Heat
heating curve	A plot of the temperature versus the amount of heat added	Phase Transitions: Melting, Boiling and Subliming
Hess's law	When chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way.	Hess's Law
heterogeneous catalyst	A catalyst that is in a different phase from one or more of the reactants	Catalysis
heterogeneous equilibrium	An equilibrium in which more than one phase of reactants or products is present	The Equilibrium Constant
heterogeneous mixture	A non-uniform combination of more than one substance	Some Basic Definitions
HOMO	The highest occupied molecular orbital	Molecular Orbitals
homogeneous catalyst	A catalyst that is present in the same phase as the reactant molecules	Catalysis
homogeneous mixture	A uniform mixture of more than one substance that behaves as a single substance	Some Basic Definitions
Hund's rule	One electron is placed in each degenerate orbital before pairing electrons in the same orbital.	Organization of Electrons in Atoms
hybridization	A mathematical mixing of atomic orbitals	Valence Bond Theory and Hybrid Orbitals
hydrocarbons	An organic compound composed of carbon and hydrogen	Hydrocarbons
hydrogen bonding	The very strong interaction between molecules due to H atoms being bonded to N, O, or F atoms	Intermolecular Forces
hydrogenation reaction	The reaction of hydrogen across a C–C double or triple bond, usually in the presence of a catalyst	Hydrocarbons
hydronium ion	The actual chemical species that represents a hydrogen ion in aqueous solution	Arrhenius Acids and Bases
hypothesis	An educated guess about how the natural universe works	Chemistry as a Science
hyrolysis	A reaction with water	Brønsted-Lowry Acids and Bases
ICE chart	A table used to calculate equilibria values featuring rows of initial, change and equlibria concentration	Calculating Equilibrium Constant Values

ideal gas	A gas that conforms exactly to the tenets of the kinetic molecular theory.	Real Gases
ideal gas law	A gas law that relates all four independent physical properties of a gas under any conditions	The Ideal Gas Law and Some Applications
indicator	A substance whose color change indicates the equivalence point of a titration	Acid-Base Titrations
initial rate	The instantaneous rate at the start of a reaction	Reaction Rates
initial rates method	A method to determine the rate law from the instantaneous reaction rate upon mixing the reactants	Rate Laws
instantaneous reaction rate	The rate of reaction at one instant in time	Reaction Rates
intermediate	A chemical species does not appear in the overall balanced equation and is generated in one elementary step but used up in a subsequent step	Reaction Mechanisms
ion	A species with an overall electric charge	Ions and Ionic Compounds
ionic compound	A compound formed from positive and negative ions	Ions and Ionic Compounds
ionic formula	The chemical formula for an ionic compound	Ions and Ionic Compounds
ionic solid	A crystalline solid composed of ions	Solids
ionization energy (IE)	The amount of energy required to remove an electron from an atom in the gas phase.	Periodic Trends
isolated system	A system that does not allow a transfer of energy or matter into or out of itself.	Energy
isomer	A molecule with the same molecular formula as another molecule but a different structure	Hydrocarbons
isothermal	A process that does not change the temperature	Phase Transitions: Melting, Boiling and Subliming
isotopes	Atoms of the same element that have different numbers of neutrons	Atomic Theory
joule	The SI unit of energy.	Energy
kelvin	The fundamental unit of temperature in SI	Other Units: Temperature and Density
ketone	A compound where the carbonyl carbon is attached to two carbon chains	Other Oxygen-Containing Functional Groups
kinetic energy	Energy due to motion	Kinetic-Molecular Theory of Gases

kinetic molecular theory of gases	A model that helps us understand gases at the molecular level and their physical properties	Kinetic-Molecular Theory of Gases
kinetics	The study of reaction rate and the factors that can influence reaction rate	Introduction to Kinetics
law of conservation of energy	Law of physics that states that the total energy of an isolated system does not increase or decrease.	Energy
law of mass action	The relationship of the amounts of reactants and products at equilibrium	The Equilibrium Constant
Le Chatelier's principle	If an equilibrium is stressed, then the reaction shifts to reduce the stress	Shifting Equilibria: Le Chatelier's Principle
Lewis diagram	A representation of the valence electrons of an atom that uses dots around the symbol of the element.	Lewis Electron Dot Diagrams
limiting reagent	The reactant that runs out first for a given chemical reaction	Limiting Reagents
line spectrum	An image that contains only certain colors of light	Quantum Numbers for Electrons
locant	The numerical position of a substituent	Branched Hydrocarbons
lock and key model	A simple model used to describe enzyme activity, where substrates must fit into appropriately shaped active sites	Catalysis
lone electron pairs	A pair of electrons that does not make a covalent bond	Covalent Bonds
LUMO	The lowest unoccupied molecular orbital	Molecular Orbitals
magnetic quantum number (mℓ)	The index that determines the orientation of the electron's spatial distribution.	Quantum Numbers for Electrons
mass-mass calculation	A calculation in which you start with a given mass of a substance and calculate the mass of another substance involved in the chemical equation	Mole-Mass and Mass-Mass Calculations
matter	Anything that has mass and takes up space.	Some Basic Definitions
mean free path	The average distance travelled by a molecule between collisions.	Molecular Effusion and Diffusion
melting	The process of a solid becoming a liquid	Phase Transitions: Melting, Boiling and Subliming
melting point	The characteristic temperature at which a solid becomes a liquid	Phase Transitions: Melting, Boiling and Subliming
meniscus	The curved surface a liquid makes as it approaches a solid barrier	Properties of Liquids

metal	An element that conducts electricity and heat well and is shiny, silvery, solid, ductile, and malleable	Some Basic Definitions
metallic solid	A solid with the characteristic properties of a metal	Solids
microstate (*W*)	A term used to describe different possible arrangements of molecular position and kinetic energy, at a particular thermodynamic state	Entropy and the Second Law of Thermodynamics
millimeters of mercury (mmHg)	The amount of pressure exerted by a column of mercury exactly 1 mm high	Pressure
mixture	A physical combination of more than one substance	Some Basic Definitions
molality (m)	The number of moles of solute per kilogram of solvent	Quantitative Units of Concentration
molar mass	The mass of 1 mol of a substance in grams	The Mole
molar volume	The volume of exactly 1 mol of a gas; equal to 22.4 L at STP.	The Ideal Gas Law and Some Applications
molarity (M)	The number of moles of solute divided by the number of liters of solution	Quantitative Units of Concentration
mole	The number of things equal to the number of atoms in exactly 12 g of carbon-12; equals 6.022×1023 things	The Mole
mole fraction	The ratio of the number of moles of a component in a mixture divided by the total number of moles in the sample	Gas Mixtures
mole fraction	The ratio of the number of moles of a component to the total number of moles in a system	Colligative Properties of Solutions
molecular formula	A formal listing of what and how many atoms are in a molecule	Molecules an Chemical Nomenclature
molecular geometry	how the atoms in a molecule are arranged	Molecular Shapes and Polarity
molecular mass	The sum of the masses of the atoms in a molecule	Masses of Atoms and Molecules
molecular orbital theory (MO theory)	A more sophisticated model of chemical bonding where new molecular orbitals are generated using a mathematical process called Linear Combination of Atomic Orbitals (LCAO)	Molecular Orbitals
molecular polarity	The vector sum of the individual bond dipoles	Molecular Shapes and Polarity
molecular solid	A crystalline solid whose components are covalently bonded molecules	Solids
molecularity	The total number of molecules that participate in the effective collision of the elementary step	Reaction Mechanisms

molecule	The smallest part of a substance that has the physical and chemical properties of that substance	Molecules an Chemical Nomenclature
mole-mass calculation	A calculation in which you start with a given number of moles of a substance and calculate the mass of another substance involved in the chemical equation, or vice versa	Mole-Mass and Mass-Mass Calculations
mole-mole calculation	A stoichiometry calculation when one starts with moles of one substance and convert to moles of another substance using the balanced chemical equation	The Mole in Chemical Reactions
monomer	The repeated unit of a polymer	Polymers
net ionic equation	A chemical equation with the spectator ions removed	Ionic Equations: A Closer Look
neutral salt	An ionic compound that does not affect the acidity of its aqueous solution	Strong and Weak Acids and Bases and Their Salts
neutralization reaction	The reaction of an acid with a base to produce water and a salt	Neutralization Reactions
neutron	A subatomic particle with no charge	Atomic Theory
node (nodal plane)	An area of zero electron density	Molecular Orbitals
nomenclature	The rules of naming in organic chemistry	Branched Hydrocarbons
nonmetal	An element that exists in various colors and phases, is brittle, and does not conduct electricity or heat well	Some Basic Definitions
nonpolar covalent bond	The equal sharing of electrons in a covalent bond	Other Aspects of Covalent Bonding
normal boiling point	The characteristic temperature at which a liquid becomes a gas when the surrounding pressure is exactly 1 atm	Phase Transitions: Melting, Boiling and Subliming
nuclear energy	The controlled harvesting of energy from fission reactions	Nuclear Energy
nuclear equation	A chemical equation that emphasizes changes in atomic nuclei	Radioactivity
nuclear model	The model of an atom that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus	Atomic Theory
nucleus	The centre of an atom that contains protons and neutrons	Atomic Theory
odd-electron molecules	A molecule with an odd number of electrons in the valence shell of an atom	Violations of the Octet Rule

orbital	The specific set of principal, angular momentum, and magnetic quantum numbers for an electron.	Quantum Numbers for Electrons
osmosis	The tendency of solvent molecules to pass through a semipermeable membrane due to concentration differences	Colligative Properties of Solutions
osmotic pressure	The tendency of a solution to pass solvent through a semipermeable membrane due to concentration differences	Colligative Properties of Solutions
oxidation	The loss of one or more electrons by an atom; an increase in oxidation number	Oxidation-Reduction Reactions
oxidation number	A number assigned to an atom that helps keep track of the number of electrons on the atom	Oxidation-Reduction Reactions
oxidation-reduction (redox) reactions	A chemical reaction that involves the transfer of electrons	Oxidation-Reduction Reactions
p block	The columns of the periodic table in which p subshells are being occupied.	Electronic Structure and the Periodic Table
parent isotope	The reactant in a nuclear equation	Radioactivity
parts per billion (ppb)	Ratio of mass of solute to total mass of sample times 1,000,000,000	Quantitative Units of Concentration
parts per million (ppm)	Ratio of mass of solute to total mass of sample times 1,000,000	Quantitative Units of Concentration
parts per thousand (ppth)	Ratio of mass of solute to total mass of sample times 1,000	Quantitative Units of Concentration
Pauli exclusion principle	No two electrons in an atom can have the same set of four quantum numbers.	Organization of Electrons in Atoms
percent yield	Actual yield divided by theoretical yield times 100% to give a percentage between 0% and 100%	Yields
percentage composition by mass (or mass percentage, % m/m)	Ratio of mass of solute to the total mass of a sample times 100	Quantitative Units of Concentration
periodic table	A chart of all the elements	Atomic Theory
periodic trends	The variation of properties versus position on the periodic table.	Periodic Trends
pH	The negative logarithm of the hydrogen ion concentration	The pH Scale
pH scale	The range of values from 0 to 14 that describes the acidity or basicity of a solution	The pH Scale
phase	An important physical property that defines whether matter is a solid, liquid, gas or supercritical fluid	Some Basic Definitions

phase diagram	A graphical representation of the equilibrium relationships that exist between the phases of a substance under specified pressures and temperatures	Properties of Liquids
photon	The name of a discrete unit of light acting as a particle.	Light
physical change	A change that occurs when a sample of matter changes one or more of its physical properties	Some Basic Definitions
physical property	A characteristic that describes matter as it exists	Some Basic Definitions
pi bond (π bond)	The sideways overlap of p orbitals, placing electron density on opposite sides of the inter-nuclear axis – a double or triple bond	Valence Bond Theory and Hybrid Orbitals
Planck's constant	The proportionality constant between the frequency and the energy of light: 6.626 × 10 to the power of −34 J·s.	Light
pOH	The negative logarithm of the hydroxide ion concentration	The pH Scale
polar covalent bond	A covalent bond between different atoms that attract the shared electrons by different amounts and cause an imbalance of electron distribution	Other Aspects of Covalent Bonding
polarity	A measure of the unequal sharing of electrons which has resulted in a dipole moment	Other Aspects of Covalent Bonding
polyatomic ions	An ion that contains more than one atom	Ions and Ionic Compounds
polymer	A long molecule made of many repeating units	Polymers
polymerization	The process of making a polymer	Polymers
polyprotic acid	An acid capable of donating more than one H+ ion	Some Special Types of Equilibria
precipitate	A solid that falls out of solution in a precipitation reaction	Types of Chemical Reactions: Single- and Double-Displacement Reactions
precipitation reaction	A chemical reaction in which two ionic compounds are dissolved in water and form a new ionic compound that does not dissolve	Types of Chemical Reactions: Single- and Double-Displacement Reactions
prefix	A prefix used with a unit that refers to a multiple or fraction of a fundamental unit to make a more conveniently sized unit for a specific quantity	Expressing Units
pressure	Force per unit area	Pressure
primary battery	A battery that cannot be recharged	Applications of Redox Reactions: Voltaic Cells

principal quantum number (n)	The index that largely determines the energy of an electron in an atom.	Quantum Numbers for Electrons
product	A final substance in a chemical equation	The Chemical Equation
proton	A subatomic particle with a positive charge	Atomic Theory
qualitative	A description of the quality of an object	Chemistry as a Science
quantitative	A description of a specific amount of something	Chemistry as a Science
quantization	When a quantity is restricted to having only certain values.	Quantum Numbers for Electrons
quantum mechanics	The theory of electrons that treats them as a wave.	Quantum Numbers for Electrons
quantum number	An index that corresponds to a property of an electron, like its energy.	Quantum Numbers for Electrons
rad	A unit of radioactive exposure equal to 0.01 J/g of tissue	Units of Radioactivity
radioactive decay	The spontaneous change of a nucleus from one element to another	Radioactivity
radioactivity	Emanations of particles and radiation from atomic nuclei	Radioactivity
Raoult's law	The mathematical formula for calculating the vapor pressure of a solution	Colligative Properties of Solutions
rate constant (k)	A proportionality constant specific to each reaction at a particular temperature	Rate Laws
rate-determining step	The slowest step in a multistep mechanism	Reaction Mechanisms
rate law	A mathematical relationship between the reaction rate and the reactant concentrations	Rate Laws
reactant	An initial substance in a chemical equation	The Chemical Equation
reaction mechanism	The bond making and bond breaking steps which occur at the molecular level during a chemical reaction	Reaction Mechanisms
reaction order	The sum of the concentration term exponents in a rate law equation	Rate Laws
reaction rate	The speed of a chemical reaction	Introduction to Kinetics
real gas	A gas that deviates from ideal behaviour.	Real Gases
redox reaction	A chemical reaction that involves the transfer of electrons	Oxidation-Reduction Reactions
reduction	The gain of one or more electrons by an atom; a decrease in oxidation number	Oxidation-Reduction Reactions

rem	A unit of radioactive exposure that includes a factor to account for the type of radioactivity	Units of Radioactivity
ribozyme	Ribonucleic acid (RNA) molecules capable of catalyzing certain chemical reactions	Catalysis
root-mean-square (rms) speed (urms)	The speed of molecules having exactly the same kinetic energy as the average kinetic energy of the sample	Kinetic-Molecular Theory of Gases
s block	The columns of the periodic table in which s subshells are being occupied	Electronic Structure and the Periodic Table
salt	Any ionic compound that is formed from a reaction between an acid and a base	Neutralization Reactions
salt	Any ionic compound that is formed from a reaction between an acid and a base	Arrhenius Acids and Bases
salt bridge	A part of a voltaic cell that contains a solution of some ionic compound whose ions migrate to either side of the voltaic cell to maintain the charge balance	Applications of Redox Reactions: Voltaic Cells
saturated hydrocarbons	A carbon compound with the maximum possible number of H atoms in its formula	Hydrocarbons
saturated solution	A solution with the maximum amount of solute dissolved in it	Some Definitions
science	The process of knowing about the natural universe through observation and experiment	Chemistry as a Science
scientific law	A specific statement that is thought to be never violated by the entire natural universe	Chemistry as a Science
scientific notation	An expression of a number using powers of 10	Expressing Numbers
screening	The repelling valence electrons by core electrons	Periodic Trends
second law of thermodynamics	A spontaneous process will increase the entropy of the universe	Entropy and the Second Law of Thermodynamics
secondary battery	A battery that can be recharged	Applications of Redox Reactions: Voltaic Cells
semimetal	An element that has properties of both metals and nonmetals	Some Basic Definitions
semipermeable membrane	A thin membrane that will pass certain small molecules but not others	Colligative Properties of Solutions
SI unit	International System of Units used by all scientists, literally translated from “le Système International d’unités.”	Expressing Units
Sievert (Sv)	Sievert (Sv) is a related unit and is defined as 100 rem	Units of Radioactivity

sigma bond (σ bond)	Orbital overlap to form a bond which has cylindrical symmetry – a single bond	Valence Bond Theory and Hybrid Orbitals
significant figures	The limit of the number of places a measurement can be properly expressed with	Significant Figures
silicones	A polymer based on a silicon and oxygen backbone	Polymers
single bond	A covalent bond composed of one pair of electrons	Covalent Bonds
single-replacement reaction	A chemical reaction in which one element is substituted for another element in a compound	Types of Chemical Reactions: Single- and Double-Displacement Reactions
solidification	The process of a liquid becoming a solid	Phase Transitions: Melting, Boiling and Subliming
solubility	The maximum amount of a solute that can be dissolved in a given amount of a solvent	Some Definitions
solubility rules	General statements that predict which ionic compounds dissolve and which do not	Types of Chemical Reactions: Single- and Double-Displacement Reactions
solute	The minor component of a solution	Some Definitions
solution	See homogeneous mixture	Some Basic Definitions
solvent	The major component of a solution.	Some Definitions
specific heat capacity	The proportionality constant between heat, mass, and temperature change; also called specific heat.	Work and Heat
spectator ion	An ion that does nothing in the overall course of a chemical reaction	Ionic Equations: A Closer Look
spin quantum number (m_s)	The index that indicates one of two spin states for an electron.	Quantum Numbers for Electrons
spontaneous process	A process that occurs without the influence of external forces or a change that moves a system towards equilibrium	Spontaneous Change
standard molar entropy (So)	The entropy of 1 mole of a substance in its standard state, at 1 atm of pressure	Measuring Entropy and Entropy Changes
standard notation	A straightforward expression of a number	Expressing Numbers
standard temperature and pressure (STP)	A set of benchmark conditions used to compare other properties of gases: 100 kPa for pressure and 273 K for temperature	The Ideal Gas Law and Some Applications
stoichiometry	The relating of one chemical substance to another using a balanced chemical reaction	Stoichiometry

strong acid	Any acid that is 100% dissociated into ions in aqueous solution	Strong and Weak Acids and Bases and Their Salts
strong base	Any base that is 100% dissociated into ions in aqueous solution	Strong and Weak Acids and Bases and Their Salts
sublimation	The process of a solid becoming a gas	Phase Transitions: Melting, Boiling and Subliming
subshell	A term used to describe electrons in a shell that have the same angular momentum quantum number.	Quantum Numbers for Electrons
substance	Matter that has the same physical and chemical properties throughout.	Some Basic Definitions
substituent	A branch off a main chain in a hydrocarbon	Branched Hydrocarbons
substrate	The reactants which are specific for a biological catalyst	Catalysis
supercritical fluid	A phase beyond the critical point, where liquid and gas phases are no longer distinct	Properties of Liquids
supersaturated solution	A unstable solution with more than the normal maximum amount of solute in it	Some Definitions
surface tension	An effect caused by an imbalance of forces on the atoms at the surface of a liquid	Properties of Liquids
surrounding atoms	An atom that makes covalent bonds to the central atom(s)	Covalent Bonds
system	The part of the universe that is under study.	Energy
temperature	A measure of the average amount of kinetic energy a system contains	Other Units: Temperature and Density
theoretical yield	An amount that is theoretically produced as calculated using the balanced chemical reaction	Yields
theory	A general statement that explains a large number of observations	Chemistry as a Science
thermochemical equation	A chemical equation that includes an enthalpy change.	Enthalpy and Chemical Reactions
thiol	The sulfur analog of an alcohol	Other Functional Groups
third law of thermodynamics	At absolute zero the entropy of a pure, perfect crystal is zero	Measuring Entropy and Entropy Changes
titrant	The reagent of known concentration	Acid-Base Titrations
titration	A chemical reaction performed quantitatively to determine the exact amount of a reagent	Acid-Base Titrations
torr	Another name for a millimeter of mercury	Pressure

tracer	A substance that can be used to follow the pathway of that substance through a structure	Uses of Radioactive Isotopes
transition state	The highest energy transitional point in the elementary step	Reaction Mechanisms
triple bond	A covalent bond composed of three pairs of bonding electrons	Covalent Bonds
unsaturated hydrocarbons	A carbon compound with less than the maximum possible number of H atoms in its formula	Hydrocarbons
unsaturated solution	A solution with less than the maximum amount of solute dissolved in it	Some Definitions
valence electron	An electron in the highest-numbered shell or in the last unfilled subshell. Valence electrons are those that are most likely to be involved in chemical reactions.	Electronic Structure and the Periodic Table
valence shell	The highest-numbered shell in an atom that contains electrons.	Electronic Structure and the Periodic Table
valence shell electron pair repulsion theory (VSEPR)	The general concept that estimates the shape of a simple molecule: electron pairs repel each other to get as far away from each other as possible	Molecular Shapes and Polarity
van der Waals equation	An equation that compensates for deviations from ideal gas behaviour, correcting for intermolecular forces and the volume of gas molecules.	Real Gases
van’t Hoff factor (i)	The number of particles each solute formula unit breaks apart into when it dissolves	Colligative Properties of Ionic Solutes
vapor	Material in the gas phase due to evaporation	Properties of Liquids
vapor pressure	The partial pressure exerted by evaporation of a liquid	Gas Mixtures
vapor pressure depression	The decrease of a solution’s vapor pressure because of the presence of a solute	Colligative Properties of Solutions
vector quantity	A quantity which has both a magnitude and direction	Molecular Shapes and Polarity
voltaic (galvanic) cell	An apparatus that allows for useful electrical work to be extracted from a redox reaction.	Applications of Redox Reactions: Voltaic Cells
wavelength	The distance between corresponding points in two adjacent light cycles.	Light
weak acid	Any acid that is less than 100% dissociated into ions in aqueous solution	Strong and Weak Acids and Bases and Their Salts
weak base	Any base that is less than 100% dissociated into ions in aqueous solution	Strong and Weak Acids and Bases and Their Salts

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third edition was published in January 2009. His publication list has over 180 items, roughly evenly distributed between research papers and articles of educational interest.

Versioning History

This page provides a record of edits and changes made to this book since its initial publication in the B.C. Open Textbook Collection. Whenever edits or updates are made, we make the required changes in the text and provide a record and description of those changes here. If the change is minor, the version number increases by 0.01. However, if the edits involve substantial updates, the version number goes up to the next full number. The files on our website always reflect the most recent version, including the print-on-demand copy.

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Version	Date	Change	Details
1.01	September 15, 2014	Book added to the B.C. Open Textbook Collection.	
1.02	September 17/15	Typos in the Conversion of Units section (pp 52-60). Division sign missing in all examples in the PDF of text.	Corrections made.
1.03	May 15, 2017	Links to videos updated. New file types added: digital .pdf and .odt files.	The updated videos are: • Chapter 1: Some Basic Definitions – “The Chemical World” • Chapter 2: Significant Figures – “Significant Figures” • Chapter 2: Converting Units – “Unit Conversion” • Chapter 5: Stoichiometry – “Stoichiometry” • Chapter 6: Molecular Effusion and Diffusion – “Diffusion” • Chapter 12: Acid-Base Titrations – “Titrations”
1.04	January 30, 2019	Error fixes and updated metadata.	Chapter: Hydrocarbons • Image showing the Lewis structure for but-2-yne: Removed the two hydrogen atoms from the third carbon atom. Chapter: Branched Hydrocarbons • A molecule was incorrectly labelled as 3-phenylheptane. It was corrected to 4-phenylheptane. • The label of the image in Answer 17 was corrected to say “3-methylheptane” Metadata • Updated copyright information and metadata based on BCcampus standards and Pressbooks updates. • Edited the About the book chapter to provide up-to-date information.

Version	Date	Change	Details
1.05	February 3, 2020	Updated style and added ISBNs.	Changed the theme from the Open Textbooks theme to Clarke. This may affect some of the styles and the PDF page count.
1.06	July 21, 2020	Error corrections to the section on Atomic Theory and Half-Life.	Two errors corrected in Atomic Theory – Example 2: The symbol for iron was corrected from F to Fe, and the mass number (235) was added above the 92 to indicate the specific isotope of uranium. And in Half-Life, "This expression works even if the number of half-lives is not a whole number" was changed to "This expression works best when the number of half-lives is a whole number."
1.07	October 27, 2021	Revised for style and fixed LaTex.	Cleaned up the style of the book and fixed all of the LaTeX to ensure it displays properly.
1.08	March 30, 2023	Fixed ordering of Chapter 8.	Moved the sections in Chapter 8 to match the order of the book this was adapted from. Renumbered figures, examples, and tables to fit the new ordering.
1.09	September 25, 2023	Links to videos updated.	The updated videos are: • Chapter 1: Some Basic Definitions – "The Chemical World" • Chapter 2: Significant Figures – "Significant Figures" • Chapter 2: Converting Units – "Unit Conversion" • Chapter 5: Stoichiometry – "Stoichiometry" • Chapter 6: Molecular Effusion and Diffusion – "Diffusion" • Chapter 12: Acid-Base Titrations – "Titrations"