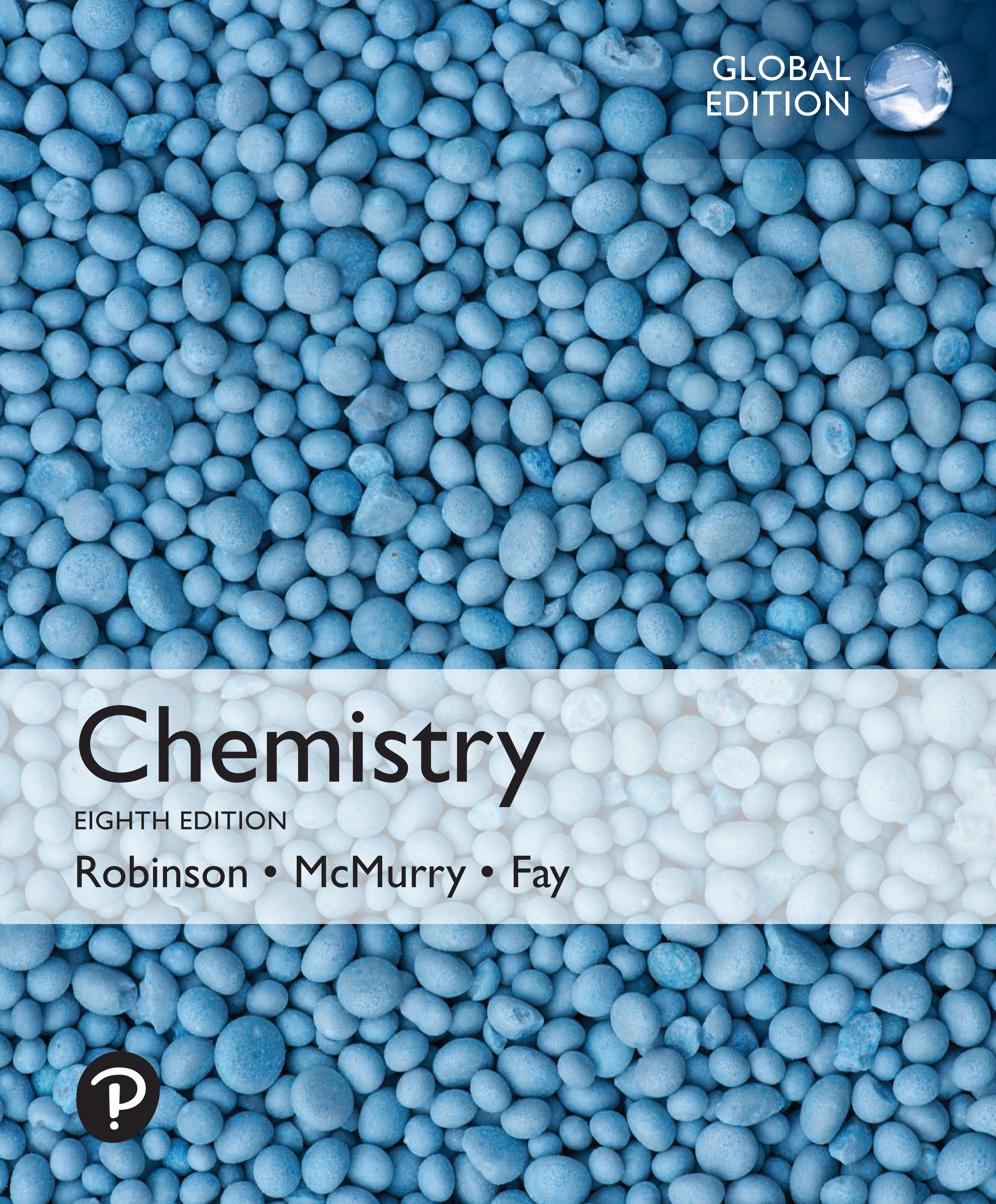


GLOBAL EDITION

Chemistry

EIGHTH EDITION

Robinson • McMurry • Fay

List of the Elements with Their Atomic Symbols and Atomic Weights

Name	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	(227)*
Aluminum	Al	13	26.981538
Americium	Am	95	(243)
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	(210)
Barium	Ba	56	137.327
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98040
Bohrium	Bh	107	(272)
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Calcium	Ca	20	40.078
Californium	Cf	98	(251)
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Cesium	Cs	55	132.90545
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copernicium	Cn	112	(285)
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Darmstadtium	Ds	110	(281)
Dubnium	Db	105	(268)
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	(252)
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	(257)
Flerovium	Fl	114	(289)
Fluorine	F	9	18.998403
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.96657
Hafnium	Hf	72	178.49
Hassium	Hs	108	(270)
Helium	He	2	4.002602
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	(262)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Livermorium	Lv	116	(293)
Lutetium	Lu	71	174.9668
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	(276)
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.96
Moscovium	Mc	115	(288)
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	(237)
Nickel	Ni	28	58.6934
Nihonium	Nh	113	(284)
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Oganesson	Og	118	(294)
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.094
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.03588
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	(280)
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(265)
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	(271)
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.989769
Strontium	Sr	38	87.62
Sulfur	S	16	32.065
Tantalum	Ta	73	180.9479
Technetium	Tc	43	(98)
Tellurium	Te	52	127.60
Tennessine	Ts	117	(292)
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.3833
Thorium	Th	90	232.0381
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.054
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.224

*Values in parentheses are the mass numbers of the most common or longest lived isotopes of radioactive elements.

Molecular Orbital Theory (Sections 8.7–8.9)

8.96 What is the difference in spatial distribution between electrons in a bonding MO and electrons in an antibonding MO?

8.97 For a given type of MO, use a σ_{2s} as an example, is the bonding or antibonding orbital higher in energy? Explain.

8.98 RAN Use the MO energy diagram in Figure 8.22b to describe the bonding in F_2^+, F_2, and F_2^-. Which of the three is likely to be stable? What is the bond order of each? Which contain unpaired electrons?

8.99 RAN Use the MO energy diagram in Figure 8.22c to describe the bonding in F_2^+, F_2, and F_2^-. Which of the three is likely to be stable? What is the bond order of each? Which contain unpaired electrons?

8.100 RAN The C_2 molecule can be represented by an MO diagram similar to that in Figure 8.22a.

(a) What is the bond order of C_2?

(b) To increase the bond order of C_2, should you add or remove an electron?

(c) Give the charge and the bond order of the new species made in part (b).

8.101 RAN Look at the molecular orbital diagram for N_2 in Figure 8.22a, and answer the following questions.

(a) What is the bond order of N_2?

(b) To decrease the bond order of N_2, should you add or remove an electron?

(c) Give the charge and the bond order of the new species made in part (b).

8.102 Look at the MO diagrams of corresponding neutral diatomic species in Figure 8.22, and predict whether each of the following ions is diamagnetic or paramagnetic. Diagrams for Li_2 and C_2 are similar to N_2; Cl_2 is similar to F_2.

(a) C_2^{2-} (b) C_2^{2+} (c) F_2^-

(d) Cl_2 (e) Li_2^+

8.103 Look at the MO diagrams of corresponding neutral diatomic species in Figure 8.22, and predict whether each of the following ions is diamagnetic or paramagnetic. MO diagrams for Li_2 and C_2 are similar to N_2; Cl_2 is similar to F_2.

(a) O_2^{2+} (b) N_2^{2+} (c) C_2^+

(d) F_2^{2+} (e) Cl_2^+

8.104 Draw a molecular orbital energy diagram for Li_2. What is the bond order? Is the molecule likely to be stable? Explain.

8.105 Calcium carbide, CaC_2, reacts with water to produce acetylene, C_2H_2, and is sometimes used as a convenient source of that substance. Use the MO energy diagram in Figure 8.22a to describe the bonding in the carbide anion, C_2^{2-}. What is its bond order?

8.106 At high temperatures, sulfur vapor is predominantly in the form of $S_2(g)$ molecules.

(a) Assuming that the molecular orbitals for third-row diatomic molecules are analogous to those for second-row molecules, construct an MO diagram for the valence orbitals of $S_2(g)$.

(b) Is S_2 likely to be paramagnetic or diamagnetic?

(c) What is the bond order of $S_2(g)$?

(d) When two electrons are added to S_2, the disulfide ion S_2^{2-} is formed. Is the bond length in S_2^{2-} likely to be shorter or longer than the bond length in S_2? Explain.

8.107 Carbon monoxide is produced by incomplete combustion of fossil fuels.

(a) Give the electron configuration for the valence molecular orbitals of CO. The orbitals have the same energy order as those of the N_2 molecule.

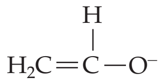
(b) Do you expect CO to be paramagnetic or diamagnetic?

(c) What is the bond order of CO? Does this match the bond order predicted by the electron-dot structure?

(d) CO can react with OH^- to form the formate ion, HCO_2^-. Draw an electron-dot structure for the formate ion, and give any resonance structures if appropriate.

8.108 Make a sketch showing the location and geometry of the *p* orbitals in the nitrite ion, NO_2^-. Describe the bonding in this ion using a localized valence bond model for σ bonding and a delocalized MO model for π bonding.

8.109 Make a sketch showing the location and geometry of the *p* orbitals in the oxy anion of allyl alcohol. Describe the bonding in this cation using a localized valence bond model for σ bonding and a delocalized MO model for π bonding.



$$H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}{-}O^-$$

Oxy anion of allyl alcohol

MULTICONCEPT PROBLEMS

8.110 RAN Propose structures for molecules that meet the following descriptions.

(a) Contains a C atom that has one π bond and three σ bonds

(b) Contains an O atom that has one π bond and one σ bond

(c) Contains an S atom that has a coordinate covalent bond

8.111 In the thiocyanate ion, NCS^-, carbon is the central atom.

(a) Draw as many resonance structures as you can for NCS^-, and assign formal charges to the atoms in each.

(b) Which resonance structure makes the greatest contribution to the resonance hybrid? Which makes the least contribution? Explain.

(c) Is NCS^- linear or bent? Explain.

(d) Which hybrid orbitals are used by the C atom, and how many Π bonds does the C atom form?

8.112 The ion I_5^- is shaped like a big "V." Draw an electron-dot structure consistent with this overall geometry.

8.113 The dichromate ion, $Cr_2O_7^{2-}$, has neither Cr—Cr nor O—O bonds.

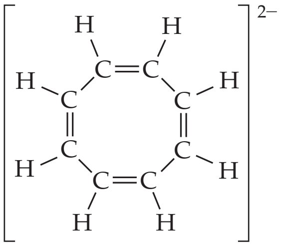
(a) Taking both 4*s* and 3*d* electrons into account, draw an electron-dot structure that minimizes the formal charges on the atoms.

(b) How many outer-shell electrons does each Cr atom have in your electron-dot structure? What is the likely geometry around the Cr atoms?

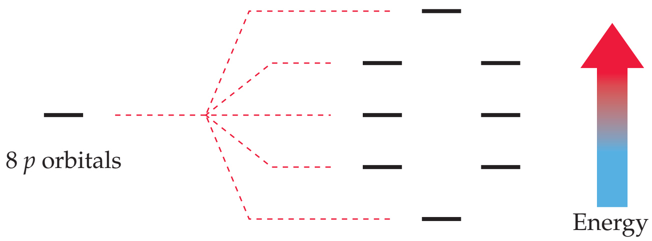
8.114 Just as individual bonds in a molecule are often polar, molecules as a whole are also often polar because of the net sum of individual bond polarities. There are three possible structures for substances with the formula $C_2H_2Cl_2$, two of which are polar overall and one of which is not.

- **(a)** Draw the three possible structures for $C_2H_2Cl_2$, predict an overall shape for each, and explain how they differ.
- **(b)** Which of the three structures is nonpolar, and which two are polar? Explain.
- **(c)** Two of the three structures can be interconverted by a process called cis–trans isomerization, in which rotation around the central carbon–carbon bond takes place when the molecules are irradiated with ultraviolet light. If light with a wavelength of approximately 200 nm is required for isomerization, how much energy in kJ/mol is involved?
- **(d)** Sketch the orbitals involved in the central carbon–carbon bond, and explain why so much energy is necessary for bond rotation to occur.

8.115 Cyclooctatetraene dianion, $C_8H_8^{2-}$, is an organic ion with the structure shown. Considering only the π bonds and not the σ bonds, cyclooctatetraene dianion can be described by the following energy diagrams of its π molecular orbitals:



Cyclooctatetraene dianion



Cyclooctatetraene dianion
pi (π) molecular orbitals

- **(a)** What is the hybridization of the 8 carbon atoms?
- **(b)** Three of the π molecular orbitals are bonding, three are antibonding, and two are *nonbonding*, meaning that they have the same energy level as isolated p orbitals. Which is which?
- **(c)** Complete the MO energy diagram by assigning the appropriate numbers of p electrons to the various molecular orbitals, indicating the electrons using up/down arrows (↑↓).
- **(d)** Based on your MO energy diagram, is the dianion paramagnetic or diamagnetic?

chapter 9

Thermochemistry: Chemical Energy

Contents

Biofuels made in a photobioreactor from algae are a renewable alternative to fossil fuels.

How do we determine the energy content of biofuels?

The answer to this question can be found on page 393 in the **INQUIRY**

Energy is important is every aspect of our lives. The food we eat provides energy to move, grow, think, and maintain a body temperature of 98.6 °F. Fossil fuels like coal, oil, and gas provide energy for electricity generation, manufacturing processes, and transportation. Projected petroleum shortages and the undesirable consequences of burning fossil fuels, including climate change and pollution, have prompted an increase in the use of renewable sources of energy such as solar cells, wind farms, and biofuels. The Inquiry at the end of the chapter describes how biofuels are made and explores their energy content.

We'll examine different forms of energy in this chapter and describe the subject of **thermochemistry,** the absorption or release of heat energy that accompanies chemical reactions. We'll also examine how heat transfer influences the very important question "Why do chemical reactions occur?" Stated simply, less stable substances with higher energy are generally converted to more stable substances with lower energy.

9.1 ENERGY AND ITS CONSERVATION

REMEMBER . . .

Energy is the capacity to supply heat or do work and is classified as either **kinetic energy**—the energy of motion—or **potential energy**—stored energy not yet released (Section 1.8).

The word *energy,* though familiar to everyone, is surprisingly hard to define in simple, nontechnical terms. A good working definition, however, is to say that **energy** is the capacity to do work or supply heat. The water falling over a dam, for instance, contains energy that can be used to turn a turbine and generate electricity. A tank of propane gas contains energy that, when released in the chemical process of combustion, can heat a house or barbecue a hamburger.

Energy is classified as either *kinetic* or *potential.* **Kinetic energy (E_K)** is the energy of motion.

Kinetic energy $E_K = \frac{1}{2}mv^2$ where m = mass and v = velocity

The derived SI unit for energy ($\text{kg} \cdot \text{m}^2/\text{s}^2$) follows from the expression for kinetic energy, $E_K = (1/2)mv^2$, and is given the name **joule (J).**

$$1\ (\text{kg} \cdot \text{m}^2/\text{s}^2) = 1\ \text{J}$$

Potential energy (E_P), by contrast, is stored energy—perhaps stored in an object because of its height or in a molecule because of reactions it can undergo. The water sitting in a reservoir behind a dam contains potential energy because of its height above the stream at the bottom of the dam. When the water is allowed to fall, its potential energy is converted to kinetic energy. Propane and other substances used as fuels contain potential energy because they can undergo a reaction with oxygen—a *combustion reaction*—that releases heat.

Let's pursue the relationship between potential energy and kinetic energy a bit further. According to the **conservation of energy law,** energy can be neither created nor destroyed; it can only be converted from one form into another.

Conservation of energy law Energy cannot be created or destroyed; it can only be converted from one form into another.

To take an example, think about a hydroelectric dam. The water sitting motionless in the reservoir behind the dam has potential energy because of its height above the outlet stream, but it has no kinetic energy because it isn't moving ($v = 0$). When the water falls through the penstocks of the dam, however, its height and potential energy decrease while its velocity and kinetic energy increase. The moving water then spins the turbine of a generator, converting its kinetic energy into electrical energy (**FIGURE 9.1**).

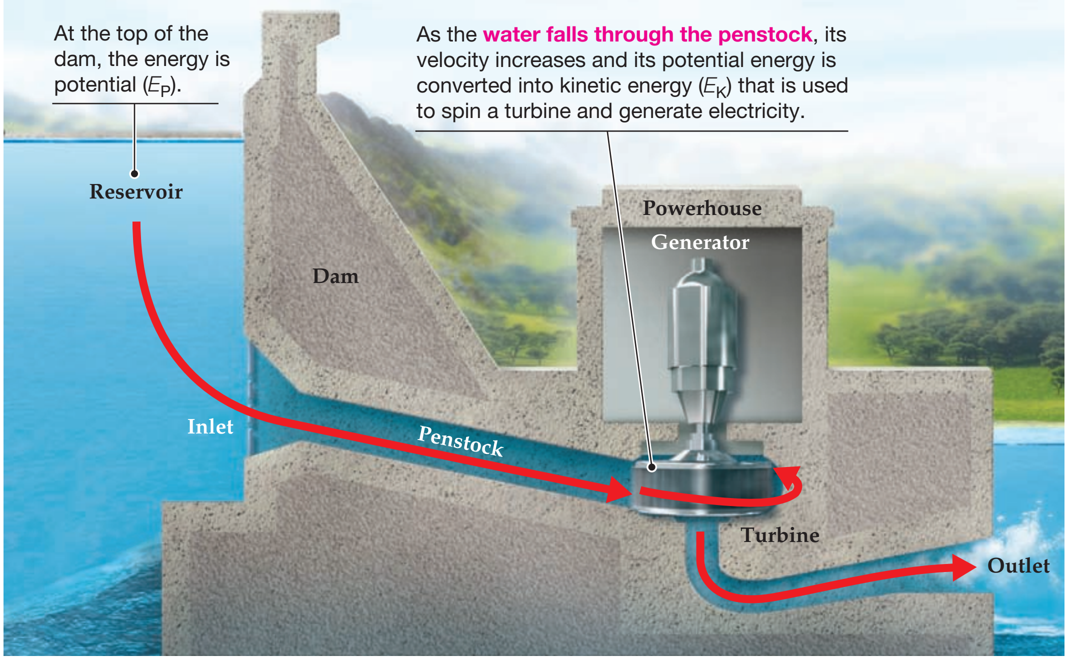


FIGURE 9.1

Conservation of energy. The total amount of energy contained by the water in the reservoir is constant.

The conversion of the kinetic energy in falling water into electricity illustrates several other important points about energy. One is that energy has many forms. Thermal energy, for example, seems different from the kinetic energy of falling water, yet is really quite similar. *Thermal energy* is just the kinetic energy of molecular motion, which we measure by finding the **temperature** of an object. An object has a low temperature and we perceive it as cold if its atoms or molecules are moving slowly. Conversely, an object has a high temperature and we perceive it as hot if its atoms or molecules are moving rapidly and are colliding forcefully with a thermometer or other measuring device.

Heat, in turn, is the amount of thermal energy transferred from one object to another as the result of a temperature difference between the two. Rapidly moving molecules in a hotter object collide with more slowly moving molecules in a colder object, transferring kinetic energy and causing the slower moving molecules to speed up.

Chemical energy is another kind of energy that seems different from that of the water in a reservoir, yet again is really quite similar. Chemical energy is a kind of potential energy in which chemical bonds act as the storage medium. Just as water releases its potential energy when it falls to a lower height, chemicals can release their potential energy in the form of heat or light when they undergo reactions and form lower-energy products. We'll explore this topic shortly.

A second point illustrated by falling water involves the conservation of energy law. To keep track of all the energy involved, it's necessary to take into account the entire chain of events that ensue from the falling water: the sound of the crashing water, the heating of the rocks at the bottom of the dam, the driving of turbines and electrical generators, the transmission of electrical power, the appliances powered by the electricity, and so on. Carrying the process to its logical extreme, it's necessary to take the entire universe into account when keeping track of all the energy in the water because the energy lost in one form *always* shows up elsewhere in another form. So important is the conservation of energy law that it's also known as the **first law of thermodynamics.**

First law of thermodynamics Energy cannot be created or destroyed; it can only be converted from one form into another.

BIG IDEA Question 1

When natural gas is burned to heat a home in the winter, _______ energy is converted to _______ energy. (Fill in the blanks with either *kinetic* or *potential*.)

9.2 INTERNAL ENERGY AND STATE FUNCTIONS

When keeping track of the energy changes in a chemical reaction, it's often helpful to think of the reaction as being isolated from the world around it. The substances we focus on in an experiment—the starting reactants and the final products—are collectively called the **system**, while everything else—the reaction flask, the solvent, the room, the building, and so on—is called the **surroundings.** If the system could be truly isolated from its surroundings so that no energy transfer could occur between them, then the total **internal energy** (***E***) of the system, defined as the sum of all the kinetic and potential energies for every molecule or ion in the system, would be conserved and remain constant throughout the reaction. In fact, this assertion is just a restatement of the first law of thermodynamics.

First law of thermodynamics (restated) The total internal energy E of an isolated system is constant.

In practice, of course, it's not possible to truly isolate a chemical reaction from its surroundings. In any real situation, the chemicals are in physical contact with the walls of a flask or container, and the container itself is in contact with the surrounding air or laboratory bench. What's important, however, is not that the system be isolated but that we be able to measure accurately any energy that enters the system from the surroundings or leaves the system and flows to the surroundings (**FIGURE 9.2**). That is, we must be able to measure any *change* in the internal energy of the system, ΔE. The energy change ΔE represents the difference in internal energy between the final state of the system after reaction and the initial state of the system before reaction:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

By convention, energy changes are measured from the point of view of the system. Any energy that flows *from* the system *to* the surroundings has a negative sign because the system has lost it (that is, E_{final} is smaller than E_{initial}). Any energy that flows *to* the system *from* the surroundings has a positive sign because the system has gained it E_{final} is larger than E_{initial}).

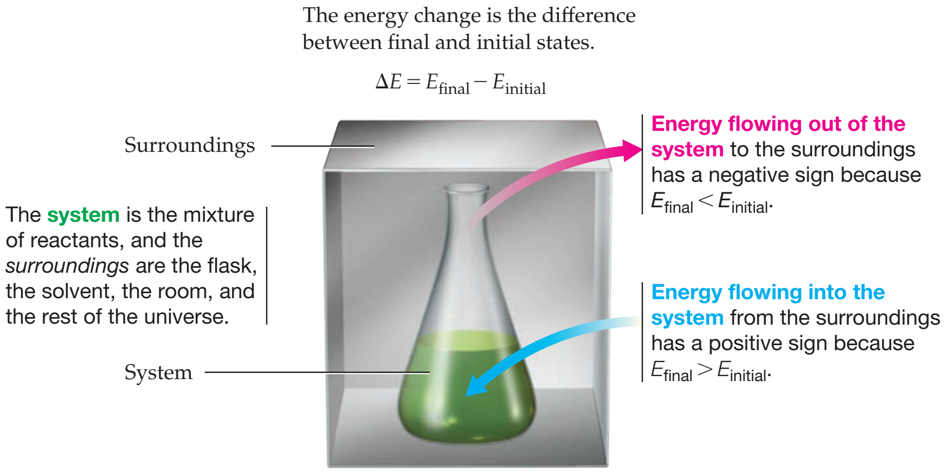
FIGURE 9.2

Energy changes in a chemical reaction.

Figure It Out

What is the sign of ΔE_{system} for a chemical reaction that causes a decrease in the temperature of the surroundings?

Answer: ΔE_{system} is positive because the chemical reaction (system) has absorbed heat from the surroundings.



If, for instance, we were to burn 1.00 mol of methane in the presence of 2.00 mol of oxygen, 802 kJ would be released as heat and transferred from the system to the surroundings. The system has 802 kJ less energy, so $\Delta E = -802$ kJ. This energy flow can be detected and measured by placing the reaction vessel in a water bath and noting the temperature rise of the bath during the reaction.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) + 802\text{ kJ energy} \qquad \Delta E = -802\text{ kJ}$$