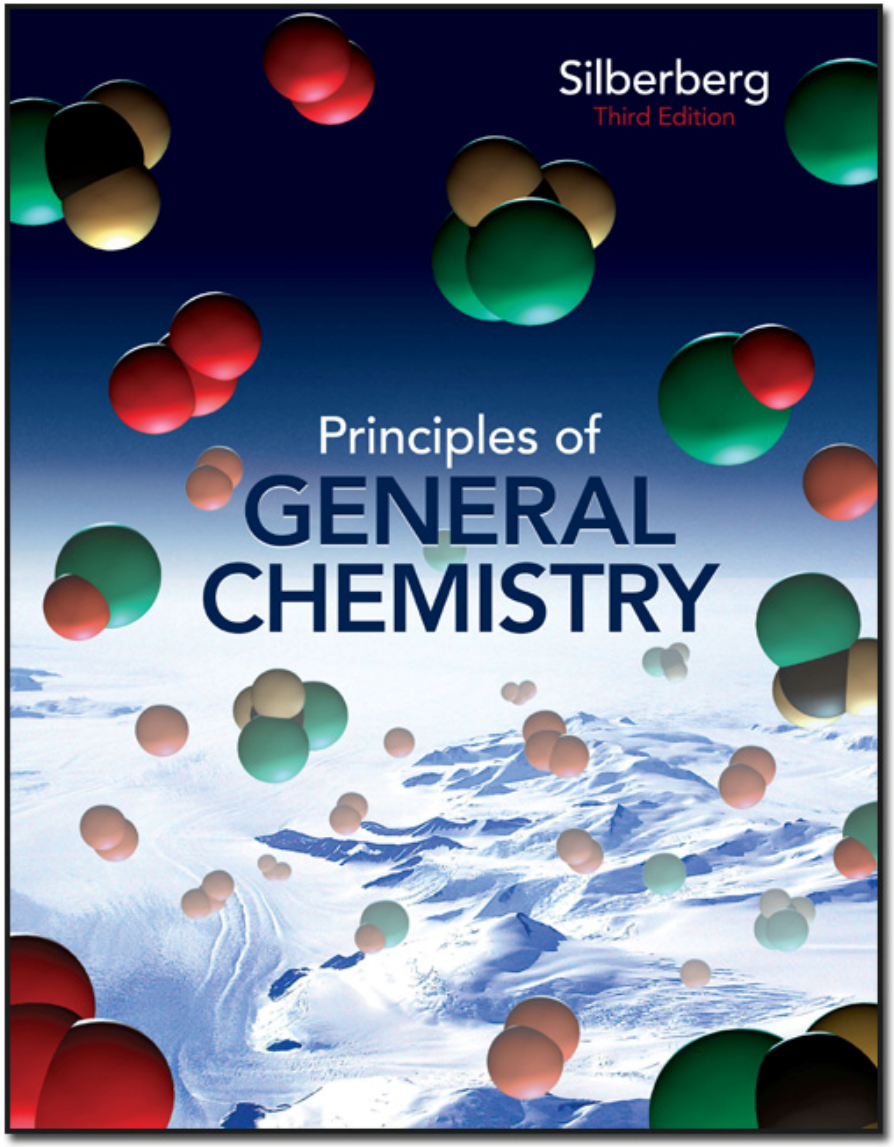

Chapter 01

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 1

Keys to the Study of Chemistry

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Chapter 1: Keys to the Study of Chemistry

1.1 Some Fundamental Definitions

1.2 The Scientific Approach: Developing a Model

1.3 Chemical Problem Solving

1.4 Measurement in Scientific Study

1.5 Uncertainty in Measurement: Significant Figures

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Chemistry

Chemistry is the study of ***matter***,

its ***properties***,

the ***changes*** that matter undergoes,

and

the ***energy*** associated with these changes.

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Definitions

Matter anything that has both mass and volume
- the “stuff” of the universe: books, planets, trees, professors, students

Composition the types and amounts of simpler substances that make up a sample of matter

Properties the characteristics that give each substance a unique identity

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Physical Properties
properties a substance shows by itself without interacting with another substance

- color, melting point, boiling point, density

Chemical Properties
properties a substance shows as it interacts with, or transforms into, other substances

- flammability, corrosiveness

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Figure 1.1 The distinction between physical and chemical change.

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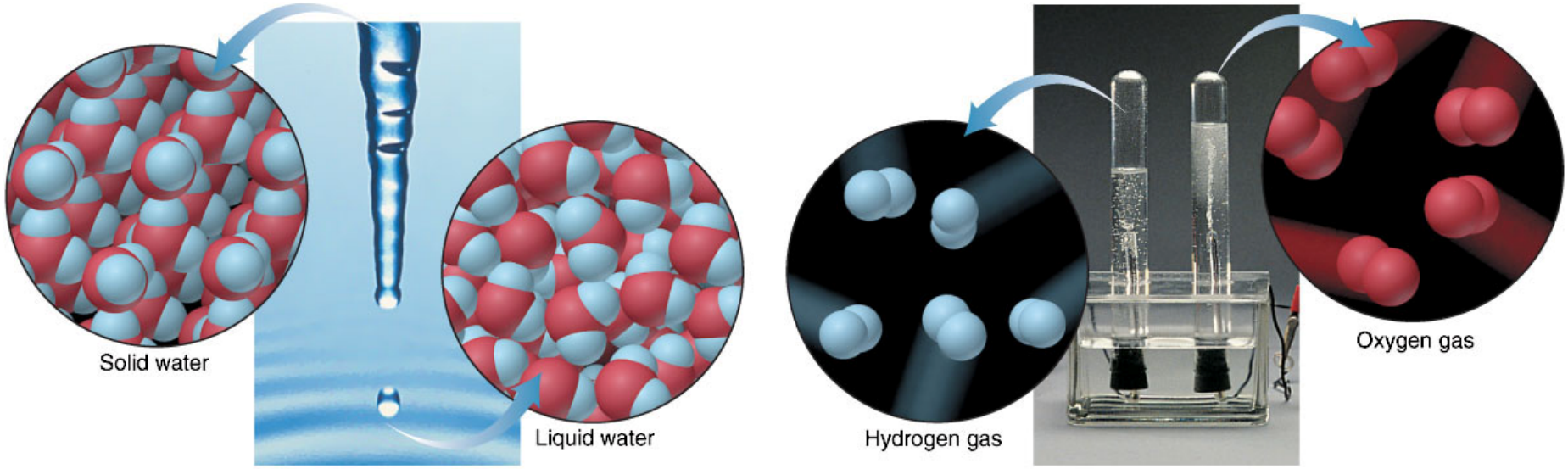

A Physical change:
Solid form of water becomes liquid form; composition does *not* change because particles are the same.

B Chemical change:
Electric current decomposes water into different substances (hydrogen and oxygen); composition *does* change because particles are different.

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Sample Problem 1.1 Visualizing Change on the Atomic Scale

PROBLEM: The scenes below represent an atomic-scale view of substance A undergoing two different changes. Decide whether each scene shows a physical or a chemical change.

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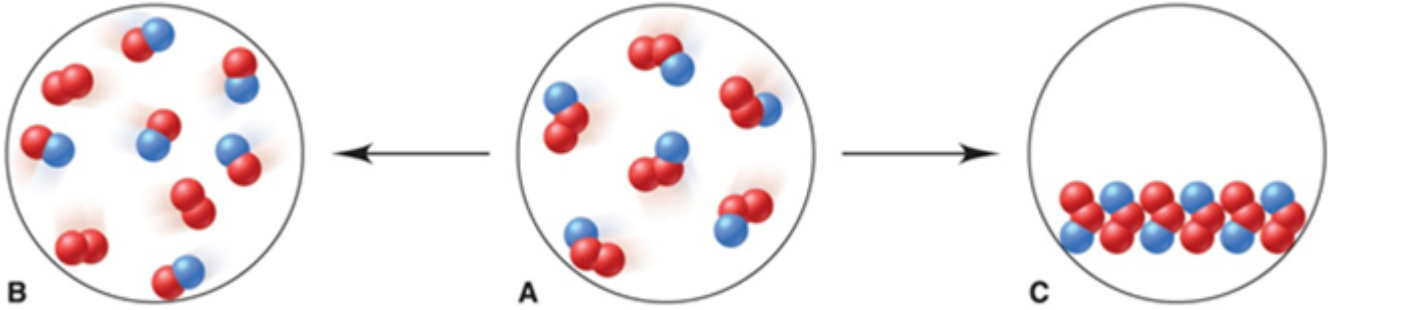

PLAN: We need to determine what change is taking place. The numbers and colors of the little spheres that represent each particle tell its "composition". If the composition does not change, the change is physical, whereas a chemical change results in a change of composition.

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Sample Problem 1.1

SOLUTION:

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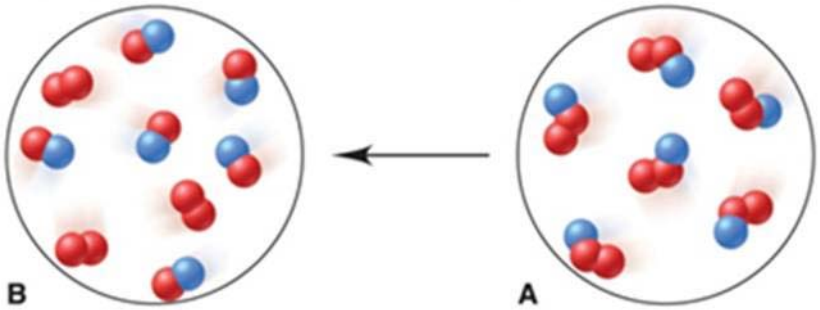

Each particle of substance A is composed of one blue and two red spheres.

Sample B is composed of two different types of particles – some have two red spheres while some have one red and one blue.

As A changes to B, the chemical composition has changed.

A → B is a **chemical change.**

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Sample Problem 1.1

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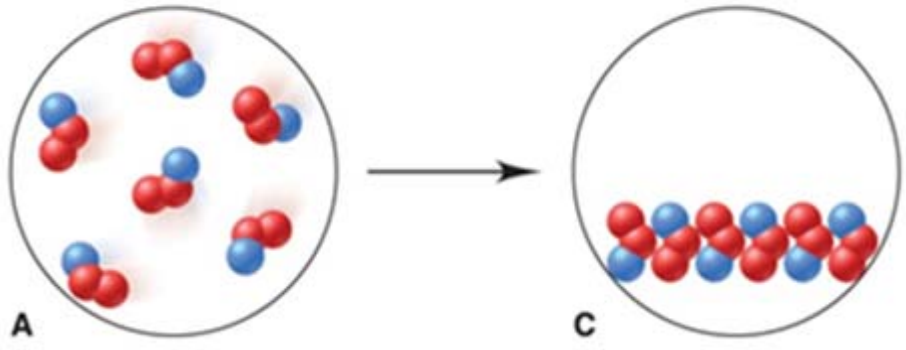

Each particle of C is still composed of one blue and two red spheres, but the particles are closer together and are more organized. The composition remains unchanged, but the physical form is different.

A → C is a **physical change**.

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The States of Matter

A ***solid*** has a fixed shape and volume. Solids may be hard or soft, rigid or flexible.

A ***liquid*** has a varying shape that conforms to the shape of the container, but a fixed volume. A liquid has an ***upper surface***.

A ***gas*** has no fixed shape or volume and therefore does not have a surface.

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Figure 1.2 The physical states of matter.

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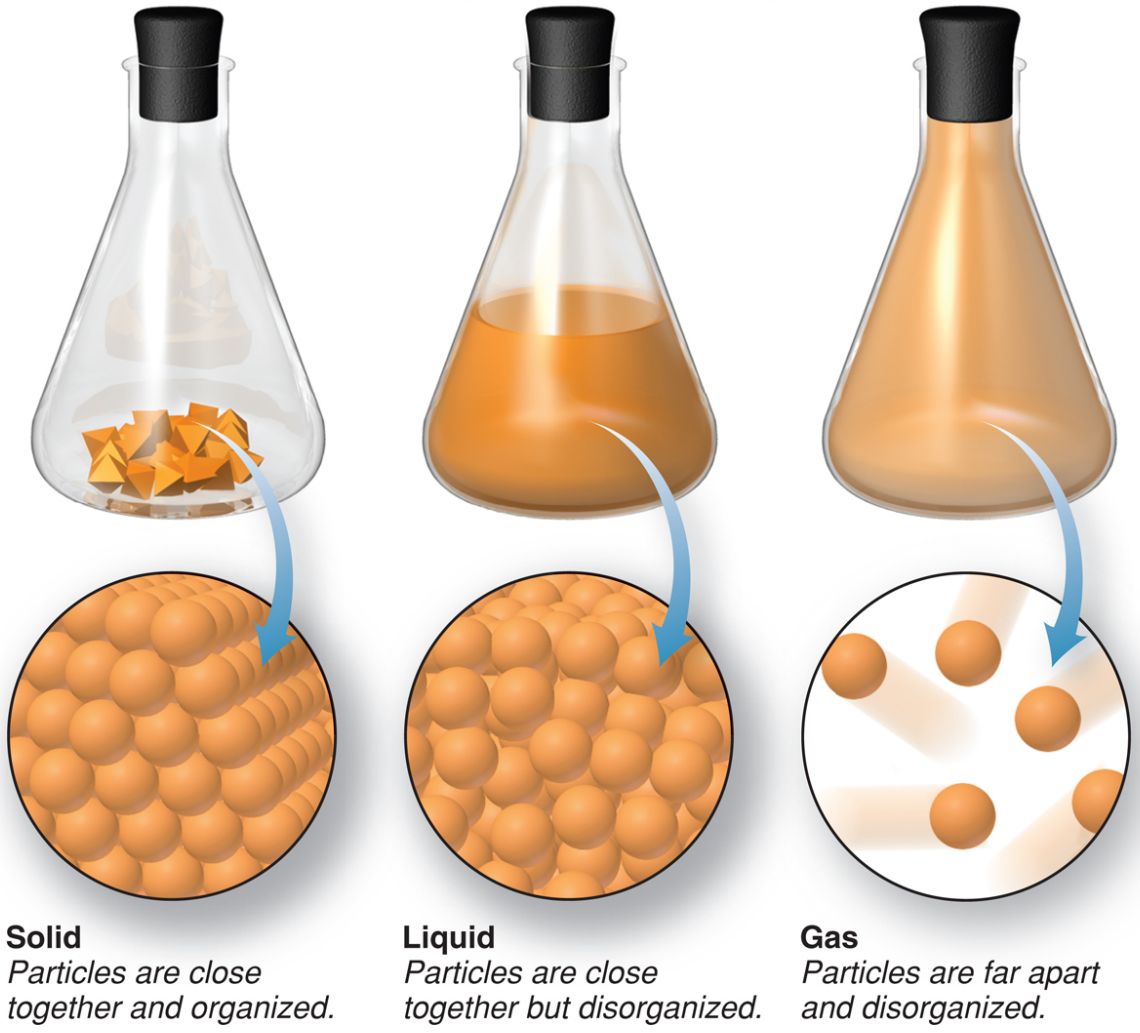

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Temperature and Change of State

- A change of state is a ***physical*** change.
  - Physical form changes, composition does not.
- Changes in physical state are ***reversible***
  - by changing the temperature.
- A chemical change cannot simply be reversed by a change in temperature.

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Sample Problem 1.2 Distinguishing Between Physical and Chemical Change

PROBLEM: Decide whether each of the following processes is primarily a physical or a chemical change, and explain briefly:

(a) Frost forms as the temperature drops on a humid winter night.

(b) A cornstalk grows from a seed that is watered and fertilized.

(c) A match ignites to form ash and a mixture of gases.

(d) Perspiration evaporates when you relax after jogging.

(e) A silver fork tarnishes slowly in air.

PLAN: "Does the substance change composition or just change form?"

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Sample Problem 1.2

SOLUTION:

(a) Frost forms as the temperature drops on a humid winter night.

physical change

(b) A cornstalk grows from a seed that is watered and fertilized.

chemical change

(c) A match ignites to form ash and a mixture of gases.

chemical change

(d) Perspiration evaporates when you relax after jogging.

physical change

(e) A silver fork tarnishes slowly in air.

chemical change

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Energy in Chemistry

Energy is the ability to do work.

Potential Energy
is energy due to the ***position*** of an object.

Kinetic Energy
is energy due to the ***movement*** of an object.

Total Energy = Potential Energy + Kinetic Energy

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Energy Changes

Lower energy states are ***more stable*** and are favored over higher energy states.

Energy is neither created nor destroyed
– it is ***conserved***
– and can be ***converted*** from one form to another.

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Figure 1.3A Potential energy is converted to kinetic energy.

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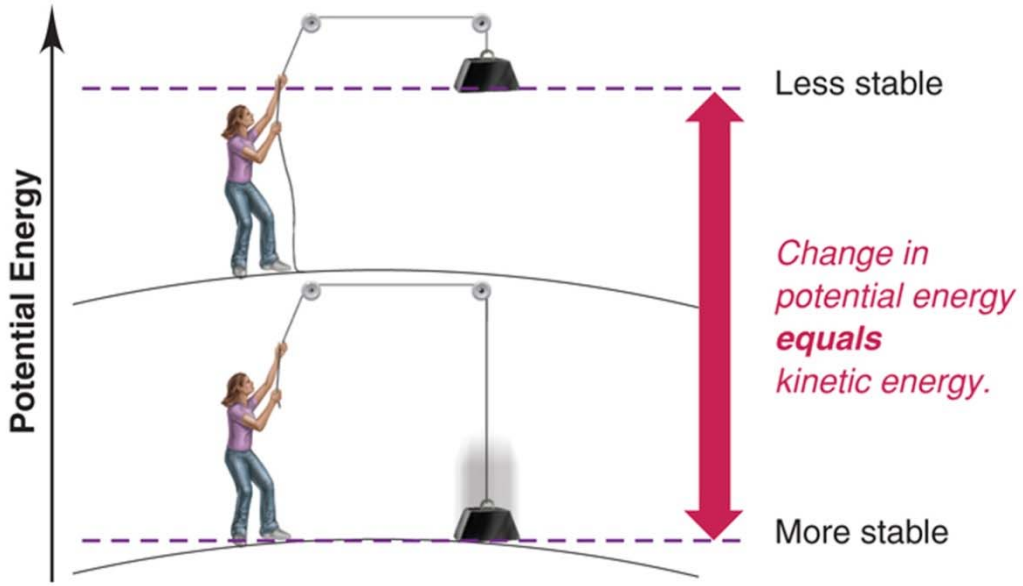

A **A gravitational system.** *Potential energy is gained when a weight is lifted. It is converted to kinetic energy as the weight falls.*

A gravitational system. The potential energy gained when a weight is lifted . It is converted to kinetic energy as the weight falls.

A lower energy state is more stable.

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Figure 1.3B Potential energy is converted to kinetic energy.

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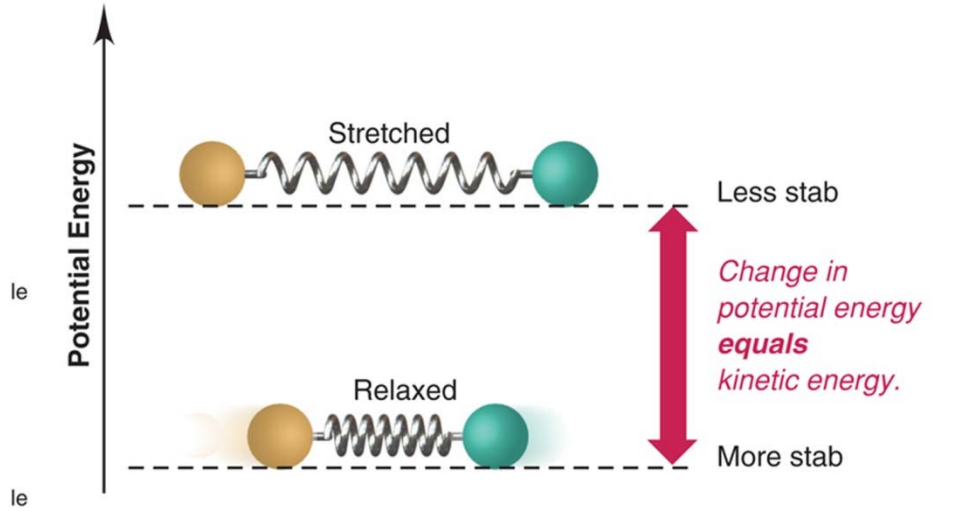

B **A system of two balls attached by a spring.** *Potential energy is gained when the spring is stretched. It is converted to the kinetic energy of the moving balls as the spring relaxes.*

A system of two balls attached by a spring. The potential energy gained by a stretched spring is converted to kinetic energy when the moving balls are released.

Energy is conserved when it is transformed.

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Figure 1.3C Potential energy is converted to kinetic energy.

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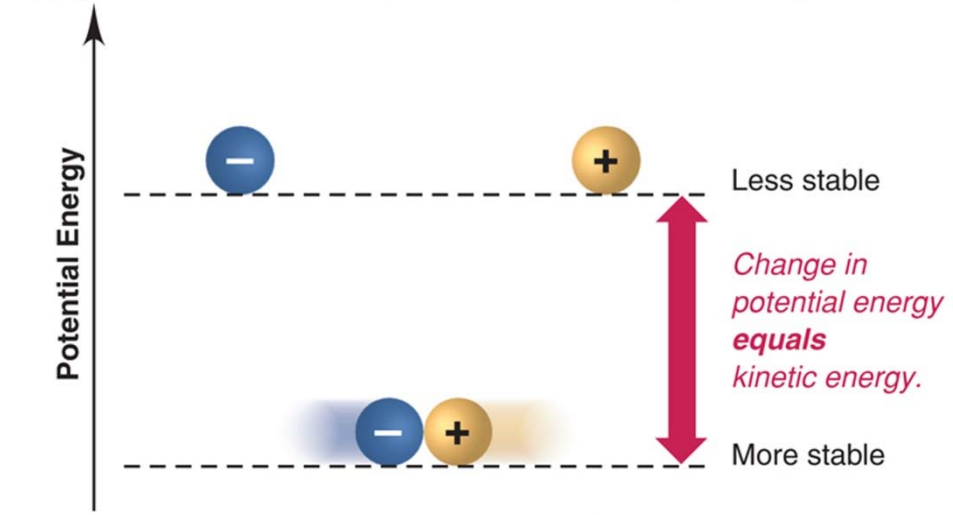

C **A system of oppositely charged particles.** *Potential energy is gained when the charges are separated. It is converted to kinetic energy as the attraction pulls the charges together.*

A system of oppositely charged particles. The potential energy gained when the charges are separated is converted to kinetic energy as the attraction pulls these charges together.

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Figure 1.3D Potential energy is converted to kinetic energy.

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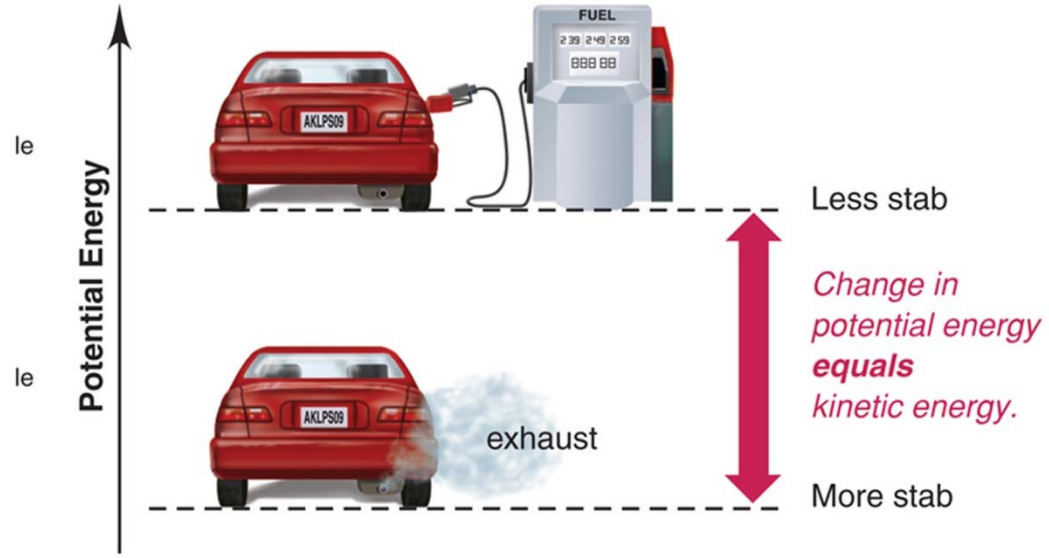

D A system of fuel and exhaust. *A fuel is higher in chemical potential energy than the exhaust. As the fuel burns, some of its potential energy is converted to the kinetic energy of the moving car.*

A system of fuel and exhaust. A fuel is higher in chemical potential energy than the exhaust. As the fuel burns, some of its potential energy is converted to the kinetic energy of the moving car.

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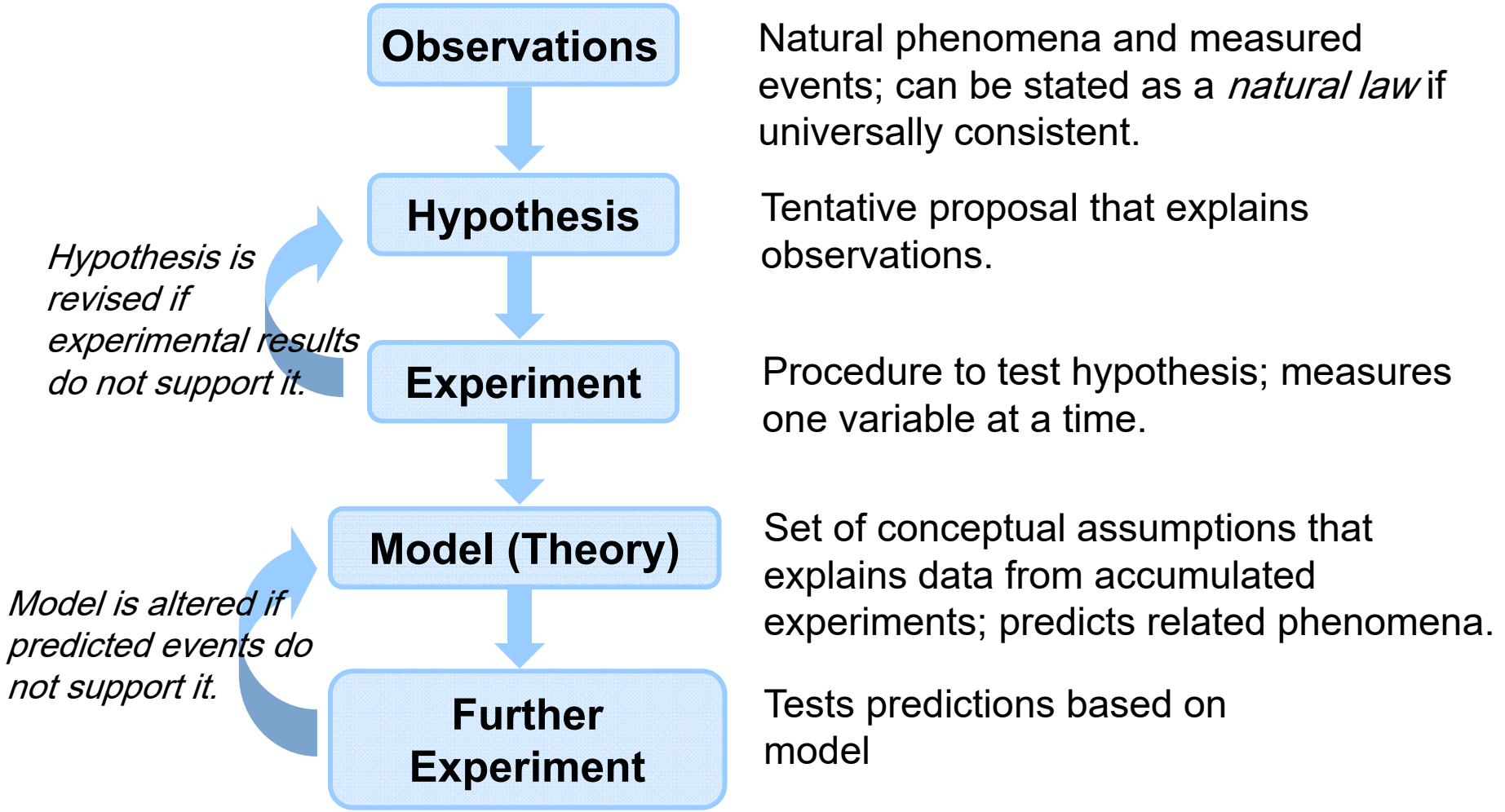
Figure 1.4 **The scientific approach to understanding nature.**



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Chemical Problem Solving

- All measured quantities consist of
  - a ***number*** and a ***unit***.
- Units are manipulated like numbers:
  - $3\ \text{ft} \times 4\ \text{ft} = 12\ \text{ft}^2$

$$\frac{350\ \text{mi}}{7\ \text{h}} = \frac{50\ \text{mi}}{1\ \text{h}} \quad \text{or } 50\ \text{mi.h}^{-1}$$

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Conversion Factors

A ***conversion factor*** is a ratio of equivalent quantities used to express a quantity in different units.

The relationship 1 mi = 5280 ft gives us the conversion factor:

$$\frac{1\text{ mi}}{5280\text{ ft}} = \frac{\cancel{5280\text{ ft}}}{\cancel{5280\text{ ft}}} = 1$$

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A conversion factor is chosen and set up so that all units cancel except those required for the answer.

PROBLEM: The height of the Angel Falls is 3212 ft. Express this quantity in miles (mi) if 1 mi = 5280 ft.

PLAN: Set up the conversion factor so that ft will cancel and the answer will be in mi.

SOLUTION:

$$3212 \text{ ft} \times \frac{1 \text{ mi}}{5280 \text{ ft}} = 0.6083 \text{ mi}$$

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Systematic Approach to Solving Chemistry Problems

- State Problem
  - Clarify the known and unknown.
- Plan
  - Suggest steps from known to unknown.
  - Prepare a visual summary of steps that includes conversion factors, equations, known variables.
- Solution
- Check
- Comment
- Follow-up Problem

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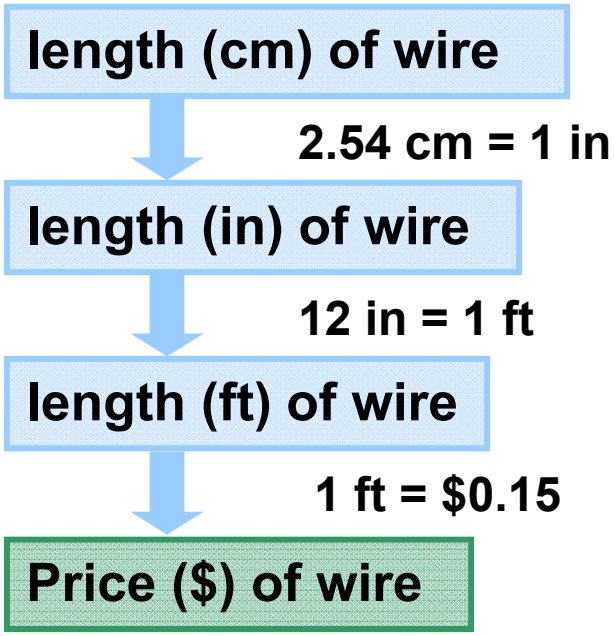
Sample Problem 1.3 Converting Units of Length

PROBLEM: To wire your stereo equipment, you need 325 centimeters (cm) of speaker wire that sells for $0.15/ft. What is the price of the wire?

PLAN: We know the length (in cm) of wire and cost per length ($/ft). We have to convert cm to inches and inches to feet. Then we can find the cost for the length in feet.



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Sample Problem 1.3

SOLUTION:

Length (in) = length (cm) x conversion factor

$$= 325 \text{ cm} \times \frac{1 \text{ in}}{2.54 \text{ cm}} = 128 \text{ in}$$

Length (ft) = length (in) x conversion factor

$$= 128 \text{ in} \times \frac{1 \text{ ft}}{12 \text{ in}} = 10.7 \text{ ft}$$

Price ($) = length (ft) x conversion factor

$$= 10.7 \text{ ft} \times \frac{\$ 0.15}{1 \text{ ft}} \quad \boxed{= \$ 1.60}$$

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Table 1.1 SI Base Units

Physical Quantity (Dimension)	Unit Name	Unit Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Amount of substance	mole	mol
Luminous intensity	candela	cd

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Table 1.2 Common Decimal Prefixes Used with SI Units

Prefix*	Prefix Symbol	Word	Conventional Notation	Exponential Notation
tera	T	trillion	1,000,000,000,000	1×10^{12}
giga	G	billion	1,000,000,000	1×10^{9}
mega	M	million	1,000,000	1×10^{6}
kilo	k	thousand	1,000	1×10^{3}
hecto	h	hundred	100	1×10^{2}
deka	da	ten	10	1×10^{1}
—	—	one	1	1×10^{0}
deci	d	tenth	0.1	1×10^{-1}
centi	c	hundredth	0.01	1×10^{-2}
milli	m	thousandth	0.001	1×10^{-3}
micro	μ	millionth	0.000001	1×10^{-6}
nano	n	billionth	0.000000001	1×10^{-9}
pico	p	trillionth	0.000000000001	1×10^{-12}
femto	f	quadrillionth	0.000000000000001	1×10^{-15}

*The prefixes most frequently used by chemists appear in bold type.

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Table 1.3 Common SI-English Equivalent Quantities

Quantity	SI to English Equivalent	English to SI Equivalent
Length	1 km = 0.6214 mile	1 mi = 1.609 km
	1 m = 1.094 yd	1 yd = 0.9144 m
	1 m = 39.37 inches	1 ft = 0.3048 m
	1 cm = 0.3937 inch	1 in = 2.54 cm
Volume	1 cubic meter (m^3) = 35.31 ft^3	1 ft^3 = 0.02832 m^3
	1 dm^3 = 0.2642 gal	1 gal = 3.785 dm^3
	1 dm^3 = 1.057 qt	1 qt = 0.9464 dm^3
	1 cm^3 = 0.03381 fluid ounce	1 qt = 946.4 cm^3
		1 fluid ounce = 29.57 cm^3
Mass	1 kg = 2.205 lb	1 lb = 0.4536 kg
	1 g = 0.03527 ounce (oz)	1 oz = 28.35 g

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Figure 1.5 Common laboratory volumetric glassware.

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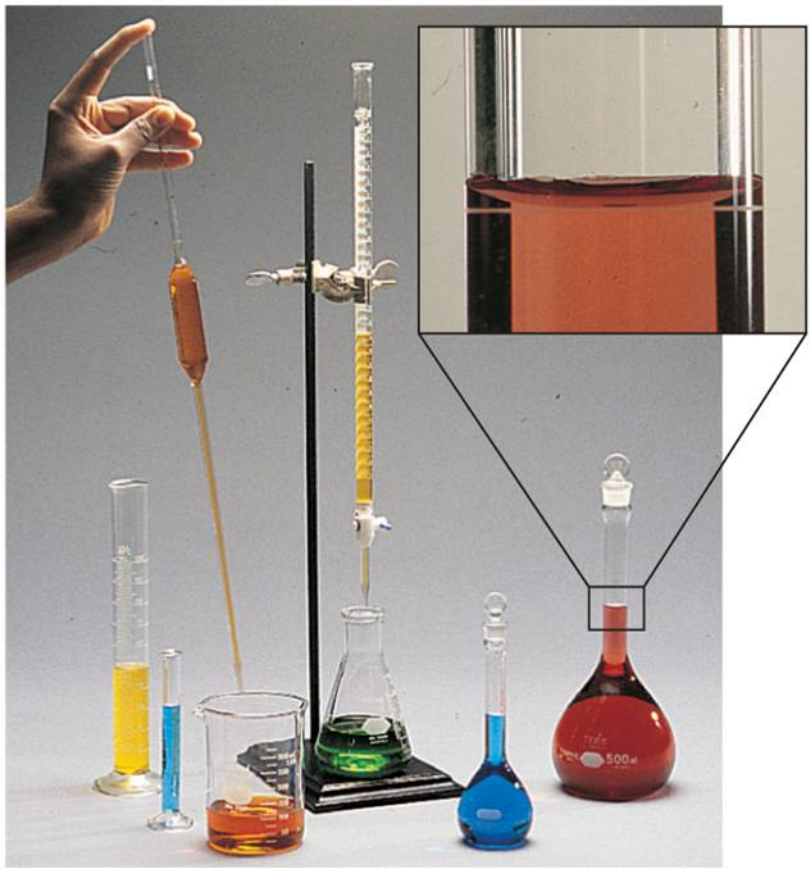

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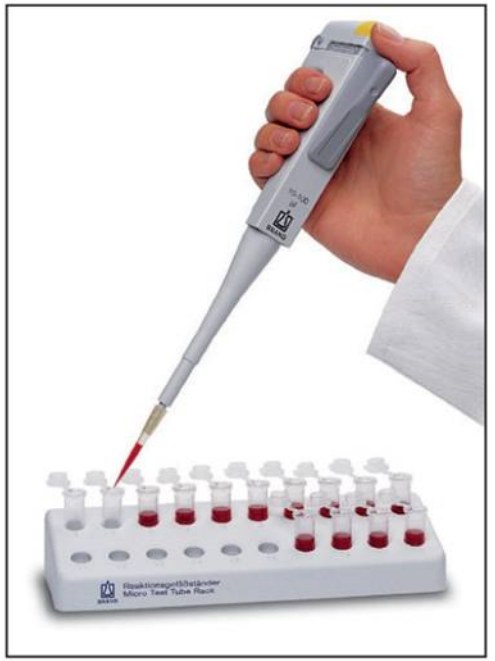

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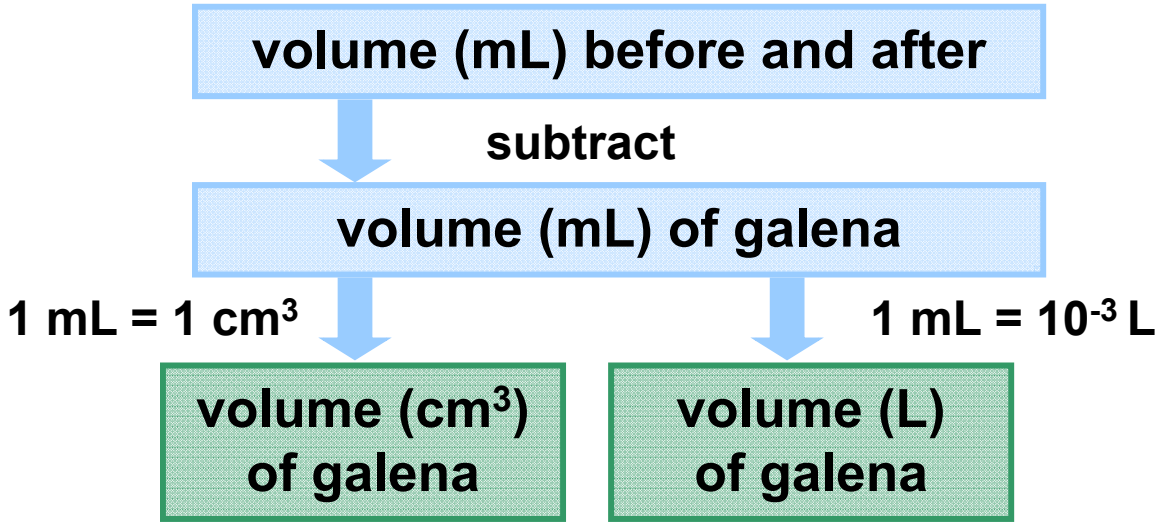
Sample Problem 1.4 **Converting Units of Volume**

PROBLEM: A graduated cylinder contains 19.9 mL of water. When a small piece of galena, an ore of lead, is added, it sinks and the volume increases to 24.5 mL. What is the volume of the piece of galena in cm^3 and in L?

PLAN: The volume of the galena is equal to the difference in the volume of the water before and after the addition.



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Sample Problem 1.4

SOLUTION:

(24.5 - 19.9) mL = volume of galena = 4.6 mL

$$4.6 \text{ mL} \times \frac{1 \text{ cm}^3}{1 \text{ mL}} = \mathbf{4.6\ cm^3}$$

$$4.6 \text{ mL} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}} = \mathbf{4.6 \times 10^{-3}\ L}$$

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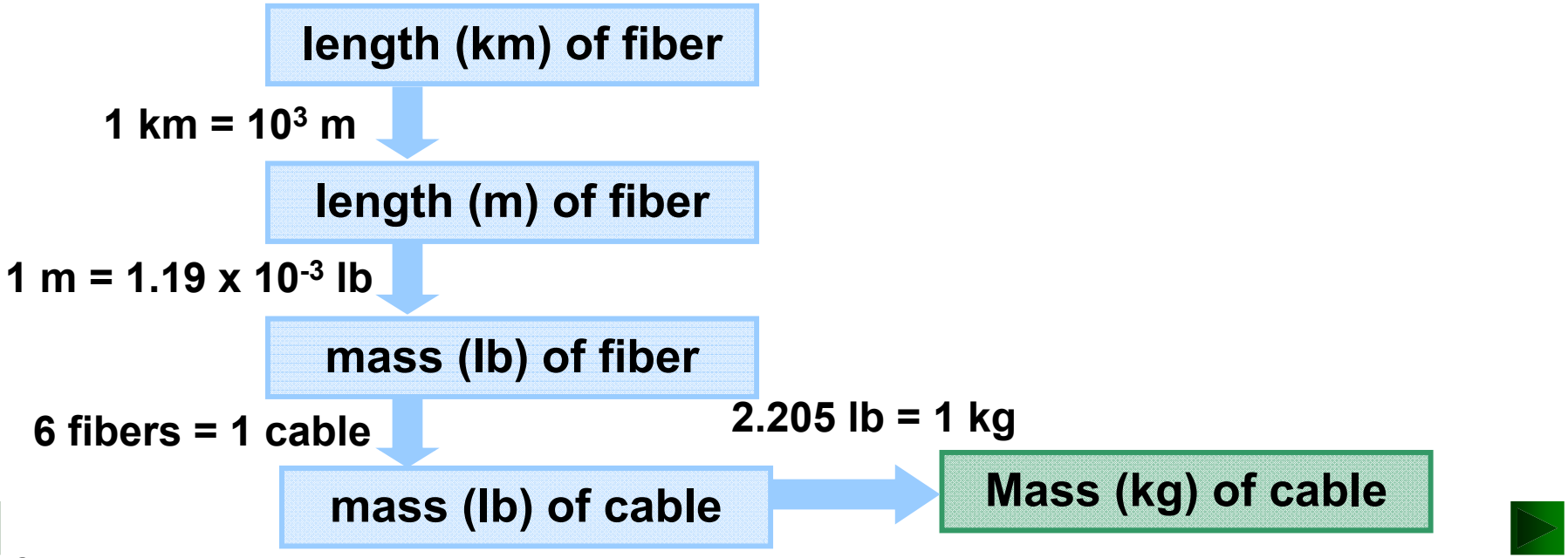
Sample Problem 1.5 **Converting Units of Mass**

PROBLEM: Many international computer communications are carried out by optical fibers in cables laid along the ocean floor. If one strand of optical fiber weighs 1.19×10^{-3} lb/m, what is the mass (in kg) of a cable made of six strands of optical fiber, each long enough to link New York and Paris (8.94×10^{3} km)?

PLAN: The sequence of steps may vary but essentially we need to find the length of the entire cable and convert it to mass.



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Sample Problem 1.5

SOLUTION:

$$8.84 \times 10^3 \cancel{\text{km}} \times \frac{10^3 \text{ m}}{1 \cancel{\text{km}}} = 8.84 \times 10^6 \text{ m}$$

$$8.84 \times 10^6 \cancel{\text{m}} \times \frac{1.19 \times 10^{-3} \text{ lb}}{1 \cancel{\text{m}}} = 1.05 \times 10^4 \text{ lb}$$

$$\frac{1.05 \times 10^4 \text{ lb}}{1 \cancel{\text{fiber}}} \times \frac{6 \cancel{\text{fibers}}}{1 \text{ cable}} = 6.30 \times 10^4 \text{ lb/cable}$$

$$\frac{6.30 \times 10^4 \cancel{\text{lb}}}{1 \text{ cable}} \times \frac{1 \text{ kg}}{2.205 \cancel{\text{lb}}}$$

$= 2.86 \times 10^4$ kg/cable

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Density

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

At a given temperature and pressure, the density of a substance is a characteristic physical property and has a specific value.

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Table 1.4 Densities of Some Common Substances*

Substance	Physical State	Density (g/cm^3)
Hydrogen	gas	0.0000899
Oxygen	gas	0.00133
Grain alcohol	liquid	0.789
Water	liquid	0.998
Table salt	solid	2.16
Aluminum	solid	2.70
Lead	solid	11.3
Gold	solid	19.3

*At room temperature (20°C) and normal atmospheric pressure (1 atm).

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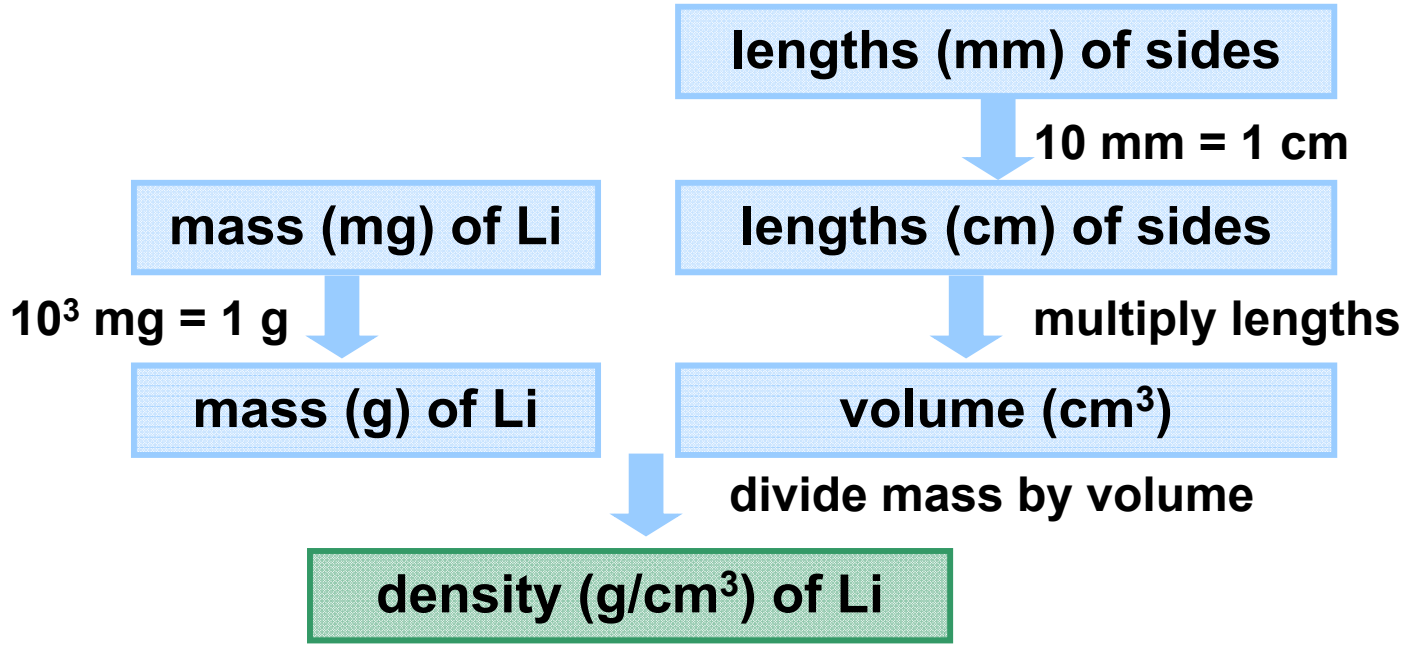
Sample Problem 1.6 Calculating Density from Mass and Length

PROBLEM: Lithium, a soft, gray solid with the lowest density of any metal, is a key component of advanced batteries. A slab of lithium weighs 1.49×10^3 mg and has sides that are 20.9 mm by 11.1 mm by 11.9 mm. Find the density of lithium in g/cm^3.

PLAN: Density is expressed in g/cm^3 so we need the mass in g and the volume in cm^3.



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Sample Problem 1.6

SOLUTION:

$$1.49 \times 10^3 \text{ mg} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 1.49 \text{ g}$$

$$20.9 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}} = 2.09 \text{ cm}$$

Similarly the other sides will be 1.11 cm and 1.19 cm, respectively.

Volume = $2.09 \times 1.11 \times 1.19 = 2.76 \text{ cm}^3$

$$\text{density of Li} = \frac{1.49 \text{ g}}{2.76 \text{ cm}^3}$$ **$= 0.540 \text{ g/cm}^3$**

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Figure 1.6 Freezing and boiling points of water in the Celsius, Kelvin (absolute) and Fahrenheit scales.

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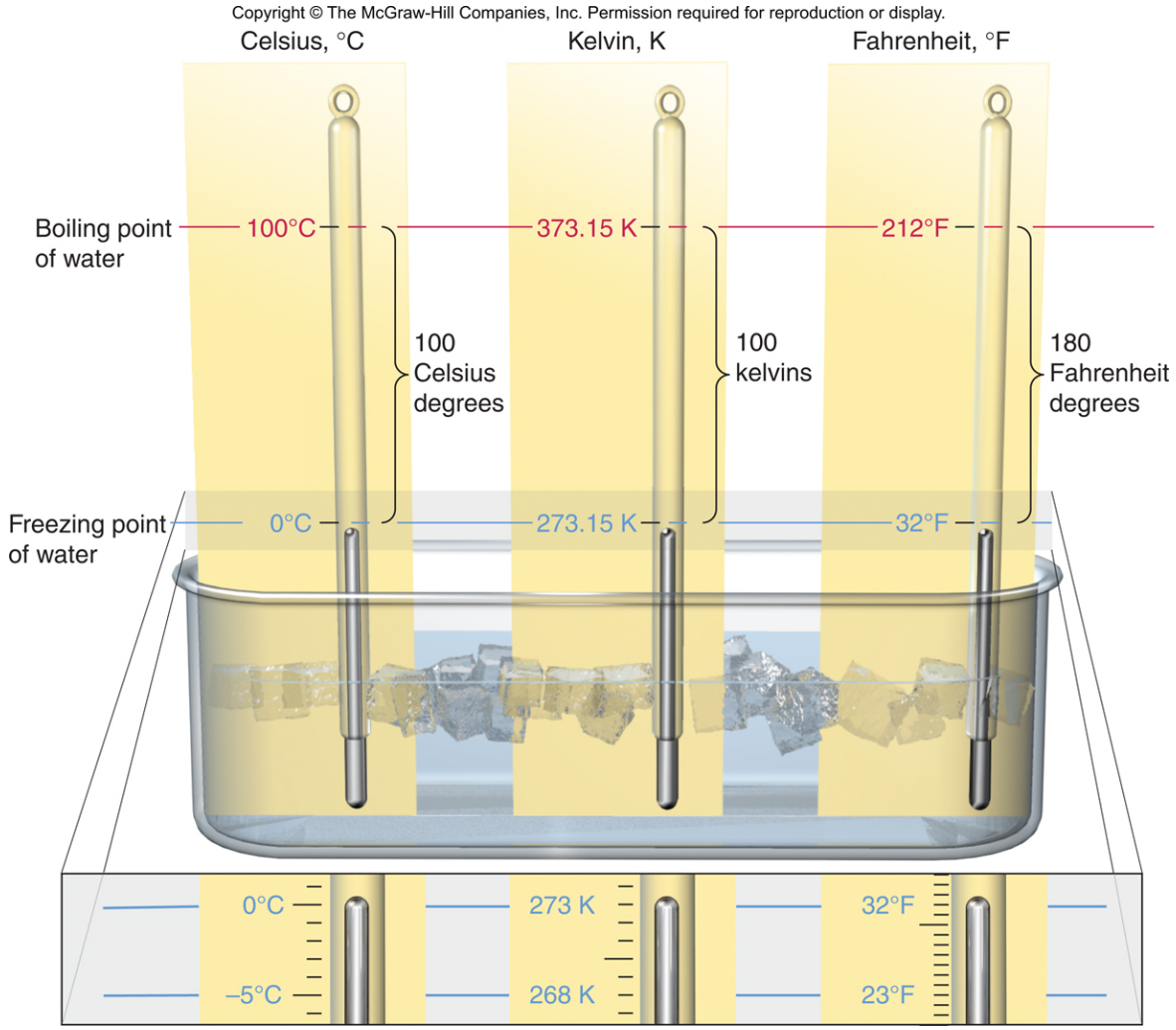

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Temperature Scales

Kelvin (K) - The “absolute temperature scale” begins at absolute zero and has only positive values. Note that the kelvin is not used with the degree sign (°).

Celsius (^{o}C) - The Celsius scale is based on the freezing and boiling points of water. This is the temperature scale used most commonly around the world. The Celsius and Kelvin scales use the **same size degree** although their starting points differ.

Fahrenheit (^{o}F) – The Fahrenheit scale is commonly used in the US. The Fahrenheit scale has a different degree size and different zero points than both the Celsius and Kelvin scales.

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Temperature Conversions

$$T\ (\text{in K}) = T\ (\text{in } ^{o}\text{C}) + 273.15$$
$$T\ (\text{in } ^{o}\text{C}) = T\ (\text{in K}) - 273.15$$

$$T\ (\text{in } ^{\circ}\text{F}) = \frac{9}{5}\ T\ (\text{in } ^{\circ}\text{C}) + 32$$

$$T\ (\text{in } ^{\circ}\text{C}) = [T\ (\text{in } ^{\circ}\text{F}) - 32]\frac{5}{9}$$

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Sample Problem 1.7 Converting Units of Temperature

PROBLEM: A child has a body temperature of 38.7°C, and normal body temperature is 98.6°F. Does the child have a fever? What is the child's temperature in kelvins?

PLAN: We have to convert °C to °F to find out if the child has a fever. We can then use the °C to Kelvin relationship to find the temperature in Kelvin.

SOLUTION:

Converting from °C to °F $\frac{9}{5}(38.7\ ^{\circ}C) + 32 =$ **101.7 °F**

Yes, the child has a fever.

Converting from °C to K 38.7 °C + 273.15 = **311.8 K**

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Significant Figures

Every measurement includes some ***uncertainty***. The ***rightmost*** digit of any quantity is always ***estimated***.

The recorded digits, both certain and uncertain, are called ***significant figures***.

The greater the number of significant figures in a quantity, the greater its certainty.

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Figure 1.7 The number of significant figures in a measurement.

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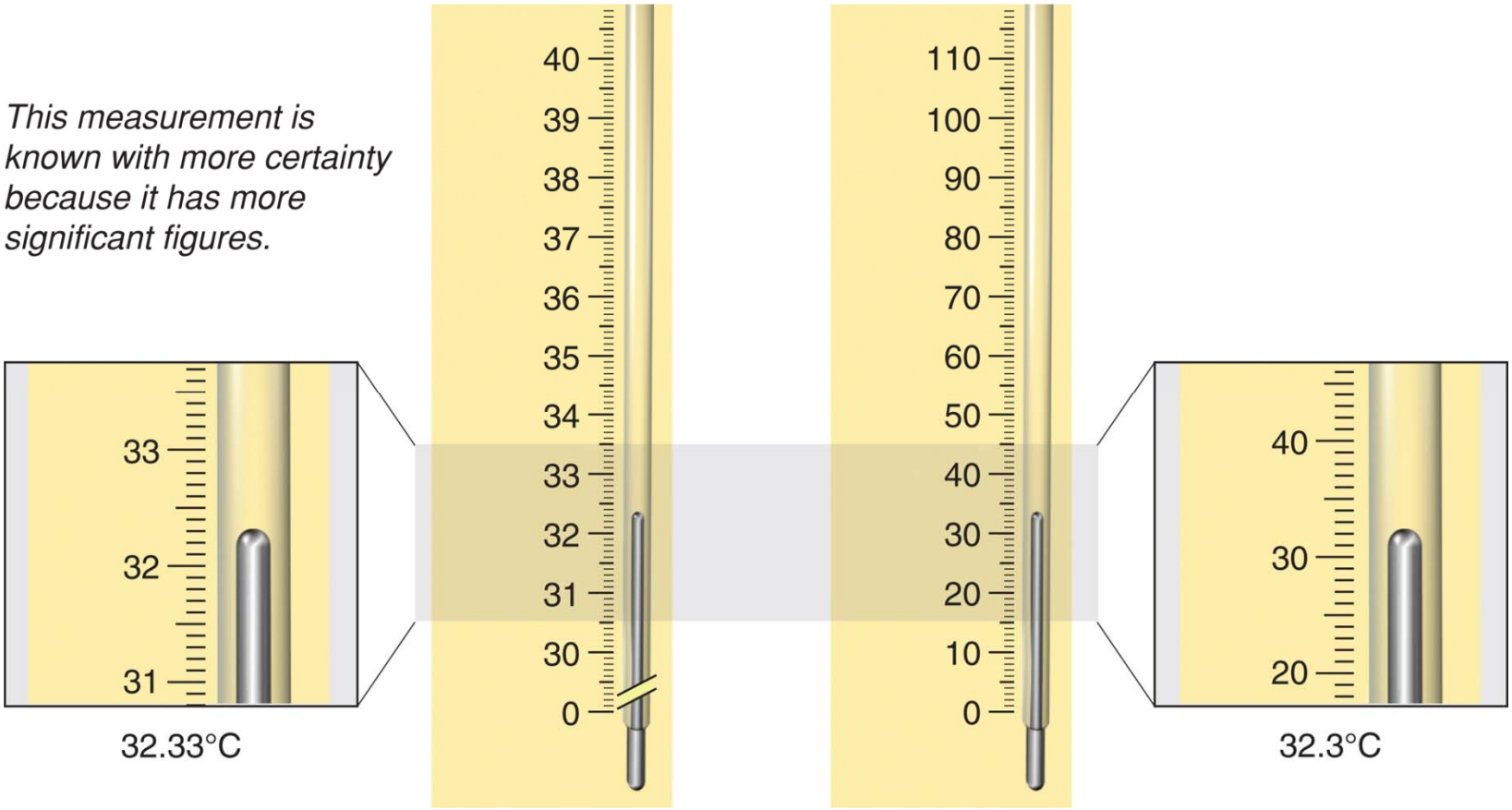

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Determining Which Digits are Significant

All digits are significant
- *except zeros that are used only to position the decimal point.*

- Make sure the measured quantity has a decimal point.
- Start at the left and move right until you reach the first nonzero digit.
- Count that digit and every digit to its right as significant.

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- Zeros that end a number are significant
  - whether they occur before or after the decimal point
  - as long as a decimal point is present.
- 1.030 mL has 4 significant figures.
- 5300. L has 4 significant figures.

- If no decimal point is present
  - zeros at the end of the number are **not** significant.
- 5300 L has only 2 significant figures.

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Sample Problem 1.8 Determining the Number of Significant Figures

PROBLEM: For each of the following quantities, underline the zeros that are significant figures (sf), and determine the number of significant figures in each quantity. For **(d)** to **(f),** express each in exponential notation first.

(a) 0.0030 L **(b)** 0.1044 g **(c)** 53,069 mL

(d) 0.00004715 m **(e)** 57,600. s **(f)** 0.0000007160 cm^3

PLAN: We determine the number of significant figures by counting digits, paying particular attention to the position of zeros in relation to the decimal point, and underline zeros that are significant.

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Sample Problem 1.8

SOLUTION:

(a) 0.0030 L has **2 sf** **(b)** 0.1044 g has **4 sf**

(c) 53,069 mL has **5 sf**

(d) 0.00004715 m = **4.715×10^{-5} m** has **4 sf**

(e) 57,600. s = **5.7600×10^{4} s** has **5 sf**

(f) 0.00000071600 cm^3 = **7.160×10^{-7} cm^3** has **4 sf**

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Rules for Significant Figures in Calculations

1. ***For multiplication and division***. The answer contains the same number of significant figures as there are in the measurement with the fewest significant figures.

Multiply the following numbers:

9.2 cm x 6.8 cm x 0.3744 cm = 23.4225 cm^3 = **23 cm^3**

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Rules for Significant Figures in Calculations

2. ***For addition and subtraction***. The answer has the *same number of decimal places as there are in the measurement with the fewest decimal places.*

Example: adding two volumes

$$\begin{array}{r} 83.5 \text{ mL} \\ +\ 23.28 \text{ mL} \\ \hline 106.78 \text{ mL} \end{array} = \mathbf{106.8}\ \text{mL}$$

Example: subtracting two volumes

$$\begin{array}{r} 865.9 \text{ mL} \\ -\ \ 2.8121 \text{ mL} \\ \hline 863.0879 \text{ mL} \end{array} = \mathbf{863.1}\ \text{mL}$$

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Rules for Rounding Off Numbers

1. If the digit removed is ***more than 5***, the preceding number increases by 1.
5.379 rounds to 5.38 if 3 significant figures are retained.

2. If the digit removed is ***less than 5***, the preceding number is unchanged.
0.2413 rounds to 0.241 if 3 significant figures are retained.

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3. If the digit removed ***is 5 followed by zeros or with no following digits***, the preceding number increases by 1 if it is odd and remains unchanged if it is even.
17.75 rounds to 17.8, but 17.65 rounds to 17.6.

If the ***5 is followed by other nonzero digits***, rule 1 is followed:

17.6500 rounds to 17.6, but 17.6513 rounds to 17.7

4. Be sure to carry two or more additional significant figures through a multistep calculation and round off the ***final*** answer ***only***.

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Exact Numbers

Exact numbers have no uncertainty associated with them.

Numbers may be exact by definition:
1000 mg = 1 g
60 min = 1 hr
2.54 cm = 1 in

Numbers may be exact by count:
exactly 26 letters in the alphabet

Exact numbers do not limit the number of significant digits in a calculation.

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Sample Problem 1.9 Significant Figures and Rounding

PROBLEM: Perform the following calculations and round each answer to the correct number of significant figures:

(a) $$\frac{16.3521\ \text{cm}^2 - 1.448\ \text{cm}^2}{7.085\ \text{cm}}$$

(b) $$\frac{4.80\times10^4\ \text{mg}\left(\frac{1\ \text{g}}{1000\ \text{mg}}\right)}{11.55\ \text{cm}^3}$$

PLAN: We use the rules for rounding presented in the text: **(a)** We subtract before we divide. **(b)** We note that the unit conversion involves an exact number.

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Sample Problem 1.9

SOLUTION:

(a) $$\frac{16.3521\ cm^2 - 1.448\ cm^2}{7.085\ cm} = \frac{14.904\ cm^{\cancel{2}}}{7.085\ \cancel{cm}}$$ **= 2.104 cm**

(b) $$\frac{4.80 \times 10^4\ \cancel{mg}\left(\frac{1\ g}{1000\ \cancel{mg}}\right)}{11.55\ cm^3} = \frac{48.0\ g}{11.55\ cm^3}$$ **= 4.16 g/ cm³**

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Precision, Accuracy, and Error

Precision refers to how close the measurements in a series are to each other.

Accuracy refers to how close each measurement is to the actual value.

Systematic error produces values that are either ***all*** higher or ***all*** lower than the actual value.

This error is part of the experimental system.

Random error produces values that are both higher and lower than the actual value.

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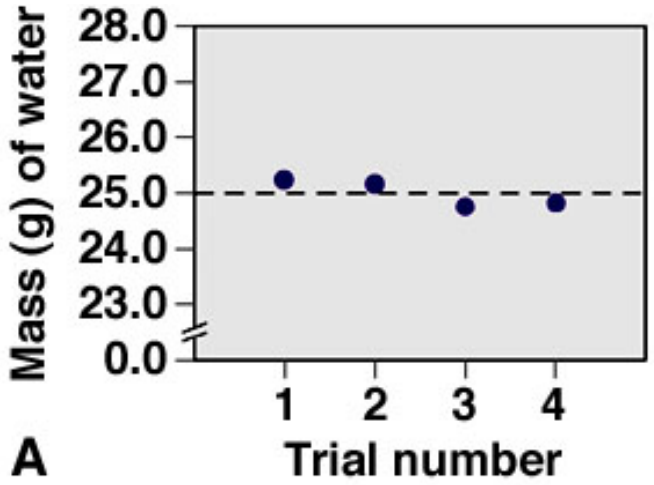
Figure 1.9 Precision and accuracy in a laboratory calibration.



precise and accurate

precise but not accurate

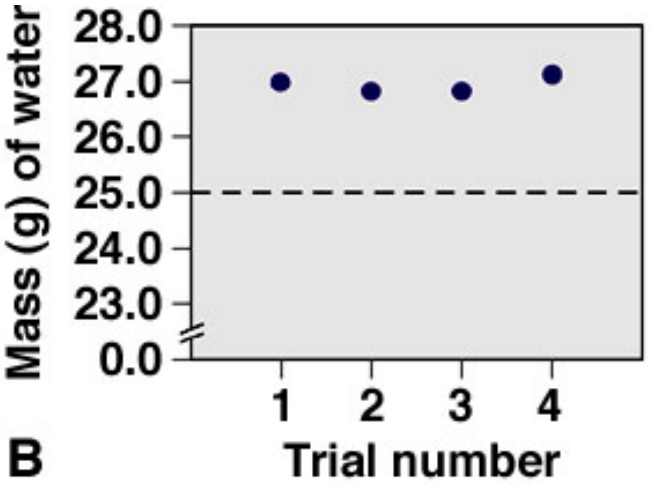


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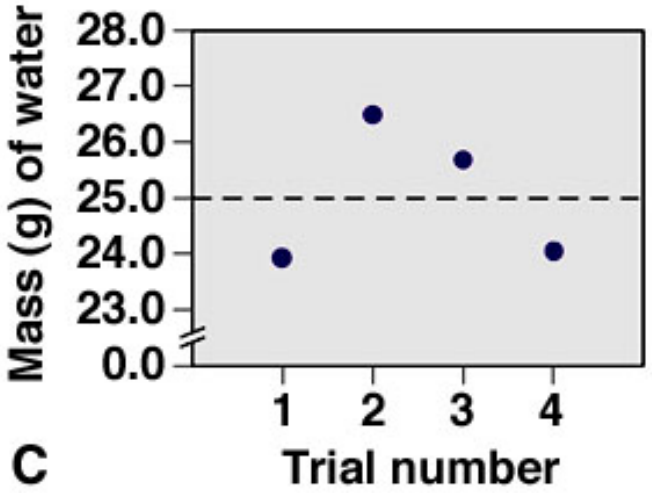
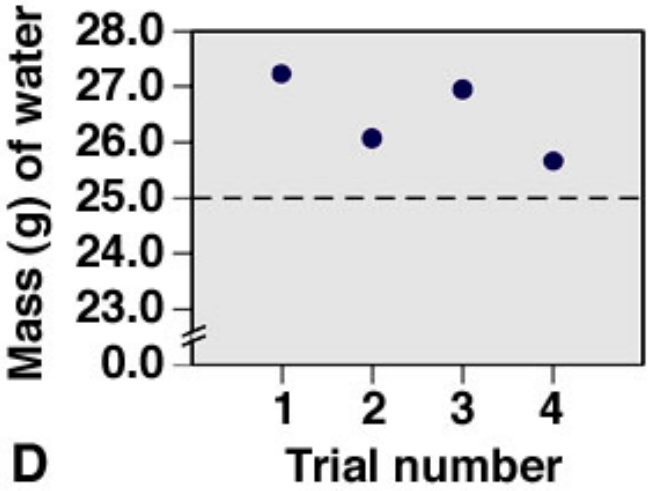
Figure 1.9 continued **Precision and accuracy in the laboratory.**



random error

systematic error



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Chapter 2

The Periodic Table and Some Properties of the Elements

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Chapter 2: The Components of Matter

2.1 Elements, Compounds, and Mixtures: An Atomic Overview

2.2 The Observations That Led to an Atomic View of Matter

2.3 Dalton's Atomic Theory

2.4 The Observations That Led to the Nuclear Atom Model

2.5 The Atomic Theory Today

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Chapter 2: The Components of Matter

2.6 Elements: A First Look at the Periodic Table

2.7 Compounds: Introduction to Bonding

2.8 Formulas, Names, and Masses of Compounds

2.9 Classification of Mixtures

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Definitions for Components of Matter

Element - the simplest type of substance with unique physical and chemical properties. *An element consists of only one type of atom.* It cannot be broken down into any simpler substances by physical or chemical means. Cu, Ag, N_2, O_2,

Molecule - a structure that consists of two or more atoms that are chemically bound together and thus behaves as an independent unit.

A Atoms of an element

B Molecules of an element

Figure 2.1

H_2O, O_3 , CO_2, NH_3, O_2

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Definitions for Components of Matter

Compound - a substance composed of two or more elements which are chemically combined.

NH_3 14 g N with 3 g H

C Molecules of a compound

Figure 2.1

D Mixture of two elements and a compound

Mixture - a group of two or more elements and/or compounds that are physically intermingled.

H_2O + NaCl

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Mixtures

A ***heterogeneous mixture*** has one or more visible boundaries between the components.

A ***homogeneous mixture*** has no visible boundaries because the components are mixed as individual atoms, ions, and molecules.

A homogeneous mixture is also called a ***solution***. Solutions in water are called ***aqueous solutions***.

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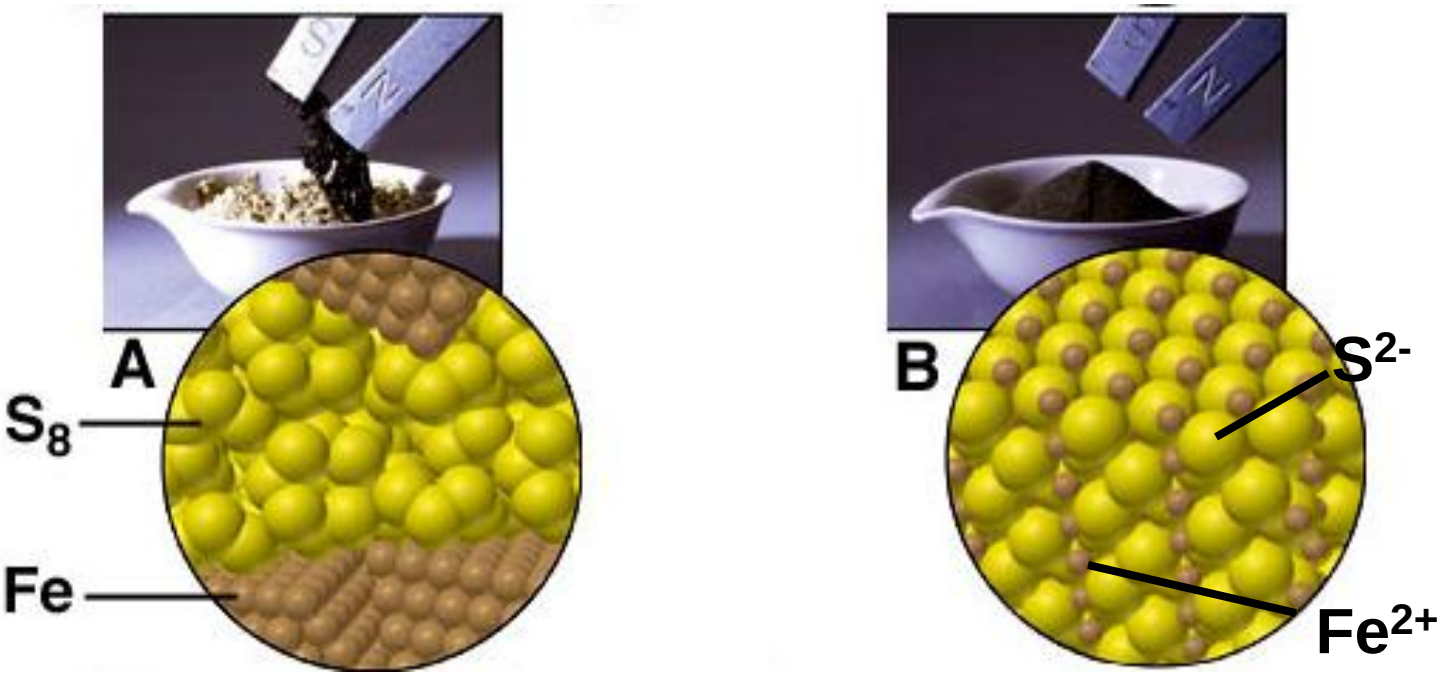
Figure 2.17 The distinction between mixtures and compounds.



A physical mixture of Fe and S_8 can be separated using a magnet.

Fe and S have reacted chemically to form the compound FeS. The elements cannot be separated by physical means.

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Table 2.1 Some Properties of Sodium, Chlorine, and Sodium Chloride

Property	Sodium +	Chlorine →	Sodium Chloride
Melting point	97.8°C	-101°C	801°C
Boiling point	881.4°C	-34°C	1413°C
Color	Silvery	Yellow-green	Colorless (white)
Density	0.97 g/cm^3	0.0032 g/cm^3	2.16 g/cm^3
Behavior in water	Reacts	Dissolves slightly	Dissolves freely

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Sample Problem 2.1 Distinguishing Elements, Compounds, and Mixtures at the Atomic Scale

PROBLEM: The following scenes represent an atomic-scale view of three samples of matter. Describe each sample as an element, compound, or mixture.

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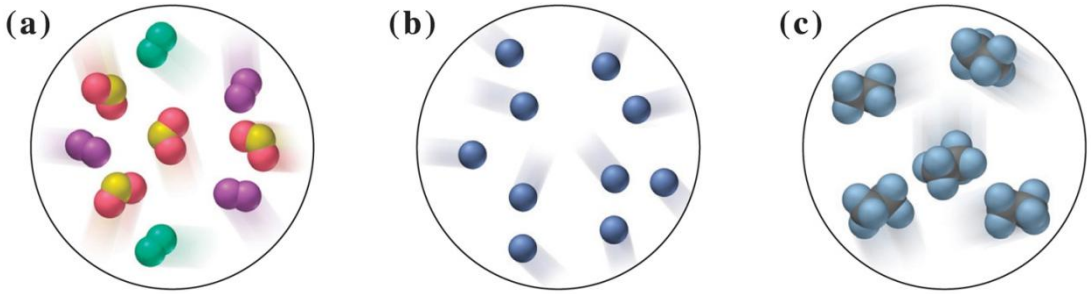

PLAN: A sample that contains only one type of particle is either an element or a compound. The particles of an element consist of only one type of atom whereas the particles of a compound have two or more types of atom bonded together.

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Sample Problem 2.1

SOLUTION:

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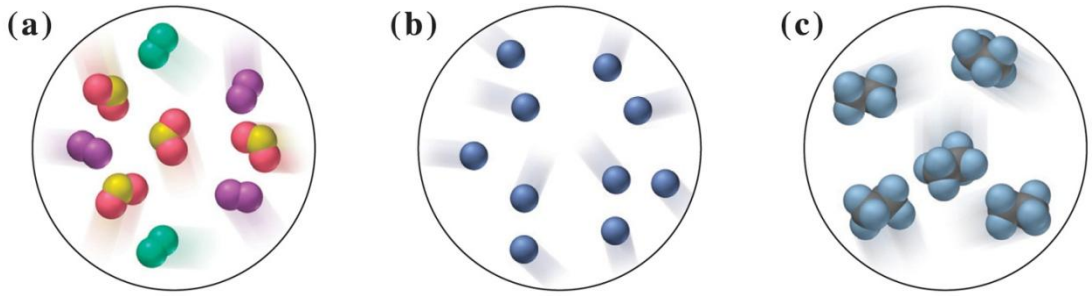

Sample (a) contains three different types of particles and is therefore a **mixture**.

Sample (b) contains only one type of particle and each particle has only one atom. This is an **element**.

Sample (c) contains only one type of particle, each of which contains two different types of atoms. This is a **compound**.

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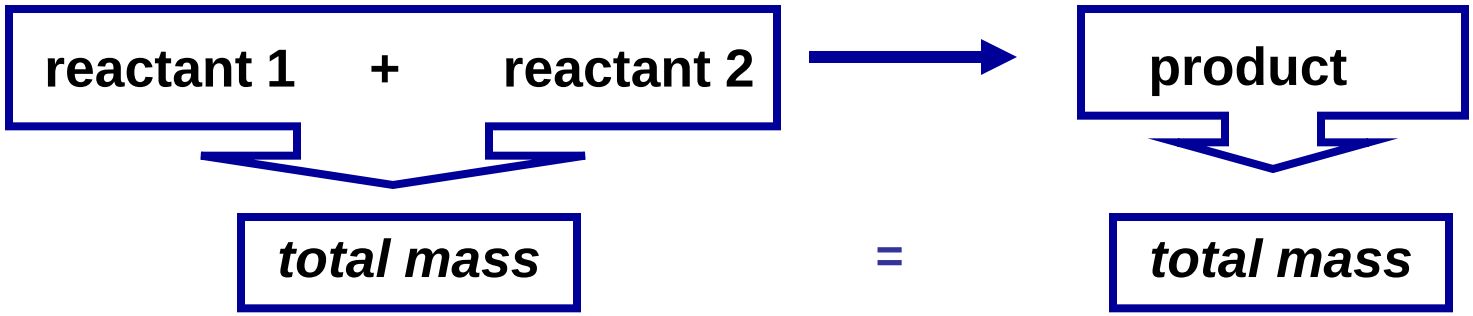
Law of Mass Conservation

The total mass of substances present does not change during a chemical reaction.



calcium oxide + carbon dioxide → calcium carbonate

$CaO + CO_2 \rightarrow CaCO_3$

56.08 g + 44.00 g → 100.08 g

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Law of Definite (or Constant) Composition

No matter the source, a particular compound is composed of the same elements in the same parts (fractions) by mass.

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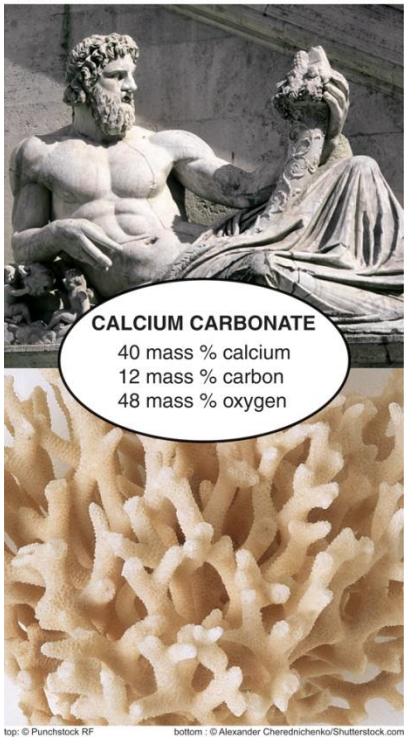

Figure 2.2

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Calcium carbonate

Analysis by Mass (grams/20.0 g)	Mass Fraction (parts/1.00 part)	Percent by Mass (parts/100 parts)
8.0 g calcium	0.40 calcium	40% calcium
2.4 g carbon	0.12 carbon	12% carbon
9.6 g oxygen	0.48 oxygen	48% oxygen
20.0 g	1.00 part by mass	100% by mass

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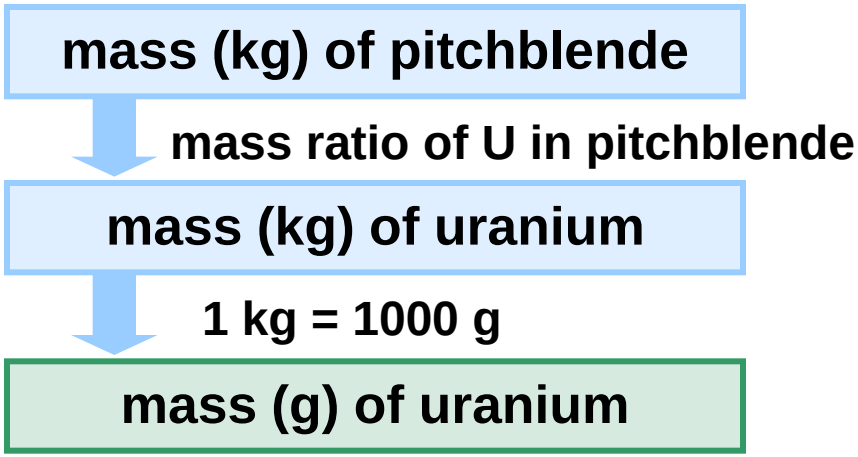
Sample Problem 2.2

Calculating the Mass of an Element in a Compound

PROBLEM: Analysis of 84.2 g of the uranium containing compound pitchblende shows it is composed of 71.4 g of uranium, with oxygen as the only other element. How many grams of uranium can be obtained from 102 kg of pitchblende?

PLAN: The mass ratio of uranium/pitchblende is the same no matter the source. We can use the ratio to find the answer.



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Sample Problem 2.2

SOLUTION:

mass (kg) of uranium =

$$\text{mass (kg) pitchblende} \times \frac{\text{mass (kg) uranium in pitchblende}}{\text{mass (kg) pitchblende}}$$

$$= 102 \text{ ~~kg pitchblende~~} \times \frac{71.4 \text{ kg uranium}}{84.2 \text{ ~~kg pitchblende~~}} = 86.5 \text{ kg uranium}$$

$$86.5 \text{ ~~kg~~ uranium} \times \frac{1000 \text{ g}}{1 \text{ ~~kg~~}}$$

= 8.65 x 10^4 g uranium

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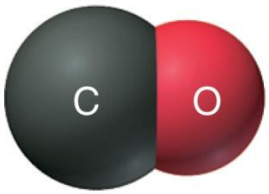
Law of Multiple Proportions

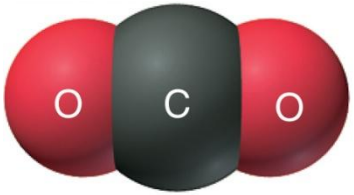
If elements A and B react to form two compounds, the different masses of B that combine with a fixed mass of A can be expressed as a ratio of small whole numbers.

Example: Carbon Oxides A & B

Carbon Oxide I : 57.1% oxygen and 42.9% carbon



Carbon oxide I
(carbon monoxide)



Carbon oxide II
(carbon dioxide)

Carbon Oxide II : 72.7% oxygen and 27.3% carbon

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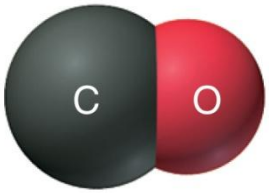
Assume that you have 100 g of each compound.

In 100 g of each compound:

g O = 57.1 g for oxide I & 72.7 g for oxide II

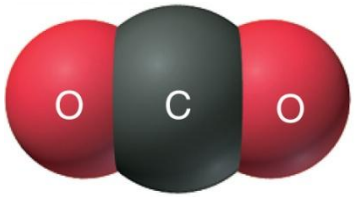
g C = 42.9 g for oxide I & 27.3 g for oxide II

For oxide I: $$\frac{\text{g O}}{\text{g C}} = \frac{57.1}{42.9} = 1.33$$



Carbon oxide I
(carbon monoxide)

For oxide II: $$\frac{\text{g O}}{\text{g C}} = \frac{72.7}{27.3} = 2.66$$



Carbon oxide II
(carbon dioxide)

$$\frac{\text{2.66 g O/g C in II}}{\text{1.33 g O/g C in I}} = \frac{2}{1}$$

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Dalton's Atomic Theory

Dalton postulated that:

1. All matter consists of ***atoms***; tiny indivisible particles of an element that cannot be created or destroyed.
2. Atoms of one element ***cannot*** be converted into atoms of another element.
3. Atoms of an element are ***identical*** in mass and other properties and are different from the atoms of any other element.
4. Compounds result from the chemical combination of a ***specific ratio*** of atoms of different elements.

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Dalton's Atomic Theory

explains the mass laws

Mass conservation

Atoms cannot be created or destroyed ***postulate 1***

or converted into other types of atoms. ***postulate 2***

Since every atom has a fixed mass, ***postulate 3***

during a chemical reaction the same atoms are present but in different combinations; therefore there is no mass change overall.

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Dalton's Atomic Theory

explains the mass laws

Definite composition

Atoms are combined in compounds in specific ratios ***postulate 4***

and each atom has a specific mass. ***postulate 3***

Each element constitutes a fixed fraction of the total mass in a compound.

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Dalton's Atomic Theory

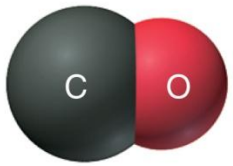
explains the mass laws

Multiple proportions

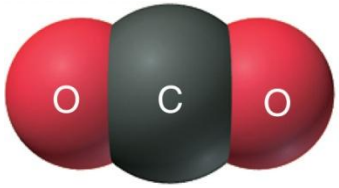
Atoms of an element have the same mass ***postulate 3***

and atoms are indivisible. ***postulate 1***

When different numbers of atoms of elements combine, they must do so in ratios of small, whole numbers.



Carbon oxide I
(carbon monoxide)



Carbon oxide II
(carbon dioxide)

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Sample Problem 2.3 Visualizing the Mass Laws

PROBLEM: The following scene represents an atomic-scale view of a chemical reaction. Which of the mass laws (mass conservation, definite composition, or multiple proportions) is (are) illustrated?

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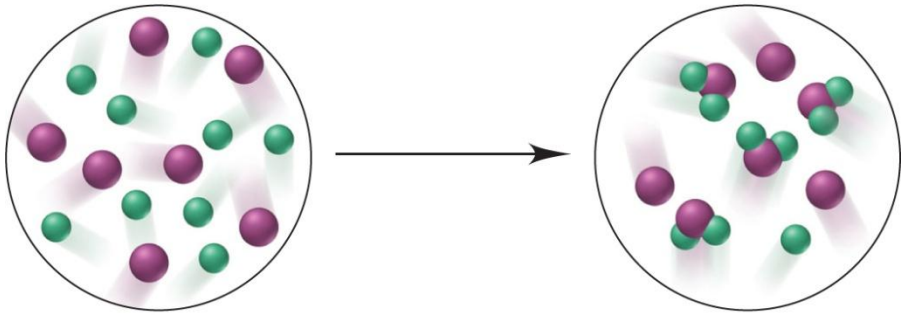

PLAN: Note the numbers, types and combination of atoms before and after the reaction.

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Sample Problem 2.3

SOLUTION:

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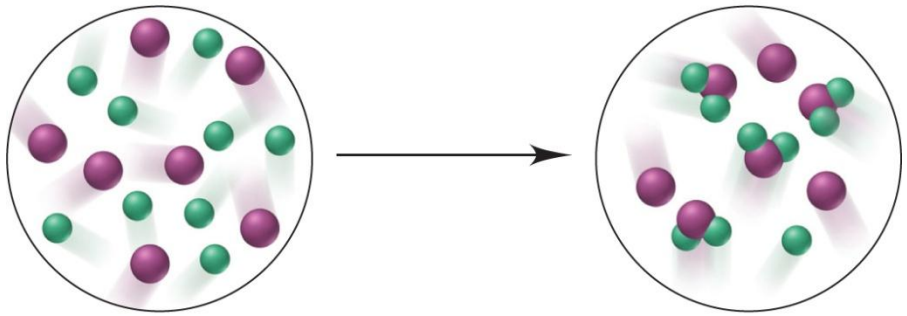

There are 7 purple and 9 green atoms both before and after the reaction. Mass is therefore conserved.

After the reaction some purple atoms remain unreacted, but some have combined with green atoms to form a compound. Each particle of this compound contains 1 purple and 2 green atoms – the composition is constant, illustrating the law of definite composition.

The ratio of the elements in the compound is a small, whole number. The ratio of their masses will also be a small, whole number. This illustrates the law of multiple proportions.

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Figure 2.3

Observations that established the properties of cathode rays.

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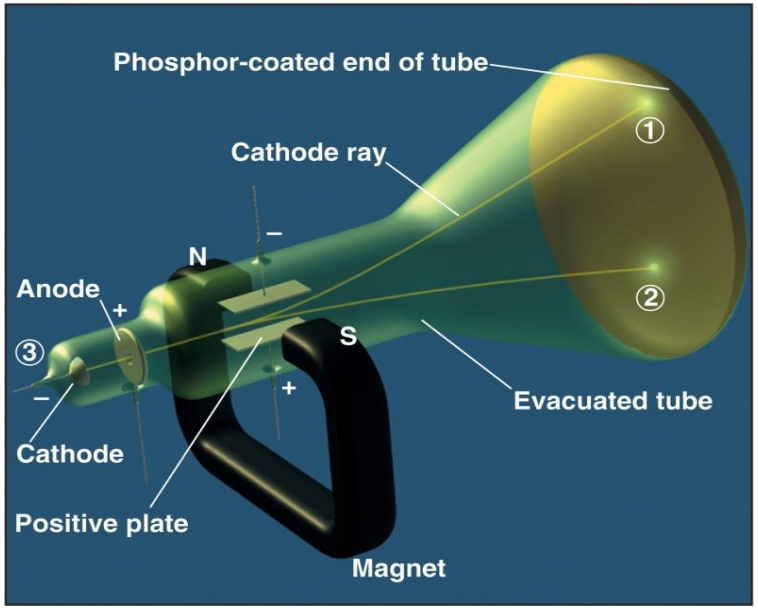

J. J Thomson, (1897) was able to measure the electron (Mass/charge) ratio = -5.686×10^{-12} Kg/C

Note: Dalton atoms are not divisible??

Observation	Conclusion
Ray bends in magnetic field.	Ray consists of charged particles.
Ray bends toward positive plate in electric field.	Ray consists of negative particles.
Ray is identical for any cathode.	These particles are found in ALL matter.

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Figure 2.4 Millikan's oil-drop experiment for measuring an electron's charge. (1909)

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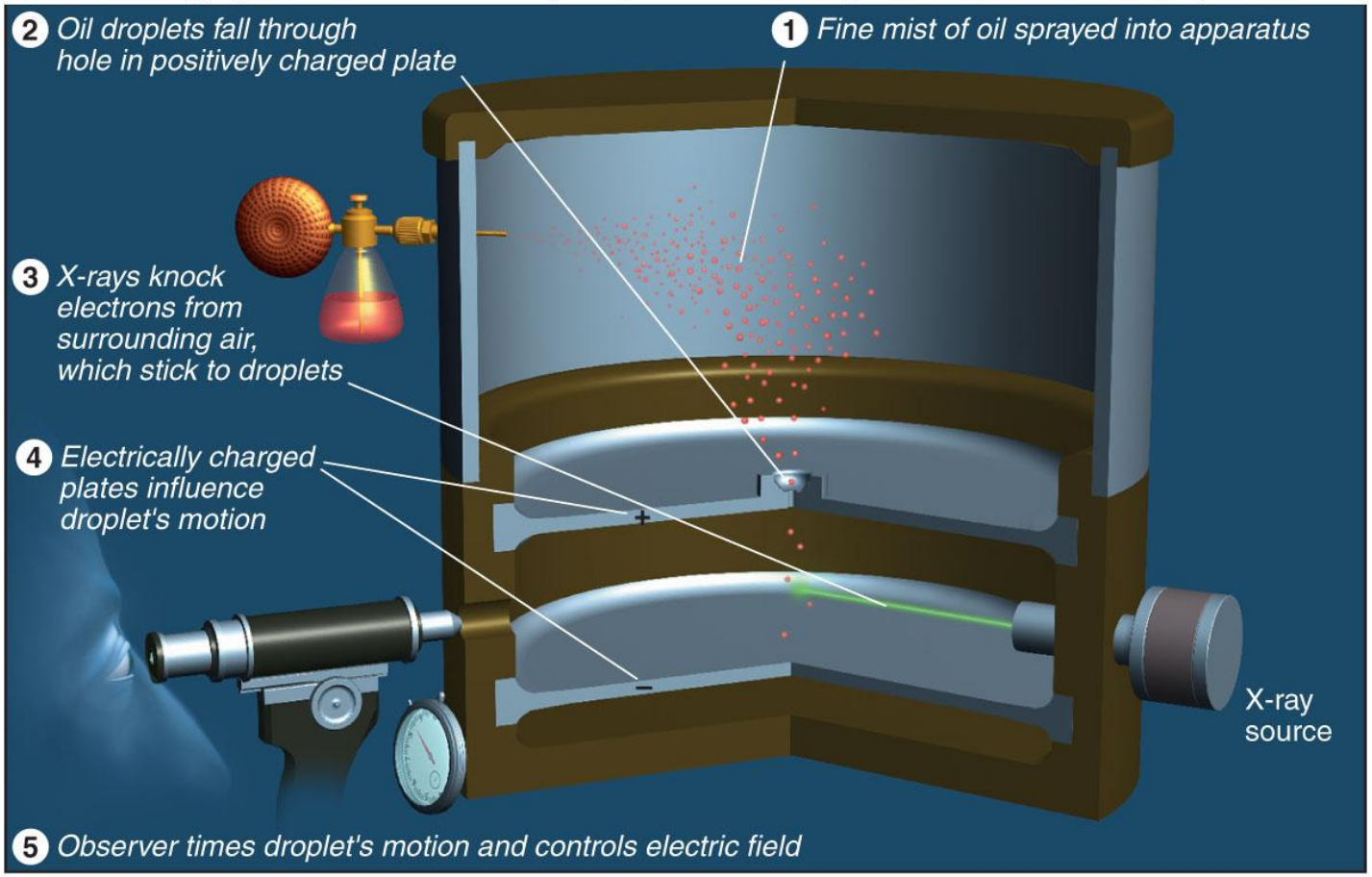

Electron charge = -1.60218×10^{-19} C (coulomb)

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Millikan's findings were used to calculate the mass of an electron.

determined by J.J. Thomson and others

$$\text{mass of electron} = \frac{\text{mass}}{\text{charge}} \times \text{charge}$$

$$= (-5.686 \times 10^{-12}\ \text{kg/}\cancel{\text{C}}) \times (-1.602 \times 10^{-19}\ \cancel{\text{C}})$$

$$= 9.109 \times 10^{-31}\ \text{kg} = 9.109 \times 10^{-28}\ \text{g}$$

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Figure 2.5 Rutherford's α-scattering experiment and discovery of the atomic nucleus. (1910)

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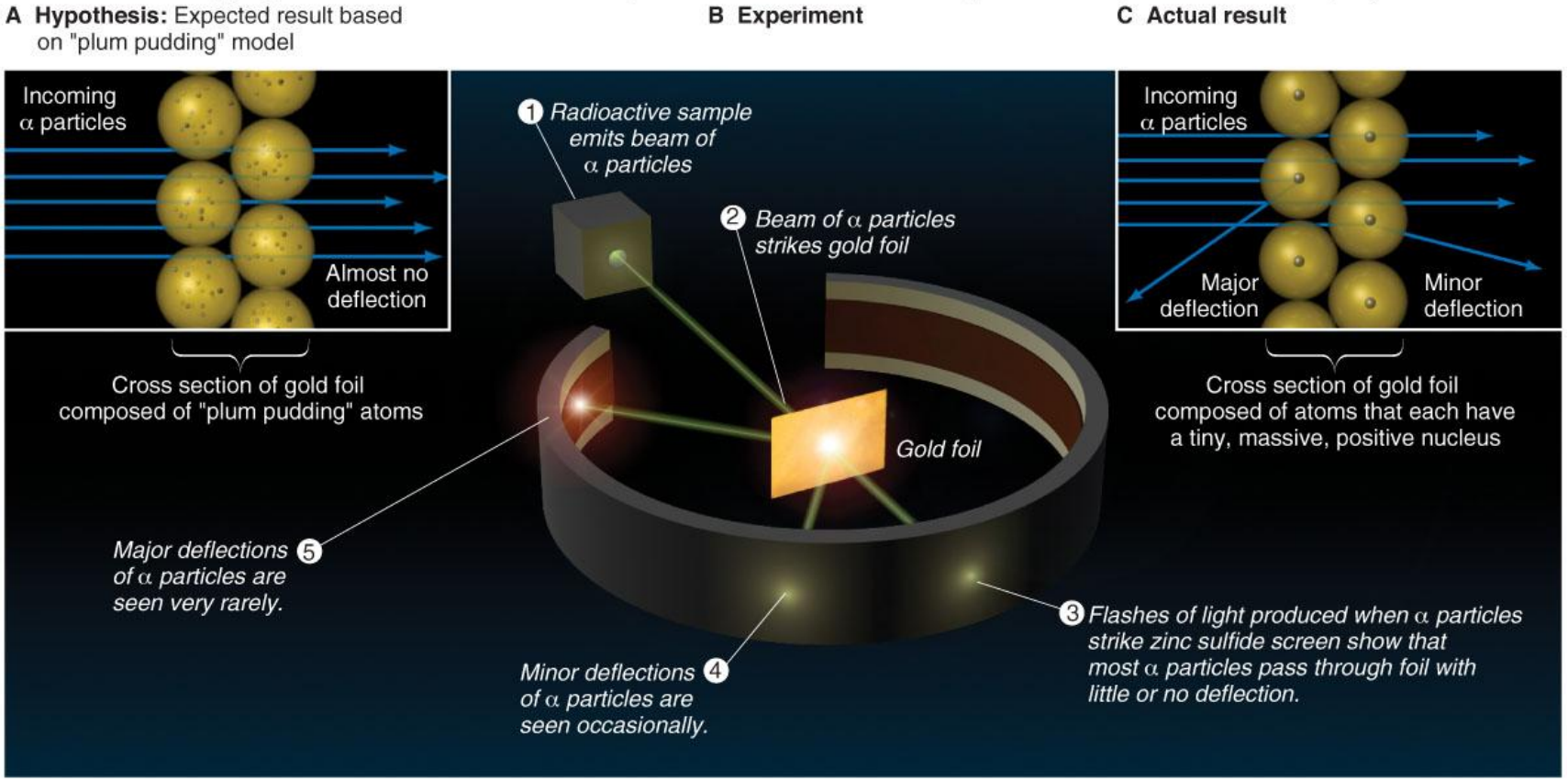

Rutherford: Atoms are empty space occupied by electrons, but in the center a tiny region he called nucleus contains all the positive particles and called them protons.

In 1932 James Chadwick discovered the Neutrons.

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Figure 2.6 General features of the atom.

The atom is an electrically neutral, spherical entity composed of a positively charged central nucleus surrounded by one or more negatively charged electrons.

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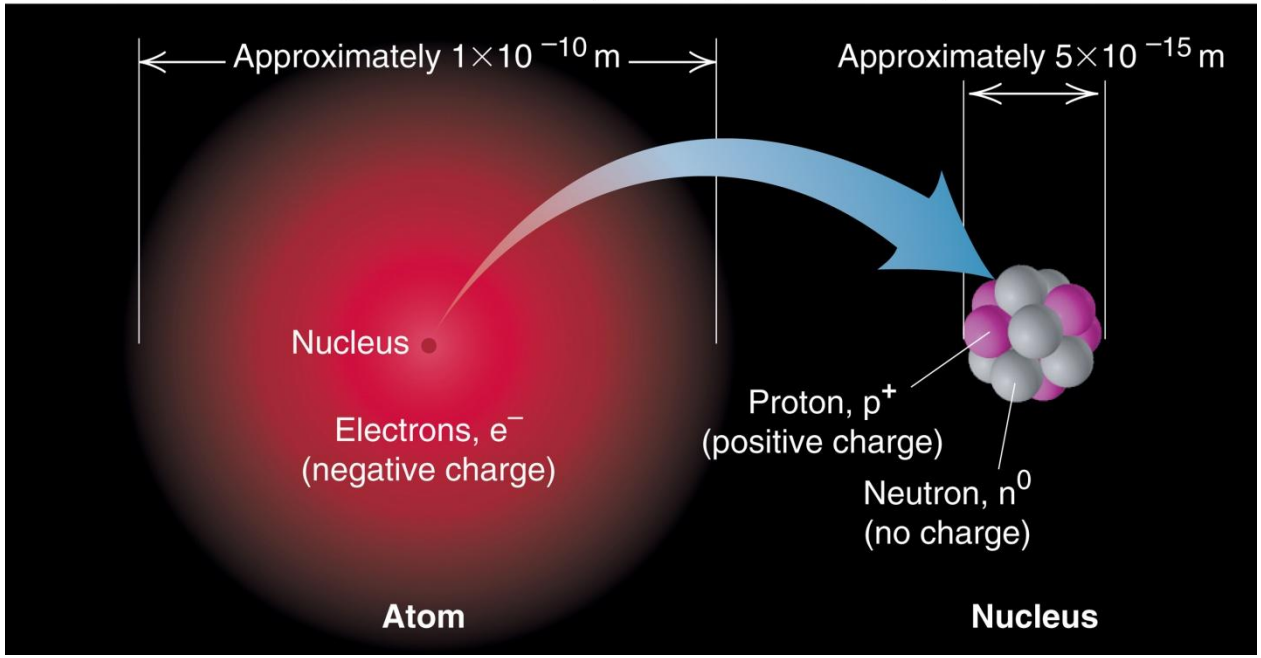

The atomic nucleus consists of protons and neutrons.

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Table 2.2 Properties of the Three Key Subatomic Properties

Name (Symbol)	Charge		Mass		Location in Atom
	Relative	Absolute (C)*	Relative (amu)†	Absolute (g)	
Proton (p^+)	1+	$+1.60218 \times 10^{-19}$	1.00727	1.67262×10^{-24}	Nucleus
Neutron (n^0)	0	0	1.00866	1.67493×10^{-24}	Nucleus
Electron (e^-)	1-	-1.60218×10^{-19}	0.00054858	9.10939×10^{-28}	Outside nucleus

* The coulomb (C) is the SI unit of charge.

† The atomic mass unit (amu) equals 1.66054×10^{-24} g.

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Atomic Number, Mass Number, and Atomic Symbol

Figure 2.7

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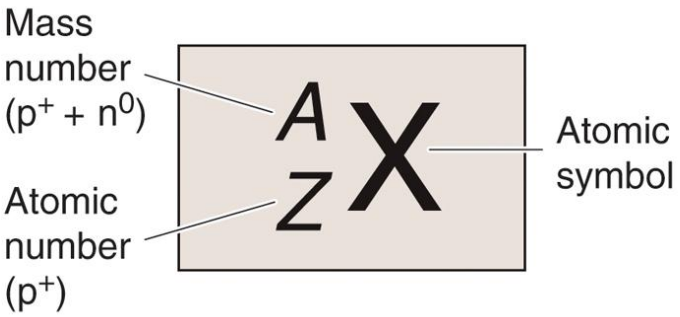


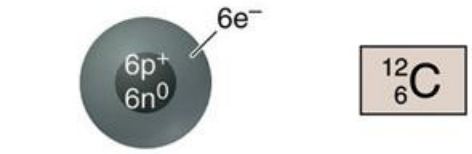
X = Atomic symbol of the element

***A* =** mass number; $A = Z + N$

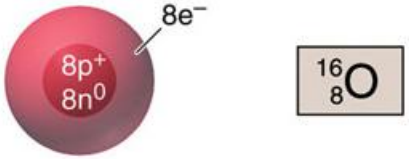
***Z* =** atomic number

(the number of protons in the nucleus)

***N* =** number of neutrons in the nucleus



An atom of carbon-12



An atom of oxygen-16

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Isotopes

Isotopes are atoms of an element with the same number of ***protons***, but a different number of ***neutrons***.

Isotopes have the same atomic number, but a different mass number.

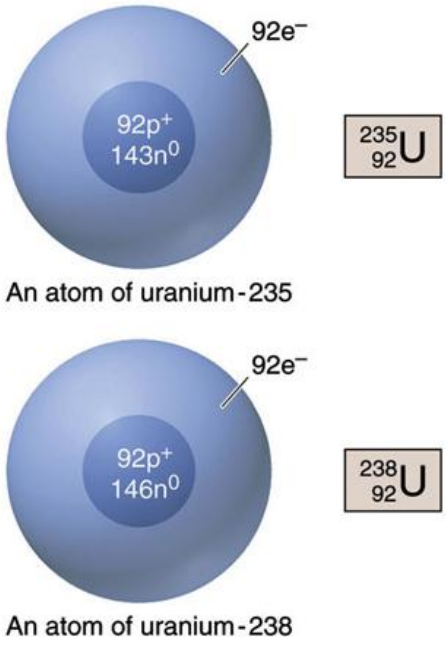

Figure 2.7

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Sample Problem 2.4

Determining the Number of Subatomic Particles in the Isotopes of an Element

PROBLEM: Silicon (Si) has three naturally occurring isotopes: ^{28}Si, ^{29}Si, and ^{30}Si. Determine the number of protons, neutrons, and electrons in each silicon isotope.

PLAN: The mass number (A) is given for each isotope and is equal to the number of protons + neutrons. The atomic number *Z*, found on the periodic table, equals the number of protons. The number of neutrons = $A - Z$, and the number of electrons equals the number of protons for a neutral atom.

SOLUTION: The atomic number of silicon is 14; therefore

^{28}Si has 14p$^+$, 14e$^-$ and 14n^0 (28-14)

^{29}Si has 14p$^+$, 14e$^-$ and 15n^0 (29-14)

^{30}Si has 14p$^+$, 14e$^-$ and 16n^0 (30-14)

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The Mass Spectrometer and Its Data

Mass Spectrometer measures the mass ratio and mass to charge ratio

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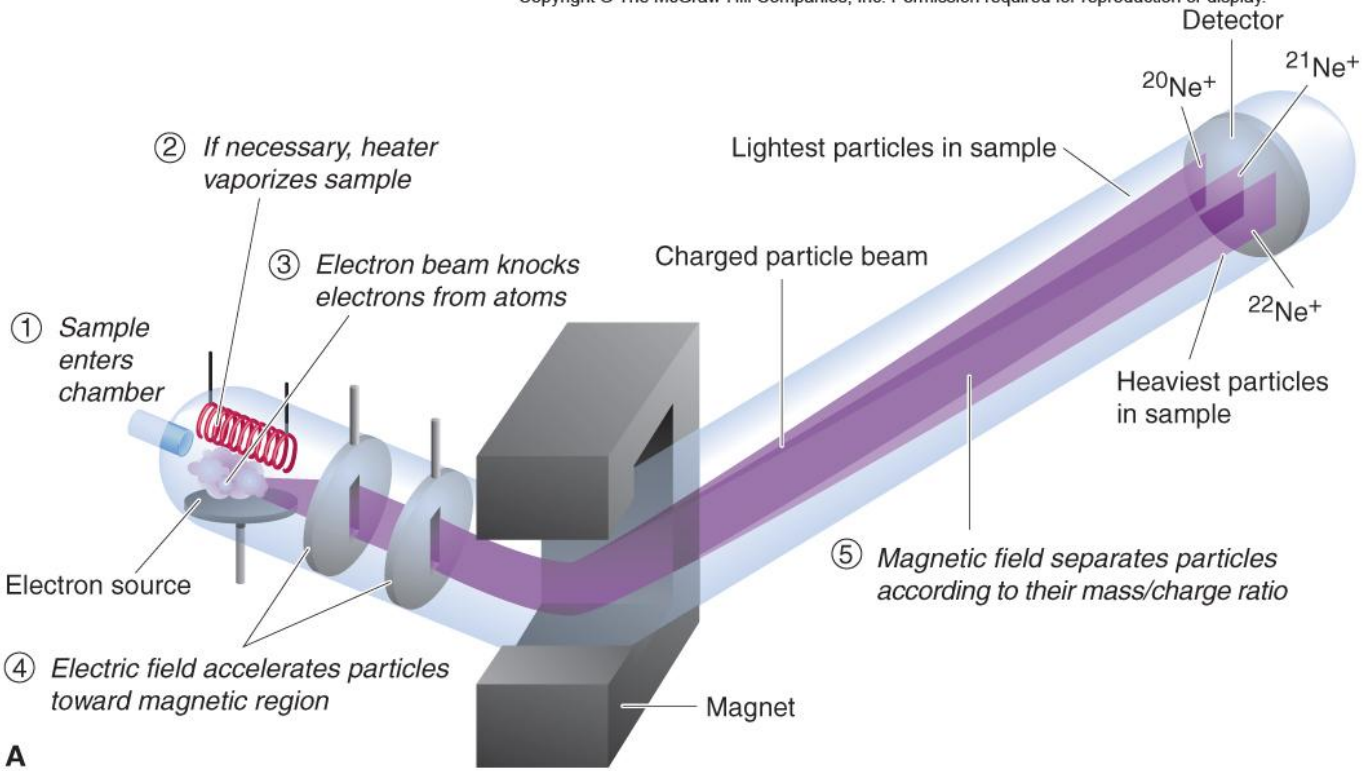

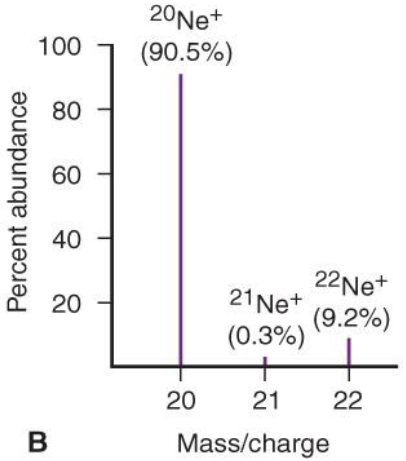

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Atomic Symbol

C Carbon **Na (Natrium) Sodium**

Note: The chemical properties of an element are determined by the number of electrons or number of protons. So having Isotopes of an element will not change its chemical properties **much**.

Mass of an atom

Atomic mass unit (amu) or Dalton (Da)

Today (u) only

$$\text{amu} = \frac{1}{12} \text{ mass of } {}^{12}C$$

So ^{12}C has a mass of 12 u

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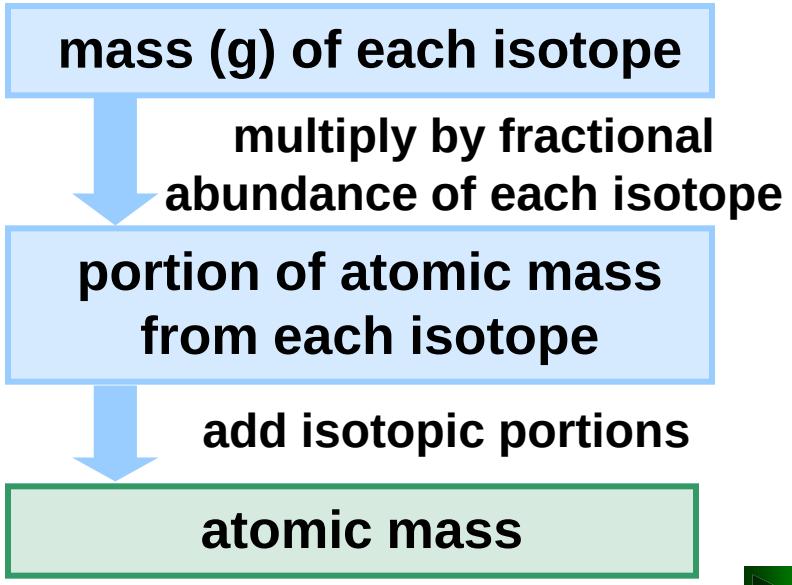
Sample Problem 2.5 Calculating the Atomic Mass of an Element

PROBLEM: Silver (Ag, Z = 47) has two naturally occurring isotopes, ^{107}Ag and ^{109}Ag. From the mass spectrometric data provided, calculate the atomic mass of Ag.

Isotope	Mass (amu)	Abundance (%)
^{107}Ag	106.90509	51.84
^{109}Ag	108.90476	48.16

PLAN: Find the weighted average of the isotopic masses.



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Sample Problem 2.5

SOLUTION:

mass portion from ^{107}Ag =

106.90509 amu x 0.5184 = 55.42 amu

mass portion from ^{109}Ag =

108.90476amu x 0.4816 = 52.45amu

atomic mass of Ag = 55.42amu + 52.45amu

= 107.87amu

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ELEMENTS: A FIRST LOOK AT THE PERIODIC TABLE.

1870 **65** elements were known

Today more than 116 elements

Dmitri Mendeleev and Meyer discovered the periodic table separately in 1869

Dmitri Mendeleev organized elements, he listed the elements by increasing atomic mass.

			Ti = 50	Zr = 90	? = 180		
			V = 51	Nb = 94	Ta = 182		
			Cr = 52	Mo = 96	W = 186		
			Mn = 55	Rh = 104,4	Pt = 197,4		
			Fe = 56	Ru = 104,4	Ir = 198		
			Ni = Co = 59	Pd = 106,6	Os = 199		
H = 1			Cu = 63,4	Ag = 108	Hg = 200		
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112			
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?		
	C = 12	Si = 28	? = 70	Sn = 118			
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?		
	O = 16	S = 32	Se = 79,4	Te = 128?			
	F = 19	Cl = 35,5	Br = 80	J = 127			
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204		
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207		
		? = 45	Ce = 92				
		?Er = 56	La = 94				
		?Yt = 60	Di = 95				
		?In = 75,6	Th = 118?				

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Figure 2.9 The modern periodic table.

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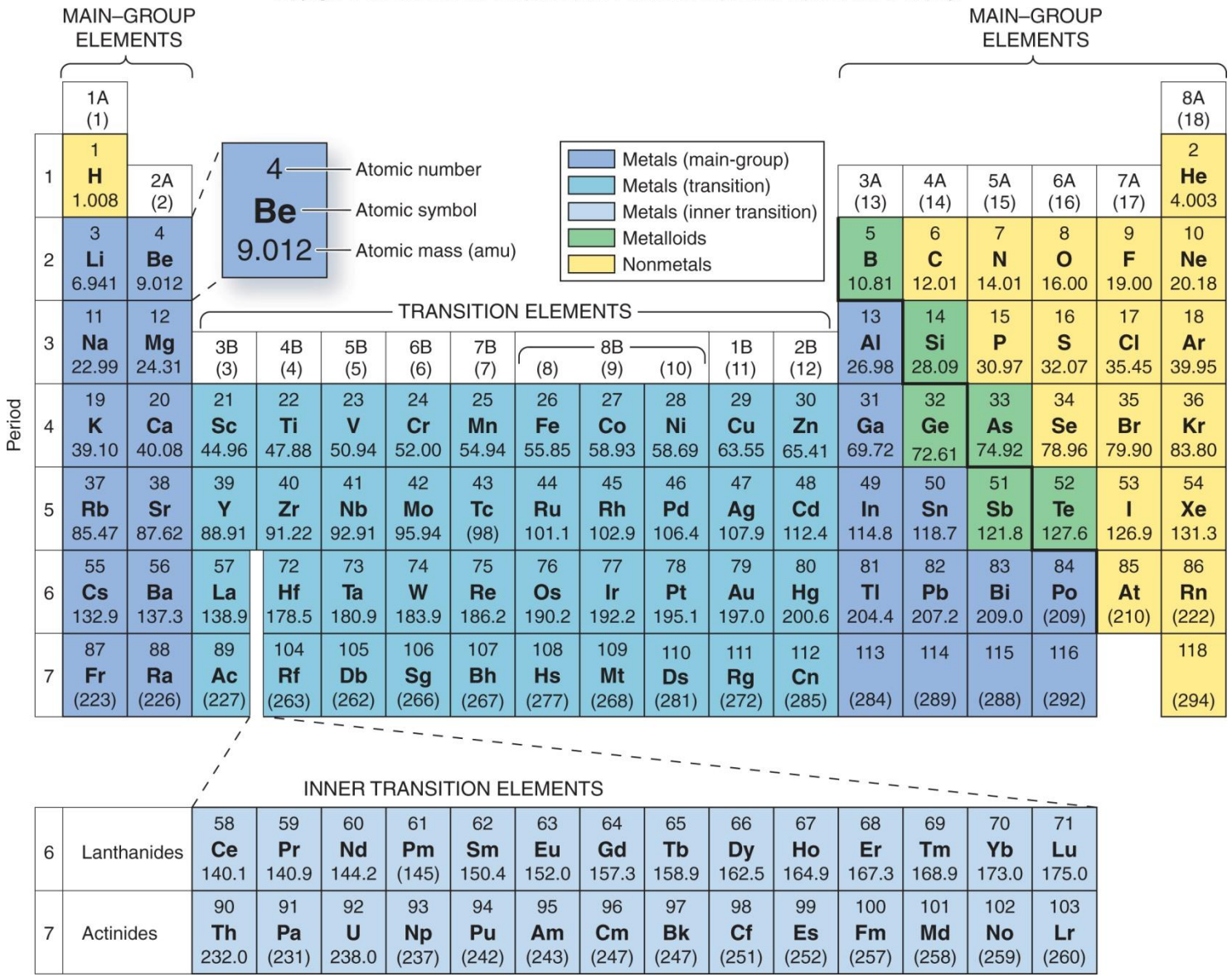

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Figure 2.10

The formation of an ionic compound.

Transferring electrons from the atoms of one element to those of another results in an ionic compound.

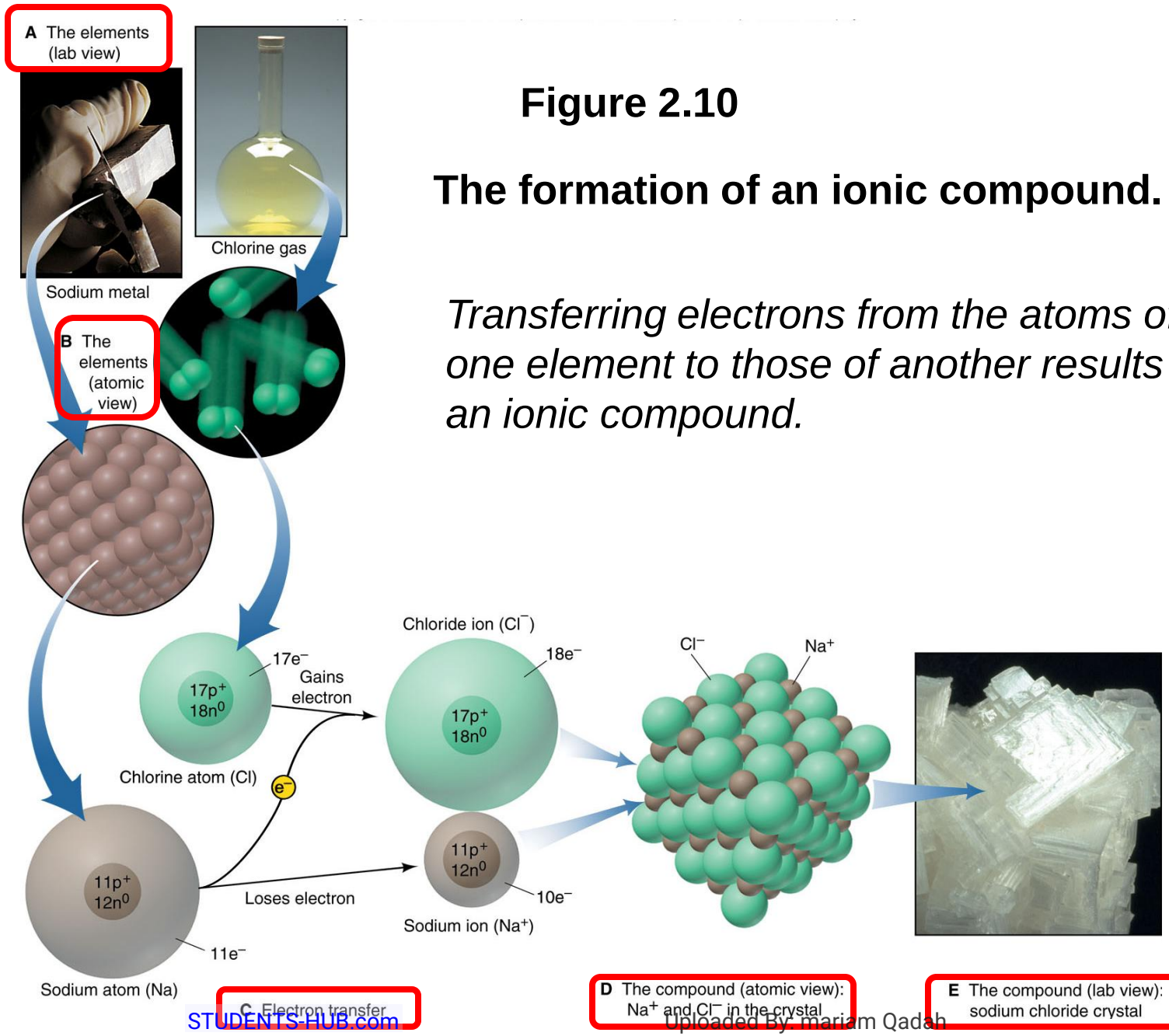

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Figure 2.11 **Factors that influence the strength of ionic bonding.**

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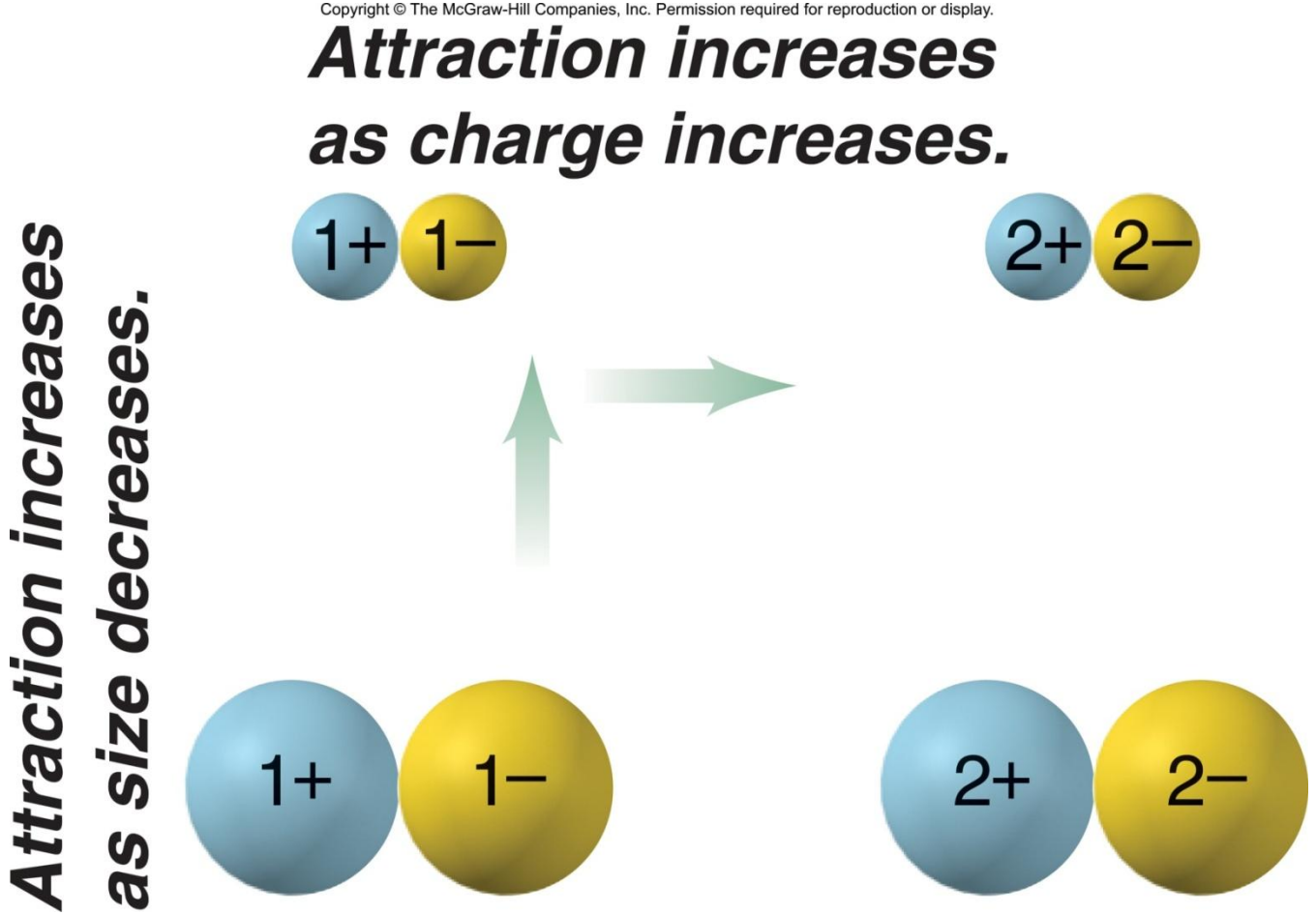

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Sample Problem 2.6 Predicting the Ion an Element Forms

PROBLEM: Predict the monoatomic ion formed by each of the following elements:

(a) Iodine ($Z = 53$) **(b)** Calcium ($Z = 20$) **(c)** Aluminum ($Z = 13$)

PLAN: Use Z to find the element on the periodic table and see where it lies relative to its **nearest** noble gas.

SOLUTION:

(a) Iodine is a nonmetal in Group 7A(17). It gains one electron to have the same number of electrons as $_{54}Xe$.

The ion is I^-

(b) Calcium is a metal in Group 2A(2). It loses two electrons to have the same number of electrons as $_{18}Ar$.

The ion is Ca^{2+}

(c) Aluminum is a metal in Group 3A(13). It loses three electrons to have the same number of electrons as $_{10}Ne$.

The ion is Al^{3+}

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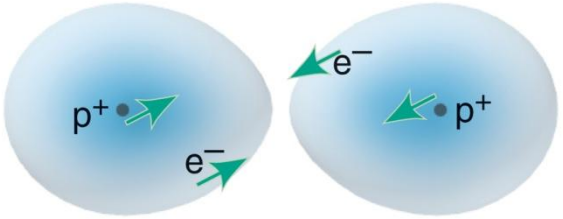
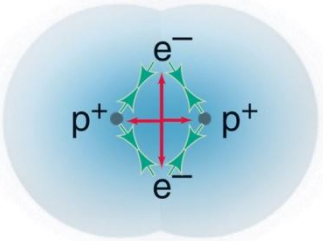
Figure 2.12 Formation of a covalent bond between two H atoms.

Covalent bonds form when elements share electrons, which usually occurs between nonmetals.

Atoms far apart: *No interactions.*



Atoms closer: *Attractions* (green arrows) *between nucleus of one atom and electron of the other increase. Repulsions between nuclei and between electrons are very weak.*



Optimum distance: *H_2 molecule forms because attractions* (green arrows) *balance repulsions* (red arrows).

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Molecules and Ions

Molecule – the basic unit of an element or covalent compound, consisting of two or more atoms bonded by the sharing of electrons.

Most covalent substances consist of molecules.

Ion – a single atom or covalently bonded group of atoms that has an overall electrical charge.

There are ***no molecules*** in an ionic compound.

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Figure 2.13 Elements that occur as molecules.

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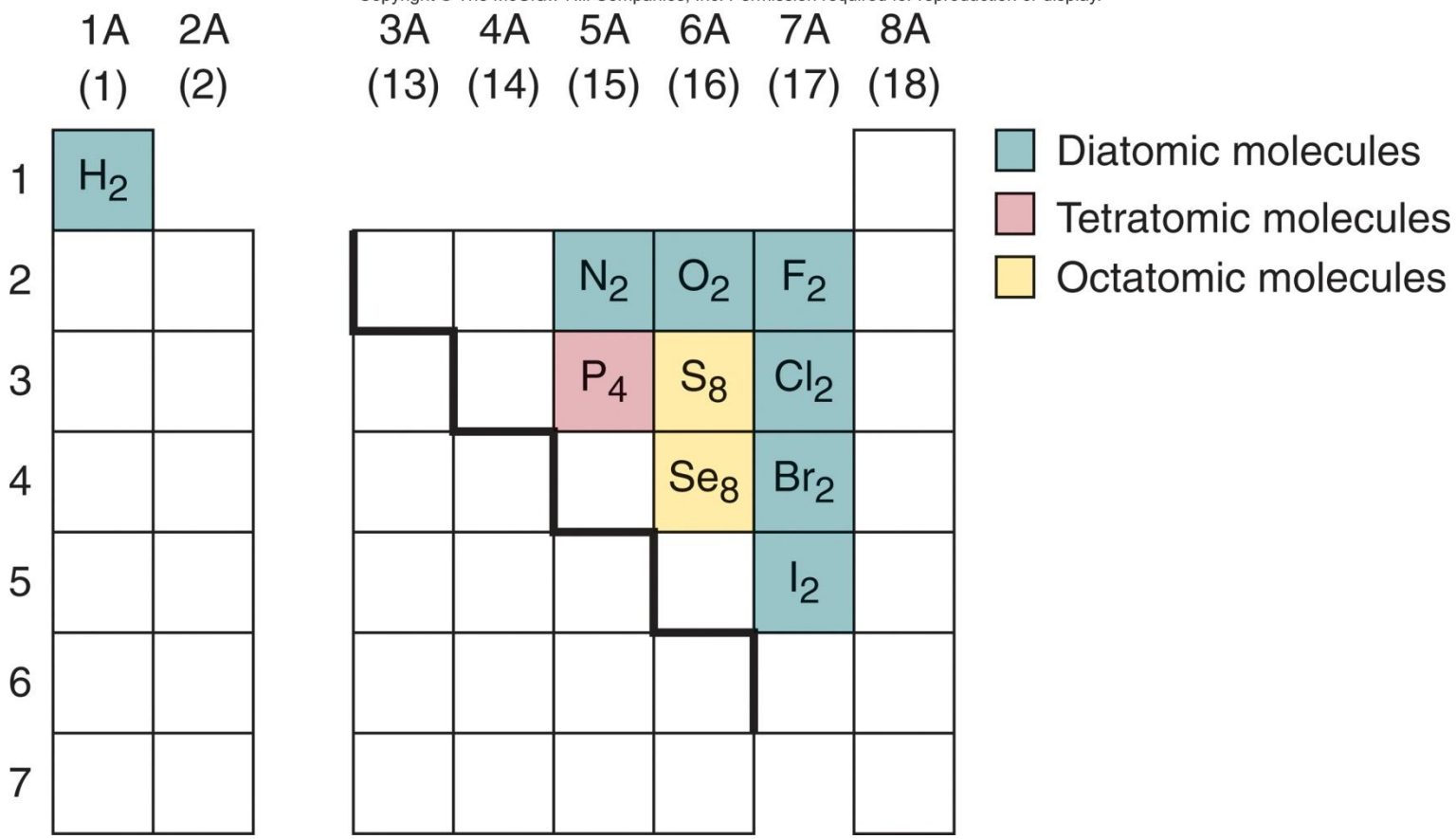

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Figure 2.14 The carbonate ion in calcium carbonate.

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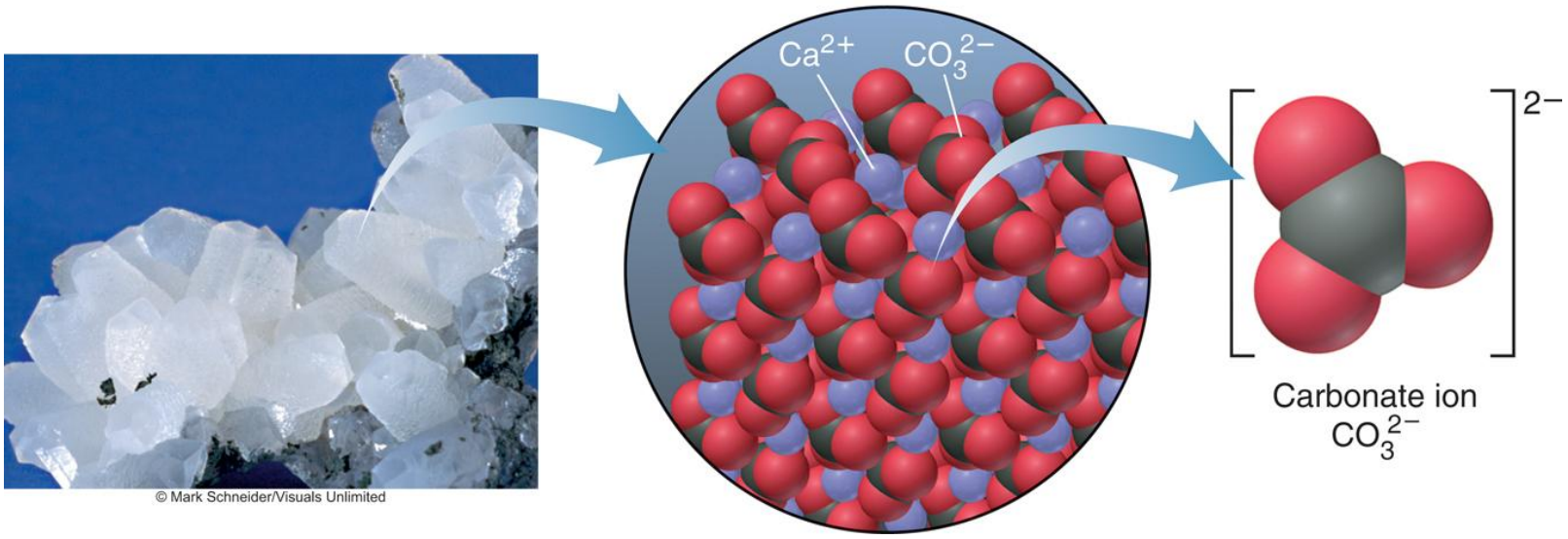

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A polyatomic ion consists of two or more atoms covalently bonded together and has an overall charge.

In many reactions the polyatomic ion will remain together as a unit.

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Chemical Formulas

- A chemical formula consists of
  - element symbols with
  - numerical subscripts.
- The chemical formula indicates the
  - **type** and **number** of each atom present
  - in the **smallest unit** of a substance.

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Naming Binary Ionic Compounds

For **all** ionic compounds, the name and formula lists the **cation** first and the **anion** second.

In a **binary ionic** compound, both the cation and the anion are monatomic.

The name of the cation is the **same** as the name of the metal. Many metal names end in -ium.

The anion is named by adding the suffix *-ide* to the root of the nonmetal name.

Calcium and bromine form calcium bromide.

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Table 2.3 Common Monatomic Ions*

Cations			Anions		
Charge	Formula	Name	Charge	Formula	Name
+1	H^+	**hydrogen**	-1	H^-	hydride
	Li^+	**lithium**		**F^-**	**fluoride**
	Na^+	**sodium**		**Cl^-**	**chloride**
	K^+	**potassium**		**Br^-**	**bromide**
	Cs^+	cesium		**I^-**	**iodide**
	Ag^+	**silver**			
+2	**Mg^{2+}**	**magnesium**	-2	**O^{2-}**	**oxide**
	Ca^{2+}	**calcium**		**S^{2-}**	**sulfide**
	Sr^{2+}	strontium			
	Ba^{2+}	**barium**			
	Zn^{2+}	**zinc**			
	Cd^{2+}	cadmium			
+3	Al^{3+}	aluminum	-3	N^{3-}	nitride

*Listed by charge; those in boldface are most common.

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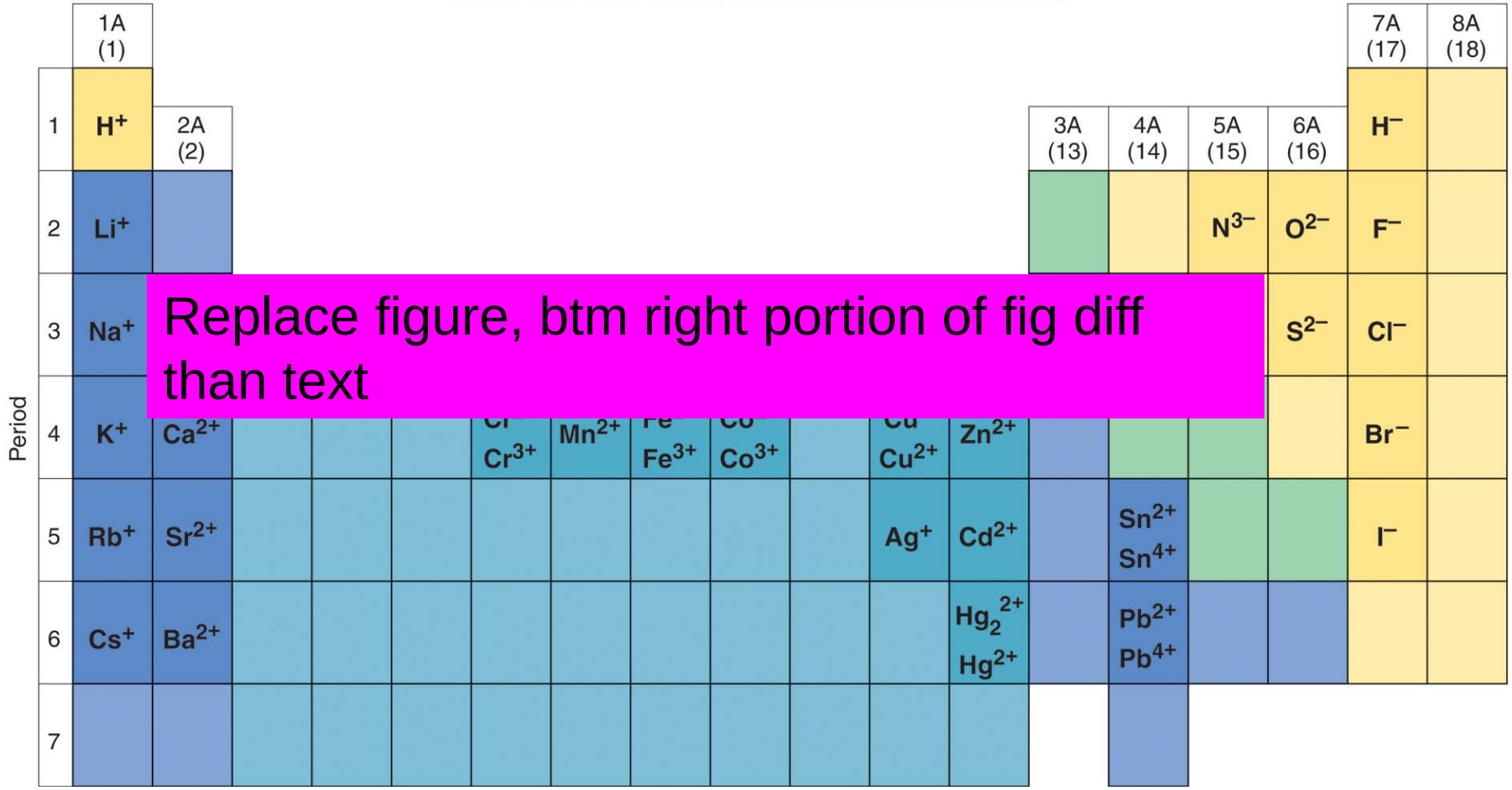
Figure 2.15 Some common monatomic ions of the elements.



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Most main-group elements form one monatomic ion.
Most transition elements form two monatomic ions.

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Sample Problem 2.7 Naming Binary Ionic Compounds

PROBLEM: Name the ionic compound formed from each of the following pairs of elements:

(a) magnesium and nitrogen **(b)** iodine and cadmium

(c) strontium and fluorine **(d)** sulfur and cesium

PLAN: Use the periodic table to decide which element is the metal and which the nonmetal. The metal (cation) is named first and the suffix-*ide* is added to the root of the non-metal name.

SOLUTION:

(a) magnesium nitride **(b) cadmium iodide**

(c) strontium fluoride **(d) cesium sulfide**

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Sample Problem 2.8

Determining Formulas of Binary Ionic Compounds

PROBLEM: Write empirical formulas for each of the compounds named in Sample Problem 2.7.

(a) magnesium nitride **(b)** cadmium iodide

(c) strontium fluoride **(d)** cesium sulfide

PLAN: A compound is neutral. We find the smallest number of each ion that will produce a neutral formula. These numbers appear as *right subscripts* to the relevant element symbol.

SOLUTION:

(a) Mg^{2+} and N^{3-}; three $Mg^{2+}(6+)$ and two $N^{3-}(6-)$; **Mg_3N_2**

(b) Cd^{2+} and I^-; one $Cd^{2+}(2+)$ and two $I^-(2-)$; **CdI_2**

(c) Sr^{2+} and F^-; one $Sr^{2+}(2+)$ and two F^- $(2-)$; **SrF_2**

(d) Cs^+ and S^{2-}; two $Cs^+(2+)$ and one S^{2-} $(2-)$; **Cs_2S**

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Table 2.4 Some Metals That Form More Than One Monatomic Ion*

Element	Ion Formula	Systematic Name	Common Name
Chromium	Cr^{2+}	chromium(II)	chromous
	Cr^{3+}	**chromium(III)**	chromic
Cobalt	Co^{2+}	cobalt(II)	
	Co^{3+}	cobalt(III)	
Copper	**Cu^{+}**	**copper(I)**	cuprous
	Cu^{2+}	**copper(II)**	cupric
Iron	**Fe^{2+}**	**iron(II)**	ferrous
	Fe^{3+}	**iron(III)**	ferric
Lead	**Pb^{2+}**	**lead(II)**	
	Pb^{4+}	lead(IV)	
Mercury	Hg_2^{2+}	mercury (I)	mercurous
	Hg^{2+}	**mercury (II)**	mercuric
Tin	**Sn^{2+}**	**tin(II)**	stannous
	Sn^{4+}	tin(IV)	stannic

*Listed alphabetically by metal name; the ions in boldface are most common.

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Sample Problem 2.9 Determining Names and Formulas of Ionic Compounds of Elements That Form More Than One Ion

PROBLEM: Give the systematic name for each formula or the formula for each name for the following compounds:

(a) tin(II) fluoride **(b)** CrI_3 **(c)** ferric oxide **(d)** CoS

PLAN: Find the smallest number of each ion that will produce a neutral formula.

SOLUTION:

(a) Tin(II) is Sn^{2+}; fluoride is F^-; so the formula is **SnF_2**.

(b) The anion I^- is iodide; $3I^-$ means that Cr (chromium) is +3. CrI_3 is **chromium(III) iodide**.

(c) Ferric is a common name for Fe^{3+}; oxide is O^{2-}; therefore the formula is **Fe_2O_3**.

(d) Co is cobalt; the anion S^{2-} is sulfide; the compound is **cobalt(II) sulfide**.

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Table 2.5 Common Polyatomic Ions*

Formula	Name	Formula	Name
		Cations	
NH_4^+	**ammonium**	**H_3O^+**	**hydronium**
		Common Anions	
CH_3COO^-	**acetate**	**CO_3^{2-}**	**carbonate**
CN^-	cyanide	**HCO_3^-**	**bicarbonate**
OH^-	**hydroxide**	CrO_4^{2-}	chromate
ClO^-	hypochlorite	**$Cr_2O_7^{2-}$**	**dichromate**
ClO_2^-	chlorite	O_2^{2-}	peroxide
ClO_3^-	**chlorate**	**PO_4^{3-}**	**phosphate**
NO_2^-	nitrite	HPO_4^{2-}	hydrogen phosphate
NO_3^-	**nitrate**	SO_3^{2-}	sulfite
MnO_4^-	**permanganate**	**SO_4^{2-}**	**sulfate**

*Bold face ions are most common. **(partial table)**

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Figure 2.16 Naming oxoanions

No. of O atoms ↑

Prefix	Root	Suffix	Example	
per	*root*	ate	ClO_4^-	perchlorate
	root	ate	ClO_3^-	chlorate
	root	ite	ClO_2^-	chlorite
hypo	*root*	ite	ClO^-	hypochlorite

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Table 2.6 Numerical Prefixes* for Hydrates and Binary Covalent Compounds

Number	Prefix	Number	Prefix	Number	Prefix
1	mono-	4	tetra-	8	octa-
2	di-	5	penta-	9	nona-
3	tri-	6	hexa-	10	deca-
		7	hepta-		

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Sample Problem 2.10

Determining Names and Formulas of Ionic Compounds Containing Polyatomic Ions

PROBLEM: Give the systematic name for each formula or the formula for each name for the following compounds:

(a) $Fe(ClO_4)_2$ **(b)** sodium sulfite **(c)** $Ba(OH)_2 \cdot 8H_2O$

PLAN: Remember to use parentheses when more than one unit of a particular polyatomic ion is present in the compound.

SOLUTION: **(a)** ClO_4^- is perchlorate; Fe must have a 2+ charge since there are 2 ClO_4^- ions. This is **iron(II) perchlorate**.

(b) The anion sulfite is SO_3^{2-}**;** therefore you need 2 Na^+ for each sulfite. The formula is $\mathbf{Na_2SO_3}$.

(c) The ionic compound is barium hydroxide. When water is included in the formula, we use the term "hydrate" and a prefix that indicates the number of molecules of H_2O. This compound is **barium hydroxide octahydrate**.

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Sample Problem 2.11

Recognizing Incorrect Names and Formulas of Ionic Compounds

PROBLEM: There is an error in the second part of each statement. Provide the correct name or formula in each case.

(a) $Ba(C_2H_3O_2)_2$ is called barium diacetate.

(b) Sodium sulfide has the formula $(Na)_2SO_3$.

(c) Iron(II) sulfate has the formula $Fe_2(SO_4)_3$.

(d) Cesium carbonate has the formula $Cs_2(CO_3)$.

SOLUTION:

(a) The charge of Ba^{2+} *must* be balanced by *two* $C_2H_3O_2^-$ ions. The prefix "di" is not required and is not used in this way when naming ionic compounds. The correct name is simply **barium acetate**.

(b) An ion of a single element does not need parentheses, and sulfide is S^{2-}, not SO_3^{2-}. The correct formula is **Na_2S**.

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Sample Problem 2.11

(c) Sulfate or SO_4^{2-} has a 2^- charge, and only ***one*** Fe^{2+} is needed to form a neutral compound. The formula should be **$FeSO_4$**.

(d) The parentheses are unnecessary, since only ***one*** CO_3^{2-} ion is present. The correct formula is **Cs_2CO_3**.

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Naming Acids

1) ***Binary acid*** solutions form when certain gaseous compounds dissolve in water.
For example, when gaseous hydrogen chloride (HCl) dissolves in water, it forms a solution called hydrochloric acid.
Prefix ***hydro-*** + anion nonmetal ***root*** + suffix ***-ic*** + the word ***acid*** -

hydro + chlor + ic + acid

hydrochloric acid

2) Oxoacid names are similar to those of the oxoanions, except for two suffix changes:
-ate in the anion becomes ***–ic*** in the acid
-ite in the anion becomes ***–ous*** in the acid
The oxoanion prefixes ***hypo-*** and ***per-*** are retained. Thus,
BrO_4^- is ***perbromate***, and $HBrO_4$ is ***perbromic*** acid;
IO_2^- is ***iodite***, and HIO_2 is ***iodous acid***.

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Sample Problem 2.12

Determining Names and Formulas of Anions and Acids

PROBLEM: Name the following anions and give the name and formula of the acid derived from each:

(a) Br^- **(b)** IO_3^- **(c)** CN^- **(d)** SO_4^{2-} **(e)** NO_2^-

SOLUTION:

(a) The anion is **bromide**; the acid is **hydrobromic acid, HBr**.

(b) The anion is **iodate**; the acid is **iodic acid, HIO_3**.

(c) The anion is **cyanide**; the acid is **hydrocyanic acid, HCN**.

(d) The anion is **sulfate**; the acid is **sulfuric acid, H_2SO_4**.

(e) The anion is **nitrite**; the acid is **nitrous acid, HNO_2**.

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Naming Binary Covalent Compounds

A binary covalent compound is typically formed by the combination of two non-metals.

Some of these compounds are very common and have *trivial* names, eg., H_2O is water.

For a binary covalent compound, the element with the ***lower*** group number in the periodic table is ***first*** in the name and formula. Its name remains unchanged.

The element that is second is named using the root with the suffix ***–ide***. Numerical prefixes indicate the number of atoms of each element present.

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Sample Problem 2.13

Determining Names and Formulas of Binary Covalent Compounds

PROBLEM: **(a)** What is the formula of carbon disulfide?

(b) What is the name of PCl_5?

(c) Give the name and formula of the compound whose molecules each consist of two N atoms and four O atoms.

SOLUTION:

(a) Carbon is C, sulfide is sulfur S and di- means two; the formula is **CS_2**.

(b) P is phosphorous, Cl is chloride, the prefix for 5 is penta-. This is **phosphorous pentachloride**.

(c) N is nitrogen and is in a lower group number than O (oxygen). The compound formula is **N_2O_4** and the name is **dinitrogen tetraoxide**.

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Sample Problem 2.14

Recognizing Incorrect Names and Formulas of Binary Covalent Compounds

PROBLEM: Explain what is wrong with the name of formula in the second part of each statement and correct it:

(a) SF_4 is monosulfur pentafluoride.

(b) Dichlorine heptaoxide is Cl_2O_6.

(c) N_2O_3 is dinitrotrioxide.

SOLUTION:

(a) The prefix mono- is not needed if there is only one atom of the first element, and the prefix for four is tetra-. So the name is **sulfur tetrafluoride**.

(b) Hepta- means 7; the formula should be **Cl_2O_7**.

(c) The first element is given its elemental name so this is **dinitrogen trioxide**.

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Naming Straight-Chain Alkanes

Hydrocarbons are compounds that contain only carbon and hydrogen atoms.

Alkanes are the simplest type of hydrocarbon.

Alkanes are named using a root name followed by the suffix ***–ane***.

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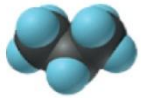
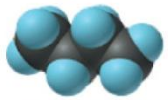
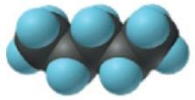
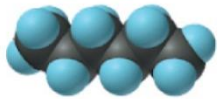
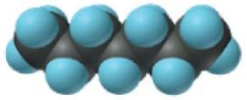
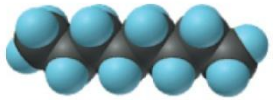
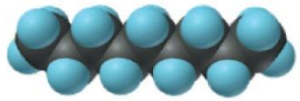
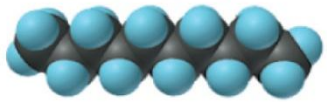
Table 2.7 The First 10 Straight-Chain Alkanes

Name (Formula)	Model
Methane (CH_4)	
Ethane (C_2H_6)	
Propane (C_3H_8)	
Butane (C_4H_{10})	
Pentane (C_5H_{12})	
Hexane (C_6H_{14})	
Heptane (C_7H_{16})	
Octane (C_8H_{18})	
Nonane (C_9H_{20})	
Decane ($C_{10}H_{22}$)	

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Molecular Masses from Chemical Formulas

Molecular mass = sum of atomic masses

For the H_2O molecule:

molecular mass =

(2 x atomic mass of H) + (1 x atomic mass of O)

= (2 x 1.008 amu) + (1 x 16.00 amu)

= 18.02 amu

*By convention, we read masses off the periodic table to **4 significant figures**.*

For **ionic compounds** we refer to a **formula mass** since ionic compounds do not consist of molecules.

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Sample Problem 2.15 — Calculating the Molecular Mass of a Compound

PROBLEM: Using the periodic table, calculate the molecular (or formula) mass of:

(a) tetraphosphorous trisulfide **(b)** ammonium nitrate

PLAN: Write the formula and then multiply the number of atoms by the respective atomic masses. Add the masses for each compound.

SOLUTION:

(a) P_4S_3

molecular mass = (4 x atomic mass of P) + (3 x atomic mass of S)

= (4 x 30.97 amu) + (3 x 32.07 amu) = **220.09 amu**

(b) NH_4NO_3

formula mass = (2 x atomic mass of N) + (4 x atomic mass of H) + (3 x atomic mass of O)

= (2 x 14.01 amu) + (4 x 1.008 amu) + (3 x 16.00 amu)

= **80.05 amu**

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Sample Problem 2.16 Using Molecular Depictions to determine Formula, Name, and Mass for a compound

PROBLEM: Each scene represents a binary compound. Determine its formula, name, and molecular (formula) mass.

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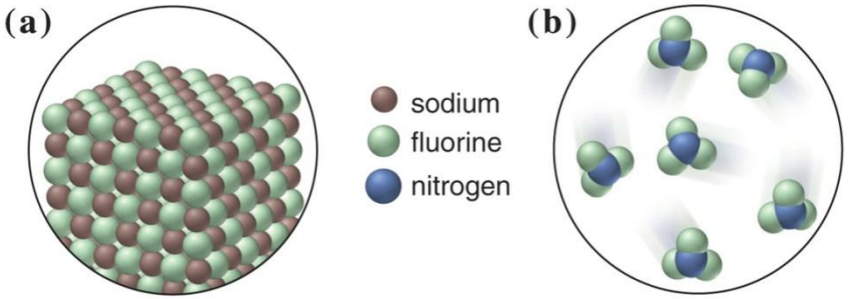

PLAN: Each compound contains only two elements. Find the simplest whole number ratio of atoms in each compound and use this formula to determine the name and the formula mass.

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Sample Problem 2.16

SOLUTION:

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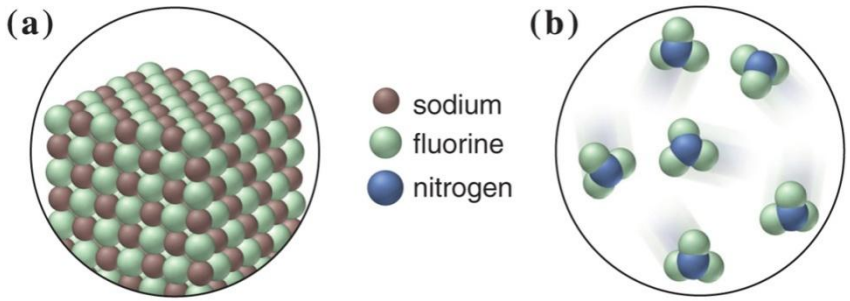

(a) There is 1 brown Na^+ for every green F^-, so the formula is **NaF**, an ionic compound, which is named **sodium fluoride**.

Formula mass = (1 x atomic mass of Na) + (1 x atomic mass of F)
= 22.99 amu + 10.00 amu = **41.99 amu**

(b) There are 3 green F for every blue N, so the formula is **NF_3**, a covalent compound, which is named **nitrogen trifluoride**.

Molecular mass = (1 x atomic mass of N) + (3 x atomic mass of F)
= 14.01 amu + (3 x 19.00) = **71.01 amu**

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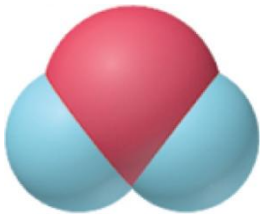
Representing Molecules with Formulas and Models

H_2O Molecular formula for water.

Structural formulas for water.

Ball-and-stick model for water.



Space-filling model for water.

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Representing Molecules with Formulas and Models

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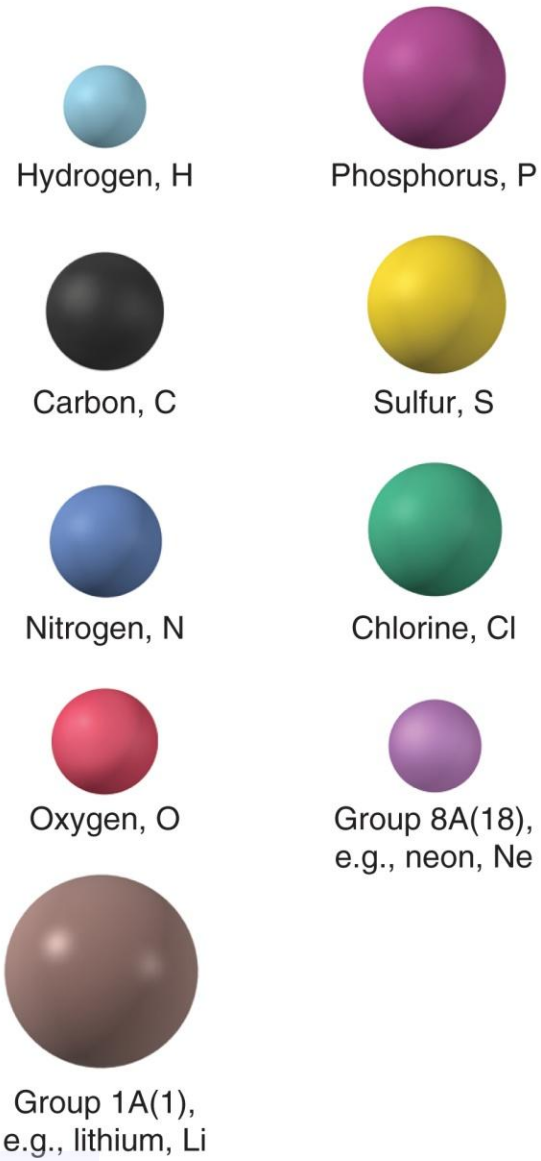

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Chapter 3

Stoichiometry of Formulas and Equations

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Mole - Mass Relationships in Chemical Systems

3.1 The Mole

3.2 Determining the Formula of an Unknown Compound

3.3 Writing and Balancing Chemical Equations

3.4 Calculating Quantities of Reactant and Product

3.5 Fundamentals of Solution Stoichiometry

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The Mole

The mole (mol) is the amount of a substance that contains the same number of entities as there are atoms in exactly 12 g of carbon-12.

> The term "***entities***" refers to atoms, ions, molecules, formula units, or electrons – in fact, any type of particle.

One mole (1 mol) contains 6.022×10^{23} entities (to four significant figures).

This number is called Avogadro's number and is abbreviated as ***N.***

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Figure 3.1 One mole (6.022×10^{23} entities) of some familiar substances.

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Determining Molar Mass

The molar mass ($\mathcal{M}$) of a substance is the mass per mole of its entities (atoms, molecules or formula units).

For **monatomic elements**, the molar mass is the same as the atomic mass in grams per mole. The atomic mass is simply read from the Periodic Table.

The molar mass of Ne = 20.18 g/mol.

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For **molecular elements** and for **compounds**, the formula is needed to determine the molar mass.

The molar mass of O_2 = 2 x $\mathcal{M}$ of O

= 2 x 16.00

= 32.00 g/mol

The molar mass of SO_2 = 1 x $\mathcal{M}$ of S + 2 x $\mathcal{M}$ of O

= 32.00 + 2(16.00)

= 64.00 g/mol

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Table 3.1 Information Contained in the Chemical Formula of Glucose, $C_6H_{12}O_6$ ($\mathcal{M}$ = 180.16 g/mol)

	Carbon (C)	Hydrogen (H)	Oxygen (O)
Atoms/molecule of compound	6 atoms	12 atoms	6 atoms
Moles of atoms/mole of compound	6 mol of atoms	12 mol of atoms	6 mol of atoms
Atoms/mole of compound	$6(6.022 \times 10^{23})$ atoms	$12(6.022 \times 10^{23})$ atoms	$6(6.022 \times 10^{23})$ atoms
Mass/molecule of compound	6(12.01 amu) = 72.06 amu	12(1.008 amu) = 12.10 amu	6(16.00 amu) = 96.00 amu
Mass/mole of compound	72.06 g	12.10 g	96.00 g

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Converting Between Amount, Mass, and Number of Chemical Entities

$$\text{Mass (g)} = \text{no. of moles} \times \frac{\text{no. of grams}}{1\ \text{mol}}$$ ← g

$$\text{No. of moles} = \text{mass (g)} \times \frac{1\ \text{mol}}{\text{no. of grams}}$$ ← $\mathcal{M}$

$$\text{No. of entities} = \text{no. of moles} \times \frac{6.022 \times 10^{23}\ \text{entities}}{1\ \text{mol}}$$

$$\text{No. of moles} = \text{no. of entities} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{entities}}$$

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Figure 3.2 Mass-mole-number relationships for elements.

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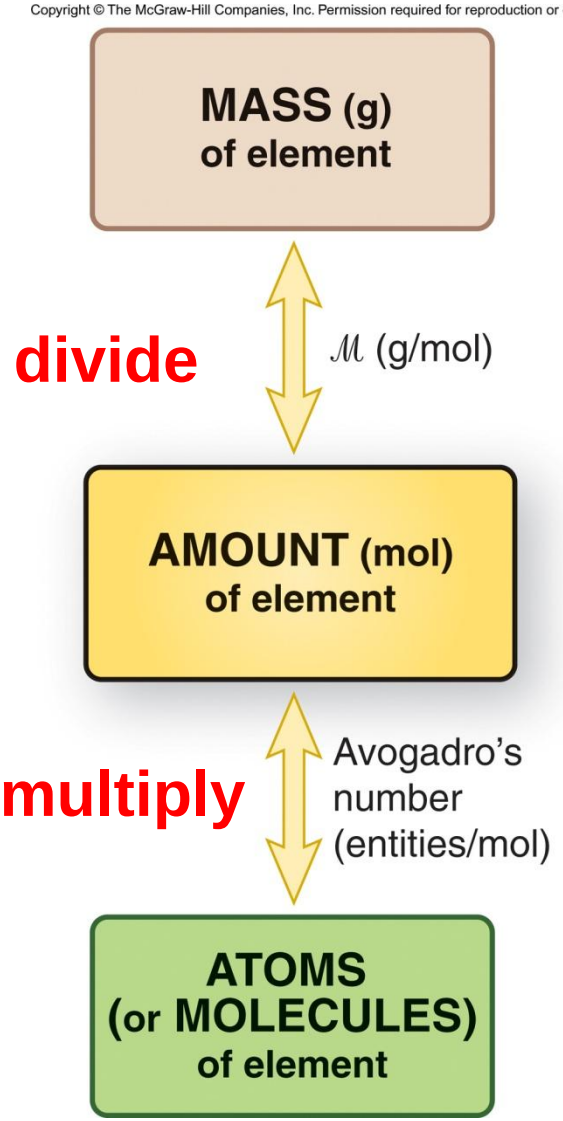

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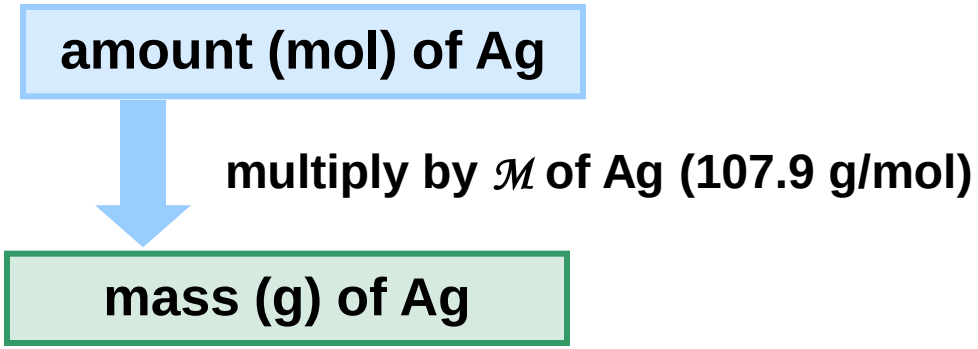
Sample Problem 3.1 Calculating the Mass of a Given Amount of an Element

PROBLEM: Silver (Ag) is used in jewelry and tableware but no longer in U.S. coins. How many grams of Ag are in 0.0342 mol of Ag?

PLAN: To convert mol of Ag to mass of Ag in g we need the molar mass of Ag.



SOLUTION:

$$0.0342 \ \cancel{\text{mol Ag}} \times \frac{107.9 \text{ g Ag}}{1 \ \cancel{\text{mol Ag}}} = \textbf{3.69 g Ag}$$

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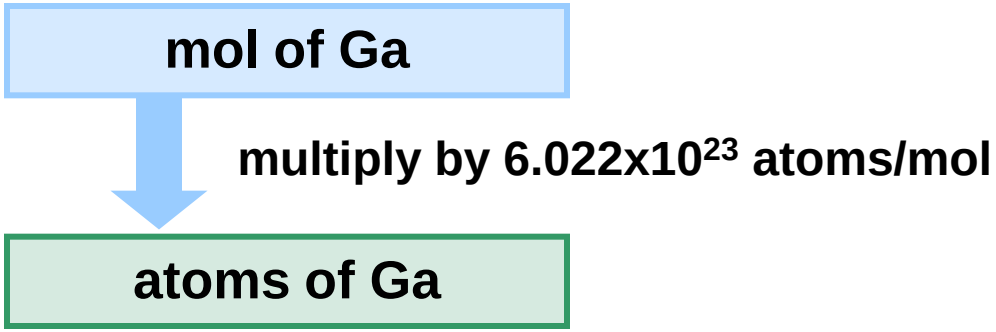
Sample Problem 3.2

Calculating the Number of Entities in a Given Amount of an Element

PROBLEM: Gallium (Ga) is a key element in solar panels, calculators, and other light-sensitive electronic devices. How many Ga atoms are in 2.85×10^{-3} mol of gallium?

PLAN: To convert mol of Ga to number of Ga atoms we need to use Avogadro's number.



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Sample Problem 3.2

SOLUTION:

$$2.85 \times 10^{-3} \cancel{\text{mol Ga atoms}} \times \frac{6.022 \times 10^{23} \text{ Ga atoms}}{1 \cancel{\text{mol Ga atoms}}}$$

$$= 1.72 \times 10^{21} \text{ Ga atoms}$$

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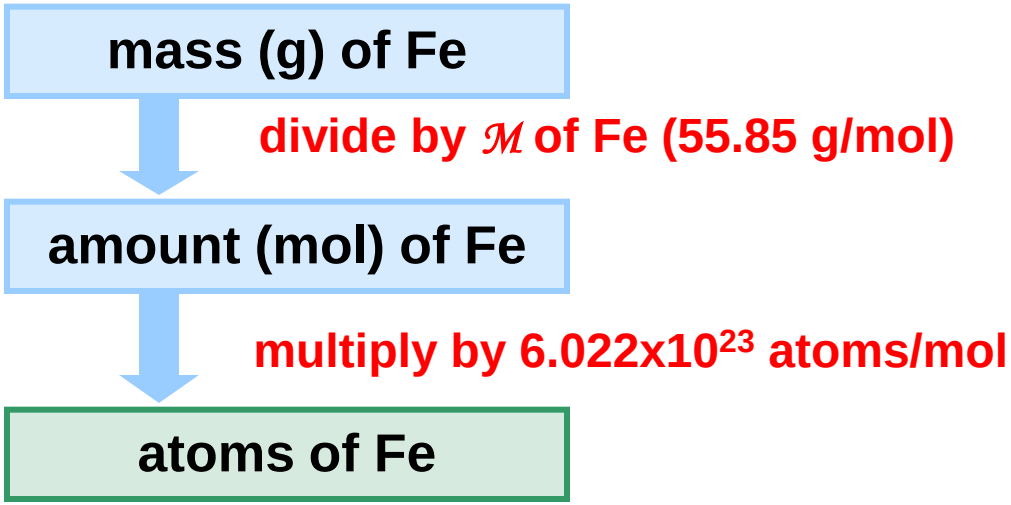
Sample Problem 3.3

Calculating the Number of Entities in a Given Mass of an Element

PROBLEM: Iron (Fe) is the main component of steel and is therefore the most important metal in society; it is also essential in the body. How many Fe atoms are in 95.8 g of Fe?

PLAN: The number of atoms cannot be calculated directly from the mass. We must first determine the number of moles of Fe atoms in the sample and then use Avogadro's number.



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Sample Problem 3.3

SOLUTION:

$$95.8 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 1.72 \text{ mol Fe}$$

$$1.72 \text{ mol Fe} \times \frac{6.022 \times 10^{23} \text{ atoms Fe}}{1 \text{ mol Fe}}$$

$= 1.04 \times 10^{24}$ atoms Fe

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Figure 3.3 Amount-mass-number relationships for compounds.

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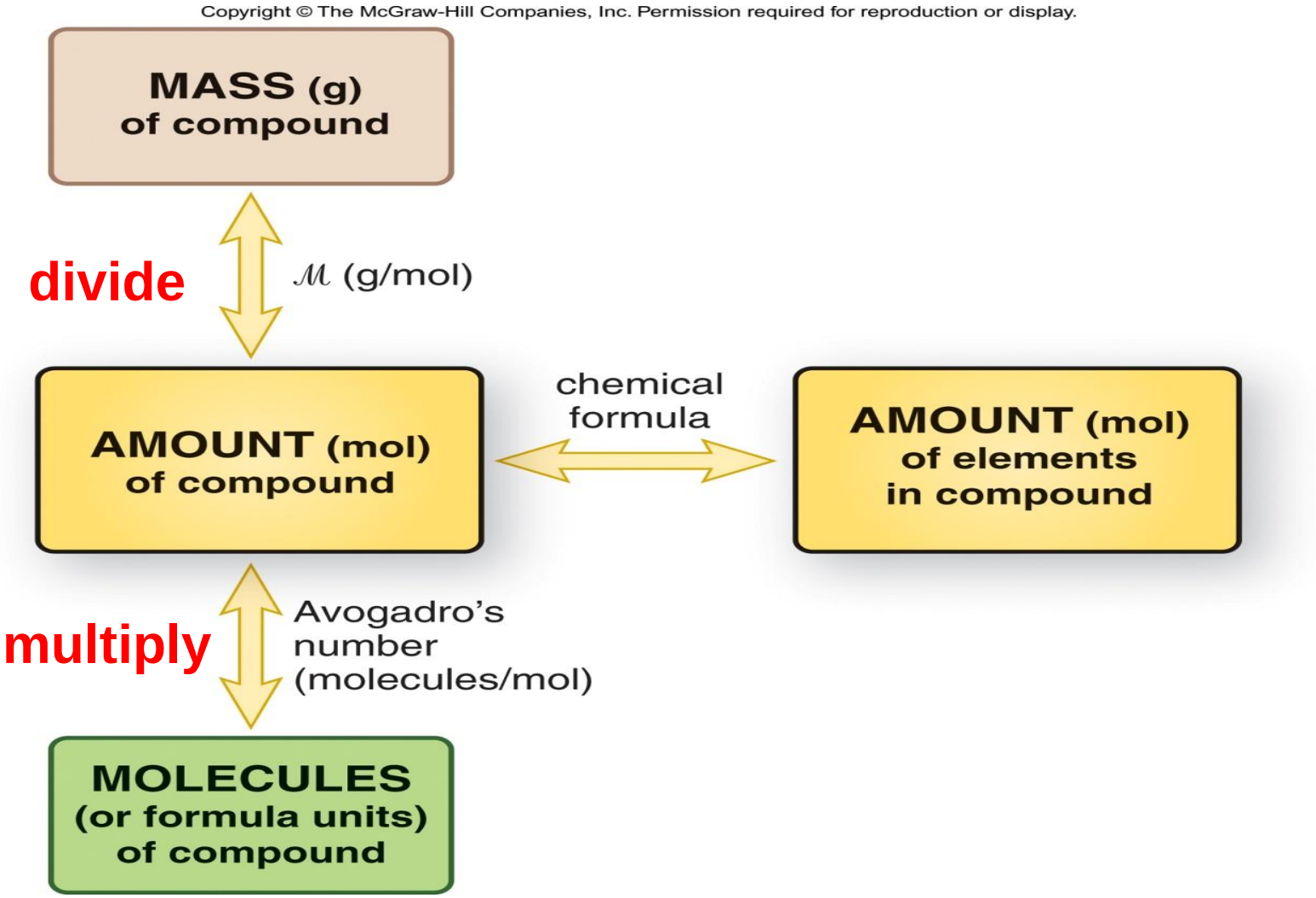

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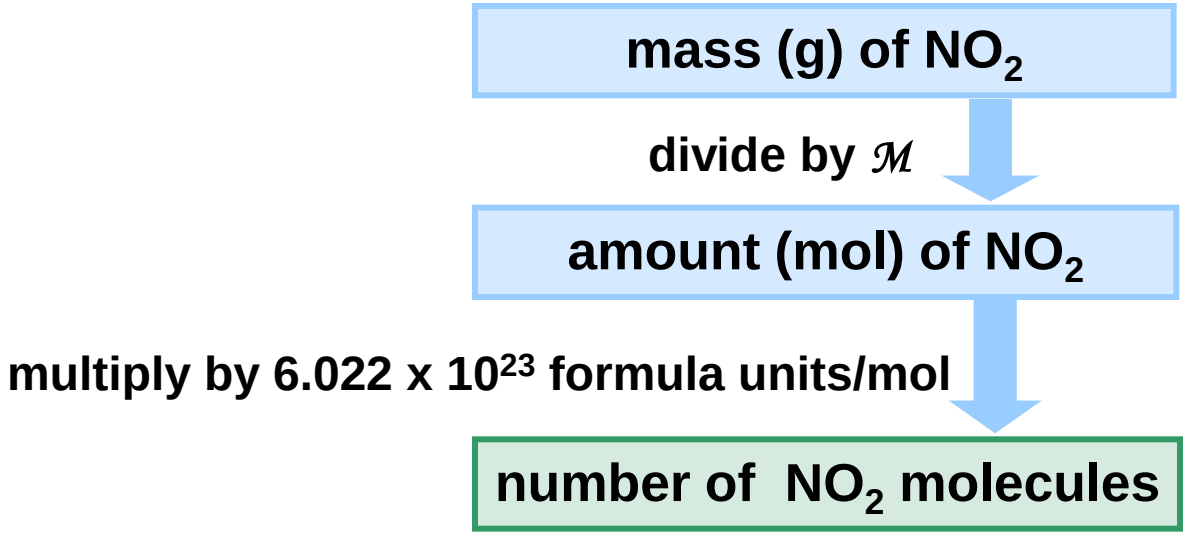
Sample Problem 3.4 Calculating the Number of Chemical Entities in a Given Mass of a Compound I

PROBLEM: Nitrogen dioxide is a component of urban smog that forms from the gases in car exhausts. How many molecules are in 8.92 g of nitrogen dioxide?

PLAN: Write the formula for the compound and calculate its molar mass. Use the given mass to calculate first the number of moles and then the number of molecules.



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Sample Problem 3.4

SOLUTION: NO_2 is the formula for nitrogen dioxide.

$\mathcal{M}$ = (1 x $\mathcal{M}$ of N) + (2 x $\mathcal{M}$ of O)

= 14.01 g/mol + 2(16.00 g/mol)

= 46.01 g/mol

$$8.92 \text{ g } NO_2 \times \frac{1 \text{ mol } NO_2}{46.01 \text{ g } NO_2} = 0.194 \text{ mol } NO_2$$

$$0.194 \text{ mol } NO_2 \times \frac{6.022 \times 10^{23} \text{ molecules } NO_2}{1 \text{ mol } NO_2}$$

= 1.17 x 10^{23} molecules NO_2

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Sample Problem 3.5

Calculating the Number of Chemical Entities in a Given Mass of a Compound II

PROBLEM: Ammonium carbonate, a white solid that decomposes on warming, is a component of baking powder.

a) How many formula units are in 41.6 g of ammonium carbonate?

b) How many O atoms are in this sample?

PLAN:

Write the formula for the compound and calculate its molar mass. Use the given mass to calculate first the number of moles and then the number of formula units.

The number of O atoms can be determined using the formula and the number of formula units.

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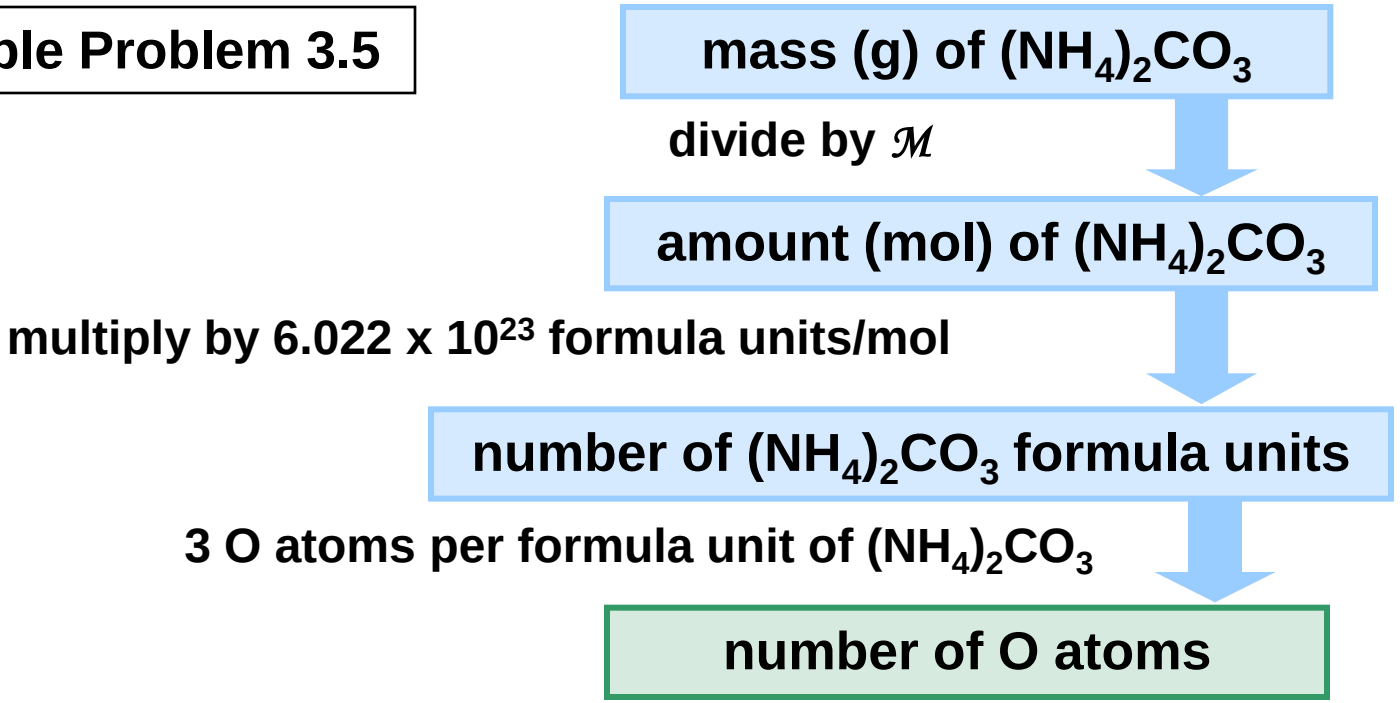
Sample Problem 3.5



SOLUTION: $(NH_4)_2CO_3$ is the formula for ammonium carbonate.

$\mathcal{M}$ = (2 x *M* of N) + (8 x $\mathcal{M}$ of H) + (1 x $\mathcal{M}$ of C) + (3 x $\mathcal{M}$ of O)

= (2 x 14.01 g/mol) + (8 x 1.008 g/mol)
+ (12.01 g/mol) + (3 x 16.00 g/mol)

= 96.09 g/mol

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Sample Problem 3.5

$$41.6 \text{ g } (NH_4)_2CO_3 \times \frac{1 \text{ mol } (NH_4)_2CO_3}{96.09 \text{ g } (NH_4)_2CO_3} = 0.433 \text{ mol } (NH_4)_2CO_3$$

$$0.433 \text{ mol } (NH_4)_2CO_3 \times \frac{6.022 \times 10^{23} \text{ formula units } (NH_4)_2CO_3}{1 \text{ mol } (NH_4)_2CO_3}$$

$= 2.61 \times 10^{23}$ formula units $(NH_4)_2CO_3$

$$2.61 \times 10^{23} \text{ formula units } (NH_4)_2CO_3 \times \frac{3 \text{ O atoms}}{1 \text{ formula unit of } (NH_4)_2CO_3}$$

$= 7.83 \times 10^{23}$ O atoms

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The Importance of Mass Percent

Mass % of element X =

$$\frac{\text{atoms of X in formula x atomic mass of X (amu)}}{\text{molecular (or formula) mass of compound (amu)}} \times 100$$

Mass % of element X =

$$\frac{\text{moles of X in formula x molar mass of X (g/mol)}}{\text{mass (g) of 1 mol of compound}} \times 100$$

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Sample Problem 3.6

Calculating the Mass Percent of Each Element in a Compound from the Formula

PROBLEM: Glucose ($C_6H_{12}O_6$) is a key nutrient for generating chemical potential energy in biological systems. What is the mass percent of each element in glucose?

PLAN: Find the molar mass of glucose, which is the mass of 1 mole of glucose. Find the mass of each element in 1 mole of glucose, using the molecular formula.

The mass % for each element is calculated by dividing the mass of that element in 1 mole of glucose by the total mass of 1 mole of glucose, multiplied by 100.

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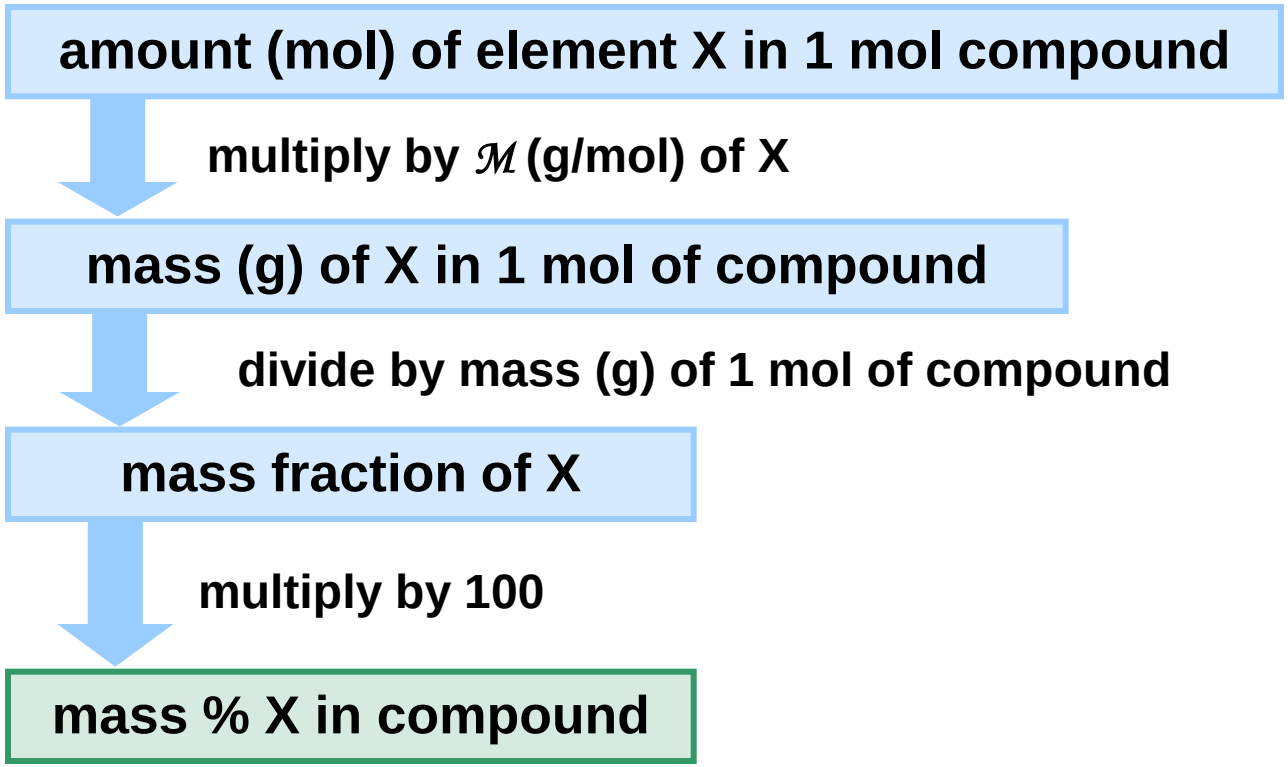
Sample Problem 3.6

PLAN:



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Sample Problem 3.6

SOLUTION:

In 1 mole of glucose there are **6** moles of C, **12** moles H, and **6** moles O.

$$6 \text{ mol C} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 72.06 \text{ g C} \qquad 12 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 12.096 \text{ g H}$$

$$6 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 96.00 \text{ g O} \qquad \mathcal{M} = 180.16 \text{ g/mol}$$

$$\text{mass percent of C} = \frac{72.06 \text{ g C}}{180.16 \text{ g glucose}} = 0.3999 \times 100 = 39.99 \text{ mass \%C}$$

$$\text{mass percent of H} = \frac{12.096 \text{ g H}}{180.16 \text{ g glucose}} = 0.06714 \times 100 = 6.714 \text{ mass \%H}$$

$$\text{mass percent of O} = \frac{96.00 \text{ g O}}{180.16 \text{ g glucose}} = 0.5329 \times 100 = 53.29 \text{ mass \%O}$$

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Determining the Mass of an Element from Its Percent

Mass percent can also be used to calculate the mass of a particular element in any mass of a compound.

Mass of element X present in sample =

$$\text{mass of compound} \times \frac{\text{mass of element in 1 mol of compound}}{\text{mass of 1 mol of compound}}$$

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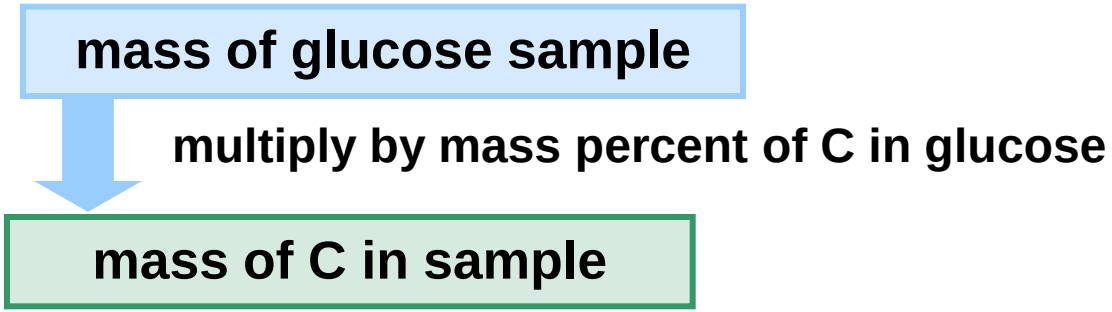
Sample Problem 3.7

Calculating the Mass of an Element in a Compound

PROBLEM: Use the information from Sample Problem 3.6 to determine the mass (g) of carbon in 16.55 g of glucose.

PLAN: The mass percent of carbon in glucose gives us the relative mass of carbon in 1 mole of glucose. We can use this information to find the mass of carbon in any sample of glucose.



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Sample Problem 3.7

SOLUTION:

Each mol of glucose contains 6 mol of C, or 72.06 g of C.

$$\text{Mass (g) of C} = \text{mass (g) of glucose} \times \frac{6 \text{ mol} \times \mathcal{M} \text{ of C (g/mol)}}{\text{mass (g) of 1 mol of glucose}}$$

$$= 16.55 \text{ g glucose} \times \frac{72.06 \text{ g C}}{180.16 \text{ g glucose}} = \mathbf{6.620 \text{ g C}}$$

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Empirical and Molecular Formulas

The empirical formula is the simplest formula for a compound that agrees with the elemental analysis. It shows the ***lowest*** whole number of moles and gives the ***relative*** number of atoms of each element present.

The empirical formula for hydrogen peroxide is HO.

The molecular formula shows the ***actual*** number of atoms of each element in a molecule of the compound.

The molecular formula for hydrogen peroxide is H_2O_2.

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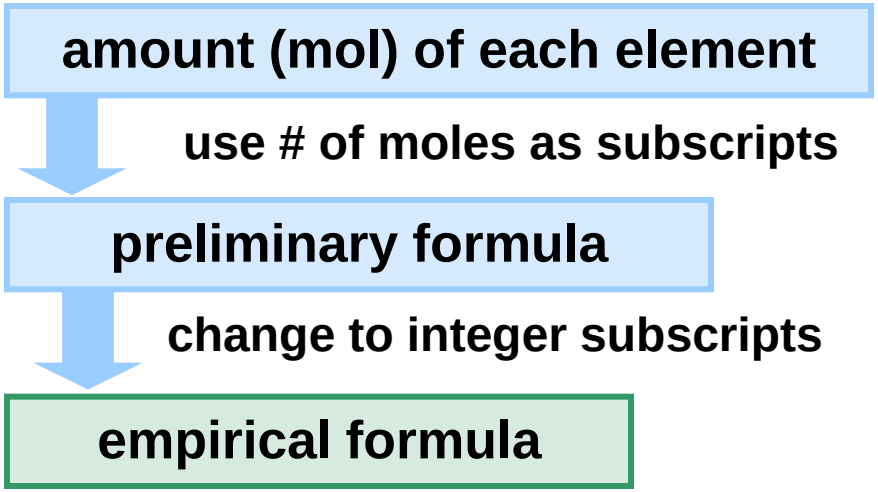
Sample Problem 3.8

Determining an Empirical Formula from Amounts of Elements

PROBLEM: A sample of an unknown compound contains 0.21 mol of zinc, 0.14 mol of phosphorus, and 0.56 mol of oxygen. What is its empirical formula?

PLAN: Find the relative number of moles of each element. Divide by the lowest mol amount to find the relative mol ratios (empirical formula).



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Sample Problem 3.8

SOLUTION: Using the numbers of moles of each element given, we write the preliminary formula $Zn_{0.21}P_{0.14}O_{0.56}$

Next we divide each fraction by the smallest one; in this case 0.14:

$$\frac{0.21}{0.14} = 1.5 \qquad \frac{0.14}{0.14} = 1.0 \qquad \frac{0.56}{0.14} = 4.0$$

This gives $Zn_{1.5}P_{1.0}O_{4.0}$

We convert to whole numbers by multiplying by the ***smallest integer*** that gives whole numbers; in this case 2:

1.5 x 2 = **3** 1.0 x 2 = **2** 4.0 x 2 = **8**

This gives us the empirical formula $Zn_3P_2O_8$

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Sample Problem 3.9

Determining an Empirical Formula from Masses of Elements

PROBLEM: Analysis of a sample of an ionic compound yields 2.82 g of Na, 4.35 g of Cl, and 7.83 g of O. What is the empirical formula and the name of the compound?

PLAN: Find the relative number of moles of each element. Divide by the lowest mol amount to find the relative mol ratios (empirical formula).

mass (g) of each element

divide by $\mathcal{M}$ (g/mol)

amount (mol) of each element

use # of moles as subscripts

preliminary formula

change to integer subscripts

empirical formula

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Sample Problem 3.9

SOLUTION: $2.82\ \cancel{g\ Na} \times \dfrac{1\ mol\ Na}{22.99\ \cancel{g\ Na}} = 0.123\ mol\ Na$

$$4.35\ \cancel{g\ Cl} \times \frac{1\ mol\ Cl}{35.45\ \cancel{g\ Cl}} = 0.123\ mol\ Cl$$

$$7.83\ \cancel{g\ O} \times \frac{1\ mol\ O}{16.00\ \cancel{g\ O}} = 0.489\ mol\ O$$

$$\text{Na and Cl} = \frac{0.123}{0.123} = 1 \quad \text{and} \quad \text{O} = \frac{0.489}{0.123} = 3.98$$

The empirical formula is $Na_1Cl_1O_{3.98}$ or $NaClO_4$; this compound is named sodium perchlorate.

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Molecular Formulas

The molecular formula gives the ***actual*** numbers of moles of each element present in 1 mol of compound.

The molecular formula is a ***whole-number multiple*** of the empirical formula.

$$\frac{\text{molar mass (g/mol)}}{\text{empirical formula mass (g/mol)}} = \text{whole-number multiple}$$

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Sample Problem 3.10

Determining a Molecular Formula from Elemental Analysis and Molar Mass

PROBLEM: Elemental analysis of lactic acid ($\mathcal{M}$ = 90.08 g/mol) shows it contains 40.0 mass % C, 6.71 mass % H, and 53.3 mass % O. Determine the empirical formula and the molecular formula for lactic acid.

PLAN:

assume 100 g lactic acid; then mass % = mass in grams

↓ **divide each mass by $\mathcal{M}$**

amount (mol) of each element

↓ **use # mols as subscripts; convert to integers**

empirical formula

↓ **divide $\mathcal{M}$ by the molar mass for the empirical formula; multiply empirical formula by this number**

molecular formula

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Sample Problem 3.10

SOLUTION: Assuming there are 100. g of lactic acid;

$$40.0\ \text{g C} \times \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 3.33\ \text{mol C}$$

$$6.71\ \text{g H} \times \frac{1\ \text{mol H}}{1.008\ \text{g H}} = 6.66\ \text{mol H}$$

$$53.3\ \text{g O} \times \frac{1\ \text{mol O}}{16.00\ \text{g O}} = 3.33\ \text{mol O}$$

$$\frac{C_{3.33}}{3.33}\ \frac{H_{6.66}}{3.33}\ \frac{O_{3.33}}{3.33} \longrightarrow CH_2O \quad \text{empirical formula}$$

$$\frac{\text{molar mass of lactate}}{\text{mass of } CH_2O} \longrightarrow \frac{90.08\ \text{g/mol}}{30.03\ \text{g/mol}} = \mathbf{3}$$

$\longrightarrow$ **$C_3H_6O_3$ is the molecular formula**

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Figure 3.4 Combustion apparatus for determining formulas of organic compounds.

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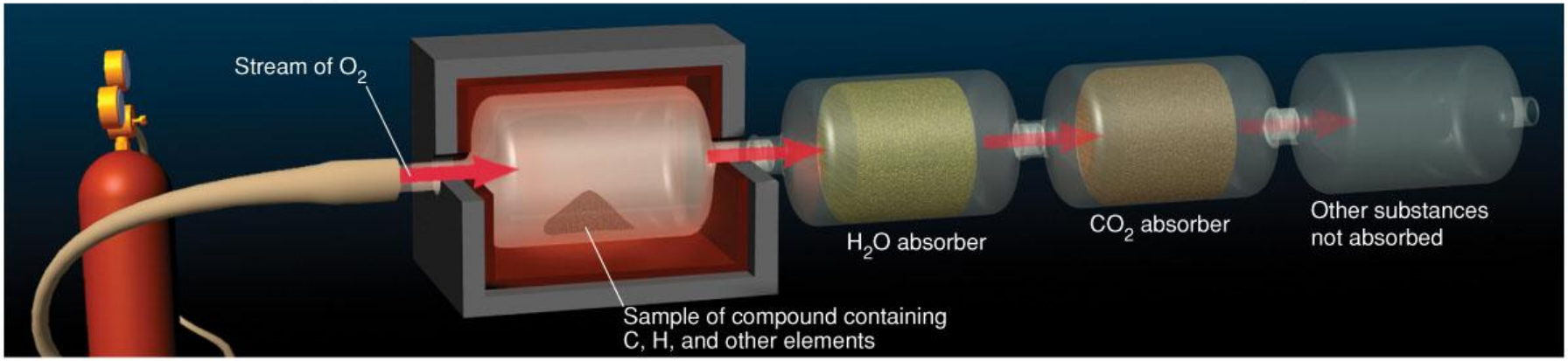

$$C_nH_m + (n+\frac{m}{4})\,O_2 = n\,CO(g) + \frac{m}{2}H_2O(g)$$

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Sample Problem 3.11

Determining a Molecular Formula from Combustion Analysis

PROBLEM:

When a 1.000 g sample of vitamin C ($\mathcal{M}$ = 176.12 g/mol) is placed in a combustion chamber and burned, the following data are obtained:

mass of CO_2 absorber after combustion = 85.35 g
mass of CO_2 absorber before combustion = 83.85 g
mass of H_2O absorber after combustion = 37.96 g
mass of H_2O absorber before combustion = 37.55 g

What is the molecular formula of vitamin C?

PLAN: The masses of CO_2 and H_2O produced will give us the masses of C and H present in the original sample. From this we can determine the mass of O.

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Sample Problem 3.11

(mass after combustion – mass before) for each absorber = mass of compound in each absorber

↓ mass of each compound x mass % of oxidized element

mass of each oxidized element

↓ mass of vitamin C – (mass of C + H)

mass of O

↓ divide each mass by $\mathcal{M}$

mol of C, H, and O

↓ use # mols as subscripts; convert to integers

empirical formula → **molecular formula**

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Sample Problem 3.11

SOLUTION: For CO_2: 85.35 g - 83.85 g = 1.50 g

$$1.50 \text{ g } CO_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g } CO_2} = 0.409 \text{ g C}$$

For H_2O: 37.96 g - 37.55 g = 0.41 g

$$0.41 \text{ g } H_2O \times \frac{2.016 \text{ g H}}{18.02 \text{ g } H_2O} = 0.046 \text{ g H}$$

mass of O = mass of vitamin C – (mass of C + mass of H)

= 1.000 g - (0.409 + 0.046) g = 0.545 g O

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Sample Problem 3.11

Convert mass to moles:

$$\frac{0.409 \text{ g C}}{12.01 \text{ g/mol C}} = 0.0341 \text{ mol C} \qquad \frac{0.046 \text{ g H}}{1.008 \text{ g/mol H}} = 0.0456 \text{ mol H}$$

$$\frac{0.545 \text{ g O}}{16.00 \text{ g/mol O}} = 0.0341 \text{ mol O}$$

Divide by smallest to get the preliminary formula:

$$\text{C} \quad \frac{0.0341}{0.0341} = 1 \qquad \text{H} \quad \frac{0.0456}{0.0341} = 1.34 \qquad \text{O} \quad \frac{0.0341}{0.0341} = 1$$

$$C_1H_{1.34}O_1 = C_3H_{4.01}O_3 \longrightarrow C_3H_4O_3$$

Divide molar mass by mass of empirical formula:

$$\frac{176.12 \text{ g/mol}}{88.06 \text{ g}} = 2.000 \text{ mol} \longrightarrow \boxed{\mathbf{C_6H_8O_6}}$$

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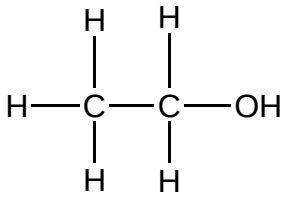
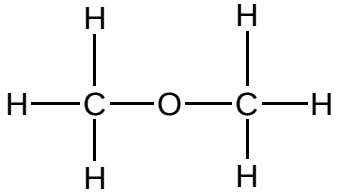
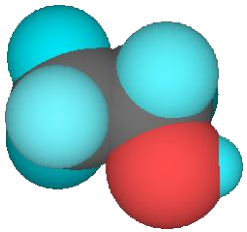
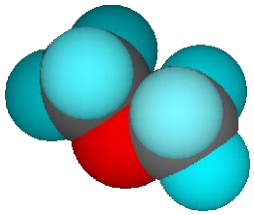
Table 3.2 Two Constitutional Isomers of C_2H_6O

Property	C_2H_6O	
	Ethanol	Dimethyl Ether
$\mathcal{M}$ (g/mol)	46.07	46.07
Boiling Point	78.5°C	-25ºC
Density at 20ºC	0.789 g/mL (liquid)	0.00195 g/mL (gas)
Structural formula		
Space-filling model		

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Writing and Balancing Chemical Equations

A ***chemical equation*** uses formulas to express the ***identities*** and ***quantities*** of substances involved in a physical or chemical change.

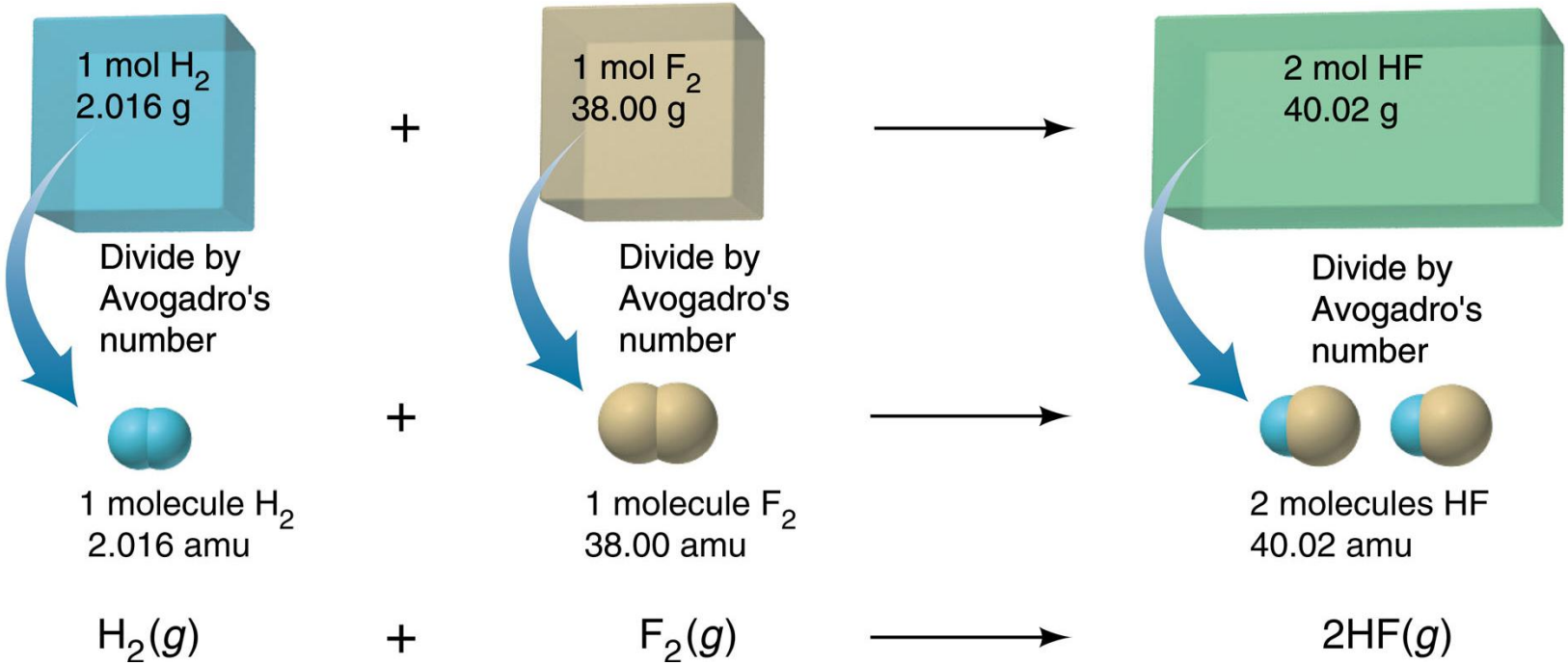

Figure 3.5

The formation of HF gas on the macroscopic and molecular levels.

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Figure 3.6 **A three-level view of the reaction between magnesium and oxygen.**

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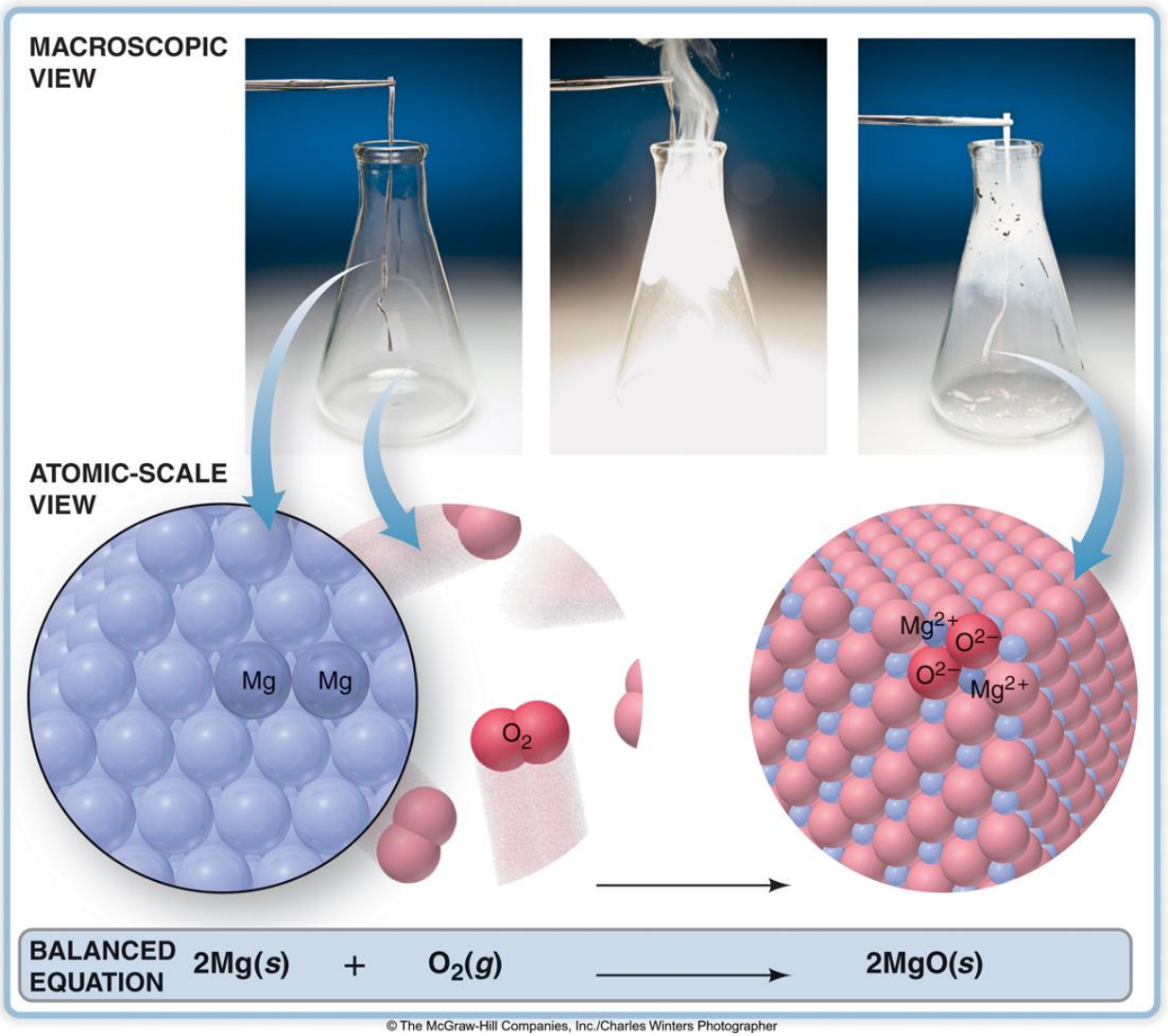

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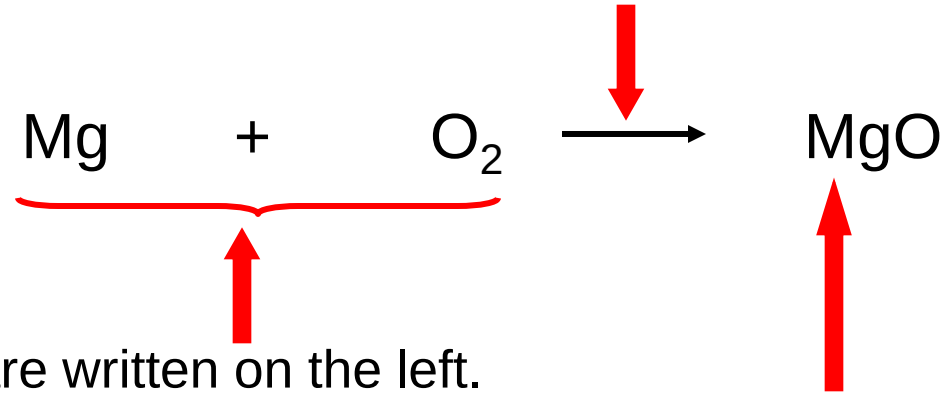
Features of Chemical Equations

A **yield arrow** points from reactants to products.



Reactants are written on the left.

Products are written on the right.

The equation must be **balanced**; the same number and type of each atom must appear on both sides.

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Balancing a Chemical Equation

translate the statement

magnesium and oxygen gas react to give magnesium oxide:

$Mg + O_2 \rightarrow MgO$

balance the atoms using *coefficients*; *formulas cannot be changed*

$\mathbf{2}Mg + O_2 \rightarrow \mathbf{2}MgO$

adjust coefficients if necessary

check that all atoms balance → **specify states of matter**

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

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Sample Problem 3.12 Balancing Chemical Equations

PROBLEM: Within the cylinders of a car's engine, the hydrocarbon octane (C_8H_{18}), one of many components of gasoline, mixes with oxygen from the air and burns to form carbon dioxide and water vapor. Write a balanced equation for this reaction.

PLAN:

translate the statement

↓

balance the atoms

↓

adjust the coefficients

↓

check the atoms balance

↓

specify states of matter

SOLUTION:

$$C_8H_{18} + O_2 \longrightarrow CO_2 + H_2O$$

$$C_8H_{18} + \frac{25}{2}O_2 \longrightarrow 8\,CO_2 + 9\,H_2O$$

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

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

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

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Molecular Scene
Combustion of Octane

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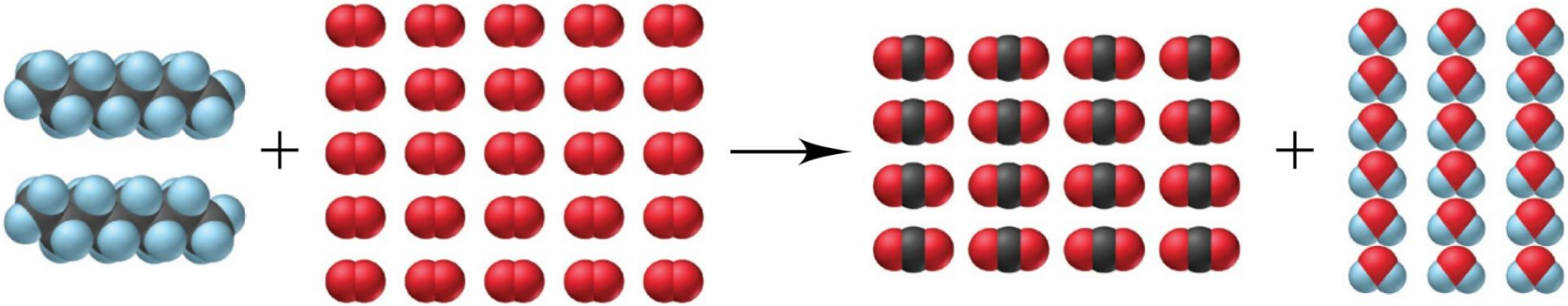

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

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Sample Problem 3.13 Balancing an Equation from a Molecular Scene

PROBLEM: The following molecular scenes depict an important reaction in nitrogen chemistry. The blue spheres represent nitrogen while the red spheres represent oxygen. Write a balanced equation for this reaction.

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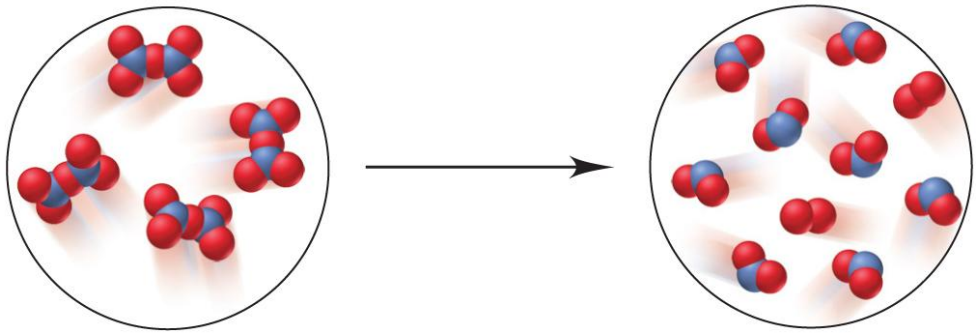

PLAN: Determine the formulas of the reactants and products from their composition. Arrange this information in the correct equation format and balance correctly, including the states of matter.

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Sample Problem 3.13

SOLUTION:

The reactant circle shows only one type of molecule, composed of 2 N and 5 O atoms. The formula is thus N_2O_5. There are 4 N_2O_5 molecules depicted.

The product circle shows two types of molecule; one has 1 N and 2 O atoms while the other has 2 O atoms. The products are NO_2 and O_2. There are 8 NO_2 molecules and 2 O_2 molecules shown.

The reaction depicted is $\mathbf{4\ N_2O_5 \rightarrow 8\ NO_2 + 2\ O_2}$.

Writing the equation with the smallest whole-number coefficients and states of matter included;

$$\mathbf{2\ N_2O_5\ (}\boldsymbol{g}\mathbf{)} \rightarrow \mathbf{4\ NO_2\ (}\boldsymbol{g}\mathbf{) + O_2\ (}\boldsymbol{g}\mathbf{)}$$

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Stoichiometric Calculations

- The coefficients in a balanced chemical equation
  - represent the relative number of reactant and product particles
  - and the relative number of moles of each.
- Since moles are related to mass
  - the equation can be used to calculate masses of reactants and/or products for a given reaction.
- The mole ratios from the balanced equation are used as conversion factors.

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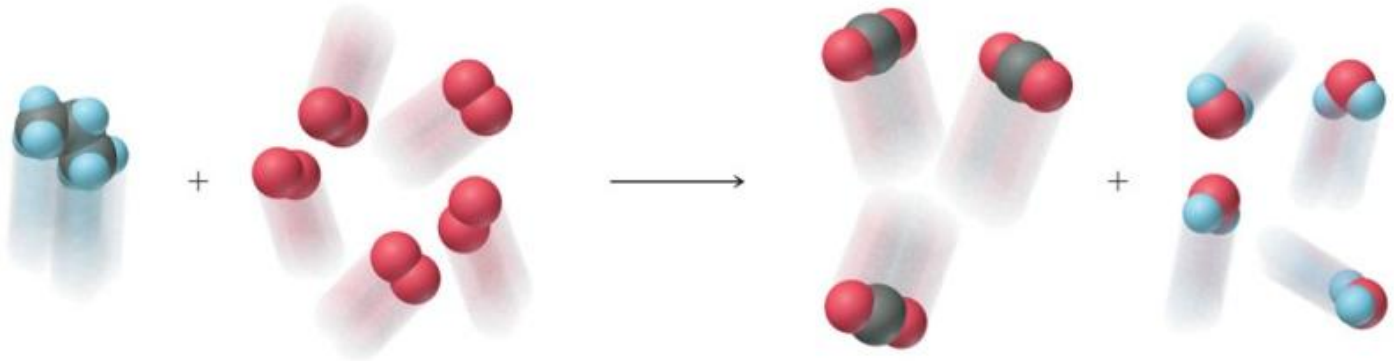
Table 3.3 Information Contained in a Balanced Equation

Viewed in Terms of	Reactants		Products
	$C_3H_8(g) + 5\ O_2(g)$	⟶	$3\ CO_2(g) + 4\ H_2O(g)$
Molecules	1 molecule C_3H_8 + 5 molecules O_2	⟶	3 molecules CO_2 + 4 molecules H_2O



Amount (mol)	1 mol C_3H_8 + 5 mol O_2	⟶	3 mol CO_2 + 4 mol H_2O
Mass (amu)	44.09 amu C_3H_8 + 160.00 amu O_2	⟶	132.03 amu CO_2 + 72.06 amu H_2O
Mass (g)	44.09 g C_3H_8 + 160.00 g O_2	⟶	132.03 g CO_2 + 72.06 g H_2O
Total Mass (g)	204.09 g	⟶	204.09 g

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Figure 3.7 **Summary of amount-mass-number relationships in a chemical equation.**

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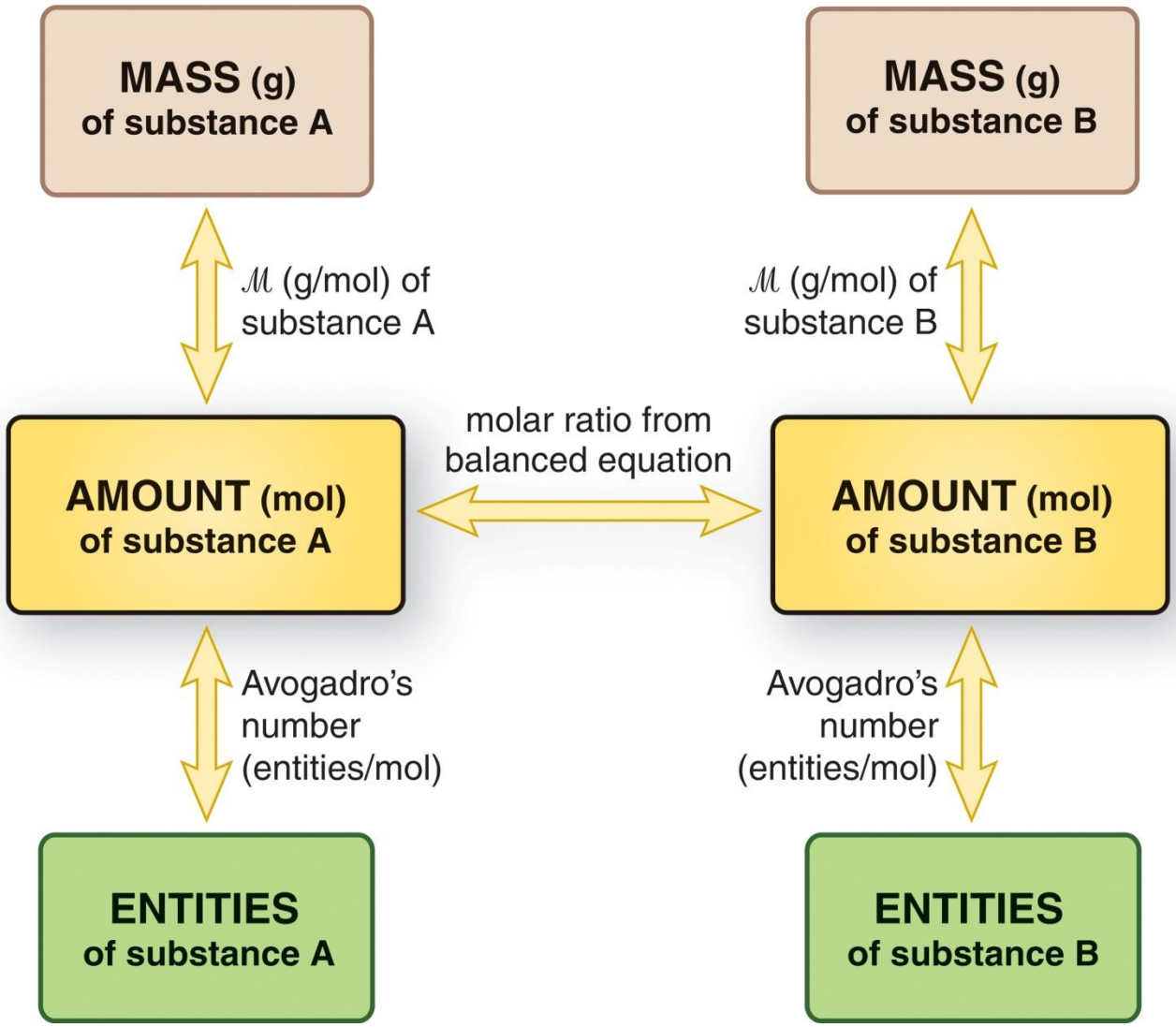

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Sample Problem 3.14

Calculating Quantities of Reactants and Products: Amount (mol) to Amount (mol)

PROBLEM: Copper is obtained from copper(I) sulfide by roasting it in the presence of oxygen gas to form powdered copper(I) oxide and gaseous sulfur dioxide.

How many moles of oxygen are required to roast 10.0 mol of copper(I) sulfide?

PLAN:

write and balance the equation

↓ **use the mole ratio as a conversion factor**

moles of oxygen

SOLUTION:

$$2\ Cu_2S\ (s) + 3\ O_2\ (g) \rightarrow 2\ Cu_2O\ (s) + 2\ SO_2\ (g)$$

$$10.0\ \text{mol } Cu_2S \times \frac{3\ \text{mol } O_2}{2\ \text{mol } Cu_2S} = \mathbf{15.0\ mol\ O_2}$$

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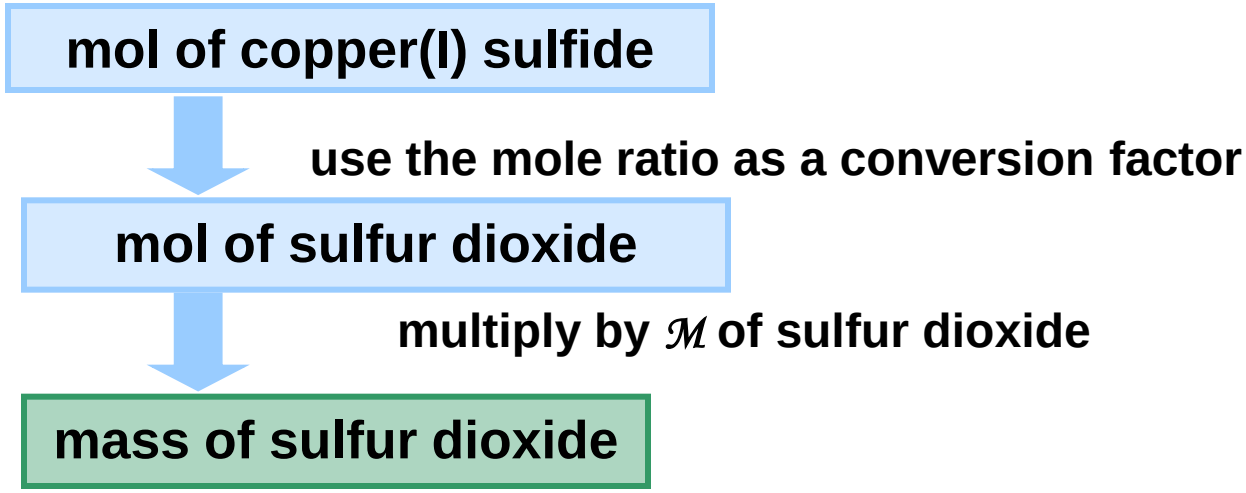
Sample Problem 3.15

Calculating Quantities of Reactants and Products: Amount (mol) to Mass (g)

PROBLEM: During the process of roasting copper(I) sulfide, how many grams of sulfur dioxide form when 10.0 mol of copper(I) sulfide reacts?

PLAN: Using the balanced equation from the previous problem, we again use the mole ratio as a conversion factor.



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Sample Problem 3.15

SOLUTION: $2\ Cu_2S\ (s) + 3\ O_2\ (g) \rightarrow 2\ Cu_2O\ (s) + 2\ SO_2\ (g)$

$$10.0\ \text{mol } Cu_2S \times \frac{2\ \text{mol } SO_2}{2\ \text{mol } Cu_2S} \times \frac{64.07\ \text{g } SO_2}{1\ \text{mol } SO_2} = \mathbf{641\ g\ SO_2}$$

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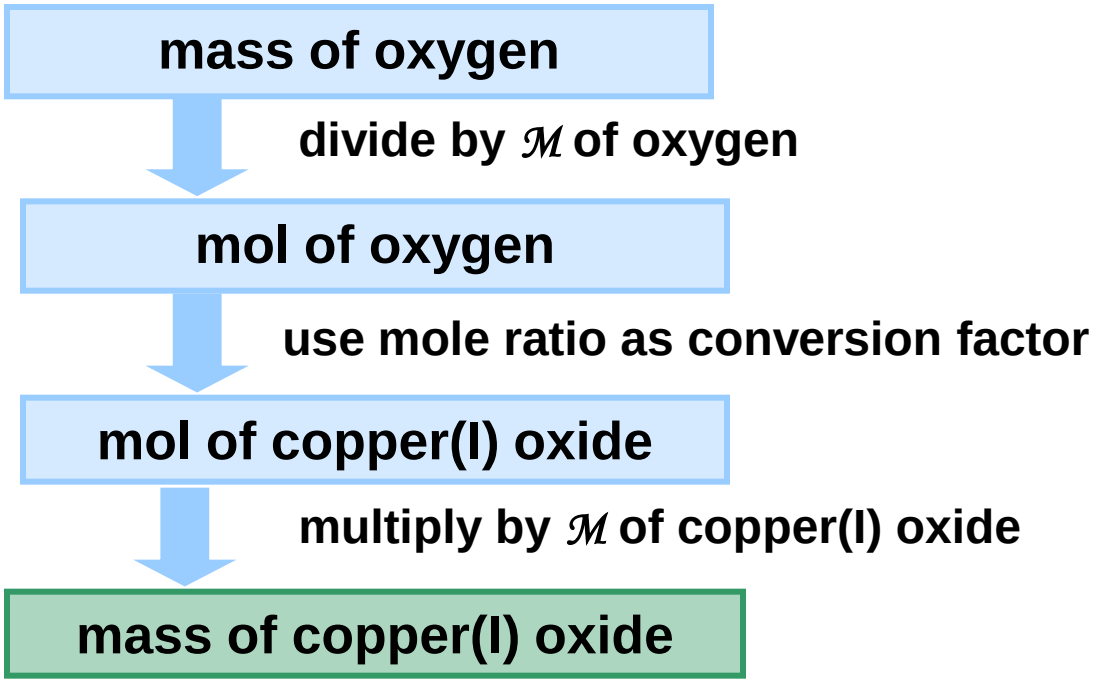
Sample Problem 3.16

Calculating Quantities of Reactants and Products: Mass to Mass

PROBLEM: During the roasting of copper(I) sulfide, how many kilograms of oxygen are required to form 2.86 kg of copper(I) oxide?

PLAN:



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Sample Problem 3.16

SOLUTION: $2\ Cu_2S\ (s) + 3\ O_2\ (g) \rightarrow 2\ Cu_2O\ (s) + 2\ SO_2\ (g)$

$$2.86\ \text{kg}\ Cu_2O \times \frac{10^3\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mol}\ Cu_2O}{143.10\ \text{g}\ Cu_2O} = 20.0\ \text{mol}\ Cu_2O$$

$$20.0\ \text{mol}\ Cu_2O \times \frac{3\ \text{mol}\ O_2}{2\ \text{mol}\ Cu_2O} \times \frac{32.00\ \text{g}\ O_2}{1\ \text{mol}\ O_2} \times \frac{1\ \text{kg}}{10^3\ \text{g}} = \mathbf{0.959\ kg\ O_2}$$

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Reactions in Sequence

- Reactions often occur in sequence.
- The product of one reaction becomes a reactant in the next.
- An overall reaction is written by combining the reactions;
  - any substance that forms in one reaction and reacts in the next can be eliminated.

$$\begin{aligned} A &\rightarrow C \\ C &\rightarrow B \\ \hline A &\rightarrow B \end{aligned}$$

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Limiting Reactants

- So far we have assumed that reactants are present in the correct amounts to react completely.
- In reality, one reactant may ***limit*** the amount of product that can form.
- The ***limiting*** reactant will be completely used up in the reaction.
- The reactant that is *not* limiting is in ***excess*** – some of this reactant will be left over.

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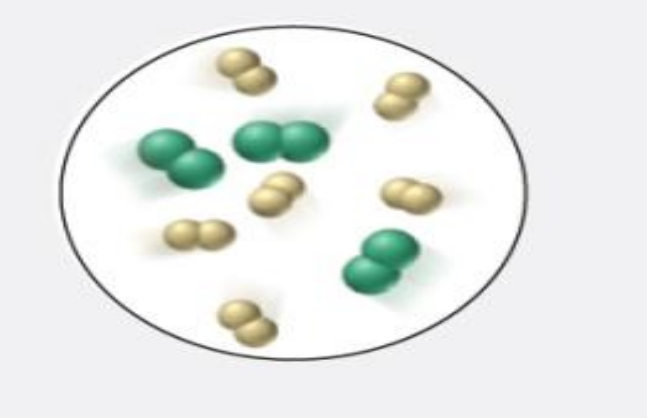
Sample Problem 3.17 Using Molecular Depictions in a Limiting-Reactant Problem

PROBLEM: Chlorine trifluoride, an extremely reactive substance, is formed as a gas by the reaction of elemental chlorine and fluorine. The molecular scene shows a representative portion of the reaction mixture before the reaction starts. (Chlorine is green, and fluorine is yellow.)



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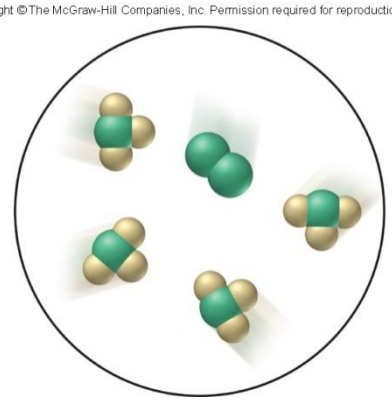

(a) Find the limiting reactant.
(b) Write a reaction table for the process.
(c) Draw a representative portion of the mixture after the reaction is complete. (Hint: The ClF_3 molecule has 1 Cl atom bonded to 3 individual F atoms).

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Sample Problem 3.17

PLAN: Write a balanced chemical equation. To determine the limiting reactant, find the number of molecules of product that would form from the given numbers of molecules of each reactant. Use these numbers to write a reaction table and use the reaction table to draw the final reaction scene.

SOLUTION: The balanced equation is $Cl_2\,(g) + 3F_2\,(g) \rightarrow 2ClF_3\,(g)$

There are 3 molecules of Cl_2 and 6 molecules of F_2 depicted:

$$3 \text{ molecules } Cl_2 \times \frac{2 \text{ molecules } ClF_3}{1 \text{ molecule } Cl_2} = 6 \text{ molecules } ClF_3$$

$$6 \text{ molecules } F_2 \times \frac{2 \text{ molecules } ClF_3}{3 \text{ molecule } Cl_2} = 4 \text{ molecules } ClF_3$$

Since the given amount of F_2 can form less product, it is the limiting reactant.

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Sample Problem 3.17

We use the amount of F_2 to determine the "change" in the reaction table, since F_2 is the limiting reactant:

Molecules	**Cl_2 (*g*) + 3F_2 (*g*) → 2ClF_3 (*g*)**		
Initial	3	6	0
Change	-2	**-6**	+4
Final	1	0	4

The final reaction scene shows that all the F_2 has reacted and that there is Cl_2 left over. 4 molecules of ClF_2 have formed:

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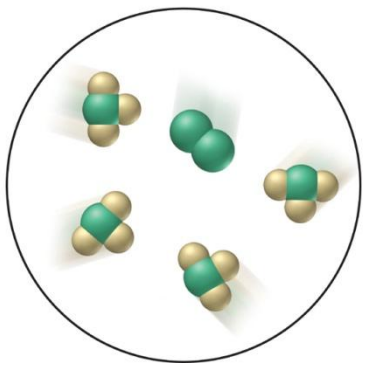

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Sample Problem 3.18

Calculating Quantities in a Limiting-Reactant Problem: Amount to Amount

PROBLEM: In another preparation of ClF_3, 0.750 mol of Cl_2 reacts with 3.00 mol of F_2.

(a) Find the limiting reactant.
(b) Write a reaction table.

PLAN: Find the limiting reactant by calculating the amount (mol) of ClF_3 that can be formed from each given amount of reactant. Use this information to construct a reaction table.

SOLUTION: The balanced equation is $Cl_2\,(g) + 3F_2\,(g) \rightarrow 2ClF_3\,(g)$

$$0.750 \text{ mol } Cl_2 \times \frac{2 \text{ mol } ClF_3}{1 \text{ mol } Cl_2} = 1.50 \text{ mol } ClF_3$$

$$3.00 \text{ mol } F_2 \times \frac{2 \text{ mol } ClF_3}{3 \text{ mol } F_2} = 2.00 \text{ mol } ClF_3$$

Cl_2 is limiting, because it yields less ClF_3.

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Sample Problem 3.18

All the Cl_2 reacts since this is the limiting reactant. For every 1 Cl_2 that reacts, 3 F_2 will react, so 3(0.750) or 2.25 moles of F_2 reacts.

Moles	**Cl_2 (*g*) +**	**$3F_2$ (*g*) →**	**$2ClF_3$ (*g*)**
Initial	0.750	3.00	0
Change	**-0.750**	- 2.25	+1.50
Final	0	0.75	1.50

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Sample Problem 3.19

Calculating Quantities in a Limiting-Reactant Problem: Mass to Mass

PROBLEM: A fuel mixture used in the early days of rocketry consisted of two liquids, hydrazine (N_2H_4) and dinitrogen tetraoxide (N_2O_4), which ignite on contact to form nitrogen gas and water vapor.

(a) How many grams of nitrogen gas form when 1.00×10^2 g of N_2H_4 and 2.00×10^2 g of N_2O_4 are mixed?

(b) Write a reaction table for this process.

PLAN: Find the limiting reactant by calculating the amount (mol) of ClF_3 that can be formed from each given mass of reactant. Use this information to construct a reaction table.

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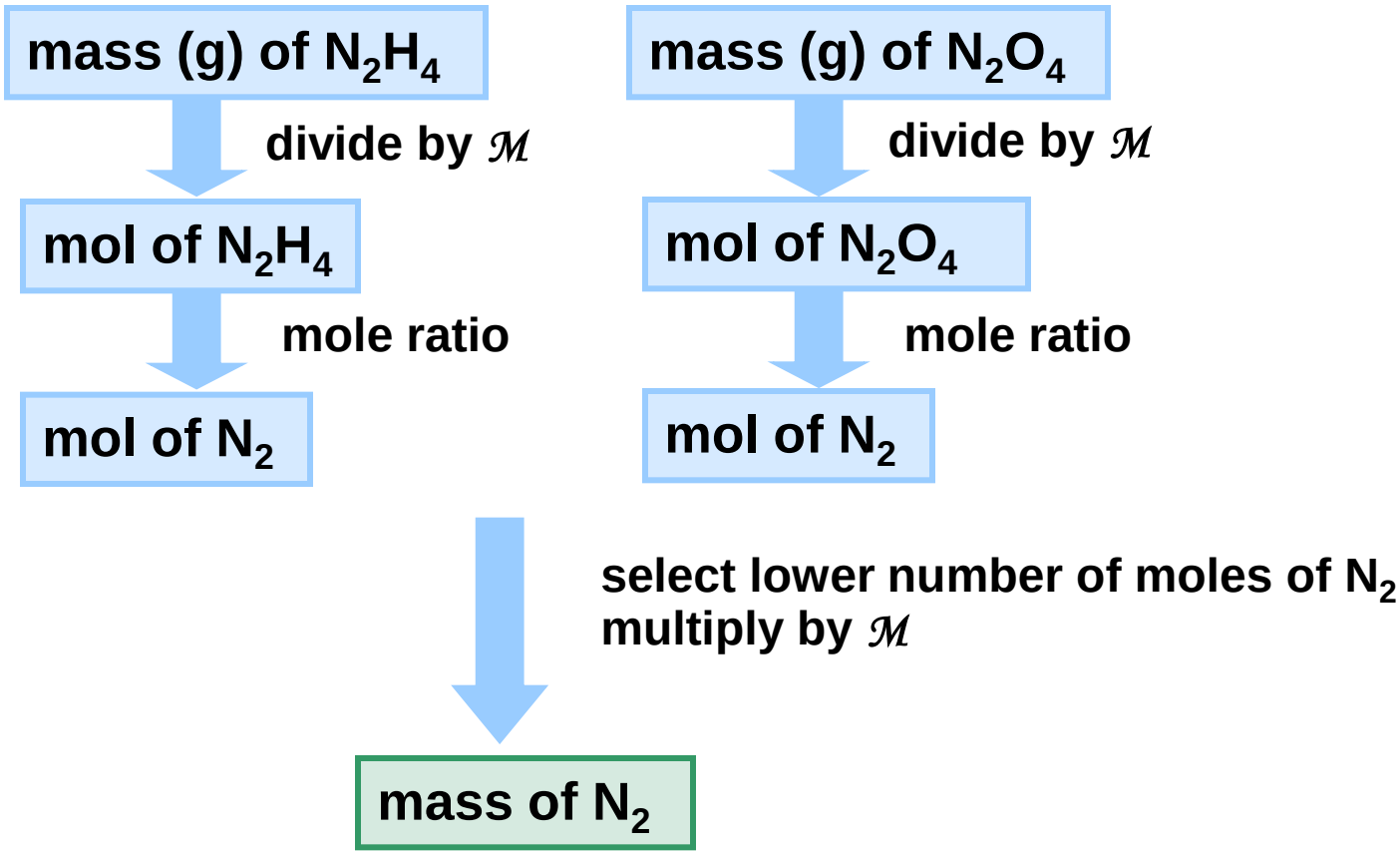
Sample Problem 3.19



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Sample Problem 3.19

SOLUTION: $2N_2H_4\,(l) + N_2O\,(l) \rightarrow 3N_2\,(g) + 4H_2O\,(g)$

For N_2H_4: 1.00×10^2 g $N_2H_4 \times \dfrac{1 \text{ mol } N_2H_4}{32.05 \text{ g } N_2H_4} = 3.12 \text{ mol } N_2H_4$

$$3.12 \text{ mol } N_2H_4 \times \frac{3 \text{ mol } N_2}{2 \text{ mol } N_2H_4} = 4.68 \text{ mol } N_2$$

For N_2O_4: 2.00×10^2 g $N_2O_4 \times \dfrac{1 \text{ mol } N_2O_4}{92.02 \text{ g } N_2O_4} = 2.17 \text{ mol } N_2$

$$2.17 \text{ mol } N_2O_4 \times \frac{3 \text{ mol } N_2}{1 \text{ mol } N_2O_4} = 6.51 \text{ mol } N_2$$

N_2H_4 is limiting and only 4.68 mol of N_2 can be produced:

$$4.68 \text{ mol } N_2 \times \frac{28.02 \text{ g } N_2}{1 \text{ mol } N_2} = \mathbf{131 \text{ g } N_2}$$

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Sample Problem 3.19

All the N_2H_4 reacts since it is the limiting reactant. For every 2 moles of N_2H_4 that react 1 mol of N_2O_4 reacts and 3 mol of N_2 form:

$$3.12 \text{ mol } N_2H_4 \times \frac{1 \text{ mol } N_2O_4}{2 \text{ mol } N_2H_4} = 1.56 \text{ mol } N_2O_4 \text{ reacts}$$

Moles	**$2N_2H_4$ (l) +**	**N_2O_4 (*l*) →**	**$3N_2$ (*g*) +**	**$4H_2O$ (*g*)**
Initial	3.12	2.17	0	0
Change	**-3.12**	**- 1.56**	**+4.68**	+6.24
Final	0	0.61	4.68	6.24

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Reaction Yields

The **theoretical yield** is the amount of product calculated using the molar ratios from the balanced equation.

The **actual yield** is the amount of product actually obtained.

The actual yield is usually less than the theoretical yield.

$$\text{\% yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

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Figure 3.8 **The effect of side reactions on the yield of the main product.**

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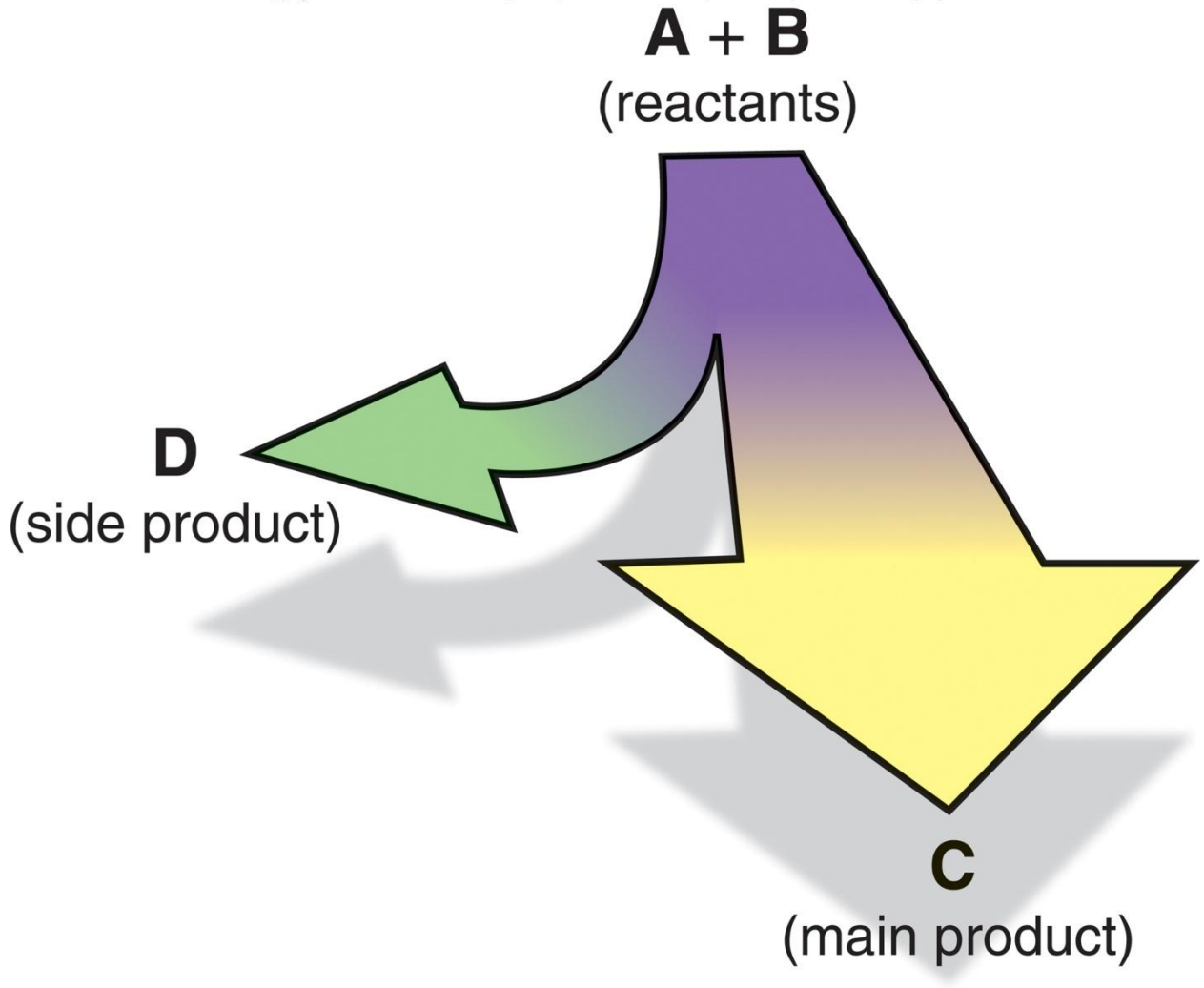

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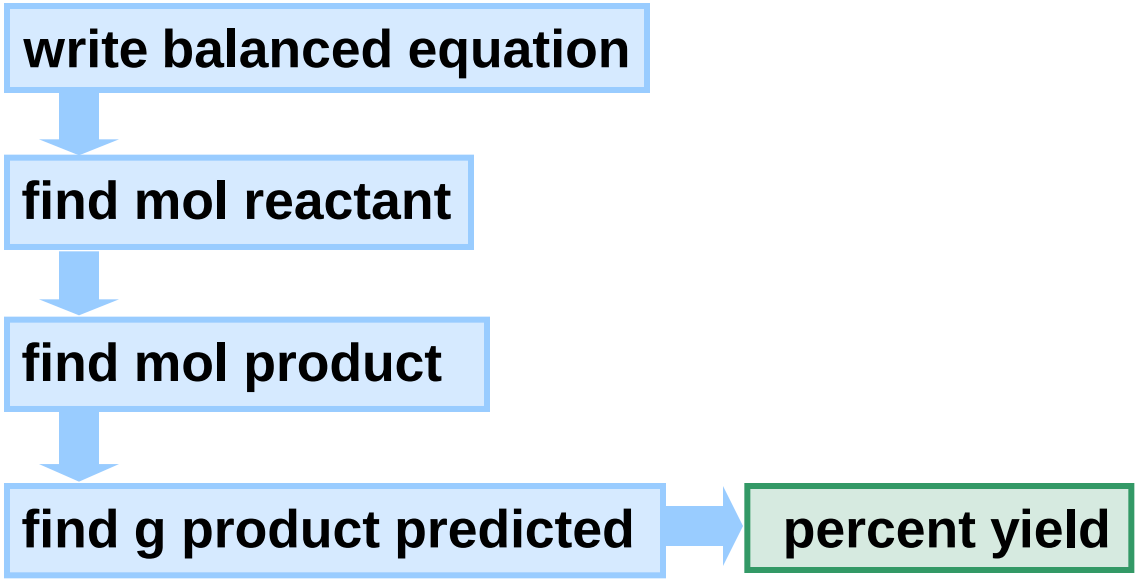
Sample Problem 3.20 Calculating Percent Yield

PROBLEM: Silicon carbide (SiC) is made by reacting sand(silicon dioxide, SiO_2) with powdered carbon at high temperature. Carbon monoxide is also formed. What is the percent yield if 51.4 kg of SiC is recovered from processing 100.0 kg of sand?

PLAN:



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Sample Problem 3.20

SOLUTION: $SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g)$

What is the percent yield if 51.4 kg of SiC is recovered from processing 100.0 kg of sand?

$$100.0 \cancel{\text{ kg SiO}_2} \times \frac{10^3 \cancel{\text{ g}}}{1 \cancel{\text{ kg}}} \times \frac{1 \text{ mol SiO}_2}{60.09 \cancel{\text{ g SiO}_2}} = 1664 \text{ mol SiO}_2$$

$$\text{mol SiO}_2 = \text{mol SiC} = 1664 \text{ mol SiC}$$

$$1664 \cancel{\text{ mol SiC}} \times \frac{40.10 \cancel{\text{ g SiC}}}{1 \cancel{\text{ mol SiC}}} \times \frac{1 \text{ kg}}{10^3 \cancel{\text{ g}}} = 66.73 \text{ kg}$$

$$\frac{51.4 \text{ kg}}{66.73 \text{ kg}} \times 100 \quad \boxed{\textbf{= 77.0\%}}$$

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Solution Stoichiometry

- Many reactions occur in solution.
- A solution consists of one or more solutes dissolved in a ***solvent***.
- The ***concentration*** of a solution is given by the quantity of solute present in a given quantity of solution.
- ***Molarity*** (*M*) is often used to express concentration.

$$\text{Molarity} = \frac{\text{moles solute}}{\text{liters of solution}} \qquad M = \frac{\text{mol solute}}{\text{L soln}}$$

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Sample Problem 3.21 Calculating the Molarity of a Solution

PROBLEM: What is the molarity of an aqueous solution that contains 0.715 mol of glycine (H_2NCH_2COOH) in 495 mL?

PLAN:

Molarity is the number of moles of solute per liter of solution.

mol of glycine

↓ **divide by volume**

concentration in mol/mL

↓ **10^3 mL = 1 L**

molarity of glycine

SOLUTION:

$$\frac{0.715 \text{ mol glycine}}{495 \cancel{\text{mL}} \text{ soln}} \times \frac{1000 \cancel{\text{mL}}}{1 \text{ L}}$$

= 1.44 *M* glycine

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Figure 3.9 **Summary of mass-mole-number-volume relationships in solution.**

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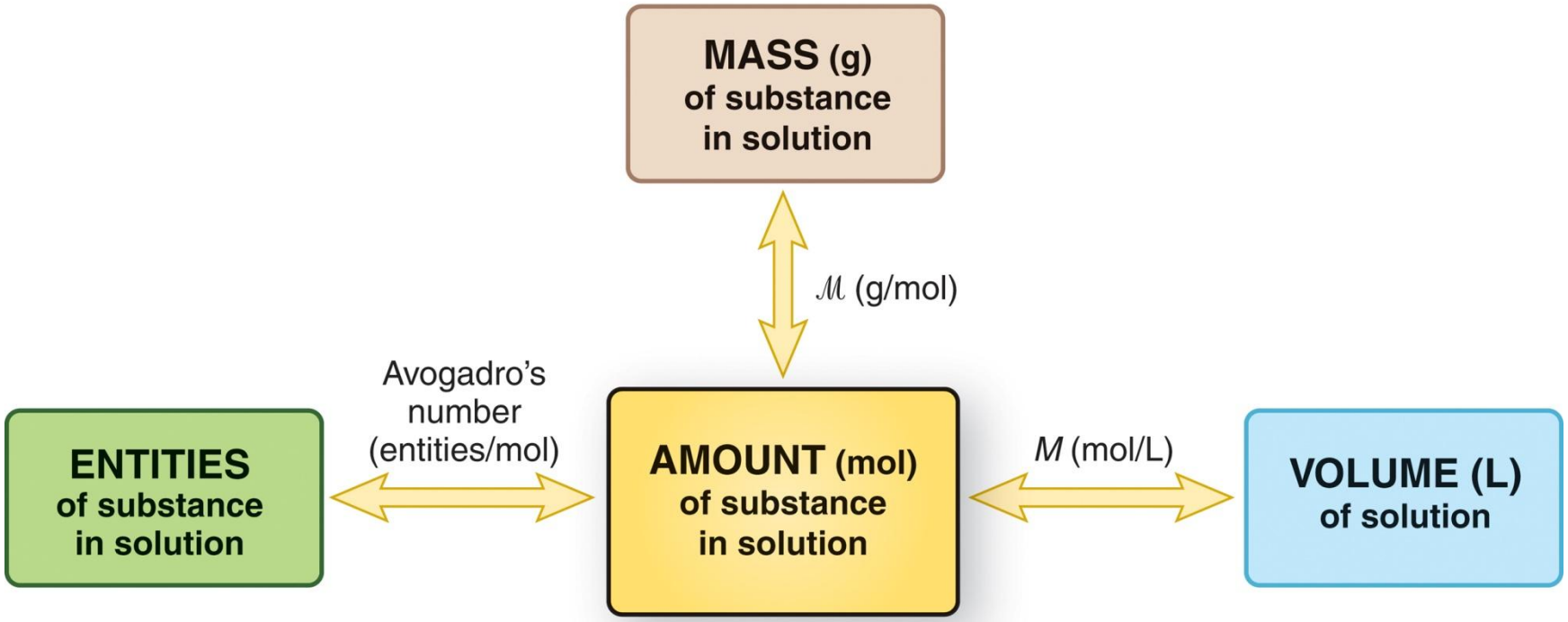

M X V = # of moles

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Sample Problem 3.22

Calculating Mass of Solute in a Given Volume of Solution

PROBLEM: How many grams of solute are in 1.75 L of 0.460 *M* sodium monohydrogen phosphate buffer solution?

PLAN: Calculate the moles of solute using the given molarity and volume. Convert moles to mass using the molar mass of the solute.

volume of solution

↓ **multiply by *M***

moles of solute

↓ **multiply by $\mathcal{M}$**

grams of solute

SOLUTION:

$$1.75 \cancel{\text{L}} \times \frac{0.460 \text{ moles}}{1 \cancel{\text{L}}} = 0.805 \text{ mol } Na_2HPO_4$$

$$0.805 \cancel{\text{mol } Na_2HPO_4} \times \frac{141.96 \text{ g } Na_2HPO_4}{1 \cancel{\text{mol } Na_2HPO_4}} = \mathbf{114 \text{ g } Na_2HPO_4}$$

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Figure 3.10 Converting a concentrated solution to a dilute solution.

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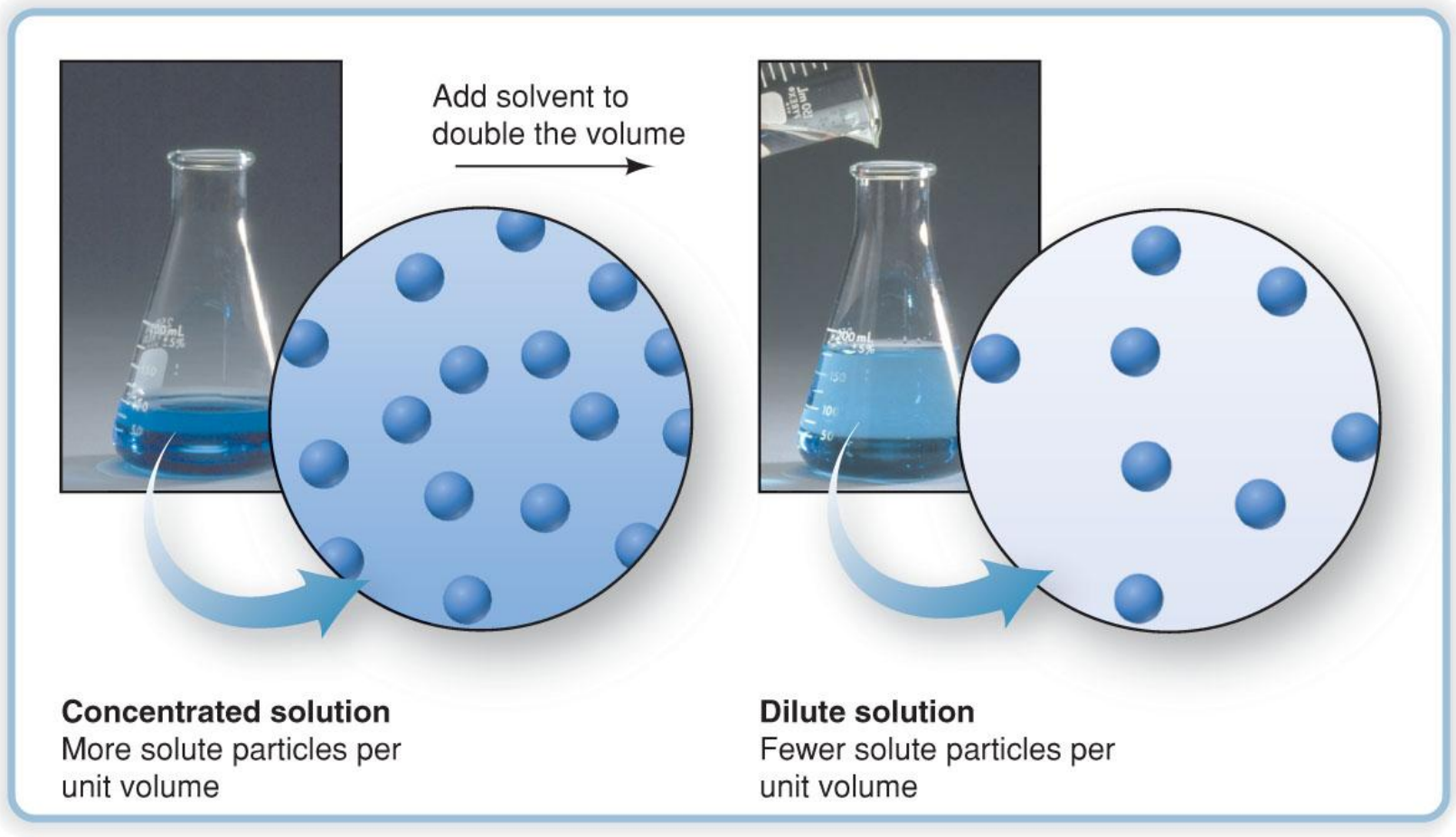

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Sample Problem 3.23

Preparing a Dilute Solution from a Concentrated Solution

PROBLEM: "Isotonic saline" is a 0.15 *M* aqueous solution of NaCl. How would you prepare 0.80 L of isotonic saline from a 6.0 *M* stock solution?

PLAN: To dilute a concentrated solution, we add only solvent, so the *moles of solute are the same in both solutions*. The volume and molarity of the dilute solution gives us the moles of solute. Then we calculate the volume of concentrated solution that contains the same number of moles.

volume of dilute soln

↓ **multiply by *M* of dilute soln**

moles of NaCl in dilute soln = mol NaCl in concentrated soln

↓ **divide by *M* of concentrated soln**

L of concentrated soln

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Sample Problem 3.23

$$M_{dil} \times V_{dil} = \#\ mol\ solute = M_{conc} \times V_{conc}$$

SOLUTION:

Using the volume and molarity for the dilute solution:

$$0.80\ \cancel{L\ soln} \times \frac{0.15\ mol\ NaCl}{1\ \cancel{L\ soln}} = 0.12\ mol\ NaCl$$

Using the moles of solute and molarity for the concentrated solution:

$$0.12\ \cancel{mol\ NaCl} \times \frac{1\ L\ soln}{6.0\ \cancel{mol\ NaCl}} = \mathbf{0.020\ L\ soln}$$

A 0.020 L portion of the concentrated solution must be diluted to a final volume of 0.80 L.

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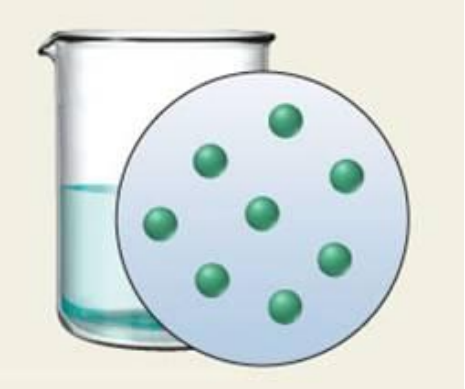
Sample Problem 3.24 Visualizing Changes in Concentration

PROBLEM: The beaker and circle represent a unit volume of solution. Draw the solution after each of these changes:

(a) For every 1 mL of solution, 1 mL of solvent is added.

(b) One third of the volume of the solution is boiled off.



PLAN: Only the volume of the solution changes; the total number of moles of solute remains the same. Find the new volume and calculate the number of moles of solute per unit volume.

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Sample Problem 3.24

SOLUTION: $N_{dil} \times V_{dil} = N_{conc} \times V_{conc}$

where N is the number of particles.

(a) $$N_{dil} = N_{conc} \times \frac{V_{conc}}{V_{dil}} = 8 \text{ particles} \times \frac{1 \text{ mL}}{2 \text{ mL}} = 4 \text{ particles}$$

(b) $$N_{conc} = N_{dil} \times \frac{V_{dil}}{V_{conc}} = 8 \text{ particles} \times \frac{1 \text{ mL}}{\frac{2}{3} \text{ mL}} = 12 \text{ particles}$$

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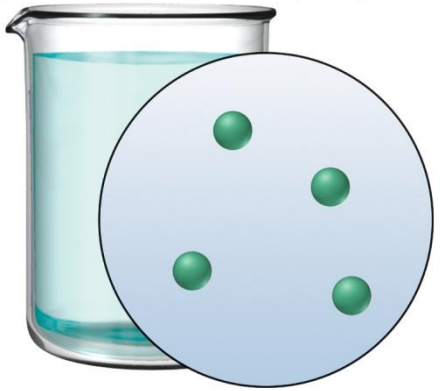

(a)

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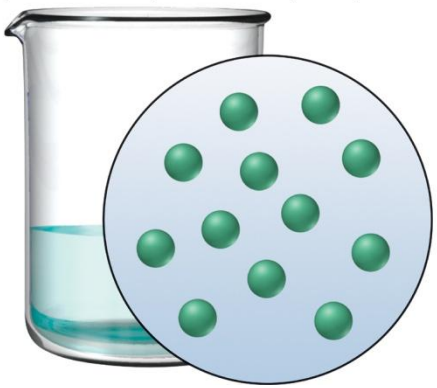

(b)

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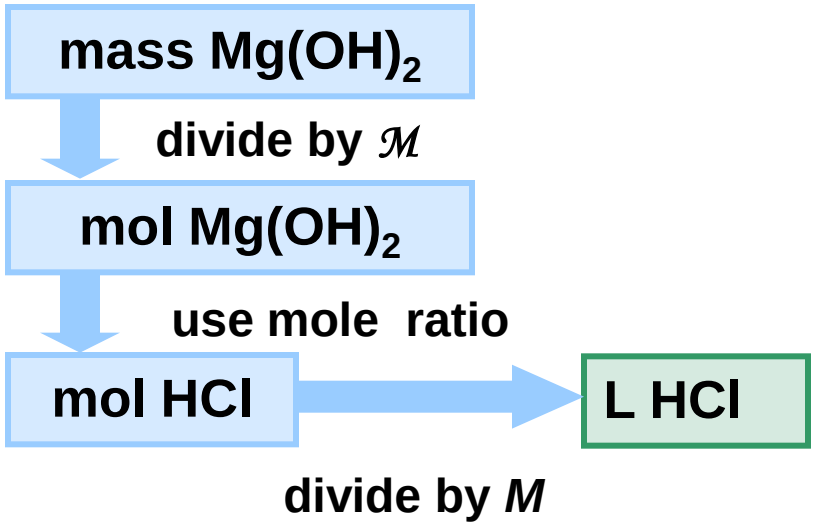
Sample Problem 3.25 Calculating Quantities of Reactants and Products for a Reaction in Solution

PROBLEM: A 0.10 *M* HCl solution is used to simulate the acid concentration of the stomach. How many liters of "stomach acid" react with a tablet containing 0.10 g of magnesium hydroxide?

PLAN: Write a balanced equation and convert the mass of $Mg(OH)_2$ to moles. Use the mole ratio to determine the moles of HCl, then convert to volume using molarity.



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Sample Problem 3.25

SOLUTION:

$$Mg(OH)_2\,(s) + 2HCl\,(aq) \rightarrow MgCl_2\,(aq) + 2H_2O\,(l)$$

$$0.10\ \text{g } Mg(OH)_2 \times \frac{1\ \text{mol } Mg(OH)_2}{58.33\ \text{g } Mg(OH)_2} = 1.7\times10^{-3}\ \text{mol } Mg(OH)_2$$

$$= 1.7\times10^{-3}\ \text{mol } Mg(OH)_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol } Mg(OH)_2} = 3.4\times10^{-3}\ \text{mol HCl}$$

$$3.4\times10^{-3}\ \text{mol HCl} \times \frac{1\text{L HCl soln}}{0.10\ \text{mol HCl}}$$

$= 3.4\times10^{-2}$ L HCl

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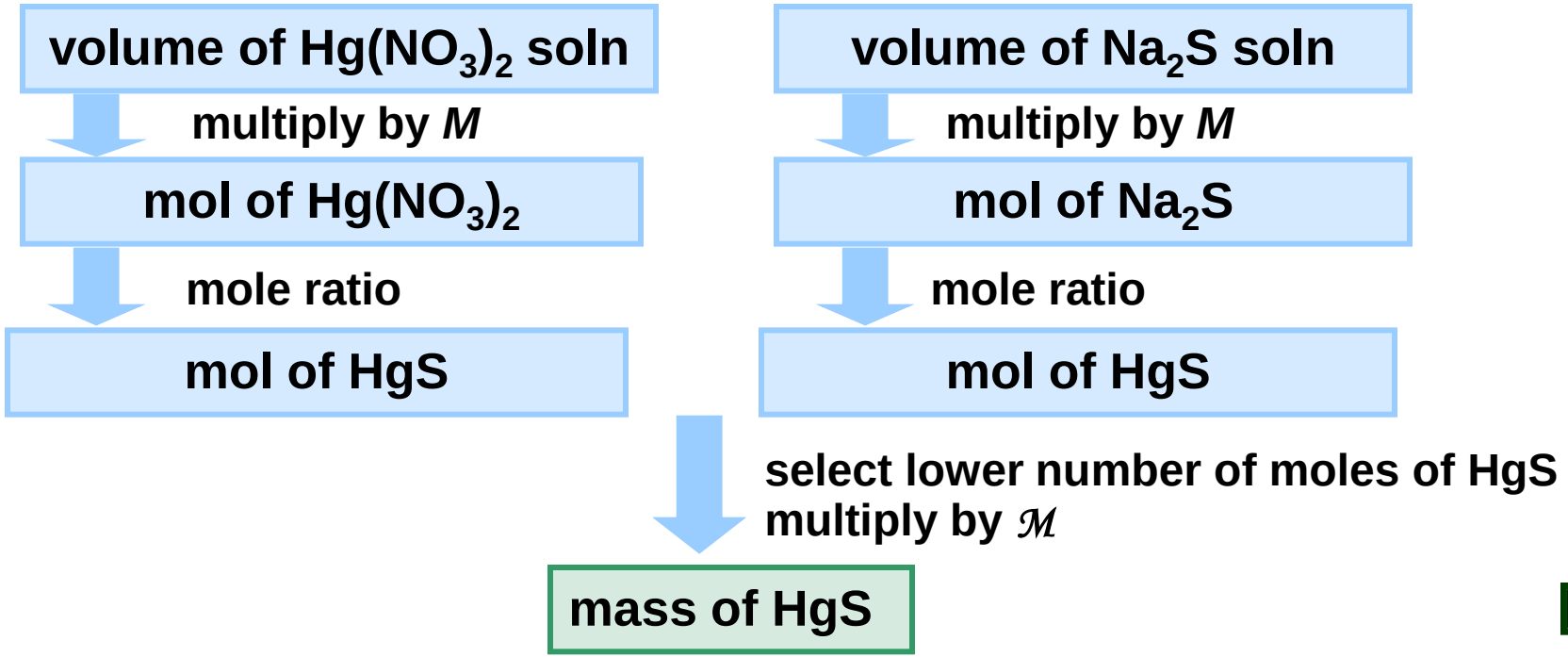
Sample Problem 3.26

Solving Limiting-Reactant Problems for Reactions in Solution

PROBLEM: In a simulation mercury removal from industrial wastewater, 0.050 L of 0.010 *M* mercury(II) nitrate reacts with 0.020 L of 0.10 *M* sodium sulfide. How many grams of mercury(II) sulfide form? Write a reaction table for this process.

PLAN: Write a balanced chemical reaction. Determine limiting reactant. Calculate the grams of mercury(II) sulfide product.



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Sample Problem 3.26

SOLUTION: $Hg(NO_3)_2\,(aq) + Na_2S\,(aq) \rightarrow HgS\,(s) + 2NaNO_3\,(aq)$

$$0.050\ \cancel{L\ Hg(NO_3)_2} \times \frac{0.010\ \cancel{mol\ Hg(NO_3)_2}}{1\ \cancel{L\ Hg(NO_3)_2}} \times \frac{1\ mol\ HgS}{1\ \cancel{mol\ Hg(NO_3)_2}}$$

$$= 5.0 \times 10^{-4}\ mol\ HgS$$

$$0.020\ \cancel{L\ Na_2S} \times \frac{0.10\ \cancel{mol\ Na_2S}}{1\ \cancel{L\ Na_2S}} \times \frac{1\ mol\ HgS}{1\ \cancel{mol\ Na_2S}} = 2.0 \times 10^{-3}\ mol\ HgS$$

$Hg(NO_3)_2$ is the limiting reactant because it yields less HgS.

$$5.0 \times 10^{-4}\ \cancel{mol\ HgS} \times \frac{232.7\ g\ HgS}{1\ \cancel{mol\ HgS}}$$

= 0.12 g HgS

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Sample Problem 3.26

The reaction table is constructed using the amount of $Hg(NO_3)_2$ to determine the changes, since it is the limiting reactant.

Amount	**$Hg(NO_3)_2$ (*aq*) +**	**Na_2S (*aq*) →**	**HgS (*s*) +**	**$2NaNO_3$ (*aq*)**
Initial	5.0×10^{-4}	2.0×10^{-3}	0	0
Change	**-5.0×10^{-4}**	**-5.0×10^{-4}**	**$+5.0 \times 10^{-4}$**	**$+1.0 \times 10^{-3}$**
Final	0	1.5×10^{-3}	5.0×10^{-4}	$+1.0 \times 10^{-3}$

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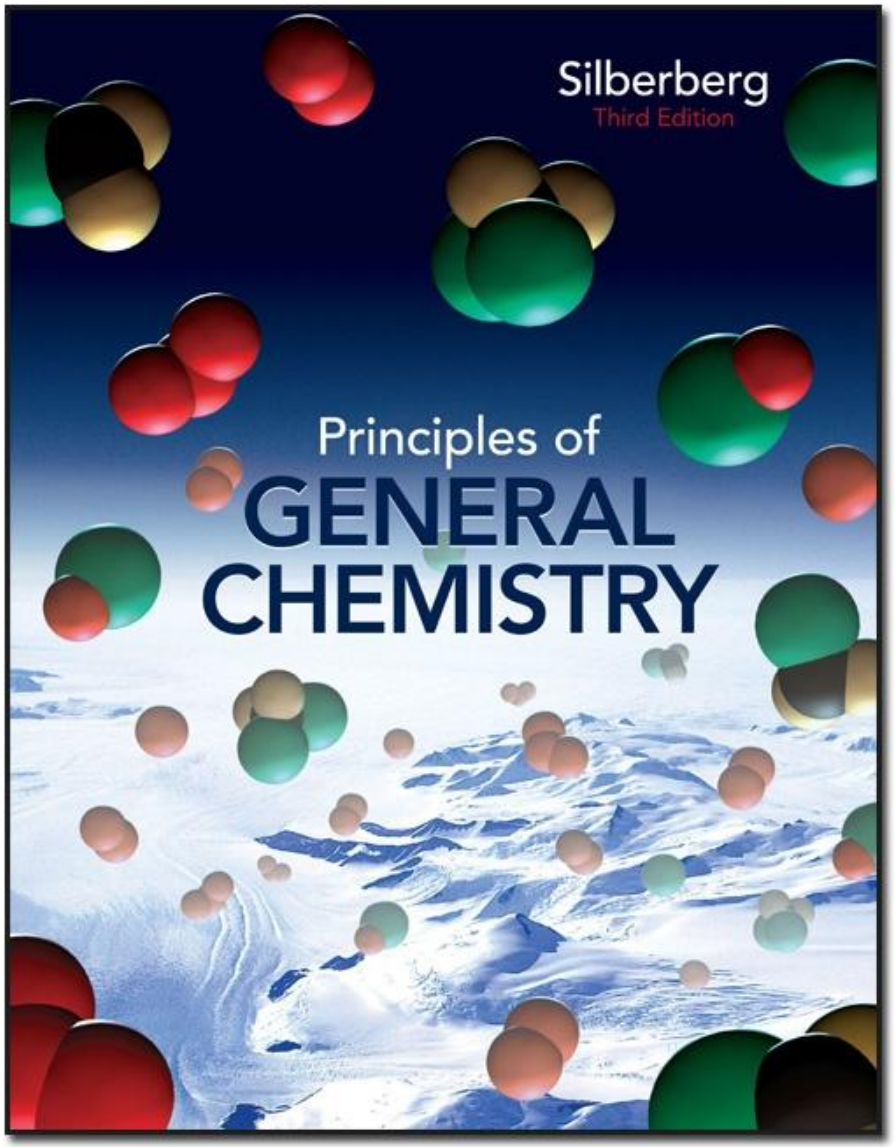

Chapter 04

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 4

Three Major Classes of Chemical Reactions

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The Major Classes of Chemical Reactions

4.1 The Role of Water as a Solvent

4.2 Writing Equations for Aqueous Ionic Reactions

4.3 Precipitation Reactions

4.4 Acid-Base Reactions

4.5 Oxidation-Reduction (Redox) Reactions

4.6 Elements in Redox Reactions

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The Role of Water as a Solvent

- Water is a polar molecule
  - since it has uneven electron distribution
  - and a bent molecular shape.
- Water readily dissolves a variety of substances.
- Water interacts strongly with its solutes and often plays an active role in aqueous reactions.

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Figure 4.1 Electron distribution in molecules of H_2 and H_2O.

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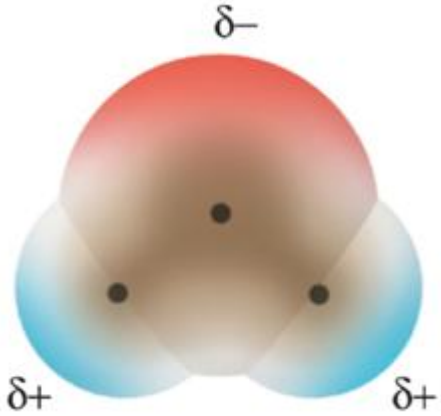
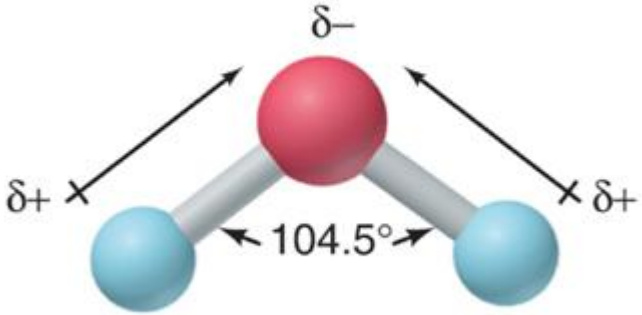
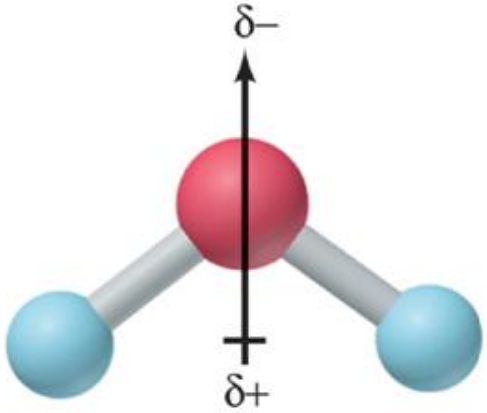
A. Electron charge distribution in H_2 is symmetrical.



B. Electron charge distribution in H_2O is asymmetrical.



C. Each bond in H_2O is polar.



D. The whole H_2O molecule is polar.

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Figure 4.2 An ionic compound dissolving in water.

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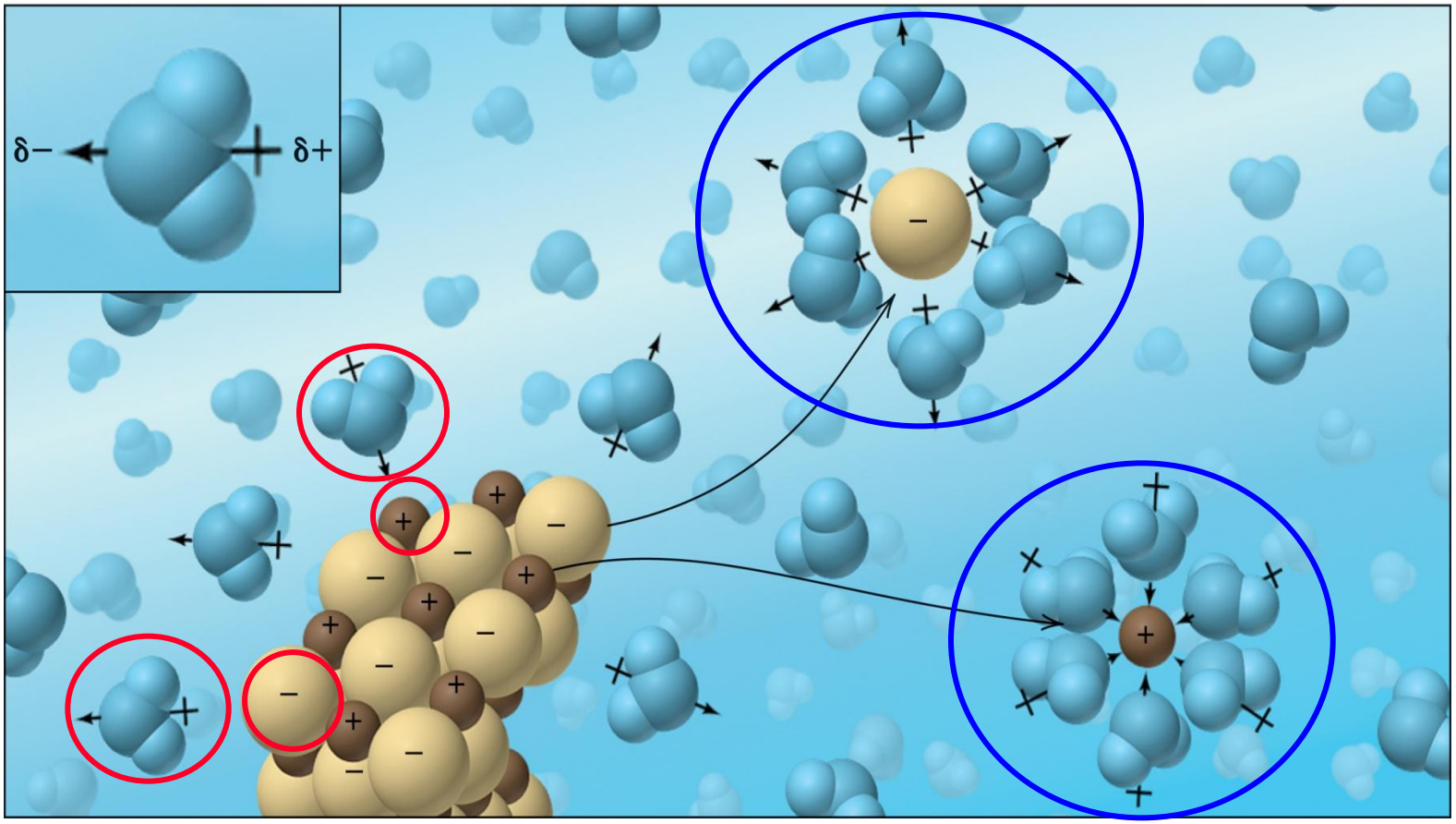

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Figure 4.3 The electrical conductivity of ionic solutions.

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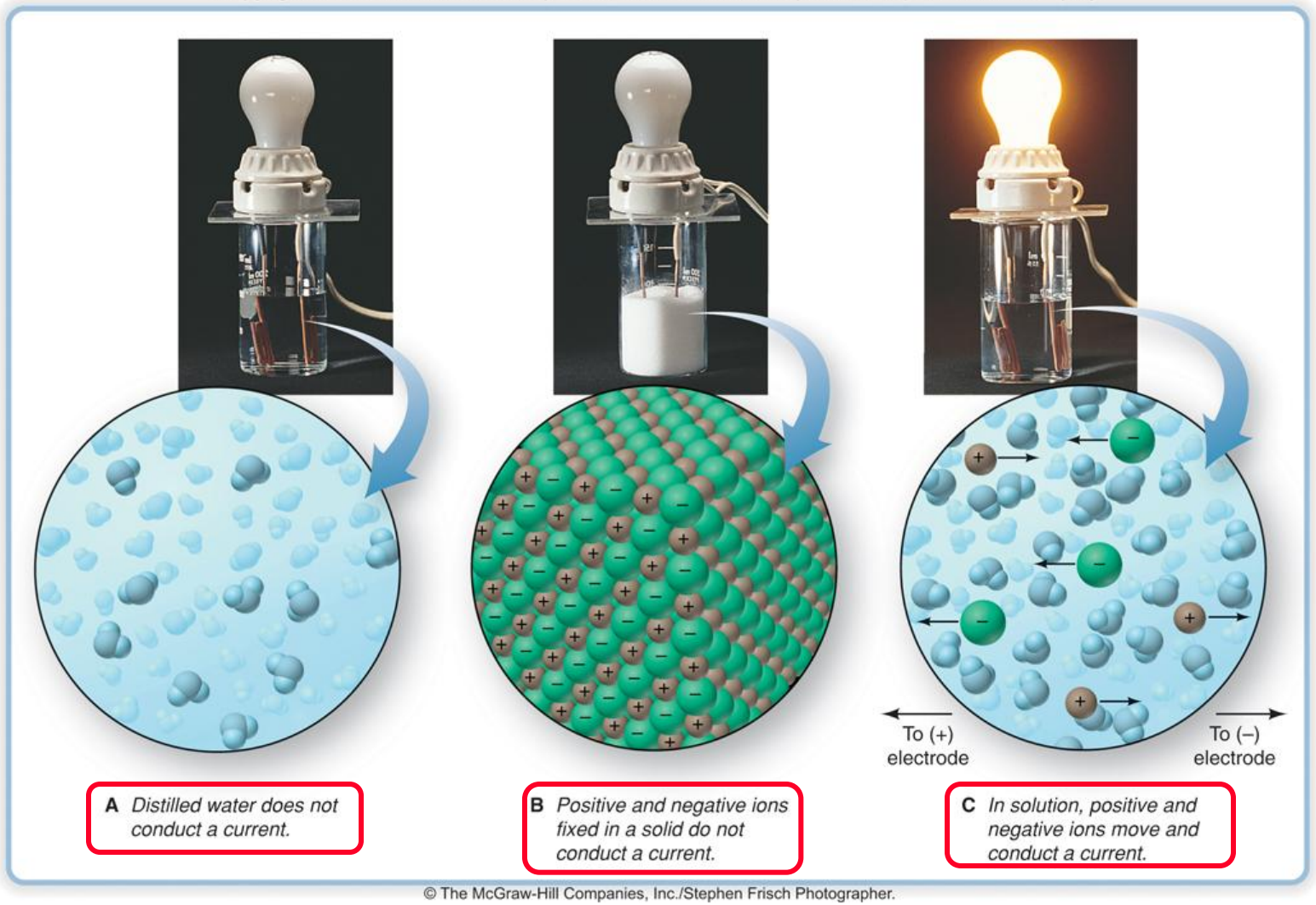

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Sample Problem 4.1

Using Molecular Scenes to Depict an Ionic Compound in Aqueous Solution

PROBLEM: The beakers shown below contain aqueous solutions of the strong electrolyte potassium sulfate.

(a) Which beaker best represents the compound in solution? (H_2O molecules are not shown).

(b) If each particle represents 0.10 mol, what is the total number of particles in solution?

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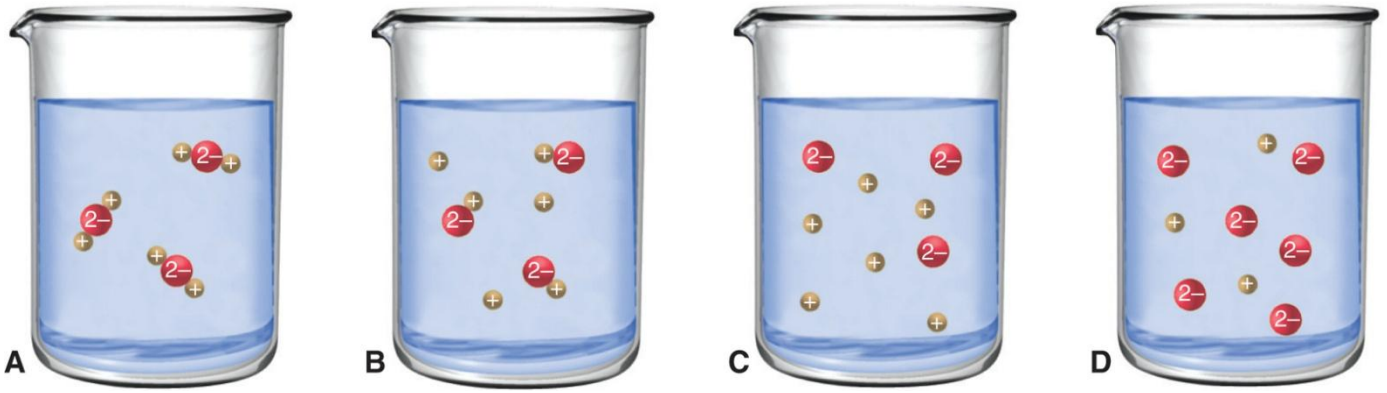

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Sample Problem 4.1

PLAN: (a) Determine the formula and write an equation for the dissociation of 1 mol of compound. Potassium sulfate is a strong electrolyte; it therefore dissociates completely in solution. *Remember that polyatomic ions remain intact in solution.*

(b) Count the number of separate particles in the relevant beaker, then multiply by 0.1 mol and by Avogadro's number.

SOLUTION:

(a) The formula is K_2SO_4, so the equation for dissociation is:

$$\mathbf{K_2SO_4\,(\mathit{s}) \rightarrow 2K^+\,(\mathit{aq}) + SO_4^{2-}\,(\mathit{aq})}$$

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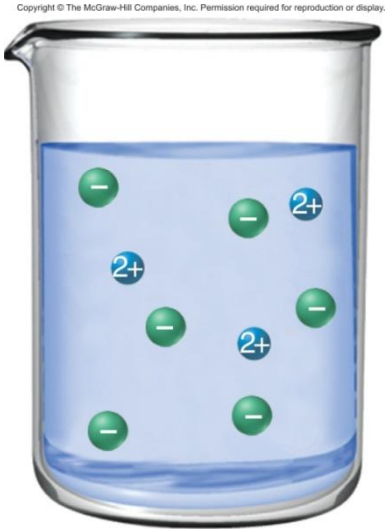
Sample Problem 4.1

There should be 2 cations for every 1 anion; beaker C represents this correctly.



(b) Beaker C contains 9 particles, 6 K^+ ions and 3 SO_4^{2-} ions.

$$9 \times 0.1 \cancel{\text{mol}} \times \frac{6.022 \times 10^{23} \text{ particles}}{1 \cancel{\text{mol}}} = \mathbf{5.420 \times 10^{23} \text{ particles}}$$

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Sample Problem 4.2 Determining Amount (mol) of Ions in Solution

PROBLEM: What amount (mol) of each ion is in each solution?

(a) 5.0 mol of ammonium sulfate dissolved in water

(b) 78.5 g of cesium bromide dissolved in water

(c) 7.42×10^{22} formula units of copper(II) nitrate dissolved in water

(d) 35 mL of 0.84 *M* zinc chloride

PLAN: Write an equation for the dissociation of 1 mol of each compound. Use this information to calculate the actual number of moles represented by the given quantity of substance in each case.

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Sample Problem 4.2

SOLUTION:

(a) The formula is $(NH_4)_2SO_4$ so the equation for dissociation is:

$(NH_4)_2SO_4$ (*s*) → $2NH_4^+$ (*aq*) + SO_4^{2-} (*aq*)

$$5.0 \text{ mol } (NH_4)_2SO_4 \times \frac{2 \text{ mol } NH_4^+}{1 \text{ mol } (NH_4)_2SO_4} = \mathbf{10.\ mol\ NH_4^+}$$

$$5.0 \text{ mol } (NH_4)_2SO_4 \times \frac{1 \text{ mol } SO_4^{2-}}{1 \text{ mol } (NH_4)_2SO_4} = 5.0 \text{ mol } SO_4^{2-}$$

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Sample Problem 4.2

SOLUTION:

(b) The formula is CsBr so the equation for dissociation is:

$CsBr\ (s) \rightarrow Cs^+\ (aq) + Br^-\ (aq)$

$$78.5\ \cancel{g\ CsBr} \times \frac{1\ \cancel{mol\ CsBr}}{212.8\ \cancel{g\ CsBr}} \times \frac{1\ mol\ Cs^+}{1\ \cancel{mol\ CsBr}} = \mathbf{0.369\ mol\ Cs^+}$$

There is one Cs^+ ion for every Br^- ion, so the number of moles of Br^- is also equation to **0.369 mol.**

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Sample Problem 4.2

SOLUTION:

(c) The formula is $Cu(NO_3)_2$ so the formula for dissociation is:

$Cu(NO_3)_2$ (*s*) → Cu^{2+} (*aq*) + 2NO_3^- (*aq*)

$$7.42\times10^{22}\ \cancel{\text{formula units}}\ Cu(NO_3)_2 \times \frac{1\ \text{mol}}{6.022\times10^{23}\ \cancel{\text{formula units}}}$$

$$= 0.123\ \text{mol}\ Cu(NO_3)_2$$

$$0.123\ \cancel{\text{mol}\ Cu(NO_3)_2} \times \frac{1\ \text{mol}\ Cu^{2+}}{1\ \cancel{\text{mol}\ Cu(NO_3)_2}}$$

= 0.123 mol Cu^{2+} ions

There are 2 NO_3^- ions for every 1 Cu^{2+} ion, so there are **0.246 mol NO_3^- ions.**

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Sample Problem 4.2

SOLUTION:

(d) The formula is $ZnCl_2$ so the formula for dissociation is:

$ZnCl_2$ (*s*) → Zn^{2+} (*aq*) + 2Cl^- (*aq*)

$$35 \text{ mL soln} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.84 \text{ mol } ZnCl_2}{1 \text{ L soln}} = \mathbf{2.9 \times 10^{-2} \text{ mol } ZnCl_2}$$

$$2.9 \times 10^{-2} \text{ mol } ZnCl_2 \times \frac{2 \text{ mol } Cl^-}{1 \text{ mol } ZnCl_2} = \mathbf{5.8 \times 10^{-2} \text{ mol } Cl^-}$$

There is 1 mol of Zn^{2+} ions for every 1 mol of $ZnCl_2$, so there are **2.9 x 10^{-2} mol Zn^{2+} ions**.

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Writing Equations for Aqueous Ionic Reactions

The **molecular equation** shows all reactants and products as if they were *intact, undissociated compounds*.

This gives the least information about the species in solution.

$$2AgNO_3\,(aq) + Na_2CrO_4\,(aq) \rightarrow Ag_2CrO_4\,(s) + 2NaNO_3\,(aq)$$

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When solutions of silver nitrate and sodium chromate mix, a brick-red precipitate of silver chromate forms.

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The **total ionic equation** shows all soluble ionic substances *dissociated into ions*.

This gives the most accurate information about species in solution.

$$2Ag^+(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s) + 2Na^+(aq) + NO_3^-(aq)$$

Spectator ions are ions that are not involved in the actual chemical change. Spectator ions appear unchanged on both sides of the total ionic equation.

$$2Ag^+(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s) + 2Na^+(aq) + 2NO_3^-(aq)$$

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The **net ionic equation** eliminates the ***spectator ions*** and shows only the *actual chemical change*.

$$2Ag^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$

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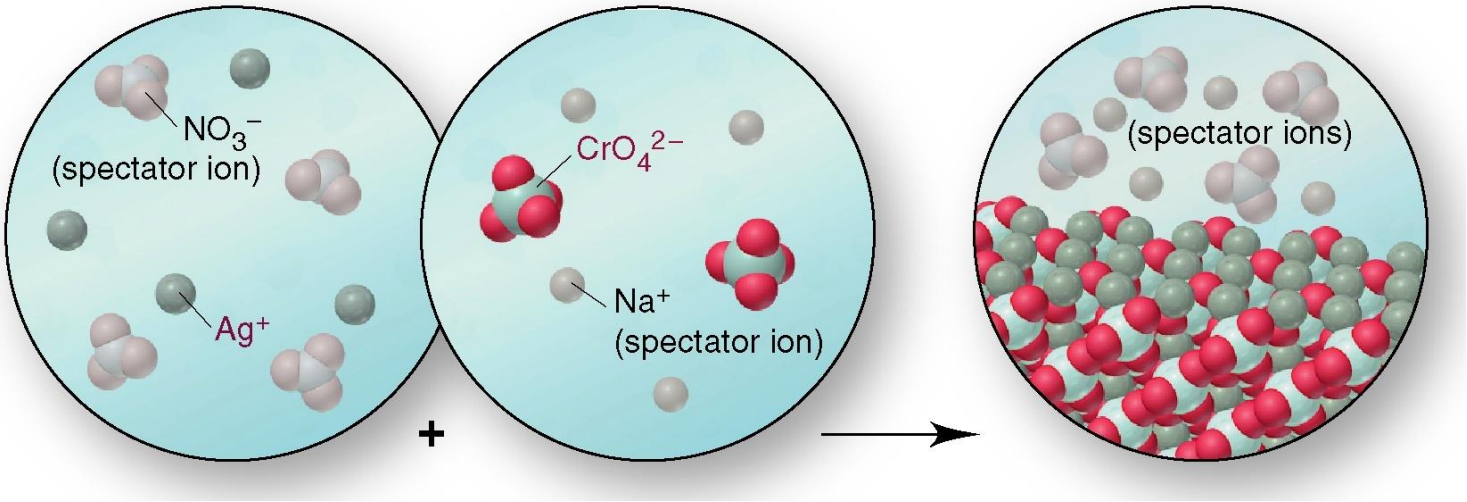

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Figure 4.4 **An aqueous ionic reaction and the three types of equations.**

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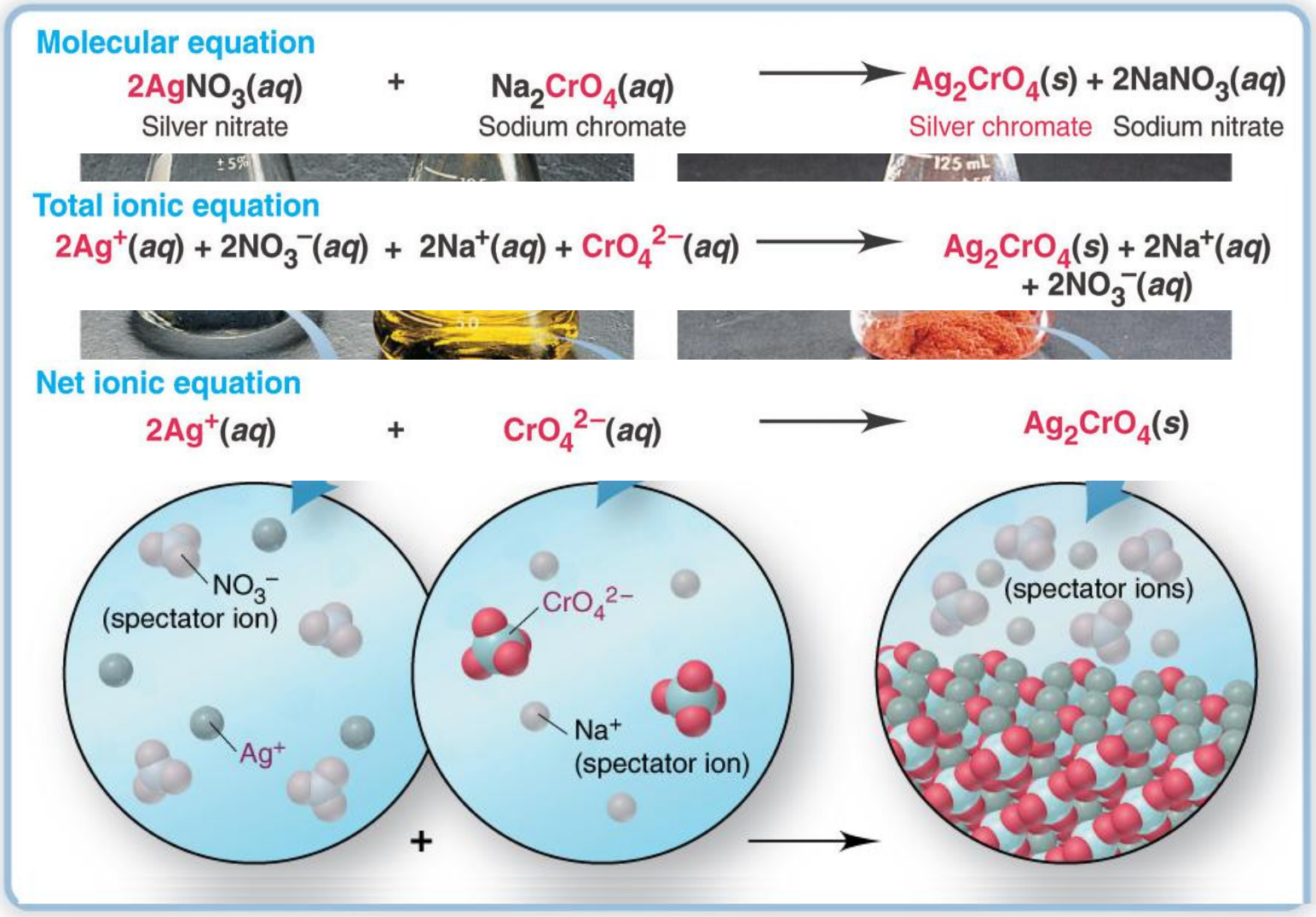

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Precipitation Reactions

- In a **precipitation reaction** two soluble ionic compounds react to give an insoluble product, called a ***precipitate***.
- The precipitate forms through the net removal of ions from solution.
- It is possible for more than one precipitate to form in such a reaction.

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Figure 4.5 The precipitation of calcium fluoride.

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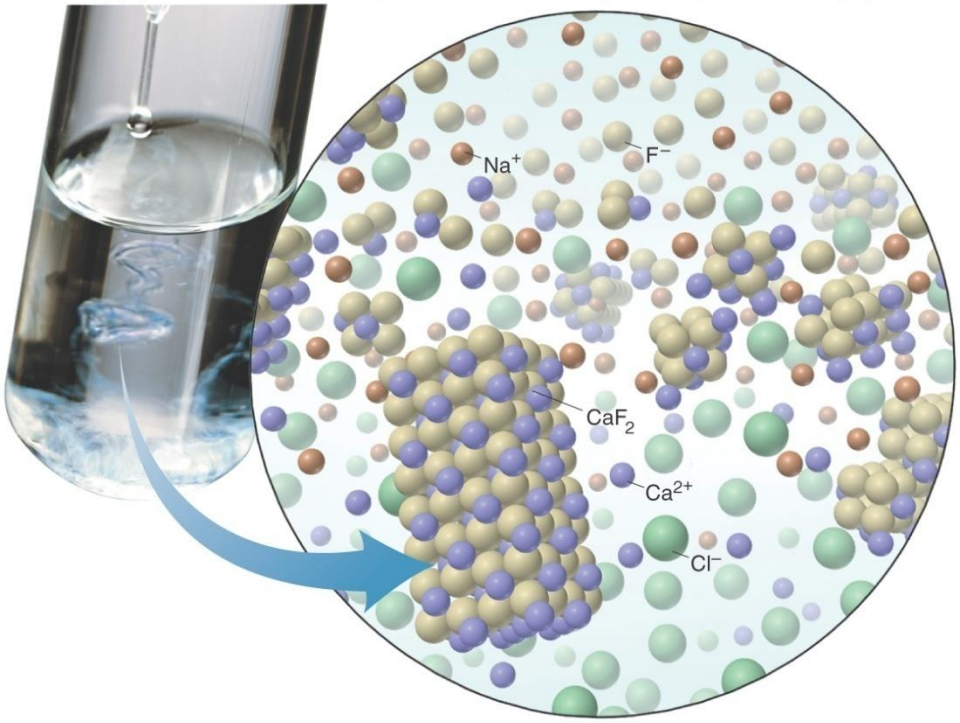

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$$2NaF\,(aq) + CaCl_2\,(aq) \longrightarrow CaF_2\,(s) + 2NaCl\,(aq)$$

$$2\,Na^+\,(aq) + 2\,F^-\,(aq) + Ca^{2+}\,(aq) + 2\,Cl^-\,(aq) \longrightarrow CaF_2(s) + 2\,Na^+\,(aq) + 2\,Cl^-\,(aq)$$

$$2\,NaF(aq) + CaCl_2\,(aq) \longrightarrow CaF_2(s) + 2\,NaCl\,(aq)$$

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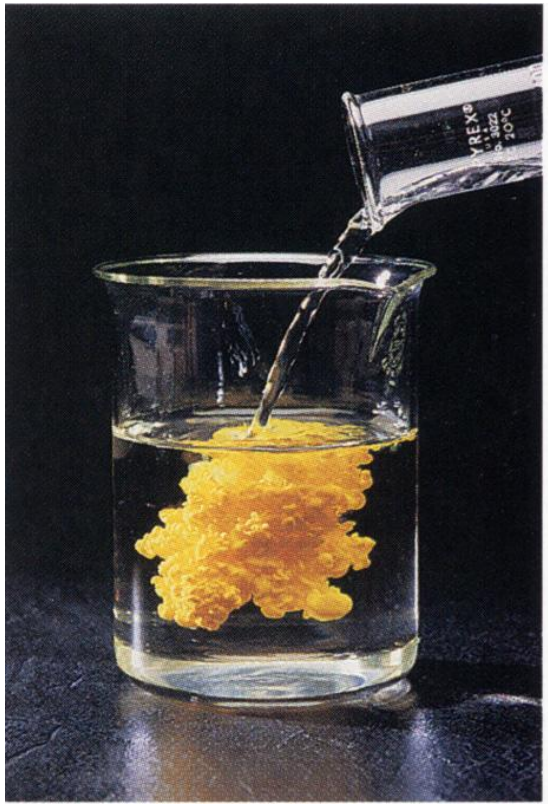
Figure 4.6 The precipitation of PbI_2, a metathesis reaction.



$$2NaI\,(aq) + Pb(NO_3)_2\,(aq) \longrightarrow PbI_2\,(s) + NaNO_3\,(aq)$$

$$2Na^+(aq) + 2I^-\,(aq) + Pb^{2+}\,(aq) + 2NO_3^-\,(aq) \longrightarrow PbI_2\,(s) + 2Na^+\,(aq) + 2NO_3^-(aq)$$

$$Pb^{2+}\,(aq) + 2I^-\,(aq) \longrightarrow PbI_2\,(s)$$

Precipitation reactions are also called **double displacement** reactions or **metathesis**.

$$2NaI\,(aq) + Pb\,(NO_3)_2\,(aq) \longrightarrow PbI_2\,(s) + 2NaNO_3\,(aq)$$

Ions exchange partners and a precipitate forms, so there is an exchange of bonds between reacting species.

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Predicting Whether a Precipitate Will Form

- Note the ions present in the reactants.
- Consider all possible cation-anion combinations.
- Use the ***solubility rules*** to decide whether any of the ion combinations is insoluble.
  - An insoluble combination identifies the precipitate that will form.

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Table 4.1 Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds

1. All common compounds of Group 1A(1) ions (Li^+, Na^+, K^+, etc.) and ammonium ion (NH_4^+) are soluble.
2. All common nitrates (NO_3^-), acetates (CH_3COO^- or $C_2H_3O_2^-$) and most perchlorates (ClO_4^-) are soluble.
3. All common chlorides (Cl^-), bromides (Br^-) and iodides (I^-) are soluble, *except* those of Ag^+, Pb^{2+}, Cu^+, and Hg_2^{2+}. All common fluorides (F^-) are soluble *except* those of Pb^{2+} and Group 2A(2).
4. All common sulfates (SO_2^{2-}) are soluble, *except* those of Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, and Pb^{2+}.

Insoluble Ionic Compounds

1. All common metal hydroxides are insoluble, *except* those of Group 1A(1) and the larger members of Group 2A(2)(beginning with Ca^{2+}).
2. All common carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble, *except* those of Group 1A(1) and NH_4^+.
3. All common sulfides are insoluble *except* those of Group 1A(1), Group 2A(2) and NH_4^+.

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Sample Problem 4.3

Predicting Whether a Precipitation Reaction Occurs; Writing Ionic Equations

PROBLEM: Predict whether or not a reaction occurs when each of the following pairs of solutions are mixed. If a reaction does occur, write balanced molecular, total ionic, and net ionic equations, and identify the spectator ions.

(a) potassium fluoride (*aq*) + strontium nitrate (*aq*) →

(b) ammonium perchlorate (*aq*) + sodium bromide (*aq*) →

PLAN: Note reactant ions, write the possible cation-anion combinations, and use Table 4.1 to decide if the combinations are insoluble.
Write the appropriate equations for the process.

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Sample Problem 4.3

SOLUTION: **(a)** The reactants are KF and $Sr(NO_3)_2$. The possible products are KNO_3 and SrF_2. KNO_3 is soluble, but SrF_2 is an insoluble combination.

Molecular equation:

$$2KF\,(aq) + Sr(NO_3)_2\,(aq) \rightarrow 2\,KNO_3\,(aq) + SrF_2\,(s)$$

Total ionic equation:

$$2K^+\,(aq) + 2F^-\,(aq) + Sr^{2+}\,(aq) + 2NO_3^-\,(aq) \rightarrow 2K^+\,(aq) + 2NO_3^-\,(aq) + SrF_2\,(s)$$

K^+ and NO_3^- are spectator ions

Net ionic equation:

$$Sr^{2+}\,(aq) + 2F^-\,(aq) \rightarrow SrF_2\,(s)$$

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Sample Problem 4.3

SOLUTION: **(b)** The reactants are NH_4ClO_4 and NaBr. The possible products are NH_4Br and $NaClO_4$. Both are soluble, so no precipitate forms.

Molecular equation:

$$\mathbf{NH_4ClO_4\ (\mathit{aq})\ +\ NaBr\ (\mathit{aq})\ \rightarrow\ NH_4Br\ (\mathit{aq})\ +\ NaClO_4\ \mathit{(aq)}}$$

Total ionic equation:

$$\mathbf{NH_4^+\ (\mathit{aq})\ +\ ClO_4^-\ (\mathit{aq})\ +\ Na^+\ (\mathit{aq})\ +\ Br^-\ (\mathit{aq})\ \rightarrow\ NH_4^+\ (\mathit{aq})\ +\ Br^-\ (\mathit{aq})\ +\ Na^+\ \mathit{(aq)}\ +\ ClO_4^-\ (\mathit{aq})}$$

All ions are spectator ions and there is no net ionic equation.

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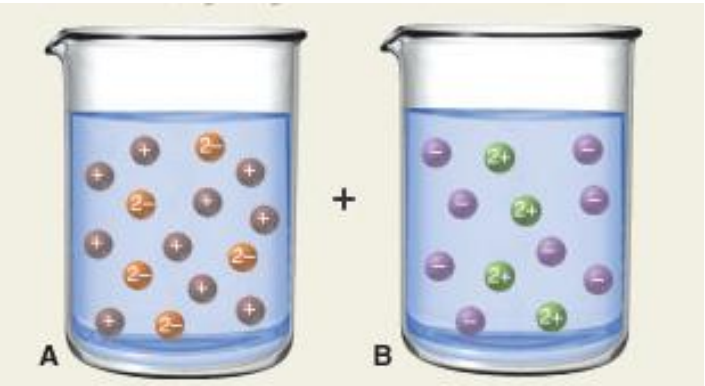
Sample Problem 4.4

Using Molecular Depictions in Precipitation Reactions

PROBLEM: The following molecular views show reactant solutions for a precipitation reaction (with H_2O molecules omitted for clarity).



(a) Which compound is dissolved in beaker A: KCl, Na_2SO_4, $MgBr_2$, or Ag_2SO_4?

(b) Which compound is dissolved in beaker B: NH_4NO_3, $MgSO_4$, $Ba(NO_3)_2$, or CaF_2?

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Sample Problem 4.4

PLAN: Note the number and charge of each kind of ion and use Table 4.1 to determine the ion combinations that are soluble.

SOLUTION:

(a) Beaker A contains two 1+ ion for each 2- ion. Of the choices given, only Na_2SO_4 and Ag_2SO_4 are possible. Na_2SO_4 is soluble while Ag_2SO_4 is not.

Beaker A therefore contains Na_2SO_4.

(b) Beaker B contains two 1- ions for each 2+ ion. Of the choices given, only CaF_2 and $Ba(NO_3)_2$ match this description. CaF_2 is not soluble while $Ba(NO_3)_2$ is soluble.

Beaker B therefore contains $Ba(NO_3)_2$.

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Sample Problem 4.4

PROBLEM: (c) Name the precipitate and spectator ions when solutions A and B are mixed, and write balanced molecular, total ionic, and net ionic equations for this process.

(d) If each particle represents 0.010 mol of ions, what is the maximum mass (g) of precipitate that can form (assuming complete reaction)?

PLAN: (c) Consider the cation-anion combinations from the two solutions and use Table 4.1 to decide if either of these is insoluble.

SOLUTION: The reactants are $Ba(NO_3)_2$ and Na_2SO_4. The possible products are $BaSO_4$ and $NaNO_3$. $BaSO_4$ is insoluble while $NaNO_3$ is soluble.

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Sample Problem 4.4

Molecular equation:

$$Ba(NO_3)_2\,(aq) + Na_2SO_4\,(aq) \rightarrow 2NaNO_3\,(aq) + BaSO_4\,(s)$$

Total ionic equation:

$$Ba^{2+}\,(aq) + 2NO_3^-\,(aq) + 2Na^+\,(aq) + SO_4^{2-}\,(aq) \rightarrow 2Na^+\,(aq) + 2NO_3^-\,(aq) + BaSO_4\,(s)$$

Na^+ and NO_3^- are spectator ions

Net ionic equation:

$$Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow BaSO_4\,(s)$$

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Sample Problem 4.4

PLAN: (d) Count the number of each kind of ion that combines to form the solid. Multiply the number of each reactant ion by 0.010 mol and calculate the mol of product formed from each. Decide which ion is the limiting reactant and use this information to calculate the mass of product formed.

SOLUTION: There are 4 Ba^{2+} particles and 5 SO_4^{2-} particles depicted.

$$4\ \cancel{Ba^{2+}\ particles} \times \frac{0.010\ \cancel{mol\ Ba^{2+}}}{1\ \cancel{particle}} \times \frac{1\ mol\ BaSO_4}{1\ \cancel{mol\ Ba^{2+}}} = 0.040\ mol\ BaSO_4$$

$$4\ \cancel{SO_4^{2-}\ particles} \times \frac{0.010\ \cancel{mol\ SO_4^{2-}}}{\cancel{1\ particle}} \times \frac{1\ mol\ BaSO_4}{1\ \cancel{mol\ SO_4^{2-}}} = 0.050\ mol\ BaSO_4$$

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Sample Problem 4.4

Ba^{2+} ion is the limiting reactant, since it yields less $BaSO_4$.

$$0.040 \cancel{\text{ mol } BaSO_4} \times \frac{233.4 \text{ g } BaSO_4}{1 \cancel{\text{ mol } BaSO_4}} = \mathbf{9.3 \text{ g } BaSO_4}$$

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Acid-Base Reactions

An **acid** is a substance that produces H^+ ions when dissolved in H_2O.

$$HX \xrightarrow{H_2O} H^+(aq) + X^-(aq)$$

A **base** is a substance that produces OH^- ions when dissolved in H_2O.

$$MOH \xrightarrow{H_2O} M^+(aq) + OH^-(aq)$$

An **acid-base reaction** is also called a **neutralization** reaction.

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Table 4.2 Strong and Weak Acids and Bases

Acids

Strong

hydrochloric acid, HCl

hydrobromic acid, HBr

hydriodic acid, HI

nitric acid, HNO_3

sulfuric acid, H_2SO_4

perchloric acid, $HClO_4$

Weak

hydrofluoric acid, HF

phosphoric acid, H_3PO_4

acetic acid, CH_3COOH (or $HC_2H_3O_2$)

Bases

Strong

Group 1A(1) hydroxides:

lithium hydroxide, LiOH

sodium hydroxide, NaOH

potassium hydroxide, KOH

rubidium hydroxide, RbOH

cesium hydroxide, CsOH

Heavy Group 2A(2) hydroxides:

calcium hydroxide, $Ca(OH)_2$

strontium hydroxide, $Sr(OH)_2$

barium hydroxide, $Ba(OH)_2$

Weak

ammonia, NH_3

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Figure 4.7 Acids and bases as electrolytes.

Strong acids and strong bases dissociate completely into ions in aqueous solution.

They are ***strong electrolytes*** and conduct well in solution.

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A Strong acid (or base) = strong electrolyte

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Figure 4.7 Acids and bases as electrolytes.

Weak acids and weak bases dissociate very little into ions in aqueous solution.

They are ***weak electrolytes*** and conduct poorly in solution.

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B Weak acid (or base) = weak electrolyte

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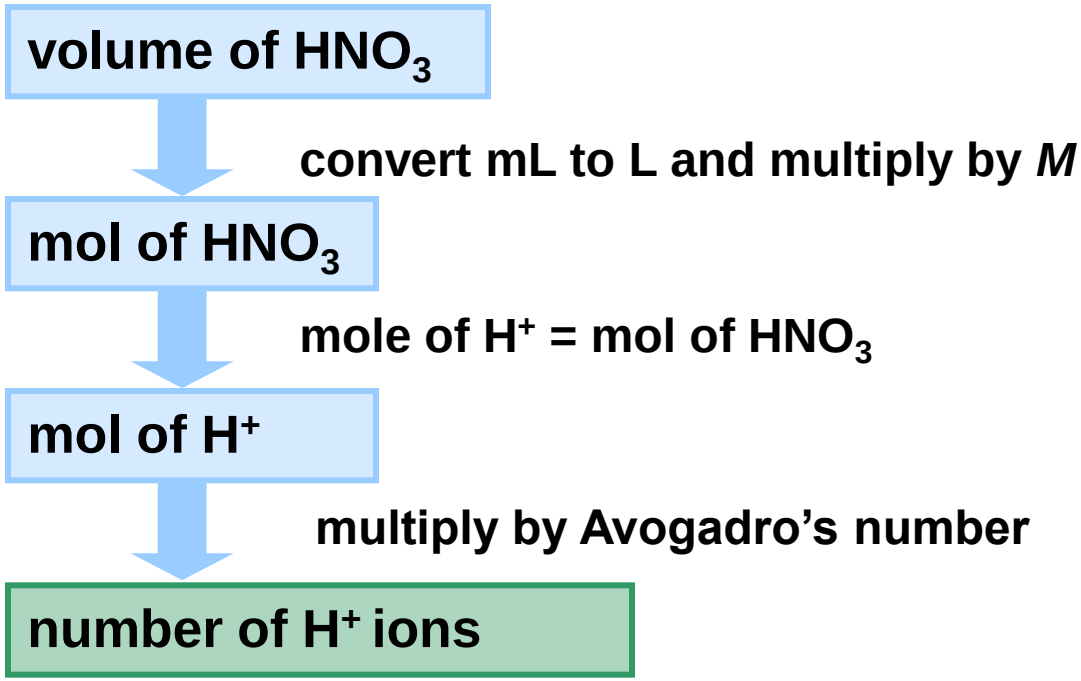
Sample Problem 4.5 Determining the Number of H^+ (or OH^-) Ions in Solution

PROBLEM: How many $H^+(aq)$ ions are in 25.3 mL of 1.4 *M* nitric acid?

PLAN: Use the volume and molarity to determine the mol of acid present. Since HNO_3 is a strong acid, moles acid = moles H^+.



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Sample Problem 4.5

SOLUTION:

$$35.3 \text{ mL soln} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{1.4 \text{ mol } HNO_3}{1 \text{ L soln}} = 0.035 \text{ mol } HNO_3$$

One mole of $H^+(aq)$ is released per mole of nitric acid (HNO_3).

$$HNO_3\,(aq) \xrightarrow{H_2O} H^+\,(aq) + NO_3^-\,(aq)$$

$$= 0.035 \text{ mol } HNO_3 \times \frac{1 \text{ mol } H^+}{1 \text{ mol } HNO_3} \times \frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol}}$$

$= 2.1 \times 10^{22}$ H^+ ions

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Sample Problem 4.6

Writing Ionic Equations for Acid-Base Reactions

PROBLEM: Write balanced molecular, total ionic, and net ionic equations for the following acid-base reactions and identify the spectator ions.

(a) hydrochloric acid (*aq*) + potassium hydroxide (*aq*) →

(b) strontium hydroxide (*aq*) + perchloric acid (*aq*) →

(c) barium hydroxide (*aq*) + sulfuric acid (*aq*) →

PLAN: All reactants are strong acids and bases (see Table 4.2). The product in each case is H_2O and an **ionic salt**.
Write the molecular reaction in each case and use the solubility rules to determine if the product is soluble or not.

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Sample Problem 4.6

SOLUTION:

(a) hydrochloric acid (*aq*) + potassium hydroxide (*aq*) $\rightarrow$

Molecular equation:

$HCl\ (aq) + KOH\ (aq) \rightarrow KCl\ (aq) + H_2O\ (l)$

Total ionic equation:

$H^+\ (aq) + Cl^-\ (aq) + K^+\ (aq) + OH^-\ (aq) \rightarrow K^+\ (aq) + Cl^-\ (aq) + H_2O\ (l)$

Net ionic equation:

$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$

Spectator ions are K^+ and Cl^-

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Sample Problem 4.6

SOLUTION:

(c) barium hydroxide (*aq*) + sulfuric acid (*aq*) →

Molecular equation:

$Ba(OH)_2$ (*aq*) + H_2SO_4 (*aq*) → $BaSO_4$ (s) + $2H_2O$ (*l*)

Total ionic equation:

Ba^{2+} (*aq*) + $2OH^-$ (*aq*) + $2H^+$ (*aq*) + SO_4^{2-} (*aq*) → $BaSO_4$ (*s*) + H_2O (*l*)

The net ionic equation is the **same** as the total ionic equation since there are **no spectator ions**.

This reaction is both a neutralization reaction and a precipitation reaction.

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Sample Problem 4.6

SOLUTION:

(b) strontium hydroxide (*aq*) + perchloric acid (*aq*) $\rightarrow$

Molecular equation:

$Sr(OH)_2\ (aq) + 2HClO_4\ (aq) \rightarrow Sr(ClO_4)_2\ (aq) + 2H_2O\ (l)$

Total ionic equation:

$Sr^{2+}\ (aq) + 2OH^-\ (aq) + 2H^+\ (aq) + 2ClO_4^-\ (aq) \rightarrow Sr^{2+}\ (aq) + 2ClO_4^-\ (aq) + 2H_2O\ (l)$

Net ionic equation:

$2H^+\ (aq) + 2OH^-\ (aq) \rightarrow 2H_2O\ (l)$ or $H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$

Spectator ions are Sr^{2+} and ClO_4^-

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Figure 4.8 An aqueous strong acid-strong base reaction as a proton-transfer process.

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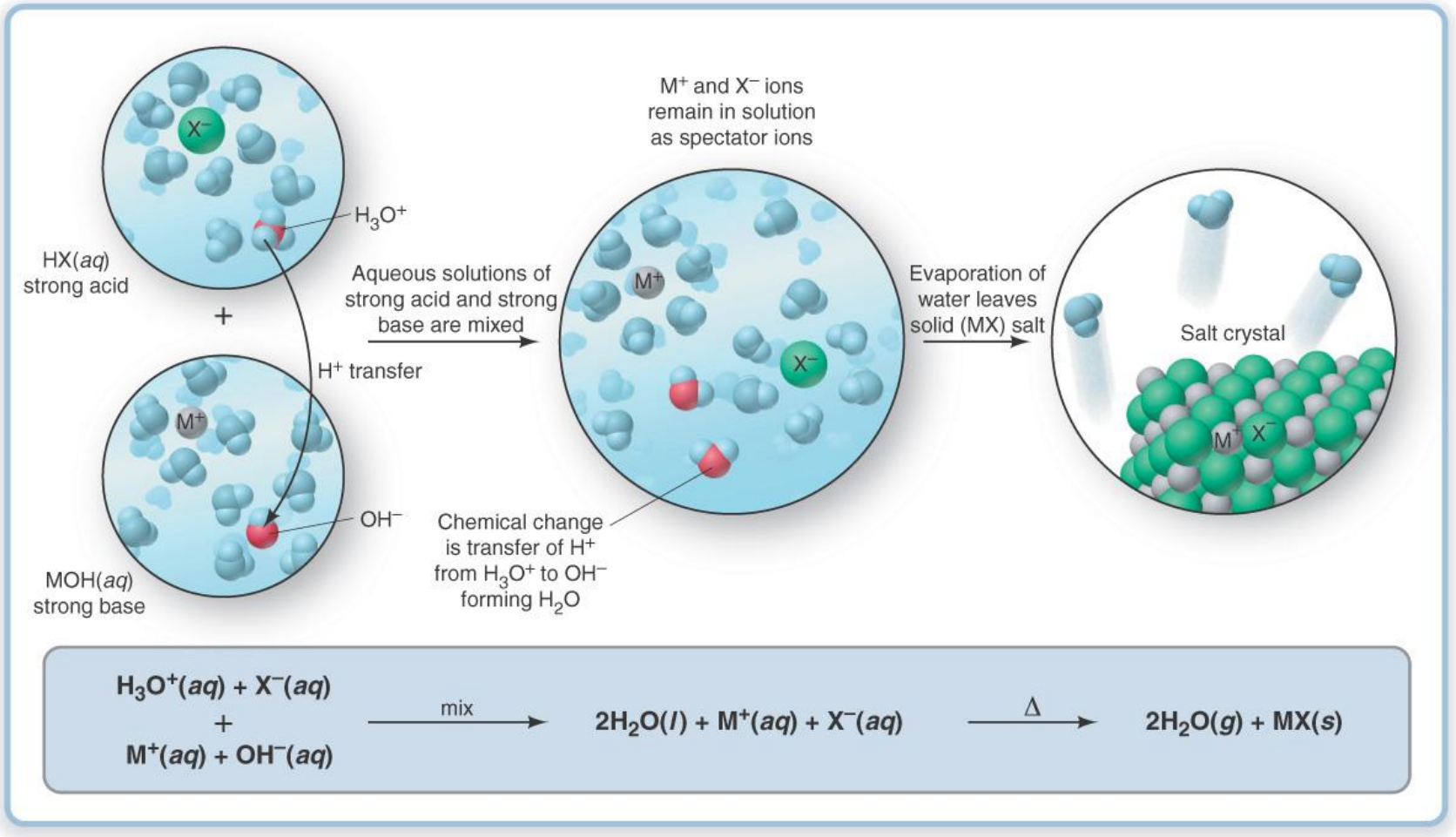

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Quantifying Acid-Base Reactions by Titration

- In a ***titration***, the concentration of one solution is used to determine the concentration of another.
- In an acid-base titration, a standard solution of base is usually added to a sample of acid of unknown molarity.
- An ***acid-base indicator*** has different colors in acid and base, and is used to monitor the reaction progress.
- At the ***equivalence point***, the mol of H^+ from the acid equals the mol of OH^- ion produced by the base.
  - Amount of H^+ ion in flask = amount of OH^- ion added
- The ***end point*** occurs when there is a slight excess of base and the indicator changes color permanently.

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Figure 4.9 An acid-base titration.

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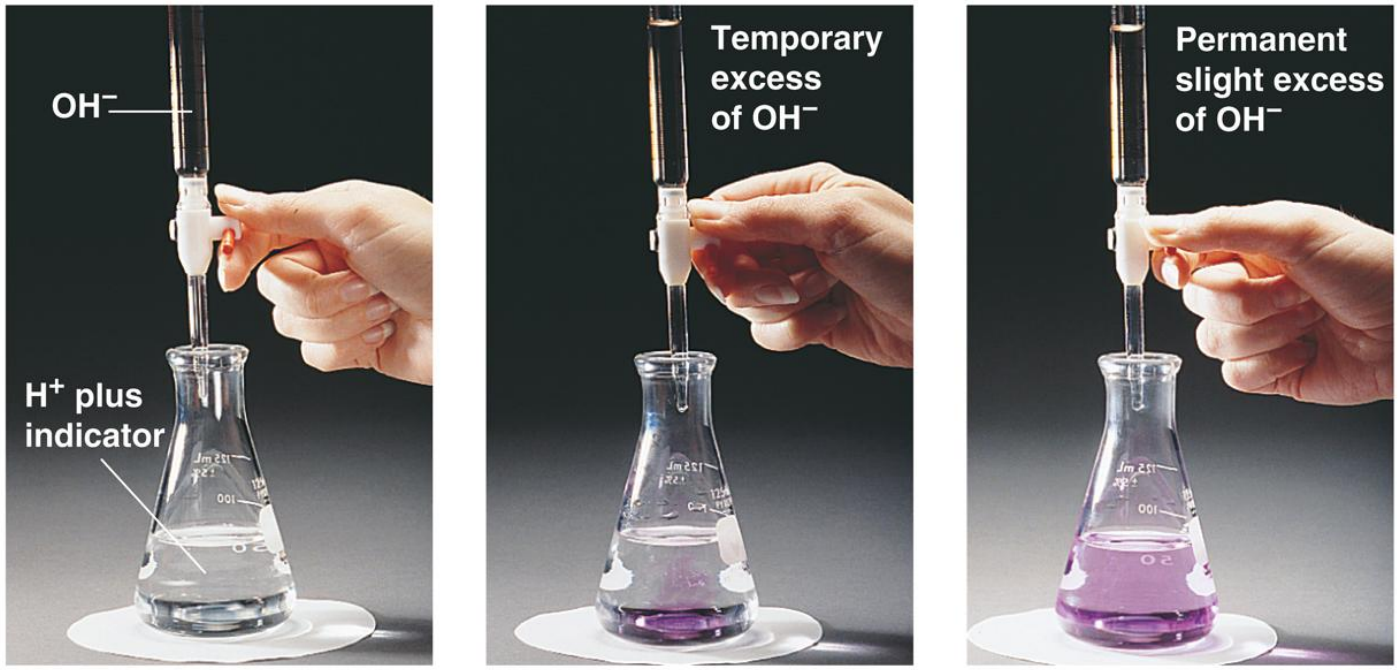

$$H^+(aq) + X^-(aq) + M^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + M^+(aq) + X^-(aq)$$

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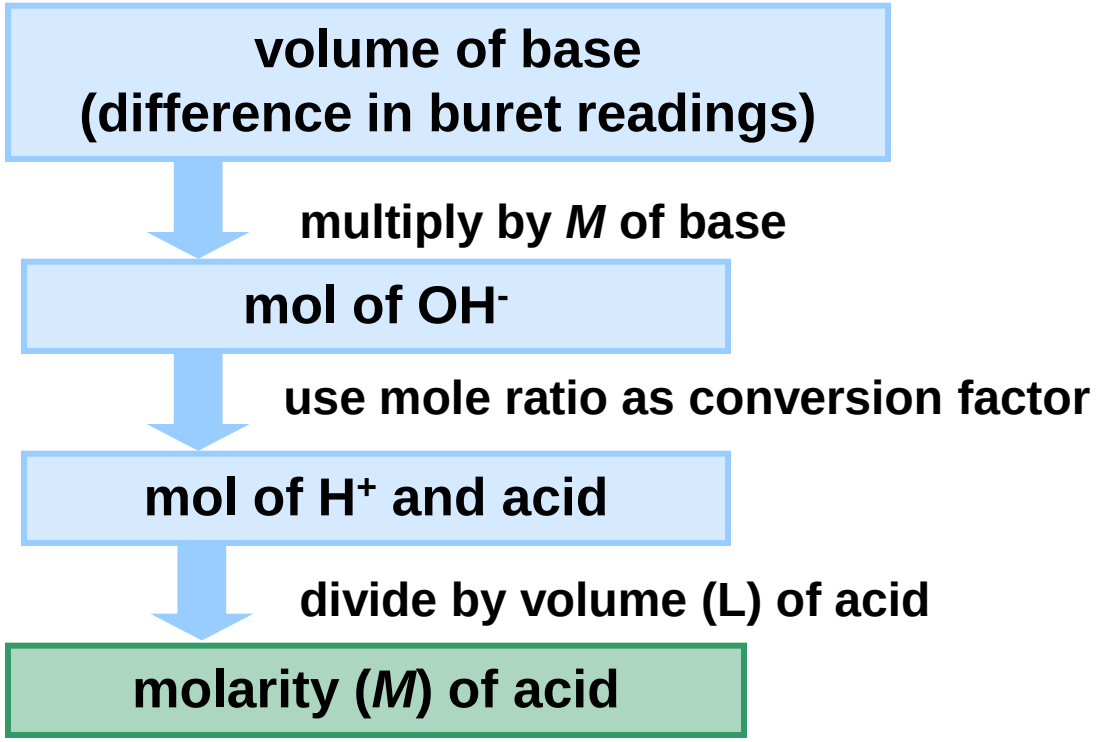
Sample Problem 4.7

Finding the Concentration of Acid from a Titration

PROBLEM: A 50.00 mL sample of HCl is titrated with 0.1524 *M* NaOH. The buret reads 0.55 mL at the start and 33.87 mL at the end point. Find the molarity of the HCl solution.

PLAN: Write a balanced equation for the reaction. Use the volume of base to find mol OH^-, then mol H^+ and finally *M* for the acid.



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Sample Problem 4.7

SOLUTION: $NaOH\,(aq) + HCl\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)$

volume of base = 33.87 mL – 0.55 mL = 33.32 mL

$$33.32\ \text{mL soln} \times \frac{1\ \text{L}}{10^3\ \text{mL}} \times \frac{0.1524\ \text{mol NaOH}}{1\ \text{L soln}} = 5.078\text{x}10^{-3}\ \text{mol NaOH}$$

Since 1 mol of HCl reacts with 1 mol NaOH, the amount of HCl = $5.078\text{x}10^{-3}$ mol.

$$\frac{5.078\text{x}10^{-3}\ \text{mol HCl}}{50.00\ \text{mL}} \times \frac{10^3\ \text{mL}}{1\ \text{L}}$$

= 0.1016 *M* HCl

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Oxidation-Reduction (Redox) Reactions

Oxidation is the ***loss*** of electrons.
The ***reducing agent*** loses electrons and is oxidized.

Reduction is the ***gain*** of electrons.
The ***oxidizing agent*** gains electrons and is reduced.

A **redox reaction** involves ***electron transfer***
Oxidation and reduction occur together.

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Figure 4.10 The redox process in the formation of (A) ionic and (B) covalent compounds from their elements.

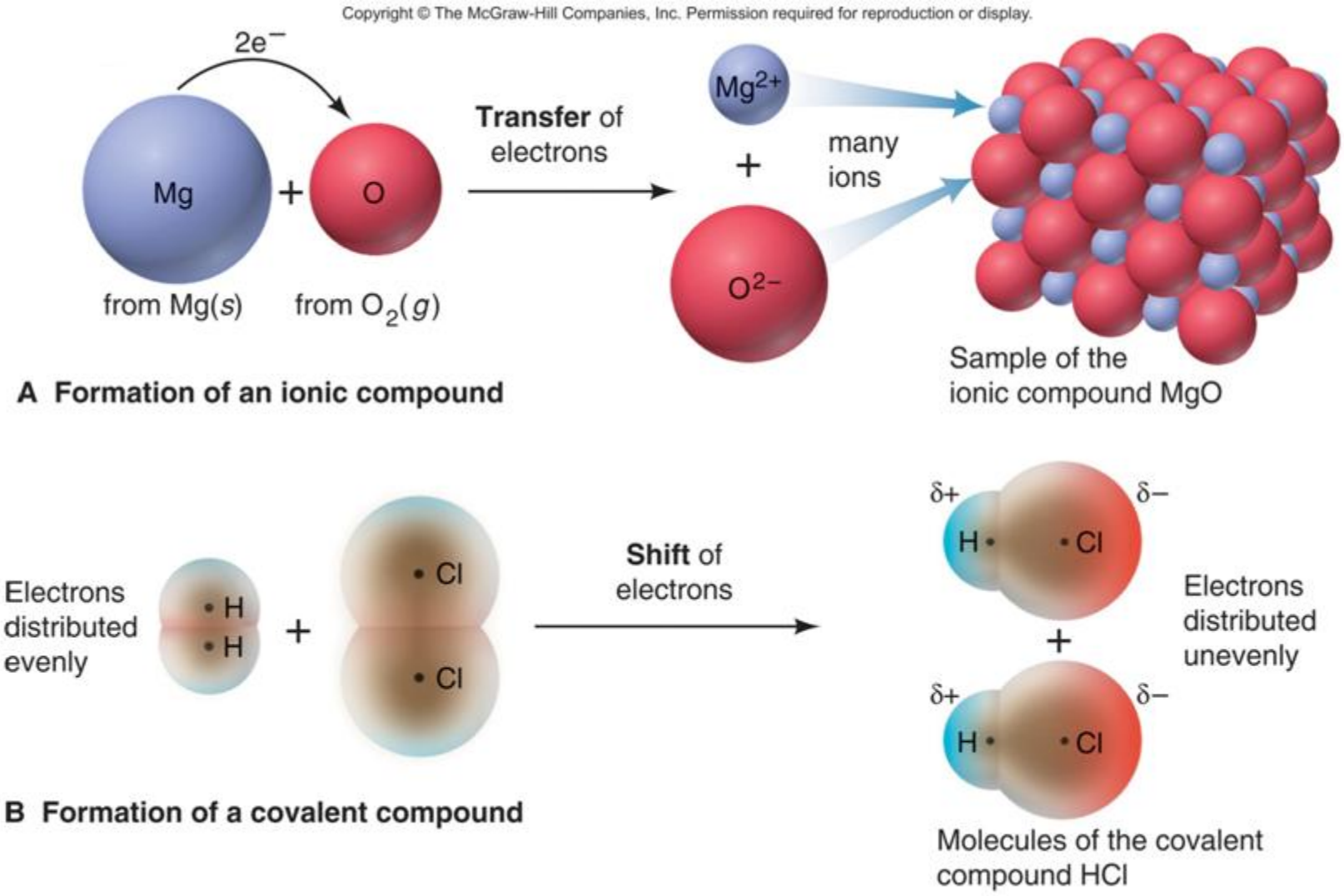

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Table 4.3 Rules for Assigning an Oxidation Number (O.N.)

General rules

1. For an atom in its elemental form (Na, O_2, Cl_2, etc.): O.N. = 0
2. For a monoatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for specific atoms or periodic table groups

1. For Group 1A(1):	O.N. = +1 in all compounds
2. For Group 2A(2):	O.N. = +2 in all compounds
3. For hydrogen:	O.N. = +1 in combination with nonmetals
4. For fluorine:	O.N. = -1 in combination with metals and boron
5. For oxygen:	O.N. = -1 in peroxides O.N. = -2 in all other compounds(except with F)
6. For Group 7A(17):	O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

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Sample Problem 4.8 Determining the Oxidation Number of Each Element in a Compound (or Ion)

PROBLEM: Determine the oxidation number (O.N.) of each element in these species:

(a) zinc chloride **(b)** sulfur trioxide **(c)** nitric acid

PLAN: The O.N.s of the ions in a polyatomic ion add up to the charge of the ion and the O.N.s of the ions in the compound add up to zero.

SOLUTION:

(a) $\mathbf{ZnCl_2}$. The O.N. for zinc is +2 and that for chloride is -1.

(b) $\mathbf{SO_3}$. Each oxygen is an oxide with an O.N. of -2. The O.N. of sulfur must therefore be +6.

(c) $\mathbf{HNO_3}$. H has an O.N. of +1 and each oxygen is -2. The N must therefore have an O.N. of +5.

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Figure 4.12 A summary of terminology for redox reactions.

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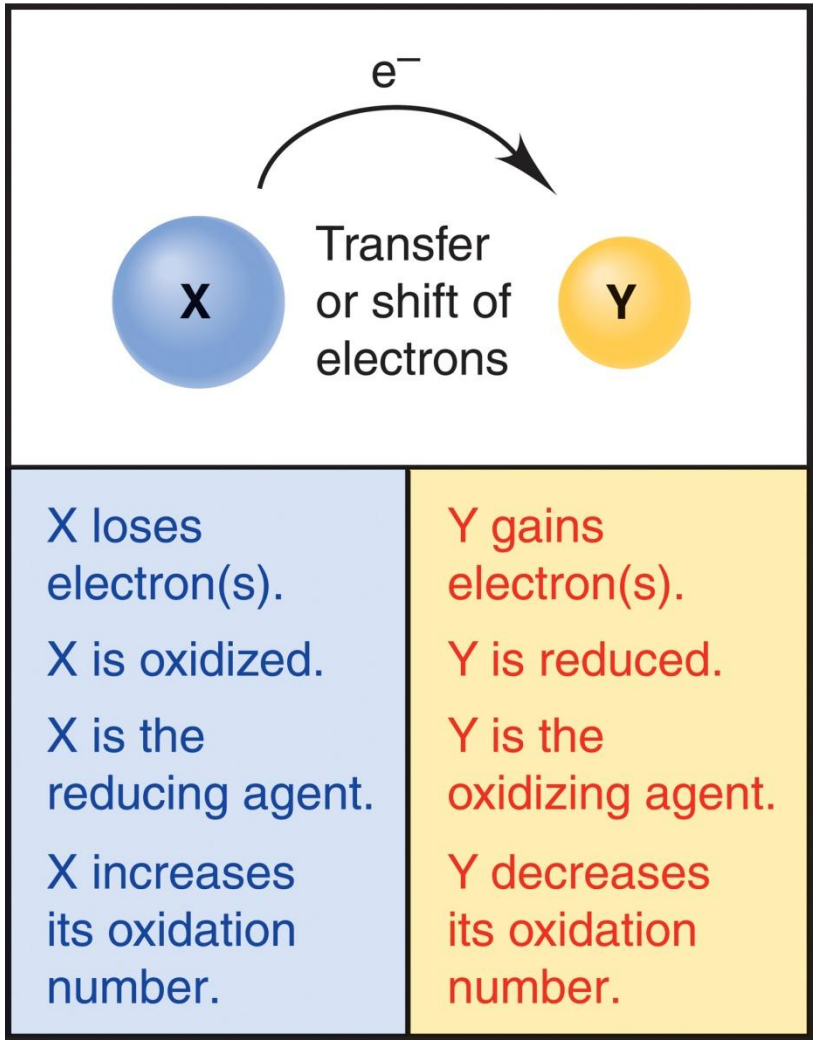

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Sample Problem 4.9

Identifying Oxidizing and Reducing Agents

PROBLEM: Identify the oxidizing agent and reducing agent in each of the following reactions:

(a) $2Al\,(s) + 3H_2SO_4\,(aq) \longrightarrow Al_2(SO_4)_3\,(aq) + 3H_2(g)$

(b) $PbO\,(s) + CO\,(g) \longrightarrow Pb\,(s) + CO_2\,(g)$

(c) $2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(g)$

PLAN: Assign an O.N. to each atom and look for those that change during the reaction.

The reducing agent contains an atom that is oxidized (increases in O.N.) while the oxidizing agent contains an atom that is reduced (decreases in O.N.).

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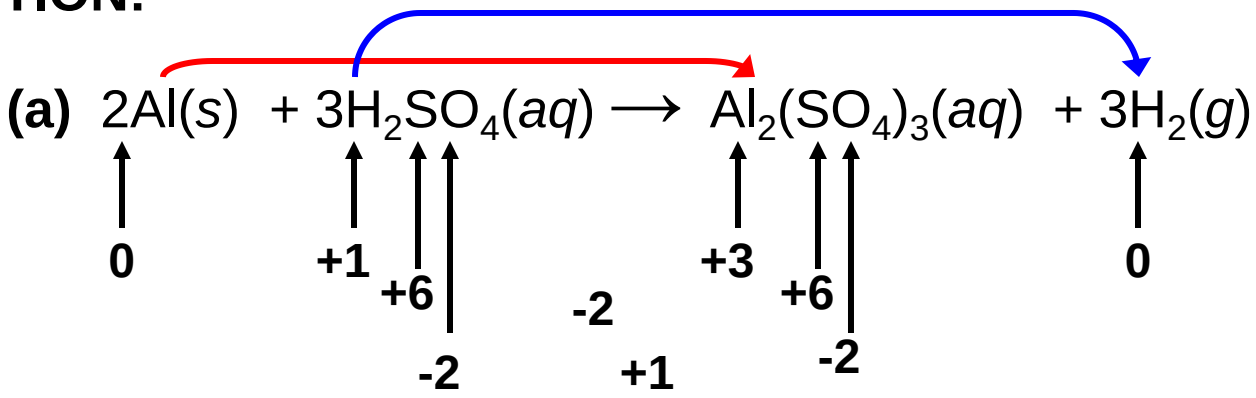
Sample Problem 4.9

SOLUTION:



Al changes O.N. from 0 to +3 and is *oxidized*.
Al is the *reducing* agent.

H changes O.N. from +1 to 0 and is *reduced*.
H_2SO_4 is the *oxidizing* agent.

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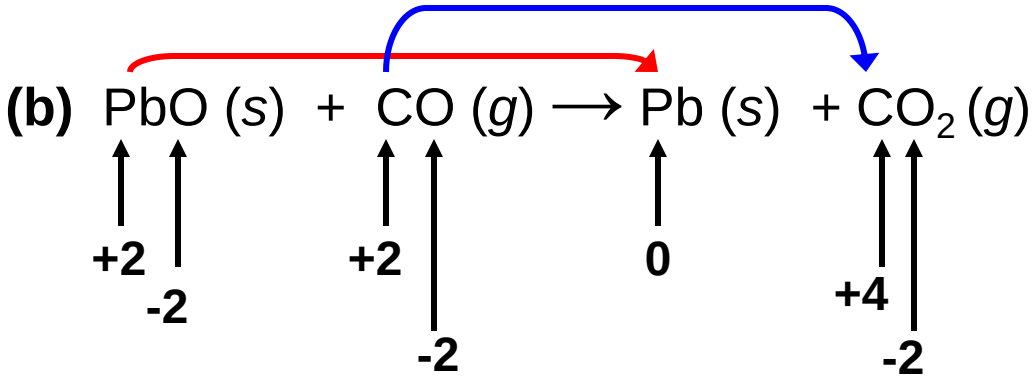
Sample Problem 4.9

SOLUTION:



Pb changes O.N. from +2 to 0 and is *reduced*.
PbO is the *oxidizing* agent.

C changes O.N. from +2 to +4 and is *oxidized*.
CO is the *reducing* agent.

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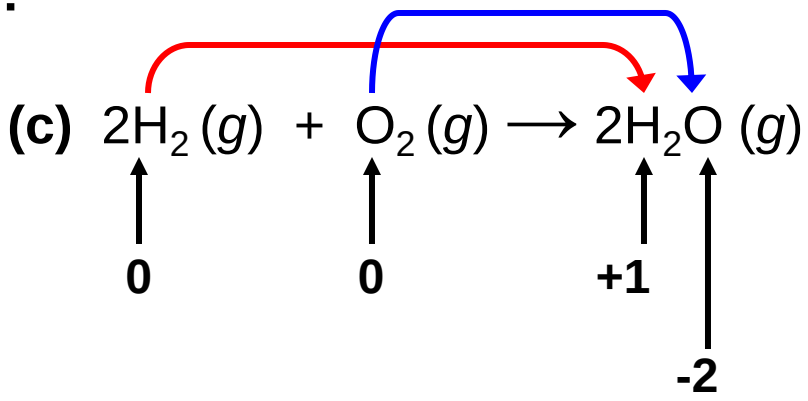
Sample Problem 4.9

SOLUTION:



H_2 changes O.N. from 0 to +1 and is *oxidized*.
H_2 is the *reducing* agent.

O changes O.N. from 0 to -2 and is *reduced*.
O_2 is the *oxidizing* agent.

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Elements in Redox Reactions

- Combination Reactions
  - Two or more reactants combine to form a new compound:
  - $X + Y \rightarrow Z$
- Decomposition Reactions
  - A single compound decomposes to form two or more products:
  - $Z \rightarrow X + Y$
- Displacement Reactions
  - double diplacement: $AB + CD \rightarrow AC + BD$
  - single displacement: $X + YZ \rightarrow XZ + Y$
- Combustion
  - the process of combining with O_2

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Figure 4.13 The active metal lithium displaces H_2 from water.

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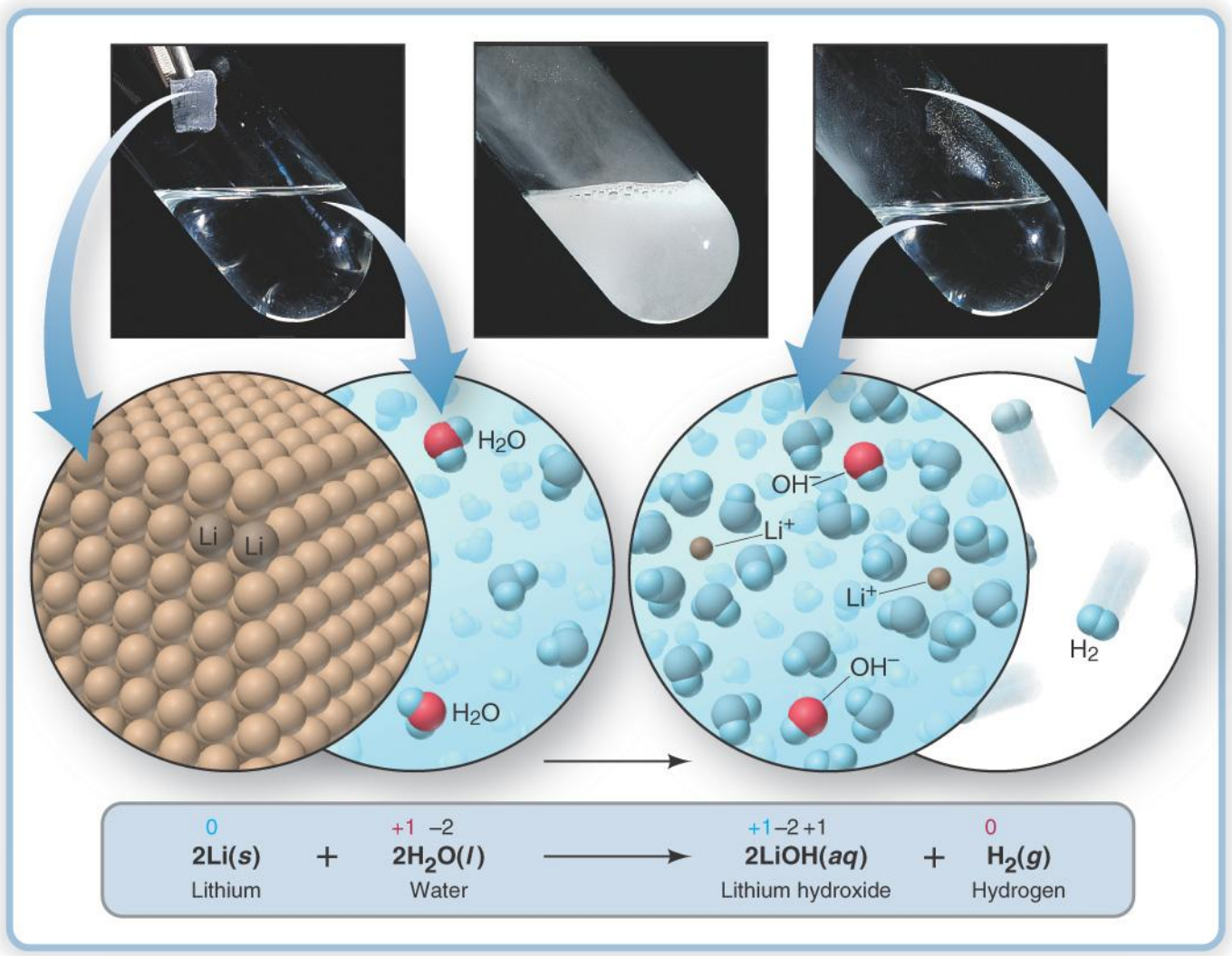

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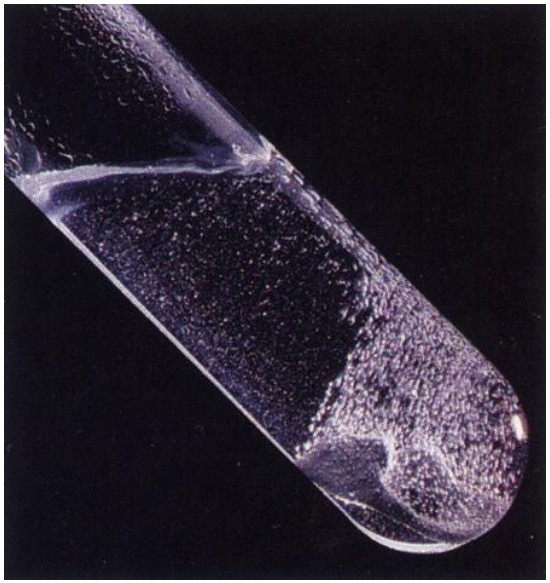
Figure 4.14 The displacement of H_2 from acid by nickel.

O.N. increasing

oxidation occurring

reducing agent



O.N. decreasing

reduction occurring

oxidizing agent

$$\overset{0}{\uparrow}\ \overset{+1}{\uparrow}\qquad\qquad \overset{+2}{\uparrow}\ \overset{0}{\uparrow}$$

$$Ni\,(s) + 2H^+\,(aq) \longrightarrow Ni^{2+}\,(aq) + H_2\,(g)$$

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Figure 4.15 A more reactive metal (Cu) displacing the ion of a less reactive metal (Ag^+) from solution.

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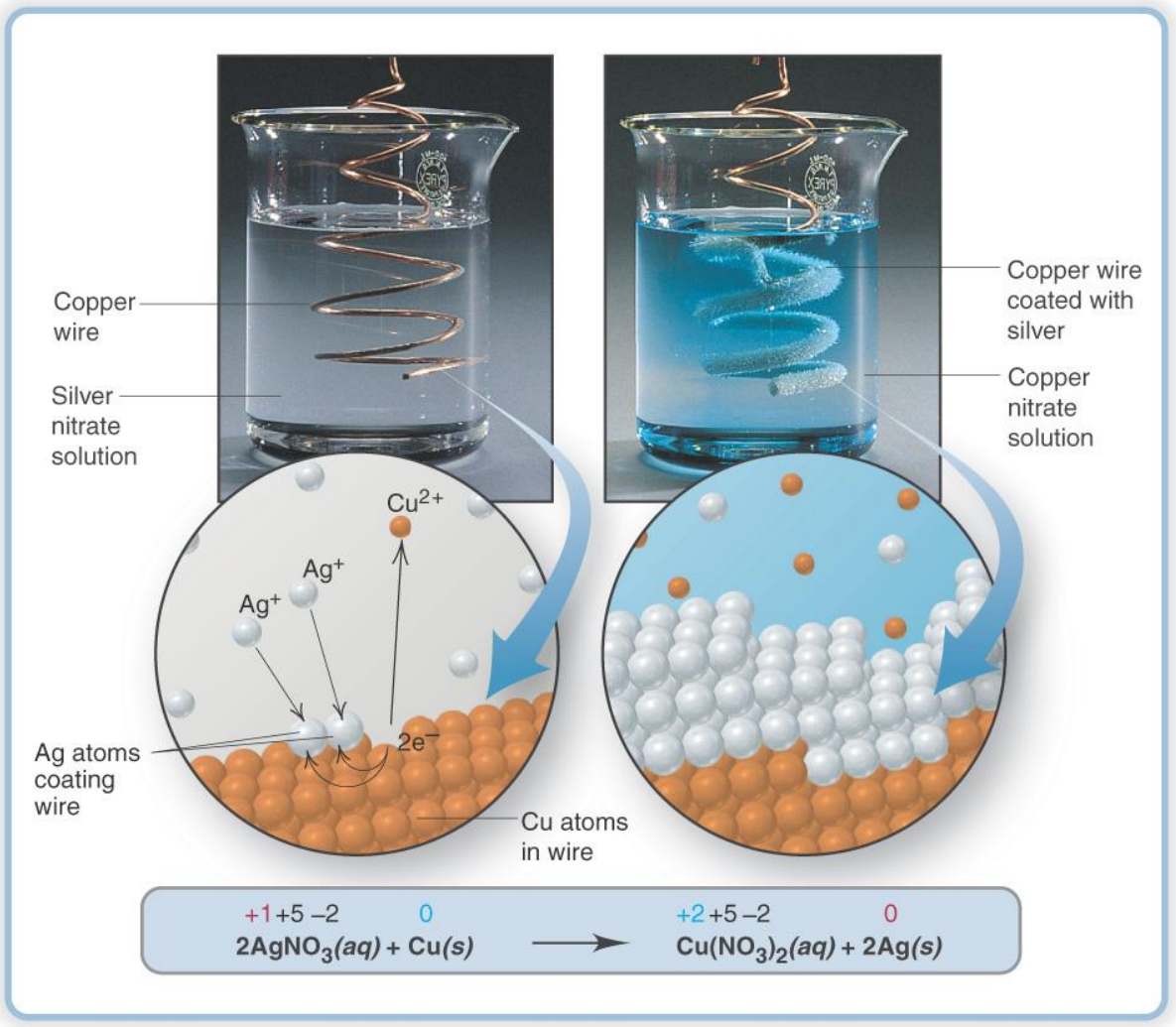

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Figure 4.16 The activity series of the metals.

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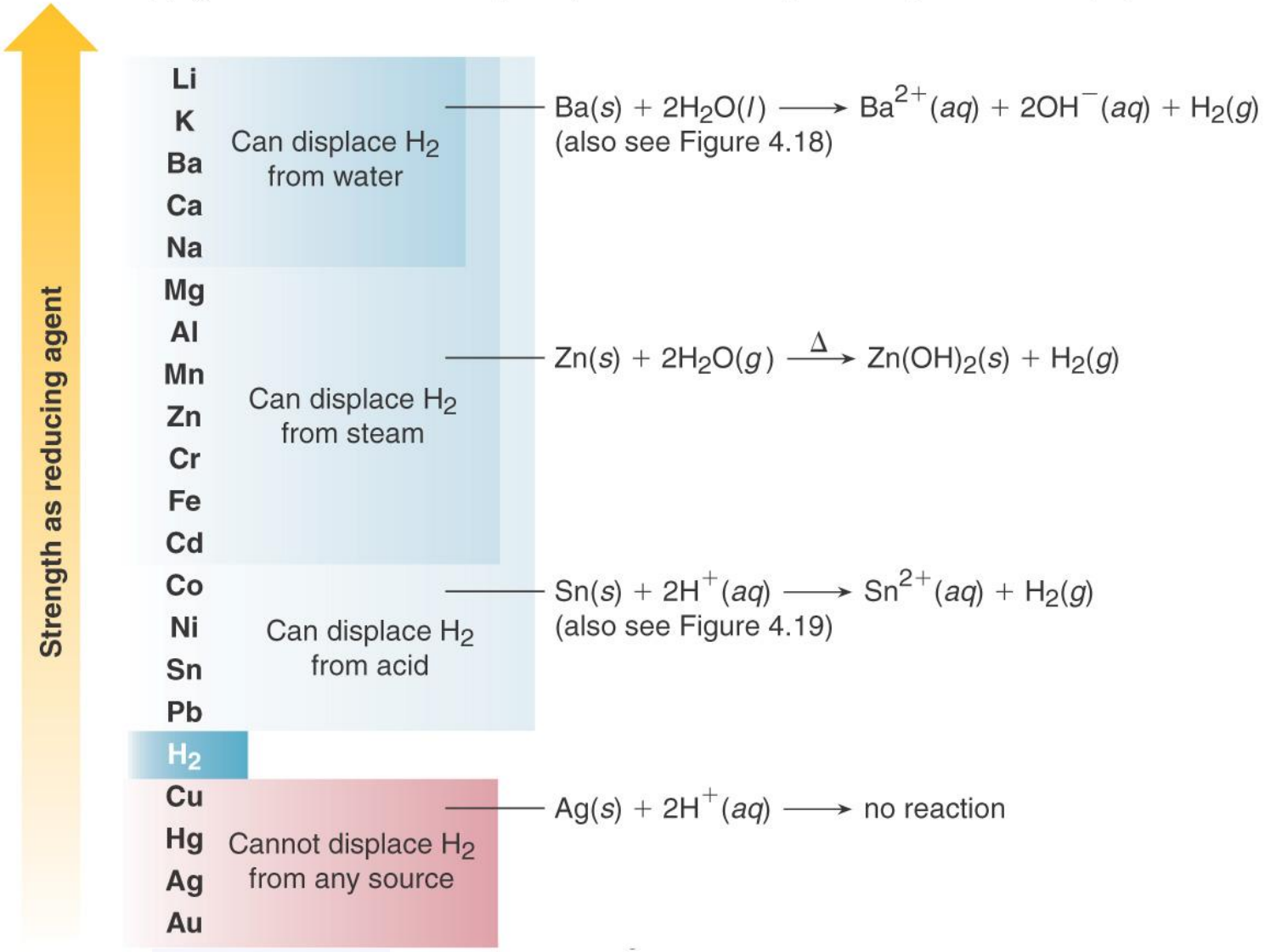

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Sample Problem 4.10 Identifying the Type of Redox Reaction

PROBLEM: Classify each of the following redox reactions as a combination, decomposition, or displacement reaction. Write a balanced molecular equation for each, as well as total and net ionic equations for part (c), and identify the oxidizing and reducing agents:

(a) magnesium (*s*) + nitrogen (*g*) ⟶ magnesium nitride (*aq*)

(b) hydrogen peroxide (*l*) ⟶ water (*l*) + oxygen gas

(c) aluminum (*s*) + lead(II) nitrate (*aq*) ⟶ aluminum nitrate (*aq*) + lead (*s*)

PLAN: Combination reactions combine reactants, decomposition reactions involve more products than reactants and displacement reactions have the same number of reactants and products.

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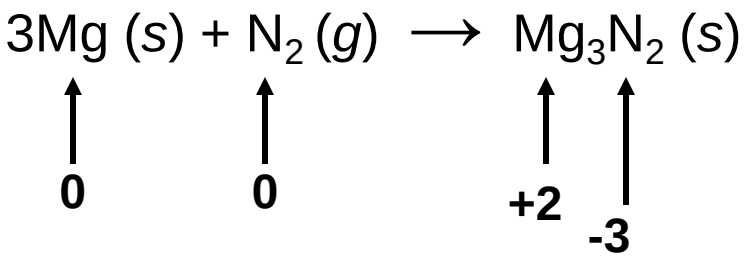
Sample Problem 4.10

SOLUTION:

(a) This is a combination reaction, since Mg and N_2 combine:



Mg is the reducing agent; N_2 is the oxidizing agent.

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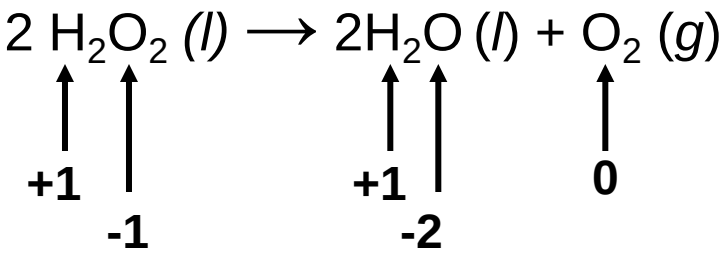
Sample Problem 4.10

(b) This is a decomposition reaction, since H_2O_2 breaks down:



H_2O_2 is *both* the reducing and the oxidizing agent.

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Sample Problem 4.10

(c) This is a displacement reaction, since Al displaces Pb^{2+} from solution.

$$2Al\,(s) + 3Pb(NO_3)_2\,(aq) \longrightarrow 2Al(NO_3)_3\,(aq) + 3Pb\,(s)$$

0 +2 +5 -2 +3 +5 -2 0

Al is the reducing agent; $Pb(NO_3)_2$ is the oxidizing agent.

The total ionic equation is:

$$2Al\,(s) + 3Pb^{2+}\,(aq) + 2NO_3^-\,(aq) \longrightarrow 2Al^{3+}\,(aq) + 3NO_3^-\,(aq) + 3Pb\,(s)$$

The net ionic equation is:

$$2Al\,(s) + 3Pb^{2+}\,(aq) \longrightarrow 2Al^{3+}\,(aq) + 3Pb\,(s)$$

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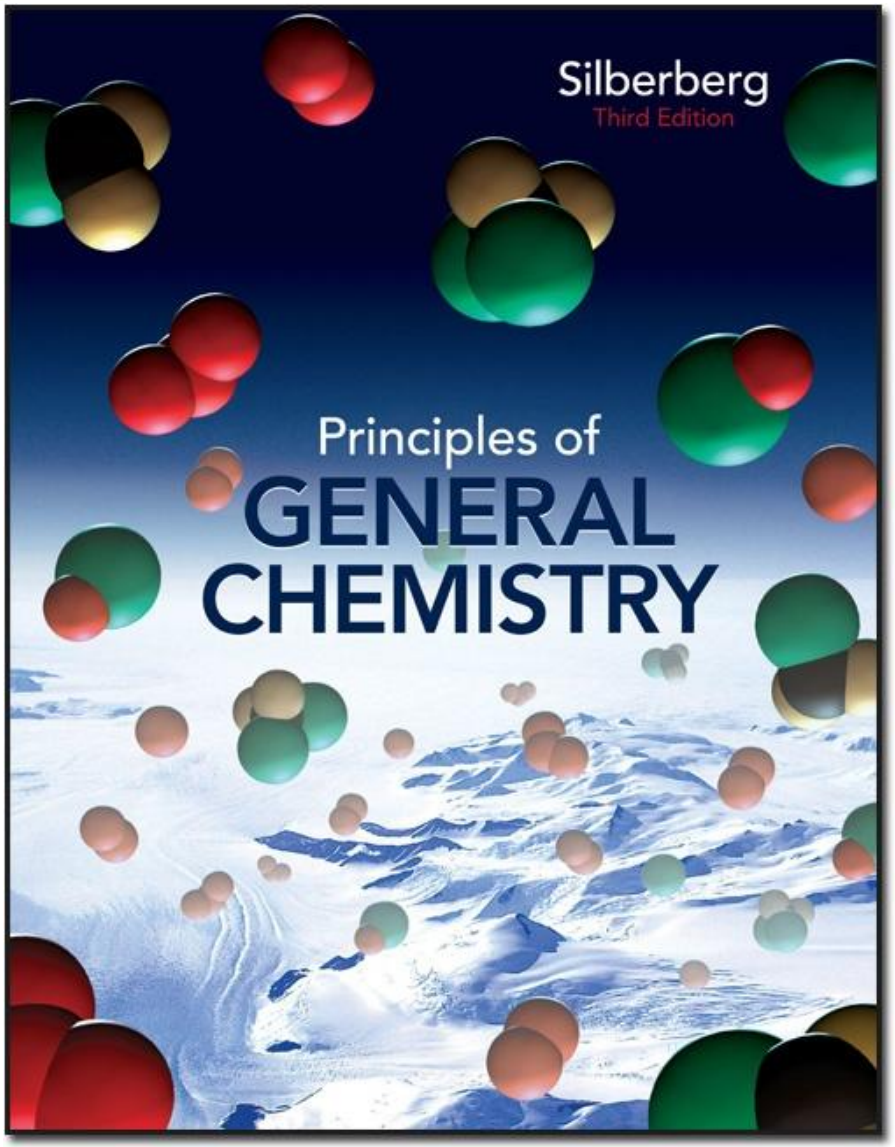

Chapter 05

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 5

Gases and the Kinetic-Molecular Theory

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Gases and the Kinetic Molecular Theory

5.1 An Overview of the Physical States of Matter

5.2 Gas Pressure and Its Measurement

5.3 The Gas Laws and Their Experimental Foundations

5.4 Rearrangements of the Ideal Gas Law

5.5 The Kinetic-Molecular Theory: A Model for Gas Behavior

5.6 Real Gases: Deviations from Ideal Behavior

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An Overview of the Physical States of Matter

Distinguishing gases from liquids and solids.

- Gas volume changes significantly with pressure.
  - Solid and liquid volumes are not greatly affected by pressure.
- Gas volume changes significantly with temperature.
  - Gases expand when heated and shrink when cooled.
  - The volume change is 50 to 100 times greater for gases than for liquids and solids.
- Gases flow very freely.
- Gases have relatively low densities.
- Gases form a solution in any proportions.
  - Gases are freely miscible with each other.

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Figure 5.1 The three states of matter.

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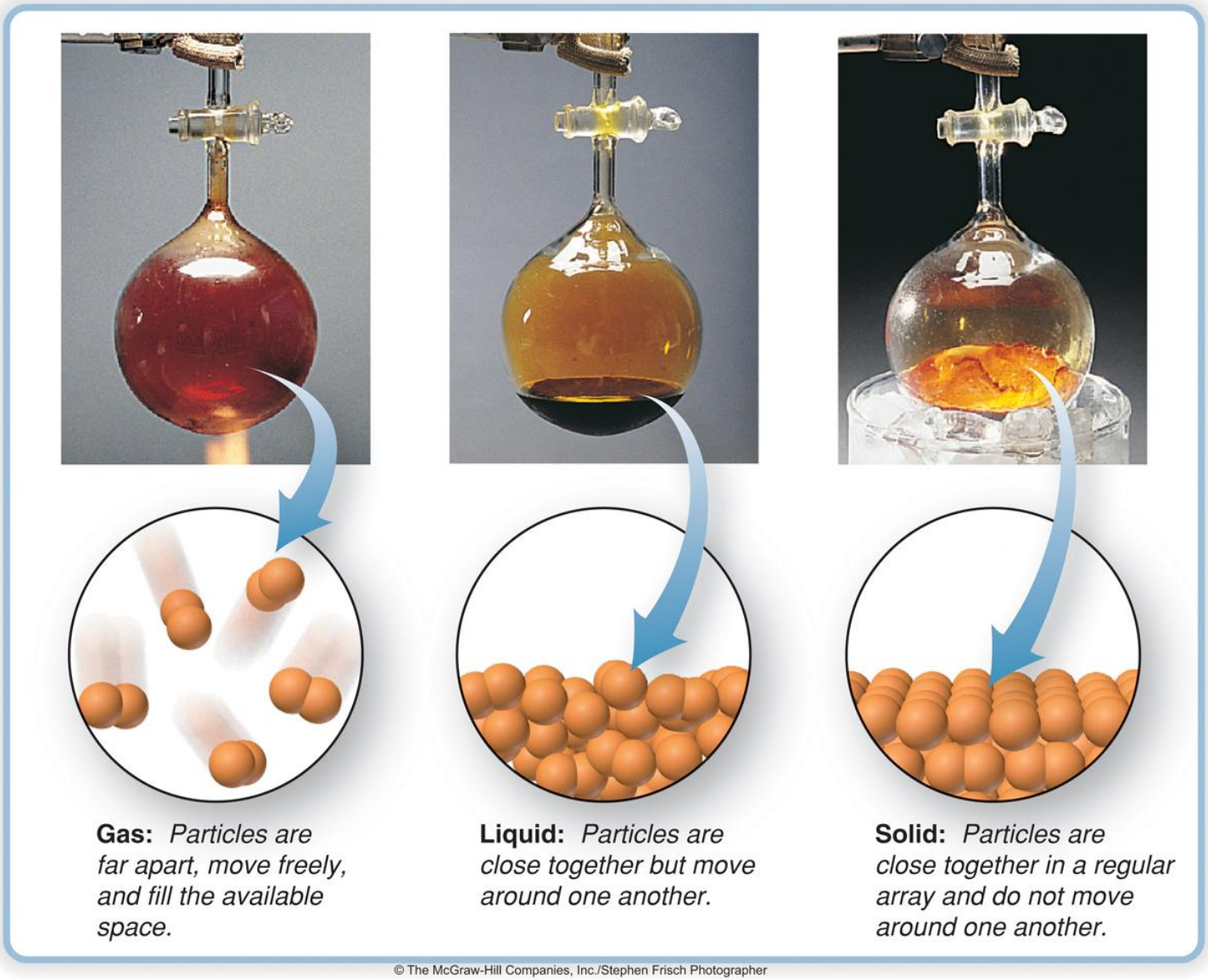

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Gas Pressure and its Measurement

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

Atmospheric pressure arises from the force exerted by atmospheric gases on the earth's surface.

Atmospheric pressure decreases with altitude.

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Figure 5.2 Effect of atmospheric pressure on a familiar object.

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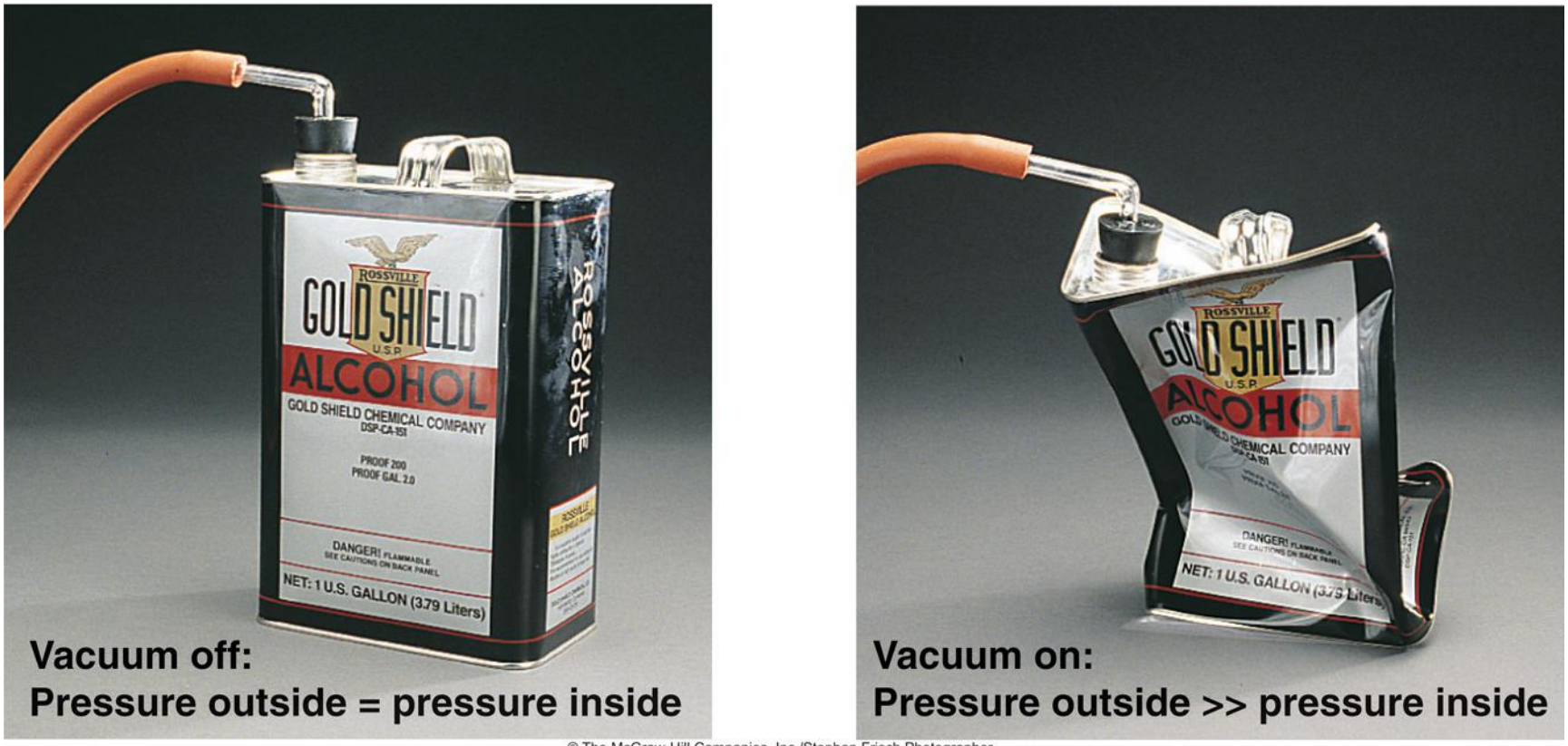

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Figure 5.3 A mercury barometer.

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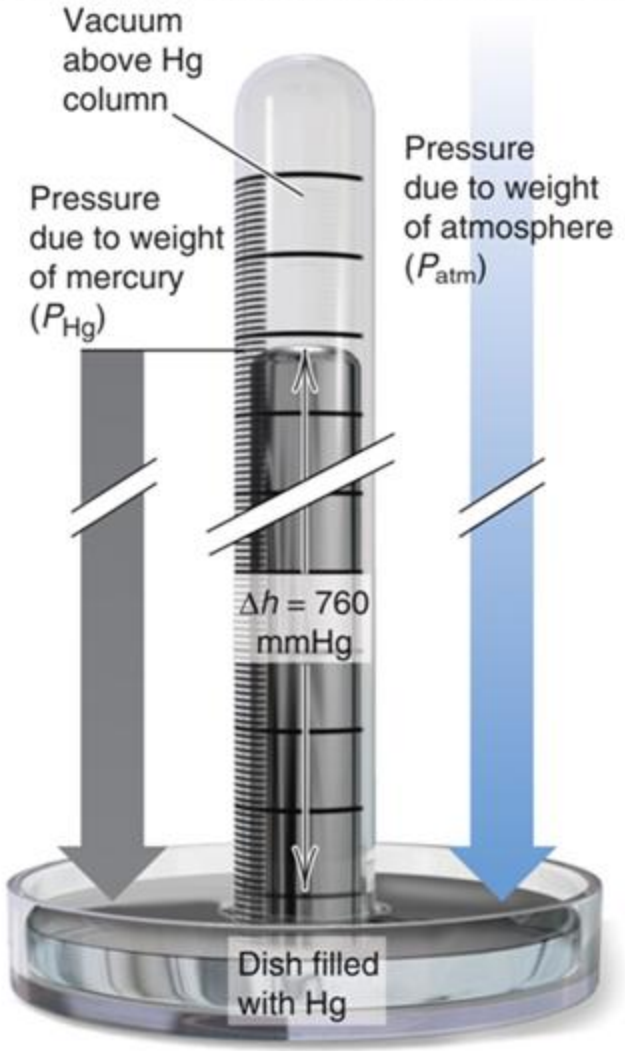

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Table 5.1 Common Units of Pressure

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Unit	Normal Atmospheric Pressure at Sea Level and 0°C
pascal (Pa); kilopascal (kPa)	1.01325×10^5 Pa; 101.325 kPa
atmosphere (atm)	1 atm*
millimeters of mercury (mmHg)	760 mmHg*
torr	760 torr*
pounds per square inch (lb/in^2 or psi)	14.7 lb/in^2
bar	1.01325 bar

*This is an exact quantity; in calculations, we use as many significant figures as necessary.

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Sample Problem 5.1 Converting Units of Pressure

PROBLEM: A geochemist heats a limestone ($CaCO_3$) sample and collects the CO_2 released in an evacuated flask attached to a closed-end manometer. After the system comes to room temperature, Δh = 291.4 mm Hg. Calculate the CO_2 pressure in torrs, atmospheres, and kilopascals.

PLAN: Construct conversion factors to find the other units of pressure.

SOLUTION:

$$291.4 \text{ mmHg} \times \frac{1 \text{ torr}}{1 \text{ mmHg}} = \mathbf{291.4 \text{ torr}}$$

$$291.4 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = \mathbf{0.3834 \text{ atm}}$$

$$0.3834 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = \mathbf{38.85 \text{ kPa}}$$

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The Gas Laws

- The gas laws describe the physical behavior of gases in terms of 4 variables:
  - pressure (*P)*
  - temperature (*T*)
  - volume (*V*)
  - amount (number of moles, *n*)
- An ***ideal gas*** is a gas that exhibits linear relationships among these variables.
- ***No ideal gas actually exists***, but most simple gases behave nearly ideally at ordinary temperatures and pressures.

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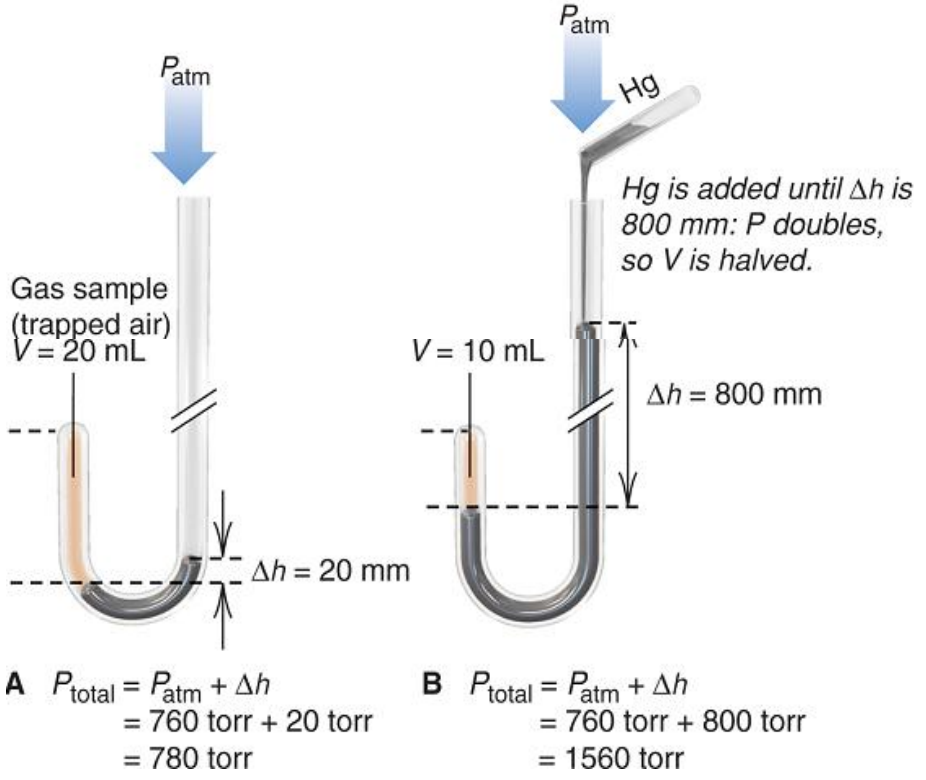
Figure 5.4 Boyle's law, the relationship between the volume and pressure of a gas.



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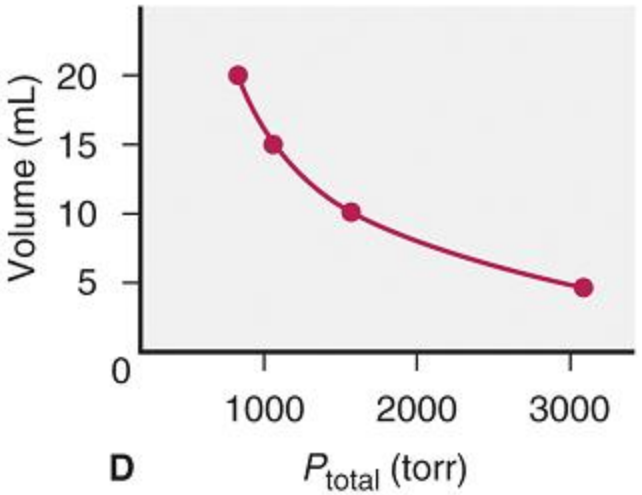
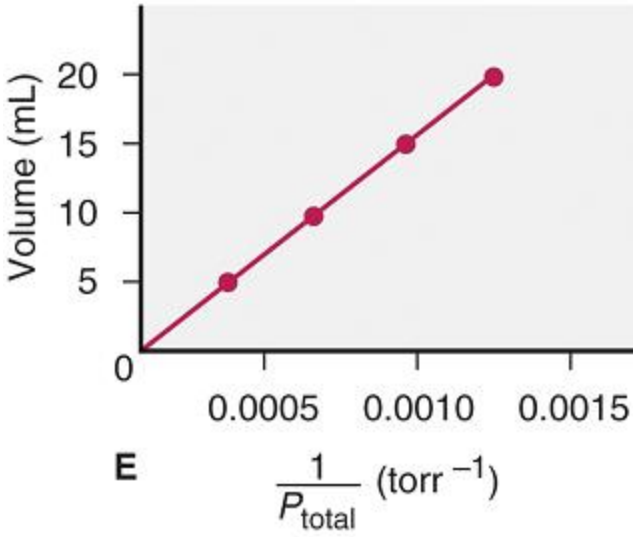
V (mL)	P (torr)			$\frac{1}{P_{total}}$	PV (torr•mL)
	Δh	+ P_{atm}	= P_{total}		
20.0	20.0	760	780	0.00128	1.56×10^4
15.0	278	760	1038	0.000963	1.56×10^4
10.0	800	760	1560	0.000641	1.56×10^4
5.0	2352	760	3112	0.000321	1.56×10^4





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Boyle's Law

At constant temperature, the volume occupied by a fixed amount of gas is ***inversely*** proportional to the external pressure.

$$V \propto \frac{1}{P} \qquad \text{or } PV = \text{constant}$$

At fixed *T* and *n*,
***P* decreases as *V* increases**
***P* increases as *V* decreases**

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Figure 5.5 AB **Charles's law, the relationship between the volume and temperature of a gas.**

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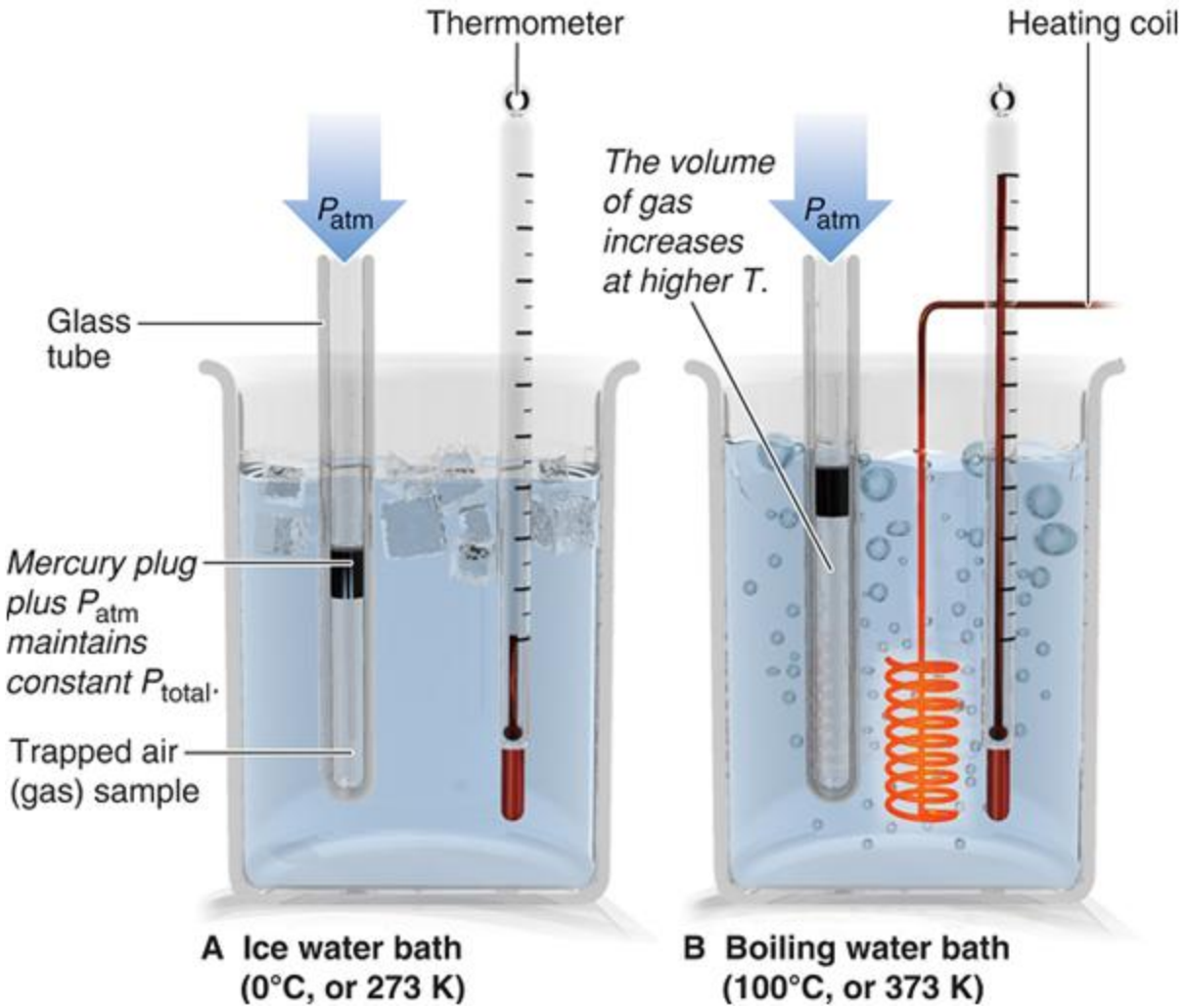

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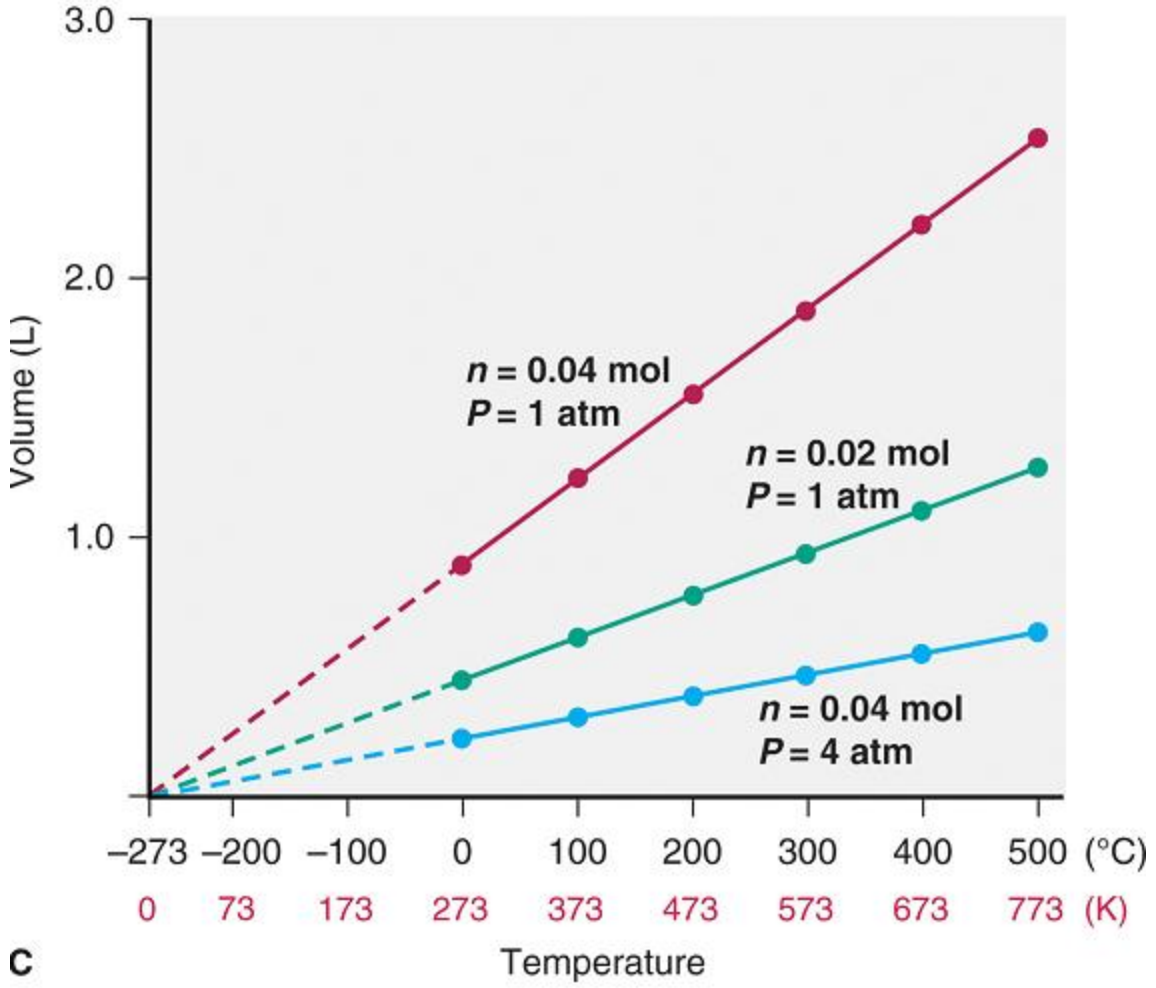
Figure 5.5 C **Absolute zero (0 K) is the temperature at which an ideal gas would have a zero volume.**



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Charles's Law

At constant pressure, the volume occupied by a fixed amount of gas is ***directly*** proportional to its absolute (Kelvin) temperature.

$$V \propto T \qquad \frac{V}{T} = \text{constant}$$

At fixed *T* and *n*,
***P* decreases as *V* increases**
***P* increases as *V* decreases**

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Figure 5.6 **The relationship between the volume and amount of a gas.**

At fixed temperature and pressure, the volume occupied by a gas is directly proportional to the amount of gas.

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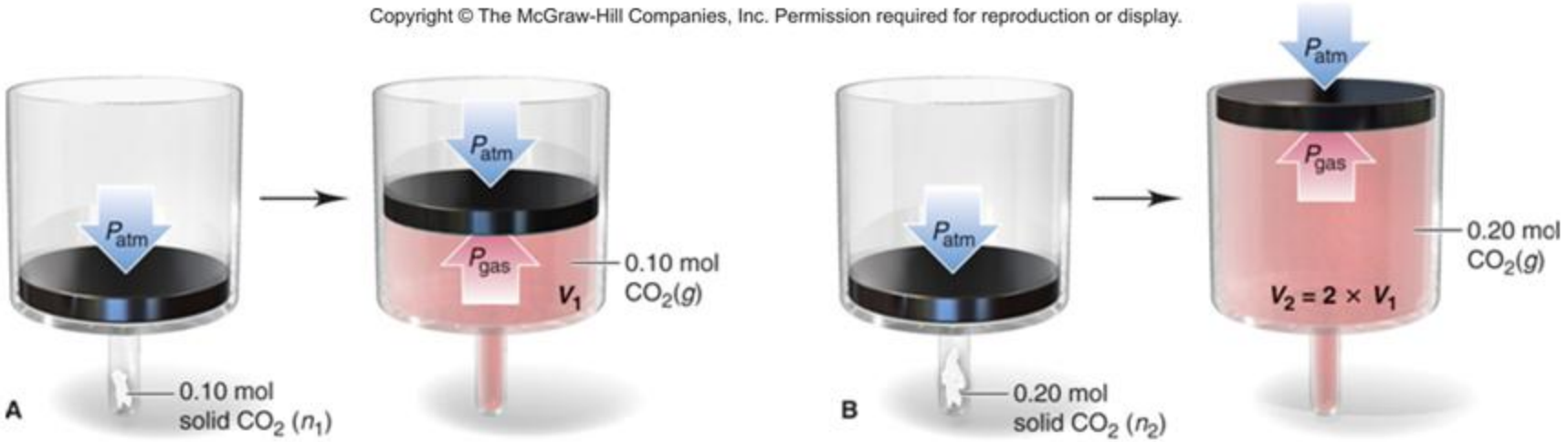

Avogadro's Law: at fixed temperature and pressure, equal volumes of ***any*** ideal gas contain equal numbers of particles (or moles).

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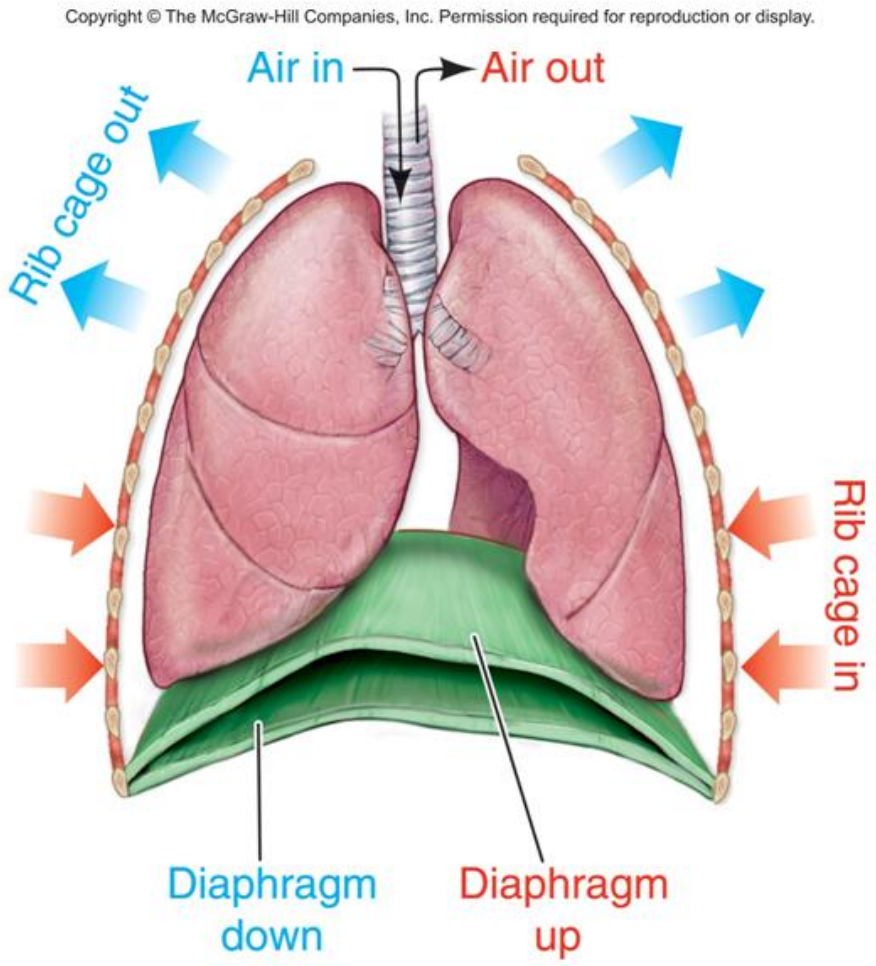
Figure 5.7 The process of breathing applies the gas laws.



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Gas Behavior at Standard Conditions

STP or **standard temperature and pressure** specifies a pressure of **1 atm (760 torr)** and a temperature of **0°C (273.15 K)**.

The **standard molar volume** is the volume of 1 mol of an ideal gas at STP.
Standard molar volume = 22.4141 L or **22.4 L**

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Figure 5.8 Standard molar volume.

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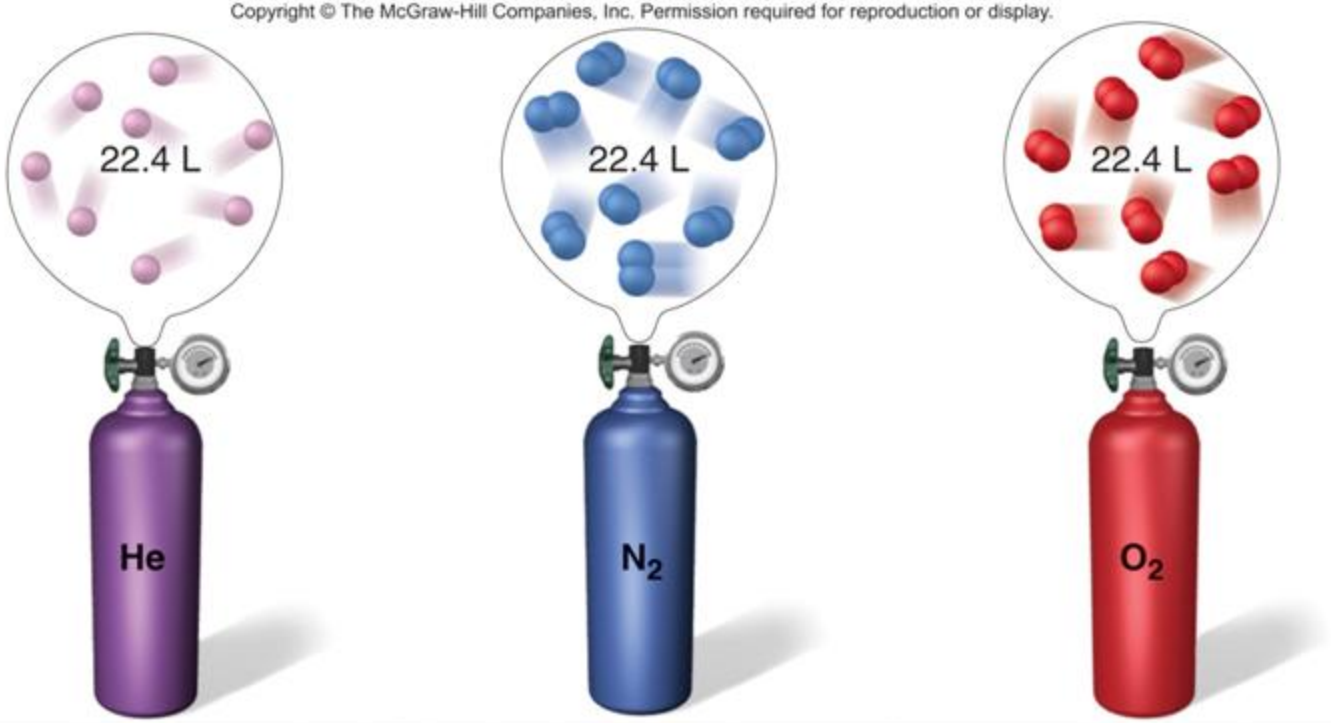

n = 1 mol	n = 1 mol	n = 1 mol
P = 1 atm (760 torr)	P = 1 atm (760 torr)	P = 1 atm (760 torr)
T = 0°C (273 K)	T = 0°C (273 K)	T = 0°C (273 K)
V = 22.4 L	V = 22.4 L	V = 22.4 L
Number of gas particles $= 6.022 \times 10^{23}$	Number of gas particles $= 6.022 \times 10^{23}$	Number of gas particles $= 6.022 \times 10^{23}$
Mass = 4.003 g	Mass = 28.02 g	Mass = 32.00 g
d = 0.179 g/L	d = 1.25 g/L	d = 1.43 g/L

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Figure 5.9 **The volume of 1 mol (22.4 L) of an ideal gas and of some familiar objects: 1 gal of milk (3.79 L), a basketball (7.50 L) and 2.00 L of a carbonated drink.**

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The Ideal Gas Law

$$pV = nRT$$

$$R = \frac{PV}{nT} = \frac{1 \text{ atm x } 22.414 \text{ L}}{1 \text{ mol x } 273.15 \text{ K}} = \frac{0.0821 \text{ atm·L}}{\text{mol·K}}$$

R is the universal gas constant;
the numerical value of *R* depends on the units used.

The ideal gas law can also be expressed by the combined equation:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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Figure 5.10 The individual gas laws as special cases of the ideal gas law.

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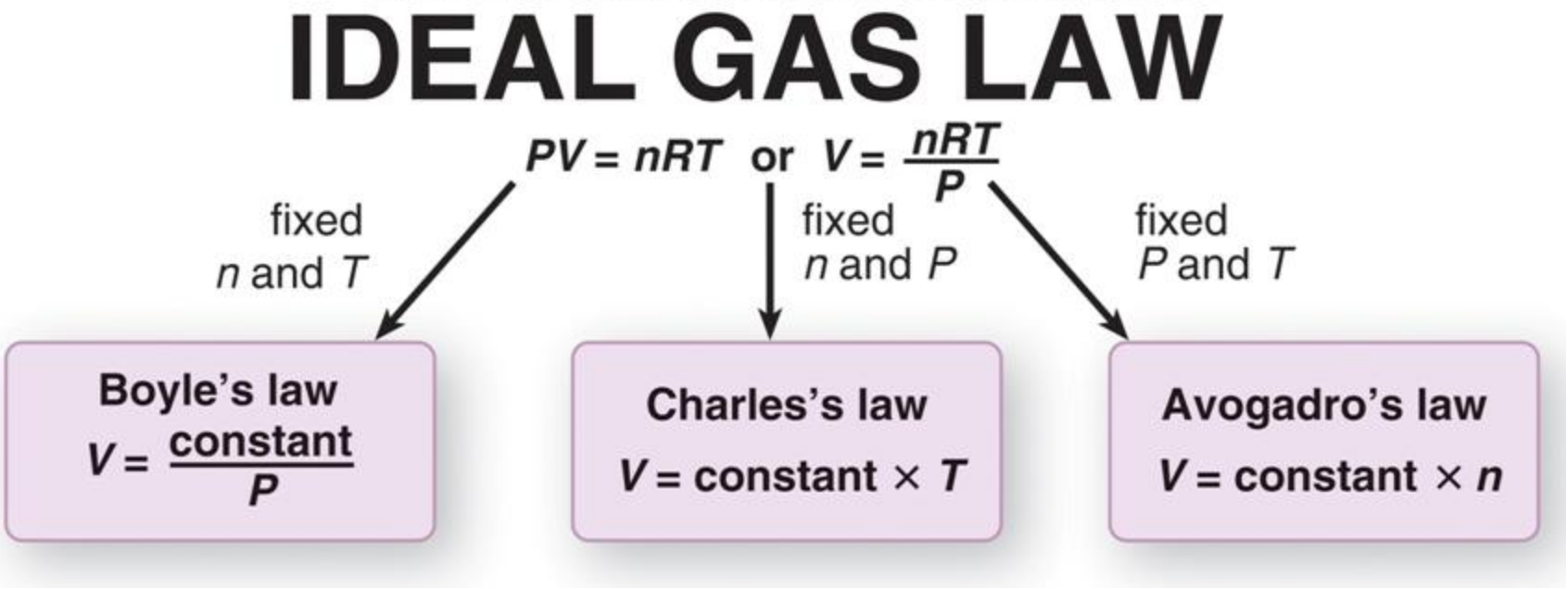

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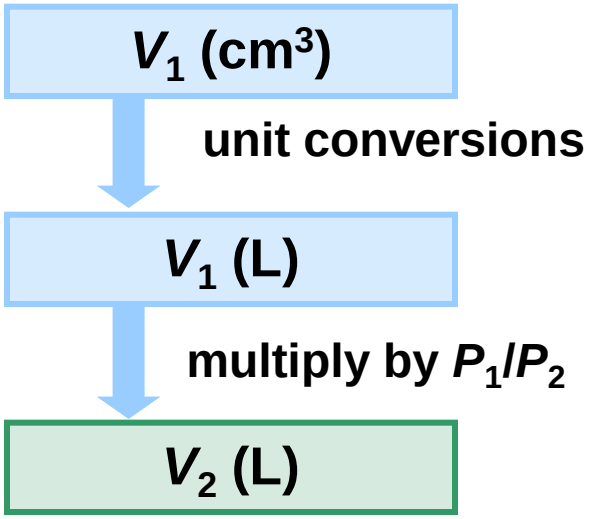
Sample Problem 5.2 Applying the Volume-Pressure Relationship

PROBLEM: Boyle's apprentice finds that the air trapped in a J tube occupies 24.8 cm^3 at 1.12 atm. By adding mercury to the tube, he increases the pressure on the trapped air to 2.64 atm. Assuming constant temperature, what is the new volume of air (in L)?

PLAN: The temperature and amount of gas are fixed, so this problem involves a change in pressure and volume only.



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Sample Problem 5.2

SOLUTION:

$P_1 = 1.12$ atm $P_2 = 2.64$ atm

$V_1 = 24.8$ cm^3 V_2 = unknown

n and *T* are constant

$$24.8 \text{ cm}^3 \times \frac{1 \text{ mL}}{1 \text{ cm}^3} \times \frac{\text{L}}{10^3 \text{ mL}} = 0.0248 \text{ L}$$

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \qquad P_1V_1 = P_2V_2$$

$$V_2 = V_1 \times \frac{P_1}{P_2} = 0.0248 \text{ L} \times \frac{1.12 \text{ atm}}{2.46 \text{ atm}}$$

= 0.0105 L

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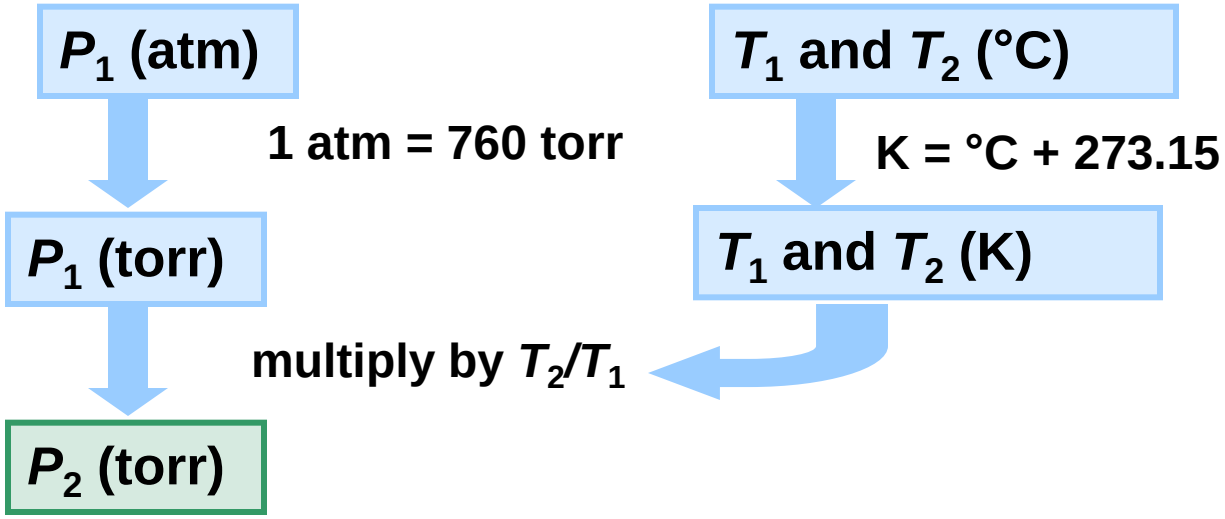
Sample Problem 5.3 Applying the Pressure-Temperature Relationship

PROBLEM: A steel tank used for fuel delivery is fitted with a safety valve that opens when the internal pressure exceeds 1.00×10^3 torr. It is filled with methane at 23°C and 0.991 atm and placed in boiling water at exactly 100°C. Will the safety valve open?

PLAN: We must determine if the pressure will exceed 1.00×10^3 torr at the new temperature. Since the gas is in a steel tank, the volume remains constant.



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Sample Problem 5.3

SOLUTION:

$P_1 = 0.991$ atm P_2 = unknown

$T_1 = 23°C$ $T_2 = 100.°C$

n and *V* are constant

$$0.991 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 753 \text{ torr}$$

$T_1 = 23 + 273.15 = 296$ K

$T_2 = 100. + 273.15 = 373$ K

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = P_1 \times \frac{T_2}{T_1} = 753 \text{ torr} \times \frac{373 \text{ K}}{296 \text{ K}}$$

= 949 torr

The safety valve will not open, since P_2 is less than 1.00×10^3 torr.

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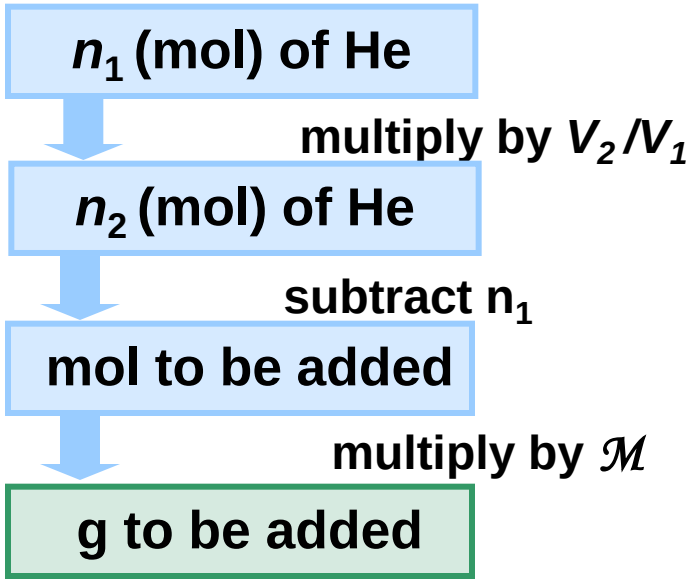
Sample Problem 5.4 Applying the Volume-Amount Relationship

PROBLEM: A scale model of a blimp rises when it is filled with helium to a volume of 55.0 dm^3. When 1.10 mol of He is added to the blimp, the volume is 26.2 dm^3. How many more grams of He must be added to make it rise? Assume constant T and P.

PLAN: The initial amount of helium (n_1) is given, as well as the initial volume (V_1) and the volume needed to make it rise (V_2). We need to calculate n_2 and hence the mass of He to be added.



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Sample Problem 5.4

SOLUTION:

$n_1 = 1.10$ mol $\quad n_2 =$ unknown

$V_1 = 26.2$ dm^3 $\quad V_2 = 55.0$ dm^3

T and P are constant

$$\frac{\cancel{P_1}V_1}{n_1\cancel{T_1}} = \frac{\cancel{P_2}V_2}{n_2\cancel{T_2}} \qquad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$n_2 = n_1 \times \frac{V_2}{V_1} = 1.10 \text{ mol} \times \frac{55.0 \cancel{\text{dm}^3}}{26.2 \cancel{\text{dm}^3}} = 2.31 \text{ mol He}$$

Additional amount of He needed = 2.31 mol – 1.10 mol = 1.21 mol He

$$1.21 \cancel{\text{mol He}} \times \frac{4.003 \text{ g He}}{1 \cancel{\text{mol He}}} = \mathbf{4.84 \text{ g He}}$$

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Sample Problem 5.5 **Solving for an Unknown Gas Variable at Fixed Conditions**

PROBLEM: A steel tank has a volume of 438 L and is filled with 0.885 kg of O_2. Calculate the pressure of O_2 at 21°C.

PLAN: We are given *V*, *T* and mass, which can be converted to moles (*n*). Use the ideal gas law to find *P*.

SOLUTION: *V* = 438 L *T* = 21°C = 294 K

n = 0.885 kg O_2 (convert to mol) *P* is unknown

$$0.885 \text{ kg } O_2 \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 27.7 \text{ mol } O_2$$

$$P = \frac{nRT}{V} = \frac{27.7 \text{ mol} \times 0.0821 \frac{\text{atm·L}}{\text{mol·K}} \times 294.15 \text{ K}}{438 \text{ L}}$$

= 1.53 atm

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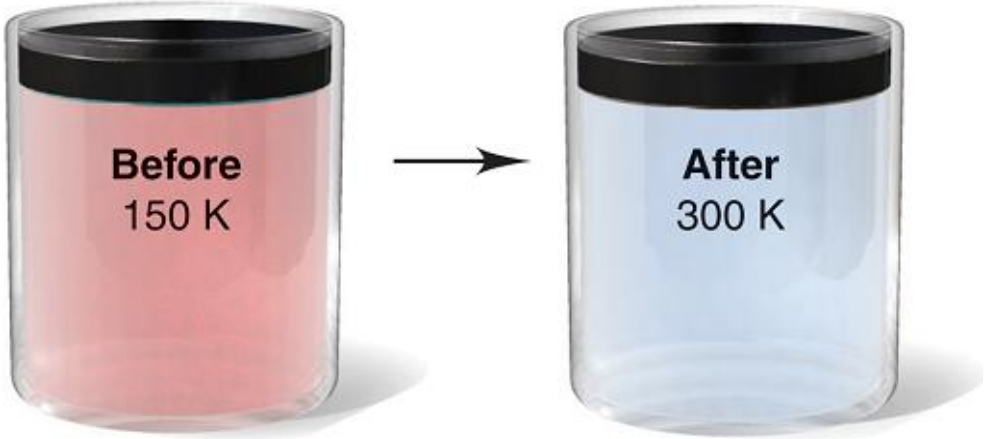
Sample Problem 5.6 — Using Gas Laws to Determine a Balanced Equation

PROBLEM: The piston-cylinder is depicted before and after a gaseous reaction that is carried out at constant pressure. The temperature is 150 K before the reaction and 300 K after the reaction. (Assume the cylinder is insulated.)



Which of the following balanced equations describes the reaction?

(1) $A_2(g) + B_2(g) \rightarrow 2AB(g)$

(2) $2AB(g) + B_2(g) \rightarrow 2AB_2(g)$

(3) $A(g) + B_2(g) \rightarrow AB_2(g)$

(4) $2AB_2(g) + A_2(g) + 2B_2(g)$

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Sample Problem 5.6

PLAN: We are told that *P* is constant for this system, and the depiction shows that *V* does not change either. Since *T* changes, the volume could not remain the same unless the amount of gas in the system also changes.

SOLUTION: $n_1T_1 = n_2T_2$ $\quad \frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{150\ \text{K}}{300\ \text{K}} = ½$

Since *T* doubles, the total number of moles of gas must halve – i.e., the moles of product must be half the moles of reactant. This relationship is shown by equation (3).

$$\mathbf{A}(g) + \mathbf{B_2}(g) \rightarrow \mathbf{AB_2}(g)$$

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The Ideal Gas Law and Gas Density

The density of a gas is
- directly proportional to its molar mass and
- inversely proportional to its temperature.

$$\text{density} = \frac{m}{V} \quad \text{and} \quad \text{moles} = \frac{m}{\mathcal{M}}$$

$$PV = \frac{m}{\mathcal{M}} RT$$

$$\frac{m}{V} = d = \frac{\mathcal{M} \times P}{RT}$$

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Sample Problem 5.7 Calculating Gas Density

PROBLEM: Find the density (in g/L) of CO_2 (*g*) and the number of molecules per liter

(a) at STP and **(b)** at room conditions (20.°C and 1.00 atm).

PLAN: We can use the molar mass of CO_2 to find its density from the ideal gas equation.

SOLUTION: (a) At STP, or 273 K and 1.00 atm:

$$d = \frac{\mathcal{M} \times P}{RT} = \frac{44.01\ \text{g/}\cancel{\text{mol}} \times 1.00\ \cancel{\text{atm}}}{0.0821\ \frac{\cancel{\text{atm}}\cdot\text{L}}{\text{mol}\cdot\cancel{\text{K}}} \times 273\ \cancel{\text{K}}}$$

= 1.96 g/L

$$\frac{1.96\ \cancel{\text{g CO}_2}}{1\ \text{L}} \times \frac{1\ \cancel{\text{mol}}\ \text{CO}_2}{44.01\ \cancel{\text{g CO}_2}} \times \frac{6.022 \times 10^{23}\ \text{molecules}}{1\ \cancel{\text{mol}}}$$

= 2.68 x 10^{22} molecules CO_2/L

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Sample Problem 5.7

SOLUTION: (b) At 20.°C and 1.00 atm:

$T = 20.°C + 273.15 = 293\ K$

$$d = \frac{\mathcal{M} \times P}{RT} = \frac{44.01\ g/\cancel{mol} \times 1.00\ \cancel{atm}}{0.0821\ \frac{atm \cdot L}{mol \cdot \cancel{K}} \times 293\ \cancel{K}}$$

= 1.83 g/L

$$\frac{1.83\ \cancel{g\ CO_2}}{1\ L} \times \frac{1\ \cancel{mol}\ CO_2}{44.01\ \cancel{g\ CO_2}} \times \frac{6.022 \times 10^{23}\ molecules}{1\ \cancel{mol}}$$

= 2.50 x 10^{22} molecules CO_2/L

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Molar Mass from the Ideal Gas Law

$$n = \frac{m}{\mathcal{M}} = \frac{PV}{RT}$$

$$\boxed{\mathcal{M} = \frac{mRT}{PV}}$$

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Sample Problem 5.8 Finding the Molar Mass of a Volatile Liquid

PROBLEM: An organic chemist isolates a colorless liquid from a petroleum sample. She places the liquid in a preweighed flask and puts the flask in boiling water, causing the liquid to vaporize and fill the flask with gas. She closes the flask and reweighs it. She obtains the following data:

Volume (*V*) of flask = 213 mL *T* = 100.0°C *P* = 754 torr

mass of flask + gas = 78.416 g mass of flask = 77.834 g

Calculate the molar mass of the liquid.

PLAN: The variables *V, T* and *P* are given. We find the mass of the gas by subtracting the mass of the flask from the mass of the flask with the gas in it, and use this information to calculate $\mathcal{M}$.

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Sample Problem 5.8

SOLUTION: *m* of gas = (78.416 - 77.834) = 0.582 g

$$V = 213\ \cancel{mL} \times \frac{1\ L}{10^3\ \cancel{mL}} = 0.213\ L \qquad T = 100.0°C + 273.15 = 373.2\ K$$

$$P = 754\ \cancel{torr} \times \frac{1\ atm}{760\ \cancel{torr}} = 0.992\ atm$$

$$\mathcal{M} = \frac{mRT}{PV} = \frac{0.582\ g \times 0.0821 \frac{atm \cdot \cancel{L}}{mol \cdot \cancel{K}} \times 373\ \cancel{K}}{0.213\ \cancel{L} \times 0.992\ \cancel{atm}}$$

= 84.4 g/mol

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Mixtures of Gases

- Gases mix homogeneously in any proportions.
  - Each gas in a mixture behaves as if it were the only gas present.
- The pressure exerted by each gas in a mixture is called its ***partial pressure***.
- Dalton's Law of partial pressures states that the total pressure in a mixture is the sum of the partial pressures of the component gases.
- The partial pressure of a gas is proportional to its mole fraction:

$$P_A = X_A \times P_{total} \qquad X_A = \frac{n_A}{n_{total}}$$

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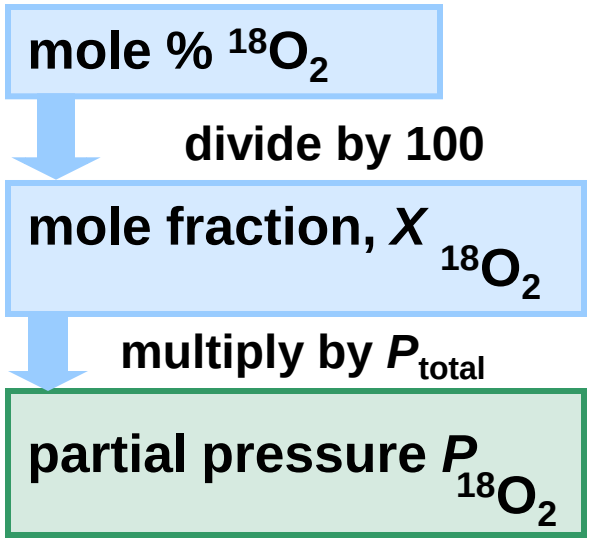
Sample Problem 5.9 Applying Dalton's Law of Partial Pressures

PROBLEM: In a study of O_2 uptake by muscle at high altitude, a physiologist prepares an atmosphere consisting of 79 mole % N_2, 17 mole % $^{16}O_2$, and 4.0 mole % $^{18}O_2$. (The isotope ^{18}O will be measured to determine the O_2 uptake.) The pressure of the mixture is 0.75 atm to simulate high altitude. Calculate the mole fraction and partial pressure of $^{18}O_2$ in the mixture.

PLAN: Find $X_{^{18}O_2}$ and $P_{^{18}O_2}$ from P_{total} and mol % $^{18}O_2$.



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Sample Problem 5.9

SOLUTION:

$$X_{^{18}O_2} = \frac{4.0 \text{ mol \% } ^{18}O_2}{100} = 0.040$$

$$P_{^{18}O_2} = X_{^{18}O_2} \times P_{total} = 0.040 \times 0.75 \text{ atm} \quad \boxed{= 0.030 \text{ atm}}$$

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Table 5.2 Vapor Pressure of Water (P_{H_2O}) + at Different T

T(^{0}C)	P_{H_2O}(torr)	T(^{0}C)	P_{H_2O}(torr)
0	4.6	40	55.3
5	6.5	45	71.9
10	9.2	50	92.5
12	10.5	55	118.0
14	12.0	60	149.4
16	13.6	65	187.5
18	15.5	70	233.7
20	17.5	75	289.1
22	19.8	80	355.1
24	22.4	85	433.6
26	25.2	90	525.8
28	28.3	95	633.9
30	31.8	100	760.0
35	42.2		

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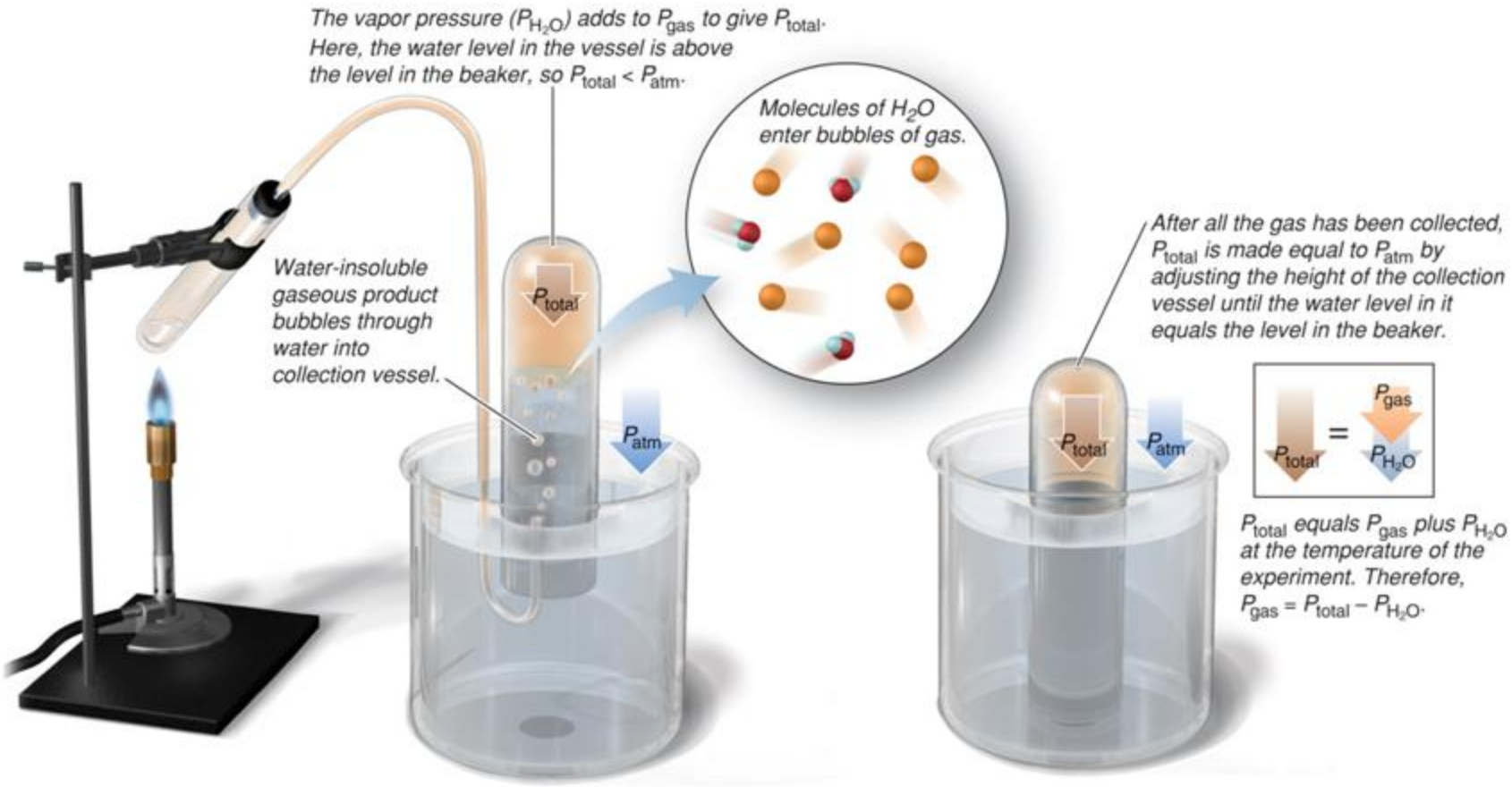
Figure 5.11 Collecting a water-insoluble gaseous product and determining its pressure.



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Sample Problem 5.10

Calculating the Amount of Gas Collected over Water

PROBLEM: Acetylene (C_2H_2) is produced in the laboratory when calcium carbide (CaC_2) reacts with water:

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

A collected sample of acetylene has a total gas pressure of 738 torr and a volume of 523 mL. At the temperature of the gas (23°C), the vapor pressure of water is 21 torr. How many grams of acetylene are collected?

PLAN: The difference in pressures will give *P* for the C_2H_2. The number of moles (*n*) is calculated from the ideal gas law and converted to mass using the molar mass.

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Sample Problem 5.10

PLAN:

P_{total}

↓ subtract P for H_2O

P of C_2H_2

↓ use ideal gas law

n of C_2H_2

↓ multiply by $\mathcal{M}$

mass of C_2H_2

SOLUTION:

$$P_{C_2H_2} = (738 - 21)\ \text{torr} = 717\ \text{torr}$$

$$P = 717\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.943\ \text{atm}$$

$$V = 523\ \cancel{\text{mL}} \times \frac{1\ \text{L}}{10^3\ \cancel{\text{mL}}} = 0.523\ \text{L}$$

$$T = 23°\text{C} + 273.15\ \text{K} = 296\ \text{K}$$

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Sample Problem 5.10

SOLUTION:

$$n_{C_2H_2} = \frac{PV}{RT} = \frac{0.943\ \cancel{atm} \times 0.523\ \cancel{L}}{0.0821\ \frac{\cancel{atm}\cdot\cancel{L}}{mol\cdot\cancel{K}} \times 296\ \cancel{K}}$$

= 0.0203 mol

$$0.0203\ \cancel{mol} \times \frac{26.04\ g\ C_2H_2}{1\ \cancel{mol}\ C_2H_2}$$

= 0.529 g C_2H_2

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The Ideal Gas Law and Stoichiometry

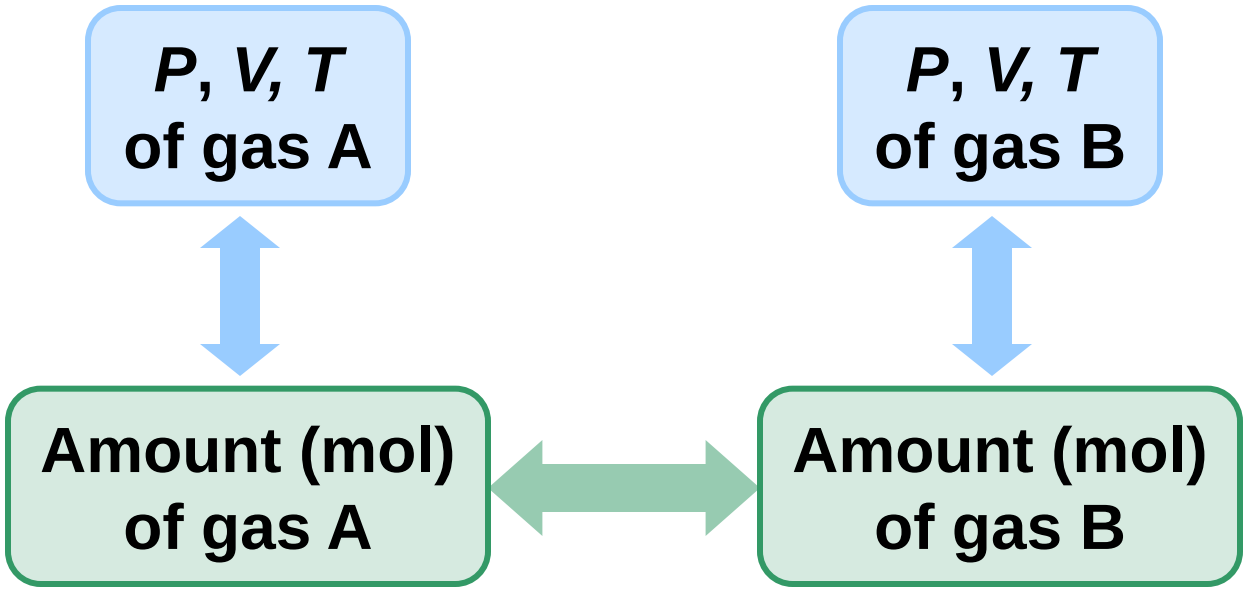

Figure 15.12

The relationships among the amount (mol, *n*) of gaseous reactant (or product) and the gas pressure (*P*), volume (*V*), and temperature (*T*).

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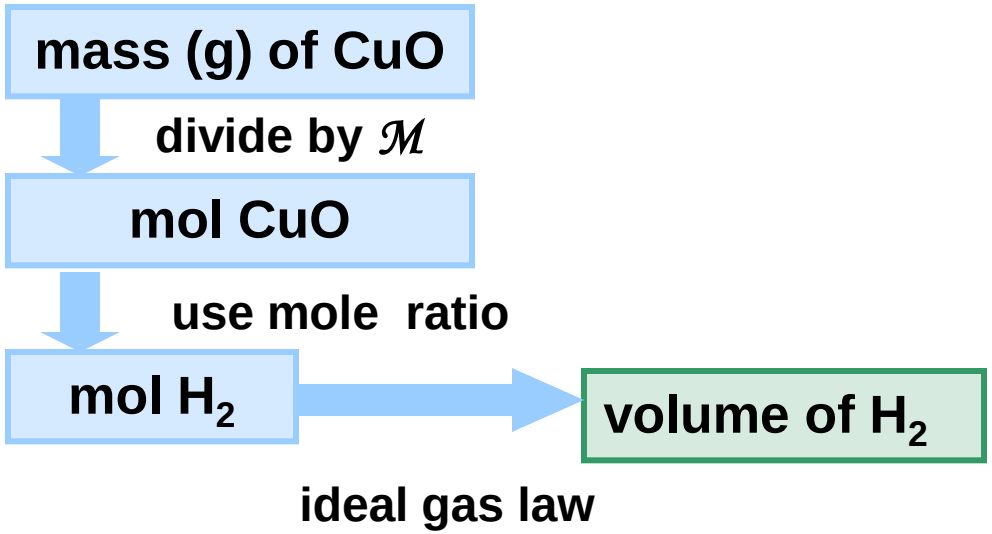
Sample Problem 5.11

Using Gas Variables to Find Amounts of Reactants and Products I

PROBLEM: What volume of H_2 gas at 765 torr and 225°C is needed to reduce 35.5 g of copper(II) oxide to form pure copper and water?

PLAN: Write a balanced equation. Convert the mass of copper (II) oxide to moles and find the moles of H_2, using the mole ratio from the balanced equation. Calculate the corresponding volume of H_2 using the ideal gas law.



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Sample Problem 5.11

SOLUTION: $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

$$35.5 \text{ g CuO} \times \frac{1 \text{ mol CuO}}{79.55 \text{ g CuO}} \times \frac{1 \text{ mol } H_2}{1 \text{ mol CuO}} = 0.446 \text{ mol } H_2$$

$$P = 765 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.01 \text{ atm} \qquad T = 225°C + 273.15 \text{ K} = 498 \text{ K}$$

$$V = \frac{nRT}{P} = \frac{0.446 \text{ mol } H_2 \times 0.0821 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 498 \text{ K}}{1.01 \text{ atm}}$$

= 18.1 L H_2

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Sample Problem 5.12

Using Gas Variables to Find Amounts of Reactants and Products II

PROBLEM: What mass of potassium chloride forms when 5.25 L of chlorine gas at 0.950 atm and 293 K reacts with 17.0 g of potassium metal?

PLAN: First we must write a balanced equation. Since the quantities of both reactants are given, we must next determine which reactant is limiting. We will use the ideal gas law to calculate the moles of Cl_2 present.

SOLUTION: The balanced equation is:

$$Cl_2(g) + 2K(s) \rightarrow 2KCl(s)$$

For Cl_2:

P = 0.950 atm V = 5.25 L

T = 293 K n = unknown

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Sample Problem 5.12

$$n_{Cl_2} = \frac{PV}{RT} = \frac{0.950\ \text{atm} \times 5.25\ \text{L}}{0.0821\ \frac{\text{atm·L}}{\text{mol·K}} \times 293\ \text{K}} = 0.207\ \text{mol}\ Cl_2$$

For Cl_2: $0.207\ \text{mol}\ Cl_2 \times \frac{2\ \text{mol KCl}}{1\ \text{mol}\ Cl_2} = 0.414\ \text{mol KCl}$

For K: $17.0\ \text{g K} \times \frac{1\ \text{mol K}}{39.10\ \text{g K}} \times \frac{2\ \text{mol KCl}}{2\ \text{mol K}} = 0.435\ \text{KCl}$

Cl_2 is the limiting reactant.

$$0.414\ \text{mol KCl} \times \frac{74.55\ \text{g KCl}}{1\ \text{mol KCl}} = \textbf{30.9 g KCl}$$

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The Kinetic-Molecular Theory: A Model for Gas Behavior

Postulate 1:

Gas particles are tiny with large spaces between them. The volume of each particle is so small compared to the total volume of the gas that it is assumed to be zero.

Postulate 2:

Gas particles are in constant, random, straight-line motion except when they collide with each other or with the container walls.

Postulate 3:

Collisions are elastic, meaning that colliding particles exchange energy but do not lose any energy due to friction. Their *total kinetic energy is constant*. Between collisions the particles do not influence each other by attractive or repulsive forces.

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Figure 5.13 Distribution of molecular speeds for N_2 at three temperatures.

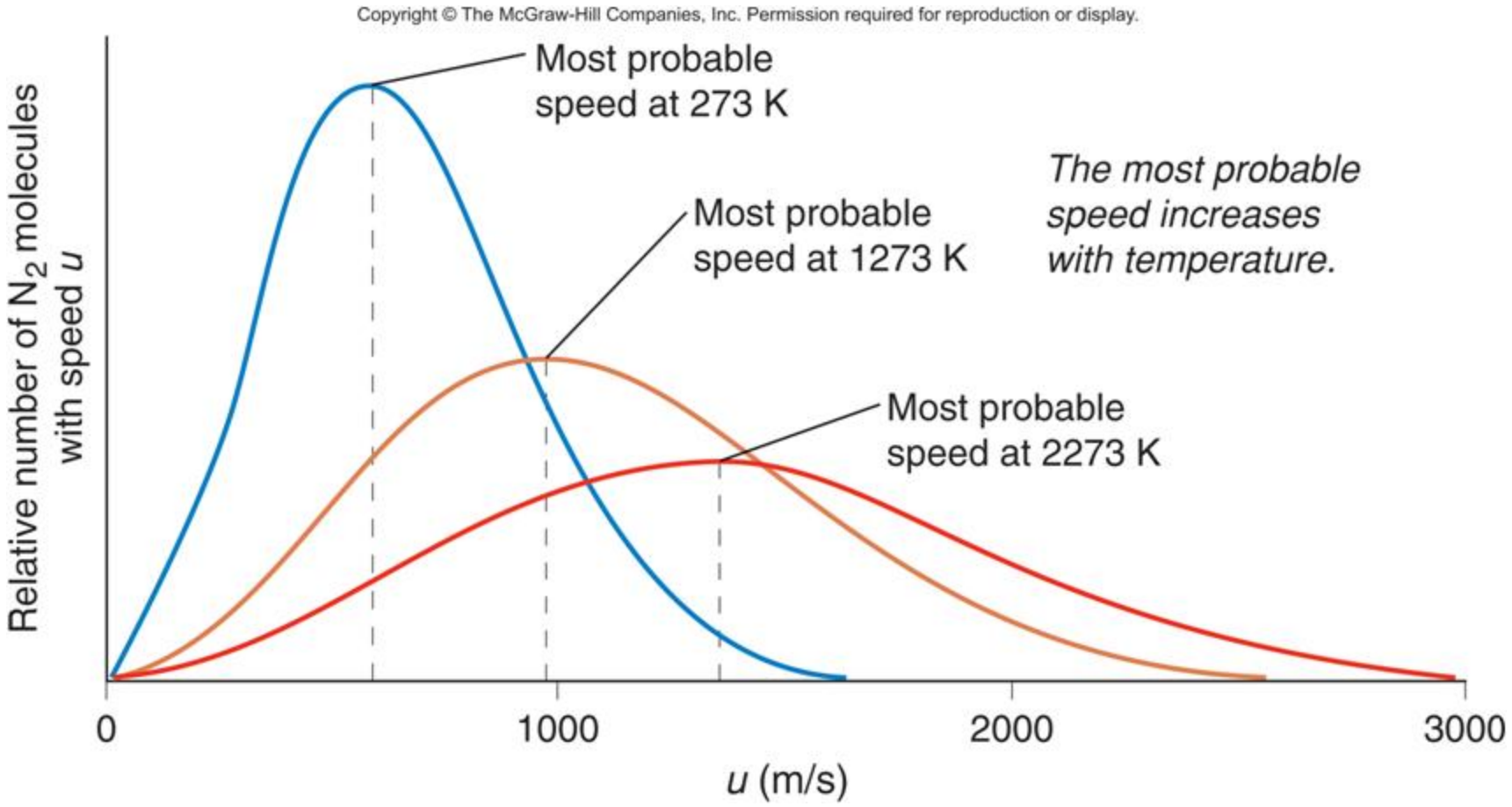

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Figure 5.14 **Pressure arises from countless collisions between gas particles and walls.**

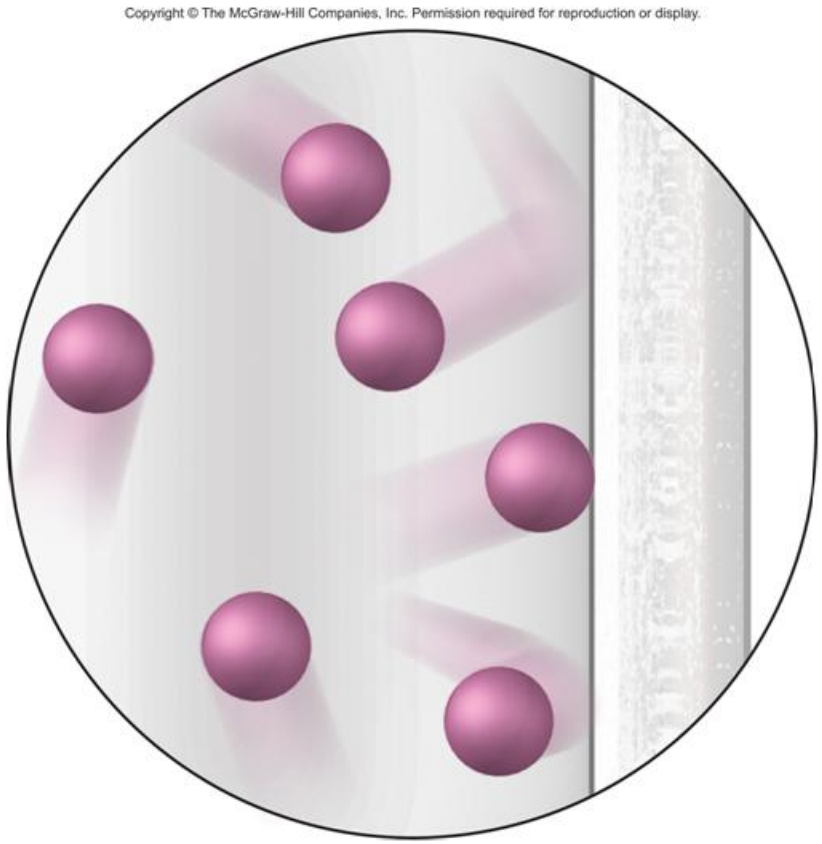

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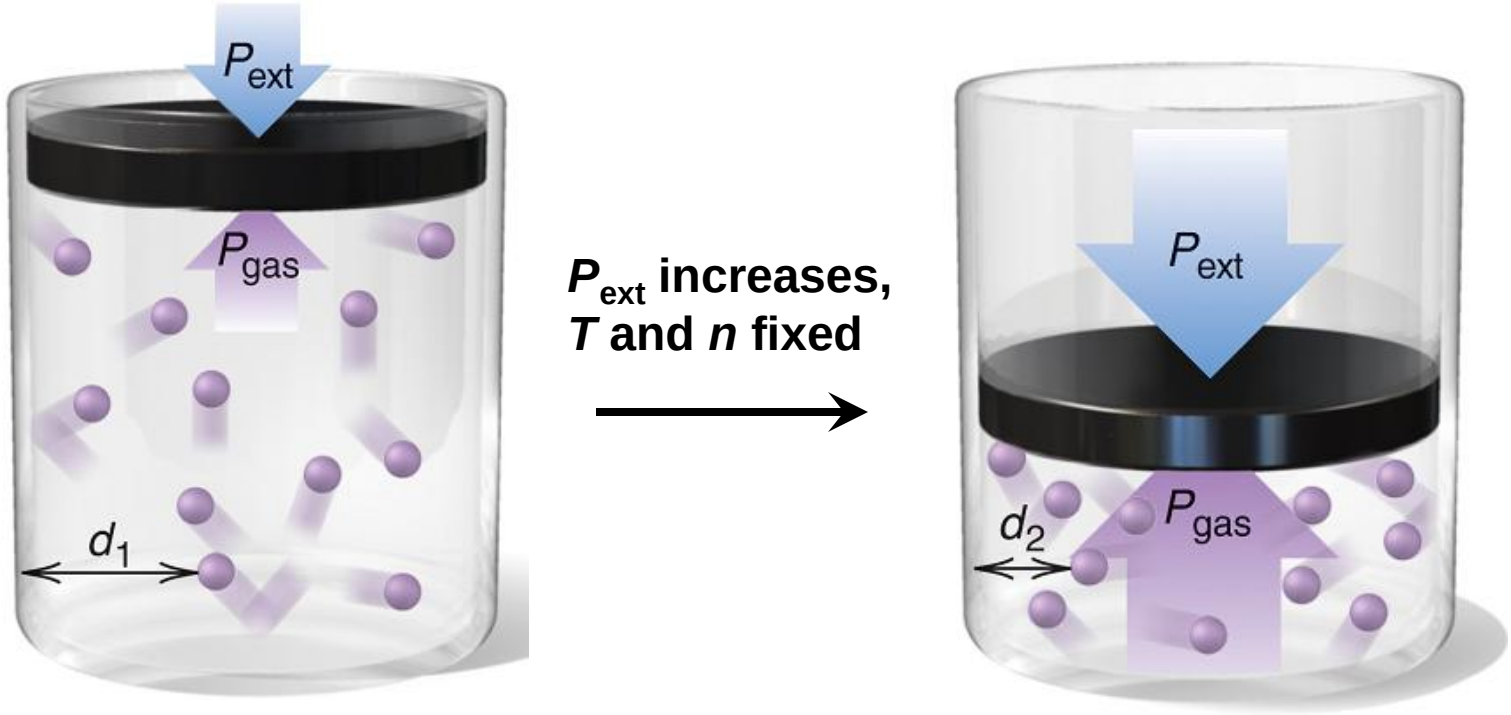
Figure 5.15 A molecular view of Boyle's law.



At any T, $P_{gas} = P_{ext}$ as particles hit the walls from an average distance, d_1.

Higher P_{ext} causes lower V, which results in more collisions, because particles hit the walls from a shorter average distance ($d_2 < d_1$). As a result, $P_{gas} = P_{ext}$ again.

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Figure 5.16 A molecular view of Dalton's law

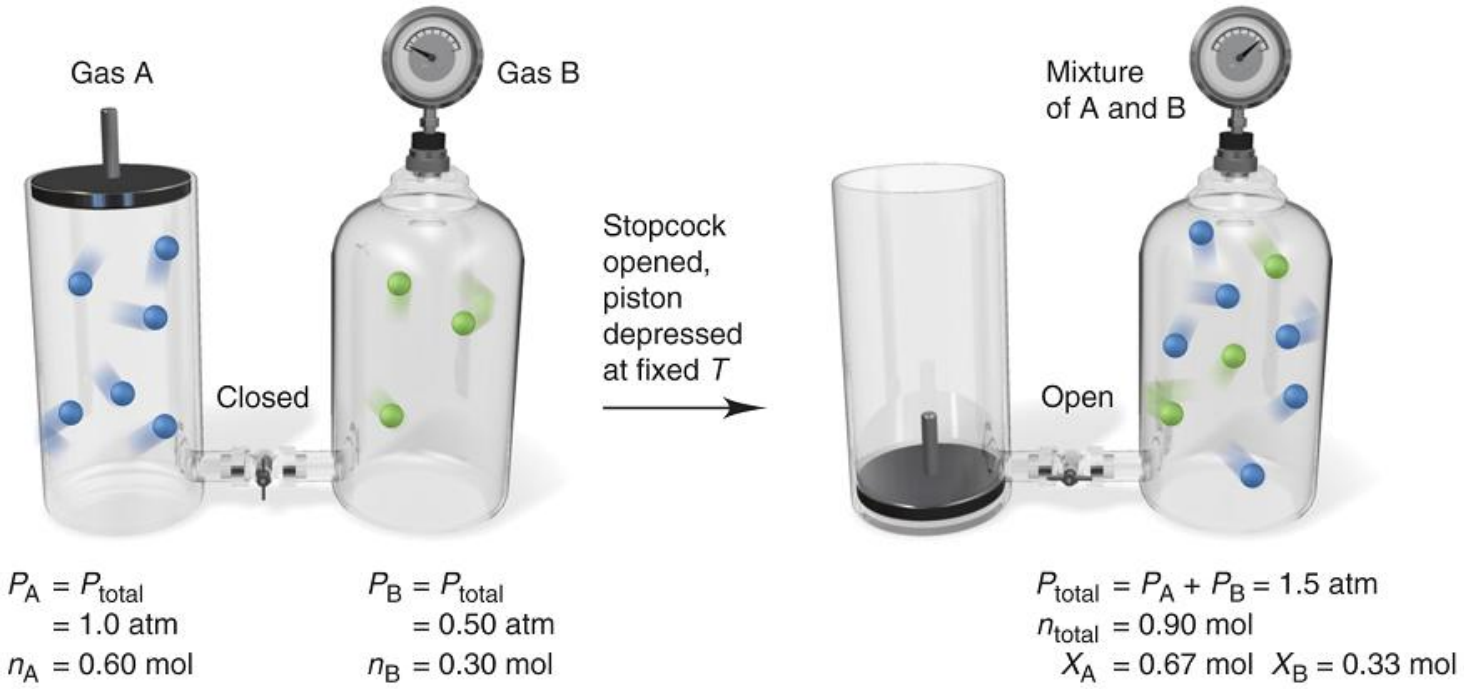

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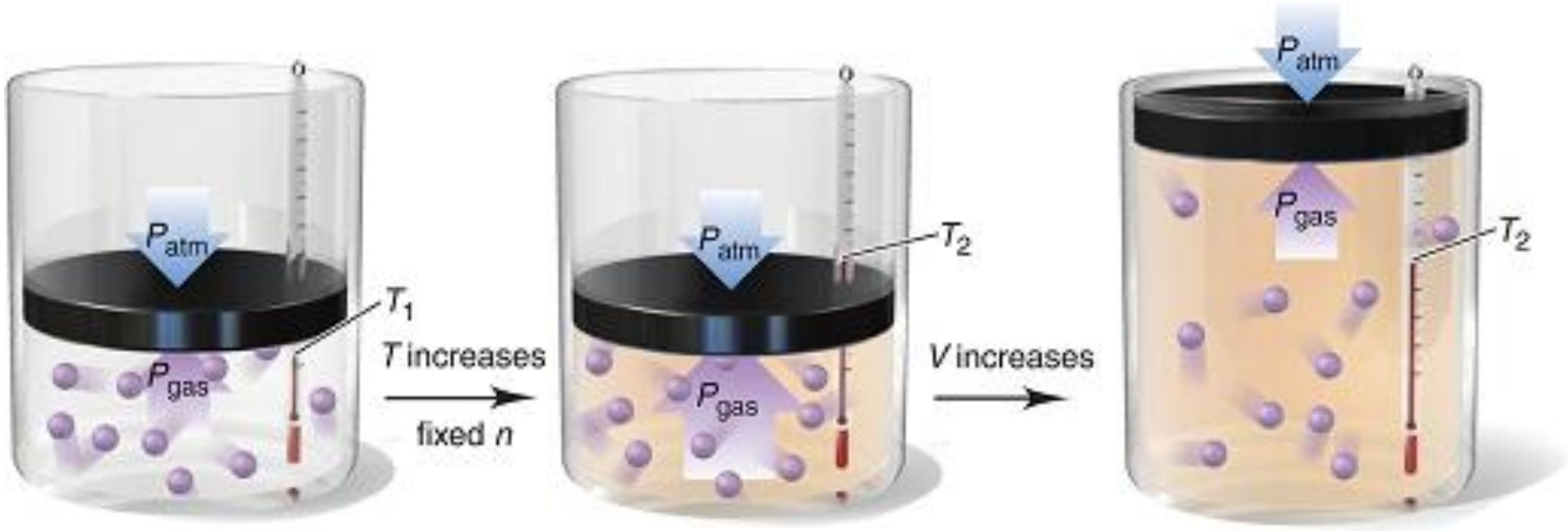
Figure 5.17 A molecular view of Charles's law



At T_1, $P_{gas} = P_{atm}$.

Higher T increases collision frequency, so $P_{gas} > P_{atm}$.

Thus, V increases until $P_{gas} = P_{atm}$ at T_2.

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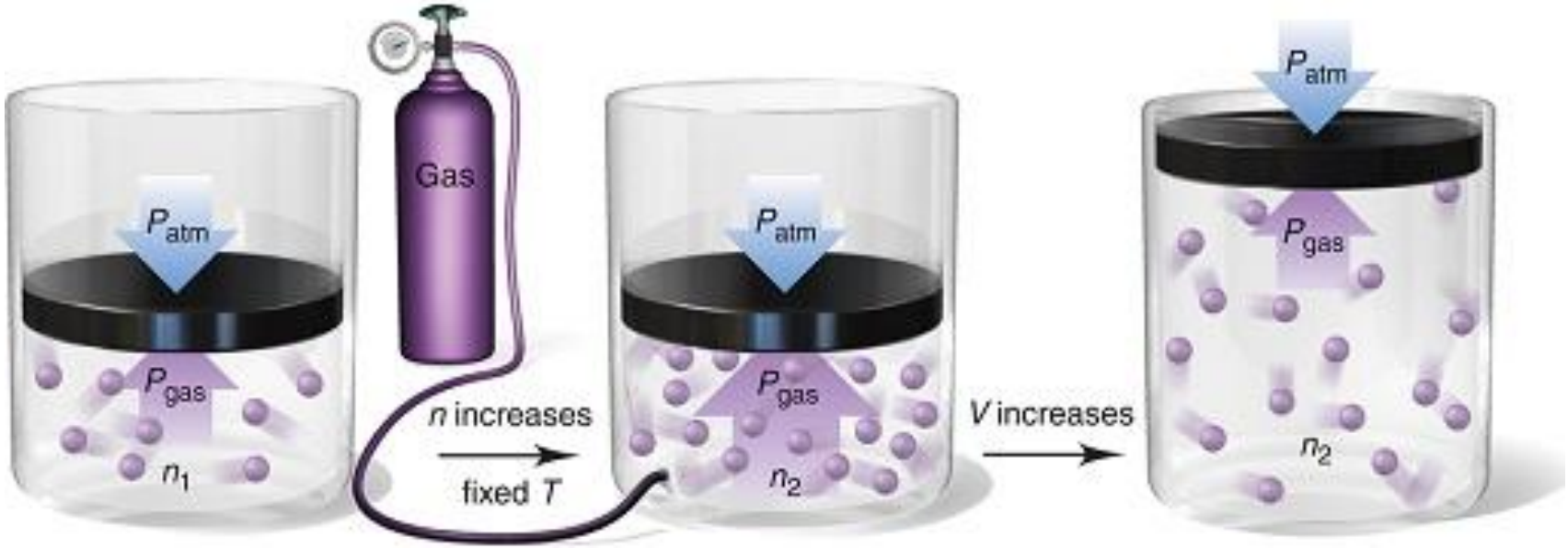
Figure 5.18 A molecular view of Avogadro's law



For a given amount, n_1, of gas, $P_{gas} = P_{atm}$.

When gas is added to reach n_2 the collision frequency of the particles increases, so $P_{gas} > P_{atm}$.

As a result, V increases until $P_{gas} = P_{atm}$ again.

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Kinetic Energy and Gas Behavior

At a given *T*, all gases in a sample have the same average kinetic energy.

$$E_k = \frac{1}{2} \text{ mass x speed}^2$$

Kinetic energy depends on both the mass and the speed of a particle.

At the same *T*, a heavier gas particle moves more slowly than a lighter one.

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Figure 5.19 The relationship between molar mass and molecular speed.

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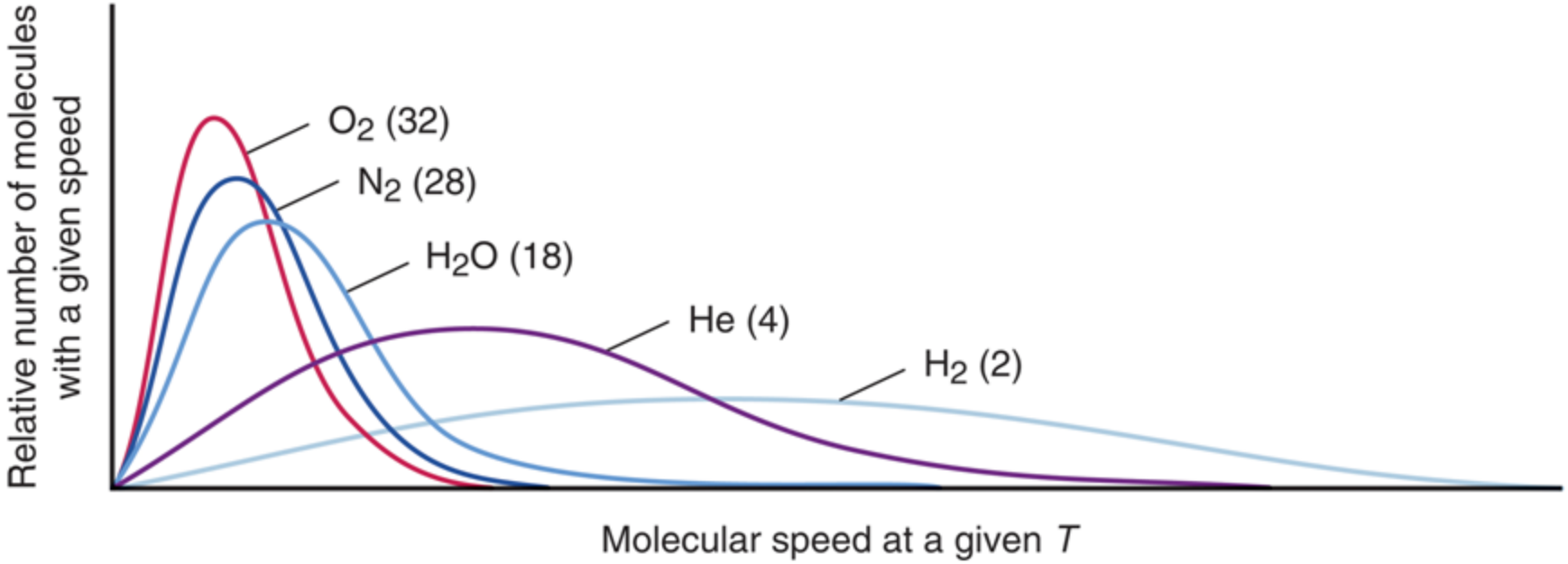

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Graham's Law of Effusion

Effusion is the process by which a gas escapes through a small hole in its container into an evacuated space.

Graham's law of effusion states that the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

A lighter gas moves more quickly and therefore has a higher rate of effusion than a heavier gas at the same *T*.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

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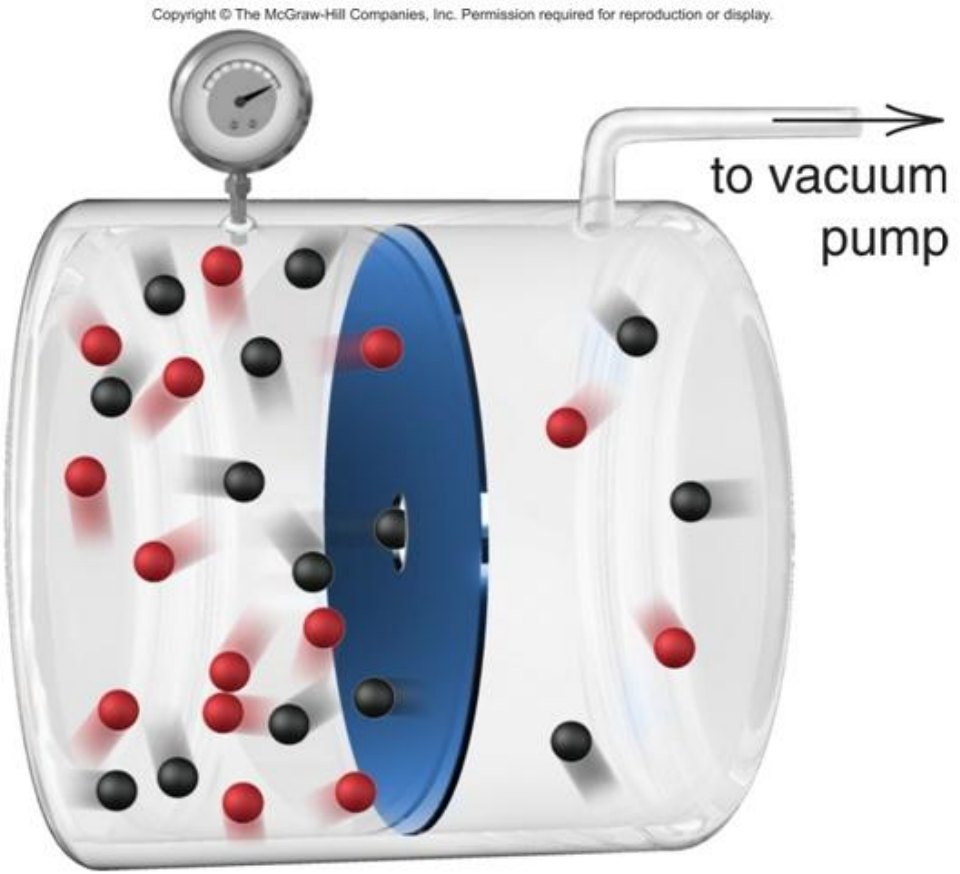
Figure 5.20 **Effusion. Lighter (*black*) particles effuse faster than heavier (*red*) particles.**



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Sample Problem 5.13 Applying Graham's Law of Effusion

PROBLEM: A mixture of helium (He) and methane (CH_4) is placed in an effusion apparatus. Calculate the ratio of their effusion rates.

PLAN: The effusion rate is inversely proportional $\sqrt{\mathcal{M}}$ for each gas, so we find the molar mass for each substance using its formula and take the square root. The ratio of the effusion rates is the inverse of the ratio of these square roots.

SOLUTION: $\mathcal{M}$ of CH_4 = 16.04 g/mol $\mathcal{M}$ of He = 4.003 g/mol

$$\frac{\text{rate}_{\text{He}}}{\text{rate}_{CH_4}} = \sqrt{\frac{16.04}{4.003}} = \mathbf{2.002}$$

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Real Gases: Deviations from Ideal Behavior

- The kinetic-molecular model describes the behavior of ideal gases. Real gases deviate from this behavior.
- Real gases have real volume.
  - Gas particles are **not** points of mass, but have volumes determined by the sizes of their atoms and the bonds between them.
- Real gases do experience attractive and repulsive forces between their particles.
- Real gases deviate most from ideal behavior at ***low temperature*** and ***high pressure***.

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Table 5.3 Molar Volume of Some Common Gases at STP (0°C and 1 atm)

Gas	Molar Volume (L/mol)	Boiling Point (°C)
He	22.435	-268.9
H_2	22.432	-252.8
Ne	22.422	-246.1
Ideal gas	**22.414**	**–**
Ar	22.397	-185.9
N_2	22.396	-195.8
O_2	22.390	-183.0
CO	22.388	-191.5
Cl_2	22.184	-34.0
NH_3	22.079	-33.4

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Figure 5.21 Deviations from ideal behavior with increasing external pressure

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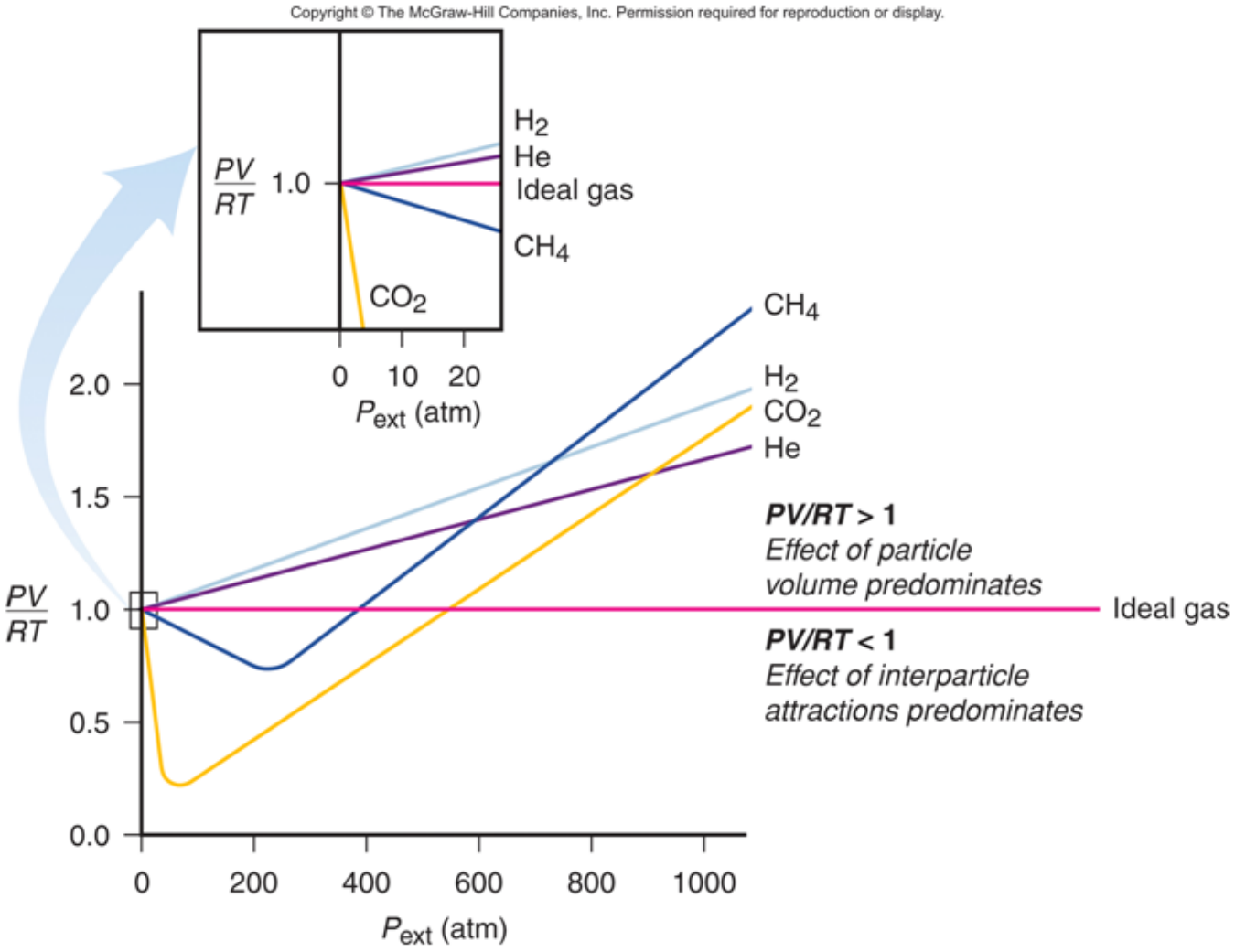

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Figure 5.22 **The effect of interparticle attractions on measured gas pressure.**

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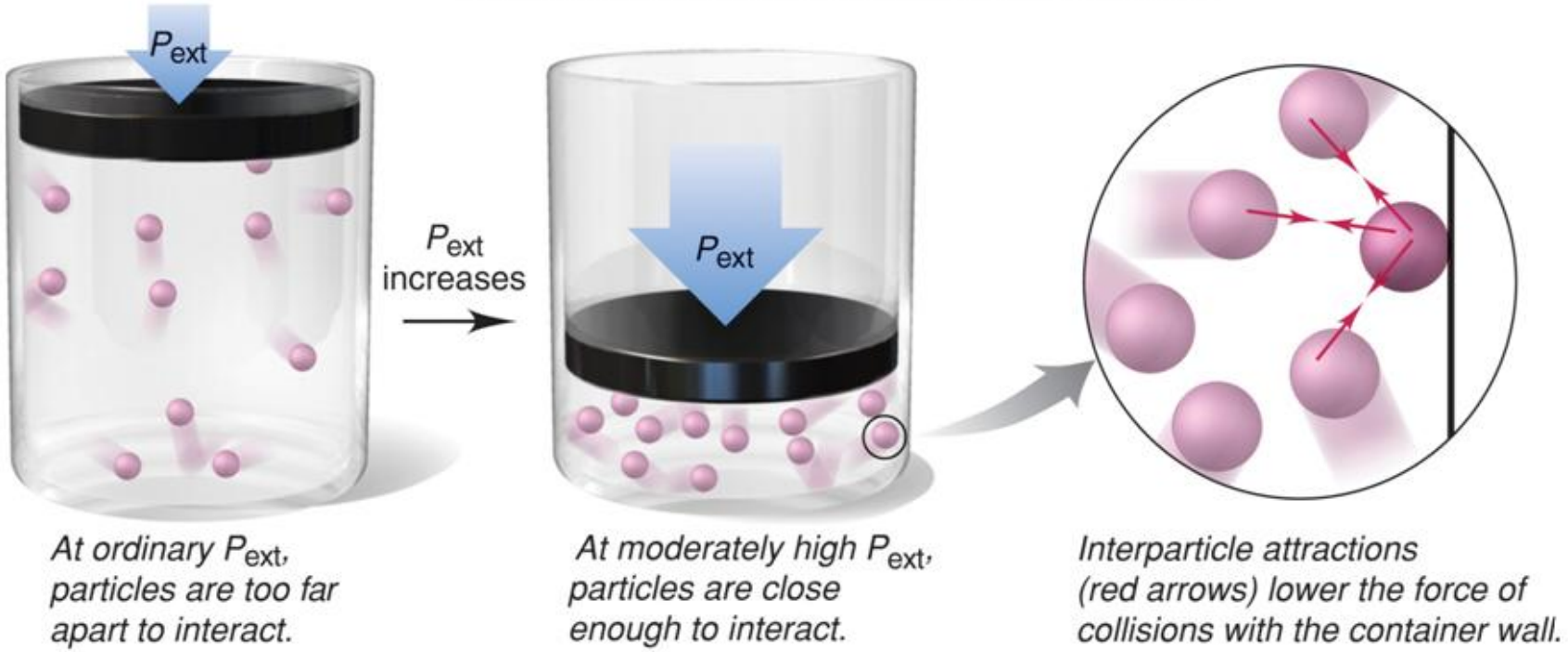

At ordinary P_{ext}, particles are too far apart to interact.

At moderately high P_{ext}, particles are close enough to interact.

Interparticle attractions (red arrows) lower the force of collisions with the container wall.

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Figure 5.23 **The effect of particle volume on measured gas volume.**

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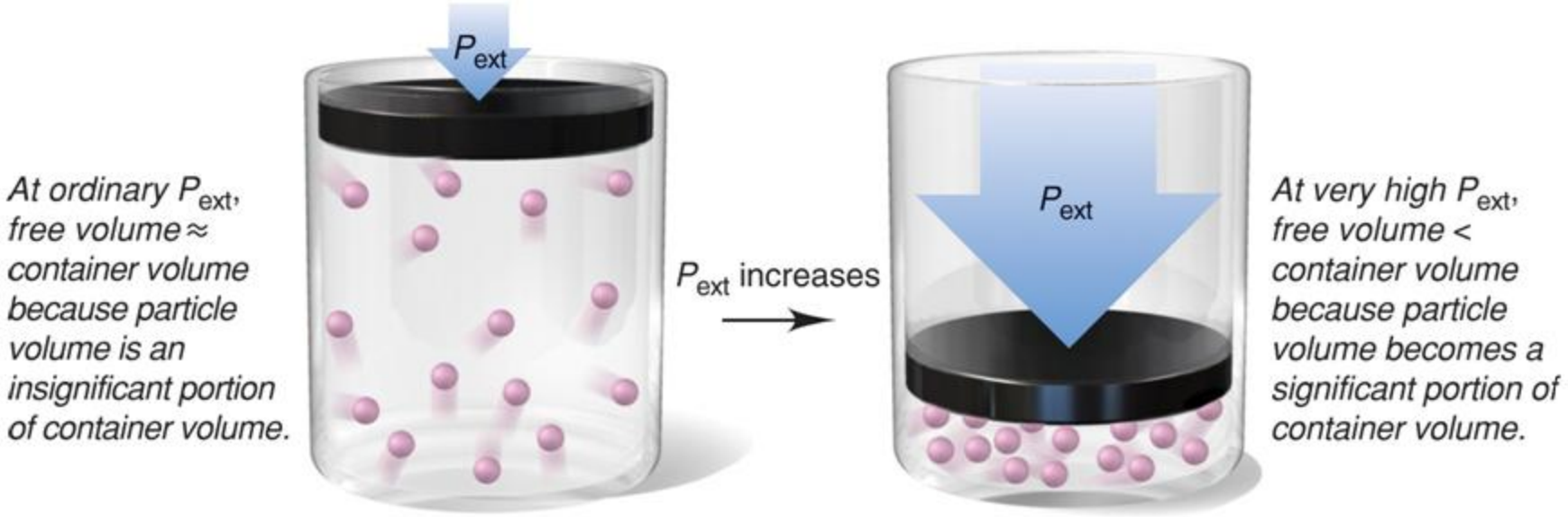

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The van der Waals equation

- The van der Waals equation adjusts the ideal gas law to take into account
  - the real volume of the gas particles and
  - the effect of interparticle attractions.

Van der Waals equation for *n* moles of a real gas

$$(P + \frac{n^2 a}{V^2})(V - nb) = nRT$$

The constant *a* relates to factors that influence the attraction between particles.

The constant *b* relates to particle volume.

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Table 5.4 Van der Waals Constants for Some Common Gases

Gas	a $\left(\frac{\text{atm}\cdot\text{L}^2}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CH_4	2.25	0.0428
CO	1.45	0.0395
CO_2	3.59	0.0427
NH_3	4.17	0.0371
H_2O	5.46	0.0305

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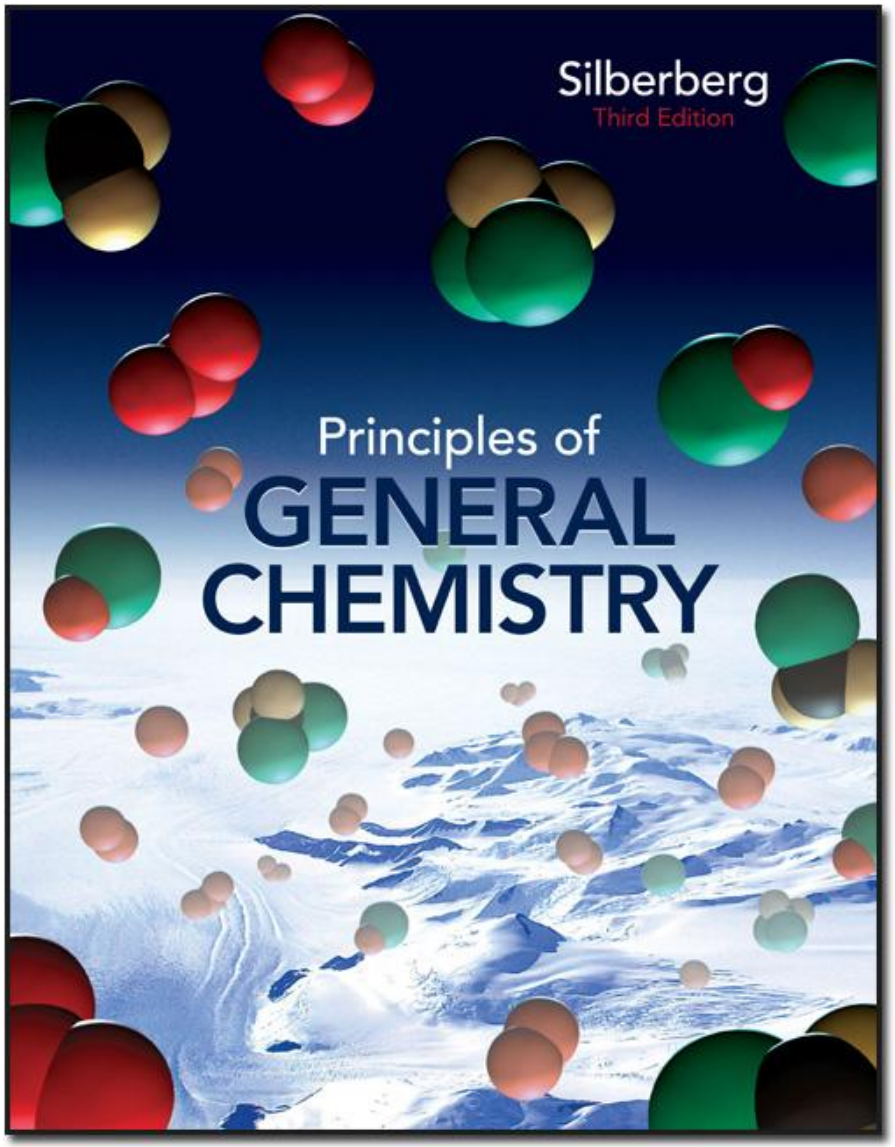

Chapter 06

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 6

Thermochemistry: Energy Flow and Chemical Change

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Thermochemistry: Energy Flow and Chemical Change

6.1 Forms of Energy and Their Interconversion

6.2 Enthalpy: Chemical Change at Constant Pressure

6.3 Calorimetry: Measuring the Heat of a Chemical or Physical Change

6.4 Stoichiometry of Thermochemical Equations

6.5 Hess's Law: Finding ΔH of Any Reaction

6.6 Standard Enthalpies of Reaction ($\Delta H°_{rxn}$)

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Transfer and Interconversion of Energy

Thermodynamics is the study of energy and its transformations.

Thermochemistry is a branch of thermodynamics that deals with the heat involved in chemical and physical changes.

When energy is transferred from one object to another, it appears as ***work*** and ***heat***.

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The System and Its Surroundings

A meaningful study of any transfer of energy requires that we first clearly define both the ***system*** and its ***surroundings***.

System + Surroundings = Universe

The ***internal energy***, ***E***, of a system is the sum of the potential and kinetic energies of all the particles present.

The total energy of the universe remains ***constant***.
A change in the energy of the system must be accompanied by an ***equal*** and ***opposite*** change in the energy of the surroundings.

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Figure 6.1 Energy diagrams for the transfer of internal energy (*E*) between a system and its surroundings.

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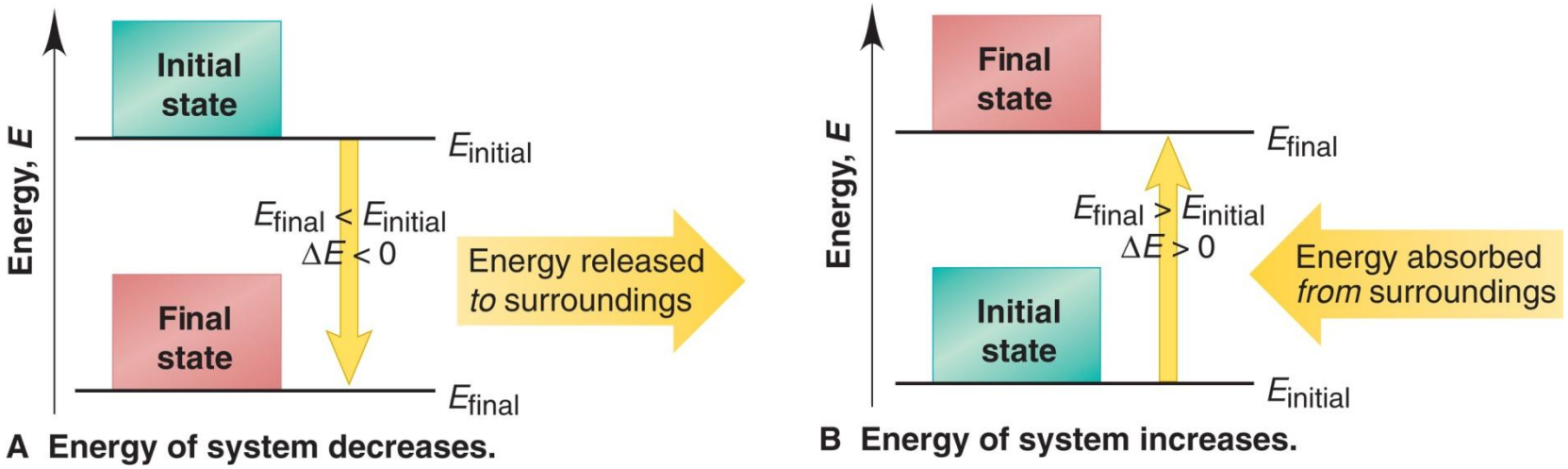

$$\Delta E = E_{final} - E_{initial} = E_{products} - E_{reactants}$$

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Figure 6.2 The two cases where energy is transferred as heat only.

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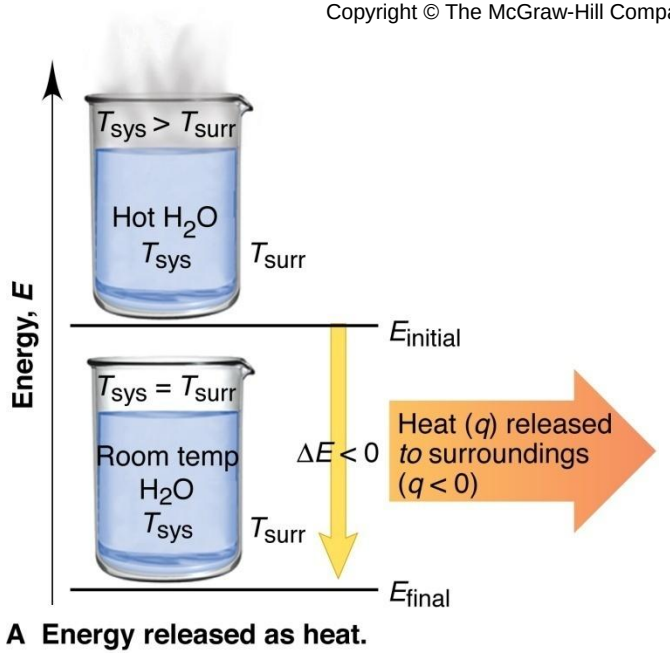
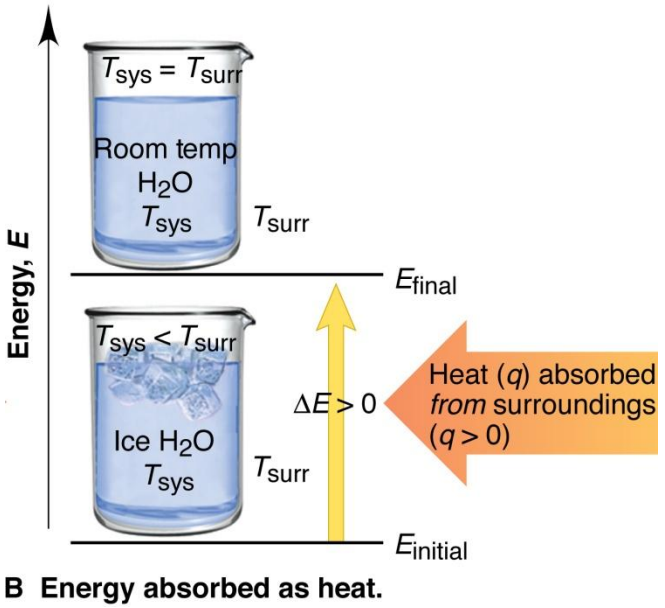


A Energy released as heat.

The system releases heat



B Energy absorbed as heat.

The system absorbs heat

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Figure 6.3A The two cases where energy is transferred as work only.

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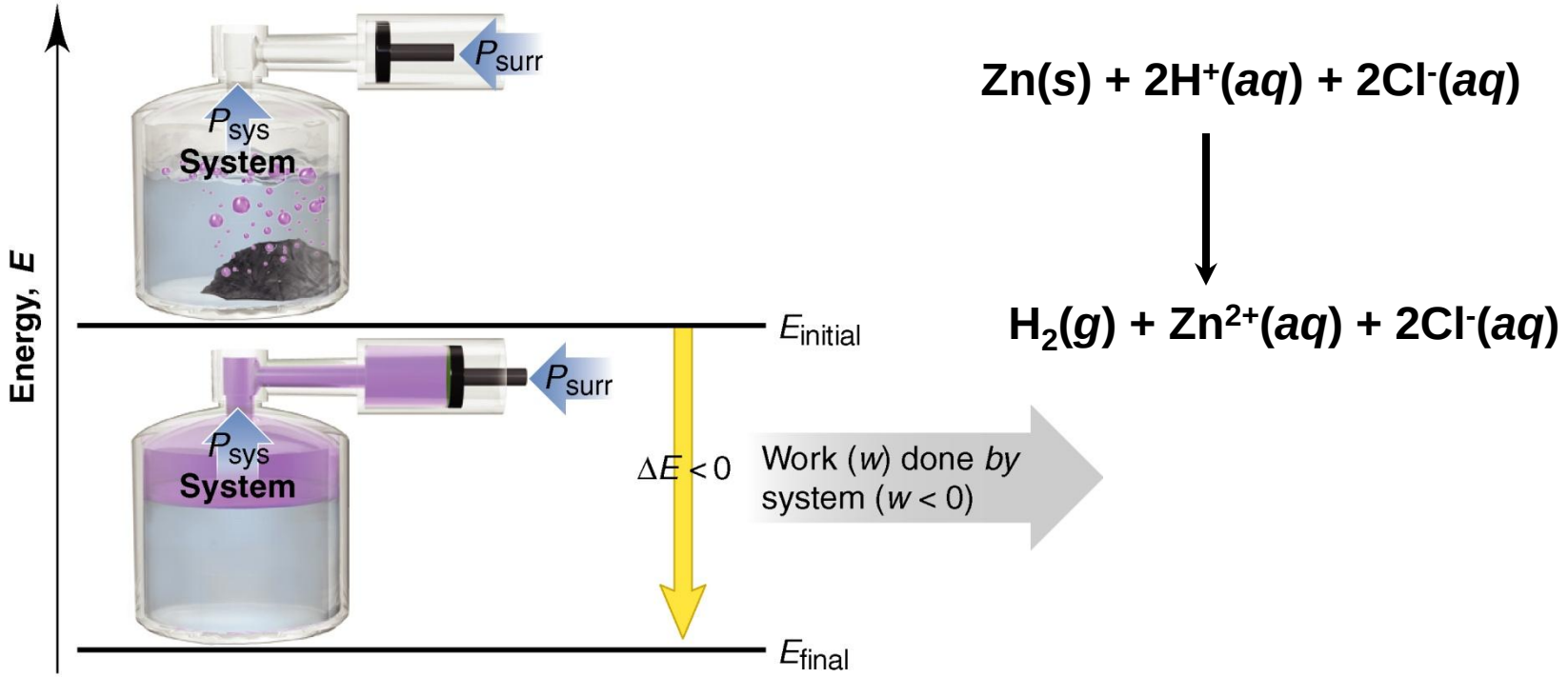

A Energy released as work.

The system does work *on* the surroundings.

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Figure 6.3B The two cases where energy is transferred as work only.

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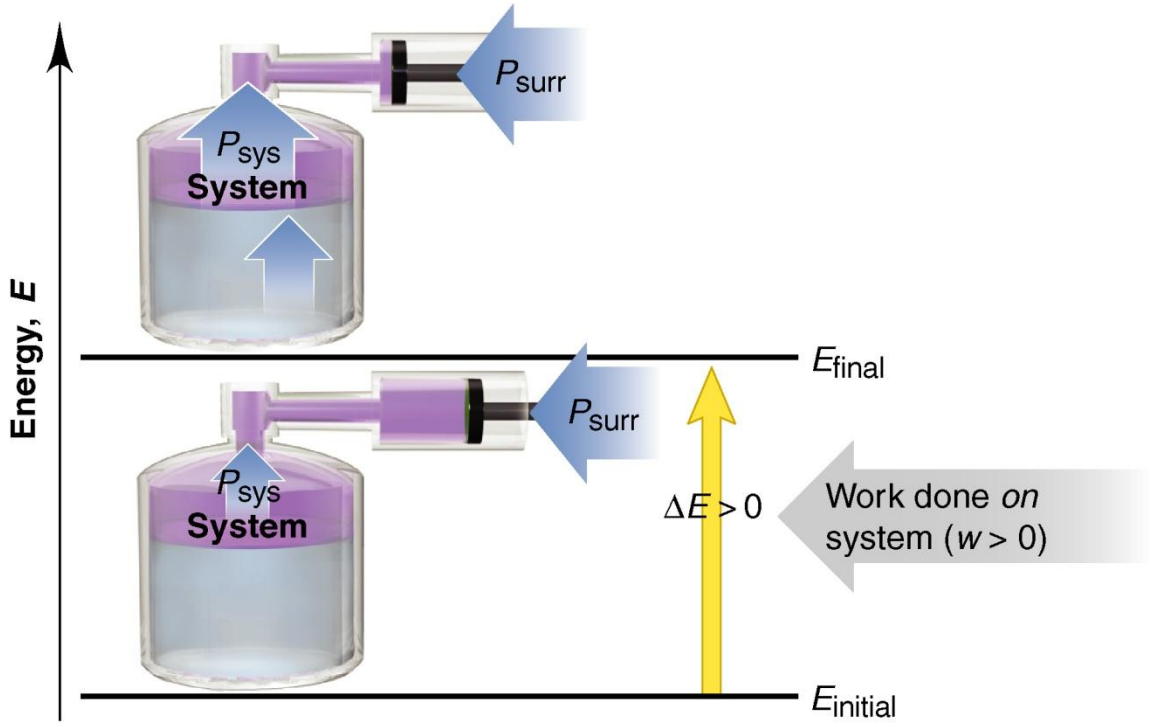

B Energy absorbed as work.

The system has work done on it *by* the surroundings.

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Table 6.1 The Sign Conventions* for *q*, *w*, and D*E*

q	+	*w*	=	Δ*E*
+ (heat *absorbed*)		+ (work done *on*)		+ (energy *absorbed*)
+ (heat *absorbed*)		− (work done *by*)		Depends on the ***sizes*** of *q* and *w*
− (heat *released*)		+ (work done *on*)		Depends on the ***sizes*** of *q* and *w*
− (heat *released*)		− (work done *by*)		− (energy *released*)

*From the perspective of the system.

Which of these are **not state functions**?

A) volume B) temperature C) pressure **D) heat** E) energy

A) internal energy B) volume C) work D) pressure E) enthalpy

A system which undergoes an adiabatic change (i.e., $q = 0$)

A system which undergoes an isothermal change (**i.e., *constant temperature***)

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The Law of Energy Conservation

The first law of Thermodynamics states that *the total energy of the universe is constant*.

Energy is conserved, and is neither created nor destroyed. Energy is transferred in the form of heat and/or work.

$$\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0$$

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Units of Energy

The SI unit of energy is the **joule (J)**.

$1\ J = 1\ kg \cdot m^2/s^2$

The **calorie** was once defined as the quantity of energy needed to raise the temperature of 1 g of water by 1°C.

1 cal = 4.184 J

The **British Thermal Unit (Btu)** is often used to rate appliances.

1 Btu is equivalent to 1055 J.

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Sample Problem 6.1 Determining the Change in Internal Energy of a System

PROBLEM: When gasoline burns in a car engine, the heat released causes the products CO_2 and H_2O to expand, which pushes the pistons outward. Excess heat is removed by the car's radiator. If the expanding gases do 451 J of work on the pistons and the system releases 325 J to the surroundings as heat, calculate the change in energy (ΔE) in J, kJ, and kcal.

PLAN: Define the system and surroundings and assign signs to ***q*** and ***w*** correctly. Then $\Delta E = q + w$. The answer can then be converted from J to kJ and to kcal.

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Sample Problem 6.1

SOLUTION:

Heat is given out by a chemical reaction, so it makes sense to define the system as the reactants and products involved. The pistons, the radiator and the rest of the car then comprise the surroundings.

Heat is given out by the system, so ***q* = - 325 J**

The gases expand to push the pistons, so the system does work on the surroundings and ***w* = - 451 J**

$$\Delta E = q + w = \quad -325\ \text{J} + (-451\ \text{J}) = \boxed{\textbf{-776 J}}$$

$$-776\ \cancel{\text{J}} \times \frac{1\ \text{kJ}}{10^3\ \cancel{\text{J}}} \boxed{\textbf{= -0.776 kJ}} \qquad -0.776\ \cancel{\text{kJ}} \times \frac{1\ \text{kcal}}{4.184\ \cancel{\text{kJ}}} \boxed{\textbf{= -0.185 kcal}}$$

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Figure 6.4 Two different paths for the energy change of a system.

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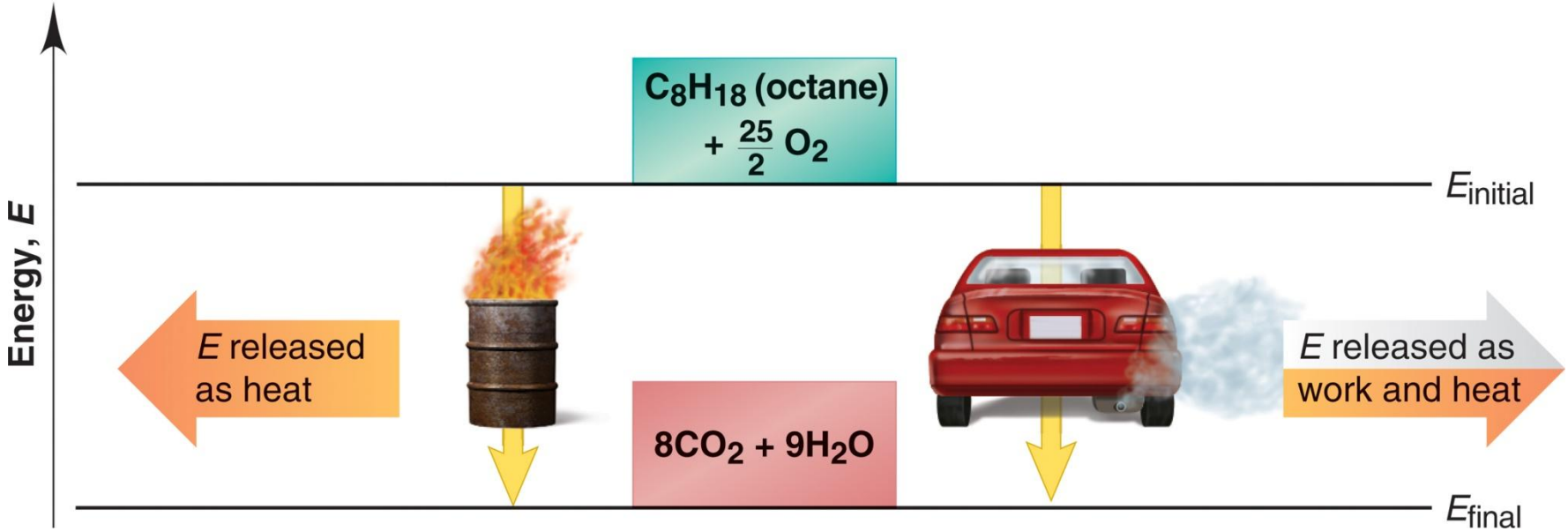

Even though *q* and *w* for the two paths are different, the total ΔE is the same for both.

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Enthalpy:
Chemical Change at Constant Pressure

$w = -P\Delta V$

$H = E + PV$

where H is enthalpy

$\Delta H = \Delta E + P\Delta V$

$q_p = \Delta E + P\Delta V = \Delta H$

$\Delta H \approx \Delta E$ in

1. Reactions that do not involve gases.

2. Reactions in which the number of moles of gas does not change.

3. Reactions in which the number of moles of gas does change but q is >>> $P\Delta V$.

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Figure 6.5 Pressure-volume work.

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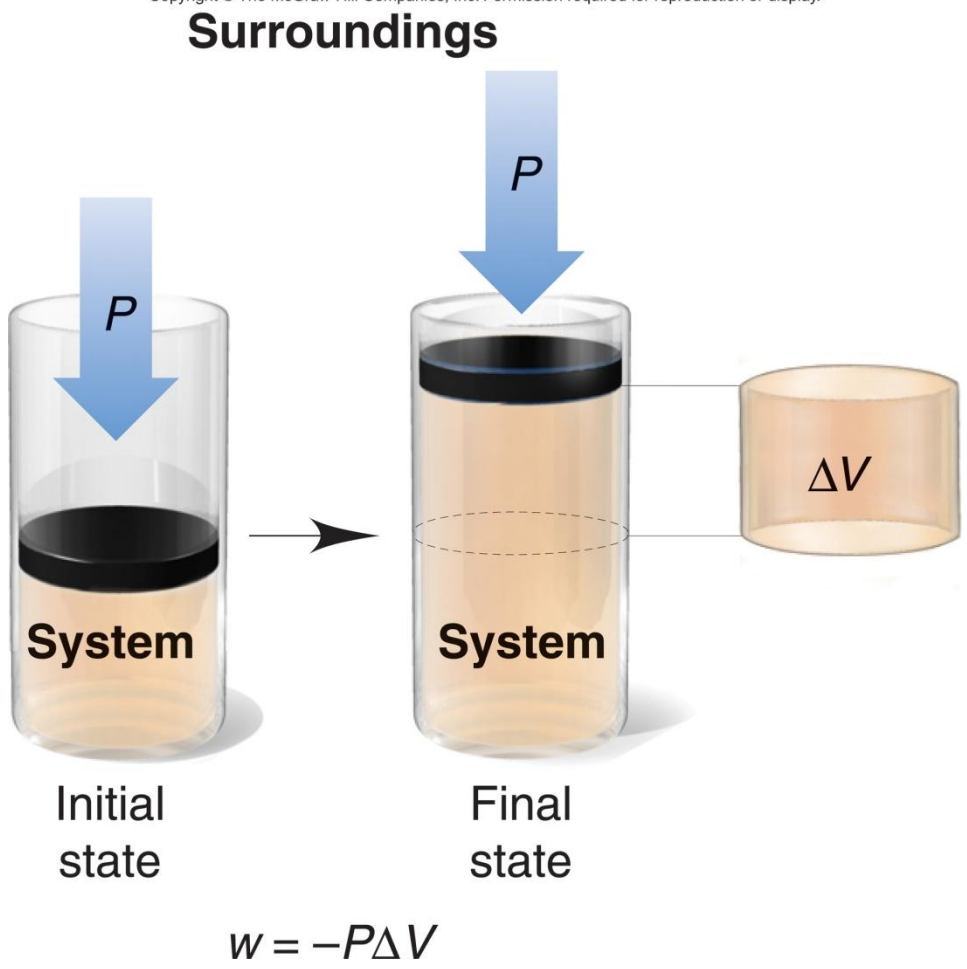

An expanding gas pushing back the atmosphere does *PV* work ($w = -P\Delta V$).

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ΔH as a measure of ΔE

- ΔH is the change in heat for a system at ***constant pressure***.

  $q_P = \Delta E + P\Delta V = \Delta H$

- $\Delta H \approx \Delta E$
  - for reactions that do not involve gases
  - for reactions in which the total amount (mol) of gas does **not** change
  - for reactions in which q_P is much larger than $P\Delta V$, even if the total mol of gas does change.

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Figure 6.6

Enthalpy diagrams for exothermic and endothermic processes.

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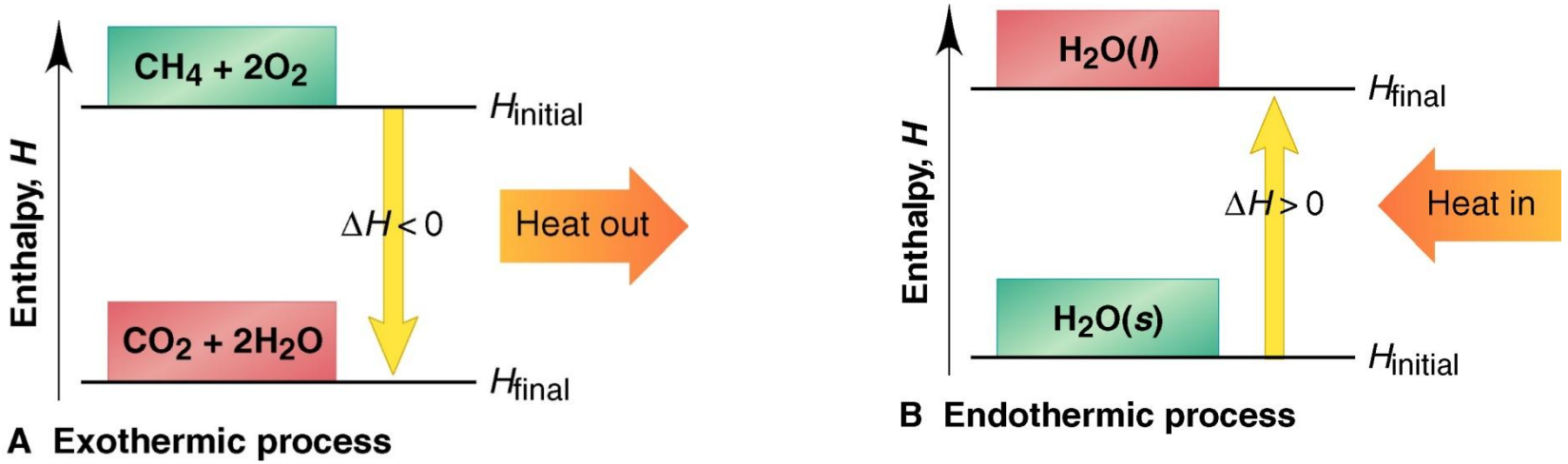
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(g)$ $\qquad$ $H_2O(s) \rightarrow H_2O(l)$



A **Exothermic process**
Heat is given out.

B **Endothermic process**
Heat is taken in.

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Sample Problem 6.2

Drawing Enthalpy Diagrams and Determining the Sign of ΔH

PROBLEM: In each of the following cases, determine the sign of ΔH, state whether the reaction is exothermic or endothermic, and draw an enthalpy diagram.

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 285.8\ kJ$

(b) $40.7\ kJ + H_2O(l) \longrightarrow H_2O(g)$

PLAN: From each equation, note whether heat is a "reactant" or a "product". If heat is taken in as a "reactant", the process is endothermic. If heat is released as a "product", the process is exothermic.

For the enthalpy diagram, the arrow always points from reactants to products. For endothermic reactions, the products are at a higher energy than the reactants, since the reactants take in heat to form the products.

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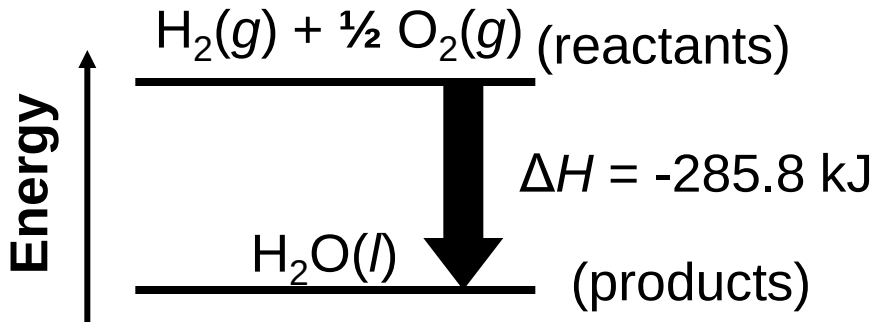
Sample Problem 6.2

SOLUTION: **(a)** $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 285.8\ kJ$

Heat is a "product" for this reaction and is therefore given out, so the reaction is exothermic. The reactants are at a higher energy than the products.



EXOTHERMIC

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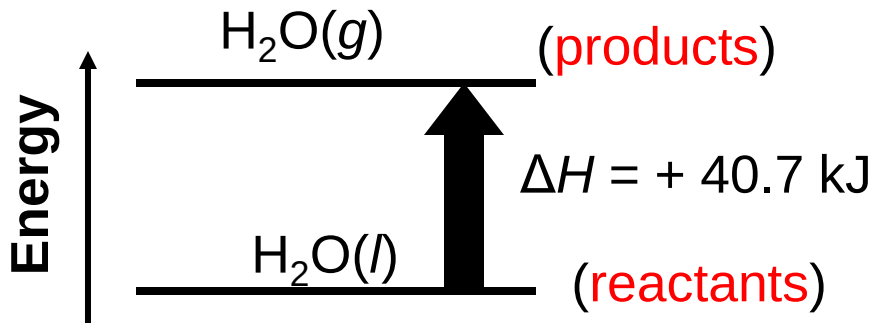
Sample Problem 6.2

SOLUTION: **(b)** 40.7 kJ + $H_2O(l) \longrightarrow H_2O(g)$

Heat is a "reactant" in this reaction and is therefore absorbed, so the reaction is endothermic. The reactants are at a lower energy than the products.



ENDOTHERMIC

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Calorimetry

$$q = c \times m \times \Delta T$$

q = heat lost or gained
c = specific heat capacity
m = mass in g
$\Delta T = T_{final} - T_{initial}$

The ***specific heat capacity*** (***c***) of a substance is the quantity of heat required to change the temperature of ***1 gram*** of the substance by ***1 K***. **(J/g·K)**

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Table 6.2 Specific Heat Capacities (*c*) of Some Elements, Compounds, and Materials

Substance	Specific Heat Capacity (J/g·K)	Substance	Specific Heat Capacity (J/g·K)*
Elements		**Solid materials**	
aluminum, Al	0.900	wood	1.76
graphite,C	0.711	cement	0.88
iron, Fe	0.450	glass	0.84
copper, Cu	0.387	granite	0.79
gold, Au	0.129	steel	0.45
Compounds			
water, $H_2O(l)$	4.184		
ethyl alcohol, $C_2H_5OH(l)$	2.46		
ethylene glycol, $(CH_2OH)_2(l)$	2.42		
carbon tetrachloride, $CCl_4(l)$	0.862		

* At 298 K (25°C).

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Sample Problem 6.3

Finding the Quantity of Heat from a Temperature Change

PROBLEM: A layer of copper welded to the bottom of a skillet weighs 125 g. How much heat is needed to raise the temperature of the copper layer from 25°C to 300.°C? The specific heat capacity (*c*) of Cu is 0.387 J/g·K.

PLAN: We know the mass (125 g) and *c* (0.387 J/g·K) of Cu and can find ΔT in °C, which equals ΔT in K. We can use the equation $q = c \times m \times \Delta T$ to calculate the heat.

SOLUTION: $\Delta T = T_{final} - T_{initial} = 300. - 25 = 275°C = 275\ K$

$$q = c \times m \times \Delta T = \frac{0.387\ J}{g \cdot K} \times 125\ \cancel{g} \times 275\ \cancel{K} = \mathbf{1.33 \times 10^4\ J}$$

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Figure 6.7 Coffee-cup calorimeter.

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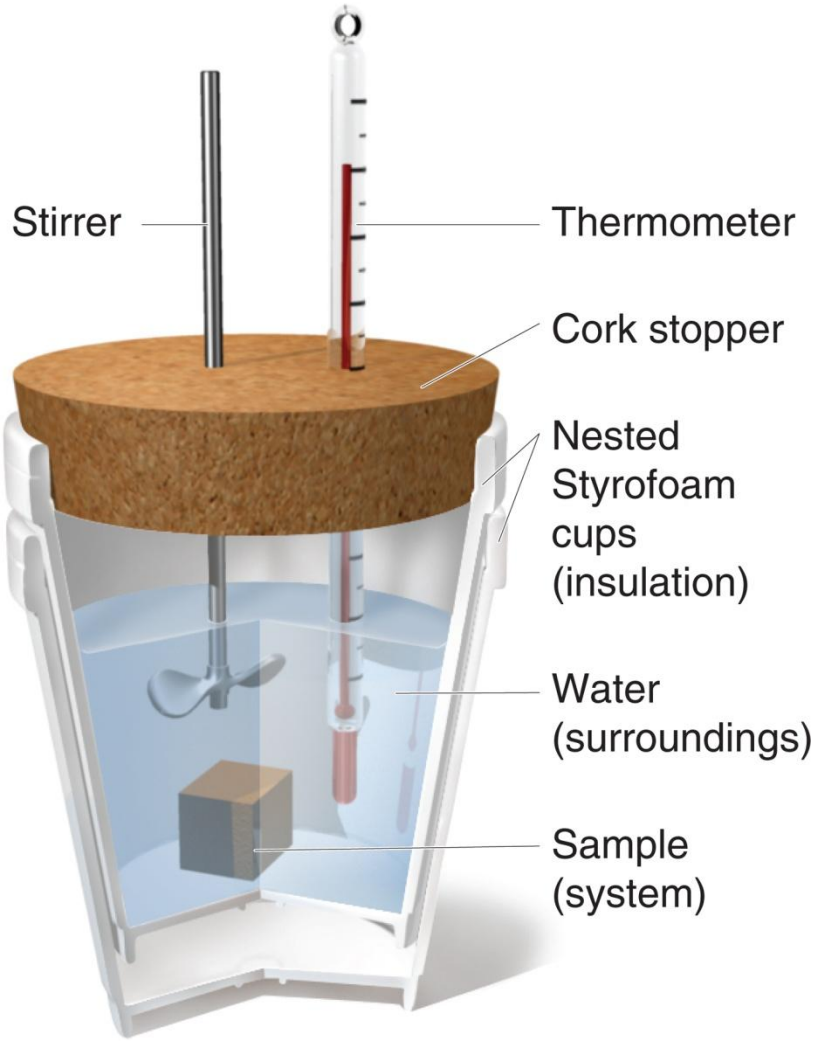

This device measures the heat transferred at constant pressure (q_P).

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Sample Problem 6.4 Determining the Specific Heat Capacity of a Solid

PROBLEM: A 22.05 g solid is heated in a test-tube to 100.00°C and added to 50.00 g of water in a coffee-cup calorimeter. The water temperature changes from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

PLAN: Since the water and the solid are in contact, heat is transferred from the solid to the water until they reach the same T_{final}. In addition, the heat given out by the solid ($-q_{solid}$) is equal to the heat absorbed by the water (q_{water}).

SOLUTION:

$$\Delta T_{water} = T_{final} - T_{initial} = (28.49°C - 25.10°C) = 3.39°C = 3.39\ K$$

$$\Delta T_{solid} = T_{final} - T_{initial} = (28.49°C - 100.00°C) = -71.51°C = -71.51\ K$$

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Sample Problem 6.4

$$c_{solid} = \frac{c_{H_2O} \text{ x mass}_{H_2O} \text{ x } \Delta T_{H_2O}}{\text{mass}_{solid} \text{ x } \Delta T_{solid}}$$

$$= \frac{4.184 \text{ J/g·K x } 50.00 \text{ g x } 3.39 \text{ K}}{22.05 \text{ g x } (-71.51 \text{ K})}$$

= 0.450 J/g·K

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Sample Problem 6.5 Determining the Enthalpy Change of an Aqueous Reaction

PROBLEM: 50.0 mL of 0.500 *M* NaOH is placed in a coffee-cup calorimeter at 25.00°C and 25.0 mL of 0.500 *M* HCl is carefully added, also at 25.00°C. After stirring, the final temperature is 27.21°C. Calculate q_{soln} (in J) and the change in enthalpy, ΔH, (in kJ/mol of H_2O formed).

Assume that the total volume is the sum of the individual volumes, that d = 1.00 g/mL and c = 4.184 J/g·K

PLAN: Heat flows from the reaction (the system) to its surroundings (the solution). Since $-q_{rxn} = q_{soln}$, we can find the heat of the reaction by calculating the heat absorbed by the solution.

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Sample Problem 6.5

SOLUTION:

(a) To find q_{soln}:

Total mass (g) of the solution = (25.0 mL + 50.0 mL) x 1.00 g/mL = 75.0 g

ΔT_{soln} = 27.21°C – 25.00°C = 2.21°C = 2.21 K

$q_{soln} = c_{soln} \times mass_{soln} \times \Delta T_{soln}$ = (4.184 J/g·K)(75.0 g)(2.21 K) **= 693 J**

(b) To find ΔH_{rxn} we first need a balanced equation:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

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Sample Problem 6.5

For HCl:

$$25.0\ \text{mL HCl} \times \frac{1\ \text{L}}{10^3\ \text{mL}} \times \frac{0.500\ \text{mol}}{1\ \text{L}} \times \frac{1\ \text{mol } H_2O}{1\ \text{mol HCl}} = 0.0125\ \text{mol } H_2O$$

For NaOH:

$$50.0\ \text{mL NaOH} \times \frac{1\ \text{L}}{10^3\ \text{mL}} \times \frac{0.500\ \text{mol}}{1\ \text{L}} \times \frac{1\ \text{mol } H_2O}{1\ \text{mol NaOH}} = 0.0250\ \text{mol } H_2O$$

HCl is limiting, and the amount of H_2O formed is 0.0125 mol.

$$\Delta H_{rxn} = \frac{q_{rxn}}{\text{mol } H_2O} = \frac{-693\ \text{J}}{0.0125\ \text{mol}} \times \frac{1\ \text{kJ}}{10^3\ \text{J}}$$

$= -55.4\ \text{kJ/mol } H_2O$

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Figure 6.8 A bomb calorimeter.

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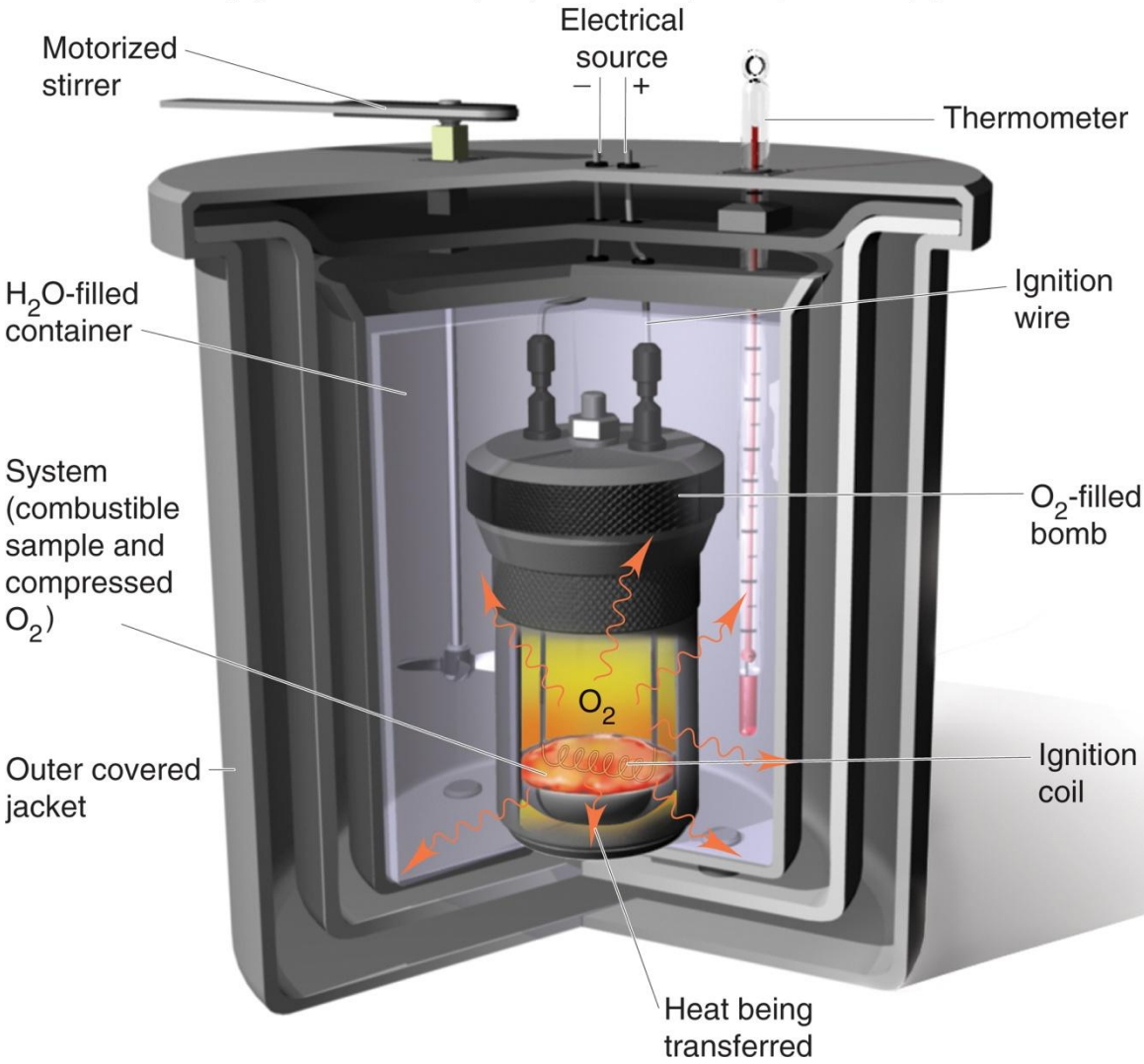

This device measures the heat released at constant volume (q_V).

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Sample Problem 6.6 Calculating the Heat of a Combustion Reaction

PROBLEM: A manufacturer claims that its new dietetic dessert has "fewer than 10 Calories per serving." To test the claim, a chemist at the Department of Consumer Affairs places one serving in a bomb calorimeter and burns it in O_2. The initial temperature is 21.862°C and the temperature rises to 26.799°C. If the heat capacity of the calorimeter is 8.151 kJ/K, is the manufacturer's claim correct?

PLAN: When the dessert (system) burns, the heat released is absorbed by the calorimeter:

$$-q_{system} = q_{calorimeter}$$

To verify the energy provided by the dessert, we calculate $q_{calorimeter}$.

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Sample Problem 6.6

SOLUTION:

$$\Delta T_{calorimeter} = T_{final} - T_{initial}$$
$$= 26.799°C - 21.862°C = 4.937°C = 4.937\ K$$

$$q_{calorimeter} = \text{heat capacity} \times \Delta T = 8.151\ kJ/K \times 4.937\ K = 40.24\ kJ$$

$$40.24\ kJ \times \frac{kcal}{4.184\ kJ}$$

= 9.63 kcal or Calories

The manufacturer's claim is true, since the heat produced is less than 10 Calories.

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Stoichiometry of Thermochemical Equations

- A ***thermochemical equation*** is a balanced equation that includes ΔH_{rxn}.
- The sign of ΔH indicates whether the reaction is exothermic or endothermic.
- The magnitude of ΔH is ***proportional to the amount of substance***.
- The value of ΔH can be used in a calculation in the same way as a mole ratio.

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Figure 6.11

The relationship between amount (mol) of substance and the energy (kJ) transferred as heat during a reaction.

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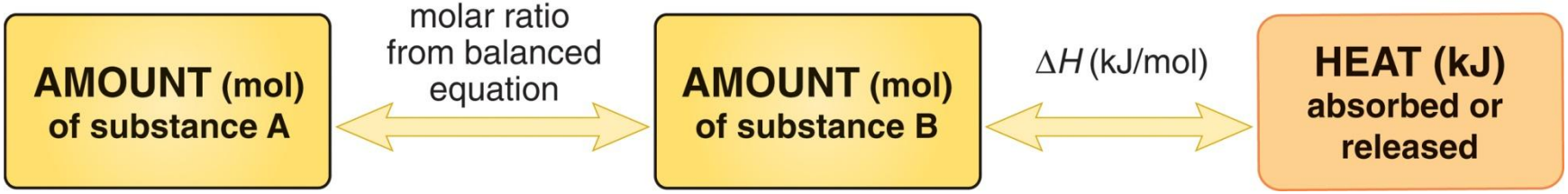

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Sample Problem 6.7

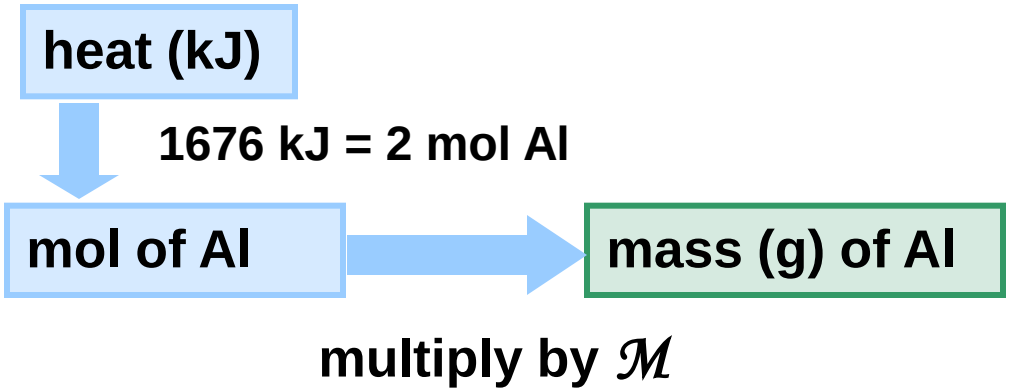
Using the Enthalpy Change of a Reaction (ΔH) to Find Amounts of Substance

PROBLEM: The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by the equation

$$Al_2O_3(s) \longrightarrow 2Al(s) + \frac{3}{2} O_2(g) \quad \Delta H_{rxn} = 1676 \text{ kJ}$$

If aluminum is produced this way, how many grams of aluminum can form when 1.000×10^3 kJ of heat is transferred?

PLAN: From the balanced equation and ΔH, we see that 2 mol of Al is formed when 1676 kJ of heat is absorbed.



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Sample Problem 6.7

SOLUTION:

$$1.000 \times 10^3 \text{ kJ} \times \frac{2 \text{ mol Al}}{1676 \text{ kJ}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = \mathbf{32.20 \text{ g Al}}$$

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Hess' Law

Hess's law states that *the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps.*

$$\Delta H_{overall} = \Delta H_1 + \Delta H_2 + \ldots\ldots\ldots + \Delta H_n$$

ΔH for an overall reaction can be calculated if the ΔH values for the individual steps are known.

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Calculating Δ*H* for an overall process

- Identify the target equation, the step whose Δ*H* is unknown.
  - Note the amount of each reactant and product.
- Manipulate each equation with known Δ*H* values so that the target amount of each substance is on the correct side of the equation.
  - Change the sign of Δ*H* when you reverse an equation.
  - Multiply amount (mol) and Δ*H* by the same factor.
- Add the manipulated equations and their resulting Δ*H* values to get the target equation and its Δ*H*.
  - All substances except those in the target equation must cancel.

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Sample Problem 6.8

Using Hess's Law to Calculate an Unknown ΔH

PROBLEM: Two gaseous pollutants that form in auto exhausts are CO and NO. An environmental chemist is studying ways to convert them to less harmful gases through the following reaction:

$$CO(g) + NO(g) \longrightarrow CO_2(g) + \tfrac{1}{2}N_2(g) \quad \Delta H = ?$$

Given the following information, calculate the unknown ΔH:

Equation A: $CO(g) + \tfrac{1}{2} O_2(g) \longrightarrow CO_2(g) \quad \Delta H_A = -283.0$ kJ

Equation B: $N_2(g) + O_2(g) \longrightarrow 2NO(g) \quad \Delta H_B = 180.6$ kJ

PLAN: Manipulate Equations A and/or B and their ΔH values to get to the target equation and its ΔH. All substances except those in the target equation must cancel.

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Sample Problem 6.8

SOLUTION:

Multiply Equation B by ½ and reverse it:

$NO(g) \longrightarrow \frac{1}{2}\ N_2(g) + \frac{1}{2}\ O_2(g)$; ΔH = - 90.3 kJ

Add the manipulated equations together:

Equation A: $CO(g) + \frac{1}{2}\ O_2(g) \longrightarrow CO_2(g)$ ΔH = -283.0 kJ

½ Equation B (reversed): $NO(g) \longrightarrow \frac{1}{2}\ N_2(g) + \frac{1}{2}\ O_2(g)$ ΔH = - 90.3 kJ

$CO(g) + NO(g) \longrightarrow CO_2(g) + \frac{1}{2}\ N_2(g)$

ΔH_{rxn} = -373.3 kJ

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Table 6.3 Selected Standard Enthalpies of Formation at 25°C (298K)

Formula	ΔH°_f (kJ/mol)
Calcium	
$Ca(s)$	0
$CaO(s)$	-635.1
$CaCO_3(s)$	-1206.9
Carbon	
C(graphite)	0
C(diamond)	1.9
$CO(g)$	-110.5
$CO_2(g)$	-393.5
$CH_4(g)$	-74.9
$CH_3OH(l)$	-238.6
$HCN(g)$	135
$CS_s(l)$	87.9
Chlorine	
$Cl(g)$	121.0
$Cl_2(g)$	0
$HCl(g)$	-92.3
Hydrogen	
$H(g)$	218
$H_2(g)$	0
Nitrogen	
$N_2(g)$	0
$NH_3(g)$	-45.9
$NO(g)$	90.3
Oxygen	
$O_2(g)$	0
$O_3(g)$	143
$H_2O(g)$	-241.8
$H_2O(l)$	-285.8
Silver	
$Ag(s)$	0
$AgCl(s)$	-127.0
Sodium	
$Na(s)$	0
$Na(g)$	107.8
$NaCl(s)$	-411.1
Sulfur	
S_8(rhombic)	0
S_8(monoclinic)	0.3
$SO_2(g)$	-296.8
$SO_3(g)$	-396.0

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Sample Problem 6.9 Writing Formation Equations

PROBLEM: Write balanced equations for the formation of 1 mol of the following compounds from their elements in their standard states and include ΔH°_f.

(a) Silver chloride, AgCl, a solid at standard conditions.

(b) Calcium carbonate, $CaCO_3$, a solid at standard conditions.

(c) Hydrogen cyanide, HCN, a gas at standard conditions.

PLAN: Write the elements as reactants and 1 mol of the compound as the product formed. Make sure all substances are in their standard states. Balance the equations and find the value of ΔH°_f in Table 6.3 or Appendix B.

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Sample Problem 6.9

SOLUTION:

(a) Silver chloride, AgCl, a solid at standard conditions.

$$Ag(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow AgCl(s) \qquad \Delta H°_f = -127.0\ kJ$$

(b) Calcium carbonate, $CaCO_3$, a solid at standard conditions.

$$Ca(s) + C(graphite) + \frac{3}{2}O_2(g) \longrightarrow CaCO_3(s) \qquad \Delta H°_f = -1206.9\ kJ$$

(c) Hydrogen cyanide, HCN, a gas at standard conditions.

$$\tfrac{1}{2}H_2(g) + C(graphite) + \tfrac{1}{2}N_2(g) \longrightarrow HCN(g) \qquad \Delta H°_f = 135\ kJ$$

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Figure 6.10

The two-step process for determining ΔH°_{rxn} from ΔH°_f values.

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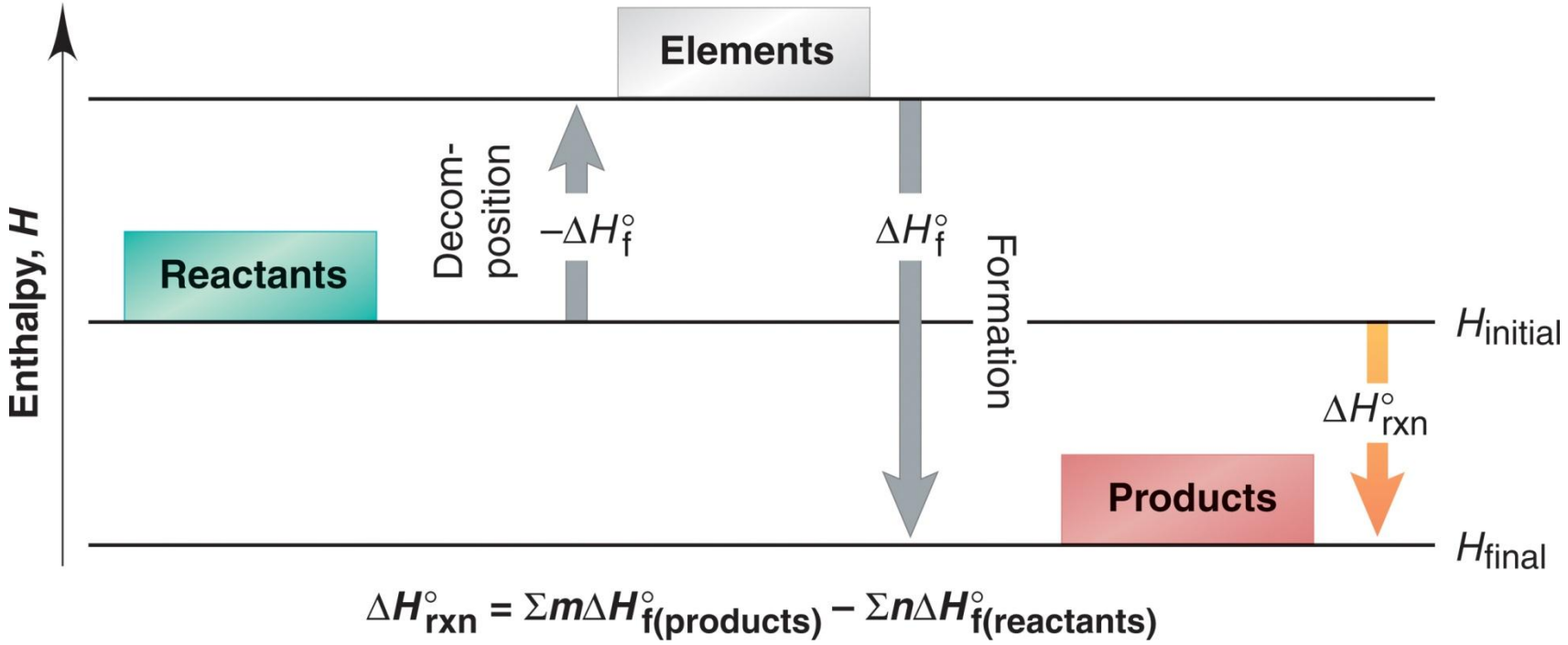

$$\Delta H^\circ_{rxn} = \Sigma m \Delta H^\circ_{f(products)} - \Sigma n \Delta H^\circ_{f(reactants)}$$

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Sample Problem 6.10 Calculating $\Delta H°_{rxn}$ from $\Delta H°_f$ Values

PROBLEM: Nitric acid, whose worldwide annual production is about 8 billion kilograms, is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

Calculate $\Delta H°_{rxn}$ from $\Delta H°_f$ values.

PLAN: Use the $\Delta H°_f$ values from Table 6.3 or Appendix B and apply the equation

$$\Delta H_{rxn} = \Sigma\, m\Delta H°_f \text{ (products)} - \Sigma\, n\Delta H°_f \text{ (reactants)}$$

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Sample Problem 6.10

SOLUTION:

$$\Delta H_{rxn} = \Sigma\, m\Delta H°_f \text{ (products)} - \Sigma\, n\Delta H°_f \text{ (reactants)}$$

$$\Delta H_{rxn} = [4(\Delta H°_f \text{ of NO}(g) + 6(\Delta H°_f \text{ of } H_2O(g)]$$
$$- [4(\Delta H \text{ of } NH_3(g) + 5(\Delta H \text{ of } O_2(g)]$$

$$= (4 \text{ mol})(90.3 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol}) –$$
$$[(4 \text{ mol})(-45.9 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ/mol})]$$
$$= -906 \text{ kJ}$$

ΔH_{rxn} = -906 kJ

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Figure 6.11 The trapping of heat by the atmosphere.

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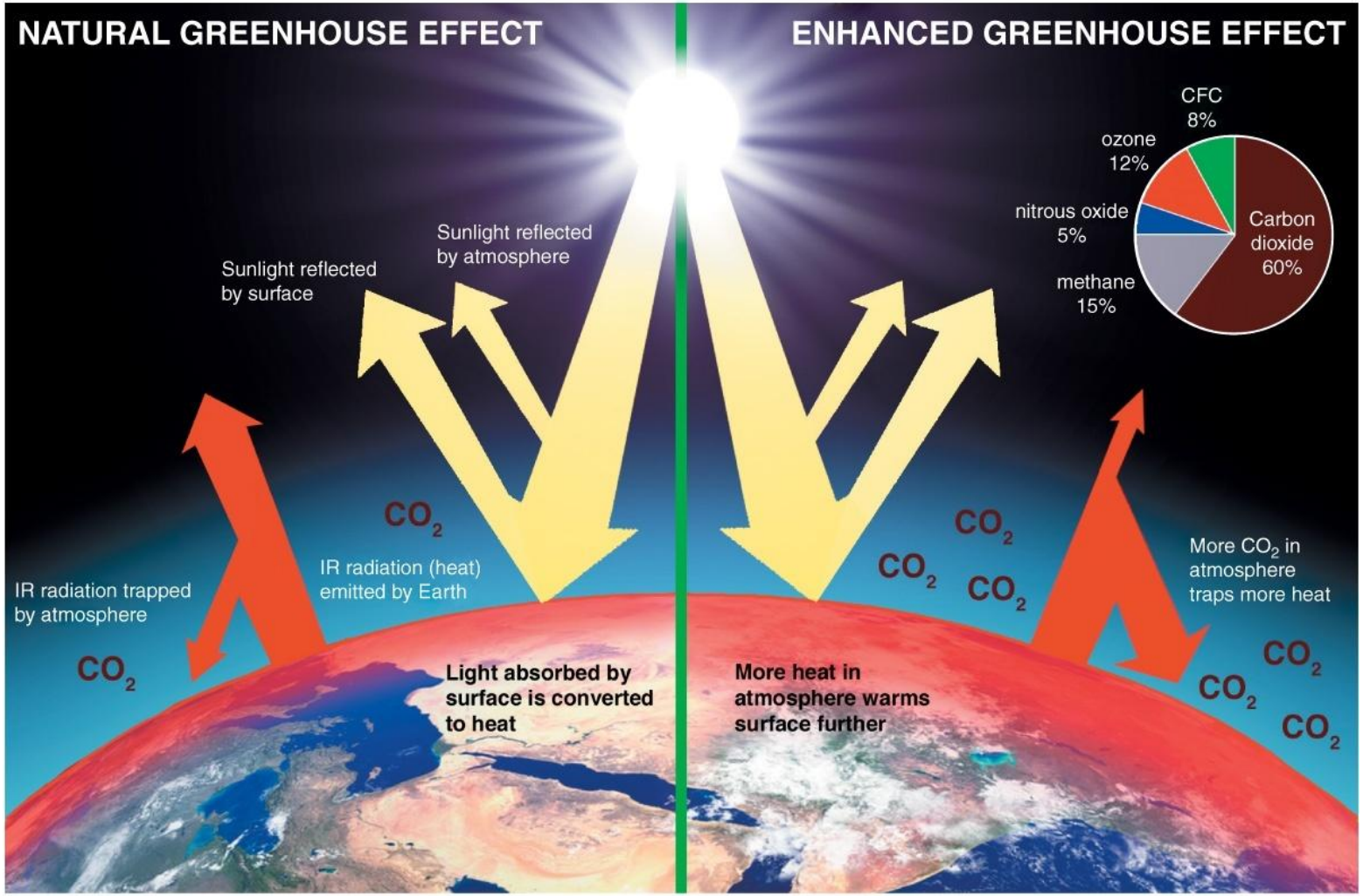

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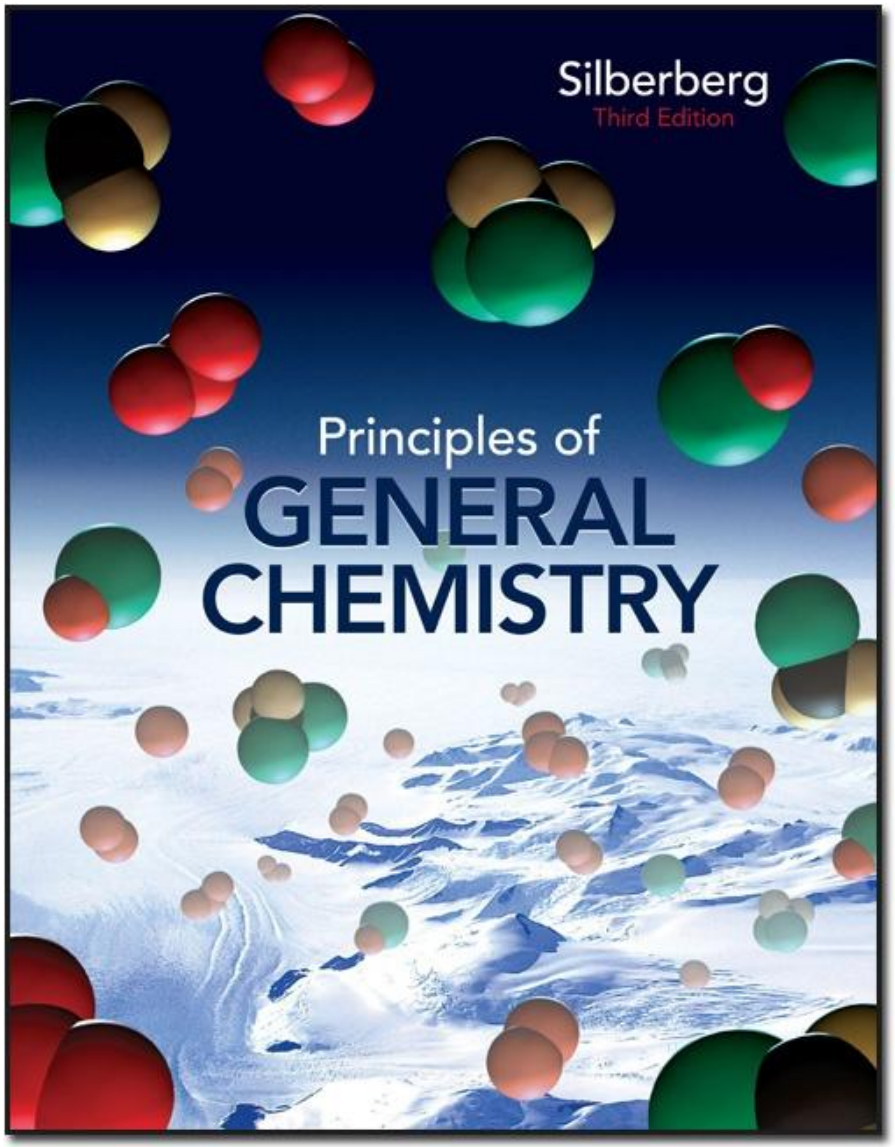

Chapter 07

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 7

Quantum Theory and Atomic Structure

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Quantum Theory and Atomic Structure

7.1 The Nature of Light

7.2 Atomic Spectra

7.3 The Wave-Particle Duality of Matter and Energy

7.4 The Quantum-Mechanical Model of the Atom

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The Wave Nature of Light

Visible light is a type of ***electromagnetic radiation***.

The wave properties of electromagnetic radiation are described by three variables:

- **frequency (**ν), cycles per second
- **wavelength (**λ**)**, the distance a wave travels in one cycle
- **amplitude**, the height of a wave crest or depth of a trough.

The ***speed of light*** is a constant:

$$c = \nu \times \lambda$$

$$= 3.00 \times 10^{8} \text{ m/s in a vacuum}$$

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Figure 7.1 The reciprocal relationship of frequency and wavelength.

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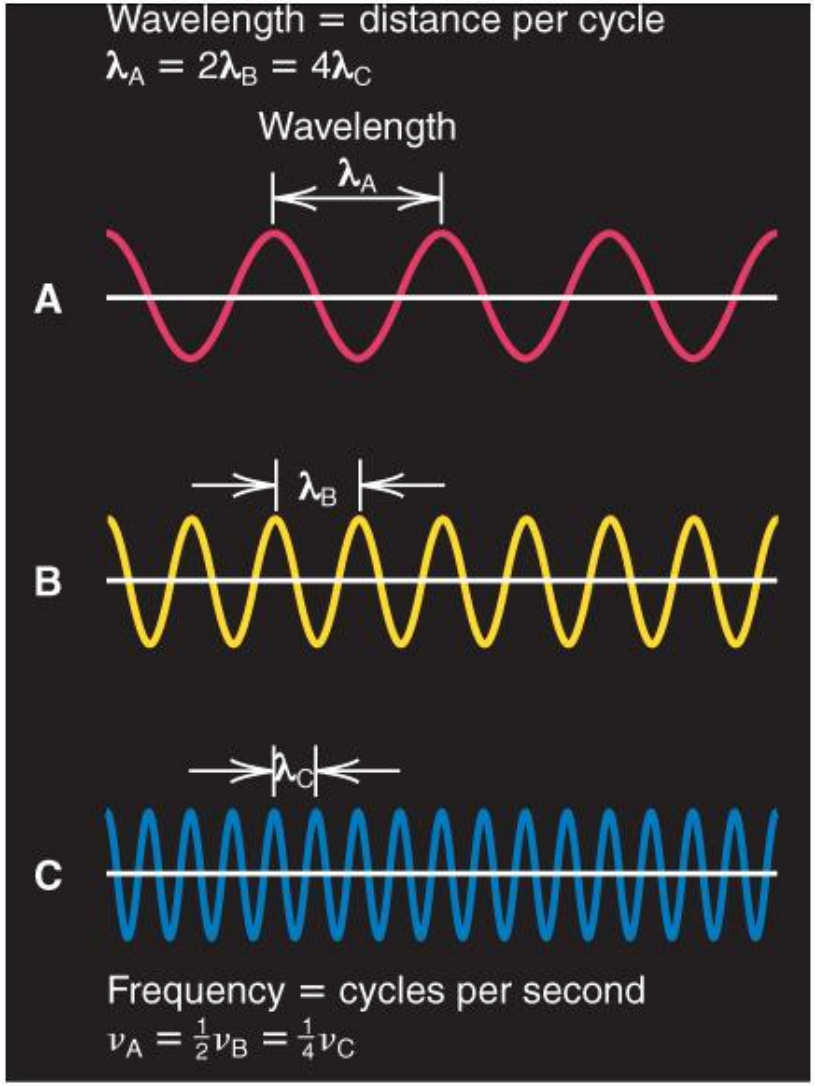

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Figure 7.2 Differing amplitude (brightness, or intensity) of a wave.

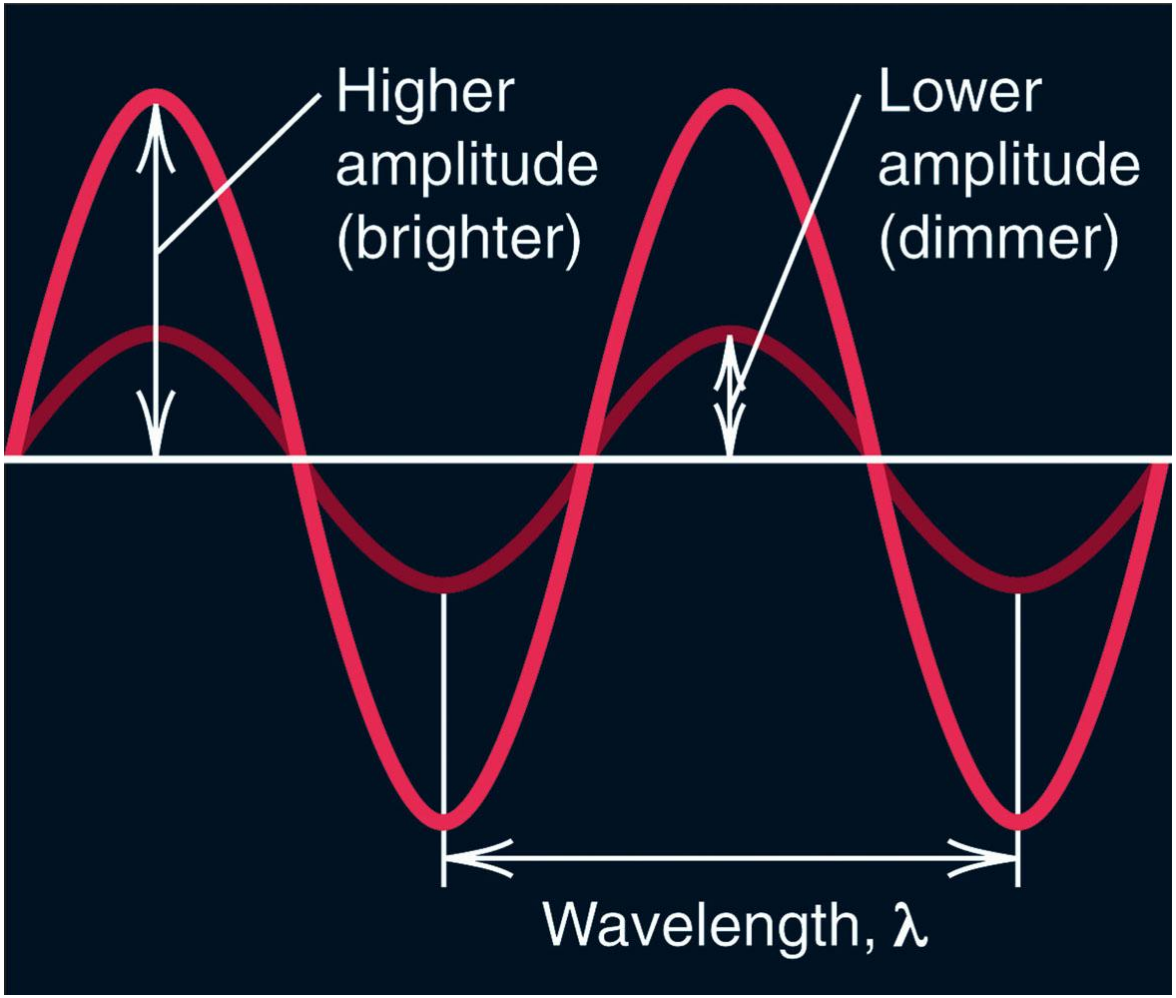

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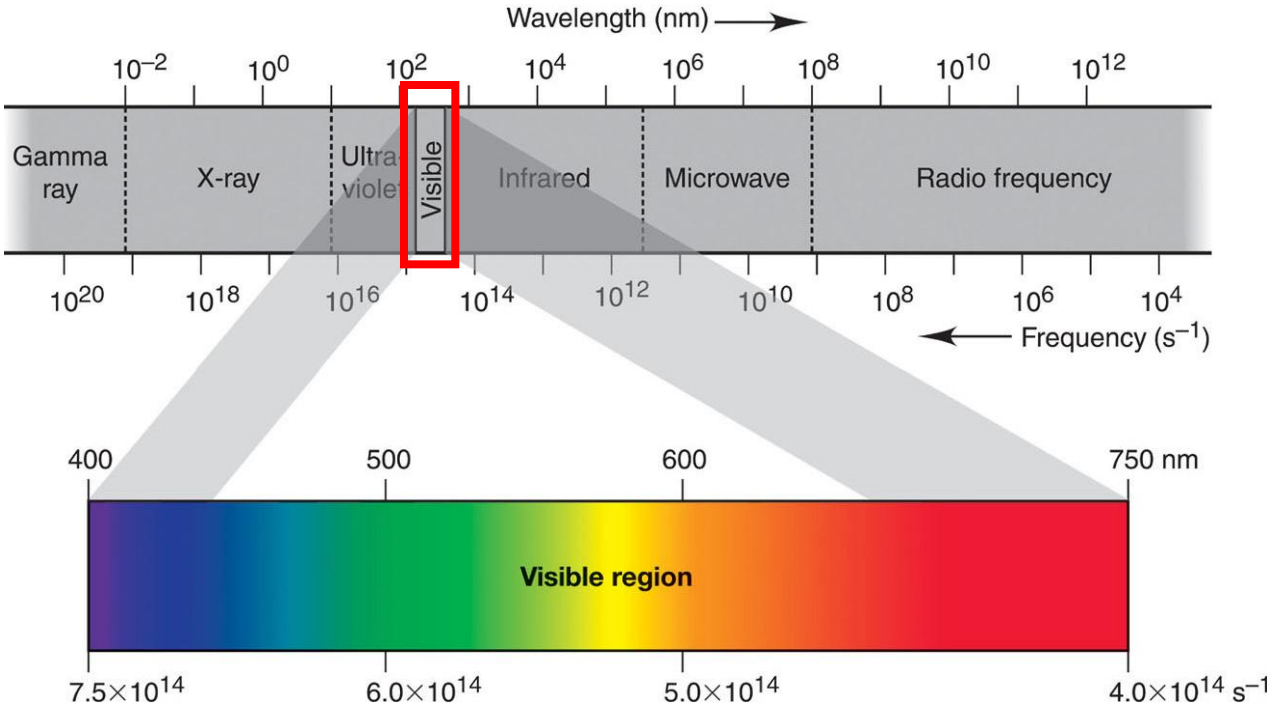
Figure 7.3 Regions of the electromagnetic spectrum.



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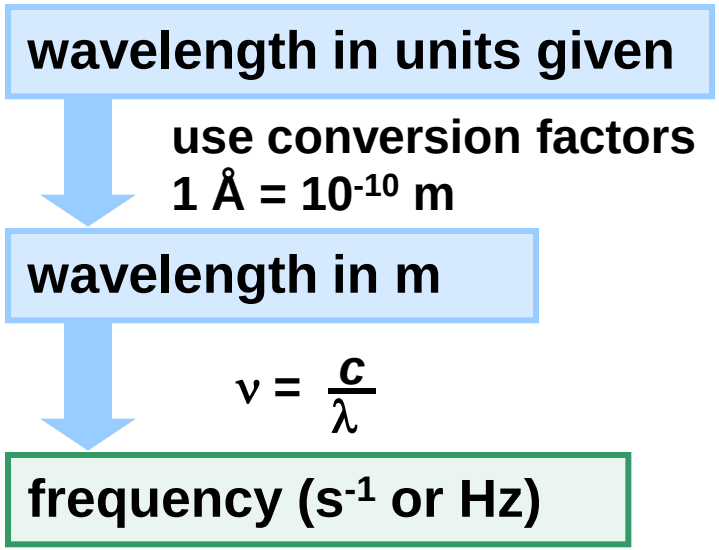
Sample Problem 7.1 Interconverting Wavelength and Frequency

PROBLEM: A dental hygienist uses x-rays (λ= 1.00Å) to take a series of dental radiographs while the patient listens to a radio station (λ = 325 cm) and looks out the window at the blue sky (λ= 473 nm). What is the frequency (in s^{-1}) of the electromagnetic radiation from each source? (Assume that the radiation travels at the speed of light, 3.00×10^8 m/s.)

PLAN: Use the equation $c = \nu\lambda$ to convert wavelength to frequency. Wavelengths need to be in meters because *c* has units of m/s.



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Sample Problem 7.1

SOLUTION:

For the x-rays: $\lambda = 1.00\ \text{Å} \times \dfrac{10^{-10}\ \text{m}}{1\ \text{Å}} = 1.00 \times 10^{-10}\ \text{m}$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{1.00 \times 10^{-10}\ \text{m}} = \mathbf{3.00 \times 10^{18}\ s^{-1}}$$

For the radio signal: $\nu = \dfrac{c}{\lambda} = \dfrac{3.00 \times 10^{8}\ \text{m/s}}{325\ \text{cm} \times \dfrac{10^{-2}\ \text{m}}{1\ \text{cm}}} = \mathbf{9.23 \times 10^{7}\ s^{-1}}$

For the blue sky: $\nu = \dfrac{c}{\lambda} = \dfrac{3.00 \times 10^{8}\ \text{m/s}}{473\ \text{nm} \times \dfrac{10^{-9}\ \text{m}}{1\ \text{nm}}} = \mathbf{6.34 \times 10^{14}\ s^{-1}}$

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Figure 7.4 Different behaviors of waves and particles.

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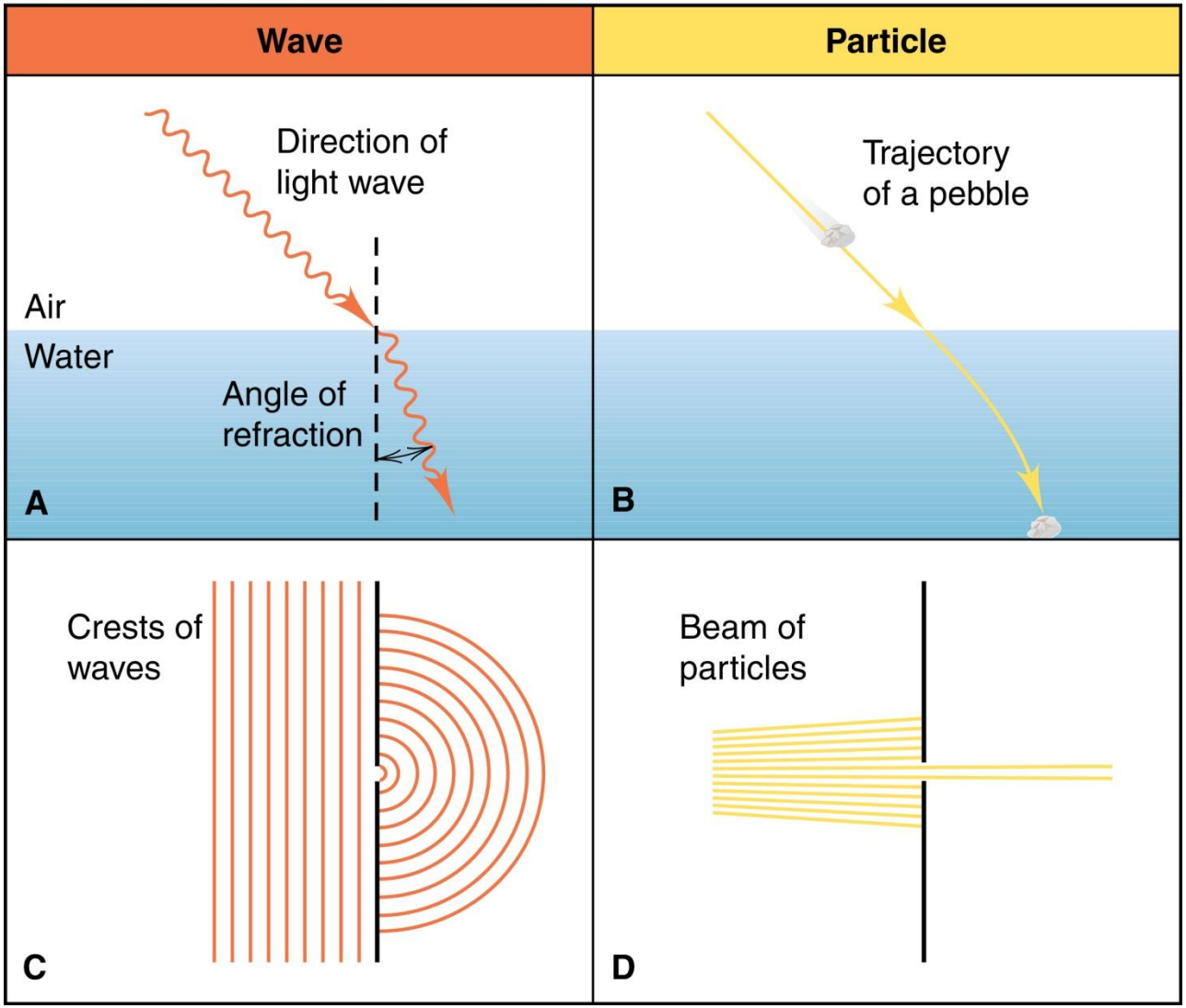

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Figure 7.5 Formation of a diffraction pattern.

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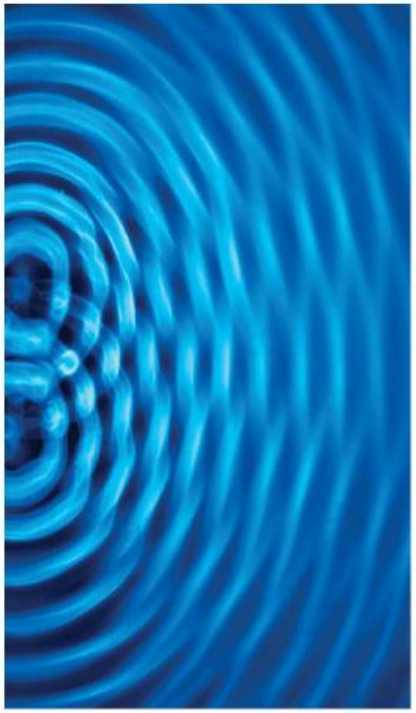
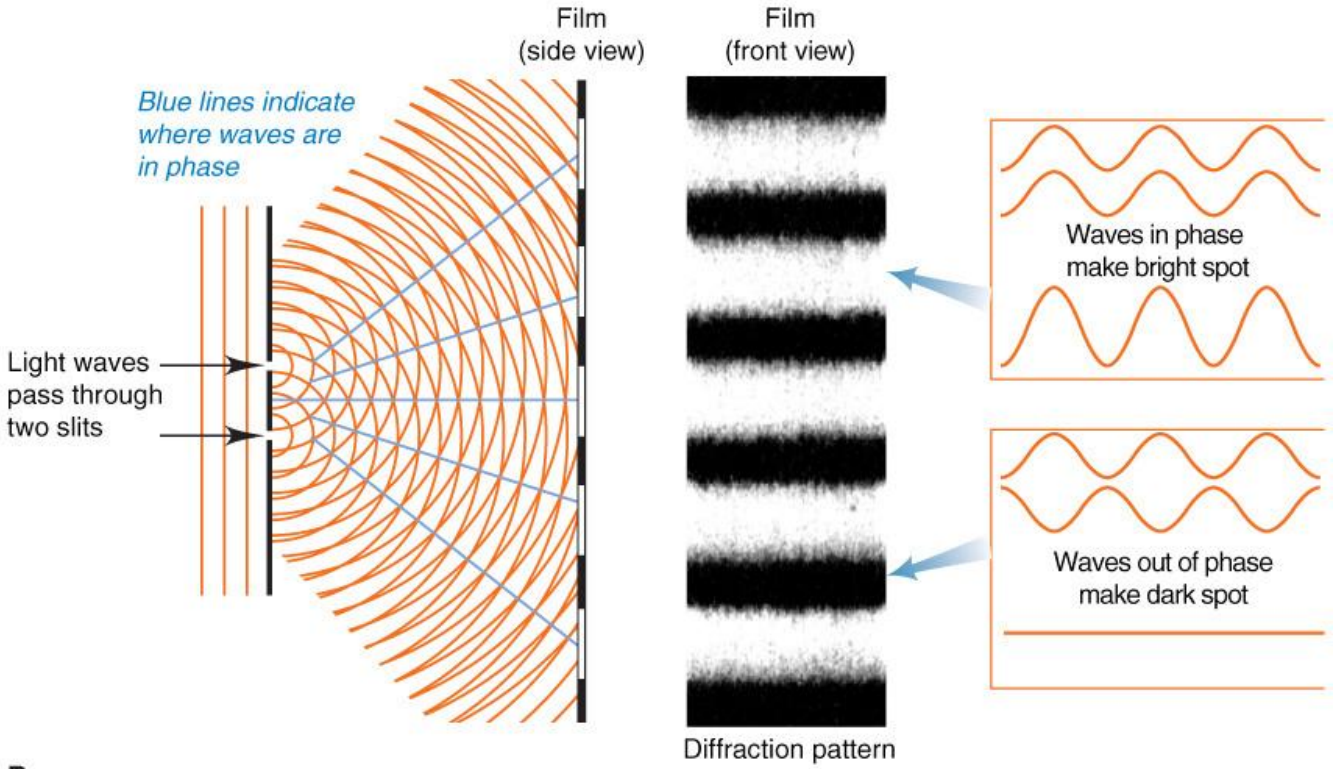


A



B

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Energy and frequency

A solid object emits visible light when it is heated to about 1000 K. This is called ***blackbody radiation***.

The *color* (and the intensity) of the light changes as the temperature changes. Color is related to ***wavelength*** and ***frequency***, while temperature is related to ***energy***.

Energy is therefore related to frequency and wavelength:

$$E = nh\nu$$

E = energy
n is a positive integer
h is Planck's constant

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The Quantum Theory of Energy

Any object (including atoms) can emit or absorb only ***certain quantities*** of energy.

Energy is ***quantized***; it occurs in fixed quantities, rather than being continuous. Each fixed quantity of energy is called a ***quantum***.

An atom changes its energy state by emitting or absorbing one or more ***quanta*** of energy.

$\Delta E = nh\nu$ where n can only be a whole number.

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Figure 7.6 The photoelectric effect.

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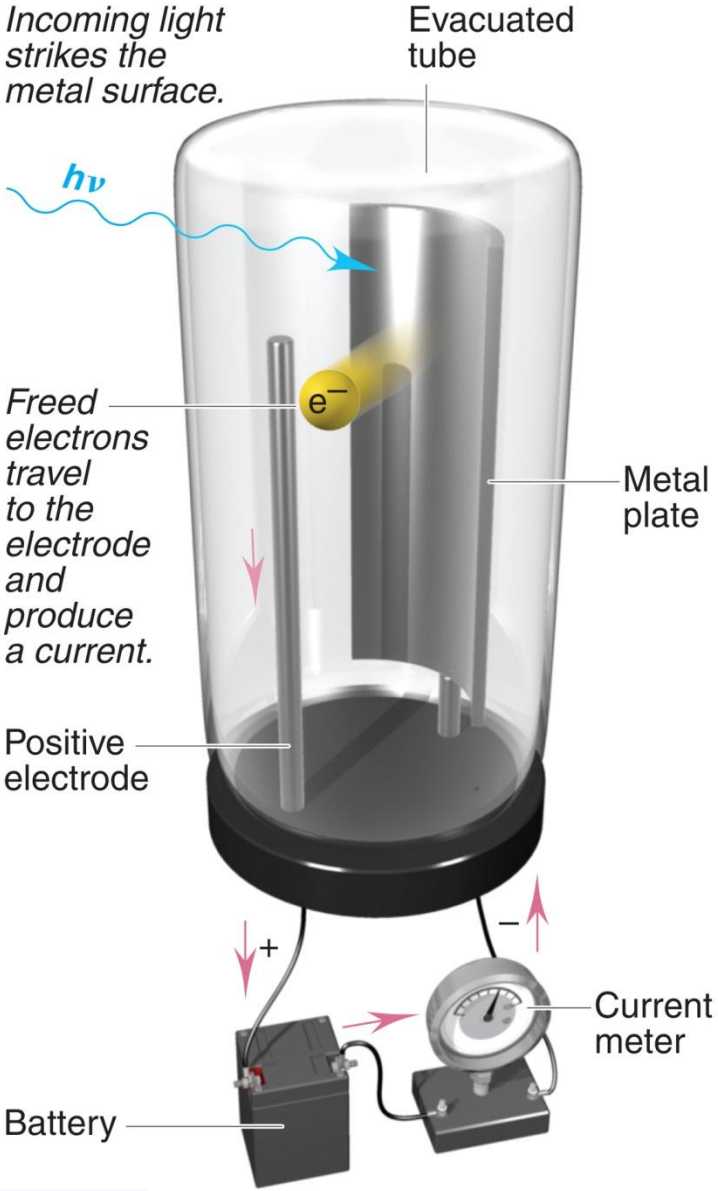

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Sample Problem 7.2 Calculating the Energy of Radiation from Its Wavelength

PROBLEM: A cook uses a microwave oven to heat a meal. The wavelength of the radiation is 1.20 cm. What is the energy of one photon of this microwave radiation?

PLAN: We know λ in cm, so we convert to m and find the frequency using the speed of light. We then find the energy of one photon using $E = h\nu$.

SOLUTION:

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})\ \text{J·s})(3.00 \times 10^{8}\ \text{m/s})}{(1.20\ \text{cm})\left(\frac{10^{-2}\ \text{m}}{1\ \text{cm}}\right)}$$

$$= 1.66 \times 10^{-23}\ \text{J}$$

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Figure 7.7A The line spectrum of hydrogen.

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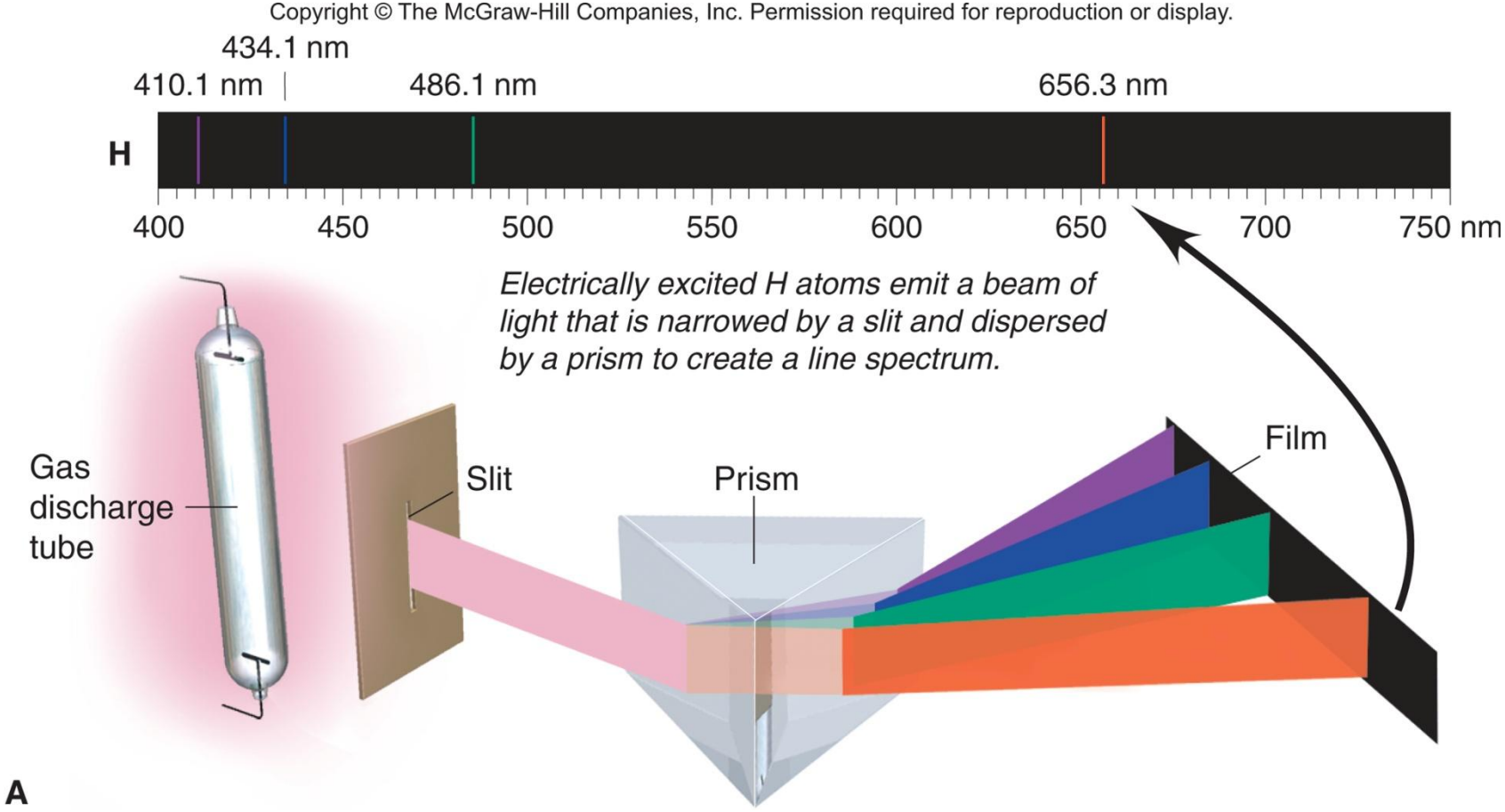

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Figure 7.7B The line spectra of Hg and Sr.

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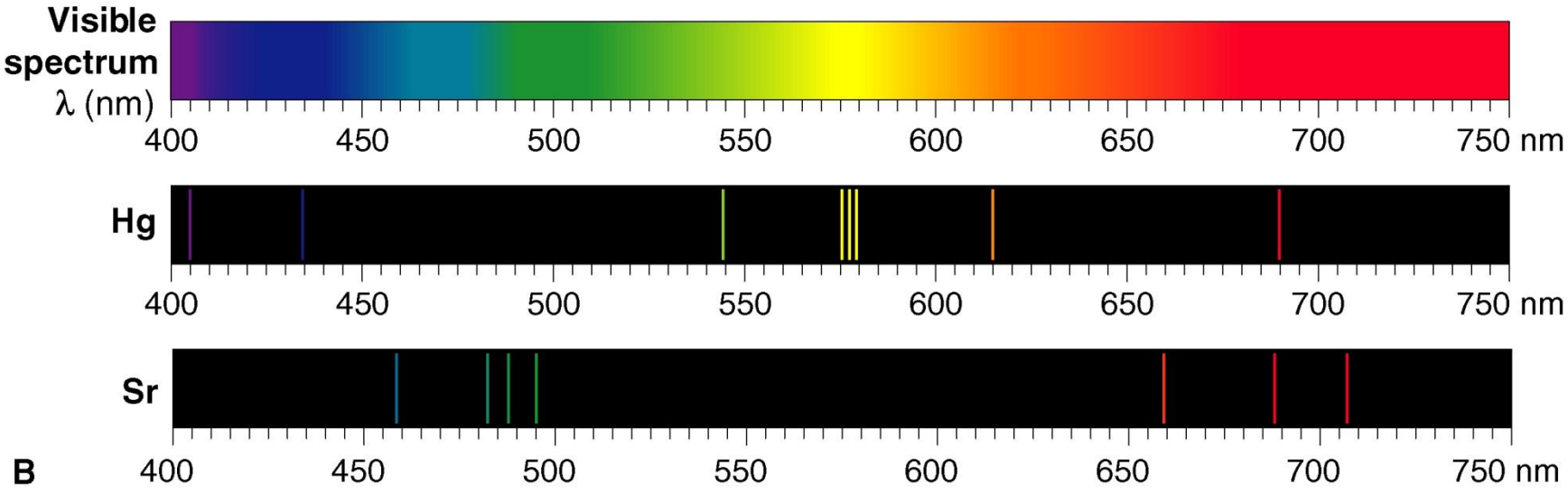

B

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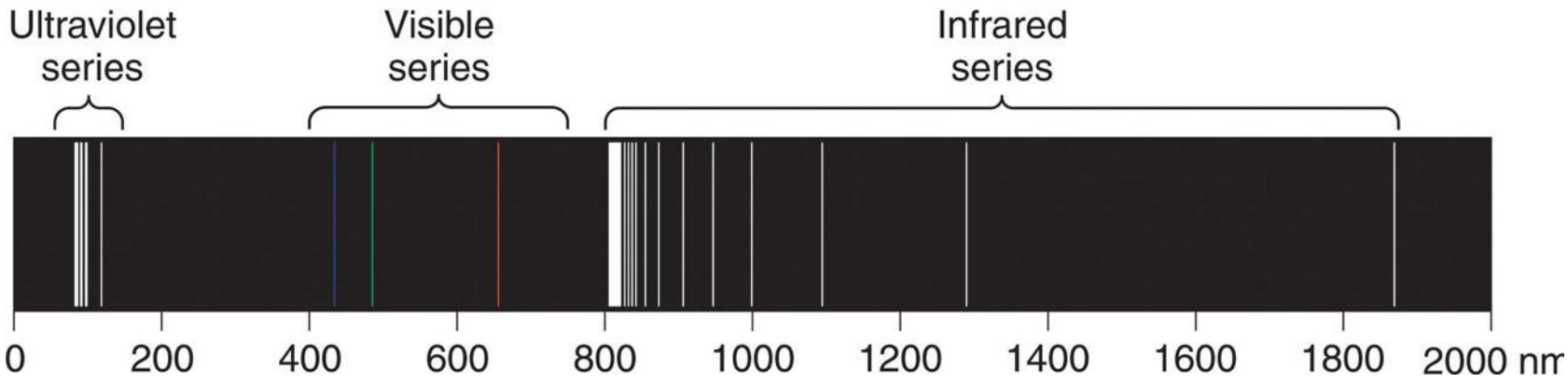
Figure 7.8 Three series of spectral lines of atomic hydrogen.



Rydberg equation $\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

R is the Rydberg constant = 1.096776x10^7 m^{-1}

for the visible series, $n_1 = 2$ and $n_2 = 3, 4, 5, ...$

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The Bohr Model of the Hydrogen Atom

Bohr's atomic model postulated the following:

- The H atom has only certain energy levels, which Bohr called ***stationary states***.
  - Each state is associated with a fixed circular orbit of the electron around the nucleus.
  - The higher the energy level, the farther the orbit is from the nucleus.
  - When the H electron is in the first orbit, the atom is in its lowest energy state, called the ***ground state***.

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- The atom does not radiate energy while in one of its stationary states.
- The atom changes to another stationary state only by absorbing or emitting a photon.
  - The energy of the photon ($h\nu$) equals the difference between the energies of the two energy states.
  - When the electron is in any orbit higher than $n = 1$, the atom is in an ***excited state***.

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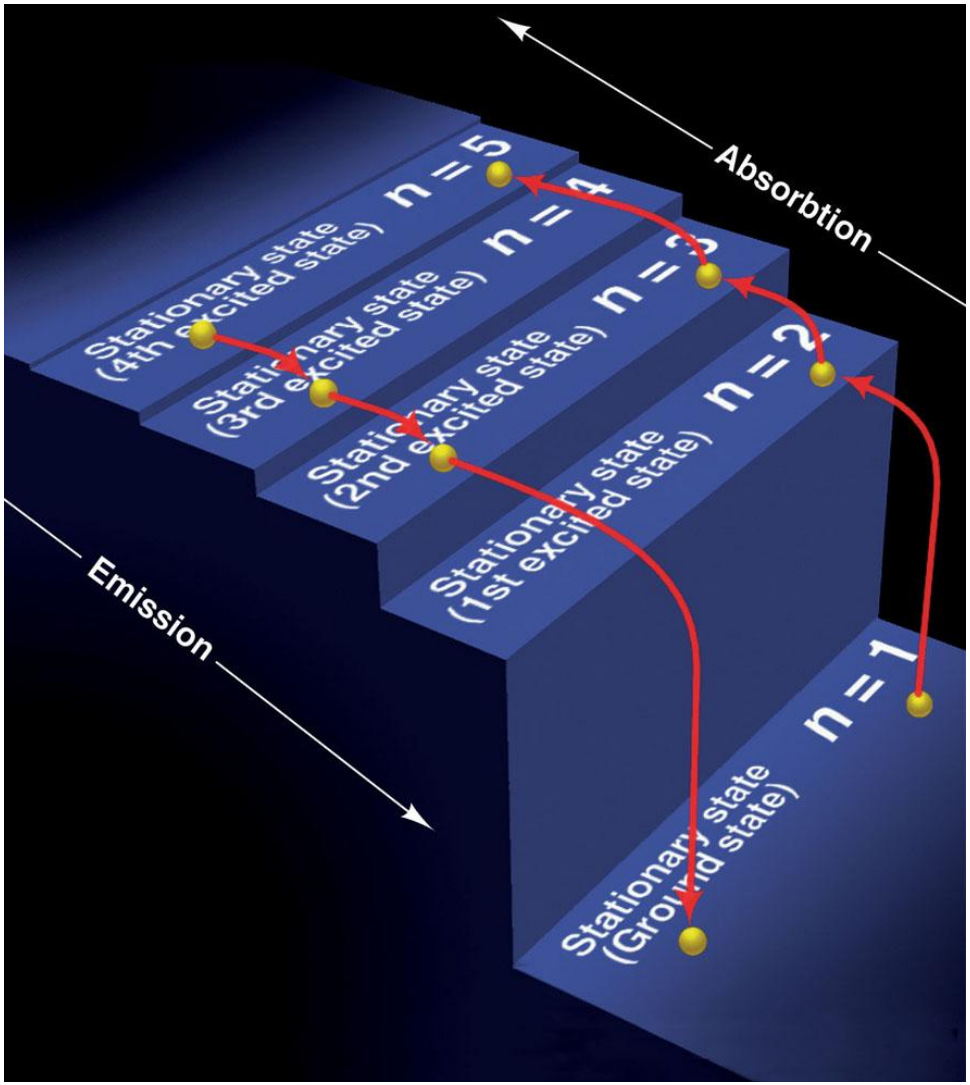
Figure 7.9 **A quantum "staircase" as an analogy for atomic energy levels.**



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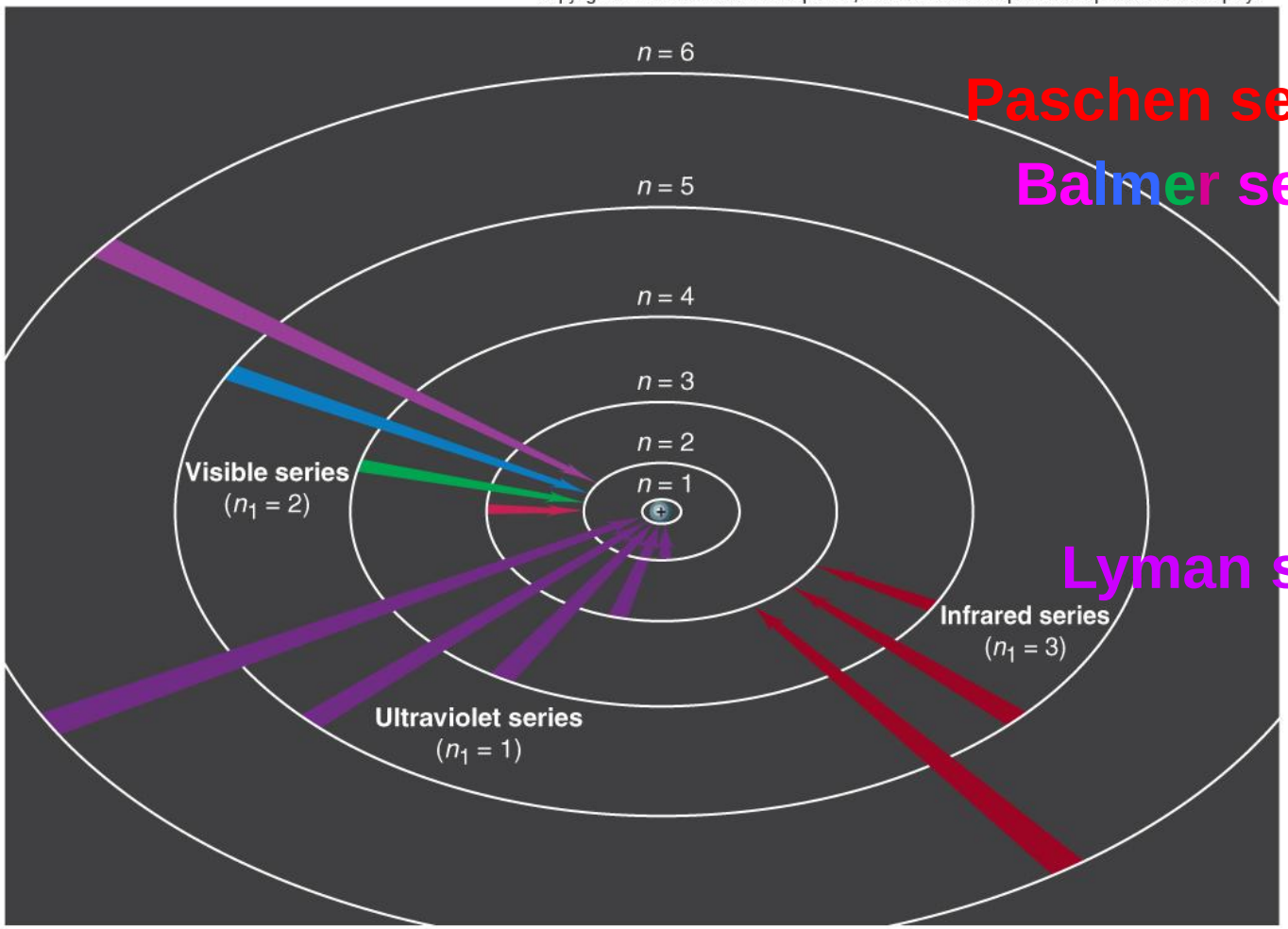

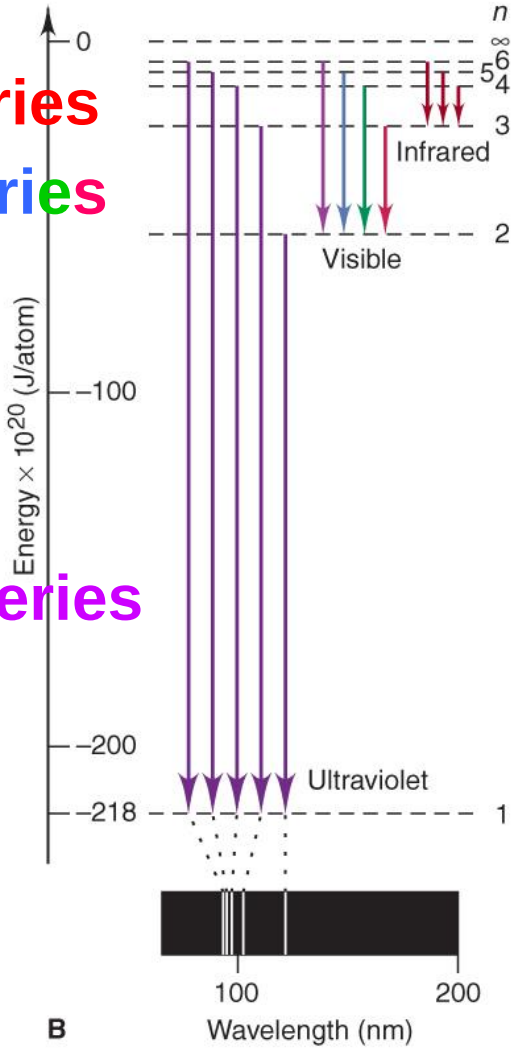

Paschen series

Balmer series

Lyman series

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A tabletop analogy for the H atom's energy.

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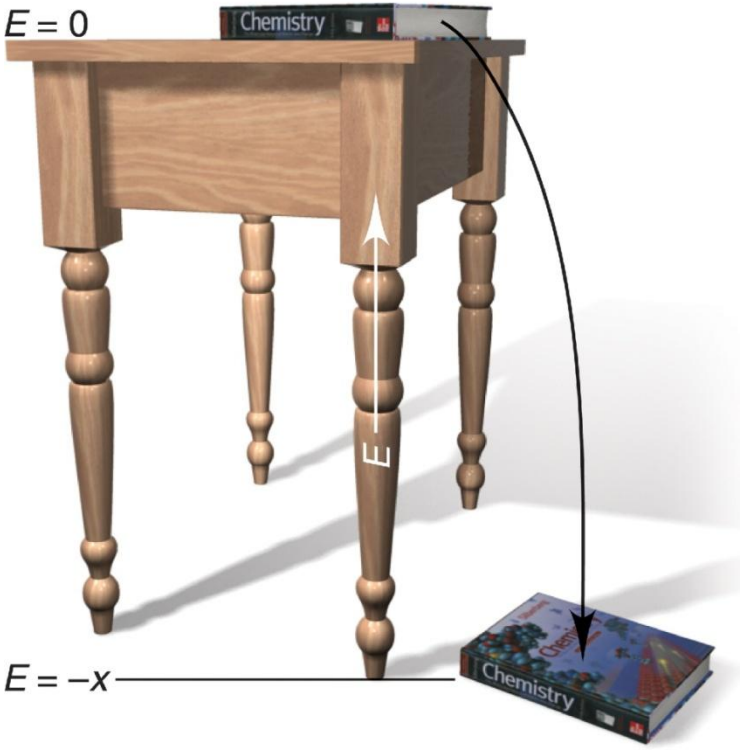

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18}\ J \left(\frac{1}{n^2_{final}} - \frac{1}{n^2_{initial}} \right)$$

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Sample Problem 7.3

Determining ΔE and λ of an Electron Transition

PROBLEM: A hydrogen atom absorbs a photon of UV light (see Figure 7.10) and its electron enters the $n = 4$ energy level. Calculate **(a)** the change in energy of the atom and **(b)** the wavelength (in nm) of the photon.

PLAN: **(a)** The H atom absorbs energy, so $E_{final} > E_{initial}$. We are given $n_{final} = 4$, and Figure 7.10 shows that $n_{initial} = 1$ because a UV photon is absorbed. We apply Equation 7.4 to find ΔE.

(b) Once we know ΔE, we find frequency and wavelength.

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Sample Problem 7.3

SOLUTION:

(a) $\Delta E = -2.18\text{x}10^{-18}\ \text{J}\left(\frac{1}{n^2_{\text{final}}} - \frac{1}{n^2_{\text{initial}}}\right) = -2.18\text{x}10^{-18}\ \text{J}\left(\frac{1}{4^2} - \frac{1}{1^2}\right)$

$= -2.18\text{x}10^{-18}\ \text{J}\left(\frac{1}{16} - \frac{1}{4}\right)$ **$= 2.04\text{x}10^{-18}$ J**

(b) $\lambda = \frac{hc}{\Delta E} = \frac{(6.626\text{x}10^{-34}\ \text{J·s})(3.00\text{x}10^{8}\ \text{m/s})}{2.04\text{x}10^{-18}\ \text{J}}$ **$= 9.74\text{x}10^{-8}$ m**

$9.74\text{x}10^{-8}\ \text{m} \times \frac{1\ \text{nm}}{10^{-9}\ \text{m}}$ **= 97.4 nm**

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Figure 7.11 Measuring chlorophyll *a* concentration in leaf extract.

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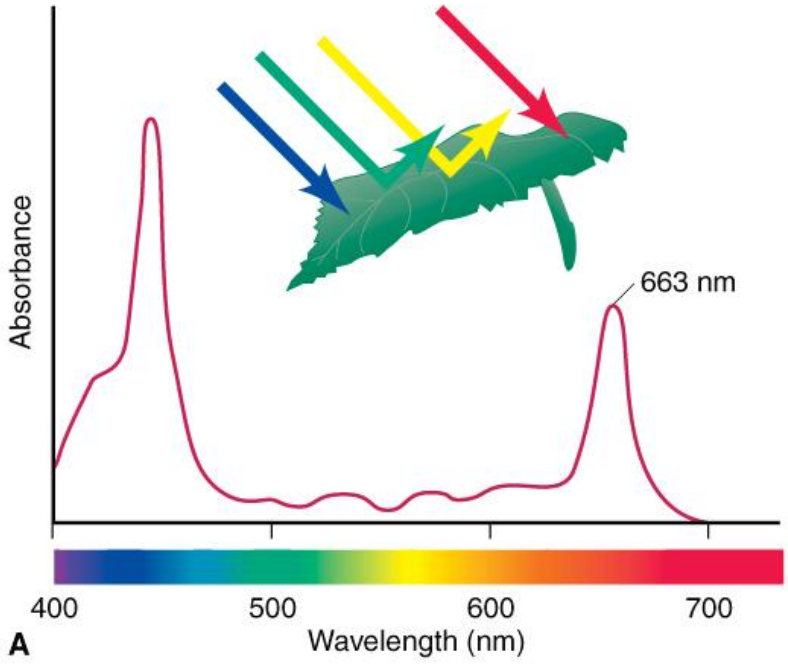

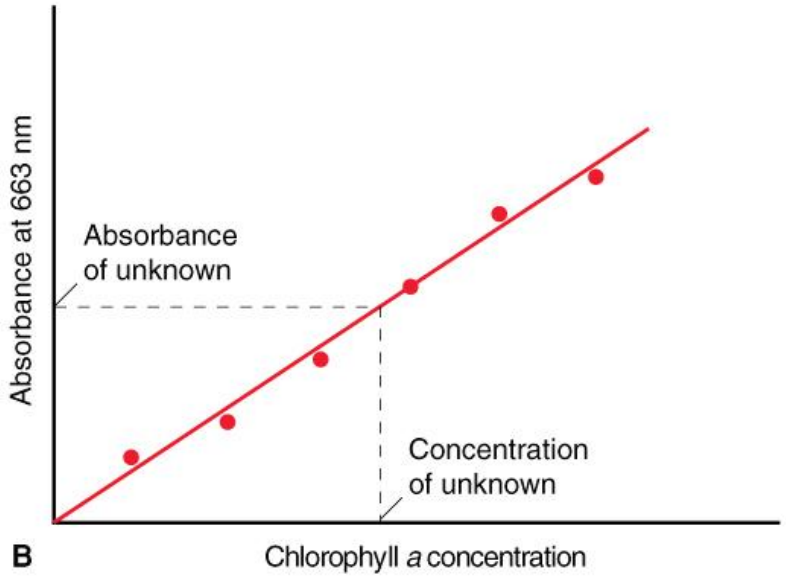

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The Wave-Particle Duality of Matter and Energy

Matter and Energy are alternate forms of the same entity.

$$E = mc^2$$

All matter exhibits properties of ***both particles and waves***. Electrons have wave-like motion and therefore have only certain allowable frequencies and energies.

Matter behaves as though it moves in a wave, and the ***de Broglie wavelength*** for any particle is given by:

$$\lambda = \frac{h}{mu}$$

m = mass

u = speed in m/s

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Figure 7.12 Wave motion in restricted systems.

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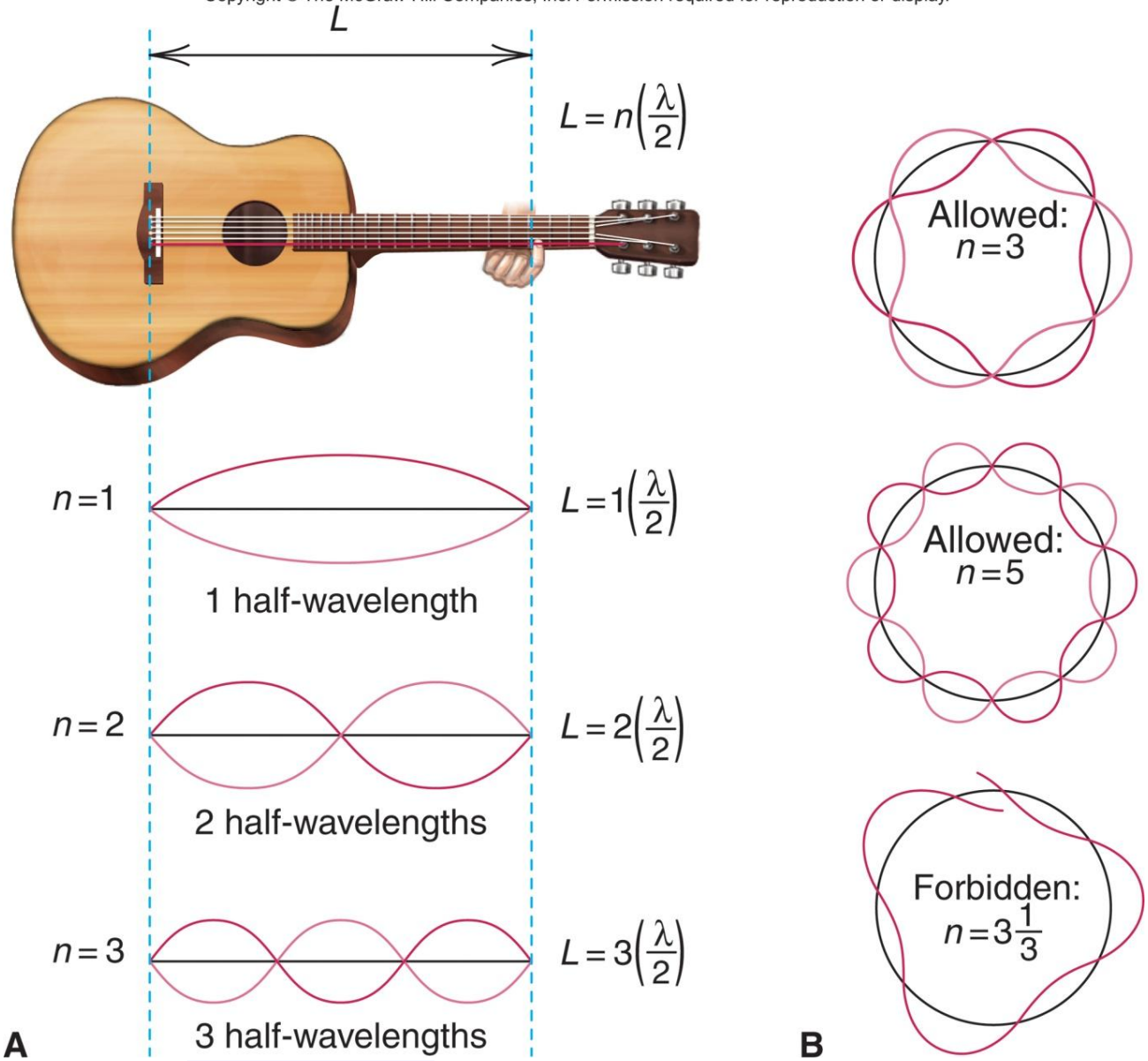

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Table 7.1 The de Broglie Wavelengths of Several Objects

Substance	Mass (g)	Speed (m/s)	λ (m)
slow electron	9×10^{-28}	1.0	7×10^{-4}
fast electron	9×10^{-28}	5.9×10^{6}	1×10^{-10}
alpha particle	6.6×10^{-24}	1.5×10^{7}	7×10^{-15}
one-gram mass	1.0	0.01	7×10^{-29}
baseball	142	25.0	2×10^{-34}
Earth	6.0×10^{27}	3.0×10^{4}	4×10^{-63}

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Sample Problem 7.4 Calculating the de Broglie Wavelength of an Electron

PROBLEM: Find the de Broglie wavelength of an electron with a speed of 1.00×10^{6} m/s (electron mass = 9.11×10^{-31} kg; $h = 6.626 \times 10^{-34}$ kg·m^2/s).

PLAN: We know the speed and mass of the electron, so we substitute these into Equation 7.5 to find λ.

SOLUTION:

$$\lambda = \frac{h}{mu}$$

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg·m}^2/\text{s}}{9.11 \times 10^{-31}\ \text{kg} \times 1.00 \times 10^{6}\ \text{m/s}}$$

$$= \mathbf{7.27 \times 10^{-10}\ m}$$

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Figure 7.13 Diffraction patterns of aluminum with x-rays and electrons.

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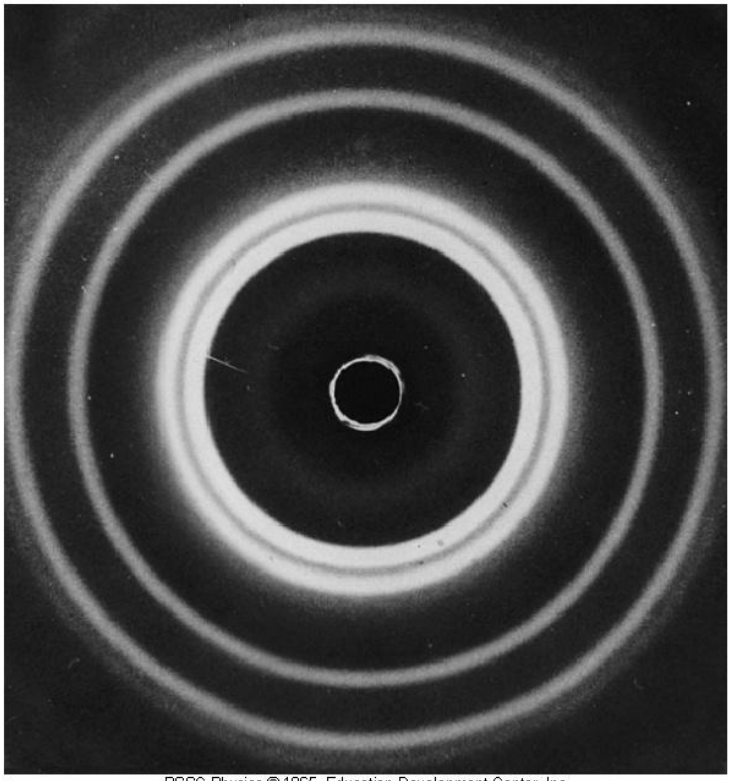

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x-ray diffraction of aluminum foil

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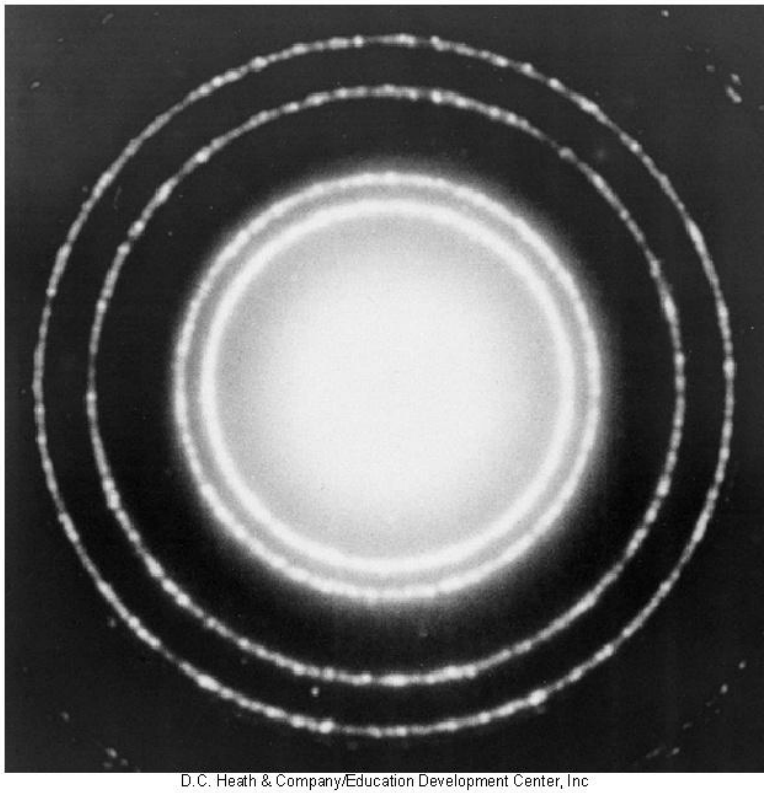

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electron diffraction of aluminum foil

This behavior implies that both X-rays, which are electromagnetic radiation, and electrons which are particles, travel in waves.

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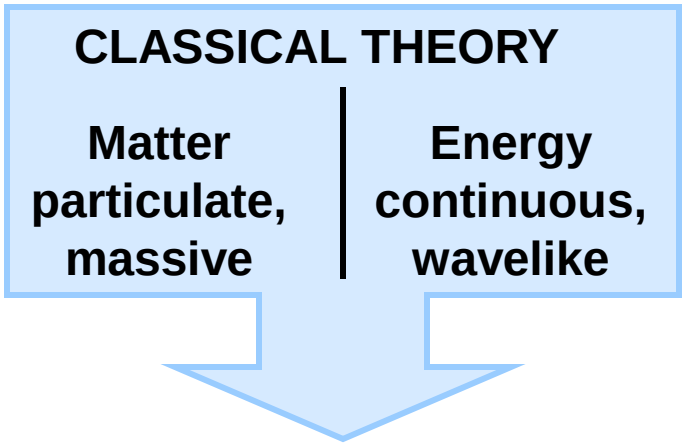

Figure 7.14

Major observations and theories leading from classical theory to quantum theory

Since *matter* is discontinuous and particulate, perhaps *energy* is discontinuous and particulate.

Observation		*Theory*	
Blackbody radiation	→	Planck:	Energy is quantized; only certain values allowed
Photoelectric effect	→	Einstein:	Light has particulate behavior (photons)
Atomic line spectra	→	Bohr:	Energy of atoms is quantized; photon emitted when electron changes orbit.

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Figure 7.14 continued

Since *energy* is wavelike, perhaps *matter* is wavelike.		
Observation		***Theory***
Davisson/Germer: Electron beam is diffracted by metal crystal	←	deBroglie: All matter travels in waves; energy of atom is quantized due to wave motion of electrons
Since *matter* has mass, perhaps *energy* has mass		
Observation		***Theory***
Compton: Photon's wavelength increases (momentum decreases) after colliding with electron	←	Einstein/deBroglie: Mass and energy are equivalent; particles have wavelength and photons have momentum.

QUANTUM THEORY

Energy *and* **Matter**

particulate, massive, wavelike

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Heisenberg's Uncertainty Principle

Heisenberg's Uncertainty Principle states that it is not possible to know both the position *and* momentum of a moving particle at the same time.

$$\Delta x \cdot m \Delta u \geq \frac{h}{4\pi}$$

x = position

u = speed

The more accurately we know the speed, the less accurately we know the position, and vice versa.

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The Quantum-Mechanical Model of the Atom

The matter-wave of the electron occupies the space near the nucleus and is continuously influenced by it.

The ***Schrödinger wave equation*** allows us to solve for the energy states associated with a particular atomic orbital.

The square of the wave function gives the ***probability density***, a measure of the ***probability*** of finding an electron of a particular energy in a particular region of the atom.

$$H\Psi = E\Psi$$

where H = the Hamiltonian operator
E = energy of the electron
Ψ = the wave function

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)\right]\Psi(x,y,z) = E\Psi(x,y,z)$$

where $$V = \frac{-Ze^2}{4\pi\varepsilon_0 r} = \frac{-Ze^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}$$

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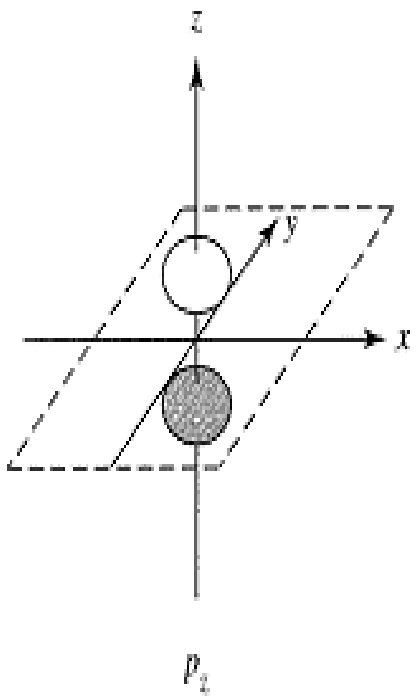
TABLE 2-5
Nodal Surfaces

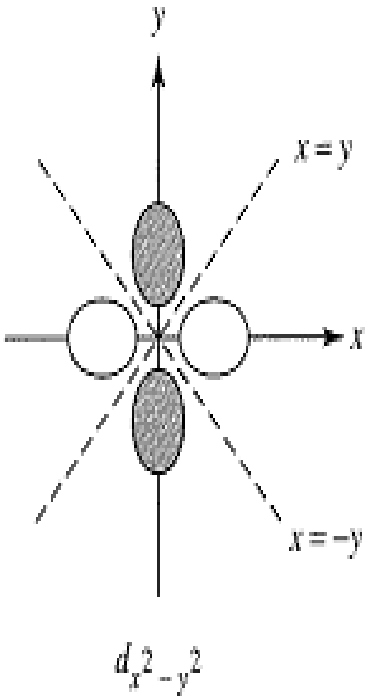
$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Spherical nodes $[R(r) = 0]$					
Examples (number of spherical nodes)					
$1s$	0	$2p$	0	$3d$	0
$2s$	1	$3p$	1	$4d$	1
$3s$	2	$4p$	2	$5d$	2

Angular nodes $[Y(\theta, \phi) = 0]$	
Examples (number of angular nodes)	
s orbitals	0
p orbitals	1 plane for each orbital
d orbitals	2 planes for each orbital except d_{z^2}
	1 conical surface for d_{z^2}



p_z



$d_{x^2-y^2}$

Number of radial nodes (spherical) = **n -L -1**

Number of angular nodes (planes) = **L**

Total number of nodes = **n - 1**

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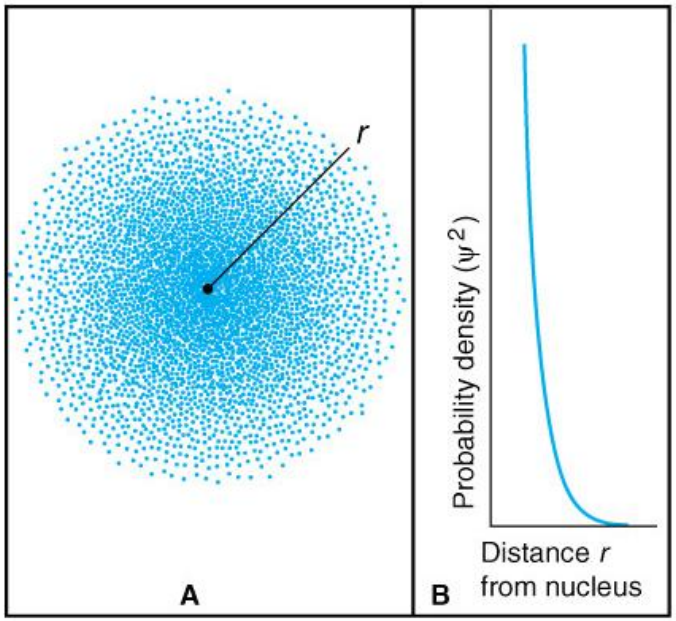


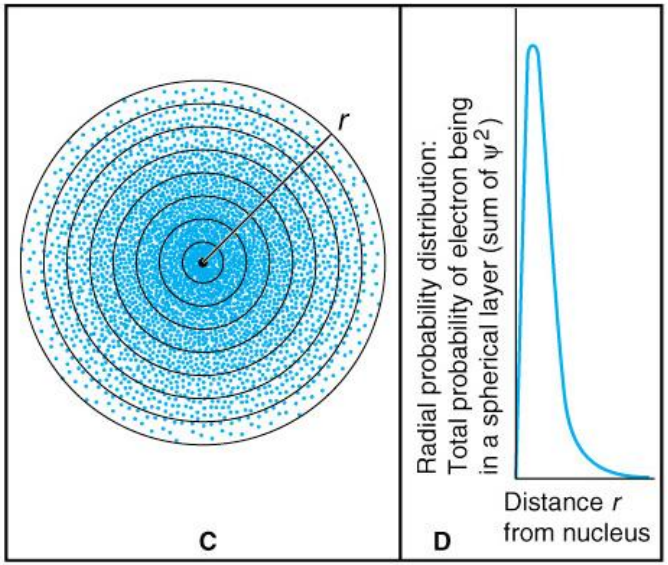
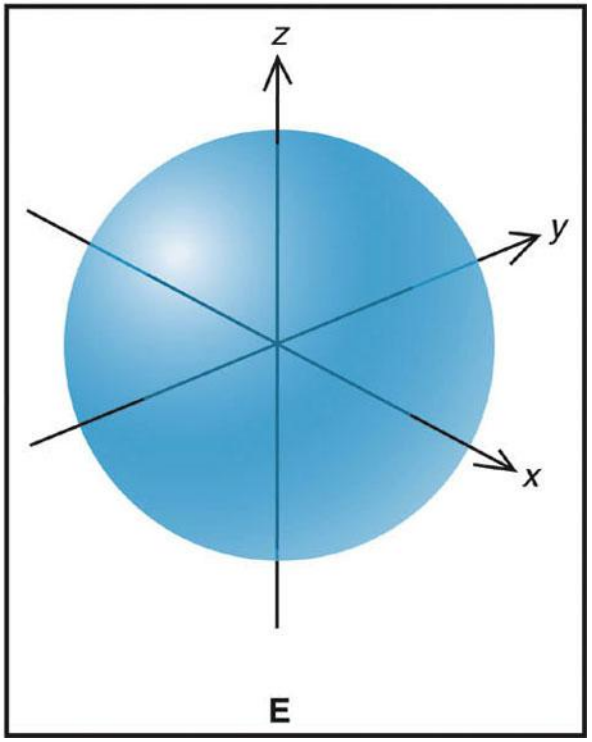


Figure 7.15

Electron probability density in the ground-state H atom.



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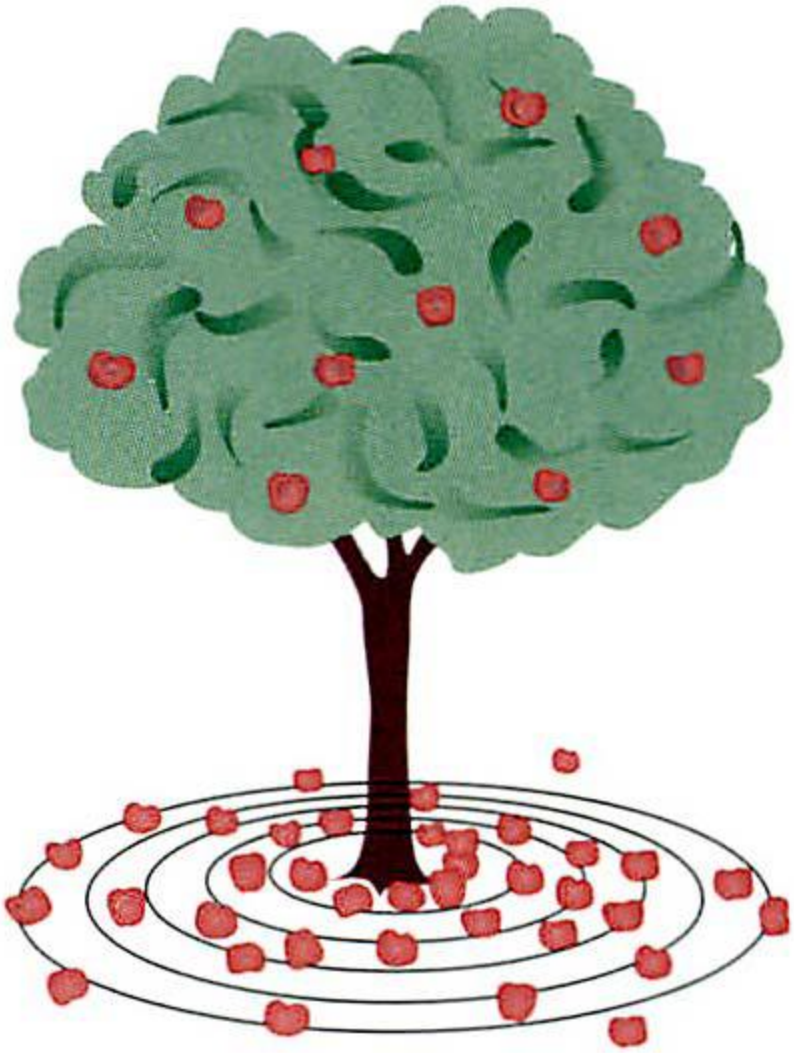

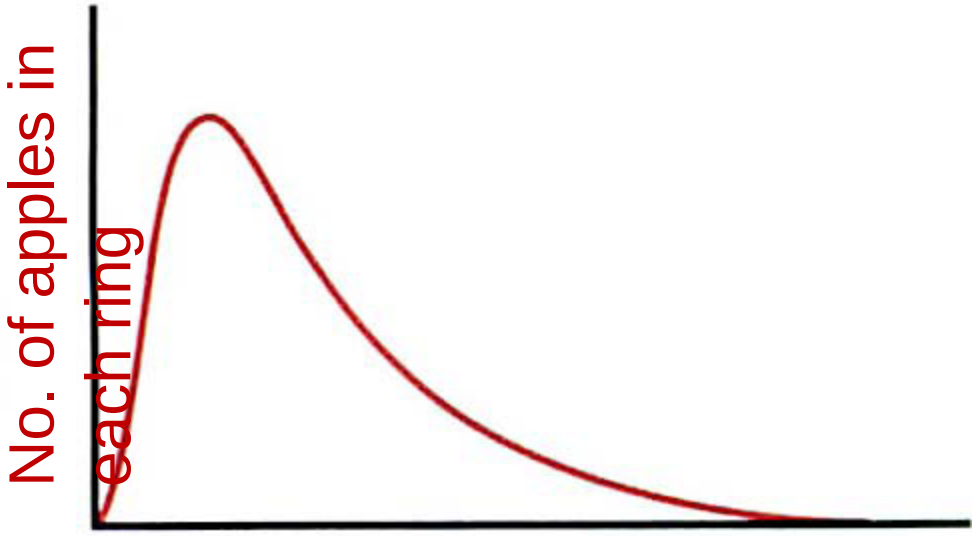

A radial probability distribution of apples

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Figure 7.16 The 1*s*, 2*s*, and 3*s* orbitals.

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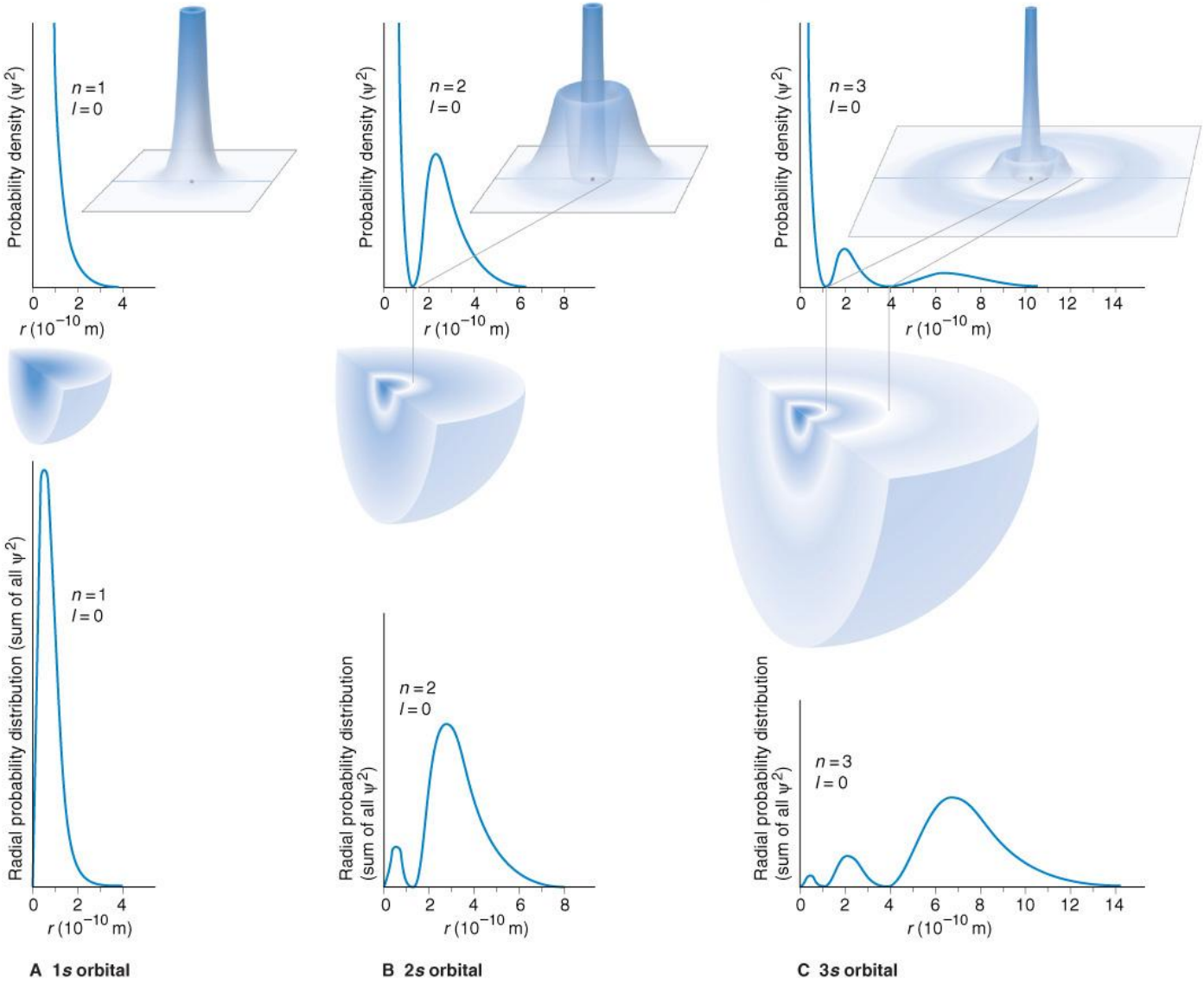

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Figure 7.17 The 2*p* orbitals.

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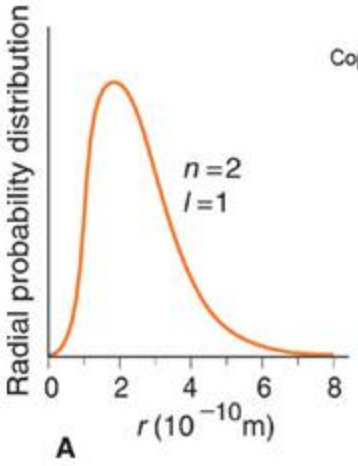
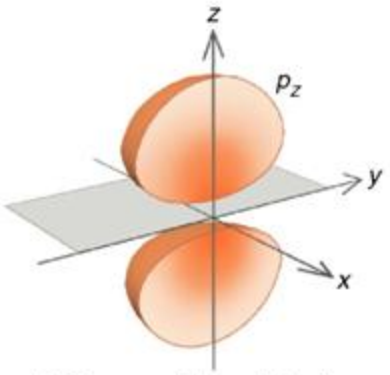
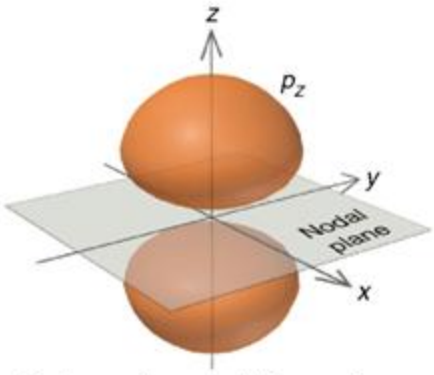


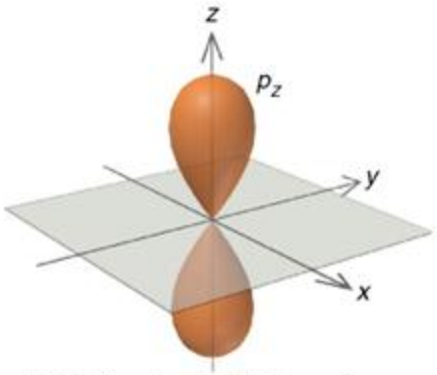
A



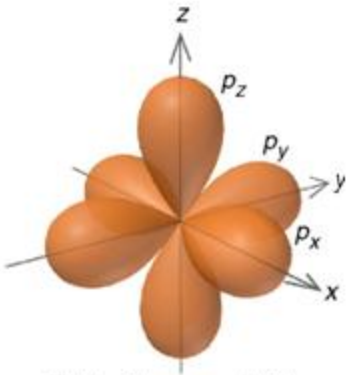
B Cross section of electron cloud depiction



C Accurate probability contour



D Stylized probability contour



E The three *p* orbitals

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Figure 7.18 The 3*d* orbitals.

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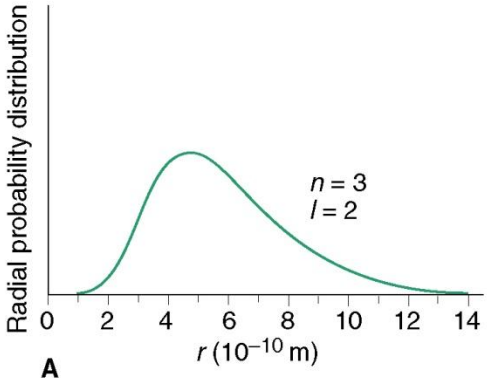

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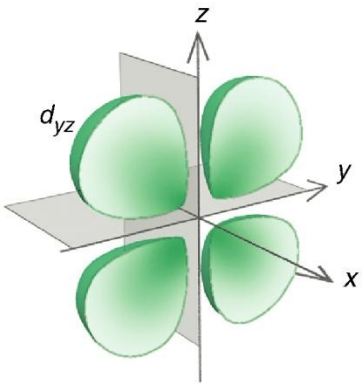
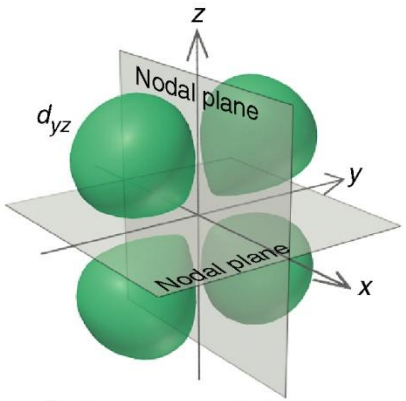
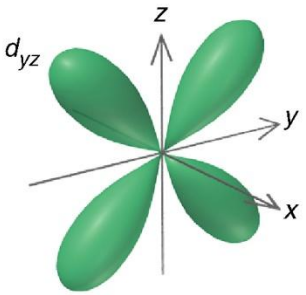


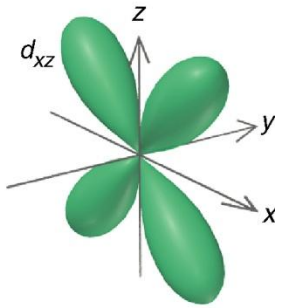
B Cross section of electron cloud depiction



C Accurate probability contour



D Stylized probability contour



E

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Figure 7.18

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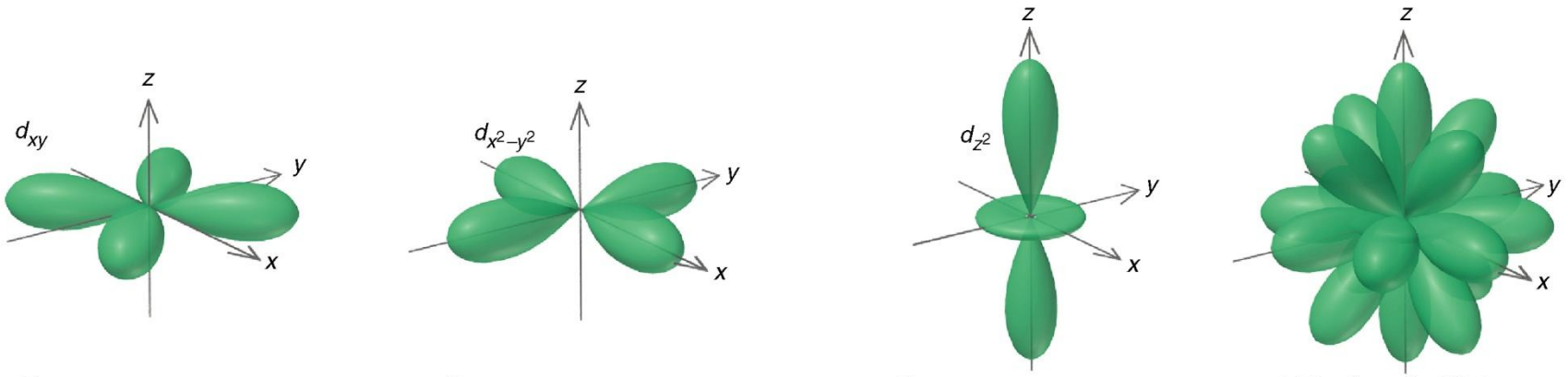

F G H I The five *d* orbitals

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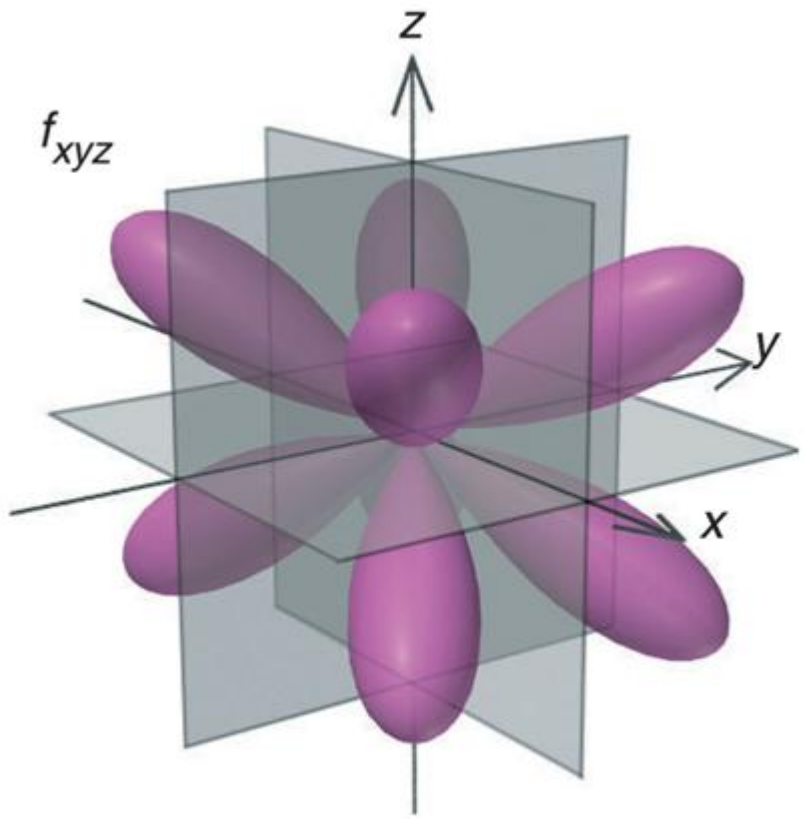
Figure 7.19 The $4f_{xyz}$ orbital, one of the seven $4f$ orbitals.



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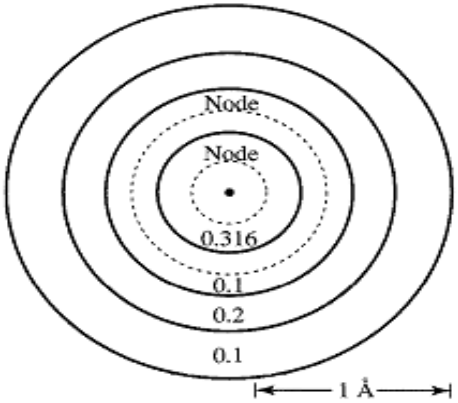
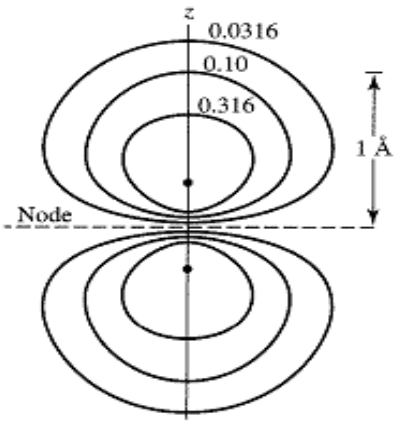
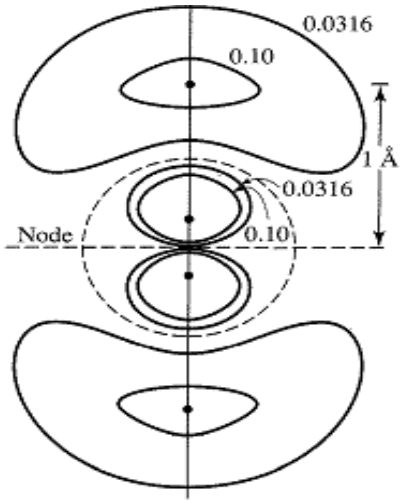


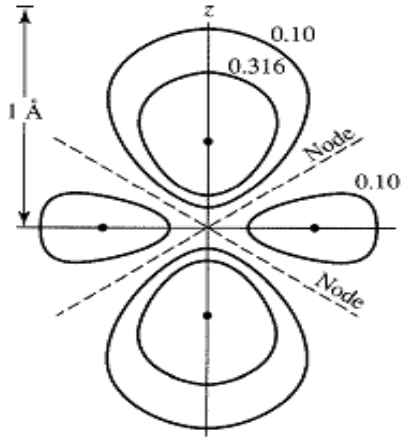
(a) Cl:3*s*



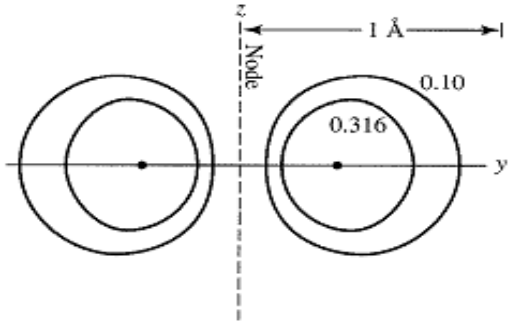
(b) C:2p_z



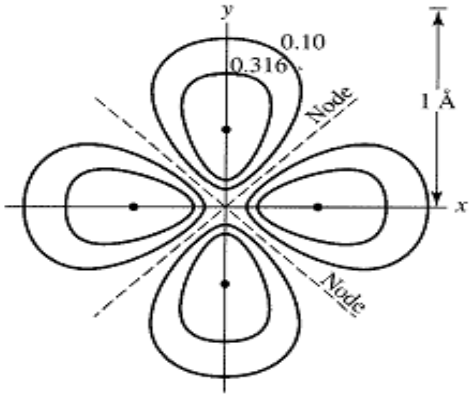
(c) Cl:3p_z



(d) Ti^{3+}:3d_{z^2}



(e) Ti^{3+}:3$d_{x^2-y^2}$



(f) Ti^{3+}:3$d_{x^2-y^2}$

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Quantum Numbers and Atomic Orbitals

An atomic orbital is specified by three quantum numbers.

The ***principal*** quantum number (***n***) is a positive integer.

The value of *n* indicates the relative ***size*** of the orbital and therefore its relative ***distance*** from the nucleus.

The ***angular momentum*** quantum number ***(l)*** is an integer from 0 to (*n* -1).

The value of *l* indicates the ***shape*** of the orbital.

The ***magnetic*** quantum number **(m_l)** is an integer with values from $-l$ to $+l$

The value of m_l indicates the spatial ***orientation*** of the orbital.

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Table 7.2 The Hierarchy of Quantum Numbers for Atomic Orbitals

Name, Symbol (Property)	Allowed Values	Quantum Numbers
Principal, n (size, energy)	Positive integer (1, 2, 3, ...)	1 2 3
Angular momentum, l (shape)	0 to $n - 1$	0 0 1 0 1 2
Magnetic, m_l (orientation)	$-l,\ldots,0,\ldots,+l$	0 0 -1 0 +1 0 -1 0 +1 -2 -1 0 +1 +2

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Sample Problem 7.5 **Determining Quantum Numbers for an Energy Level**

PROBLEM: What values of the angular momentum (l) and magnetic (m_l) quantum numbers are allowed for a principal quantum number (n) of 3? How many orbitals are allowed for $n = 3$?

PLAN: Values of l are determined from the value for n, since l can take values from 0 to (n-1). The values of m_l then follow from the values of l.

SOLUTION: For $n = 3$, allowed values of l are = 0, 1, and 2

For $l = 0$ $m_l = 0$

For $l = 1$ $m_l = -1, 0,$ or $+1$

For $l = 2$ $m_l = -2, -1, 0, +1,$ or $+2$

There are 9 m_l values and therefore 9 orbitals with $n = 3$.

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Sample Problem 7.6 Determining Sublevel Names and Orbital Quantum Numbers

PROBLEM: Give the name, magnetic quantum numbers, and number of orbitals for each sublevel with the following quantum numbers:

(a) $n = 3$, $l = 2$ **(b)** $n = 2$, $l = 0$ **(c)** $n = 5$, $l = 1$ **(d)** $n = 4$, $l = 3$

PLAN: Combine the n value and l designation to name the sublevel. Knowing l, we can find m_l and the number of orbitals.

SOLUTION:

	n	l	sublevel name	possible m_l values	# of orbitals
(a)	3	2	3*d*	-2, -1, 0, 1, 2	5
(b)	2	0	2*s*	0	1
(c)	5	1	5*p*	-1, 0, 1	3
(d)	4	3	4*f*	-3, -2, -1, 0, 1, 2, 3	7

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Sample Problem 7.7 Identifying Incorrect Quantum Numbers

PROBLEM: What is wrong with each of the following quantum numbers designations and/or sublevel names?

	n	l	m_l	Name
(a)	1	1	0	1*p*
(b)	4	3	+1	4*d*
(c)	3	1	-2	3*p*

SOLUTION:

(a) A sublevel with $n = 1$ can only have $l = 0$, not $l = 1$. The only possible sublevel name is 1*s*.

(b) A sublevel with $l = 3$ is an *f* sublevel, to a *d* sublevel. The name should be 4*f*.

(c) A sublevel with $l = 1$ can only have m_l values of -1, 0, or +1, not -2.

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Figure 7.20 **Energy levels of the H atom.**

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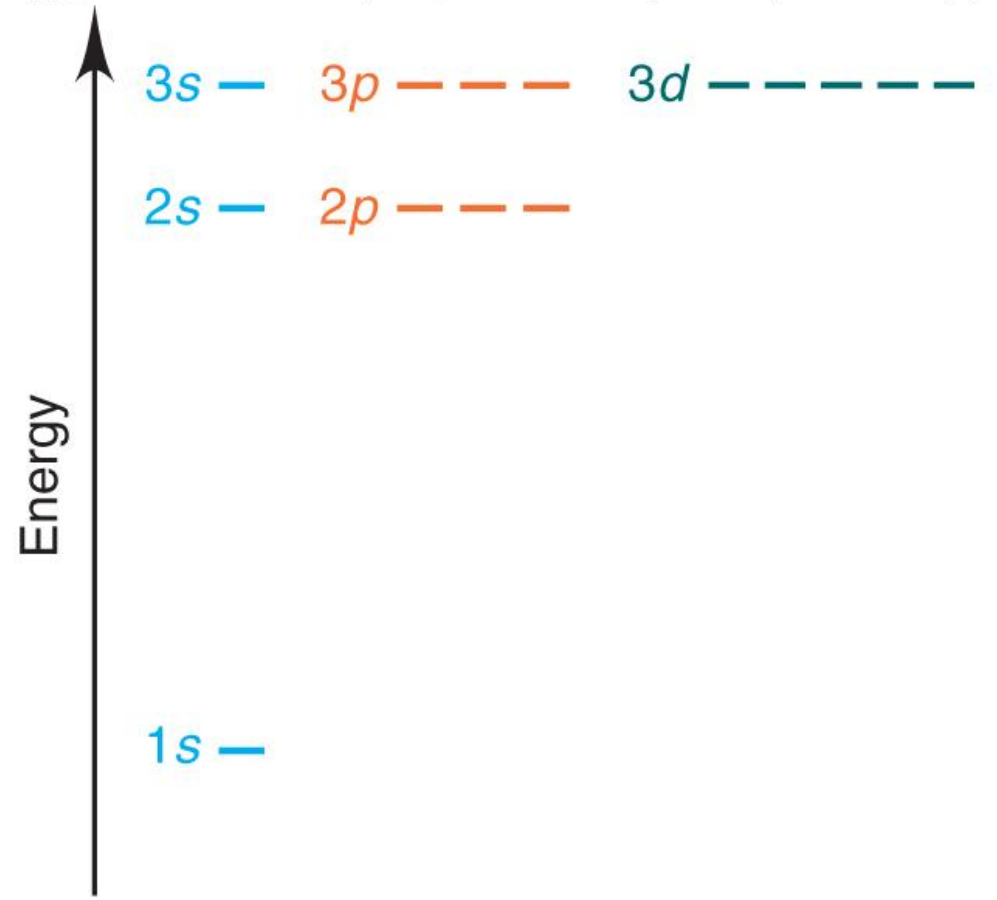

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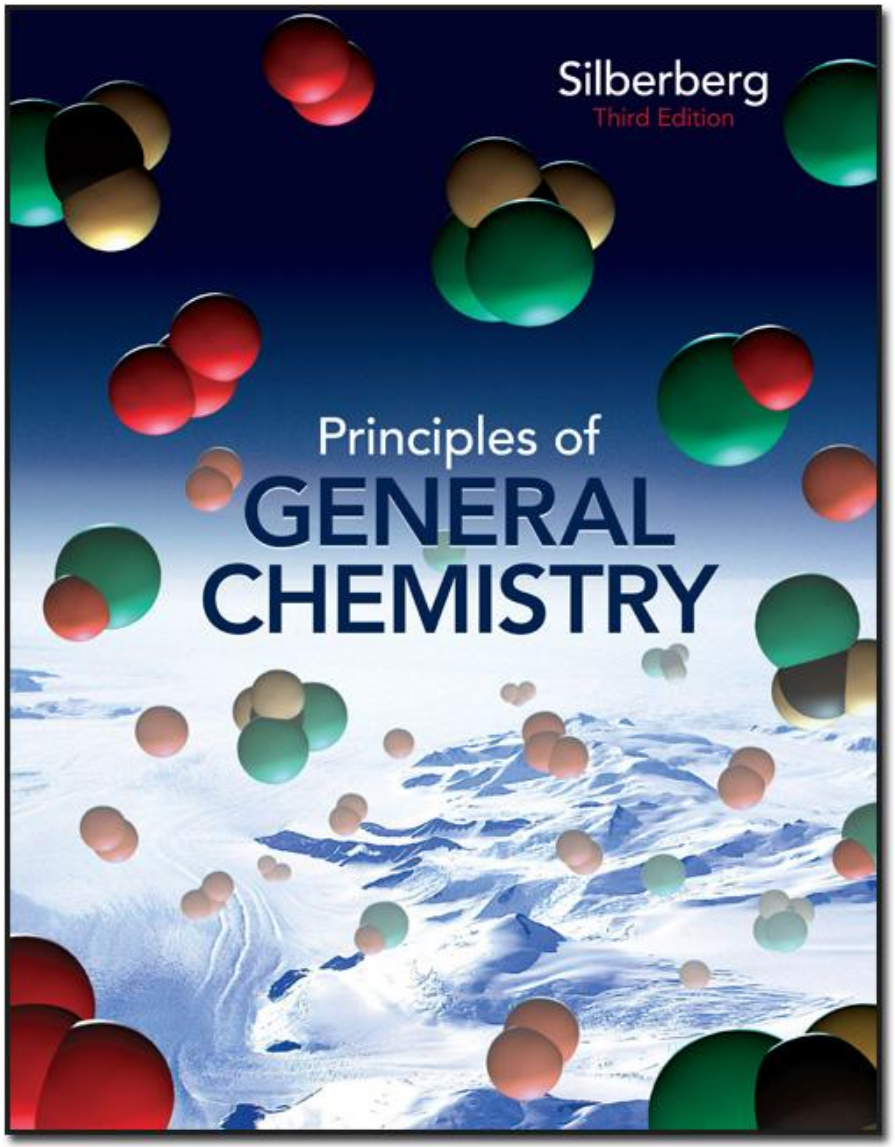

Chapter 08

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 8

Electron Configuration and Chemical Periodicity

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Electron Configuration and Chemical Periodicity

8.1 Characteristics of Many-Electron Atoms

8.2 The Quantum-Mechanical Model and the Periodic Table

8.3 Trends in Three Atomic Properties

8.4 Atomic Properties and Chemical Reactivity

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Figure 8.1 **The effect of electron spin.**

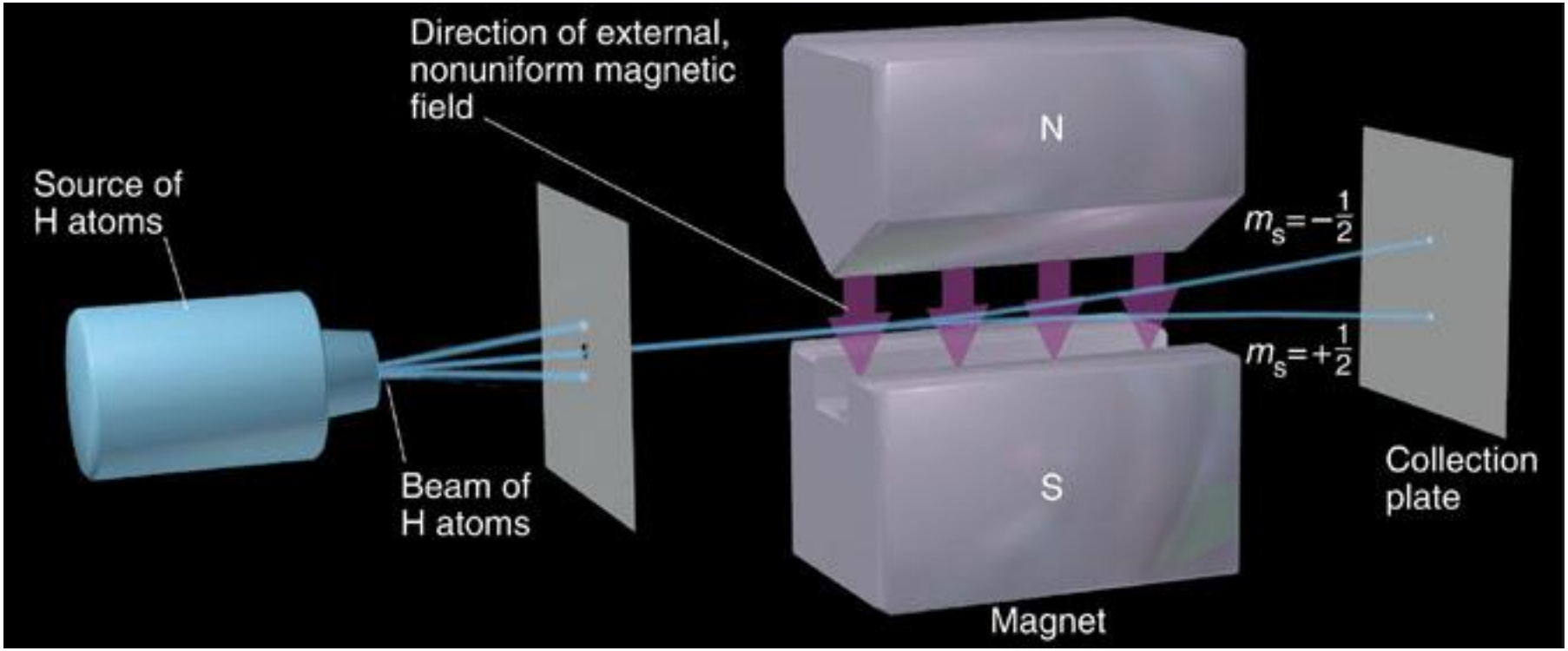

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Table 8.1 Summary of Quantum Numbers of Electrons in Atoms

Name	Symbol	Permitted Values	Property
principal	n	positive integers (1, 2, 3, …)	orbital energy (size)
angular momentum	l	integers from 0 to n-1	orbital shape (The l values 0, 1, 2, and 3 correspond to *s*, *p*, *d*, and *f* orbitals, respectively.)
magnetic	m_l	integers from -l to 0 to +l	orbital orientation
spin	m_s	+½ or -½	direction of e^- spin

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Quantum Numbers and The Exclusion Principle

Each electron in any atom is described completely by a set of ***four*** quantum numbers.

The first three quantum numbers describe the orbital, while the fourth quantum number describes electron spin.

Pauli's **exclusion principle** states that *no two electrons in the same atom can have the same four quantum numbers*.

An atomic orbital can hold a ***maximum of two electrons*** and they must have ***opposing spins***.

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Factors Affecting Atomic Orbital Energies

- The energies of atomic orbitals are affected by
  - nuclear charge (Z) and
  - shielding by other electrons.
- A **higher nuclear charge** increases nucleus-electron interactions and lowers sublevel energy.
- **Shielding** by other electrons reduces the full nuclear charge to an ***effective nuclear charge*** ($\boldsymbol{Z_{eff}}$).
  - Z_{eff} is the nuclear charge an electron actually experiences.
- **Orbital shape** also affects sublevel energy.

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Shielding and Orbital Energy

- Electrons in the ***same*** energy level shield each other to some extent.
- Electrons in ***inner*** energy levels shield the outer electrons very effectively.
  - The farther from the nucleus an electron is, the lower the Z_{eff} for that particular electron.

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Figure 8.2 Penetration and sublevel energy.

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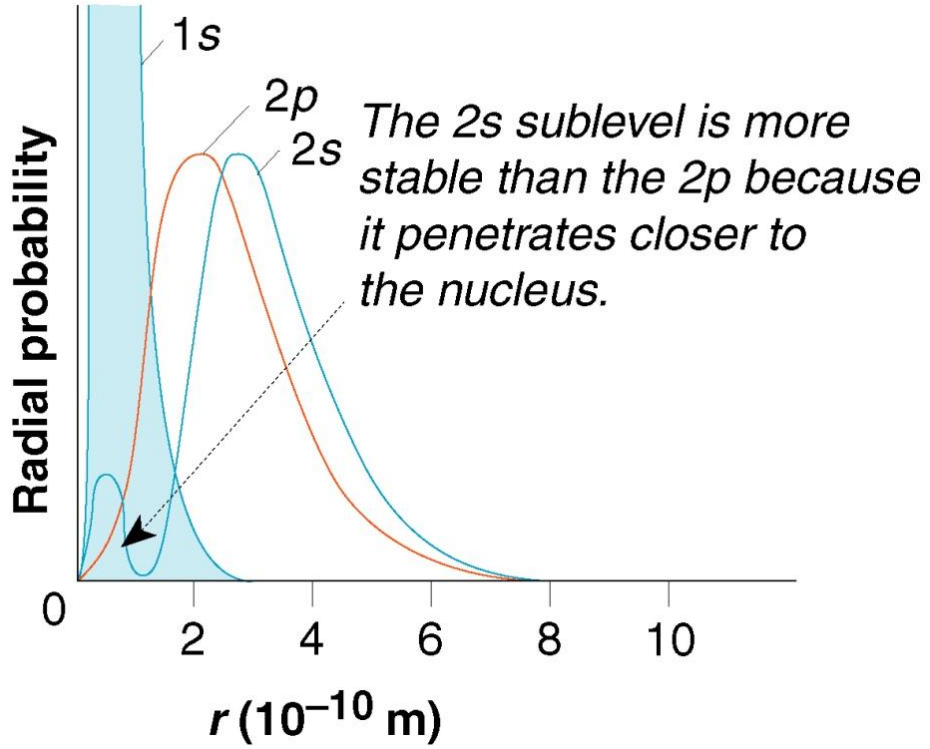

Orbital shape causes electrons in some orbitals to “penetrate” close to the nucleus.

Penetration increases nuclear attraction and decreases shielding.

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Splitting of Levels into Sublevels

Each energy level is split into ***sublevels*** of differing energy.

Splitting is caused by penetration and its effect on shielding.

For a given *n* value, a lower *l* value indicates a lower energy sublevel.

Order of sublevel energies: *s* < *p* < *d* < *f*

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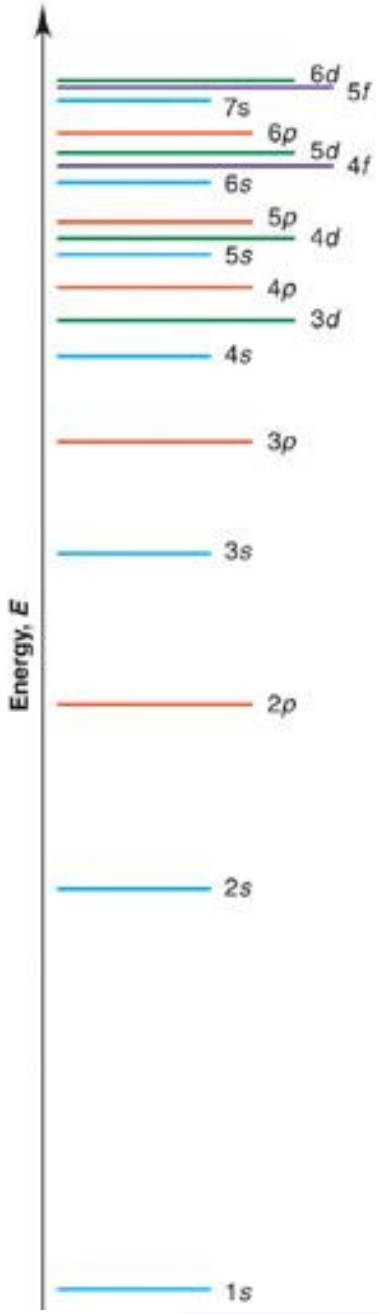

Figure 8.3

Order for filling energy sublevels with electrons.

In general, energies of sublevels increase as n increases ($1 < 2 < 3$, etc.)
and as l increases ($s < p < d < f$).

As n increases, some sublevels overlap.

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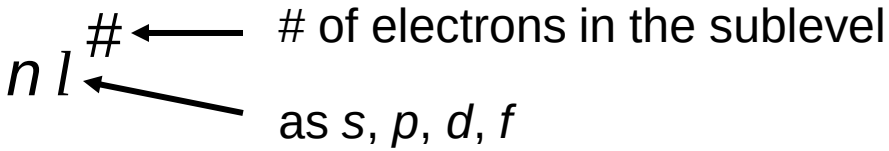
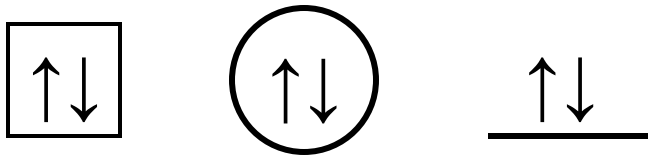
Electron Configurations and Orbital Diagrams

Electron configuration is indicated by a shorthand notation:



Orbital diagrams make use of a box, circle, or line for each orbital in the energy level. An arrow is used to represent an electron *and* its spin.



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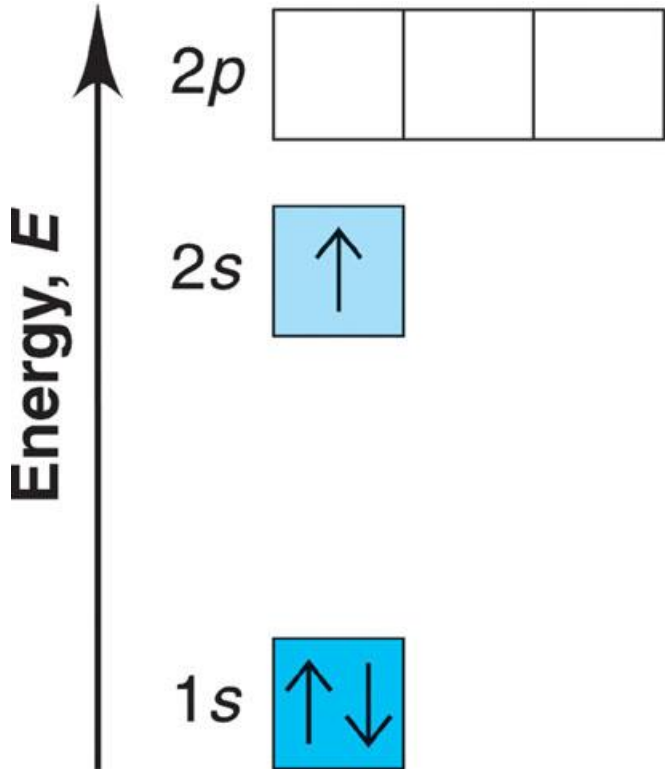
A vertical orbital diagram for the Li ground state.



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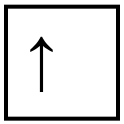
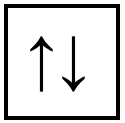
Building Orbital Diagrams

The **aufbau principle** is applied – electrons are always placed in the lowest energy sublevel available.

H (Z = 1) $1s^1$ 

1*s*

The **exclusion principle** states that each orbital may contain a maximum of 2 electrons, which must have opposite spins.

He (Z = 2) $1s^2$ 

1*s*

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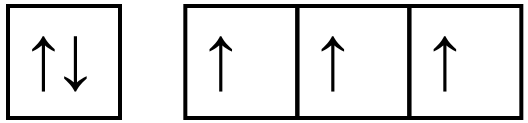
Building Orbital Diagrams

Hund's rule specifies that when orbitals of equal energy are available, the lowest energy electron configuration has the maximum number of unpaired electrons with parallel spins.

N (Z = 7) $1s^2 2s^2 2p^3$



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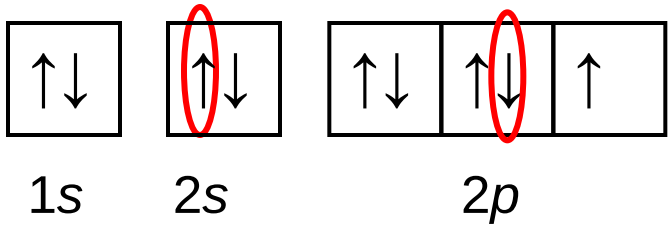
Sample Problem 8.1 Determining Quantum Numbers from Orbital Diagrams

PROBLEM: Write a set of quantum numbers for the third electron and a set for the eighth electron of the F atom.

PLAN: Identify the electron of interest and note its level (n), sublevel, (l), orbital (m_l) and spin (m_s). Count the electrons in the order in which they are placed in the diagram.

SOLUTION:

F (Z = 9) $1s^2 2s^2 2p^5$



For the 3rd electron: $n = 2$, $l = 0$, $m_l = 0$, $m_s = +½$

For the 8th electron: $n = 2$, $l = 1$, $m_l = -1$, $m_s = -½$

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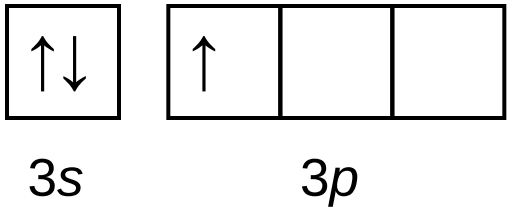
Partial Orbital Diagrams and Condensed Configurations

A ***partial orbital diagram*** shows only the highest energy sublevels being filled.

Al (Z = 13) $1s^2 2s^2 2p^6 3s^2 3p^1$



A ***condensed electron configuration*** has the element symbol of the ***previous*** noble gas in square brackets.

Al has the condensed configuration [Ne]$3s^2 3p^1$

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Table 8.2 Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 3.

Atomic Number	Element	Partial Orbital Diagram (3*s* and 3*p* Sublevels Only)	Full Electron Configuration†	Condensed Electron Configuration
		3*s* 3*p*		
11	Na	↑	$[1s^2 2s^2 2p^6]\ 3s^1$	[Ne] $3s^1$
12	Mg	↑↓	$[1s^2 2s^2 2p^6]\ 3s^2$	[Ne] $3s^2$
13	Al	↑↓ ↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^1$	[Ne] $3s^2 3p^1$
14	Si	↑↓ ↑ ↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^2$	[Ne] $3s^2 3p^2$
15	P	↑↓ ↑ ↑ ↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^3$	[Ne] $3s^2 3p^3$
16	S	↑↓ ↑↓ ↑ ↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^4$	[Ne] $3s^2 3p^4$
17	Cl	↑↓ ↑↓ ↑↓ ↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^5$	[Ne] $3s^2 3p^5$
18	Ar	↑↓ ↑↓ ↑↓ ↑↓	$[1s^2 2s^2 2p^6]\ 3s^2 3p^6$	[Ne] $3s^2 3p^6$

*Colored type indicates the sublevel to which the last electron is added.
†The full configuration is not usually written with square brackets; they are included here to show how the [Ne] designation arises.

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Electron Configuration and Group

Elements in the same group of the periodic table have the same outer electron configuration.

Elements in the same group of the periodic table exhibit similar chemical behavior.

Similar outer electron configurations correlate with similar chemical behavior.

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Figure 8.4 Condensed electron configurations in the first three periods.

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Period	1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 **H** $1s^1$							2 **He** $1s^2$
2	3 **Li** [He] $2s^1$	4 **Be** [He] $2s^2$	5 **B** [He] $2s^2 2p^1$	6 **C** [He] $2s^2 2p^2$	7 **N** [He] $2s^2 2p^3$	8 **O** [He] $2s^2 2p^4$	9 **F** [He] $2s^2 2p^5$	10 **Ne** [He] $2s^2 2p^6$
3	11 **Na** [Ne] $3s^1$	12 **Mg** [Ne] $3s^2$	13 **Al** [Ne] $3s^2 3p^1$	14 **Si** [Ne] $3s^2 3p^2$	15 **P** [Ne] $3s^2 3p^3$	16 **S** [Ne] $3s^2 3p^4$	17 **Cl** [Ne] $3s^2 3p^5$	18 **Ar** [Ne] $3s^2 3p^6$

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Table 8.3 Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 4.

Atomic Number	Element	Partial Orbital Diagram (4*s*, 3*d*, and 4*p* Sublevels Only)	Full Electron Configuration	Condensed Electron Configuration
		4*s* 3*d* 4*p*		
19	K	↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	[Ar] $4s^1$
20	Ca	↑↓	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	[Ar] $4s^2$
21	Sc	↑↓ ↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	[Ar] $4s^2 3d^1$
22	Ti	↑↓ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	[Ar] $4s^2 3d^2$
23	V	↑↓ ↑ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	[Ar] $4s^2 3d^3$
24	Cr	↑ ↑ ↑ ↑ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	[Ar] $4s^1 3d^5$
25	Mn	↑↓ ↑ ↑ ↑ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	[Ar] $4s^2 3d^5$
26	Fe	↑↓ ↑↓ ↑ ↑ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	[Ar] $4s^2 3d^6$
27	Co	↑↓ ↑↓ ↑↓ ↑ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	[Ar] $4s^2 3d^7$

*Colored type indicates the sublevel to which the last electron is added.

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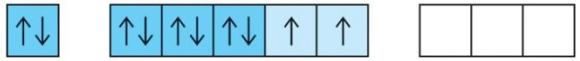
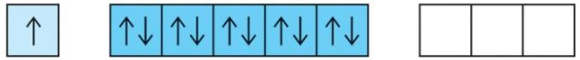
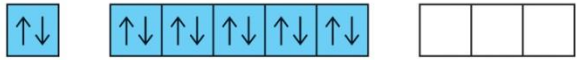
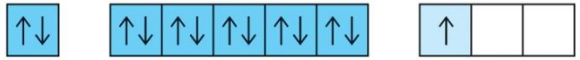
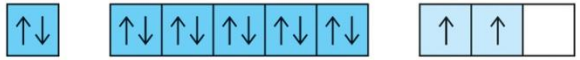
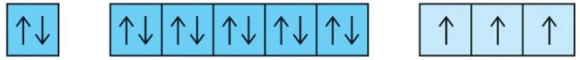
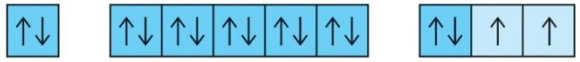
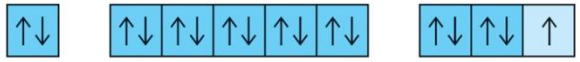
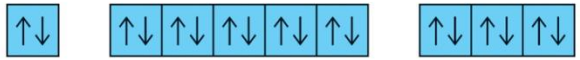
Table 8.3 Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 4.

Atomic Number	Element	Partial Orbital Diagram (4*s*, 3*d*, and 4*p* Sublevels Only)	Full Electron Configuration	Condensed Electron Configuration
28	Ni		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	[Ar] $4s^2 3d^8$
29	Cu		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	[Ar] $4s^1 3d^{10}$
30	Zn		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	[Ar] $4s^2 3d^{10}$
31	Ga		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$	[Ar] $4s^2 3d^{10} 4p^1$
32	Ge		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$	[Ar] $4s^2 3d^{10} 4p^2$
33	As		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$	[Ar] $4s^2 3d^{10} 4p^3$
34	Se		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$	[Ar] $4s^2 3d^{10} 4p^4$
35	Br		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$	[Ar] $4s^2 3d^{10} 4p^5$
36	Kr		$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$	[Ar] $4s^2 3d^{10} 4p^6$

*Colored type indicates the sublevel to which the last electron is added.

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Figure 8.5 A periodic table of partial ground-state electron configurations.

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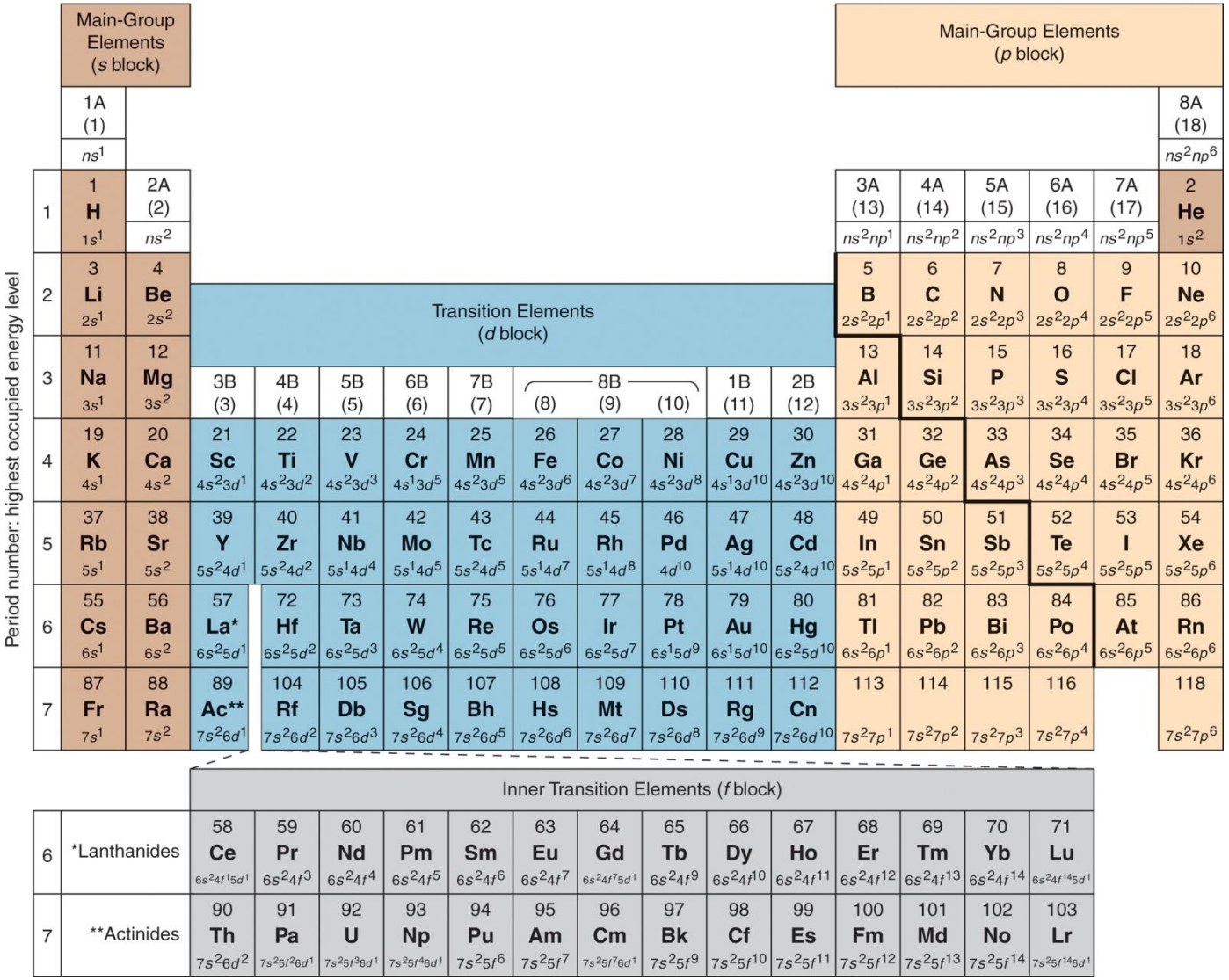

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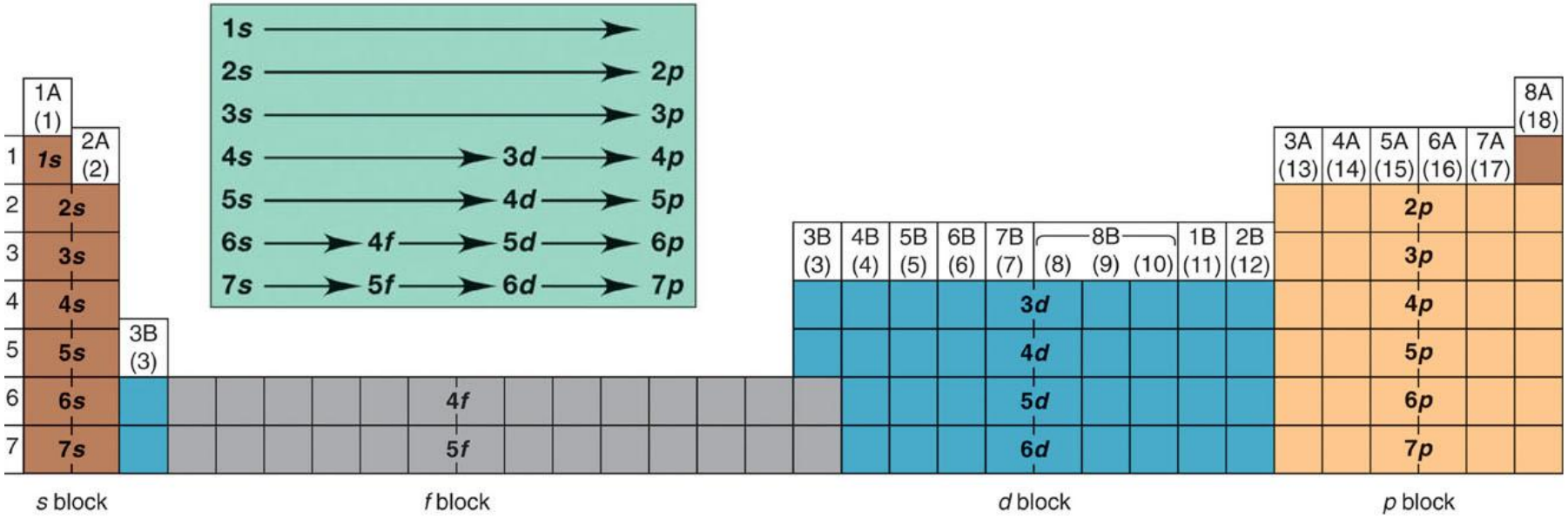
Figure 8.6 **Orbital filling and the periodic table.**



The order in which the orbitals are filled can be obtained directly from the periodic table.

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Aid to memorizing sublevel filling order.

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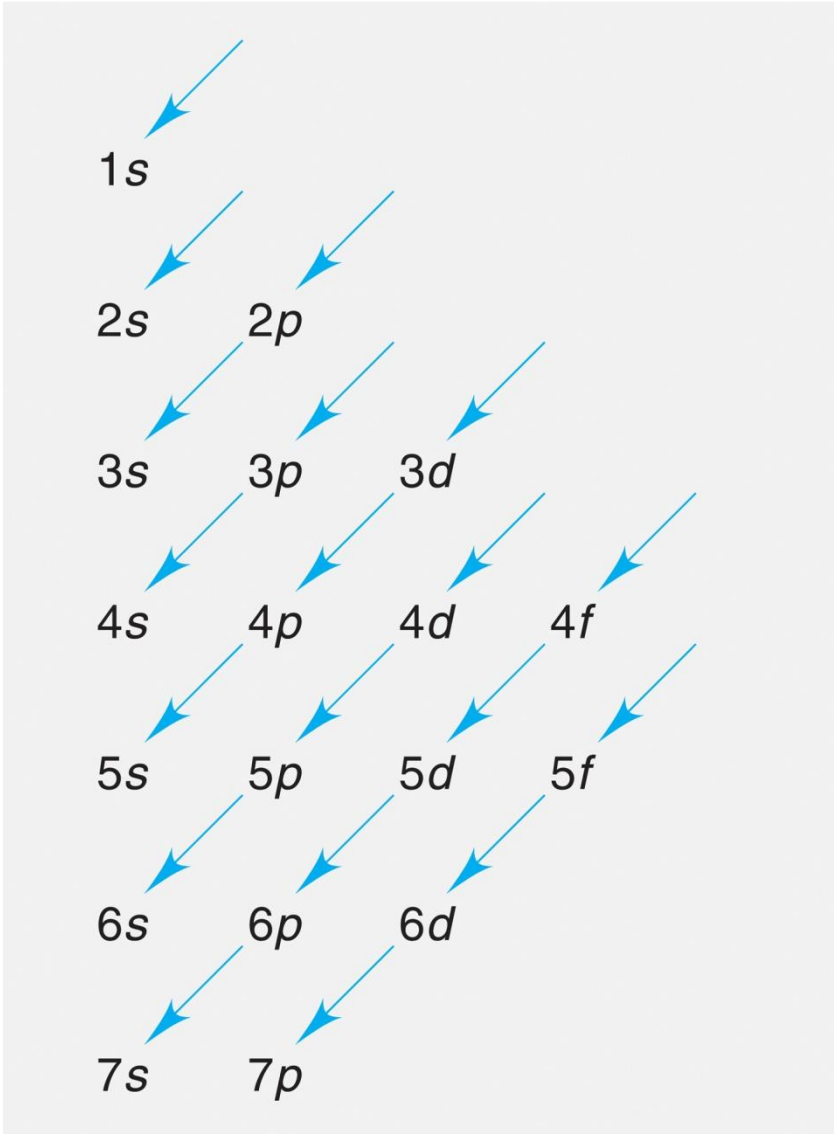

The *n* value is constant horizontally.
The *l* value is constant vertically.
n + *l* is constant diagonally.

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Categories of Electrons

Inner (core) electrons are those an atom has in common with the pervious noble gas and any ***completed*** transition series.

Outer electrons are those in the ***highest*** energy level (highest *n* value).

Valence electrons are those involved in forming compounds.

For **main group** elements, the valence electrons ***are*** the outer electrons.

For **transition elements**, the valence electrons include the outer electrons and any (*n*-1)*d* electrons.

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Sample Problem 8.2 Determining Electron Configurations

PROBLEM: Using the periodic table on the inside cover of the text (not Figure 8.5 or Table 8.3), give the full and condensed electron configurations, partial orbital diagrams showing valence electrons only, and number of inner electrons for the following elements:

(a) potassium (K; $Z = 19$)

(b) technetium (Tc; $Z = 43$)

(c) lead (Pb; $Z = 82$)

PLAN: The atomic number gives the number of electrons, and the periodic table shows the order for filling orbitals. The partial orbital diagram includes all electrons added after the previous noble gas except those in filled inner sublevels.

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Sample Problem 8.2

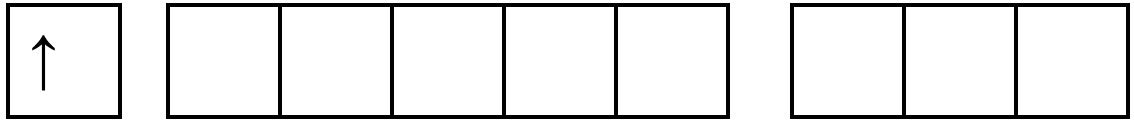
SOLUTION:

(a) For K (Z = 19)

full configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

condensed configuration [Ar] $4s^1$

partial orbital diagram



There are 18 inner electrons.

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Sample Problem 8.2

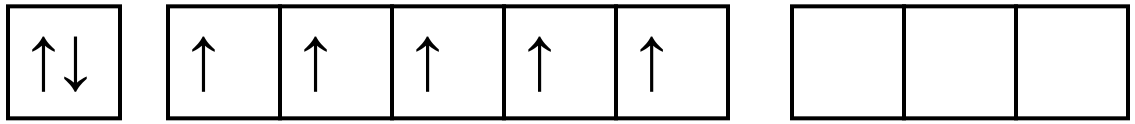
SOLUTION:

(b) For Tc (Z = 43)

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

condensed configuration $[Kr]5s^2 4d^5$

partial orbital diagram



There are 36 inner electrons.

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Sample Problem 8.2

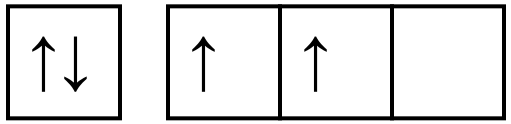
SOLUTION:

(a) For Pb (Z = 82)

full configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^2$

condensed configuration [Xe] $6s^2 4f^{14} 5d^{10} 6p^2$

partial orbital diagram



There are 78 inner electrons.

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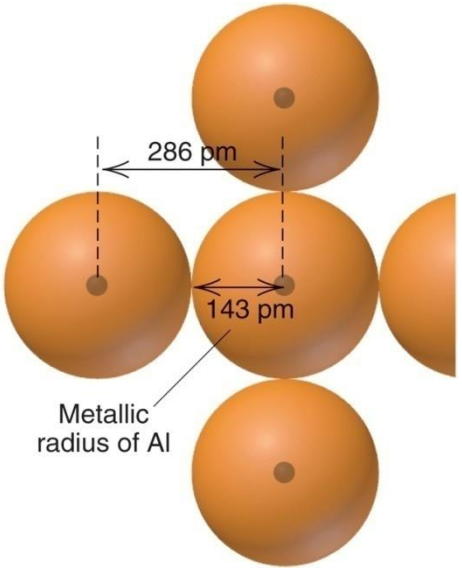
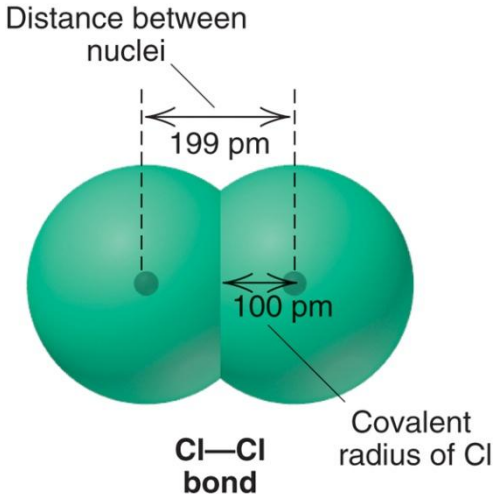
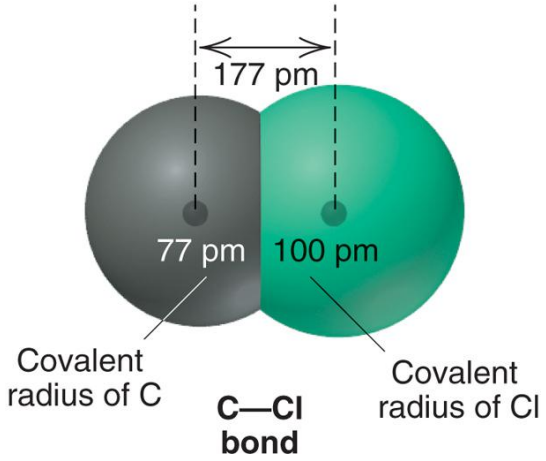
Figure 8.7 Defining atomic size.



A. The metallic radius of aluminum.



B. The covalent radius of chlorine.



C. Known covalent radii and distances between nuclei can be used to find unknown radii.

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Trends in Atomic Size

Atomic size ***increases*** as the principal quantum number *n* ***increases***.

As *n* increases, the probability that the outer electrons will be farther from the nucleus increases.

Atomic size ***decreases*** as the effective nuclear charge Z_{eff} ***increases***.

As Z_{eff} increases, the outer electrons are pulled closer to the nucleus.

For ***main group elements***:
atomic size ***increases*** down a group in the periodic table and ***decreases*** across a period.

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Figure 8.8

Atomic radii of the main-group and transition elements.

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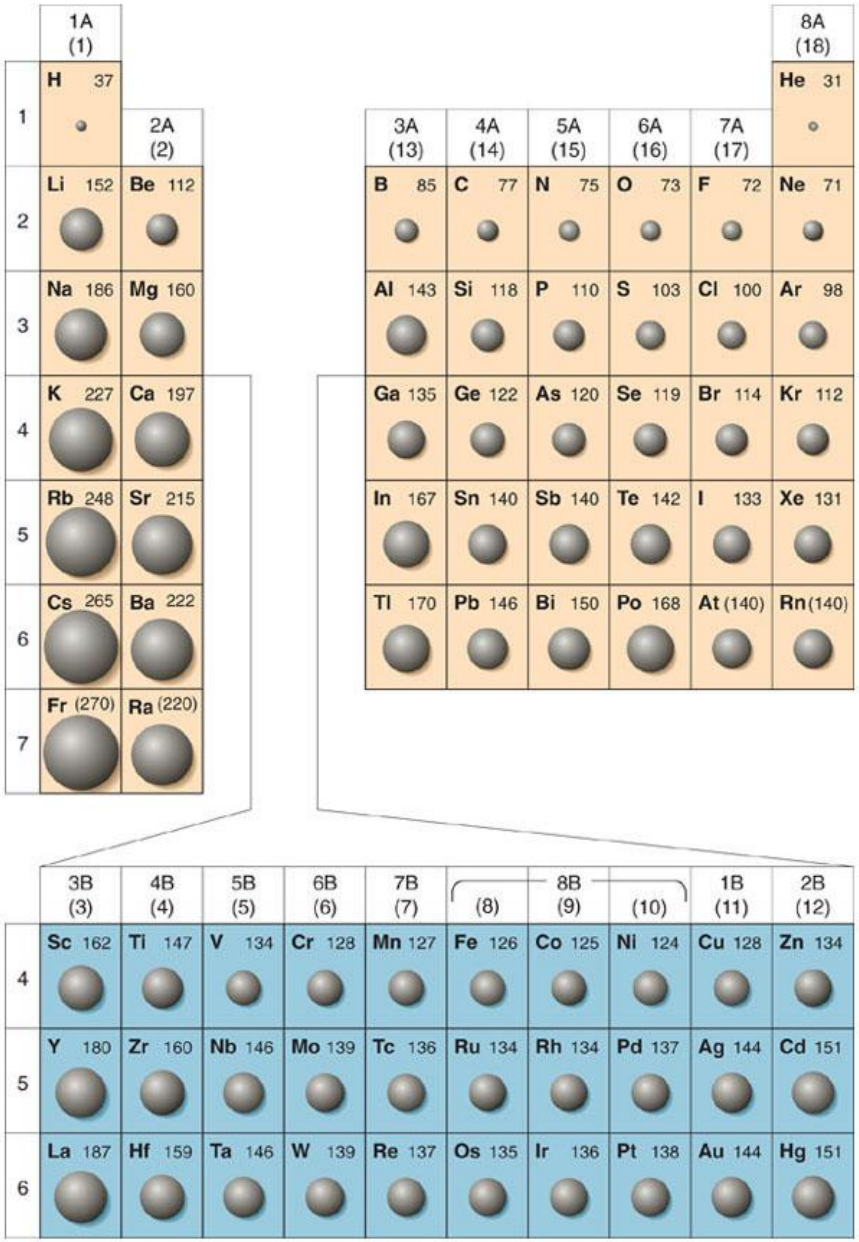

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Figure 8.9 Periodicity of atomic radius.

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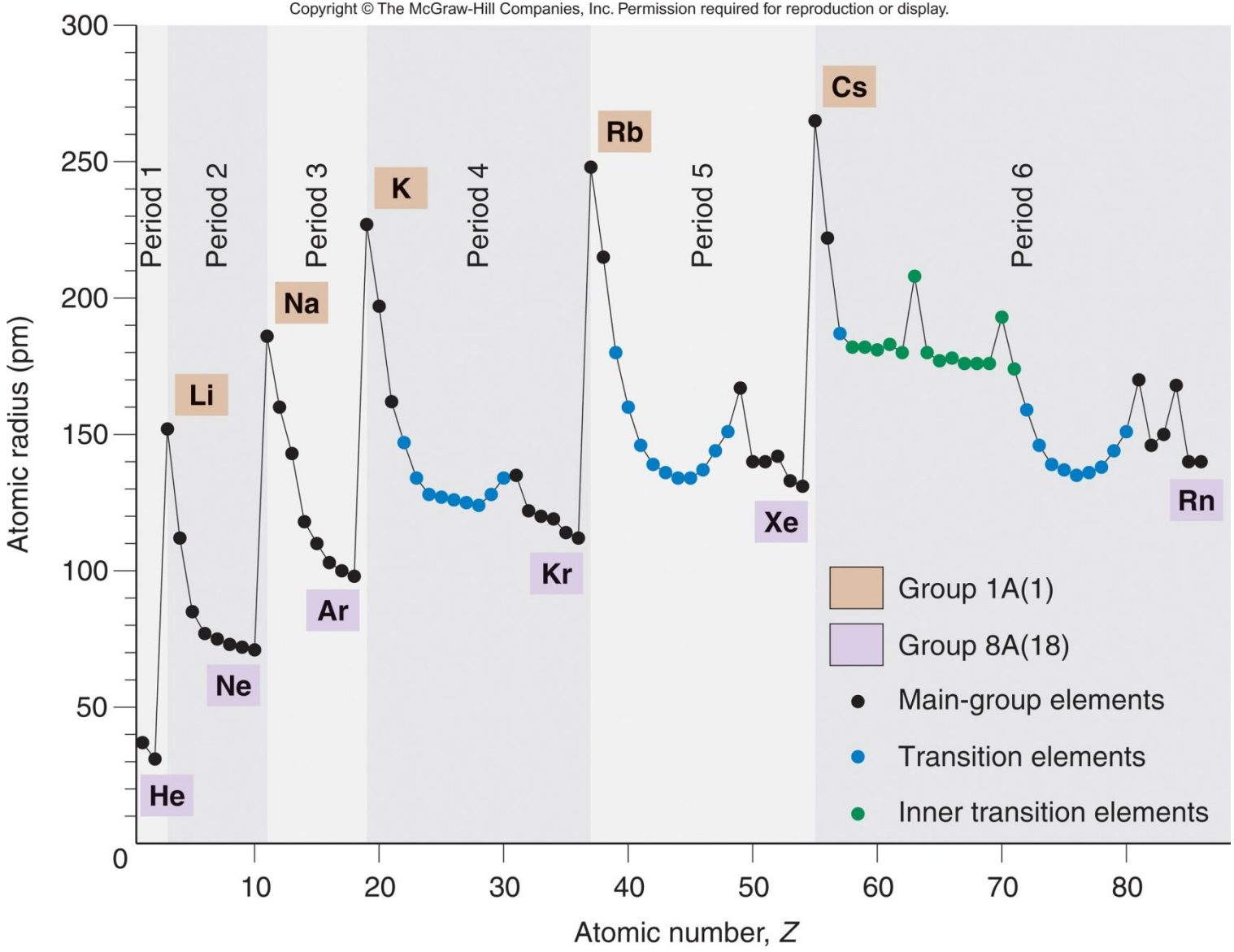

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Sample Problem 8.3 Ranking Elements by Atomic Size

PROBLEM: Using only the periodic table (not Figure 8.8), rank each set of main-group elements in order of *decreasing* atomic size:

(a) Ca, Mg, Sr

(b) K, Ga, Ca

(c) Br, Rb, Kr

(d) Sr, Ca, Rb

PLAN: Locate each element on the periodic table. Main-group elements increase in size down a group and decrease in size across the period.

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Sample Problem 8.3

SOLUTION:

(a) Sr > Ca > Mg

Ca, Mg, and Sr are in Group 2A. Size increases down the group.

(b) K > Ca > Ga

K, Ga, and Ca are all in Period 4. Size decreases across the period.

(c) Rb > Br > Kr

Rb is the largest because it has one more energy level than the other elements. Kr is smaller than Br because Kr is further to the right in the same period.

(d) Rb > Sr > Ca

Ca is the smallest because it has one fewer energy level. Sr is smaller than Rb because it is smaller to the right in the same period.

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Trends in Ionization Energy

Ionization energy (IE) is the energy required for the ***complete removal*** of 1 mol of electrons from 1 mol of gaseous atoms or ions.

Atoms with a ***low IE*** tend to form ***cations***.
Atoms with a ***high IE*** tend to form ***anions*** (except the noble gases).

Ionization energy tends to ***decrease*** down a group and ***increase*** across a period.

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Figure 8.10 Periodicity of first ionization energy (IE_1).

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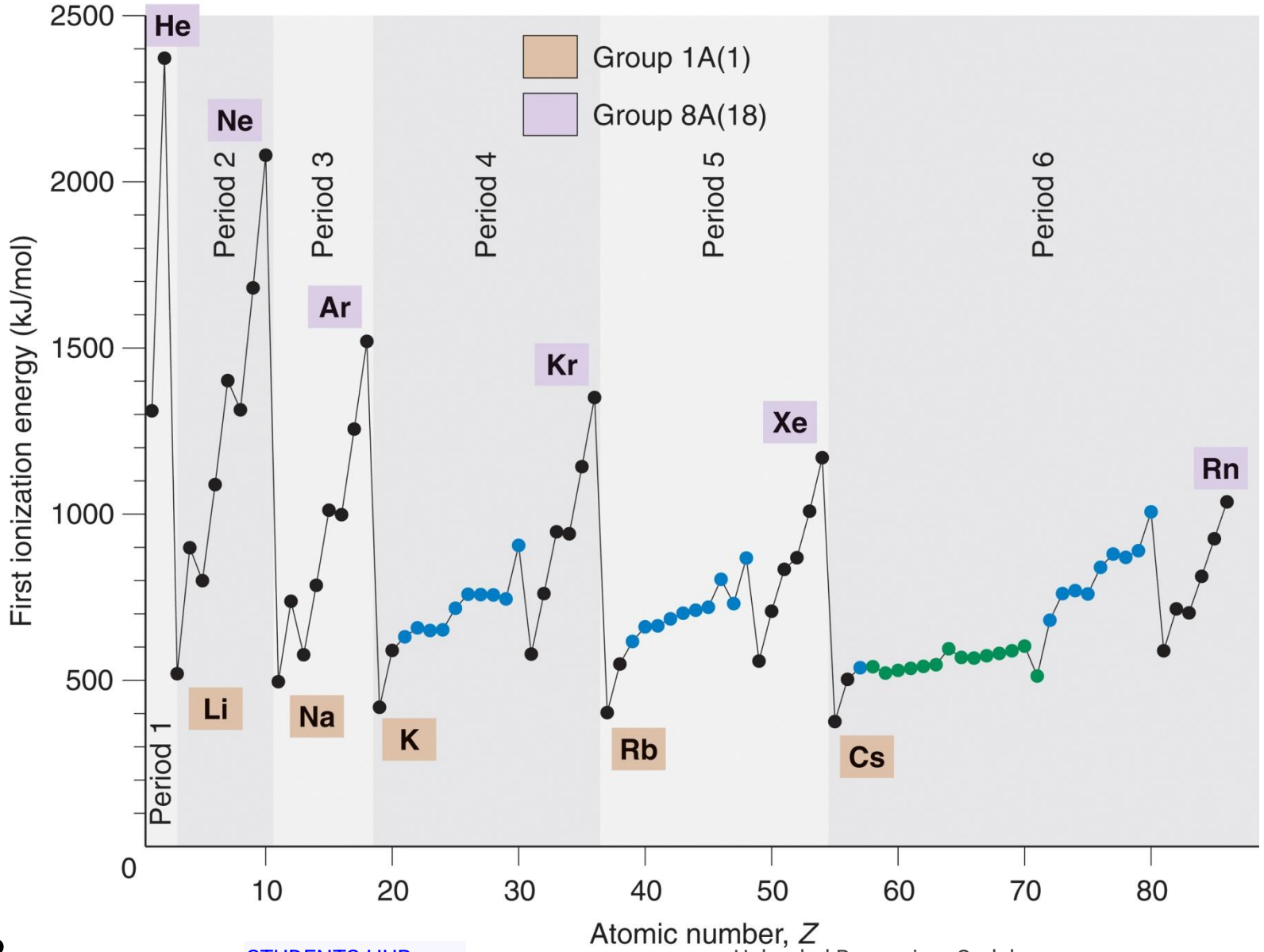

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Figure 8.11 First ionization energies of the main-group elements.

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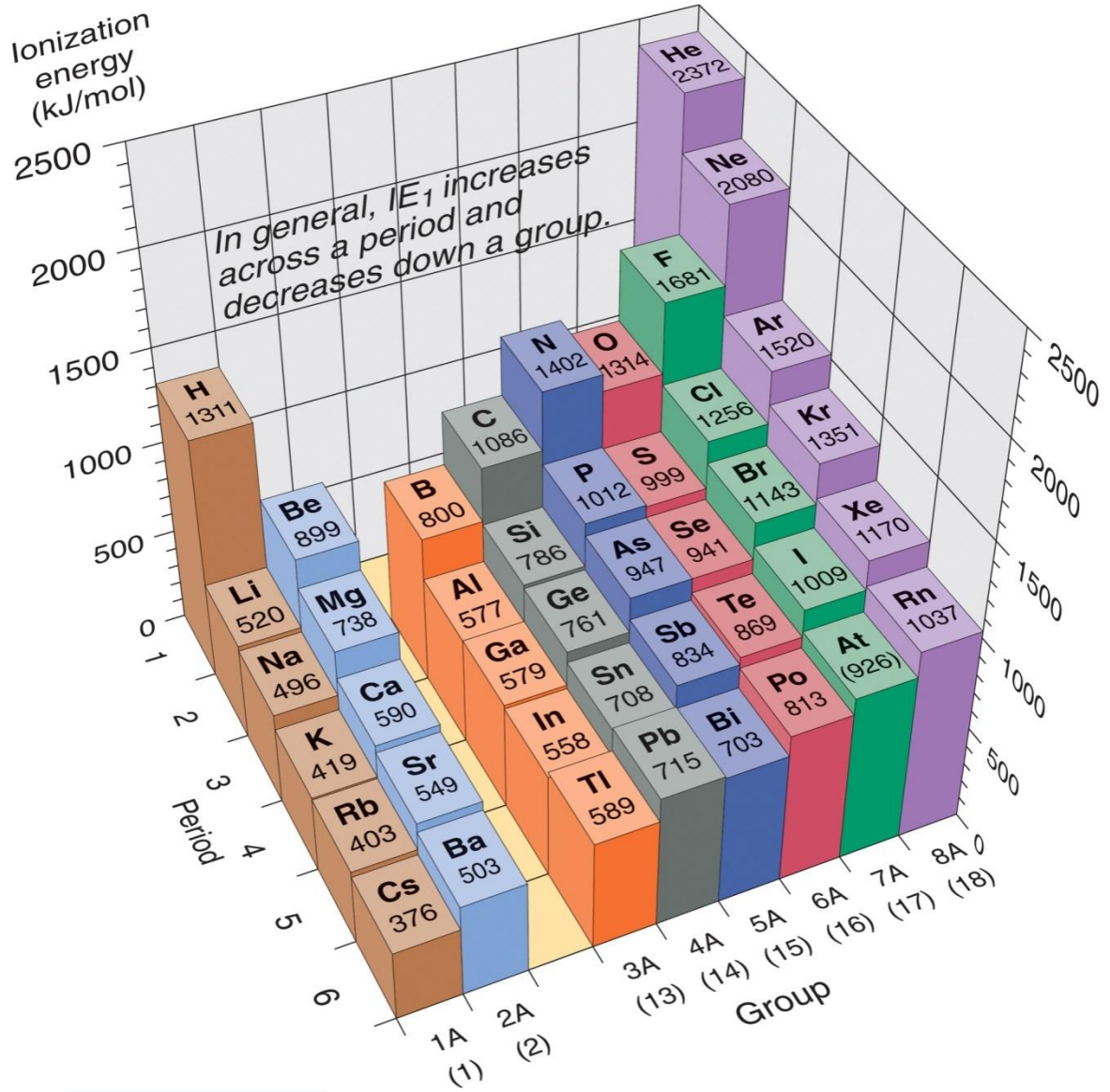

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Sample Problem 8.4

Ranking Elements by First Ionization Energy

PROBLEM: Using the periodic table only, rank the elements in each of the following sets in order of *decreasing* IE_1:

(a) Kr, He, Ar

(b) Sb, Te, Sn

(c) K, Ca, Rb

(d) I, Xe, Cs

PLAN: Find each element on the periodic table. IE_1 generally decreases down a group and increases across a period.

SOLUTION:

(a) He > Ar > Kr

Kr, He, and Ar are in Group 8A. IE_1 decreases down the group.

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Sample Problem 8.4

SOLUTION:

(b) Te > Sb > Sn

Sb, Te, and Sn are in Period 5. IE_1 increases across a period.

(c) Ca > K > Rb

K has a higher IE_1 than Rb because K is higher up in Group 1A. Ca has a higher IE_1 than K because Ca is further to the right in Period 4.

(d) Xe > I > Cs

Xe has a higher IE_1 than I because Xe is further to the right in the same period. Cs has a lower IE_1 than I because it is further to the left in a higher period.

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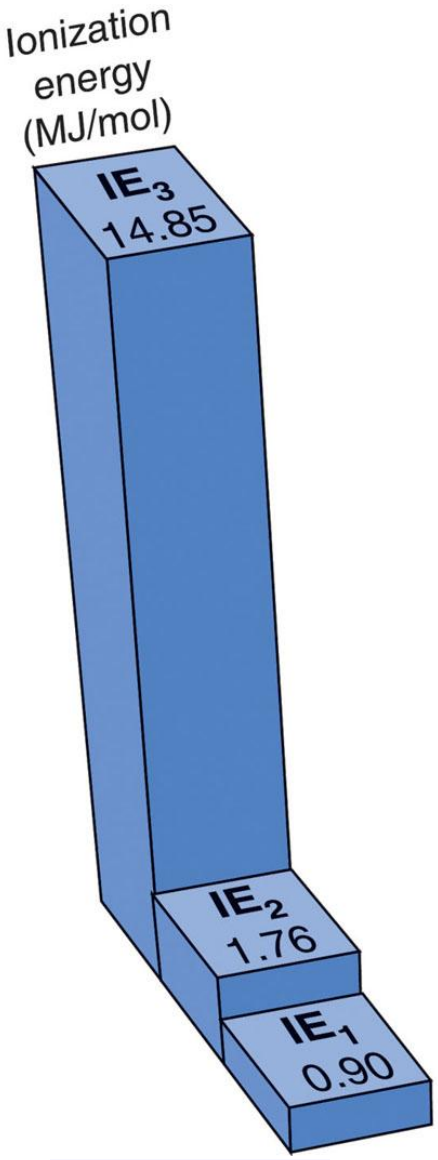
Figure 8.12 The first three ionization energies of beryllium.



Beryllium has 2 valence electrons, so IE_3 is much larger than IE_2.

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Table 8.4 Successive Ionization Energies of the Elements Lithium Through Sodium

Z	Element	Number of Valence Electrons	Ionization Energy (MJ/mol)*									
			IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
3	Li	1	0.52	7.30	11.81							
4	Be	2	0.90	1.76	14.85	21.01			CORE ELECTRONS			
5	B	3	0.80	2.43	3.66	25.02	32.82					
6	C	4	1.09	2.35	4.62	6.22	37.83	47.28				
7	N	5	1.40	2.86	4.58	7.48	9.44	53.27	64.36			
8	O	6	1.31	3.39	5.30	7.47	10.98	13.33	71.33	84.08		
9	F	7	1.68	3.37	6.05	8.41	11.02	15.16	17.87	92.04	106.43	
10	Ne	8	2.08	3.95	6.12	9.37	12.18	15.24	20.00	23.07	115.38	131.43
11	Na	1	0.50	4.56	6.91	9.54	13.35	16.61	20.11	25.49	28.93	141.37

*MJ/mol, or megajoules per mole = 10^3 kJ/mol.

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Sample Problem 8.5 — Identifying an Element from Its Ionization Energies

PROBLEM: Name the Period 3 element with the following ionization energies (in kJ/mol) and write its electron configuration:

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
1012	1903	2910	4956	6278	22,230

PLAN: Look for a large increase in IE, which occurs after all valence electrons have been removed.

SOLUTION:

The largest increase occurs after IE_5, that is, after the 5th valence electron has been removed. The Period 3 element with 5 valence electrons is **phosphorus (P; Z = 15**).

The complete electron configuration is **$1s^2 2s^2 2p^6 3s^2 3p^3$**.

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Trends in Electron Affinity

Electron Affinity (EA) is the energy change that occurs when 1 mol of electrons is ***added*** to 1 mol of gaseous atoms or ions.

Atoms with a ***low EA*** tend to form ***cations***.
Atoms with a ***high EA*** tend to form ***anions***.

The trends in electron affinity are not as regular as those for atomic size or IE.

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Figure 8.13 Electron affinities of the main-group elements (in kJ/mol).

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1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
H −72.8							He (0.0)
Li −59.6	Be ≤0	B −26.7	C −122	N +7	O −141	F −328	Ne (+29)
Na −52.9	Mg ≤0	Al −42.5	Si −134	P −72.0	S −200	Cl −349	Ar (+35)
K −48.4	Ca −2.37	Ga −28.9	Ge −119	As −78.2	Se −195	Br −325	Kr (+39)
Rb −46.9	Sr −5.03	In −28.9	Sn −107	Sb −103	Te −190	I −295	Xe (+41)
Cs −45.5	Ba −13.95	Tl −19.3	Pb −35.1	Bi −91.3	Po −183	At −270	Rn (+41)

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Behavior Patterns for IE and EA

Reactive nonmetals have high IEs and highly negative EAs.
These elements attract electrons strongly and tend to form negative ions in ionic compounds.

Reactive metals have low IEs and slightly negative EAs.
These elements lose electrons easily and tend to form positive ions in ionic compounds.

Noble gases have very high IEs and slightly positive EAs.
These elements tend to neither lose nor gain electrons.

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Figure 8.14 Trends in three atomic properties.

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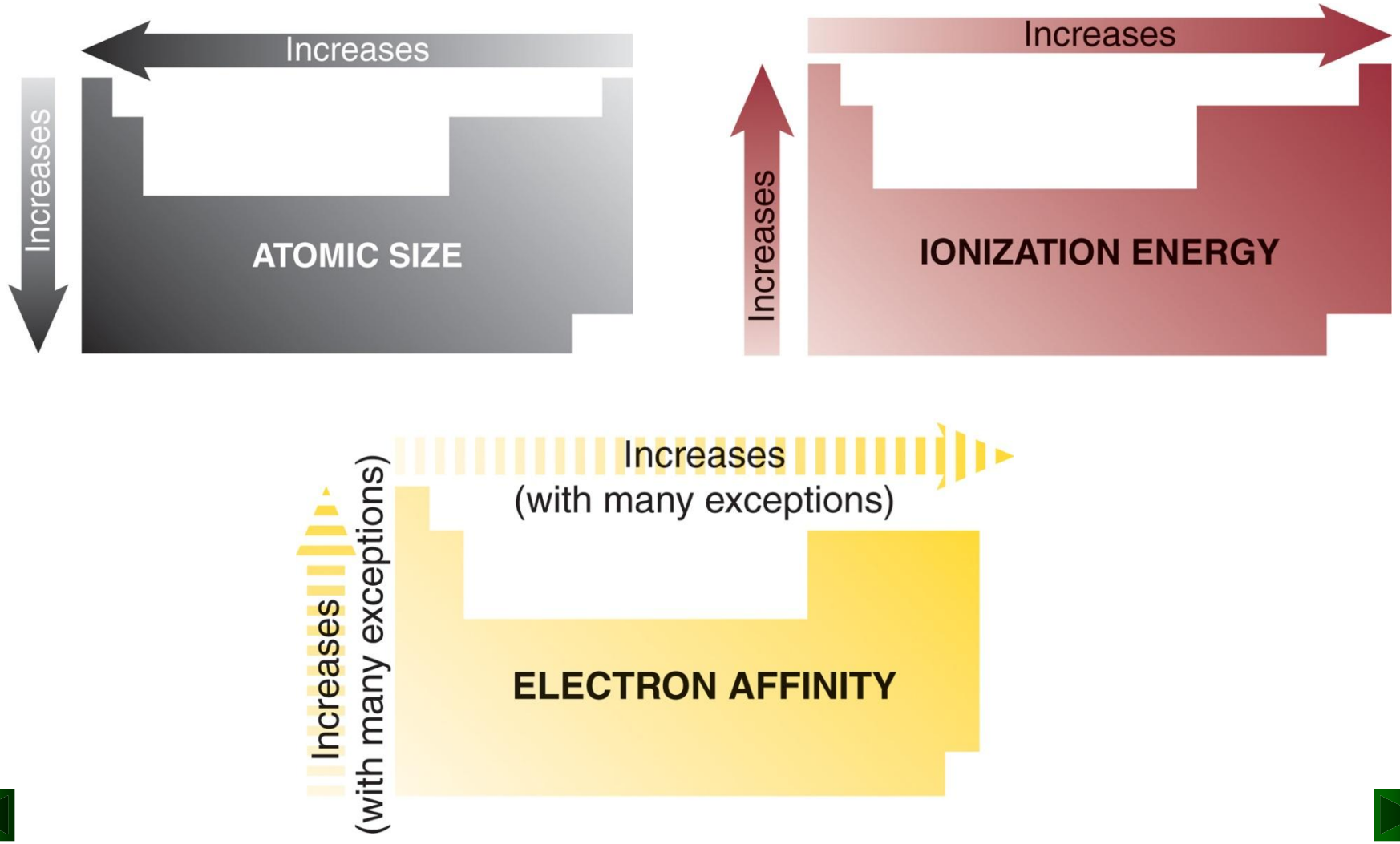

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Metallic Behavior

- Metals are typically shiny solids with moderate to high melting points.
- Metals are good conductors of heat and electricity, and can easily be shaped.
- Metals tend to lose electrons and form cations, i.e., they are easily ***oxidized***.
- Metals are generally ***strong reducing agents***.
- Most metals form ionic oxides, which are ***basic*** in aqueous solution.

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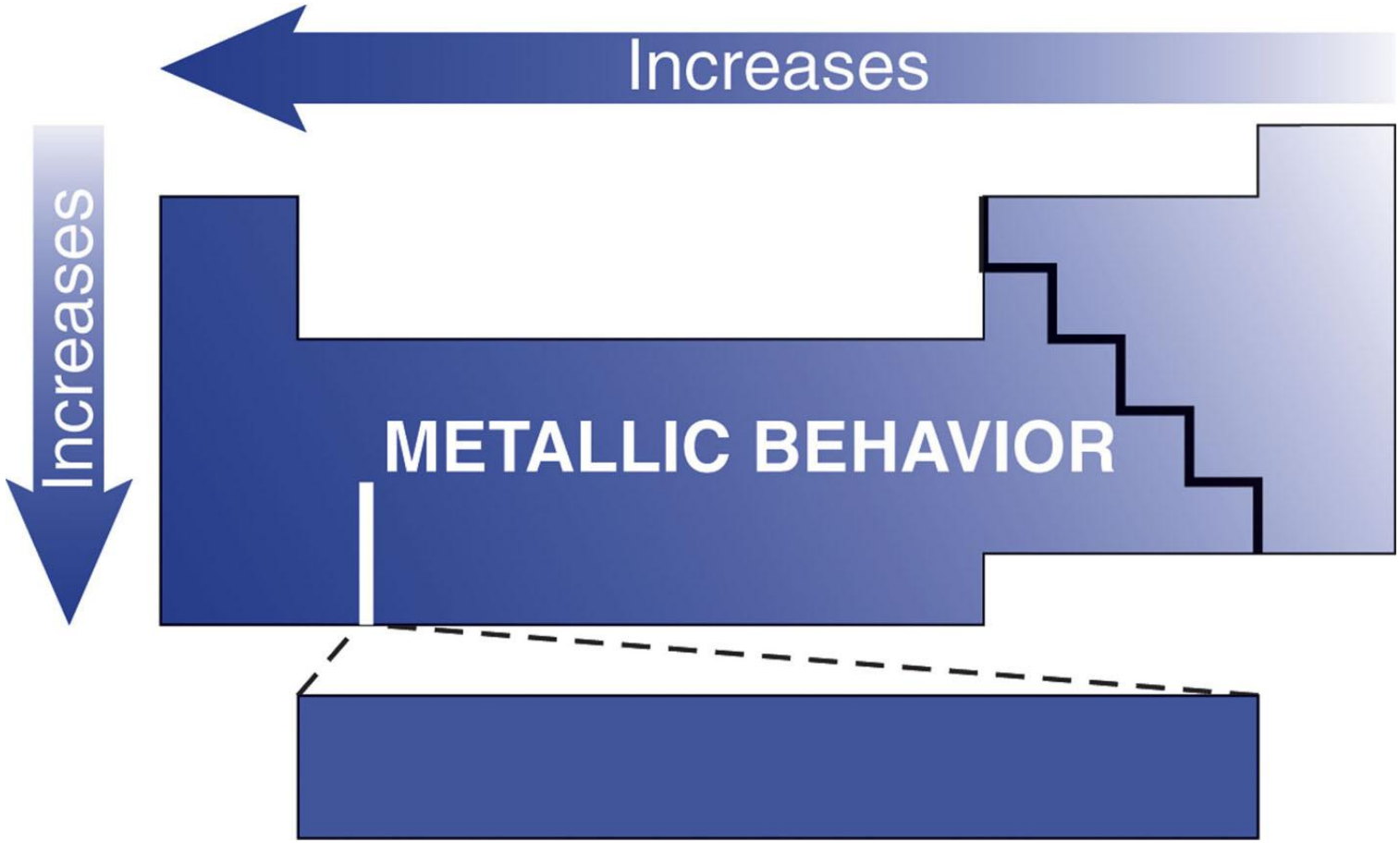
Figure 8.15 Trends in metallic behavior.



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Acid-Base Behavior of Oxides

Main-group metals form ***ionic oxides***, which are ***basic*** in aqueous solution.

Main-group nonmetals form ***covalent oxides***, which are ***acidic*** in aqueous solution.

Some metals and metalloids form ***amphoteric oxides***, which can act as acids or bases in water:

$$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$

$$Al_2O_3(s) + 2NaOH(aq) \rightarrow 2NaAl(OH)_4(aq)$$

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Figure 8.16 Acid-base behavior of some element oxides.

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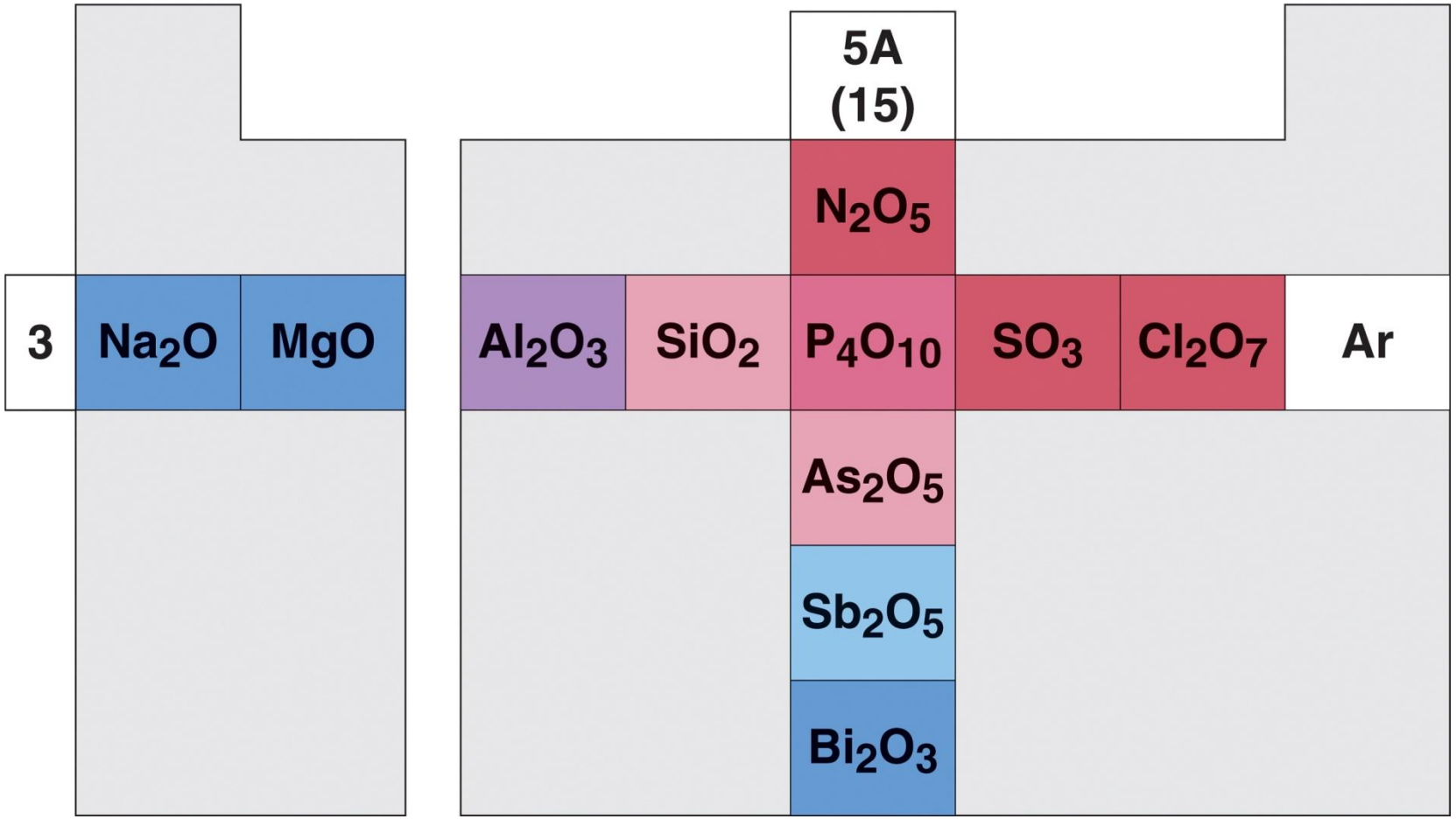

Oxides become more basic down a group and more acidic across a period.

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Electron configurations of Monatomic Ions

Elements at either end of a period gain or lose electrons to attain a filled outer level. The resulting ion will have a ***noble gas electron configuration*** and is said to be ***isoelectronic*** with that noble gas.

$Na(1s^2 2s^2 2p^6 \mathbf{3s^1}) \rightarrow \mathbf{e^-} + Na^+([He]2s^2 2p^6)$

[isoelectronic with Ne]

$Br([Ar]4s^2 3d^{10} \mathbf{4p^5}) + \mathbf{e^-} \rightarrow Br^- ([Ar]4s^2 3d^{10} 4p^6)$

[isoelectronic with Kr]

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Figure 8.17 **Main-group elements whose ions have noble gas electron configurations.**

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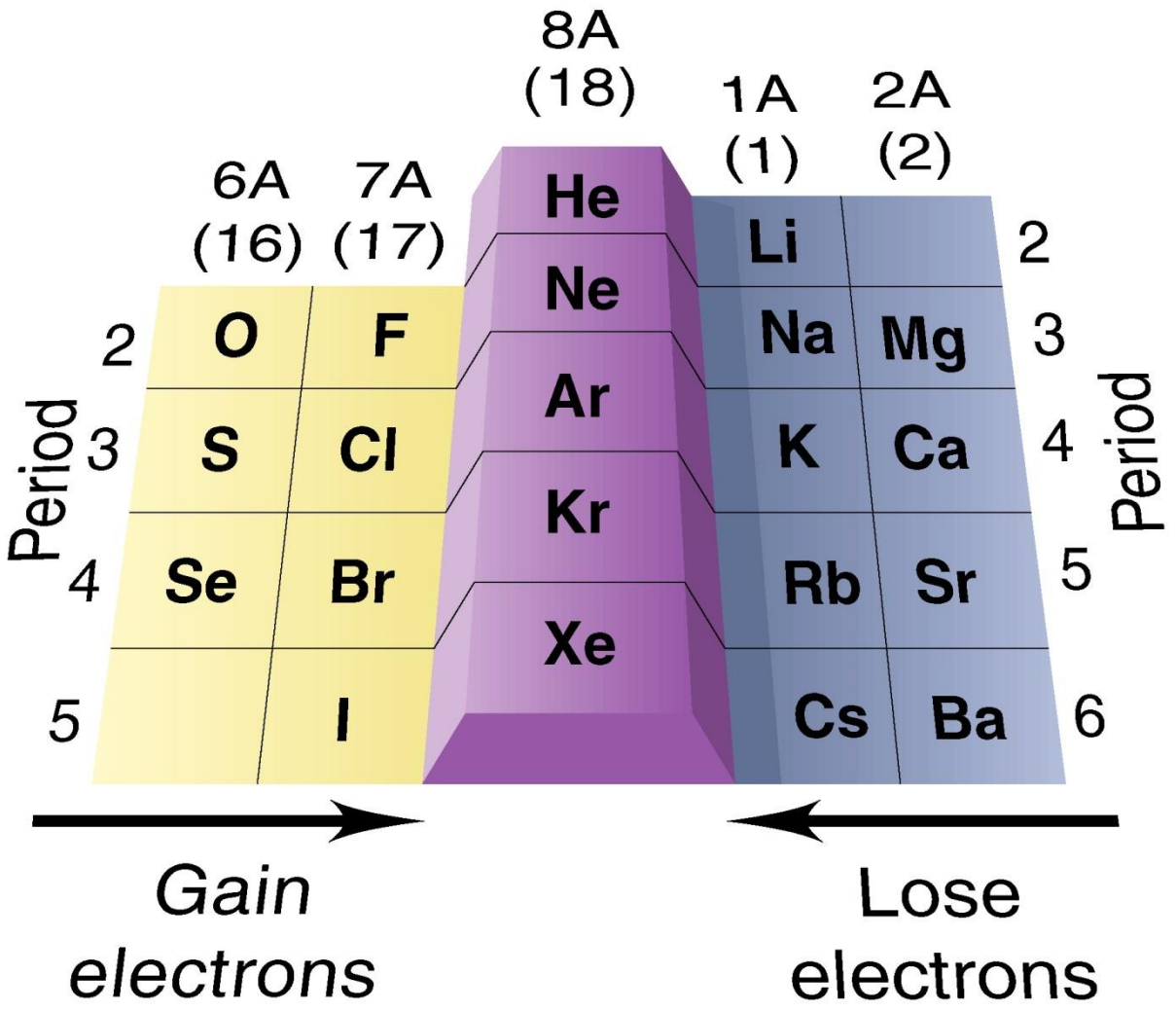

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Electron Configurations of Monatomic Ions

A ***pseudo-noble gas configuration*** is attained when a metal atom empties its highest energy level.
The ion attains the stability of empty *ns* and *np* sublevels and a filled (*n*-1)*d* sublevel.

$$Sn([Kr]\mathbf{5s^2}4d^{10}\mathbf{5p^2}) \rightarrow \mathbf{4e^-} + Sn^{4+}([Kr]4d^{10})$$

A metal may lose only the *np* electrons to attain an ***inert pair configuration***.
The ion attains the stability of a filled *ns* and (*n*-1)*d* sublevels.

$$Sn([Kr]5s^24d^{10}\mathbf{5p^2}) \rightarrow \mathbf{2e^-} + Sn^{2+}([Kr]5s^24d^{10})$$

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Sample Problem 8.6 Writing Electron Configurations of Main-Group Ions

PROBLEM: Using condensed electron configurations, write reactions for the formation of the common ions of the following elements:

(a) Iodine (Z = 53) **(b)** Potassium (Z = 19) **(c)** Indium (Z = 49)

PLAN: Identify the position of each element on the periodic table and recall that:

- Ions of elements in Groups 1A(1), 2A(2), 6A(16), and 7A(17) are usually isoelectronic with the nearest noble gas.
- Metals in Groups 3A(13) to 5A(15) can lose the *ns* and *np* electrons or just the *np* electrons.

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Sample Problem 8.6

SOLUTION:

(a) Iodine (Z = 53) is in Group 7A(17) and will gain one electron to be isoelectronic with Xe: $I\ ([Kr]\ 5s^2 4d^{10} 5p^5) + e^- \longrightarrow I^-\ ([Kr]\ 5s^2 4d^{10} 5p^6)$

(b) Potassium (Z = 19) is in Group 1A(1) and will lose one electron to be isoelectronic with Ar: $K\ ([Ar]\ 4s^1) \longrightarrow K^+\ ([Ar]) + e^-$

(c) Indium (Z = 49) is in Group 3A(13) and can lose either one electron or three electrons: $In\ ([Kr]\ 5s^2 4d^{10} 5p^1) \longrightarrow In^+\ ([Kr]\ 5s^2 4d^{10}) + e^-$

$In\ ([Kr]\ 5s^2 4d^{10} 5p^1) \longrightarrow In^{3+}([Kr]\ 4d^{10}) + 3e^-$

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Figure 8.18 The crossover of sublevel energies in Period 4.

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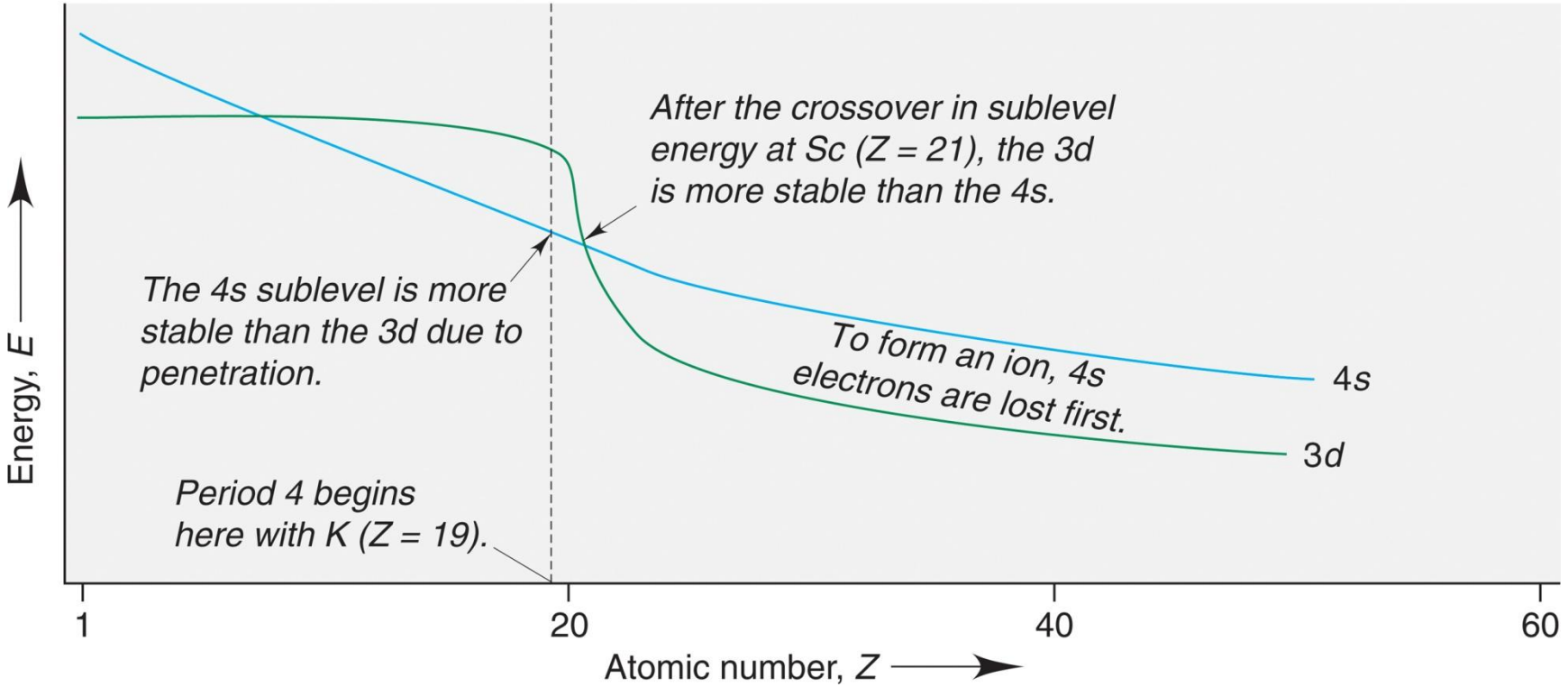

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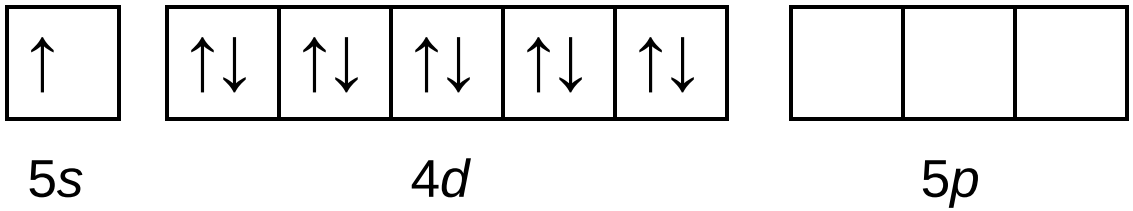
Magnetic Properties of Transition Metal Ions

A species with one or more unpaired electrons exhibits ***paramagnetism*** – it is attracted by a magnetic field.

Ag (Z = 47)



A species with all its electrons paired exhibits ***diamagnetism*** – it is not attracted (and is slightly repelled) by a magnetic field.

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Figure 8.19 Measuring the magnetic behavior of a sample.

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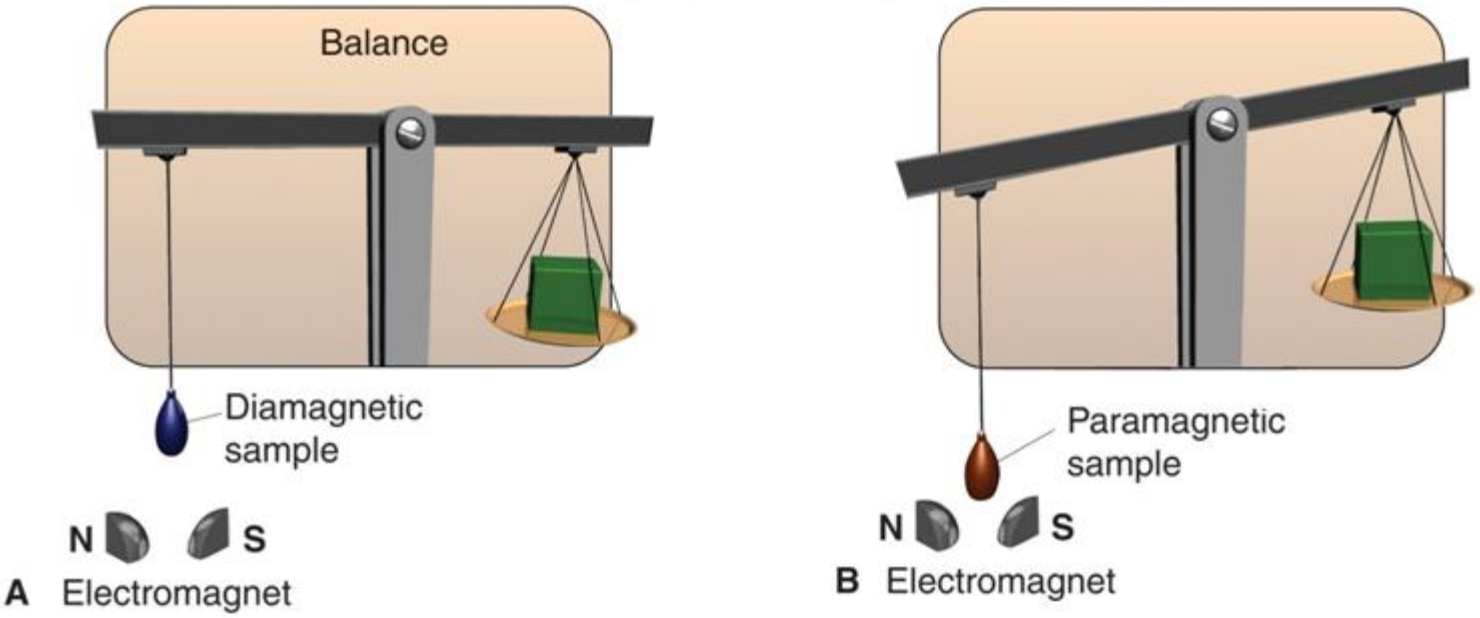

The apparent mass of a diamagnetic substance is unaffected by the magnetic field.

The apparent mass of a paramagnetic substance increases as it is attracted by the magnetic field.

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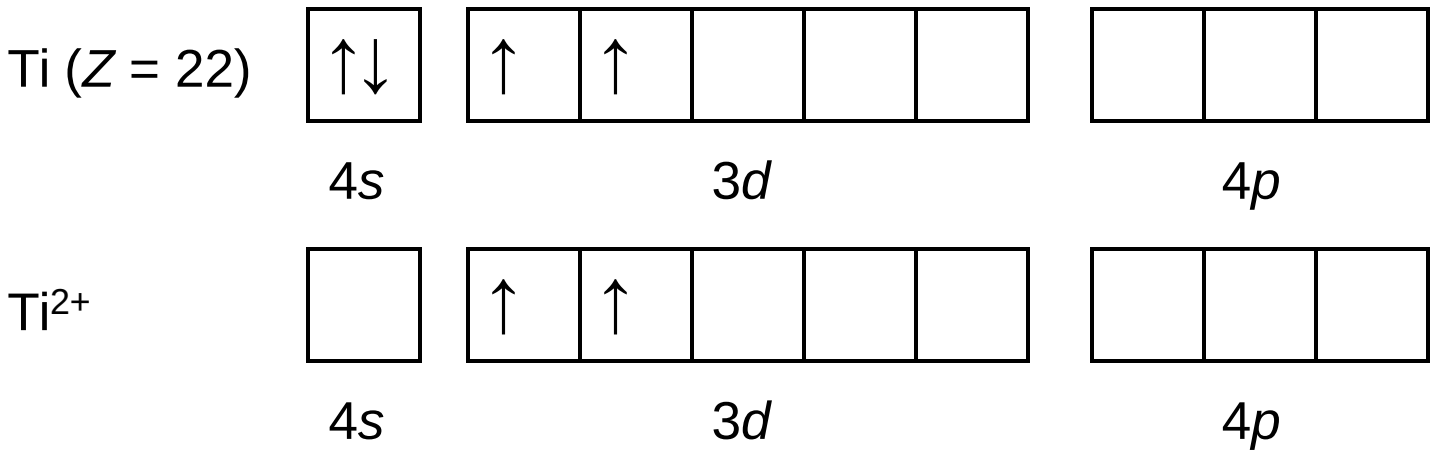
Magnetic Properties of Transition Metal ions

Magnetic behavior can provide evidence for the electron configuration of a given ion.



Ti^{2+} has 2 unpaired electrons and is paramagnetic, providing evidence that the 4*s* electrons are lost before the 3*d* electrons.

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Sample Problem 8.7

Writing Electron Configurations and Predicting Magnetic Behavior of Transition Metal Ions

PROBLEM: Use condensed electron configurations to write the reaction for the formation of each transition metal ion, and predict whether the ion is paramagnetic or diamagnetic.

(a) $Mn^{2+}(Z = 25)$ **(b)** $Cr^{3+}(Z = 24)$ **(c)** $Hg^{2+}(Z = 80)$

PLAN: Write the condensed electron configuration for each atom, recalling the irregularity for Cr. Remove electrons, beginning with the *ns* electrons, and determine if there are any unpaired electrons.

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Sample Problem 8.7

SOLUTION:

(a) $Mn^{2+}(Z = 25)$ Mn ([Ar] $4s^2 3d^5$) $\longrightarrow$ Mn^{2+} ([Ar] $3d^5$) + $2e^-$

Since there are 5 *d* electrons they are all unpaired. Mn^{2+} is **paramagnetic**.

(b) $Cr^{3+}(Z = 24)$ Cr ([Ar] $4s^1 3d^5$) $\longrightarrow$ Cr^{3+} ([Ar] $3d^3$) + $3e^-$

Since there are 3 *d* electrons they are all unpaired. Cr^{3+} is **paramagnetic.**

(c) $Hg^{2+}(Z = 80)$ Hg ([Xe] $6s^2 4f^{14} 5d^{10}$) $\longrightarrow$ Hg^{2+} ([Xe] $4f^{14} 5d^{10}$) + $2e^-$

The 4*f* and the 5*s* sublevels are filled, so there are no unpaired electrons. Hg^{2+} is **diamagnetic**.

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Ionic Size vs. Atomic Size

Cations are ***smaller*** than their parent atoms while anions are ***larger***.

Ionic radius ***increases*** down a group as *n* increases.

Cation size ***decreases*** as charge ***increases***.

An ***isoelectronic series*** is a series of ions that have the same electron configuration. Within the series, ion size ***decreases*** with increasing nuclear charge.

3- > 2- > 1- > 1+ > 2+ > 3+

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Figure 8.20 **Ionic radius.**

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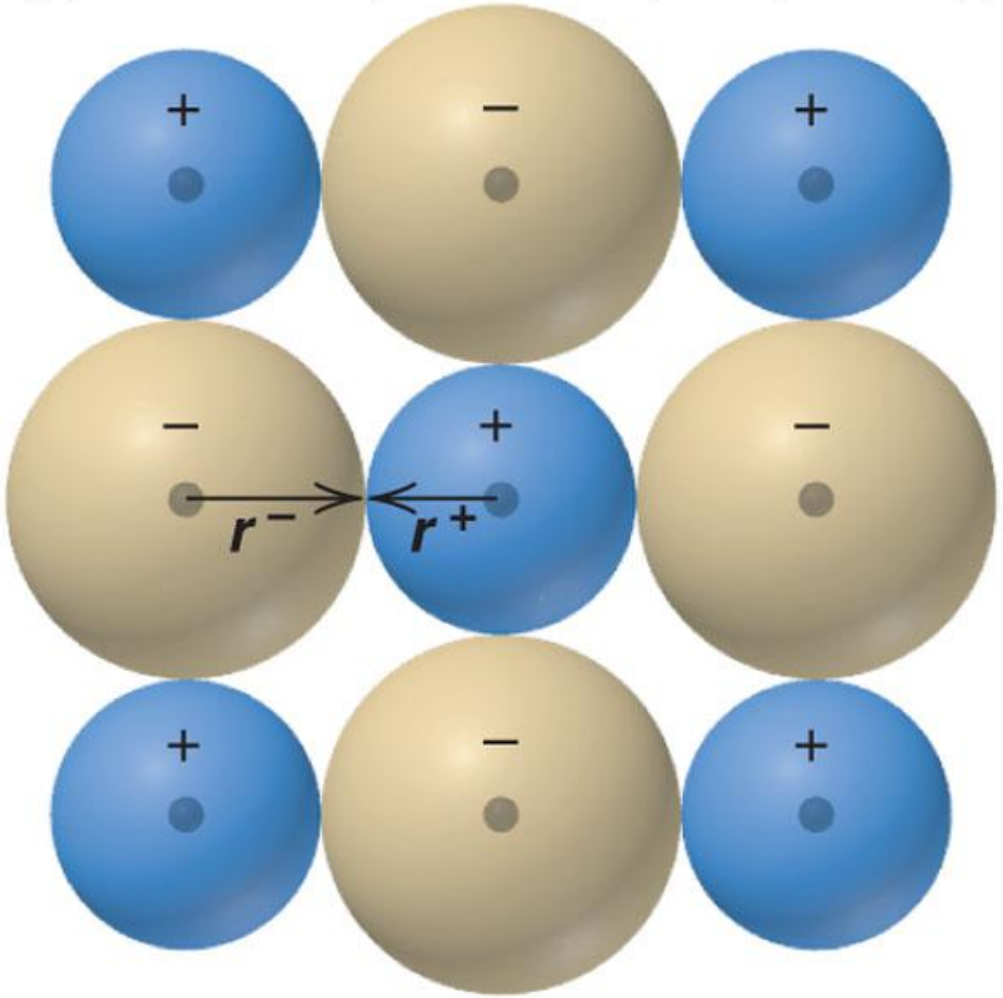

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Figure 8.21 Ionic vs. atomic radii.

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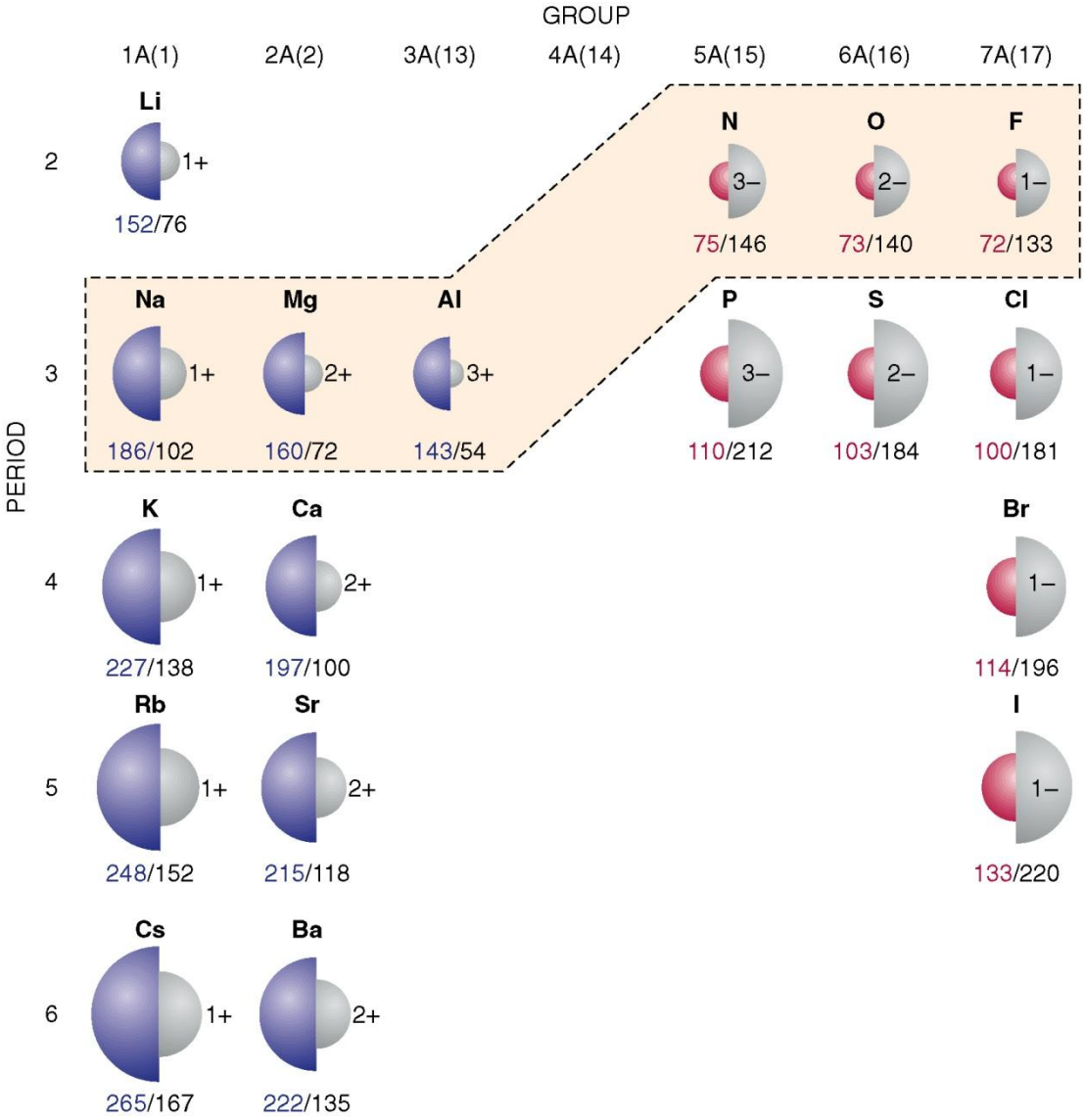

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Sample Problem 8.8 Ranking Ions by Size

PROBLEM: Rank each set of ions in order of *decreasing* size, and explain your ranking:

(a) Ca^{2+}, Sr^{2+}, Mg^{2+} **(b)** K^{+}, S^{2-}, Cl^{-} **(c)** Au^{+}, Au^{3+}

PLAN: Find the position of each element on the periodic table and apply the trends for ionic size.

SOLUTION:

(a) $\mathbf{Sr^{2+} > Ca^{2+} > Mg^{2+}}$

All these ions are from Group 2A, so size increases down the group.

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Sample Problem 8.8

SOLUTION:

(b) $S^{2-} > Cl^{-} > K^{+}$

These ions are isoelectronic, so size decreases as nuclear charge increases.

(c) $Au^{+} > Au^{3+}$

Cation size decreases as charge increases.

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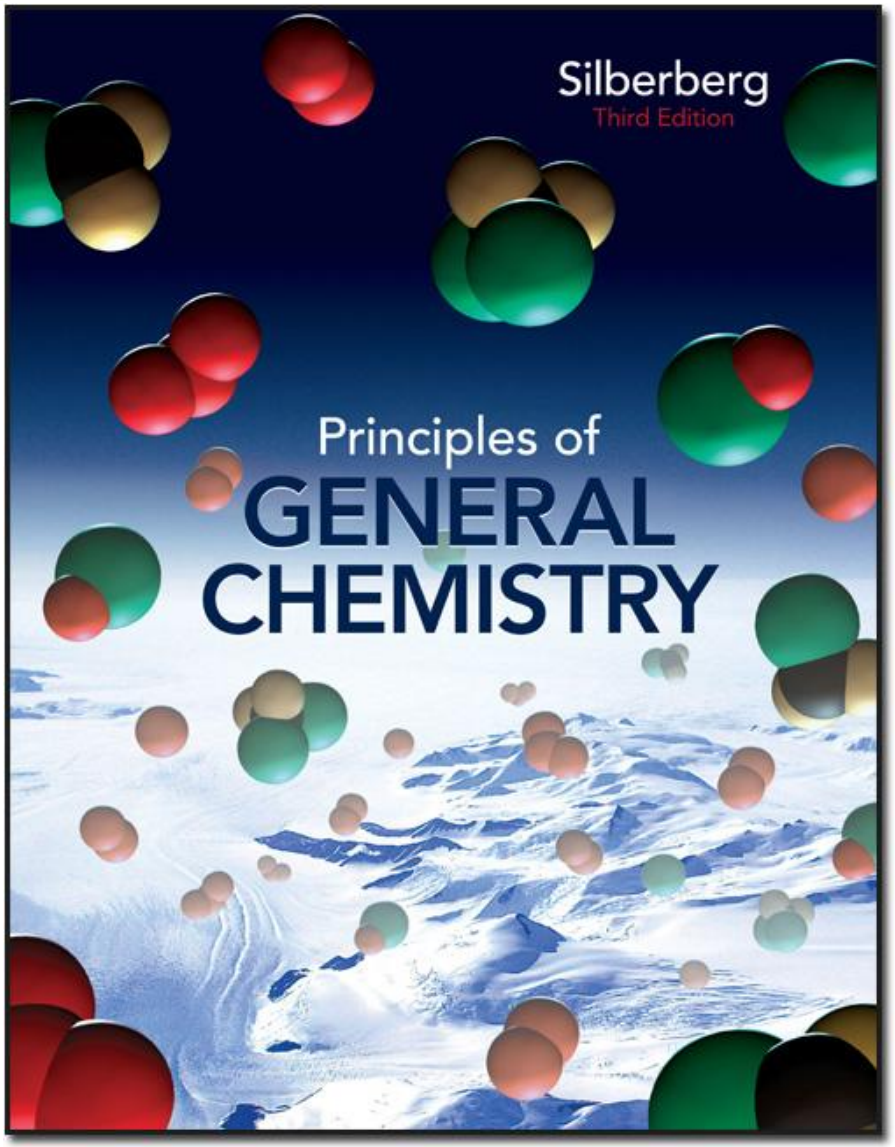

Chapter 09

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 9

Models of Chemical Bonding

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Models of Chemical Bonding

9.1 Atomic Properties and Chemical Bonds

9.2 The Ionic Bonding Model

9.3 The Covalent Bonding Model

9.4 Bond Energy and Chemical Change

**9.5 Between the Extremes:
Electronegativity and Bond Polarity**

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Figure 9.1 A comparison of metals and nonmetals.

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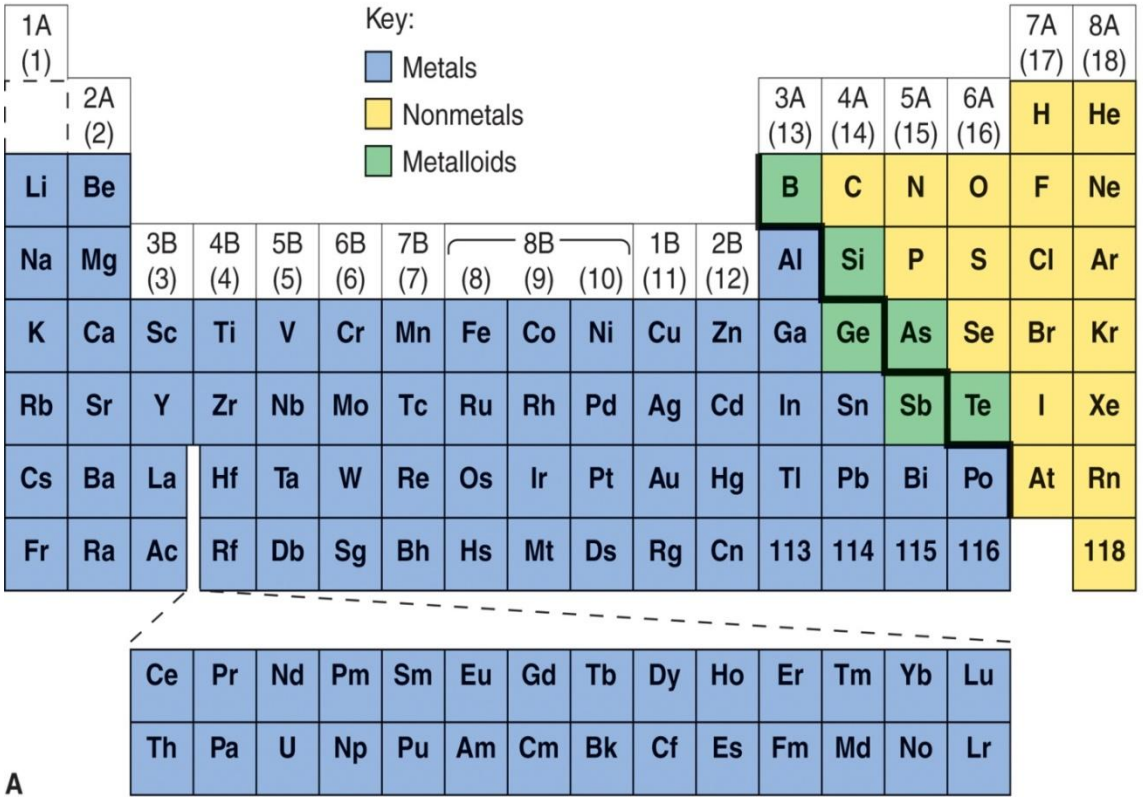

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PROPERTY	METAL ATOM	NONMETAL ATOM
Atomic size	Larger	Smaller
Z_{eff}	Lower	Higher
IE	Lower	Higher
EA	Less negative	More negative

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Types of Chemical Bonding

Ionic bonding involves the ***transfer*** of electrons and is usually observed when a ***metal*** bonds to a ***nonmetal***.

Covalent bonding involves the ***sharing*** of electrons and is usually observed when a ***nonmetal*** bonds to a ***nonmetal***.

Metallic bonding involves ***electron pooling*** and occurs when a ***metal*** bonds to another ***metal***.

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Figure 9.2 Three models of chemical bonding.

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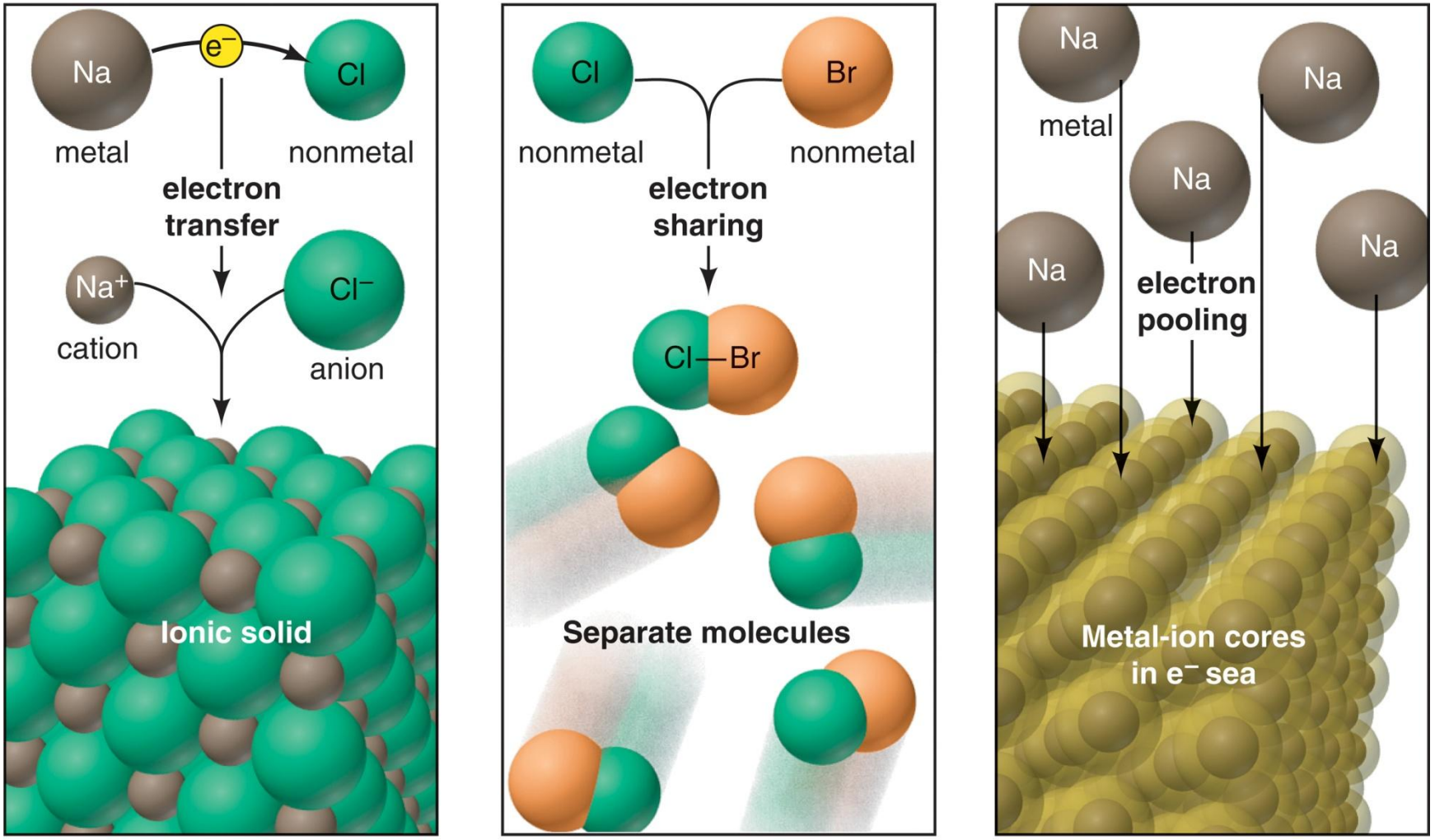

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Figure 9.3 **Gradations in bond type among Period 3 (*black type*) and Group 4A (*red type*) elements.**

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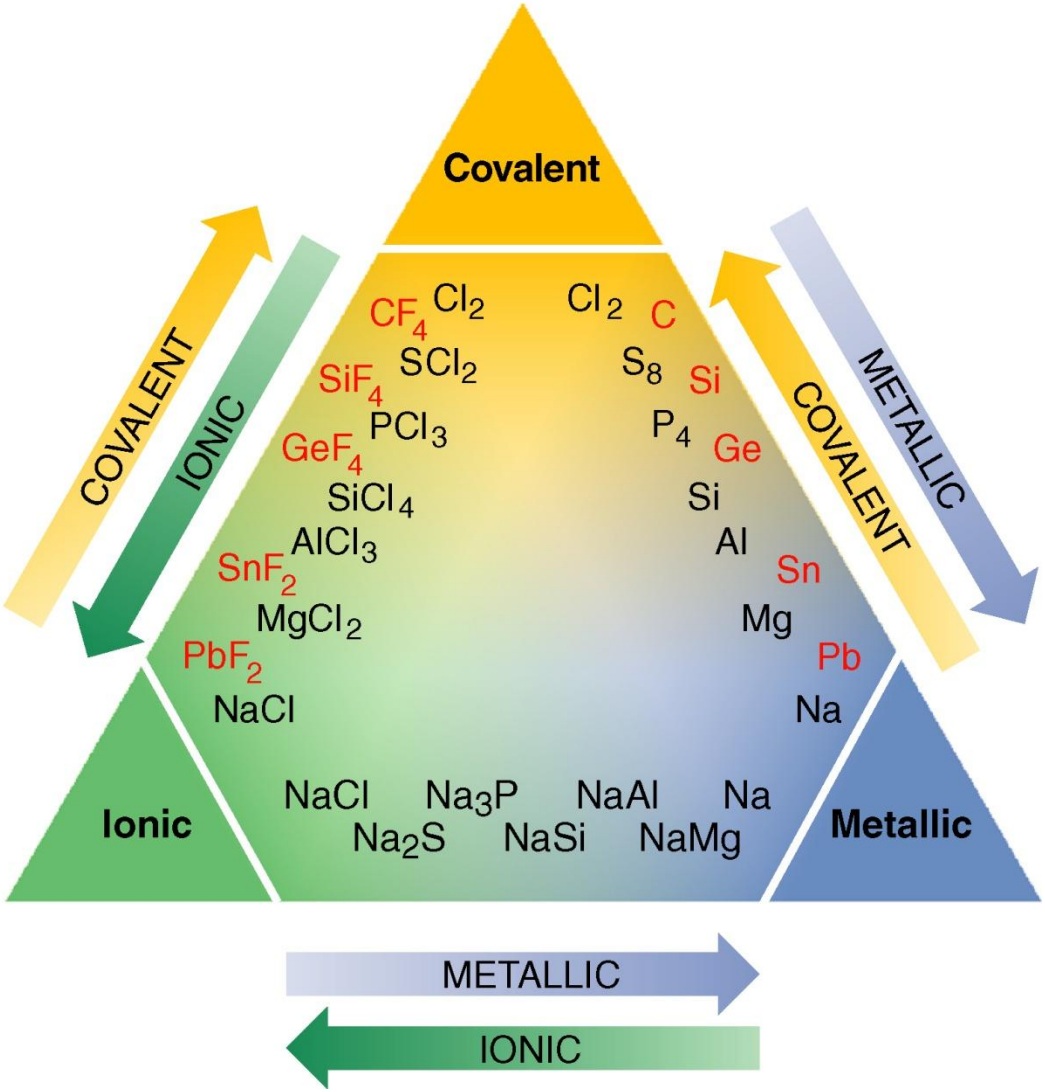

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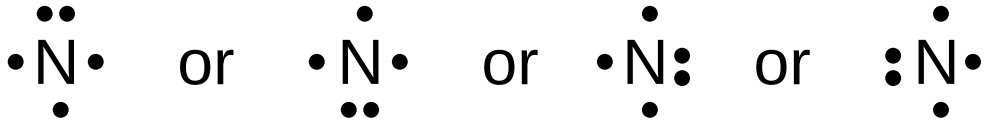
Lewis Electron-Dot Symbols

To draw the Lewis symbol for any main-group element:

- Note the A-group number, which gives the number of valence electrons.
- Place one dot at a time on each of the four sides of the element symbol.
- Keep adding dots, pairing them, until all are used up.

Example:

Nitrogen, N, is in Group 5A and therefore has 5 valence electrons.



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Lewis Symbols and Bonding

For a ***metal***, the ***total*** number of dots in the Lewis symbol is the number of electrons the atom loses to form a cation.

For a ***nonmetal***, the number of unpaired dots equals

- the number of electrons the atom ***gains*** to form an anion
- or the number it ***shares*** to form covalent bonds.

The ***octet rule*** states that when atoms bond, they lose, gain, or share electrons to attain a ***filled outer level of 8 electrons*** (or 2, for H and Li).

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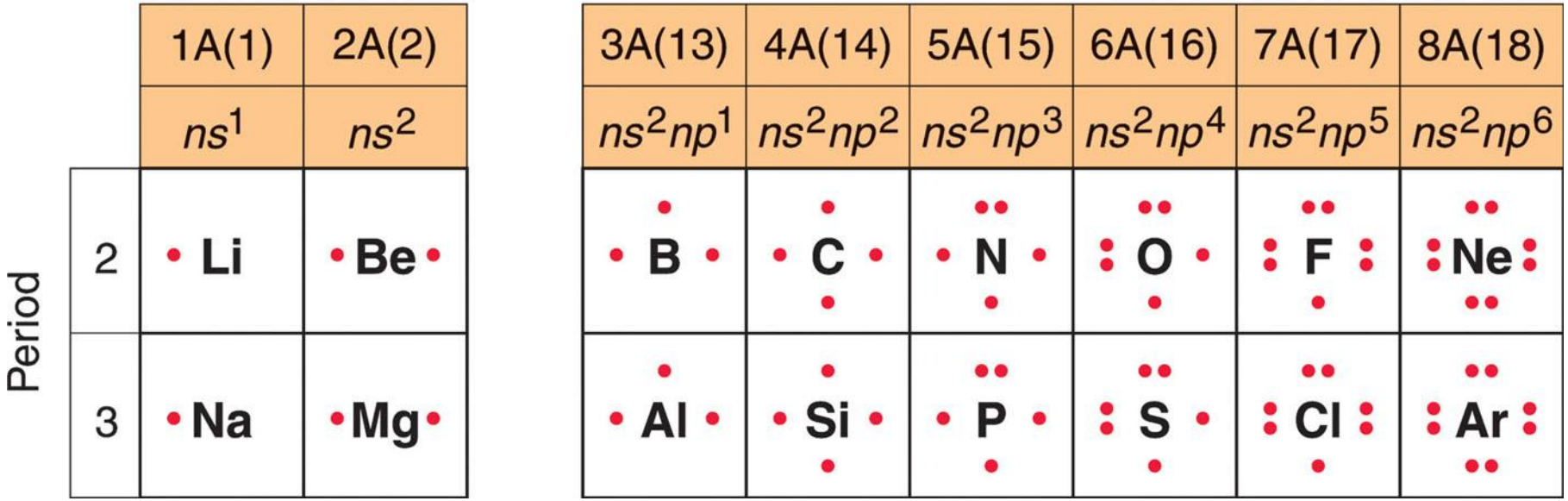
Figure 9.4

Lewis electron-dot symbols for elements in Periods 2 and 3.



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The Ionic Bonding Model

An ionic bond is formed when a metal ***transfers*** electrons to a nonmetal to form ***ions***, which attract each other to give a solid compound.

The total number of electrons lost by the metal atom(s) equals the total number of electrons gained by the nonmetal atoms.

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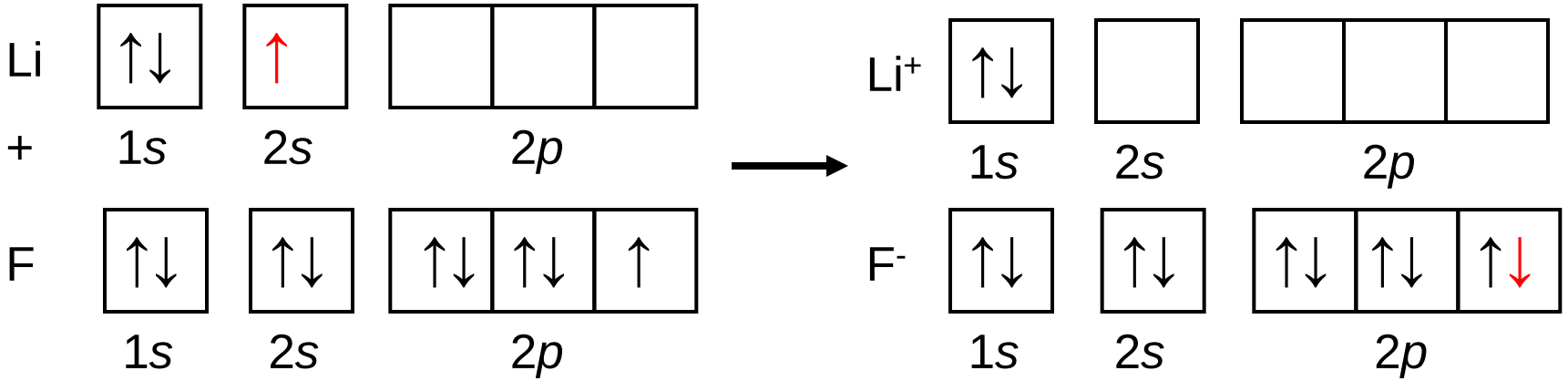
Figure 9.5 Three ways to depict electron transfer in the formation of Li^+ and F^-.

Electron configurations Li $1s^2 2s^1$ + F $1s^2 2p^5$ ⟶ Li^+ $1s^2$ + F^- $1s^2 2s^2 2p^6$

Orbital diagrams



Lewis electron-dot symbols

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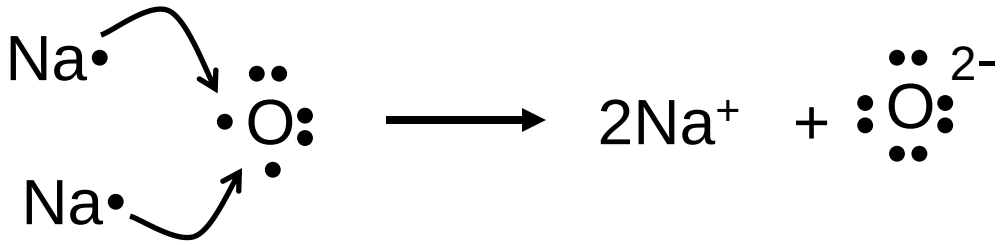
Sample Problem 9.1 Depicting Ion Formation

PROBLEM: Use partial orbital diagrams and Lewis symbols to depict the formation of Na^+ and O^{2-} ions from the atoms, and determine the formula of the compound formed.

PLAN: Draw orbital diagrams and Lewis symbols for Na and O atoms. To attain filled outer levels, Na loses one electron and O gains two. Two Na atoms are needed for each O atom so that the number of electrons lost equals the number of electrons gained.

SOLUTION:



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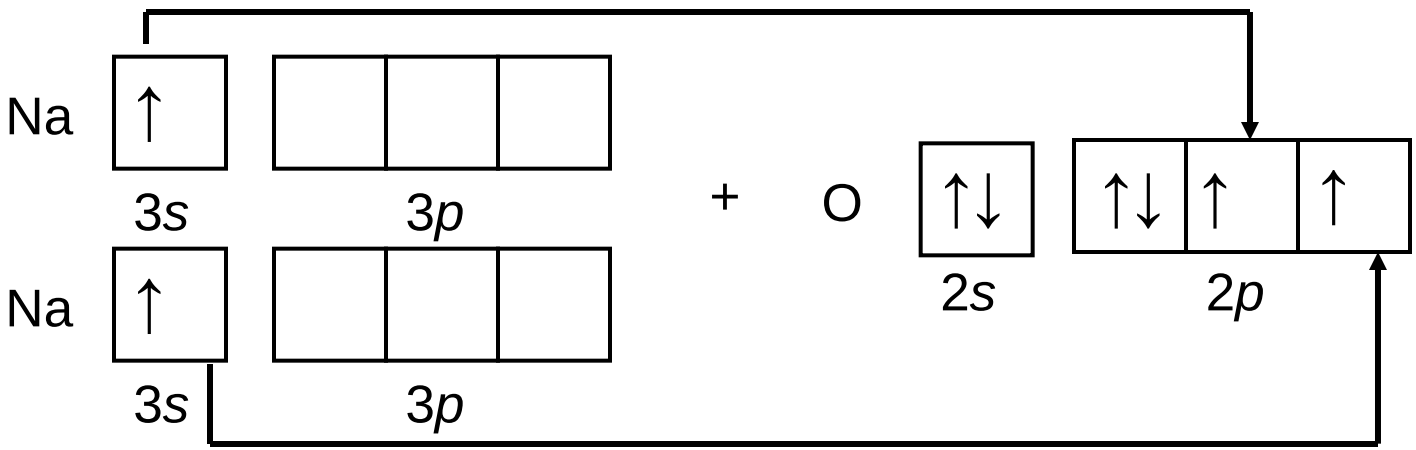
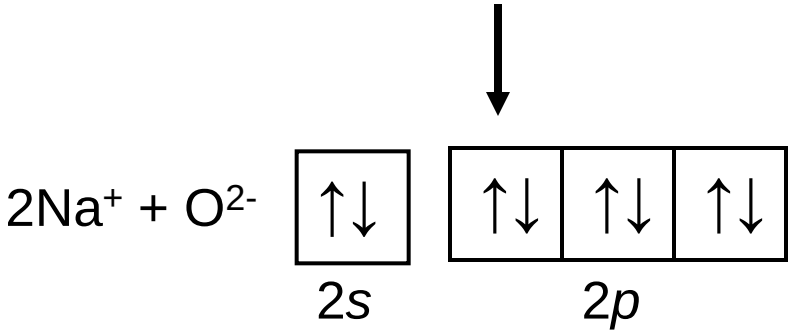
Sample Problem 9.1





The formula is Na_2O

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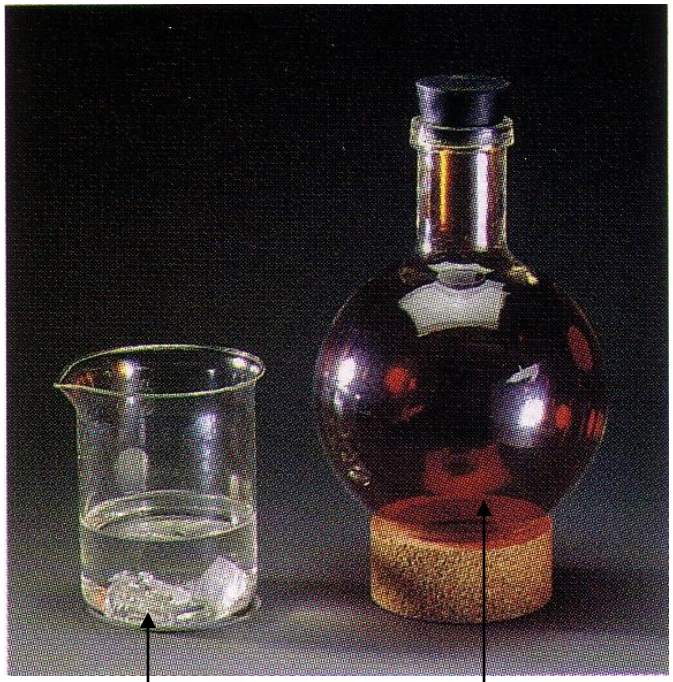
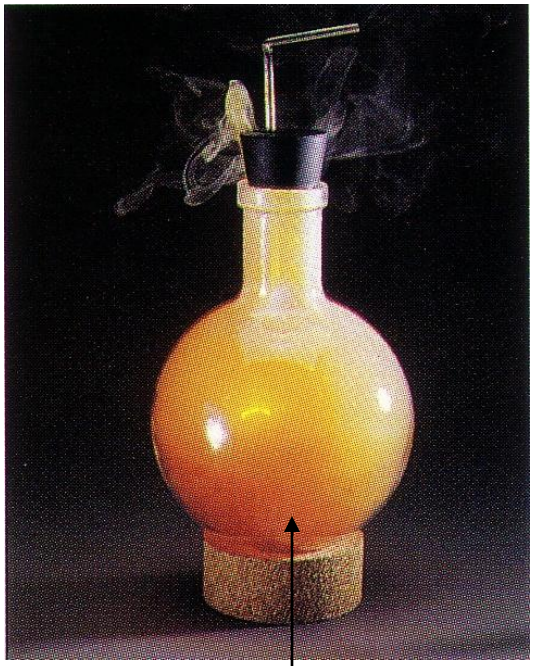
Figure 9.6 The exothermic formation of sodium bromide.



Na(*s*) $Br_2(l)$



NaBr(*l*)

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Periodic Trends in Lattice Energy

Lattice energy is the energy required to separate 1 mol of an ionic solid into gaseous ions.

Lattice energy is a measure of the strength of the ionic bond.

Coloumb's Law

$$\text{Electrostatic energy} \propto \frac{\text{charge A x charge B}}{\text{distance}}$$

$$\text{Electrostatic energy} \propto \frac{\text{cation charge x anion charge}}{\text{cation radius + anion radius}} \propto \Delta H^{o}_{\text{lattice}}$$

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Periodic Trends in Lattice Energy

Lattice energy is affected by ***ionic size*** and ***ionic charge***.

As ionic size ***increases***, lattice energy ***decreases***. Lattice energy therefore decreases down a group on the periodic table.

As ionic charge ***increases***, lattice energy ***increases***.

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Figure 9.7 Trends in lattice energy.

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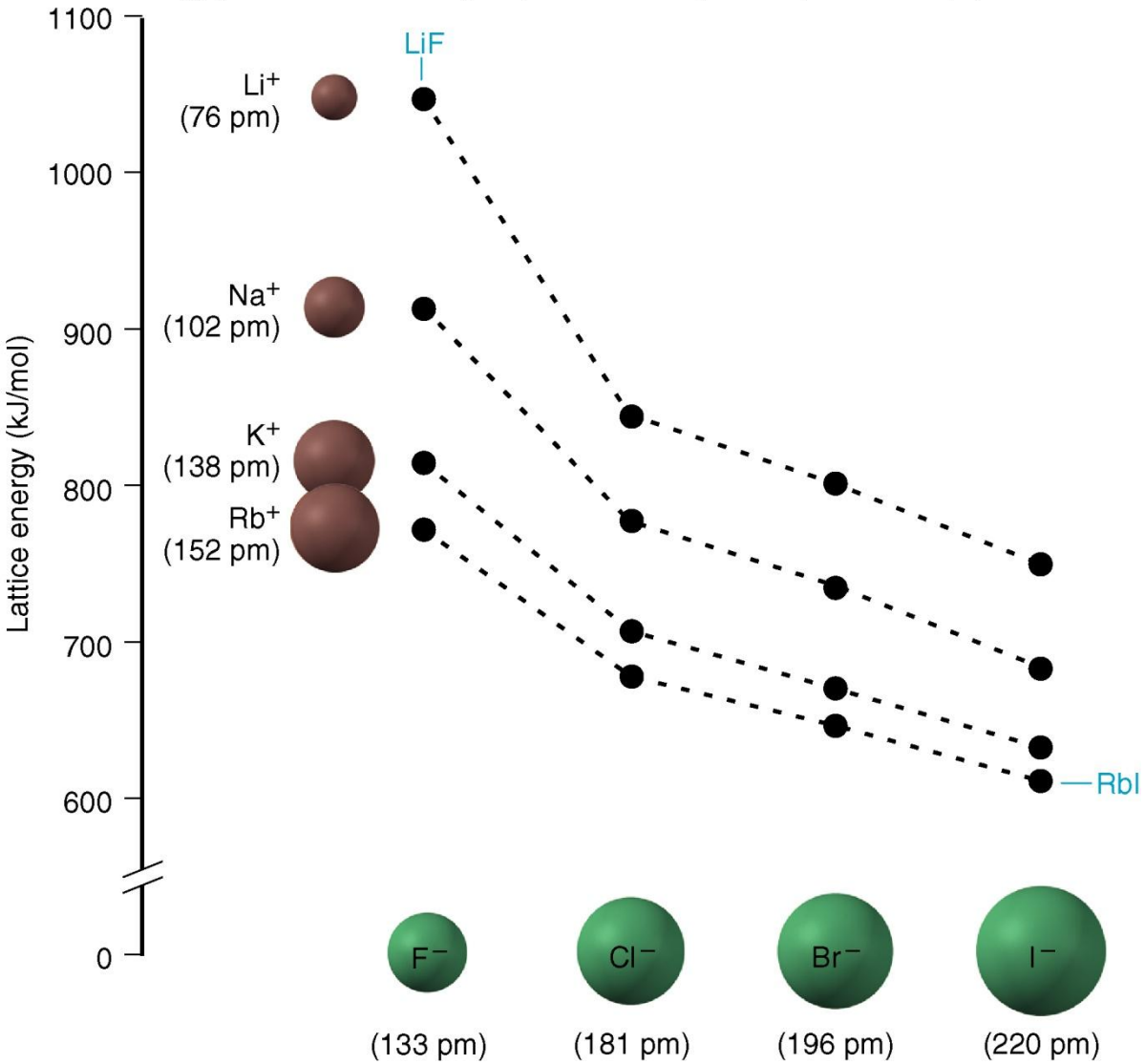

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Properties of Ionic Compounds

- Ionic compounds tend to be hard, rigid, and brittle, with high melting points.
- Ionic compounds do not conduct electricity in the solid state.
  - In the solid state, the ions are fixed in place in the lattice and do not move.
- Ionic compounds conduct electricity when melted or dissolved.
  - In the liquid state or in solution, the ions are free to move and carry a current.

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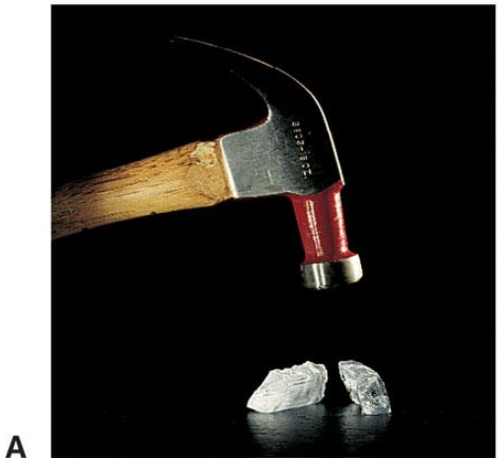
Figure 9.8 Why ionic compounds crack.



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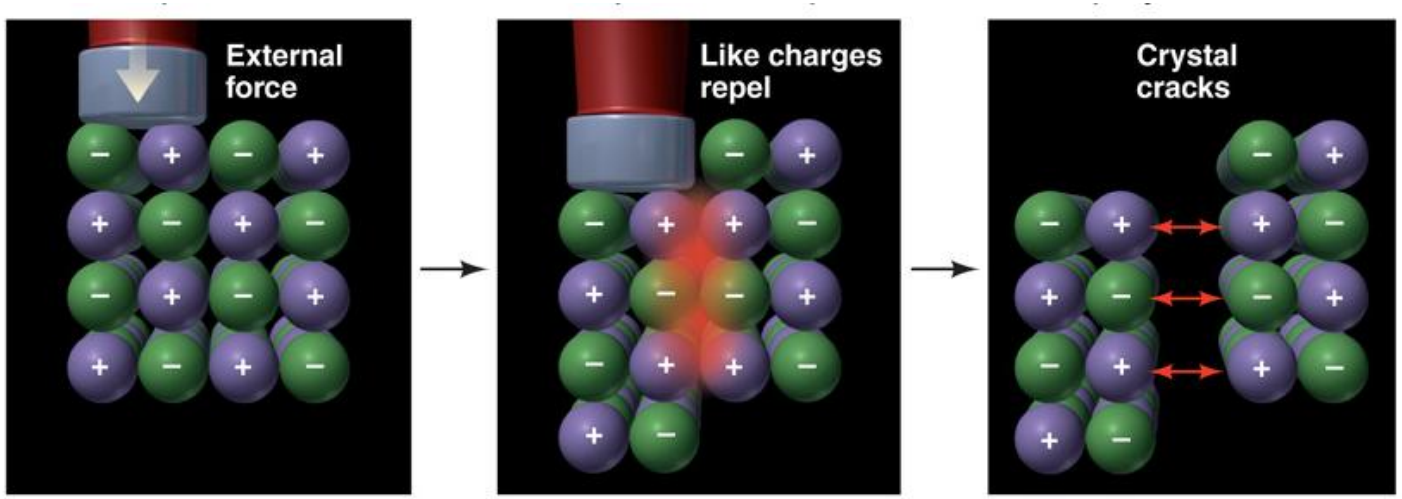

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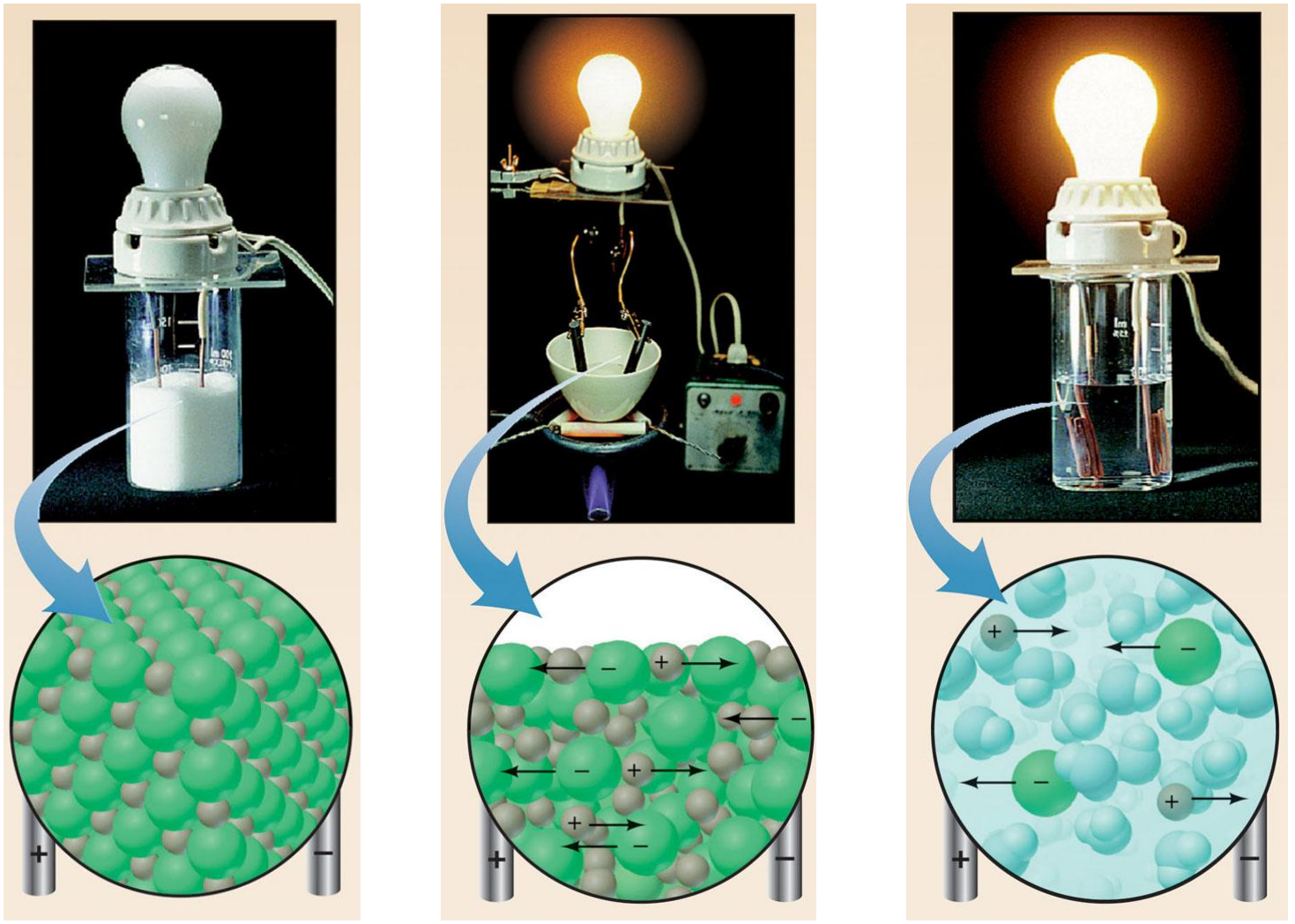
Figure 9.9 Electrical conductance and ion mobility.



Solid ionic compound

Molten ionic compound

Ionic compound dissolved in water

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Table 9.1 Melting and Boiling Points of Some Ionic Compounds

Compound	mp (°C)	bp (°C)
CsBr	636	1300
NaI	661	1304
$MgCl_2$	714	1412
KBr	734	1435
$CaCl_2$	782	>1600
NaCl	801	1413
LiF	845	1676
KF	858	1505
MgO	2852	3600

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Figure 9.10 Covalent bond formation in H_2.

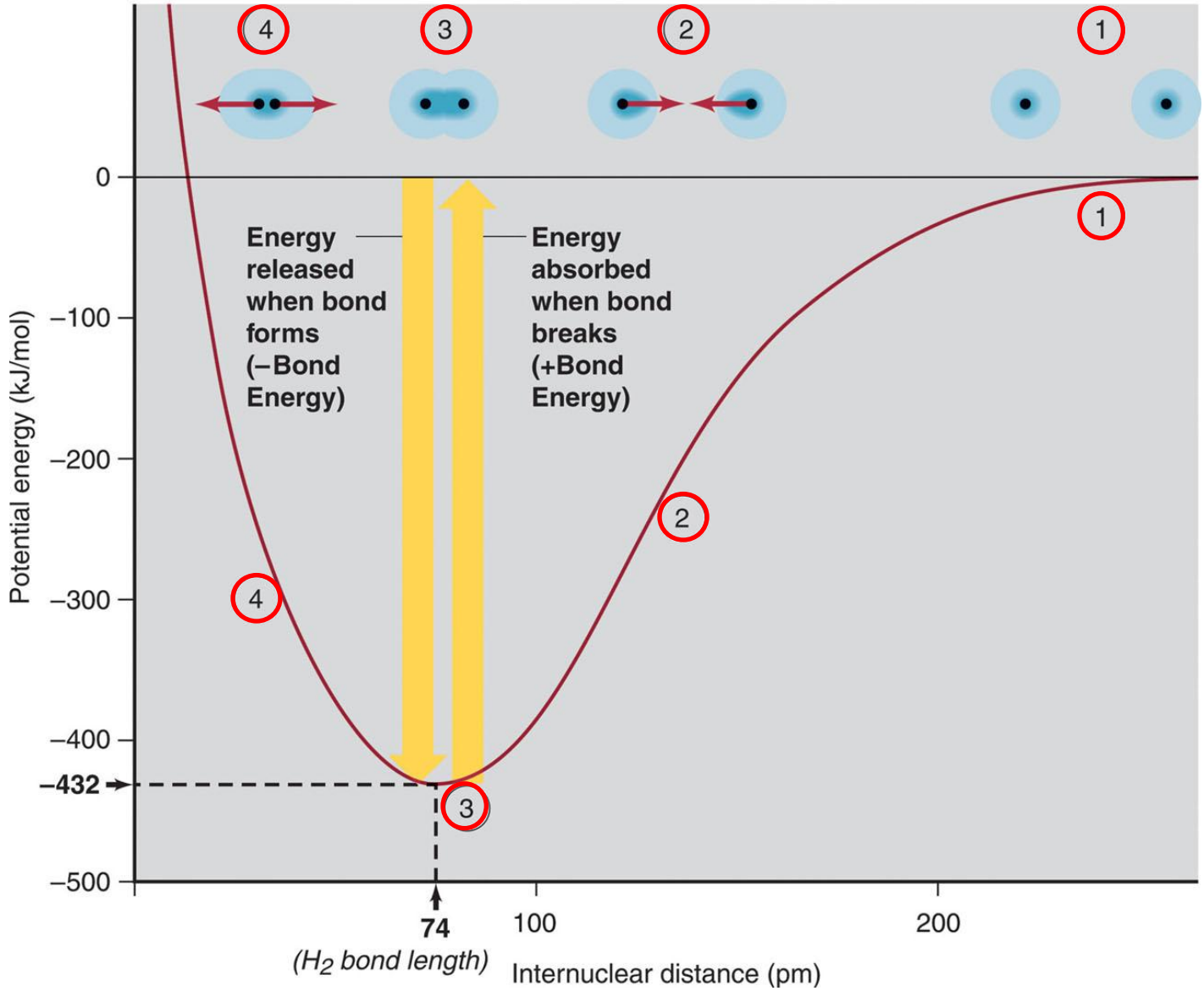

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Figure 9.11 Distribution of electron density in H_2.

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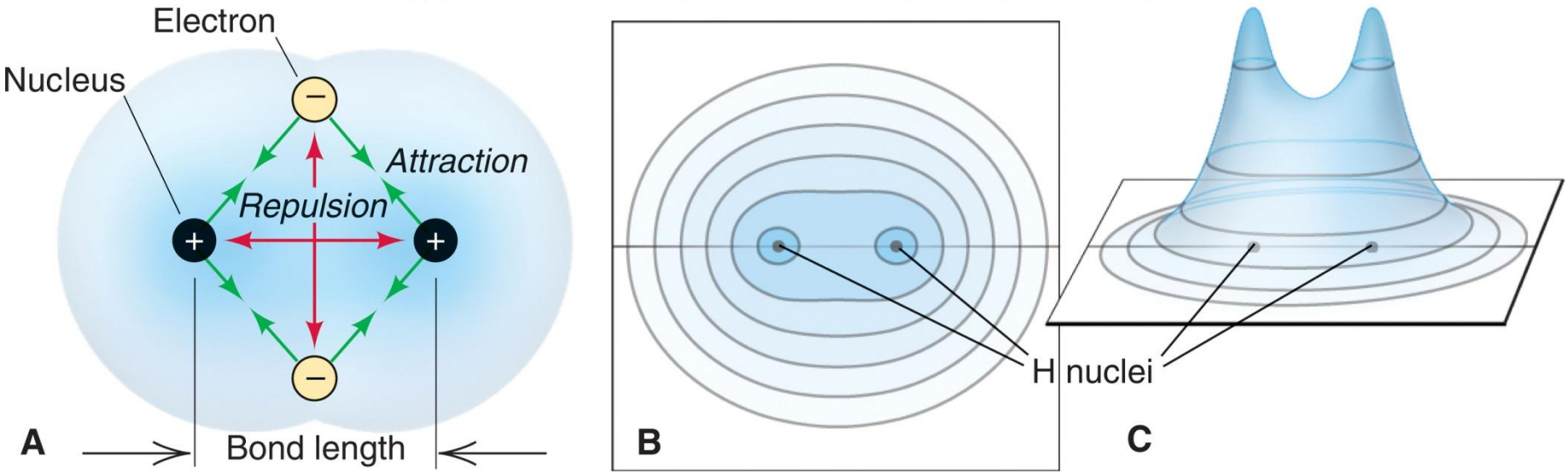

At some distance (bond length), attractions balance repulsions.

Electron density is high around and between the nuclei.

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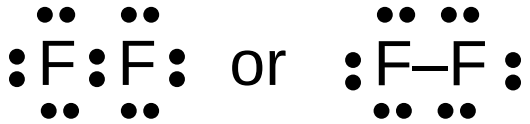
Bonding Pairs and Lone Pairs

Atoms share electrons to achieve a full outer level of electrons. The shared electrons are called a ***shared pair*** or ***bonding pair***.

The shared pair is represented as a pair of dots or a line:

H:H or H–H

An outer-level electron pair that is not involved in bonding is called a ***lone pair***, or ***unshared pair***.

 or

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Properties of a Covalent Bond

The ***bond order*** is the number of electron pairs being shared by a given pair of atoms.

A single bond consists of one bonding pair and has a bond order of 1.

The ***bond energy*** (BE) is the energy needed to overcome the attraction between the nuclei and the shared electrons. The ***stronger*** the bond the ***higher*** the bond energy.

The ***bond length*** is the distance between the nuclei of the bonded atoms.

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Trends in bond order, energy, and length

For a given pair of atoms, a ***higher bond order*** results in a ***shorter bond length*** and ***higher bond energy***.

For a given pair of atoms, a shorter bond is a stronger bond.

Bond length ***increases*** down a group in the periodic table and ***decreases*** across the period.

Bond energy shows the opposite trend.

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Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
Single Bonds											
H—H	432	74	N—H	391	101	Si—H	323	148	S—H	347	134
H—F	565	92	N—N	160	146	Si—Si	226	234	S—S	266	204
H—Cl	427	127	N—P	209	177	Si—O	368	161	S—F	327	158
H—Br	363	141	N—O	201	144	Si—S	226	210	S—Cl	271	201
H—I	295	161	N—F	272	139	Si—F	565	156	S—Br	218	225
			N—Cl	200	191	Si—Cl	381	204	S—I	~170	234
C—H	413	109	N—Br	243	214	Si—Br	310	216			
C—C	347	154	N—I	159	222	Si—I	234	240	F—F	159	143
C—Si	301	186							F—Cl	193	166
C—N	305	147	O—H	467	96	P—H	320	142	F—Br	212	178
C—O	358	143	O—P	351	160	P—Si	213	227	F—I	263	187
C—P	264	187	O—O	204	148	P—P	200	221	Cl—Cl	243	199
C—S	259	181	O—S	265	151	P—F	490	156	Cl—Br	215	214
C—F	453	133	O—F	190	142	P—Cl	331	204	Cl—I	208	243
C—Cl	339	177	O—Cl	203	164	P—Br	272	222	Br—Br	193	228
C—Br	276	194	O—Br	234	172	P—I	184	246	Br—I	175	248
C—I	216	213	O—I	234	194				I—I	151	266
Multiple Bonds											
C=C	614	134	N=N	418	122	C≡C	839	121	N≡N	945	110
C=N	615	127	N=O	607	120	C≡N	891	115	N≡O	631	106
C=O	745 (799 in CO_2)	123	O_2	498	121	C≡O	1070	113			

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Table 9.3 The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C=O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C=C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N=N	2	122	418
N≡N	3	110	945

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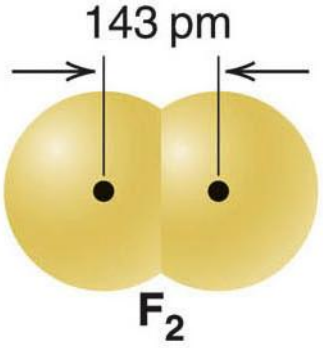
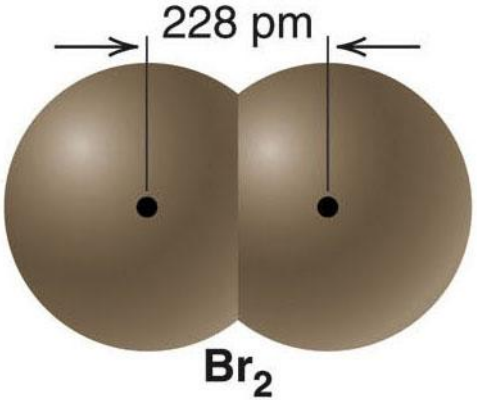
Figure 9.12 Bond length and covalent radius.

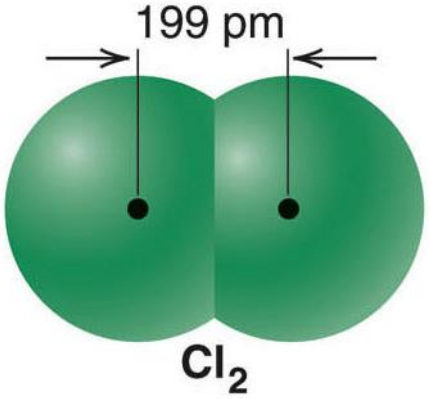
Internuclear distance (bond length)	Covalent radius
143 pm	72 pm



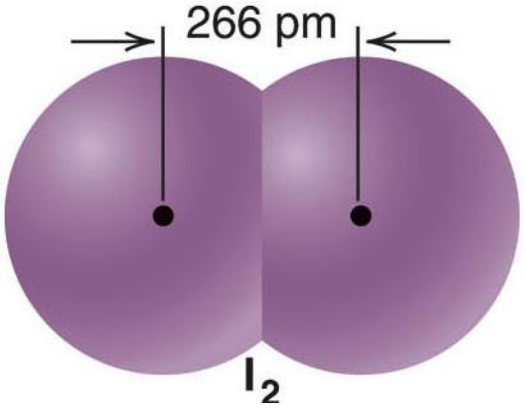
Internuclear distance (bond length)	Covalent radius
228 pm	114 pm



Internuclear distance (bond length)	Covalent radius
199 pm	100 pm



Internuclear distance (bond length)	Covalent radius
266 pm	133 pm



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Sample Problem 9.2 Comparing Bond Length and Bond Strength

PROBLEM: Using the periodic table, but not Tables 9.2 or 9.3, rank the bonds in each set in order of *decreasing* bond length and decreasing bond strength:

(a) S–F, S–Br, S–Cl **(b)** C=O, C–O, C≡O

PLAN: (a) S is singly bonded to three different halogen atoms, so the bond order is the same. Bond length increases and bond strength decreases as the atomic radius of the halogen increases.

(b) The same two atoms are bonded in each case, but the bond orders differ. Bond strength increases and bond length decreases as bond order increases.

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Sample Problem 9.2

SOLUTION:

(a) Atomic size increases going down a group, so F < Cl < Br.

Bond length: S–Br > S–Cl > S–F

Bond strength: S–F > S–Cl > S–Br

(b) By ranking the bond orders, we get

Bond length: C–O > C=O > C≡O

Bond strength: C≡O > C=O > C–O

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Figure 9.13

Strong forces within molecules and weak forces between them.

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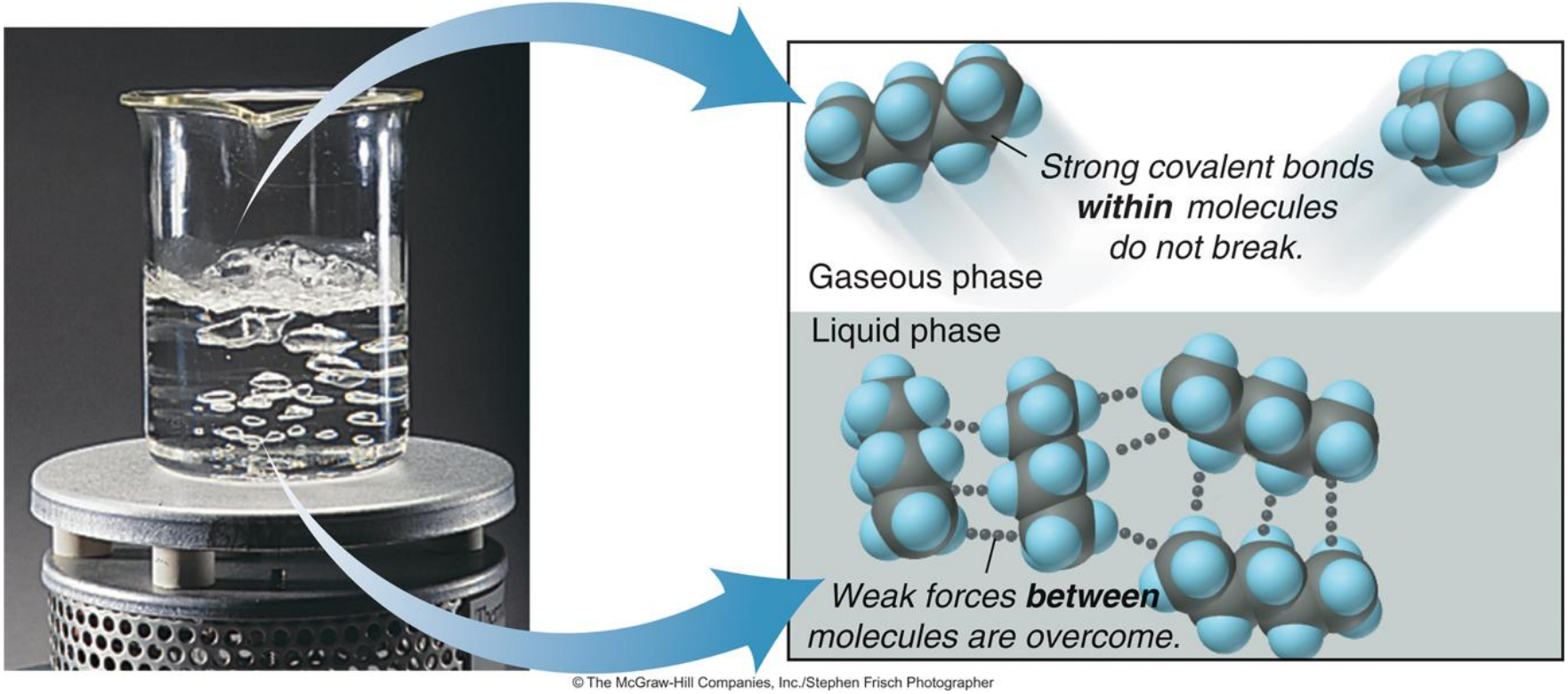

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Figure 9.14 **Covalent bonds of network covalent solids: quartz and diamond.**

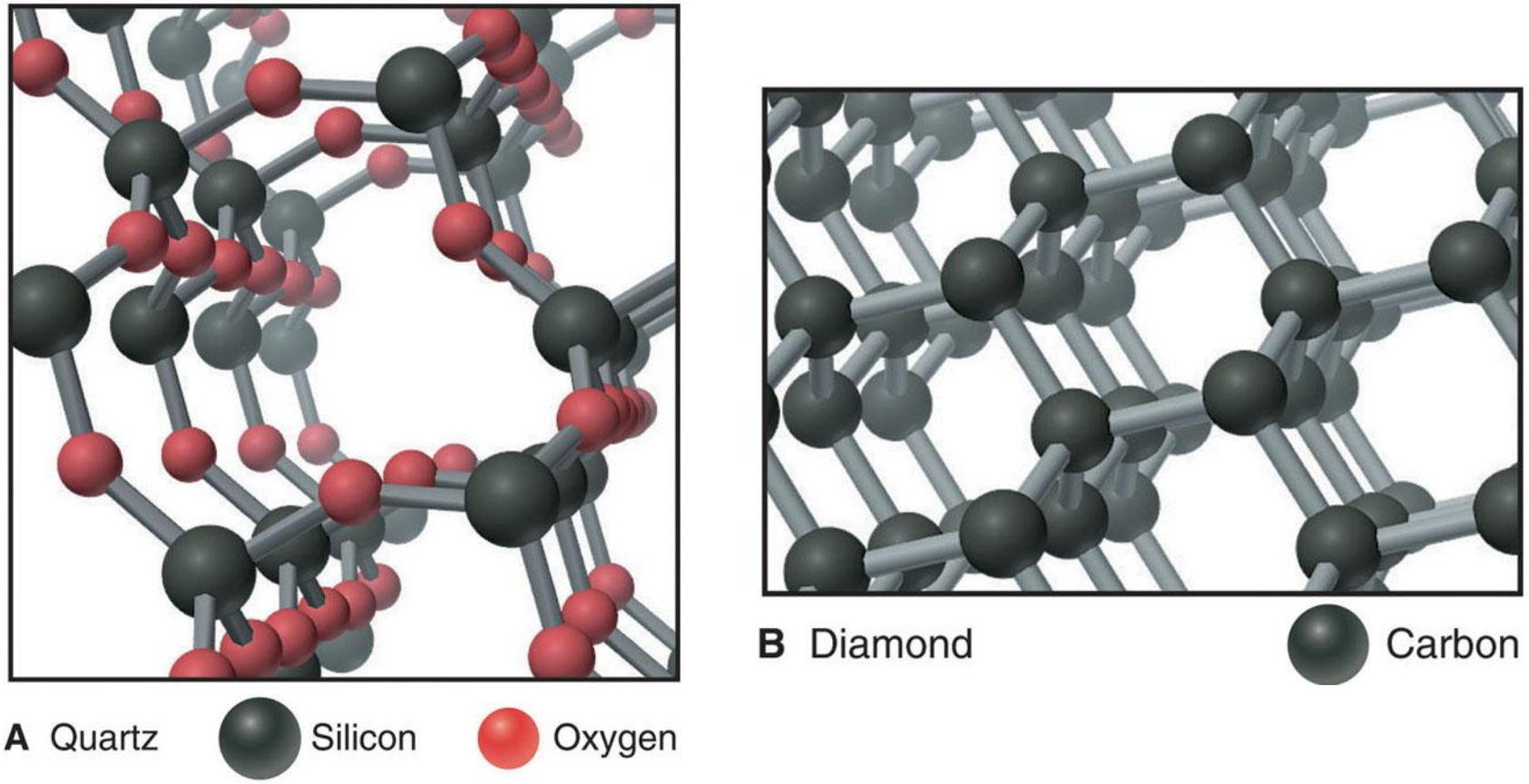

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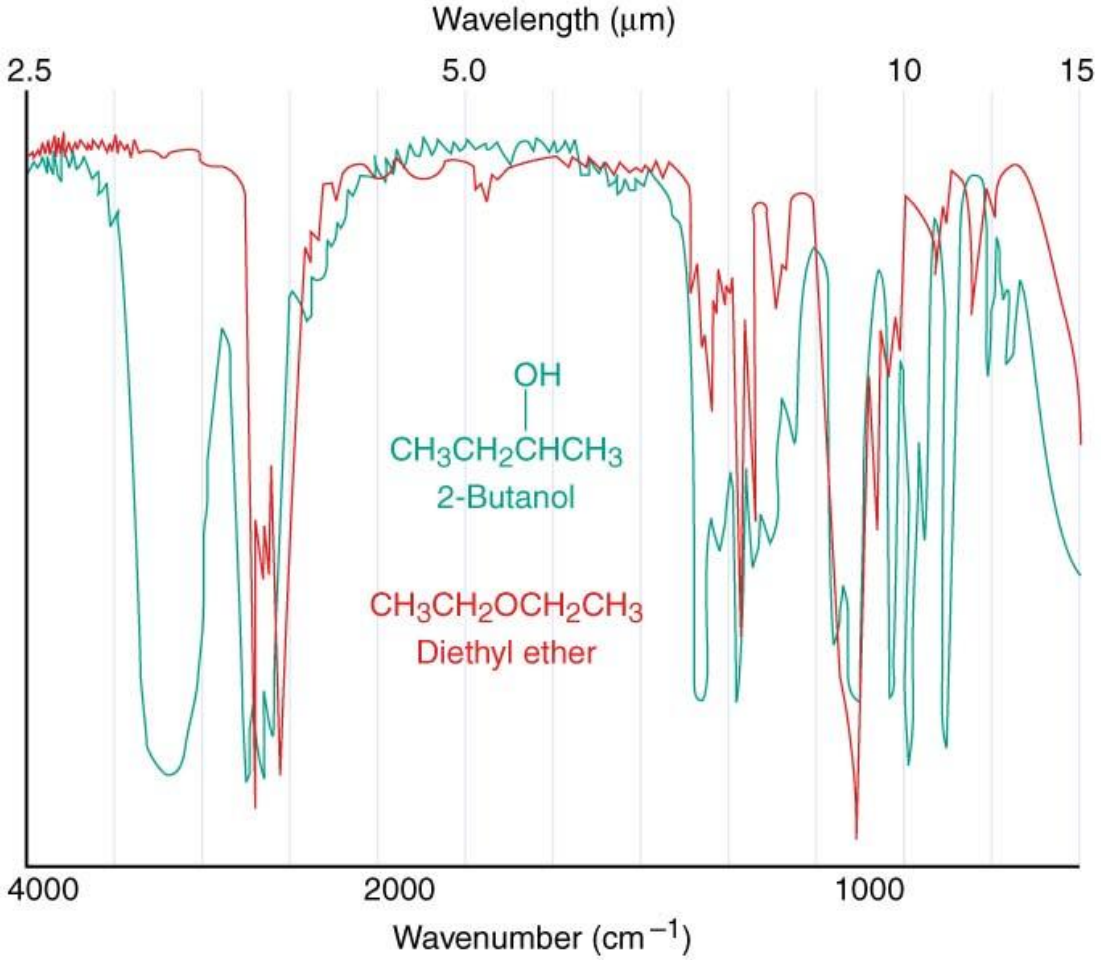
Figure 9.15 The infrared (IR) spectra of 2-butanol (*green*) and diethyl ether (*red*).



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Bond Energies and ΔH^{o}_{rxn}

The heat released or absorbed during a chemical change is due to differences between the bond energies of reactants and products.

$$\Delta H°_{rxn} = \Sigma \Delta H°_{\text{reactant bonds broken}} + \Sigma \Delta H°_{\text{product bonds formed}}$$

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Figure 9.16 Using bond energies to calculate $\Delta H°_{rxn}$ for HF formation.

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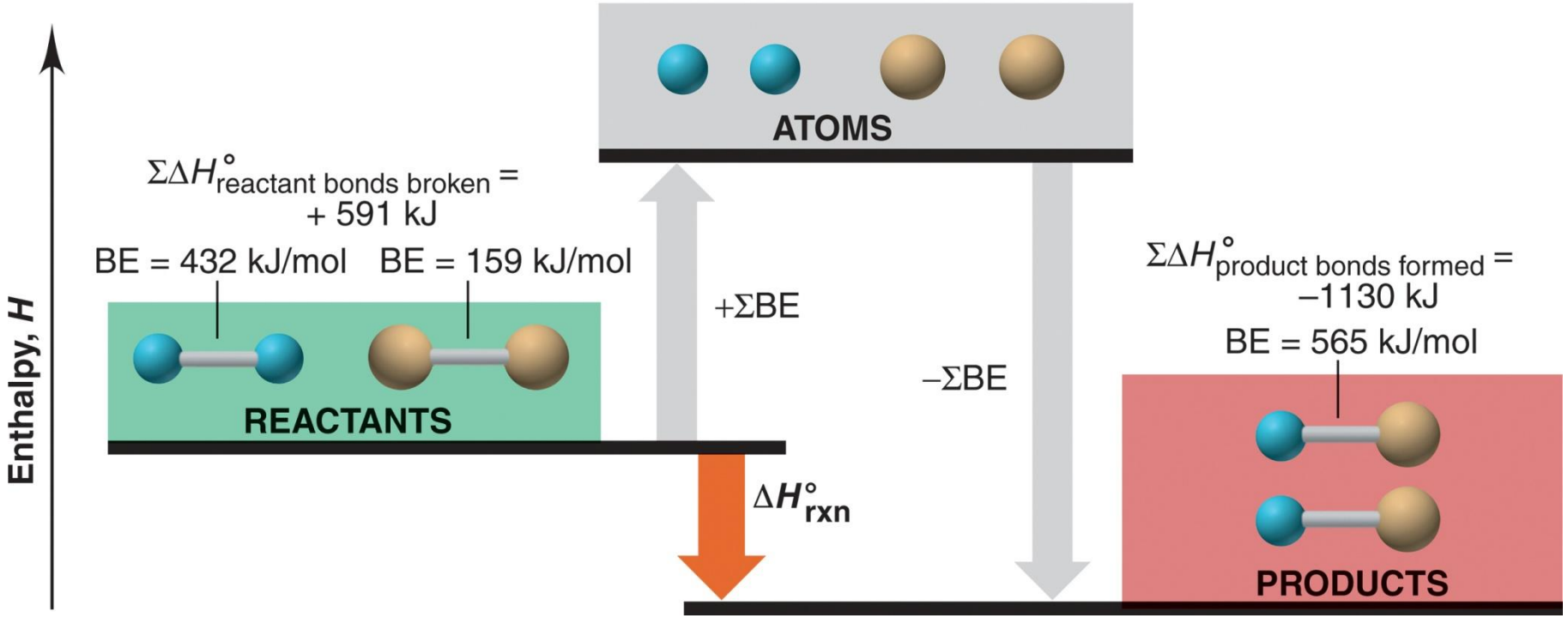

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Figure 9.17 Using bond energies to calculate ΔH°_{rxn} for the combustion of methane.

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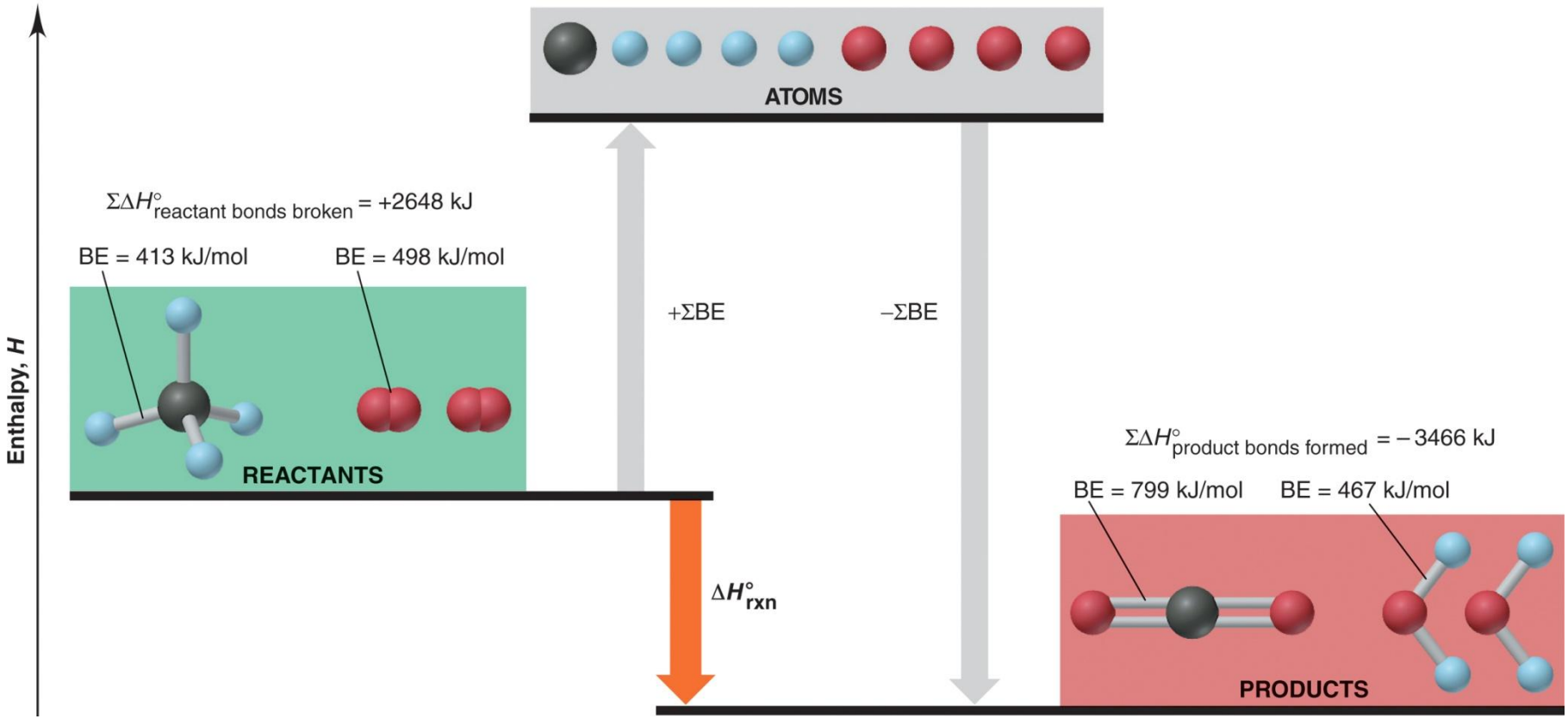

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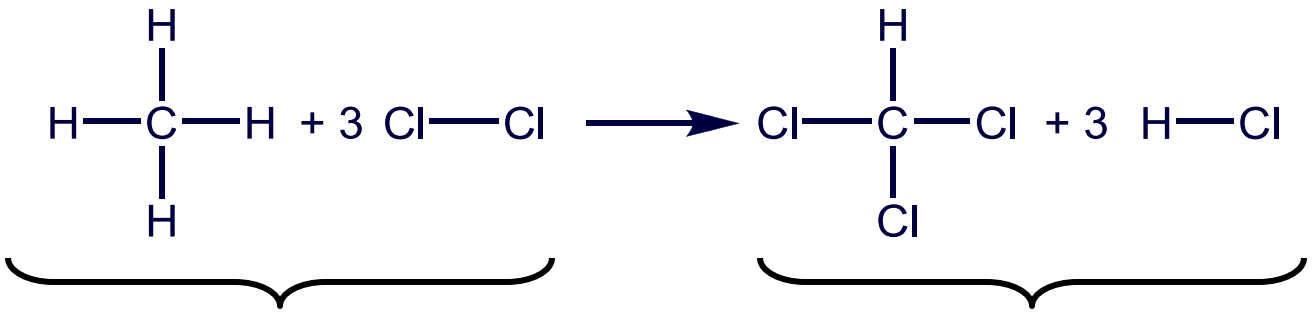
Sample Problem 9.3

Using Bond Energies to Calculate $\Delta H°_{rxn}$

PROBLEM: Calculate $\Delta H°_{rxn}$ for the chlorination of methane to form chloroform.



bonds broken
$\Sigma\Delta H°$ positive

bonds formed
$\Sigma\Delta H°$ negative

PLAN: All the reactant bonds break, and all the product bonds form. Find the bond energies in Table 9.2 and substitute the two sums, with correct signs, into Equation 9.2.

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Sample Problem 9.3

SOLUTION:

For bonds broken:

4 x C-H = (4 mol)(413 kJ/mol) = 1652 kJ

3 x Cl-Cl = (3 mol)(243 kJ/mol) = 729 kJ

$\Sigma \Delta H^\circ_{\text{bonds broken}}$ = 2381 kJ

For bonds formed:

3 x C-Cl = (3 mol)(-339 kJ/mol) = -1017 kJ

1 x C-H = (1 mol)(-413 kJ/mol) = -413 kJ

3 x H-Cl = (3 mol)(-427 kJ/mol) = -1281 kJ

$\Sigma \Delta H^\circ_{\text{bonds formed}}$ = -2711 kJ

$\Delta H^\circ_{\textbf{reaction}} = \Sigma \Delta H^\circ_{\text{bonds } \textbf{broken}} + \Sigma \Delta H_{\textbf{ bonds formed}}$

= 2381 kJ + (-2711 kJ) = - 330 kJ

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Electronegativity and Bond Polarity

A covalent bond in which the shared electron pair is not shared equally, but remains closer to one atom than the other, is a ***polar covalent bond***.

The ability of an atom in a covalent bond to attract the shared electron pair is called its ***electronegativity***.

Unequal sharing of electrons causes the more electronegative atom of the bond to be *partially* negative and the less electronegative atom to be *partially* positive.

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Figure 9.18 Bonding between the models.

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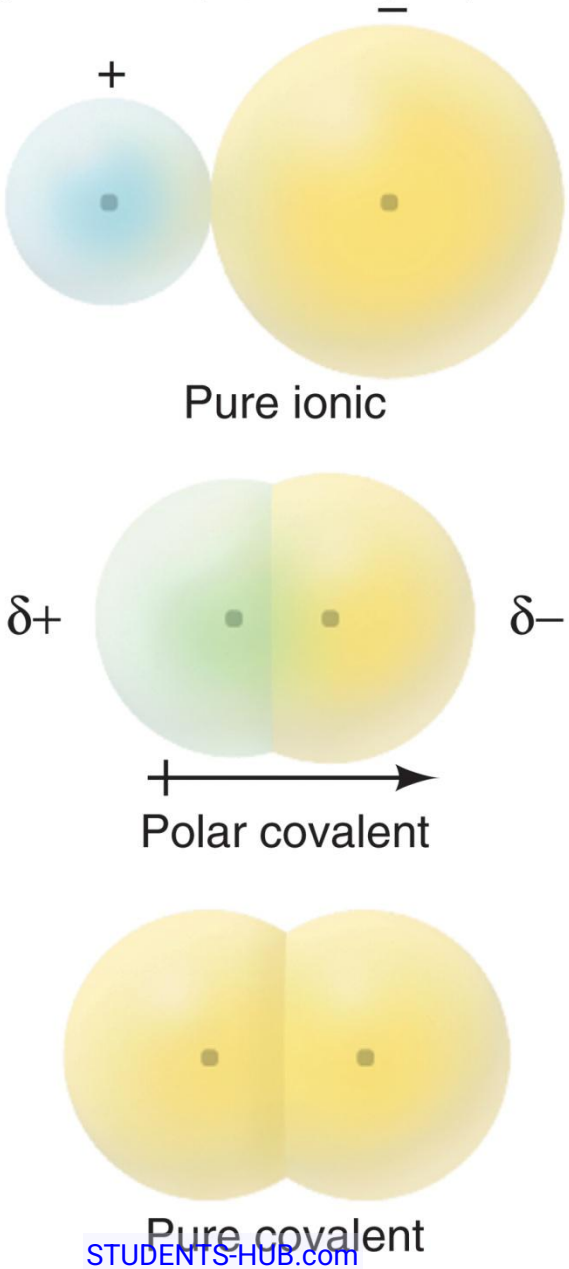

Polar covalent bonds are much more common than either pure ionic or pure covalent bonds.

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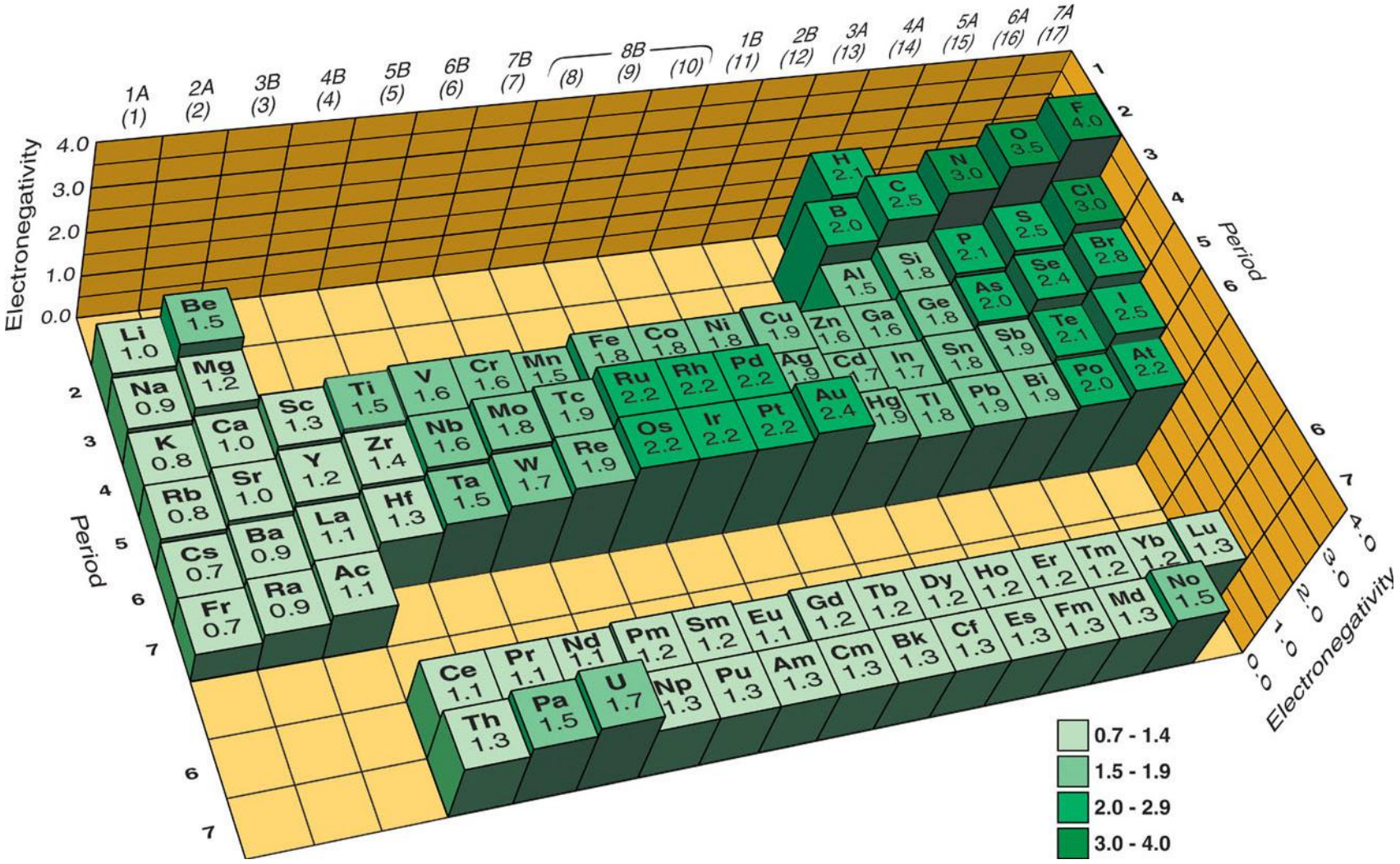
Figure 9.19 The Pauling electronegativity (EN) scale.



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Trends in Electronegativity

The most electronegative element is ***fluorine.***

In general electronegativity ***decreases*** down a group as atomic size ***increases***.

In general electronegativity ***increases*** across a period as atomic size ***decreases***.

Nonmetals are ***more*** electronegative than metals.

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Electronegativity and Oxidation Number

Electronegativities can be used to assign oxidation numbers:

- The more electronegative atom is assigned ***all*** the ***shared*** electrons.
- The less electronegative atom is assigned ***none*** of the shared electrons.
- Each atom in a bond is assigned ***all*** of its ***unshared*** electrons.
- O.N. = # of valence e^- (# of shared e^- + # of unshared e^-)

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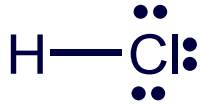
Example: 

Cl is more electronegative than H, so for Cl:

valence e^- = 7

shared e^- = 2

unshared e^- = 6

O.N. = 7 – (2 + 6) = -1

H is less electronegative than Cl, so for H:

valence e^- = 1

shared e^- = 0 (all shared e^- assigned to Cl)

unshared e^- = 0

O.N. = 1 – (0 + 0) = +1

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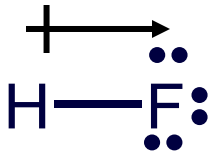
Depicting Polar Bonds

The unequal sharing of electrons can be depicted by a polar arrow. The head of the arrow points to the ***more electronegative element***.



A polar bond can also be marked using δ+ and δ- symbols.

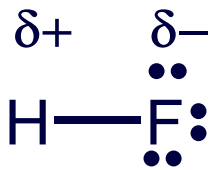


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Figure 9.20 Electron density distributions in H_2, F_2, and HF.

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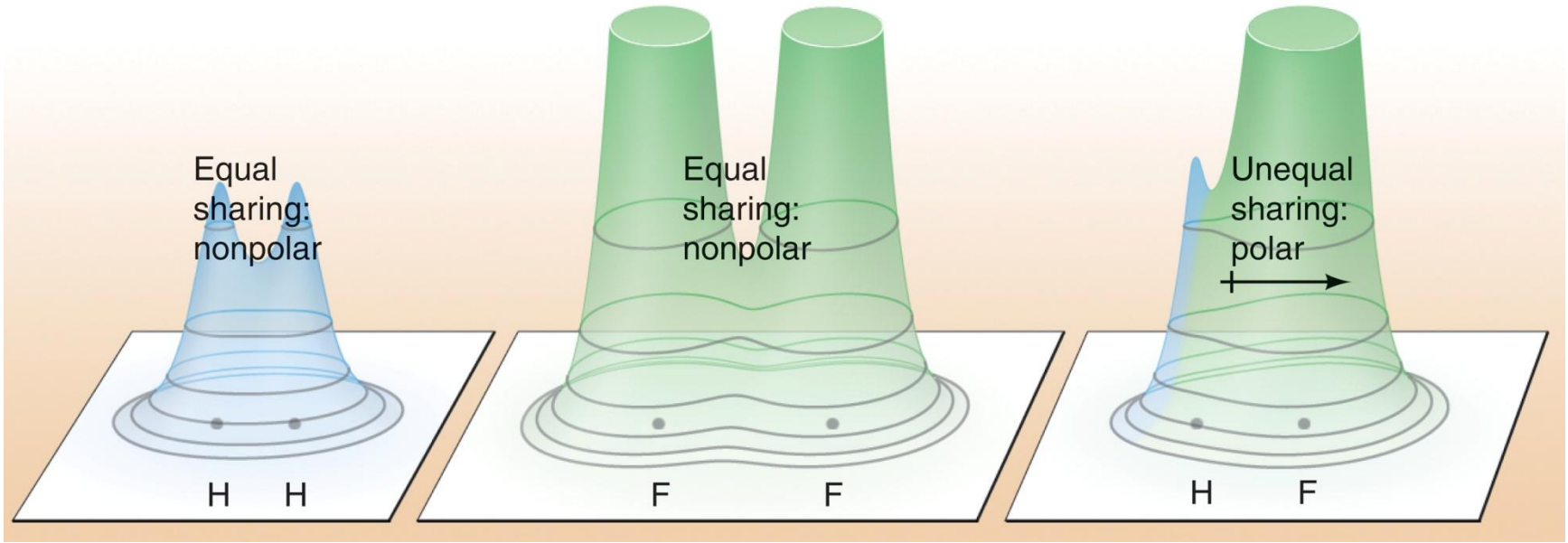

In HF, the electron density shifts from H to F.

The H–F bond has partial ionic character.

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Figure 9.21 ΔEN ranges for classifying the partial ionic character of bonds.

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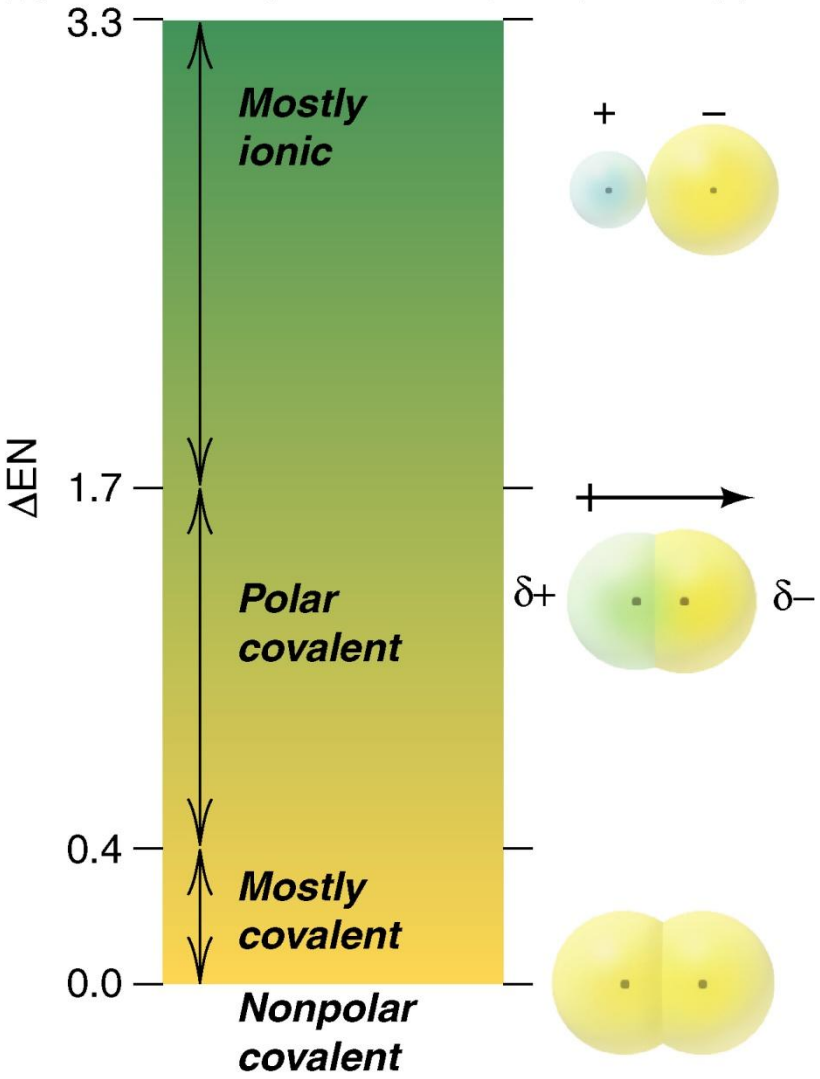

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Figure 9.22 Percent ionic character as a function of ΔEN.

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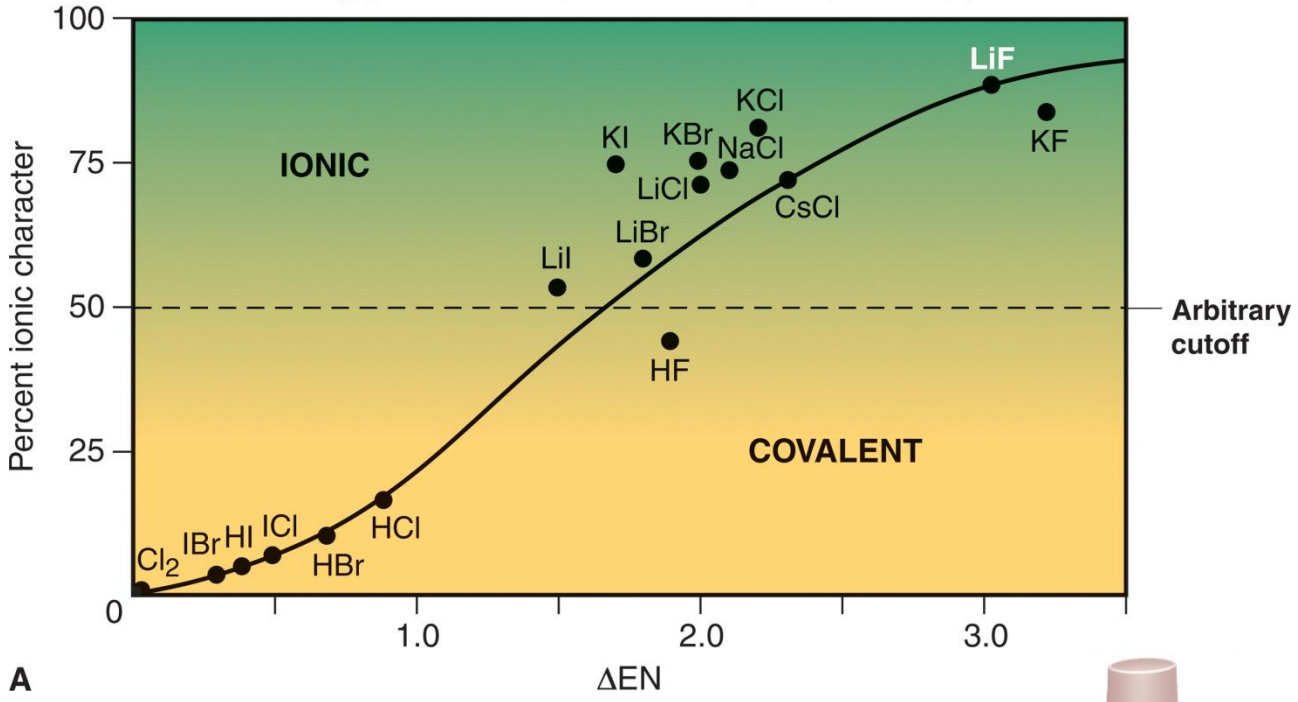

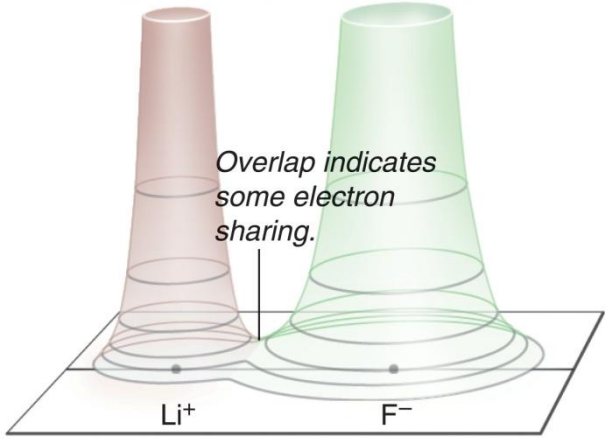

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Sample Problem 9.4 Determining Bond Polarity from EN Values

PROBLEM: **(a)** Use a polar arrow to indicate the polarity of each bond: N–H, F–N, I–Cl.

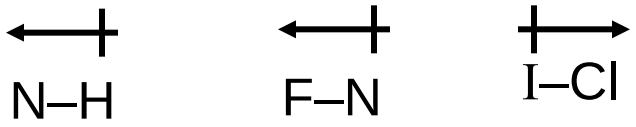
(b) Rank the following bonds in order of increasing polarity: H–N, H–O, H–C.

PLAN: **(a)** We use Figure 9.21 to find the EN values for each element. The polar arrow points toward the more electronegative element.

(b) The greater the ΔEN between the atoms, the more polar the bond.

SOLUTION: **(a)** The EN values are:

N = 3.0, H = 2.1; F = 4.0; I = 2.5, Cl = 3.0



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Sample Problem 9.4

(b) The EN values are:

N = 3.0, H = 2.1; O = 3.5; C = 2.5

ΔEN for H–N = 3.0 – 2.1 = 0.9

ΔEN for H–O = 3.5 – 2.1 = 1.4

ΔEN for H–C = 2.5 – 2.1 = 0.4

H-C < H-N < H-O

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Figure 9.23 Properties of the Period 3 chlorides.

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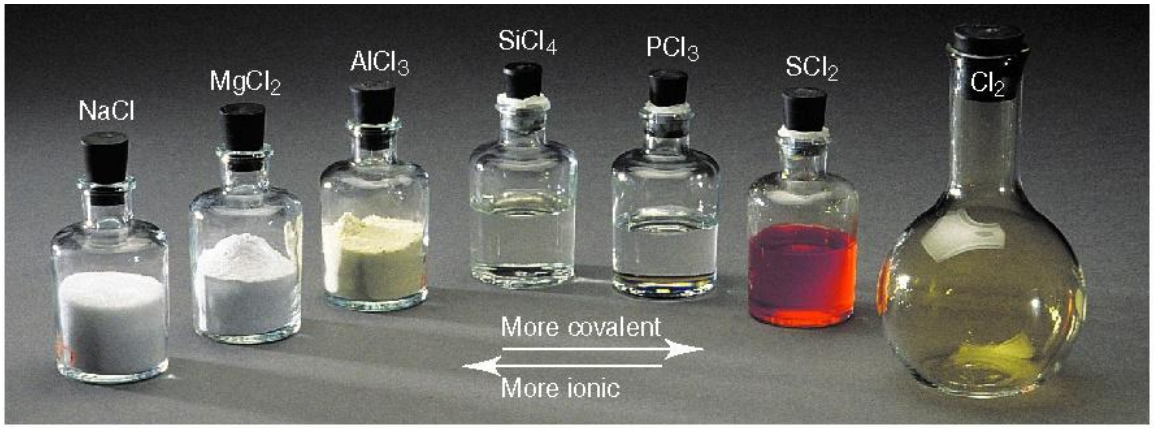

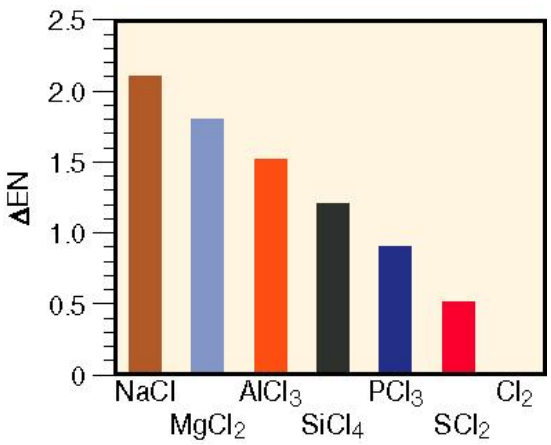

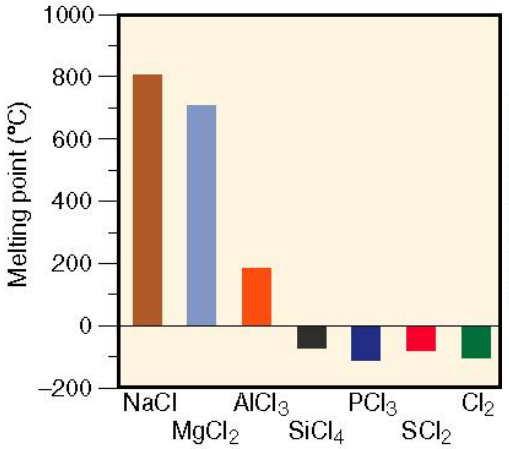

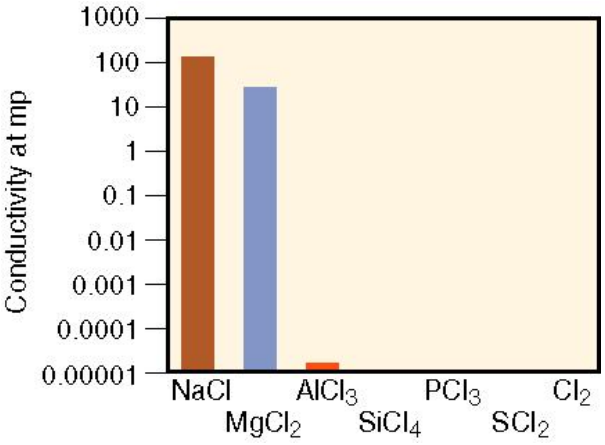

As ΔEN decreases, melting point and electrical conductivity decrease because the bond type changes from ionic to polar covalent to nonpolar covalent.

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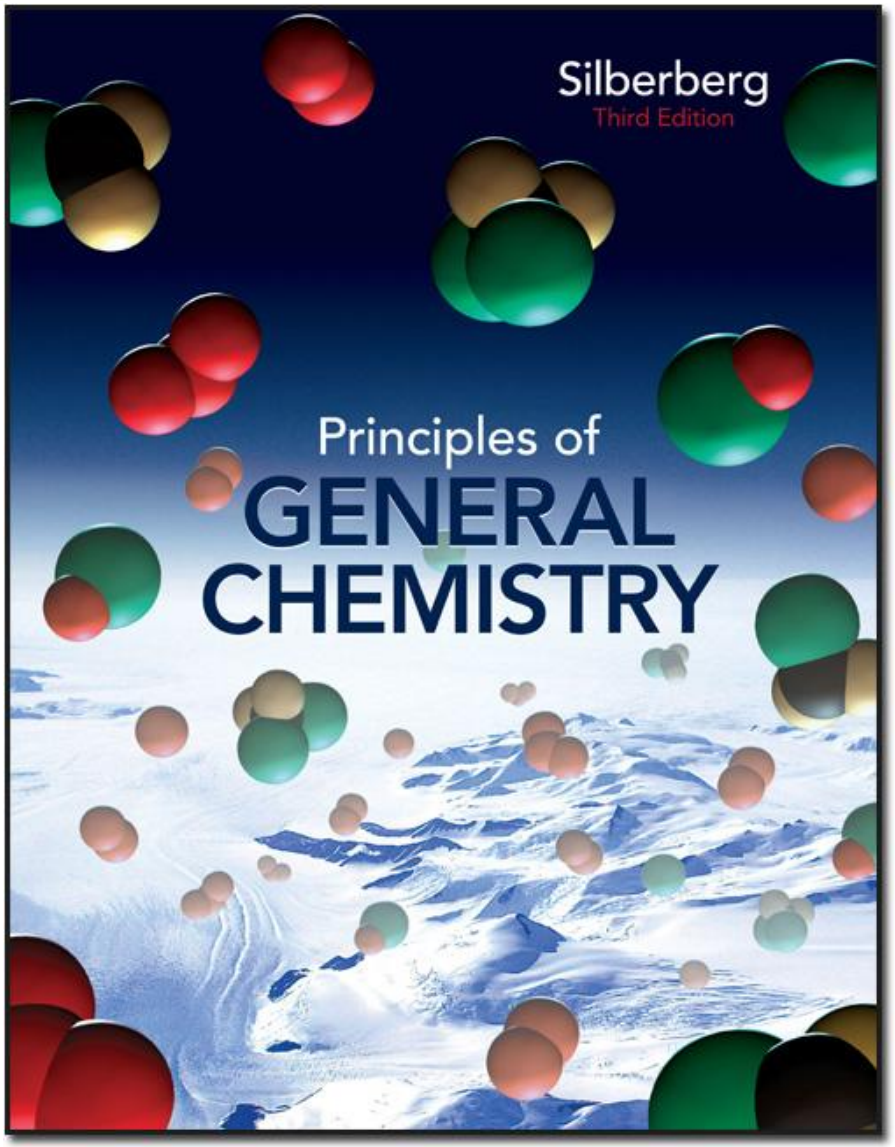

Chapter 10

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 10

The Shapes of Molecules

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The Shapes of Molecules

10.1 Depicting Molecules and Ions with Lewis Structures

10.2 Valence-Shell Electron-Pair Repulsion (VSEPR) Theory and Molecular Shape

10.3 Molecular Shape and Molecular Polarity

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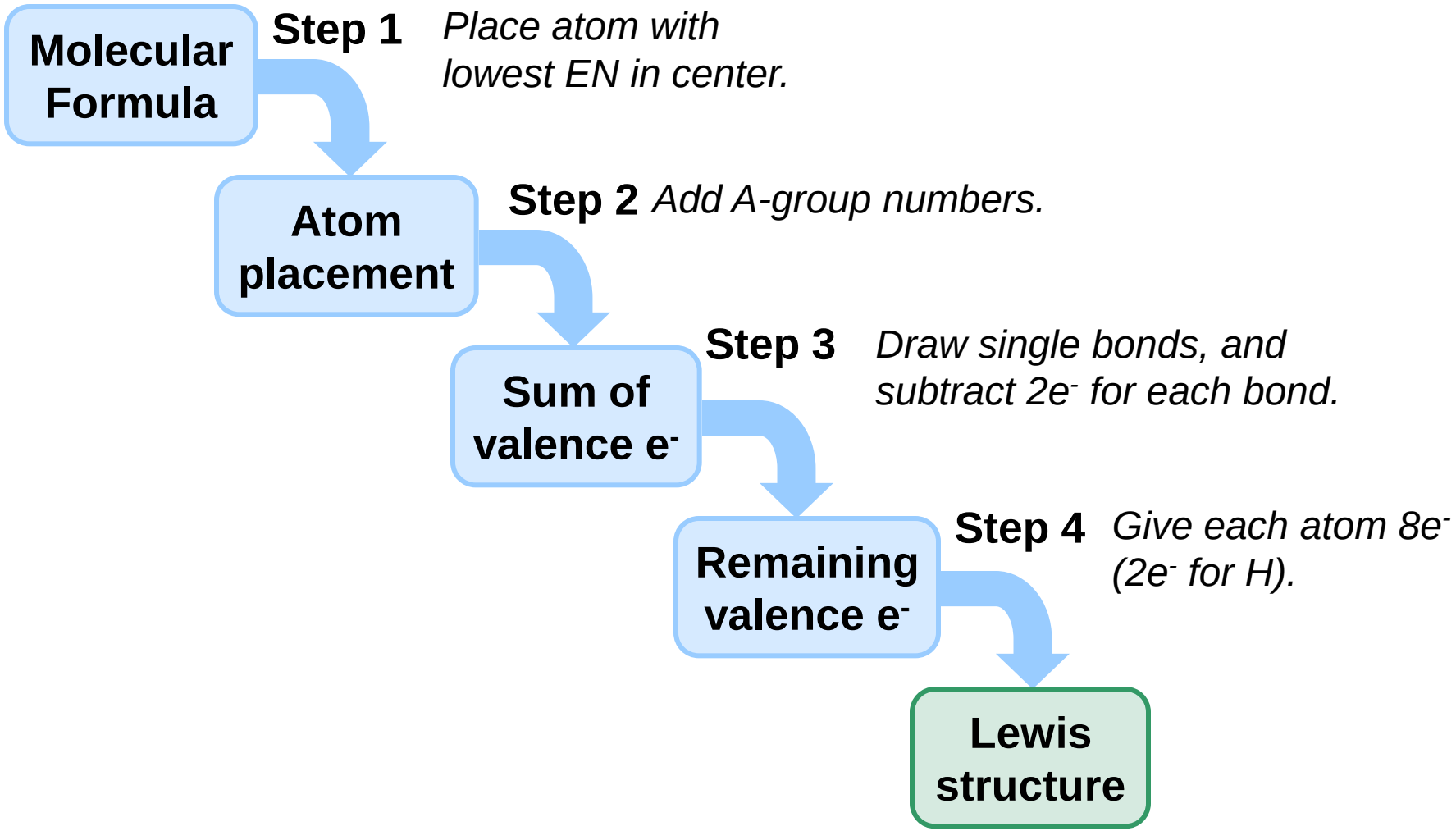
Figure 10.1 **The steps in converting a molecular formula into a Lewis structure.**



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Example: NF_3

Molecular Formula

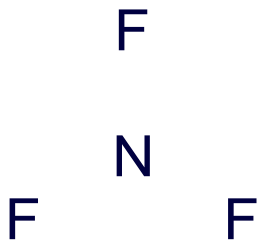
Atom placement

Sum of valence e⁻

Remaining valence e⁻

Lewis structure

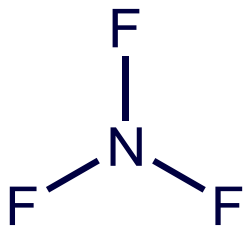
N has a lower EN than F, so N is placed in the center.

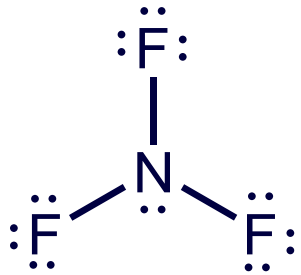


1 x N = 1 x 5 = 5e⁻

3 x F = 3 x 7 = 21 e⁻

Total = 28 e⁻





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Sample Problem 10.1 Writing Lewis Structures for Molecules with One Central Atom

PROBLEM: Write a Lewis structure for CCl_2F_2, one of the compounds responsible for the depletion of stratospheric ozone.

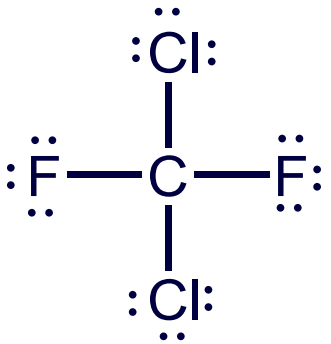
SOLUTION:

Step 1: Carbon has the lowest EN and is the central atom. The other atoms are placed around it.

Cl
F C F
Cl

Step 2: [1 x C($4e^-$)] + [2 x F($7e^-$)] + [2 x Cl($7e^-$)] = 32 valence e^-

Step 3-4: Add single bonds, then give each atom a full octet.



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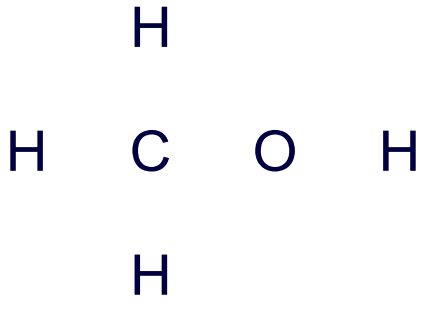
Sample Problem 10.2 Writing Lewis Structures for Molecules with More than One Central Atom

PROBLEM: Write the Lewis structure for methanol (molecular formula CH_4O), an important industrial alcohol that is being used as a gasoline alternative in car engines.

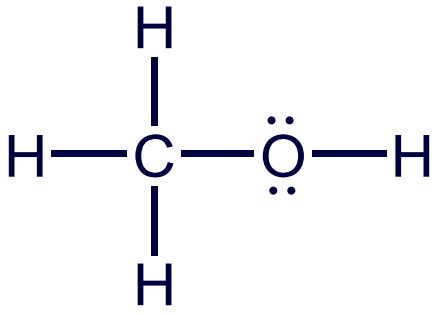
SOLUTION:

Step 1: Place the atoms relative to each other. H can only form one bond, so C and O must be central and adjacent to each other.



Step 2: [1 x C($4e^-$)] + [1 x O($6e^-$)] + [4 x H($1e^-$)] = 14 valence e^-

Step 3-4: Add single bonds, then give each atom (other than H) a full octet.



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Multiple Bonds

If there are not enough electrons for the ***central*** atom to attain an octet, a multiple bond is present.

Step 5: If the central atom does not have a full octet, change a lone pair on a surrounding atom into another bonding pair to the central atom, thus forming a multiple bond.

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Sample Problem 10.3 **Writing Lewis Structures for Molecules with Multiple Bonds**

PROBLEM: Write Lewis structures for the following:

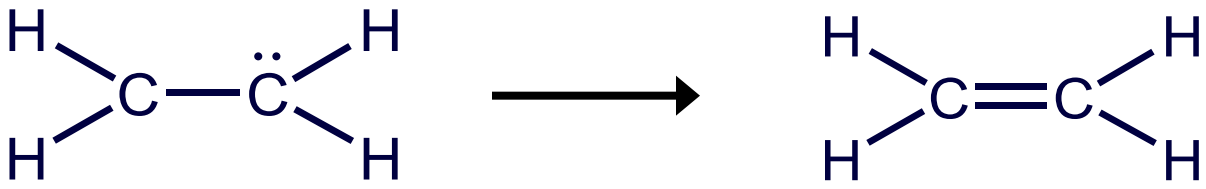
(a) Ethylene (C_2H_4), the most important reactant in the manufacture of polymers

(b) Nitrogen (N_2), the most abundant atmospheric gas

PLAN: After following steps 1 to 4 we see that the central atom does not have a full octet. We must therefore add step 5, which involves changing a lone pair to a bonding pair.

SOLUTION:

(a) C_2H_4 has 2(4) + 4(1) = 12 valence e^-. H can have only one bond per atom.



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Sample Problem 10.3

(b) N_2 has 2(5) = 10 valence e^-.

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Resonance Structures

O_3 can be drawn in 2 ways:

I II

These are two different reasonable Lewis structures for the ***same*** molecule.

Neither structure depicts O_3 accurately, because in reality the O-O bonds are identical in length and energy.

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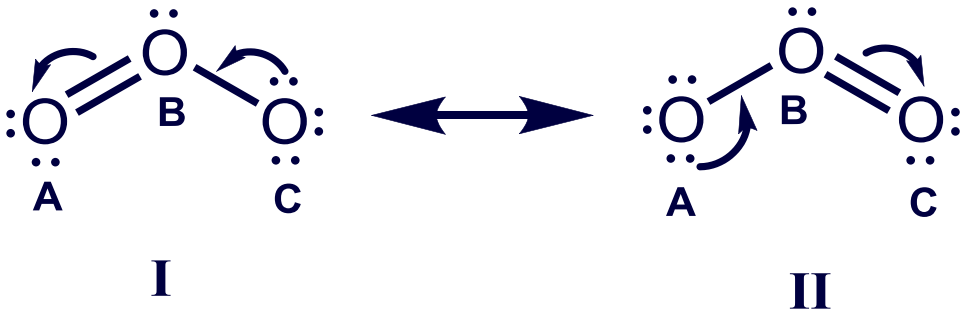
Resonance Structures

The structure of O_3 is shown more correctly using both Lewis structures, called ***resonance structures***.

A two-headed resonance arrow is placed between them.



Resonance structures have the *same relative placement of atoms but different locations of bonding and lone electron pairs.*

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The Resonance Hybrid

A species like O_3, which can be depicted by more than one valid Lewis structure, is called a ***resonance hybrid***.

Resonance forms ***are not real bonding depictions***.

O_3 does ***not*** change back and forth between its two resonance forms.

The ***real structure*** of a resonance hybrid is an ***average*** of its contributing resonance forms.

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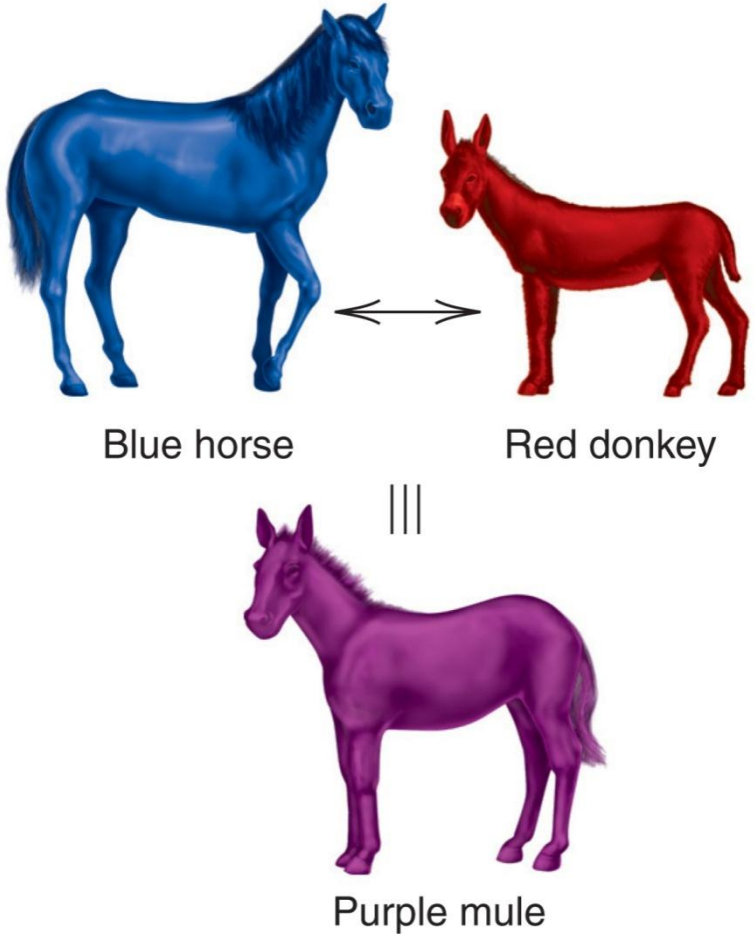

A mule is a genetic mix, a hybrid, of a horse and a donkey. It is not a horse one instant and a donkey the next. Likewise, a resonance hybrid has a **single** structure although it retains characteristics of its resonance forms.

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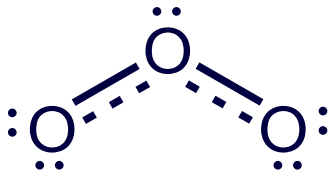
Electron Delocalization

Lewis structures depict electrons as ***localized*** either on an individual atom (lone pairs) or in a bond between two atoms (shared pair).

In a resonance hybrid, electrons are ***delocalized***: their density is "spread" over a few adjacent atoms.



Dotted lines are used to show delocalized electrons.

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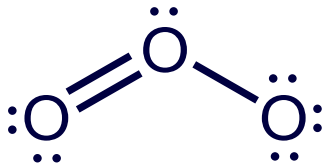
Fractional Bond Orders

Resonance hybrids often have ***fractional bond orders*** due to partial bonding.

For O_3, bond order = $\frac{\text{3 electron pairs}}{\text{2 bonded-atom pairs}}$ = 1½



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Sample Problem 10.4 Writing Resonance Structures

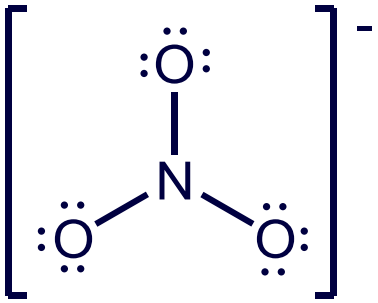
PROBLEM: Write resonance structures for the nitrate ion, NO_3^- and find the bond order.

PLAN: Write the Lewis structure, remembering to add $1e^-$ to the total number of valence e^- for the -1 charge. We apply Step 5 to form multiple bonds. Since multiple bonds can be formed in more than one location, there are resonance forms.

SOLUTION:

Nitrate has [1 x N($5e^-$)] + [3 x O($6e^-$)] + $1e^-$] = 24 valence e^-

After Steps 1-4:



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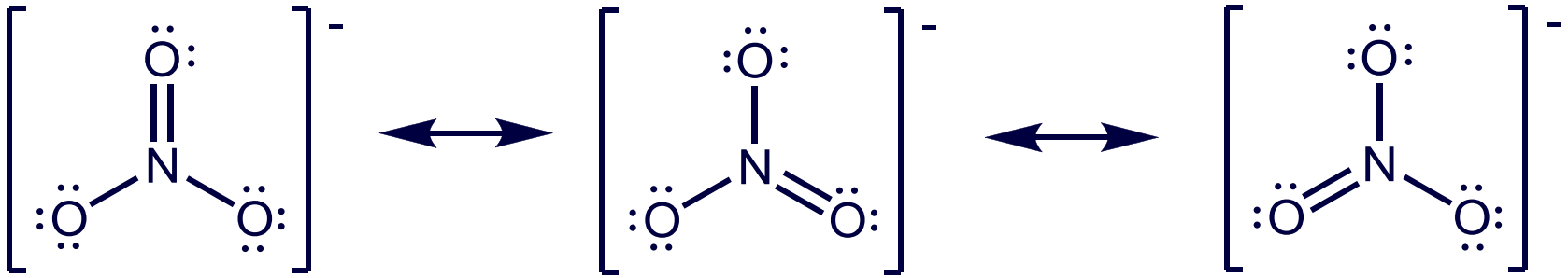
Sample Problem 10.4

Step 5. Since N does not have a full octet, we change a lone pair from O to a bonding pair to form a double bond.



$$\text{Bond order} = \frac{\text{4 shared electron pairs}}{\text{3 bonded-atom pairs}} = 1\frac{1}{3}$$

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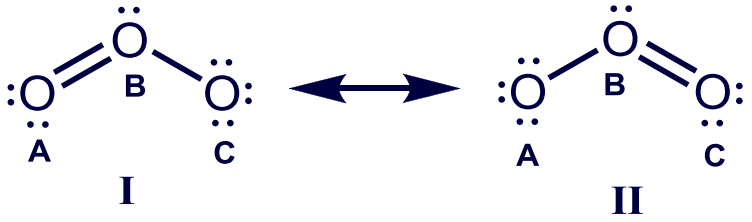
Formal Charge

Formal charge is the charge an atom would have if all electrons were shared ***equally***.

Formal charge of atom =

# of valence e^- - (# of unshared valence e^- + ½ # of shared valence e^-)



For O_A in resonance form I, the formal charge is given by

6 valence e^- - (4 unshared e^- + ½(4 shared e^-) = 6 – 4 – 2 = 0

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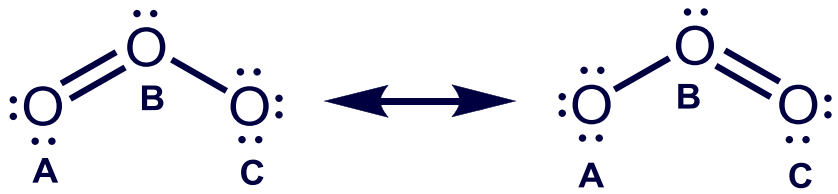
Formal Charge

Formal charges must sum to the actual charge on the species for ***all*** resonance forms.



O_A [6 – 4 – ½(4)] = 0
O_B [6 – 2 – ½(6)] = +1
O_C [6 – 6 – ½(2)] = -1

O_A [6 – 6 – ½(2)] = -1
O_B [6 – 2 – ½(6)] = +1
O_C [6 – 4 – ½(4)] = 0

For both these resonance forms the formal charges sum to zero, since O_3 is a neutral molecule.

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Choosing the More Important Resonance Form

- Smaller formal charges (positive or negative) are preferable to larger ones.

- The ***same*** nonzero formal charges on adjacent atoms are not preferred.

  Avoid like charges on adjacent atoms.

- A more negative formal charge should reside on a more electronegative atom.

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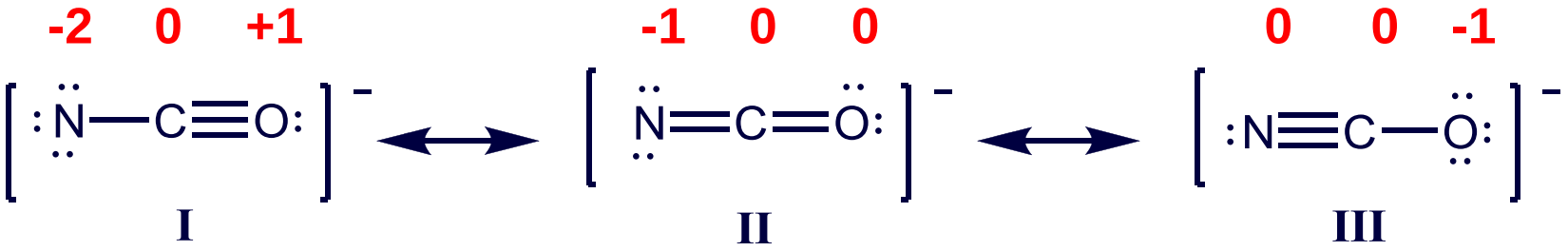
Example: NCO^- has 3 possible resonance forms:



Resonance forms with smaller formal charges are preferred.
Resonance form I is therefore ***not*** an important contributor.

A negative formal charge should be placed on a more electronegative atom, so resonance form III is preferred to resonance form II.

The overall structure of the NCO^- ion is still an ***average*** of all three forms, but **resonance form III** contributes ***most*** to the average.

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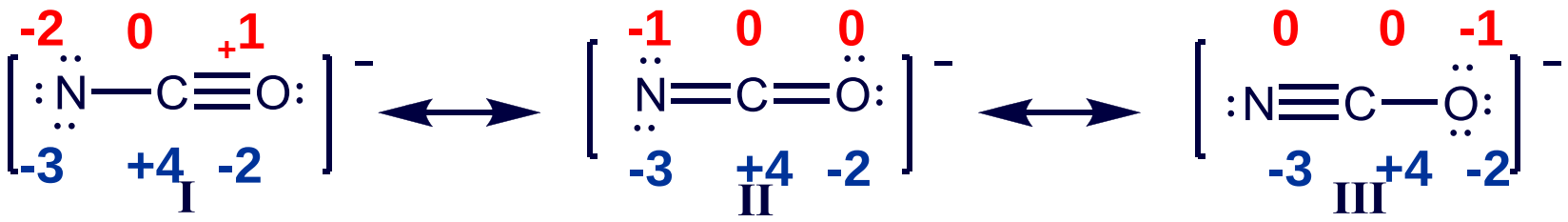
Formal Charge Versus Oxidation Number

For a ***formal charge***, bonding electrons are ***shared equally*** by the atoms.

The formal charge of an atom may change between resonance forms.

Formal charges



Oxidation numbers

For an ***oxidation number***, bonding electrons are ***transferred*** to the ***more*** electronegative atom.

The oxidation number of an atom is the ***same*** in all resonance forms.

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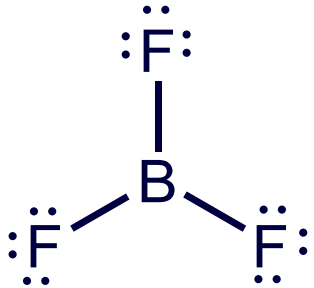
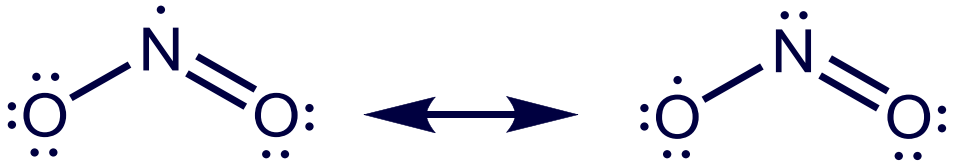
Exceptions to the Octet Rule

Molecules with Electron-Deficient Atoms



B and Be are commonly electron-deficient.

Odd-Electron Species



A molecule with an odd number of electrons is called a ***free radical***.

enigma - something that baffles understanding and cannot be explained; "how it got out is a mystery"; "it remains one of nature's secrets"

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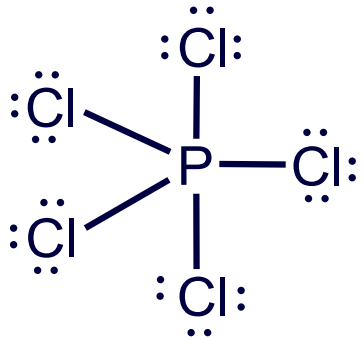
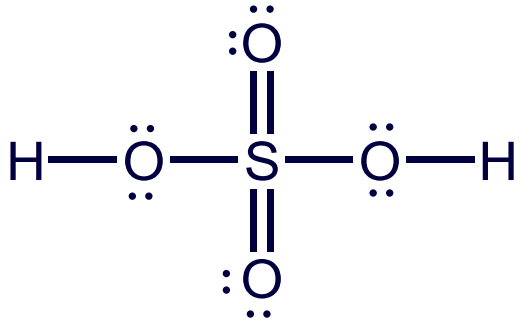
Exceptions to the Octet Rule

Expanded Valence Shells





An expanded valence shell is only possible for ***nonmetals from Period 3 or higher*** because these elements have available ***d orbitals***.

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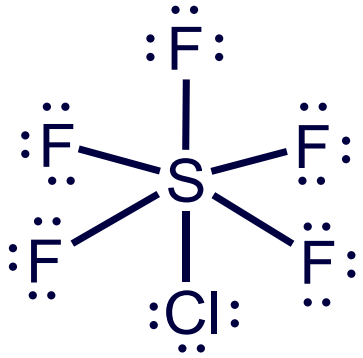
Sample Problem 10.5 **Drawing Lewis Structures for Octet-Rule Exceptions**

PROBLEM: Write a Lewis structure and identify the octet-rule exception for **(a)** $SClF_5$; **(b)** H_3PO_4 (draw two resonance forms and select the more important); **(c)** $BFCl_2$.

PLAN: Draw each Lewis structure and examine it for exceptions to the octet rule. Period 3 elements can have an expanded octet, while B commonly forms electron-deficient species.

SOLUTION:

(a) The central atom is S, which is in Period 3 and can have an expanded valence shell.



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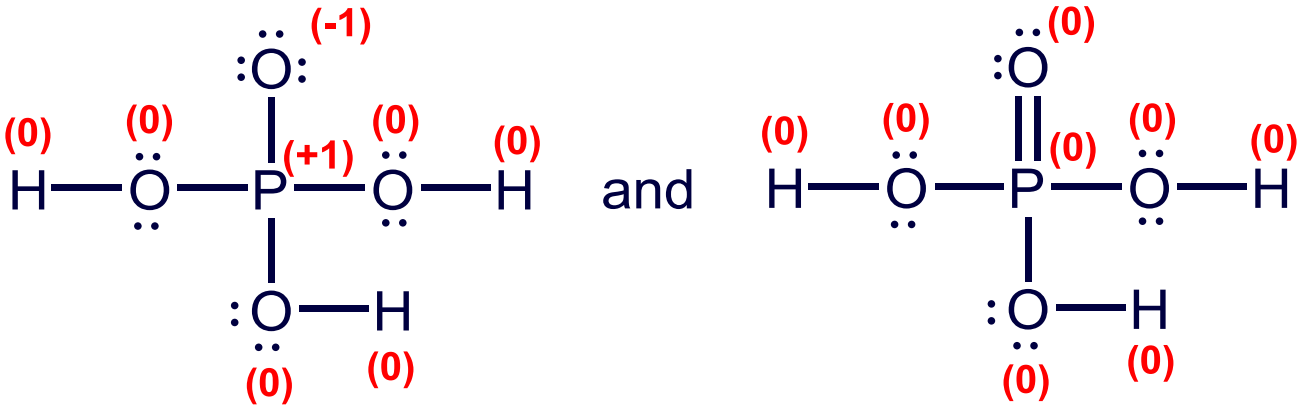
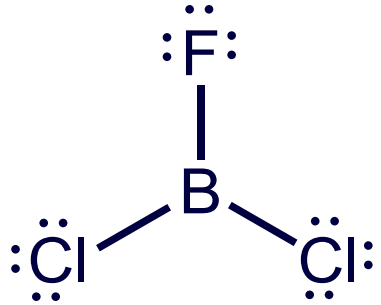
Sample Problem 10.5

(b) H_3PO_4 has two resonance forms and formal charges indicate the more important form.



(c) $BFCl_2$ is an electron-deficient molecule. B has only six electrons surrounding it.



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Valence-Shell Electron-Pair Repulsion Theory (VSEPR) and Molecular Shape

Each group of valence electrons around a central atom is located as far as possible from the others, to minimize repulsions.

A “group” of electrons is any number of electrons that occupies a localized region around an atom.

A single bond, double bond, triple bond, lone pair, or single electron all count as a single group.

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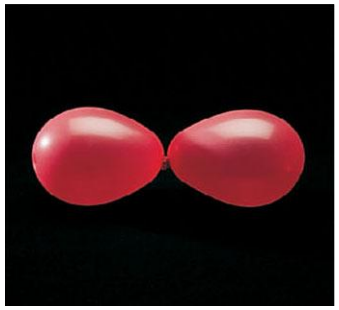
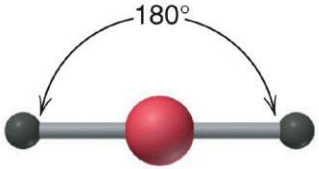
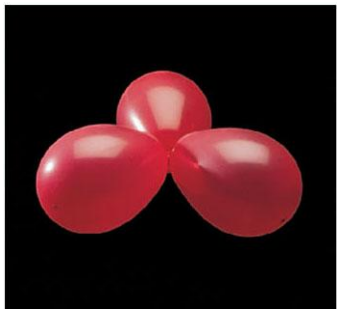
Figure 10.2 Electron-group repulsions and molecular shapes.

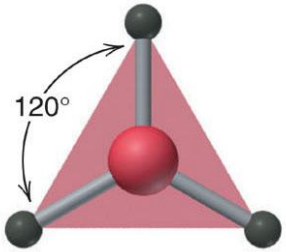


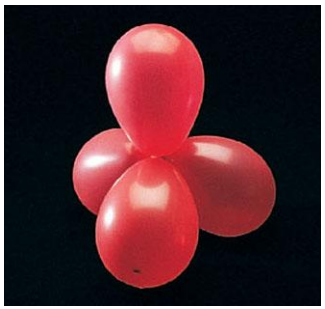
linear



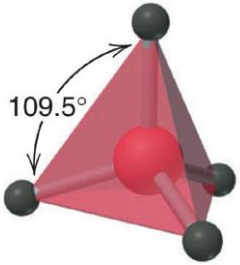


trigonal planar

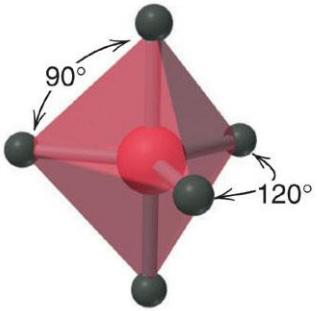




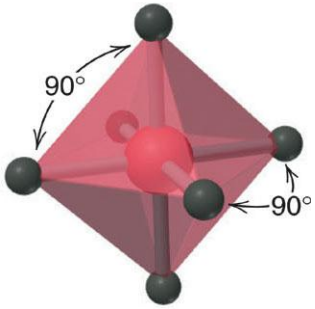
tetrahedral



trigonal bipyramidal



octahedral



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Electron-group Arrangement and Molecular Shape

The ***electron-group arrangement*** is defined by both bonding and nonbonding electron groups.

The ***molecular shape*** is the three-dimensional arrangement of nuclei joined by the bonding groups. This is defined only by the relative positions of the nuclei.

Molecular shape is classified using the designation

$\mathbf{AX}_m\mathbf{E}_n$

A = central atom
X = surrounding atom
E = nonbonding valence-electron group
m and *n* are integers

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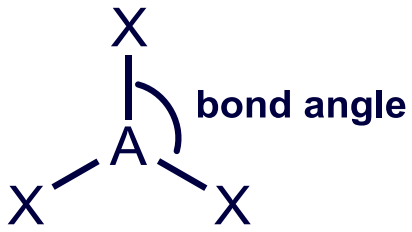
Bond Angle

The ***bond angle*** is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom.



The angles shown in Figure 10.2 are ***ideal*** bond angles, determined by basic geometry alone. Real bond angles deviate from the ideal value in many cases.

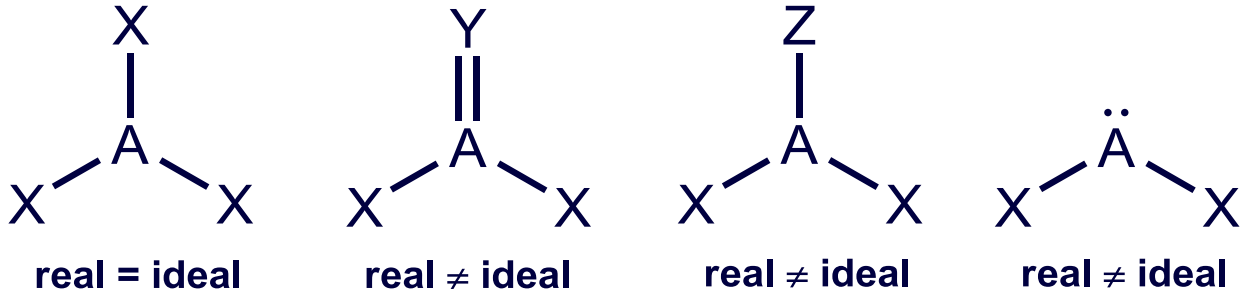


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Figure 10.3 **The single molecular shape of the linear electron-group arrangement.**

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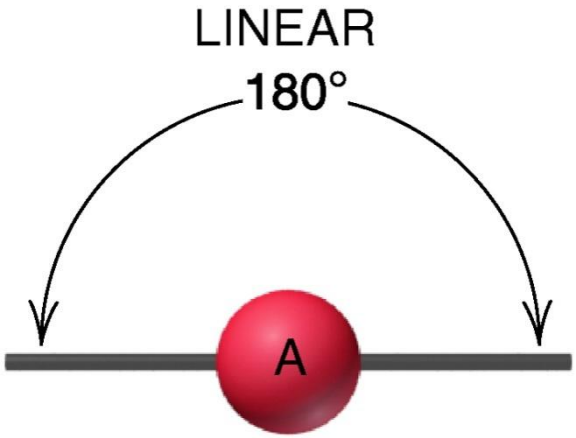
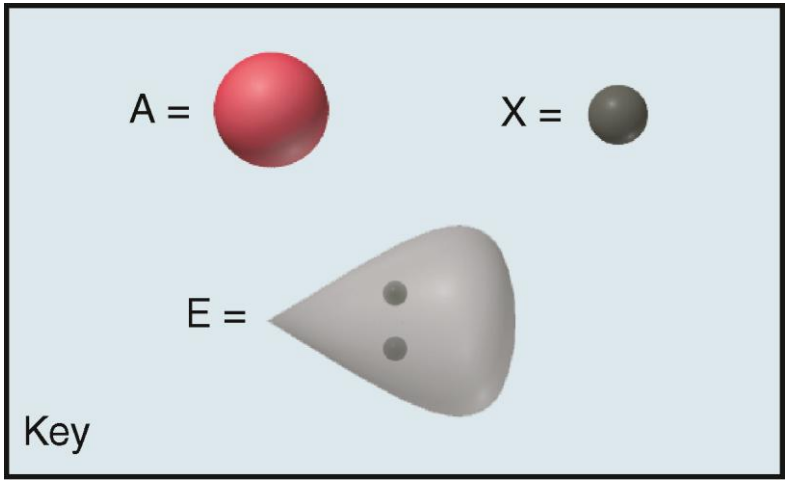


AX_2

Linear

Examples:
CS_2, HCN, BeF_2



This key refers to Figures 10.3 through 10.8.

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Figure 10.4 The two molecular shapes of the trigonal planar electron-group arrangement.

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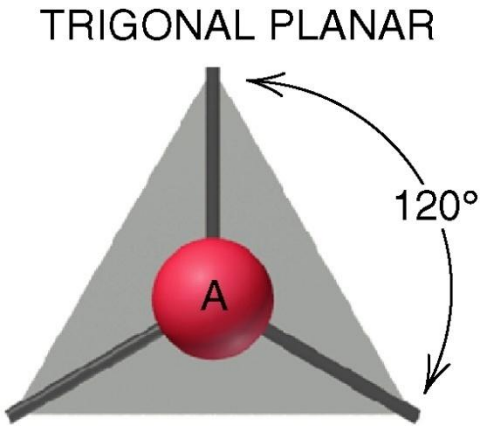
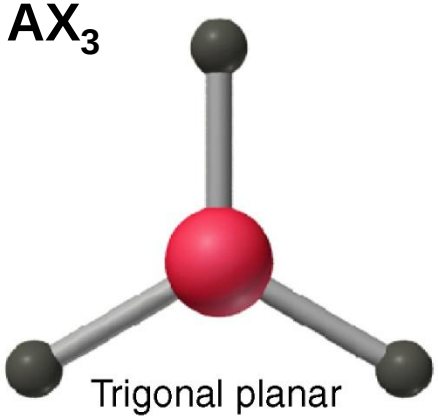
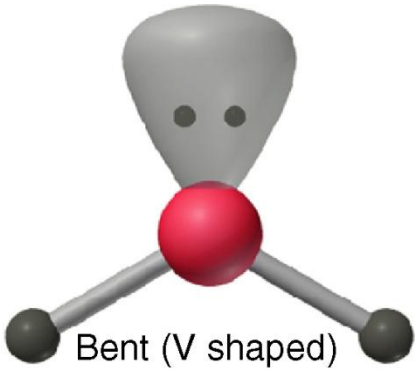


AX_3



Examples:
SO_3, BF_3, NO_3^-, CO_3^{2-}

AX_2E



Examples:
SO_2, O_3, $PbCl_2$, $SnBr_2$

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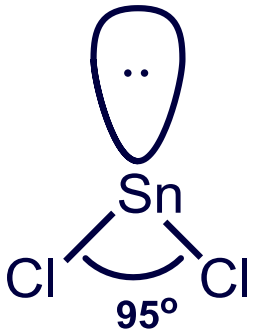
Factors Affecting Bond Angles

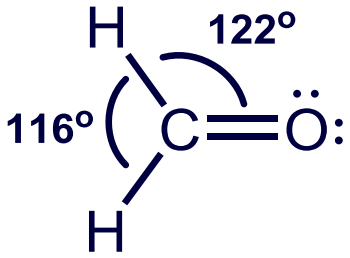
Nonbonding (Lone) Pairs



A lone pair repels bonding pairs more strongly than bonding pairs repel each other. This decreases the angle between the bonding pairs.

Repulsion of: Lp/Lp > Lp/Bp > Bp/Bp

Double Bonds



The ideal angle is 120°.

A double bond has greater electron density than a single bond, and repels the single bond electrons more than they repel each other.

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Figure 10.5 The three molecular shapes of the tetrahedral electron-group arrangement.

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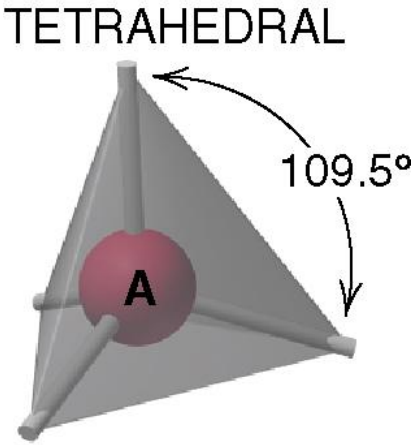
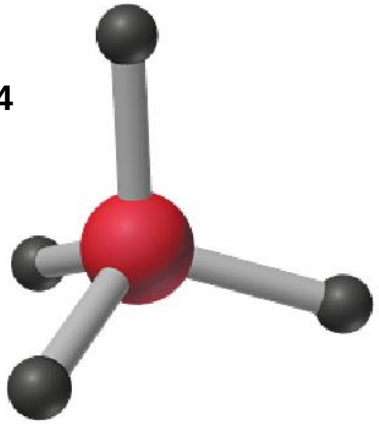


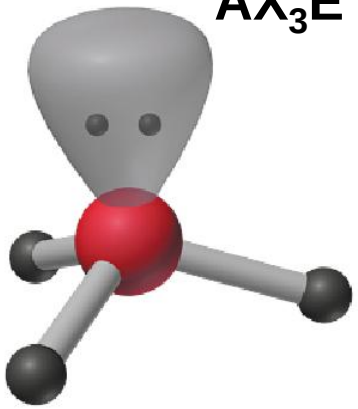
AX_4



Tetrahedral

Examples:
CH_4, $SiCl_4$,
SO_4^{2-}, ClO_4^-

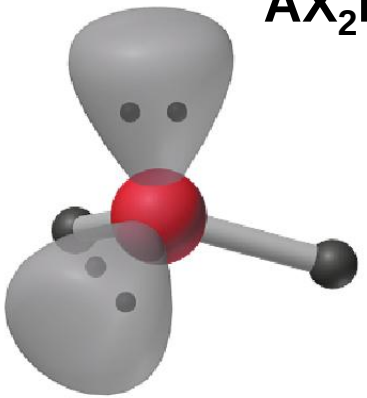
AX_3E



Trigonal pyramidal

Examples:
NH_3, PF_3
ClO_3^-, H_3O^+

AX_2E_2



Bent (V shaped)

Examples:
H_2O, OF_2, SCl_2

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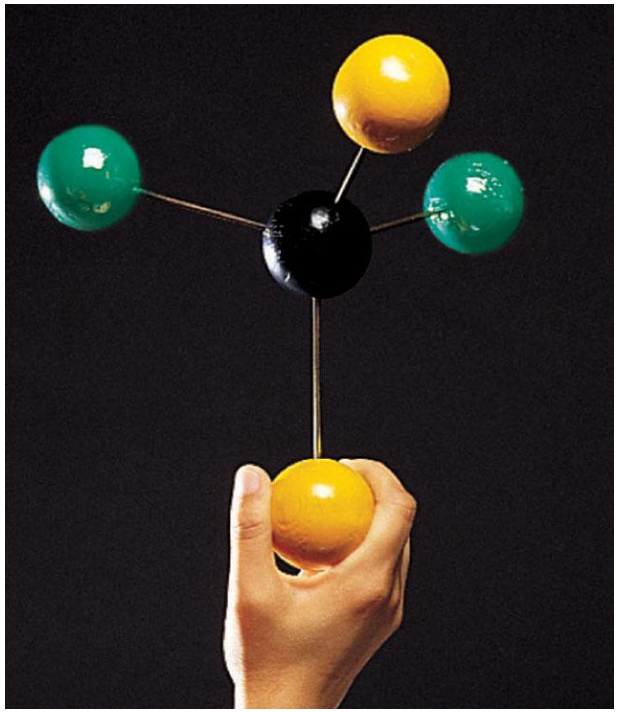
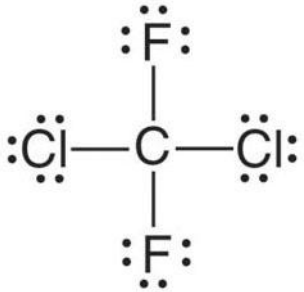
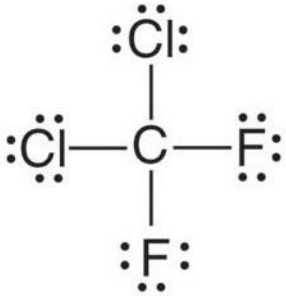
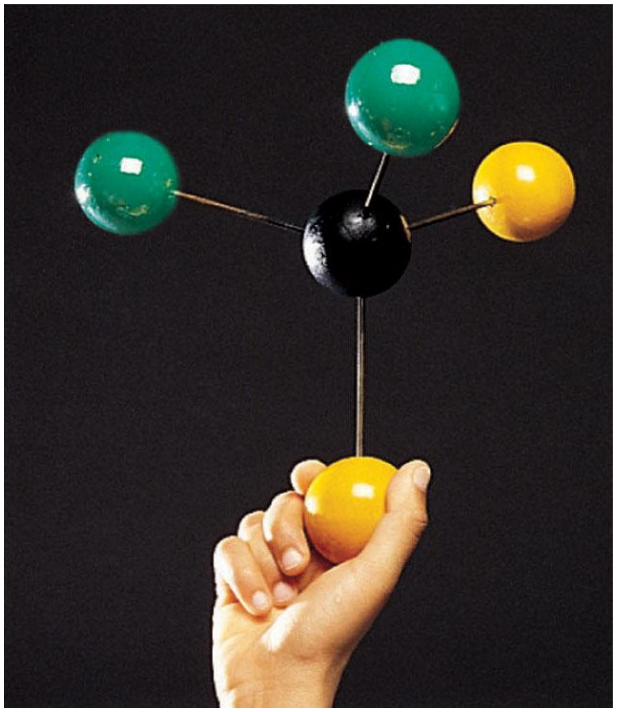
Figure 10.6 Lewis structures do not indicate molecular shape.





same as





twist to the right

twist to the left

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Figure 10.7 The four molecular shapes of the trigonal bipyramidal electron-group arrangement.

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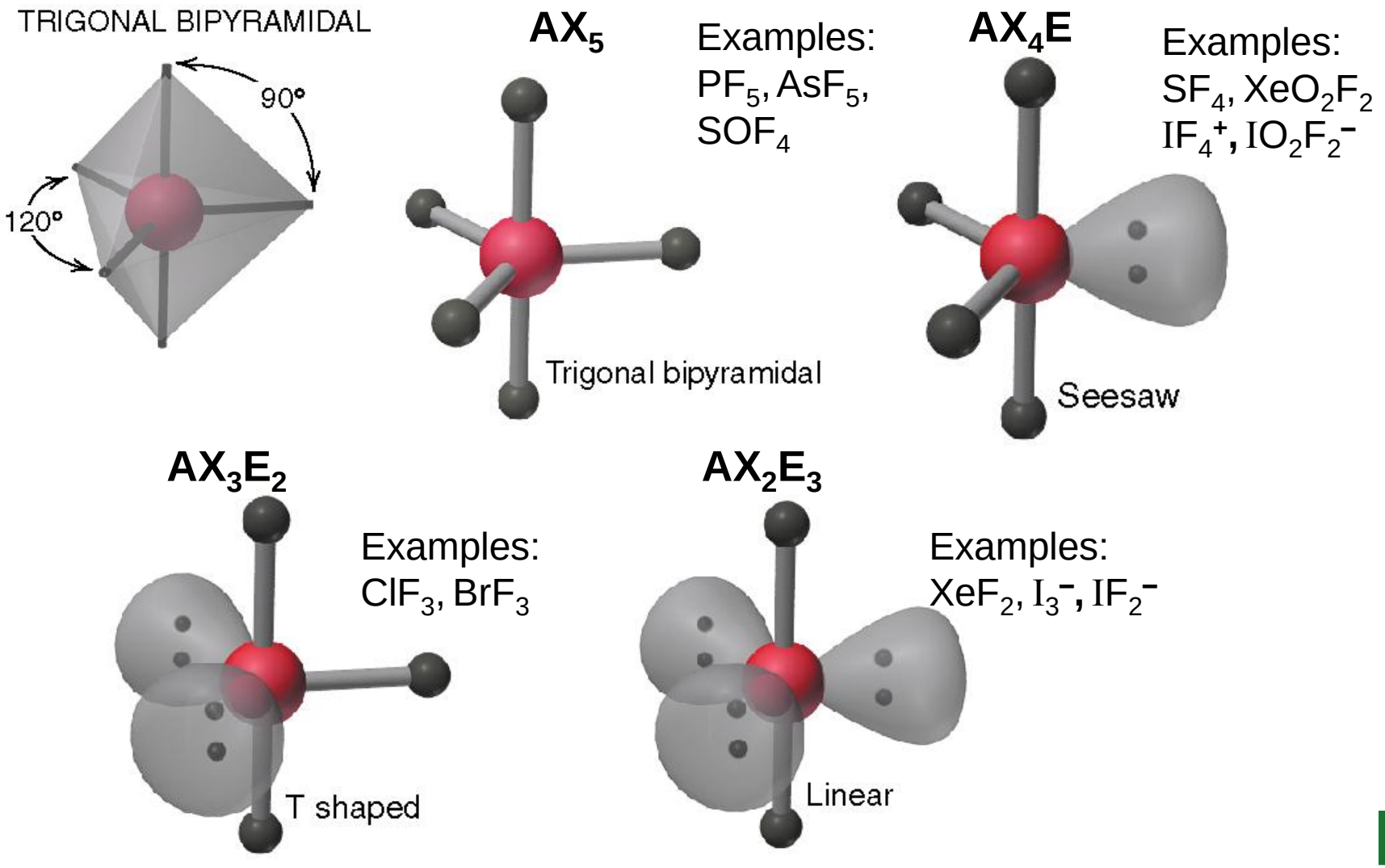

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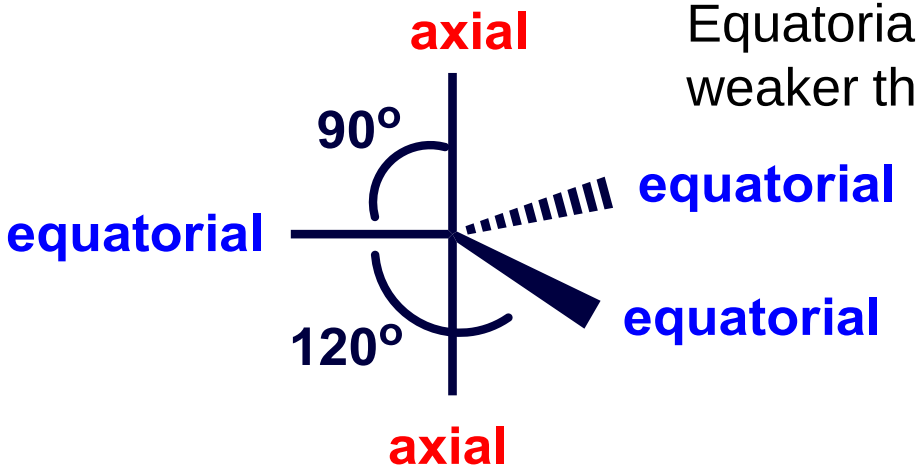
Axial and Equatorial Positions

A five electron-group system has two different positions for electron groups, and two ideal bond angles.



Equatorial-equatorial repulsions are weaker than axial-equatorial repulsions.

Where possible, lone pairs in a five electron-group system occupy ***equatorial*** positions.

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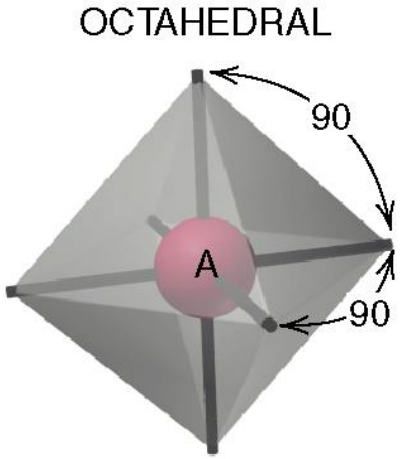
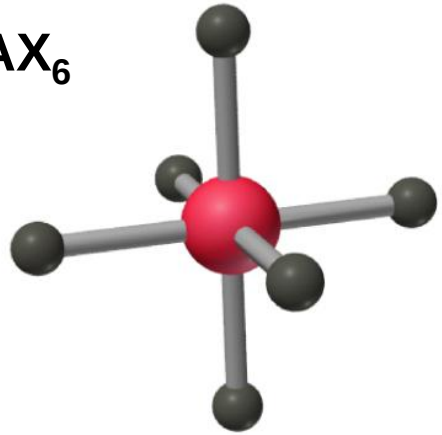
Figure 10.8 **The three molecular shapes of the octahedral electron-group arrangement.**



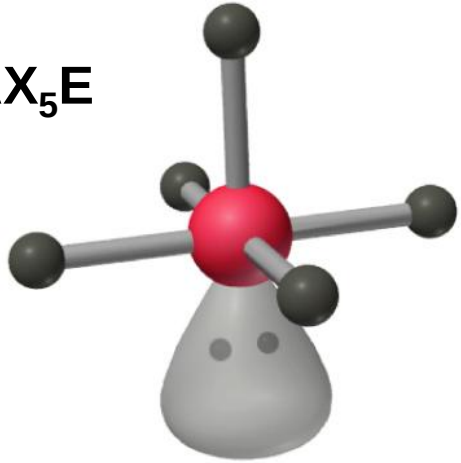
AX_6



Octahedral

Examples:
SF_6, IOF_5

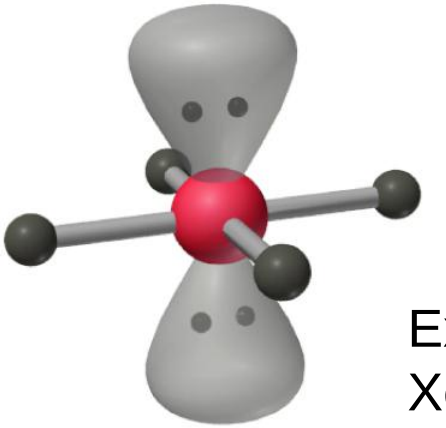
AX_5E



Square pyramidal

Examples:
BrF_5, TeF_5^-,
$XeOF_4$

AX_4E_2



Square planar

Examples:
XeF_4, ICl_4^-

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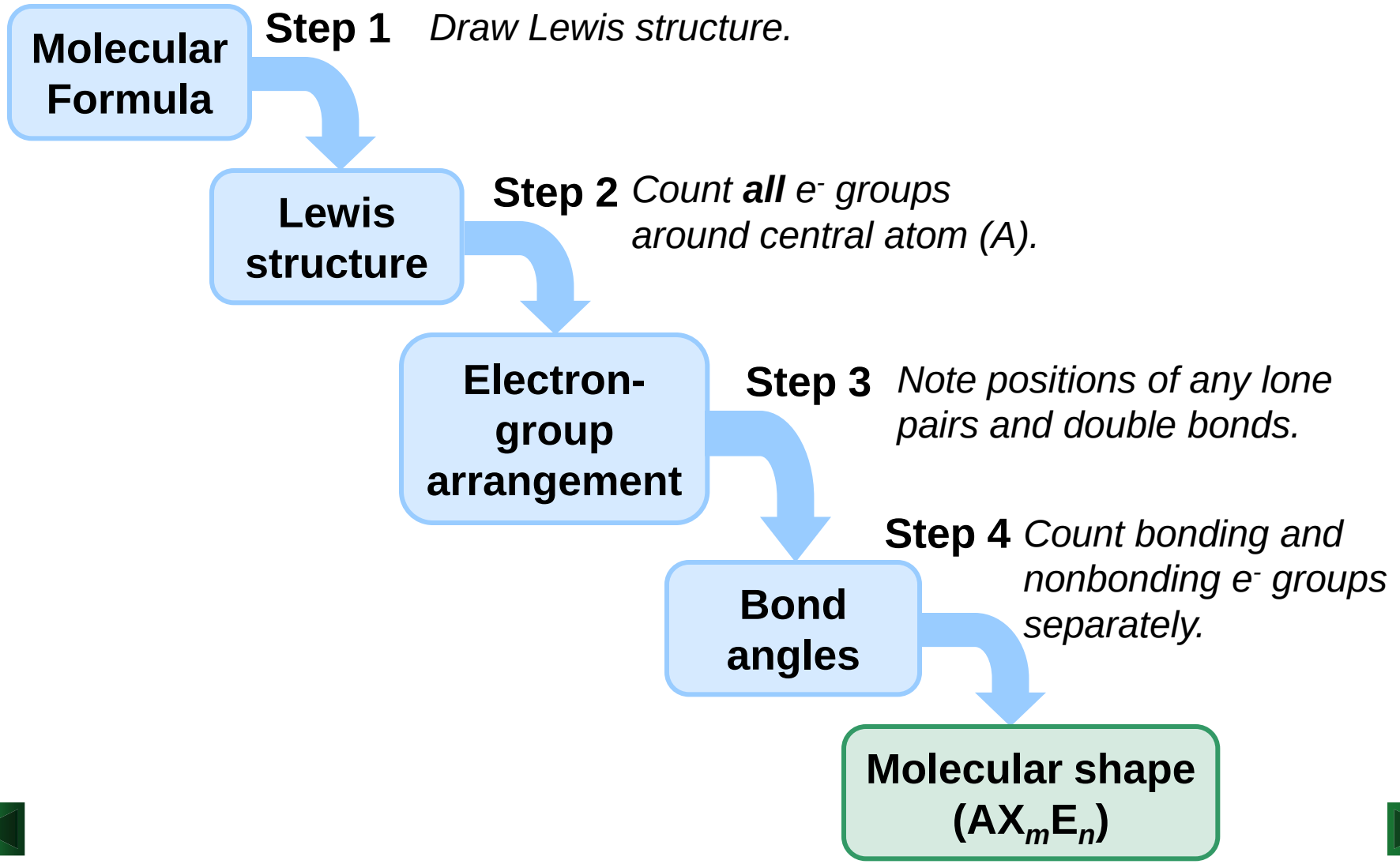
Figure 10.9 **The four steps in converting a molecular formula to a molecular shape**



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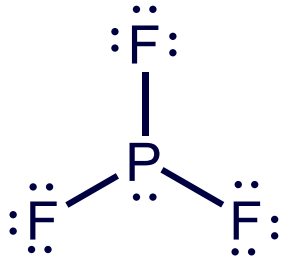
Sample Problem 10.6 **Examining Shapes with Two, Three, or Four Electron Groups**

PROBLEM: Draw the molecular shape and predict the bond angles (relative to the ideal bond angles) of **(a)** PF_3 and **(b)** $COCl_2$.

SOLUTION:

(a) For PF_3, there are 26 valence electrons. The Lewis structure is



There are four electron groups around P, giving a tetrahedral electron-group arrangement. **The ideal bond angle is therefore 109.5°.**

There is one lone pair and three bonding pairs, so the actual bond angle will be **less than 109.5°.**

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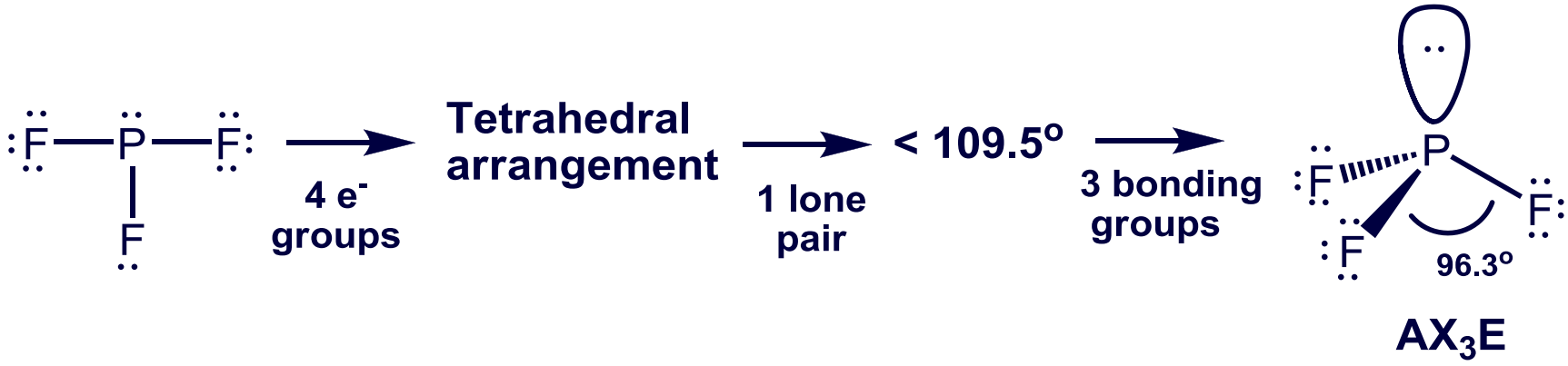
Sample Problem 10.6

The molecular shape for PF_3 is **trigonal pyramidal** (**AX_3E**).



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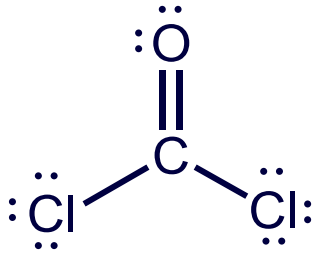
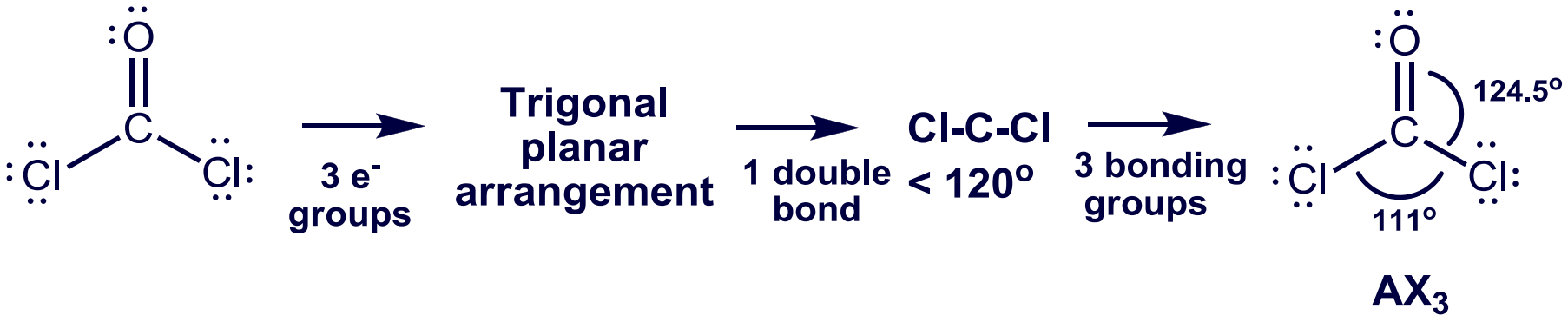
Sample Problem 10.6

(b) For $COCl_2$ there are 24 valence e^-. The Lewis structure is



There are three electron groups around C, giving a trigonal planar electron-group arrangement. **The ideal bond angle is 120°**, but the double bond will compress the Cl-C-Cl angle to **less than 120°.**



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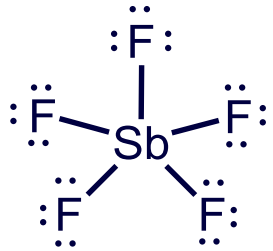
Sample Problem 10.7

Examining Shapes with Five or Six Electron Groups

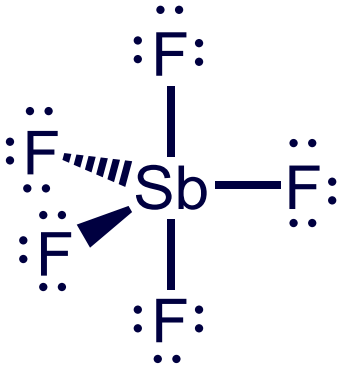
PROBLEM: Draw the molecular shapes and predict the bond angles (relative to the ideal bond angles) of **(a)** SbF_5 and **(b)** BrF_5.

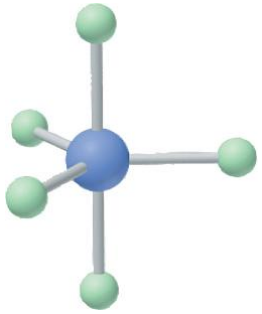
SOLUTION:

(a) SbF_5 has 40 valence e^-. The Lewis structure is



There are five electron groups around Sb, giving a trigonal bipyramidal electron-group arrangement. **The ideal bond angles are 120° between equatorial groups and 90° between axial groups.**





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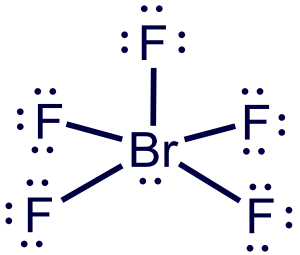
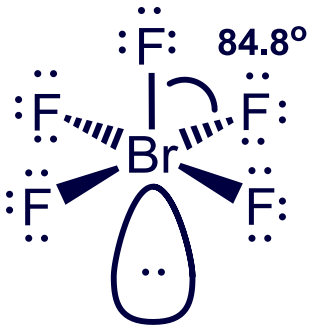
Sample Problem 10.7

(b) BrF_5 has 42 valence e$^-$. The Lewis structure is



There are six electron groups around Br, giving an octahedral electron-group arrangement. **The ideal bond angles are 90°**. There is one lone pair, so the bond angles will be **less than 90°** and the molecular shape is **square pyramidal**.



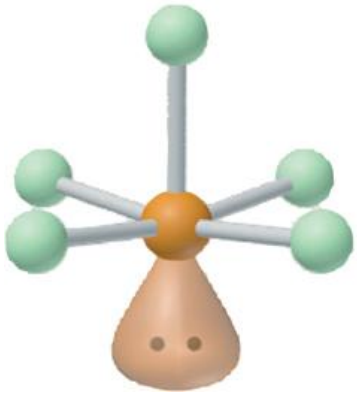


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Figure 10.10 **The tetrahedral shapes around the central atoms and the overall shapes of ethane (A) and ethanol (B).**

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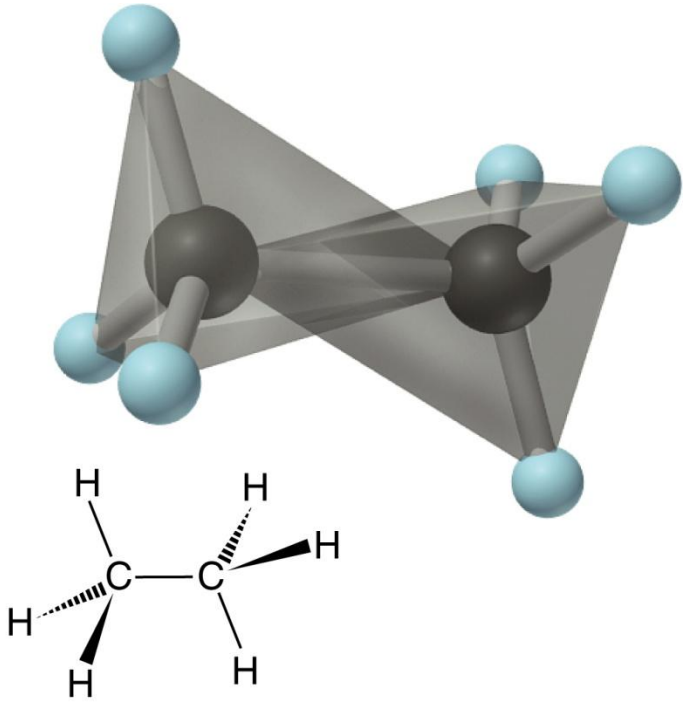
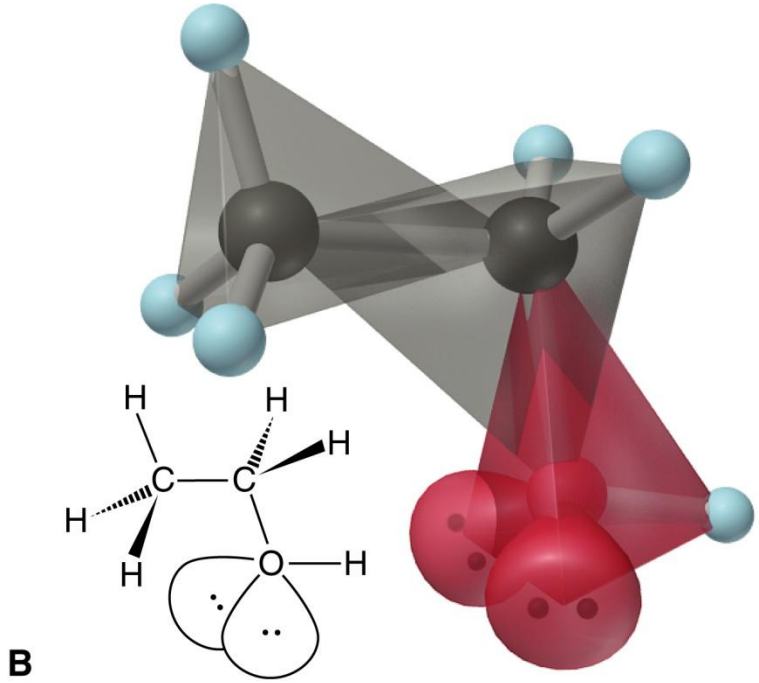


A

ethane

CH_3CH_3



B

ethanol

CH_3CH_2OH

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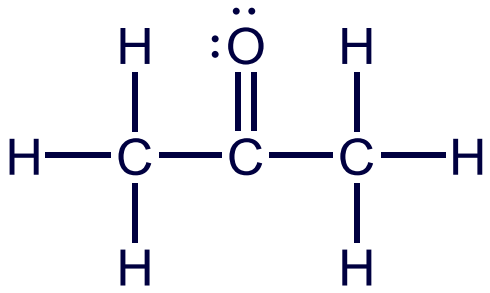
Sample Problem 10.8 **Predicting Molecular Shapes with More Than One Central Atom**

PROBLEM: Determine the shape around each of the central atoms in acetone, $(CH_3)_2CO$.

PLAN: There are three central C atoms, two of which are in CH_3– groups. We determine the shape around one central atom at a time.

SOLUTION:

Step 1: The Lewis structure is



Step 2: Each CH_3– group has four electron groups around its central C, so the electron-group arrangement is *tetrahedral*. The third C atom has three electron groups around it, with a *trigonal planar* arrangement.

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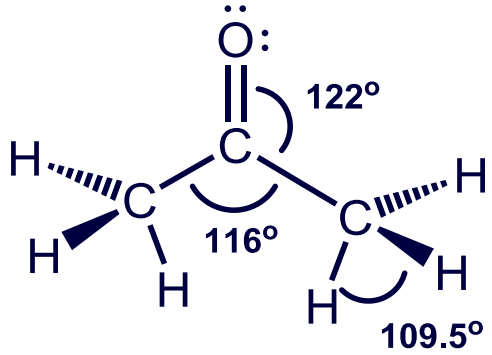
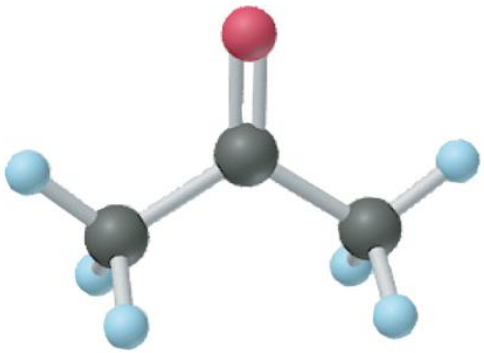
Sample Problem 10.8

Step 3: The H-C-H bond angle in each CH_3– group should be near the ideal value of 109.5°. The C=O double bond will compress the C-C-C angle to less than the ideal angle of 120°.

Step 4: The shape around the C in each CH_3– group is **tetrahedral** (**AX_4**). The shape around the middle C is **trigonal planar** (**AX_3).**





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Molecular Shape and Molecular Polarity

Overall ***molecular polarity*** depends on both ***shape*** and ***bond polarity***.

The polarity of a molecule is measured by its ***dipole moment*** (**μ**), which is given in the unit *debye* (D).

A molecule is polar if

- it contains one or more ***polar bonds*** and
- the individual bond dipoles ***do not cancel***.

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Figure 10.11 The orientation of polar molecules in an electric field.

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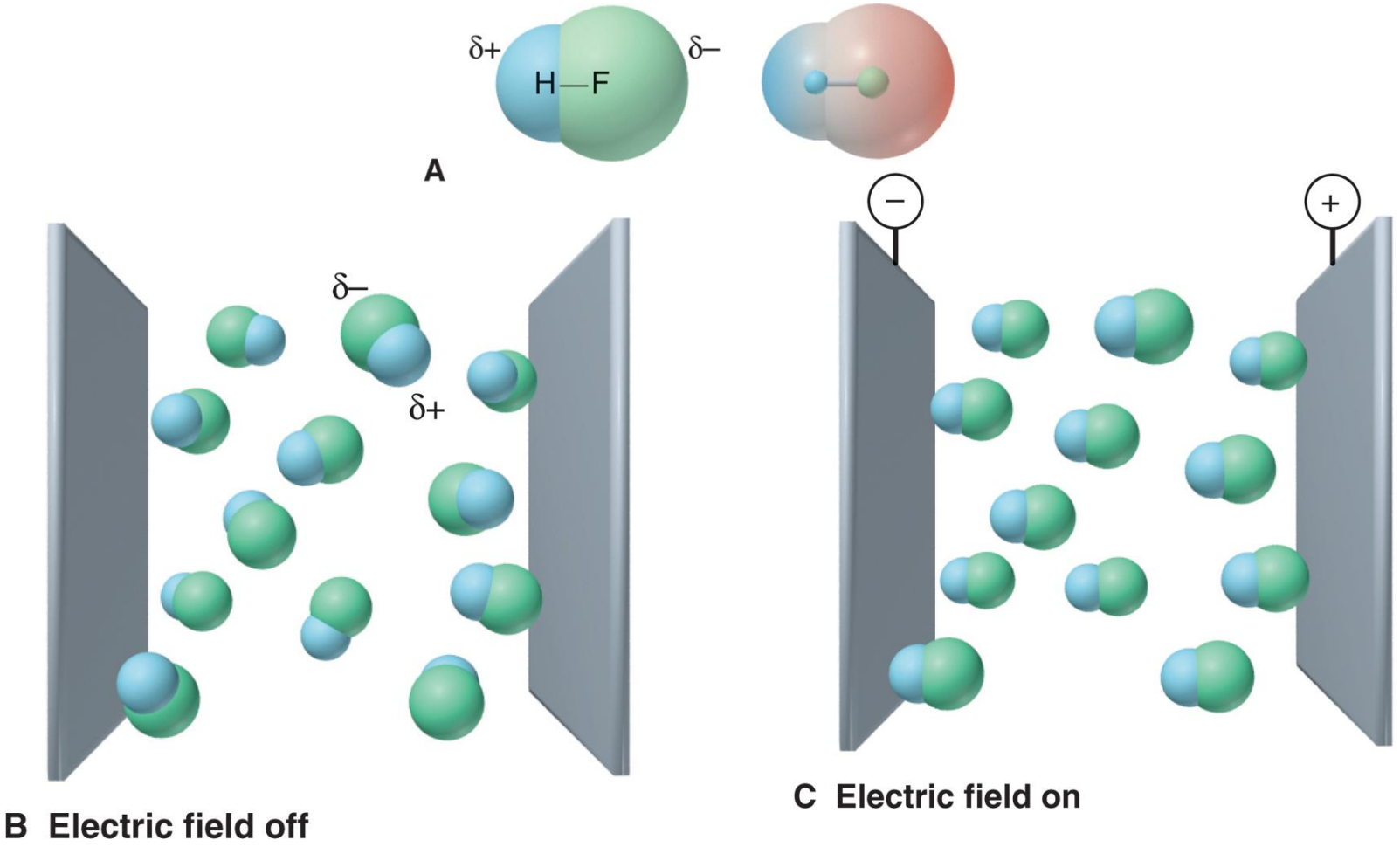

Molecules are randomly oriented.

Molecules become oriented when the field is turned on.

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Bond Polarity, Bond Angle, and Dipole Moment

Example: CO_2

The ΔEN between C (EN = 2.5) and O (EN = 3.5) makes each C=O bond polar.

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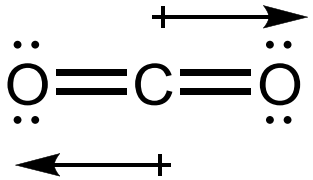

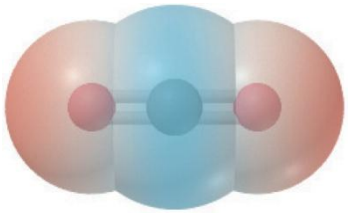

CO_2 is linear, the bond angle is 180°, and the individual bond polarities therefore cancel. The molecule has ***no net dipole moment*** (μ = 0 D).

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Bond Polarity, Bond Angle, and Dipole Moment

Example: H_2O

The ΔEN between H (EN = 2.1) and O (EN = 3.5) makes each H-O bond polar.

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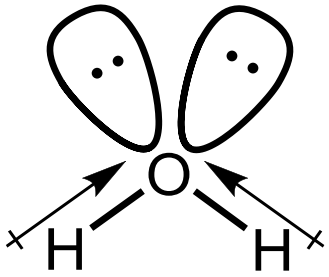

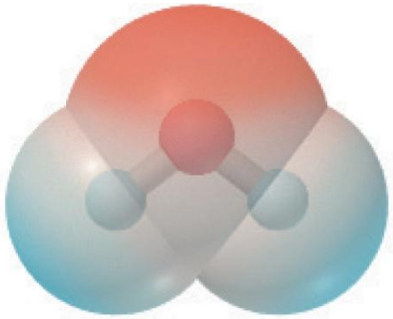

H_2O has a V shaped geometry and the individual bond polarities do **not** cancel. This molecule has an ***overall molecular polarity***. The O is partially negative while the H atoms are partially positive.

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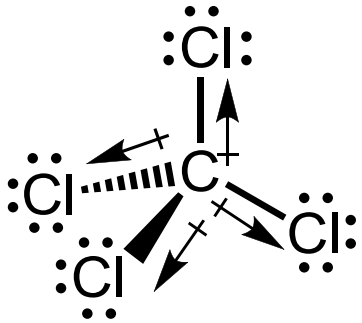
Bond Polarity, Bond Angle, and Dipole Moment

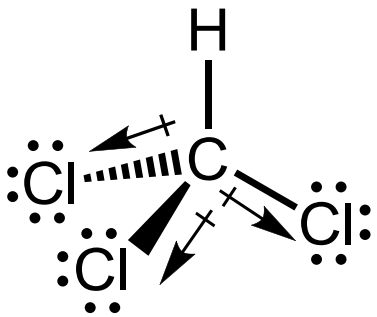
Molecules with the same shape may have different polarities.

CCl_4



Bonds are polar, but individual bond polarities cancel.

$CHCl_3$



Bond polarities do not cancel. This molecule is polar (μ = 1.01 D).

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Sample Problem 10.9 Predicting the Polarity of Molecules

PROBLEM: For each of the following use the molecular shape and EN values and trends (Figure 9.20, p. 349) to predict the direction of bond and molecular polarity, if present.

(a) Ammonia, NH_3 **(b)** Boron trifluoride, BF_3

(c) Carbonyl sulfide, COS (atom sequence SCO)

PLAN: We draw and name the molecular shape, and mark each polar bond with a polar arrow pointing toward the atom with the higher EN. If bond polarities balance one another, the molecule is nonpolar. If they reinforce each other, we show the direction of overall molecular polarity.

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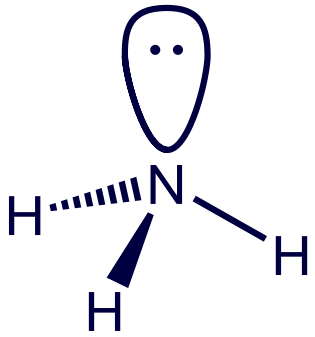
Sample Problem 10.9

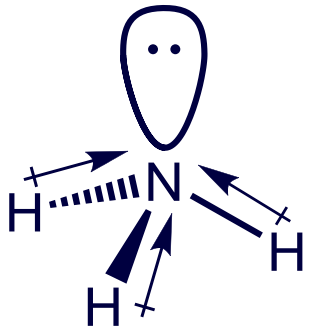
SOLUTION:

(a) NH_3 has 8 valence e^- and a trigonal pyramidal molecular shape.

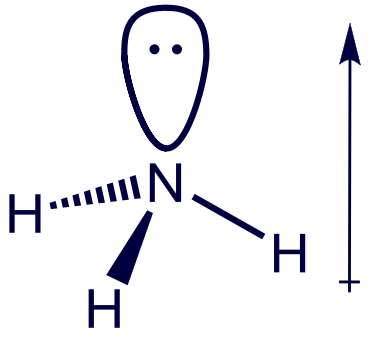
N (EN = 3.0) is more electronegative than H (EN = 2.1) so bond polarities point towards N.



molecular shape



bond polarities



molecular polarity

Ammonia is polar overall.

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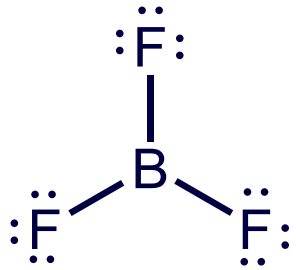
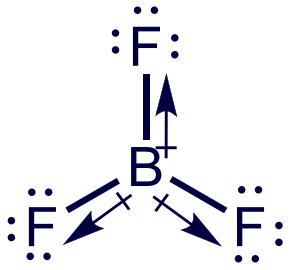
Sample Problem 10.9

(b) BF_3 has 24 valence e^- and a trigonal planar molecular shape.

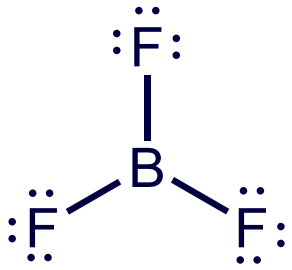
F (EN = 4.0) is more electronegative than B (EN = 2.0) so bond polarities point towards F.



molecular shape



bond polarities



molecular polarity

Individual bond polarities balance each other and BF_3 has no molecular polarity.

Boron trifluoride is nonpolar.

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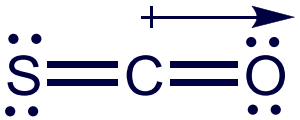
Sample Problem 10.9

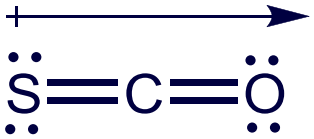
(c) COS has a linear shape.

C and S have the same EN (2.5) but the C=O bond (ΔEN = 1.0) is quite polar.

molecular shape



bond polarities



molecular polarity

Carbonyl sulfide is polar overall.

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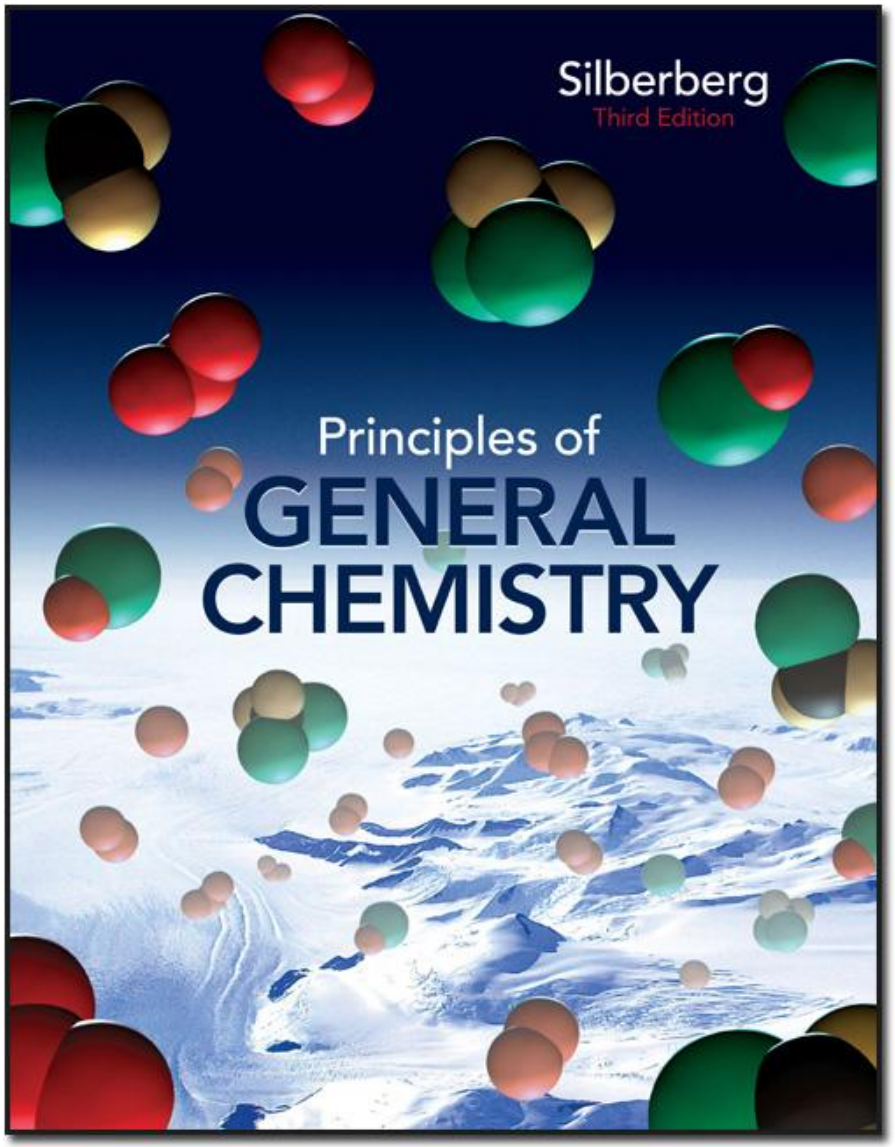

Chapter 11

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 11

Theories of Covalent Bonding

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Theories of Covalent Bonding

11.1 Valence Bond (VB) Theory and Orbital Hybridization

11.2 Modes of Orbital Overlap and the Types of Covalent Bonds

11.3 Molecular Orbital (MO) Theory and Electron Delocalization

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Valence Bond (VB) Theory

The basic principle of VB theory:

A covalent bond forms when the orbitals of two atoms ***overlap*** and a pair of electrons occupy the overlap region.

The space formed by the overlapping orbitals can accommodate a ***maximum of two electrons*** and these electrons must have ***opposite (paired) spins***.

The greater the orbital overlap, the stronger the bond.

Extent of orbital overlap depends on orbital shape and direction.

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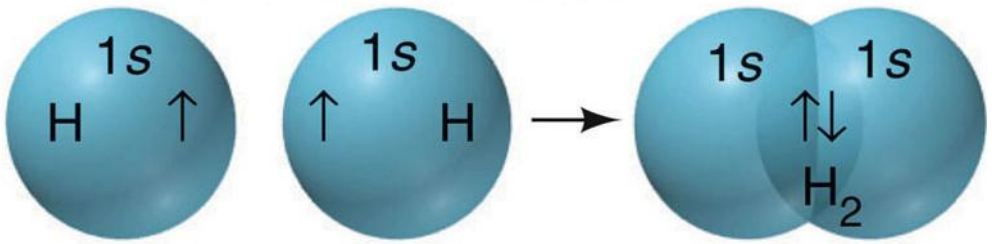
Figure 11.1 Orbital overlap and spin pairing in H_2.



A covalent bond results from the overlap of orbitals from two atoms.

The shared space is occupied by two electrons, which have opposite spins.

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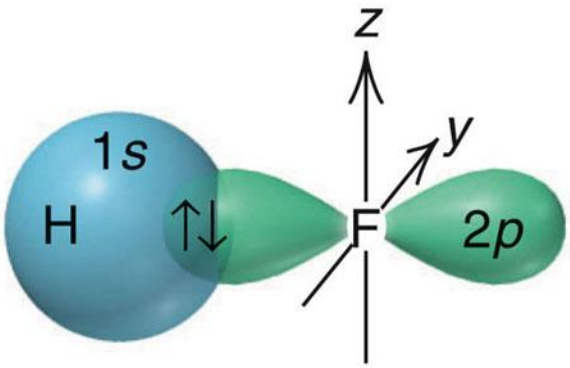
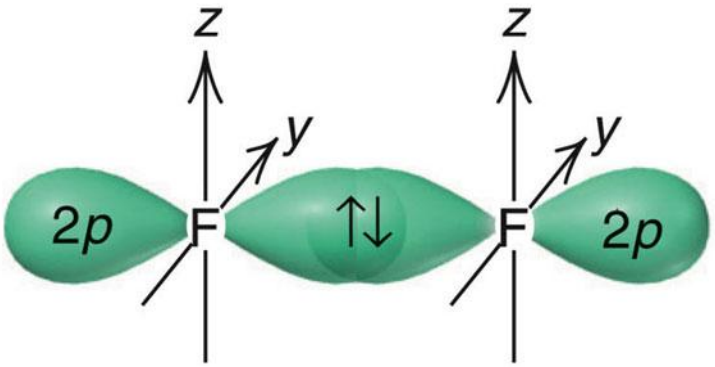
Figure 11.1 Orbital orientation and maximum overlap.



Hydrogen fluoride, HF.



Fluorine, F_2.

The greater the extent of orbital overlap, the stronger the bond.

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VB Theory and Orbital Hybridization

The orbitals that form when bonding occurs are ***different*** from the atomic orbitals in the isolated atoms.

If no change occurred, we could not account for the molecular shapes that are observed.

Atomic orbitals “mix” or ***hybridize*** when bonding occurs to form ***hybrid orbitals***.

The spatial orientation of these hybrid orbitals correspond with observed molecular shapes.

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Features of Hybrid Orbitals

The ***number*** of hybrid orbitals formed ***equals*** the number of atomic orbitals mixed.

The ***type*** of hybrid orbitals formed ***varies*** with the types of atomic orbitals mixed.

The ***shape*** and ***orientation*** of a hybrid orbital ***maximizes*** overlap with the other atom in the bond.

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Figure 11.2 Formation and orientation of *sp* hybrid orbitals and the bonding in $BeCl_2$.

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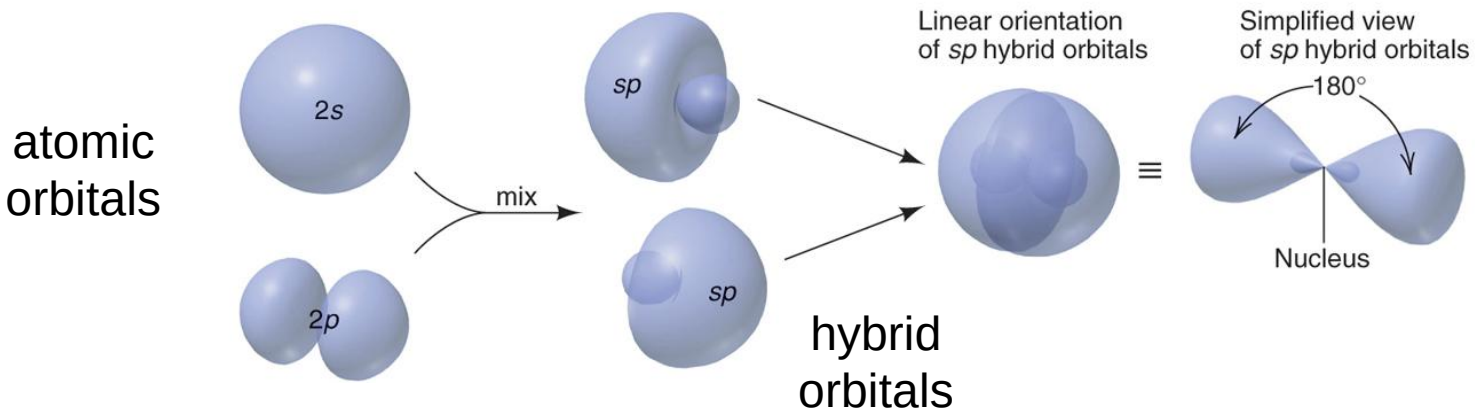

One 2*s* and one 2*p* atomic orbital mix to form two sp hybrid orbitals.

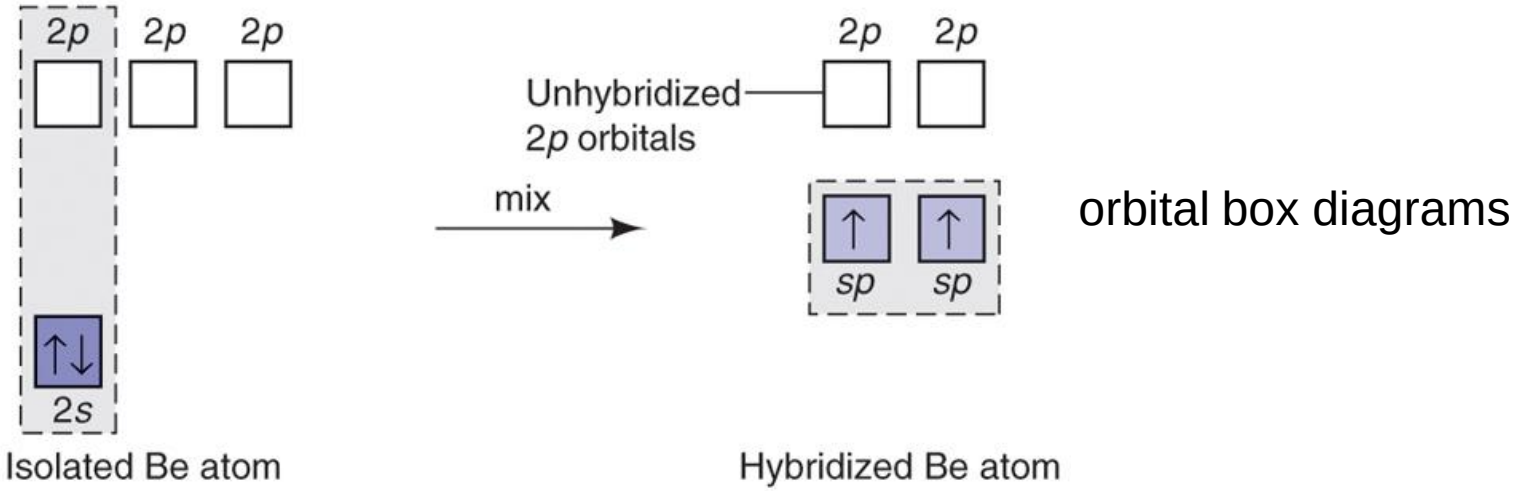

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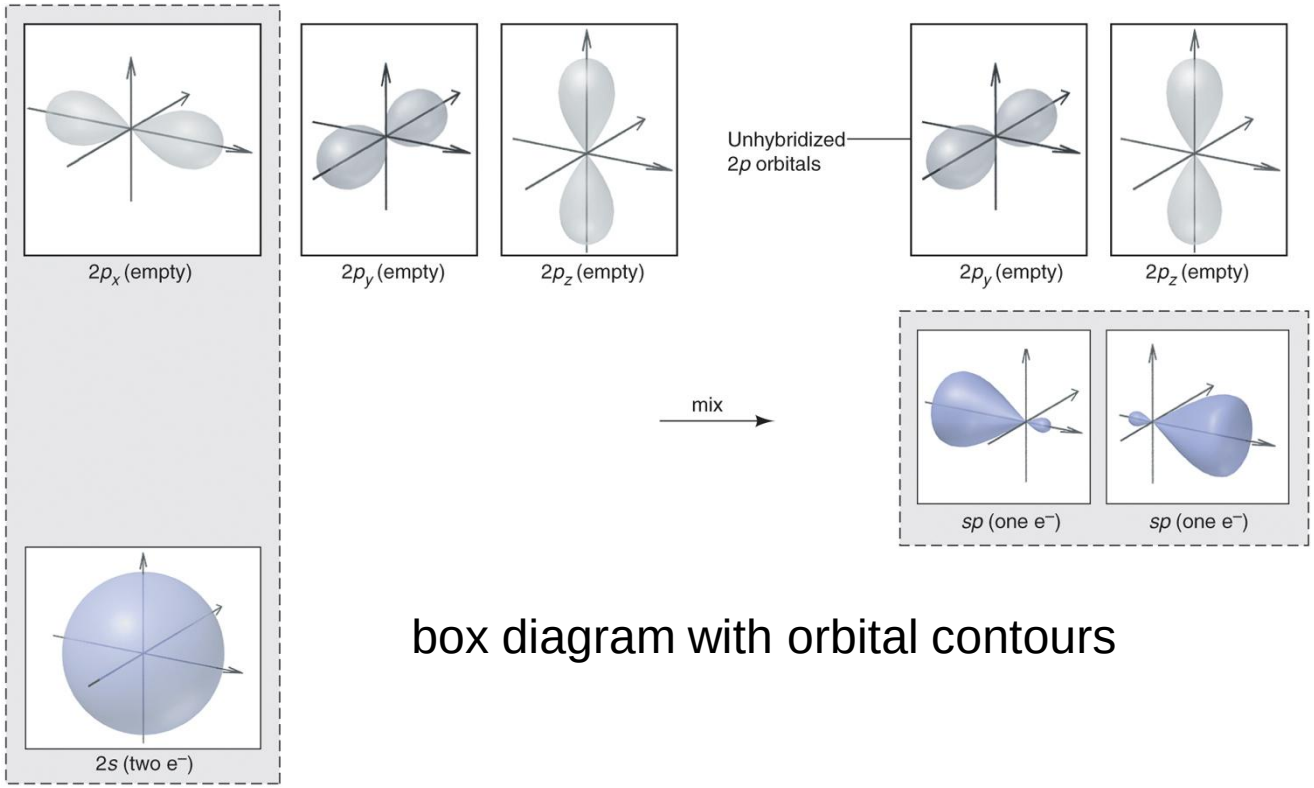
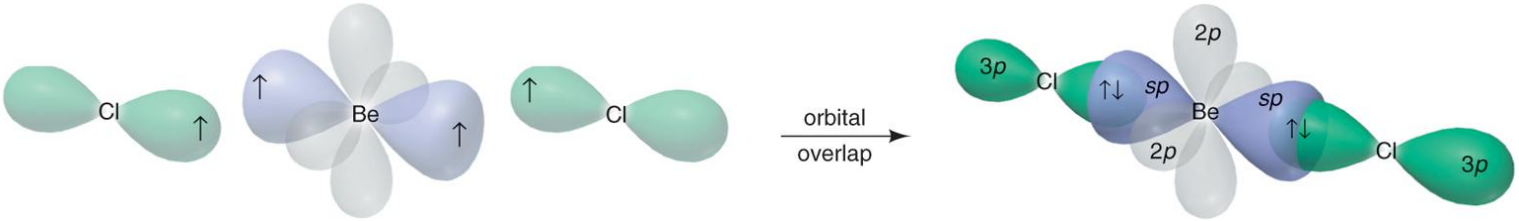
Figure 11.2 continued



box diagram with orbital contours



Overlap of Be and Cl orbitals to form $BeCl_2$.

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Figure 11.3 The sp^2 hybrid orbitals in BF_3.

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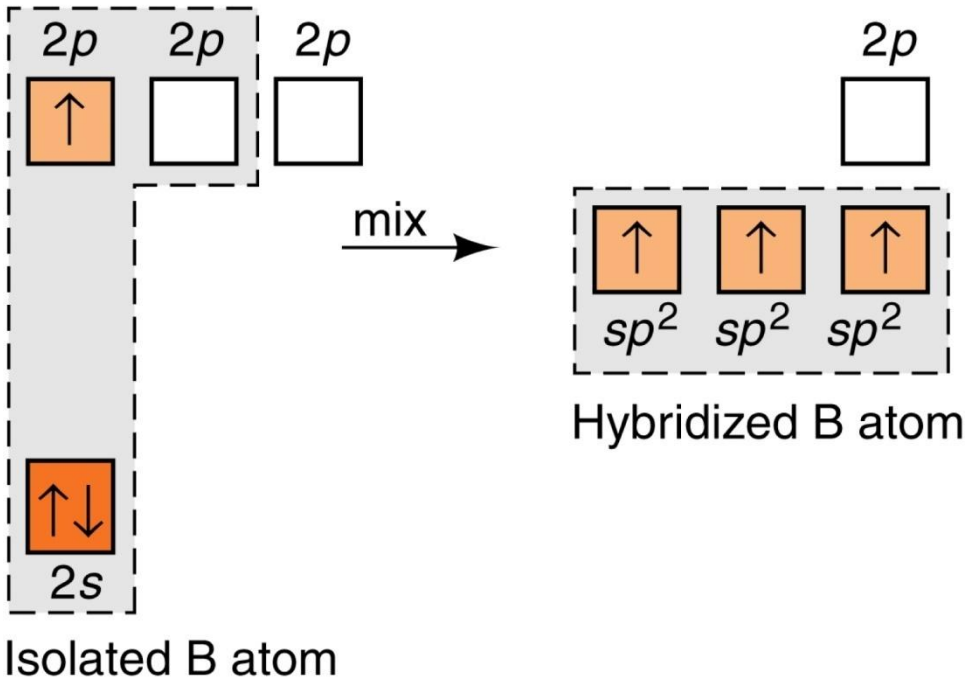

Mixing one *s* and two *p* orbitals gives three sp^2 hybrid orbitals. The third 2*p* orbital remains unhybridized.

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Figure 11.3 continued

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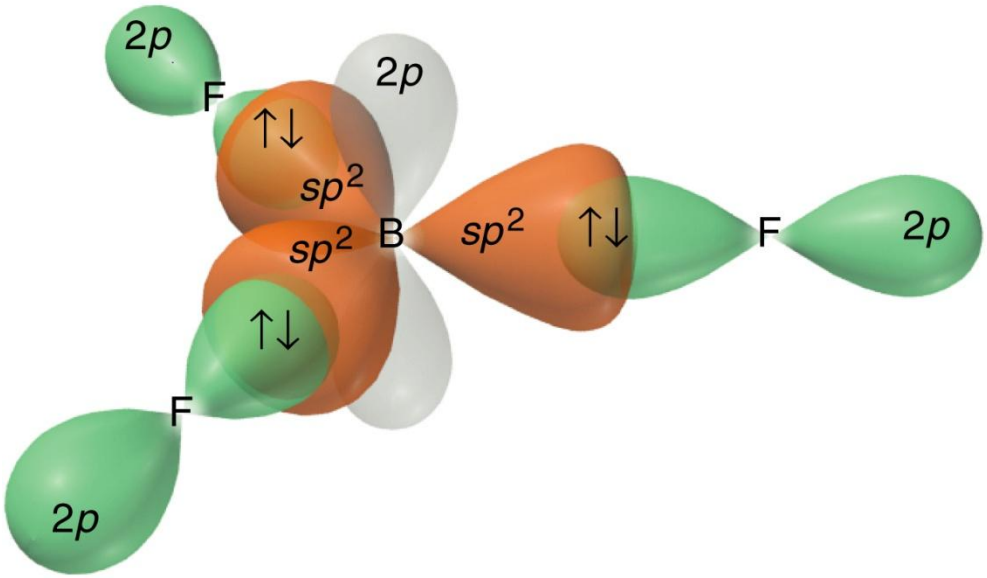

The three sp^2 orbitals point to the corners of an equilateral triangle, their axes 120° apart.

Each half-filled sp^2 orbital overlaps with the half-filled $2p$ orbital of a F atom.

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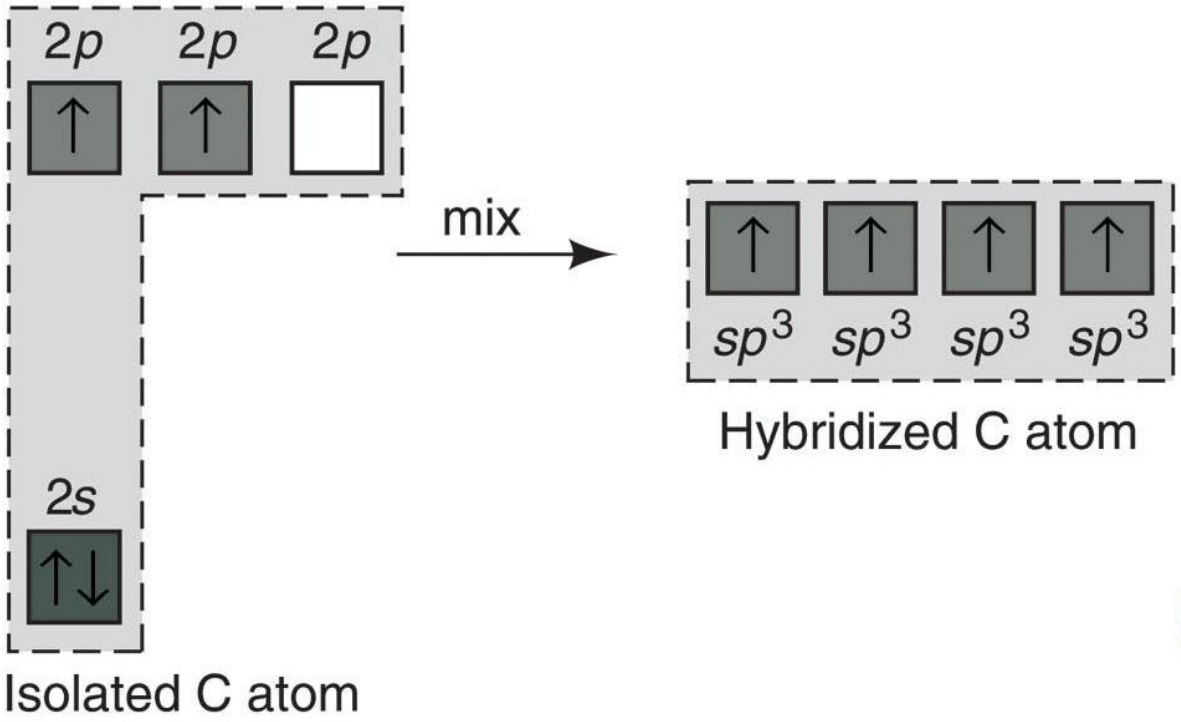
Figure 11.4 The sp^3 hybrid orbitals in CH_4.



The four sp^3 orbitals adopt a tetrahedral shape.

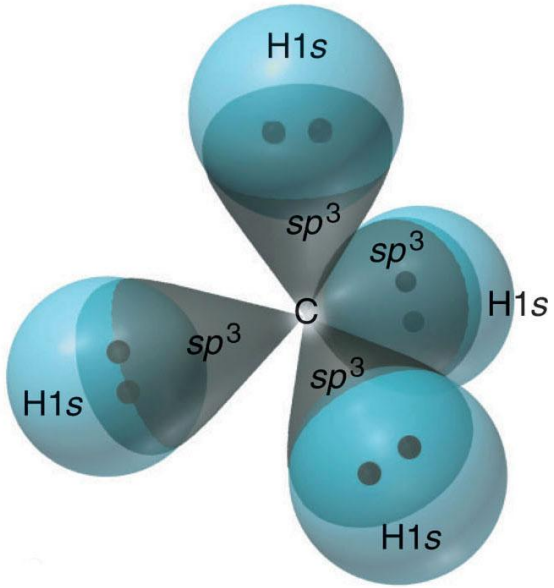


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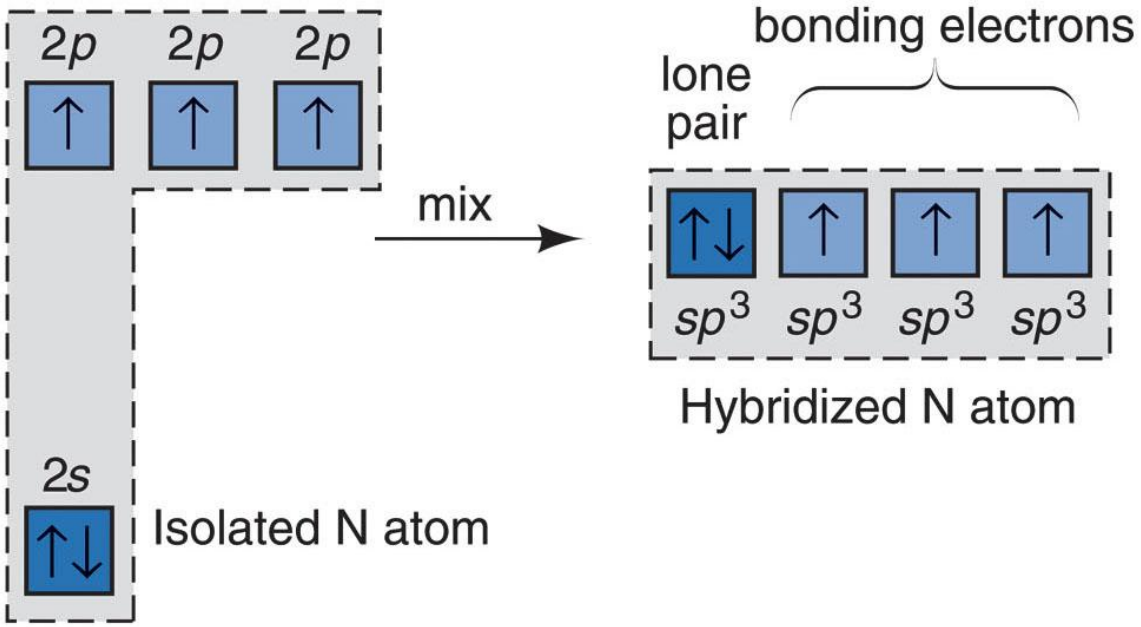
Figure 11.5 The sp^3 hybrid orbitals in NH_3.



The N lone pair occupies an sp^3 hybrid orbital, giving a trigonal pyramidal shape.

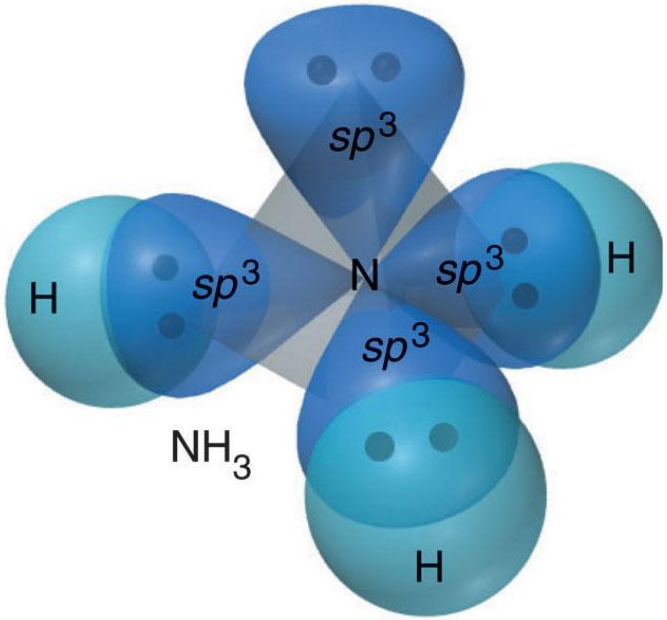


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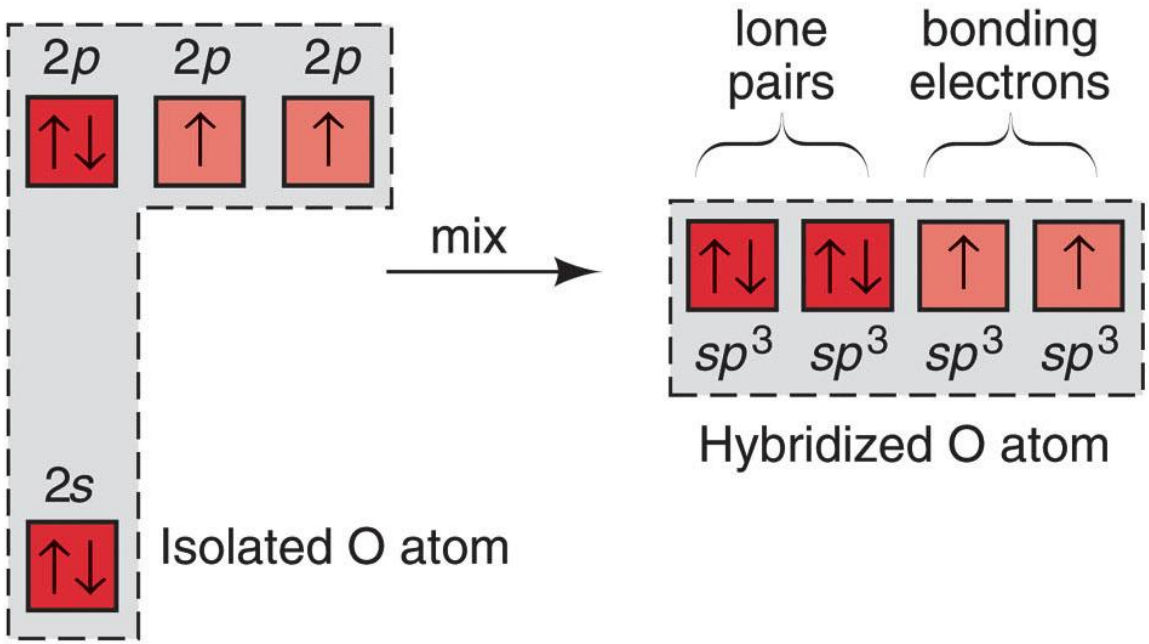
Figure 11.5 continued **The sp^3 hybrid orbitals in H_2O.**



The O lone pairs occupy sp^3 hybrid orbitals, giving a bent shape.

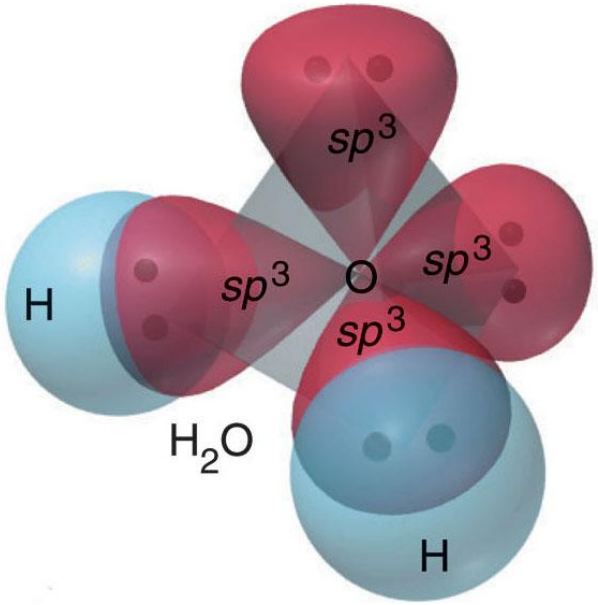


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Figure 11.6 The sp^3d hybrid orbitals in PCl_5.

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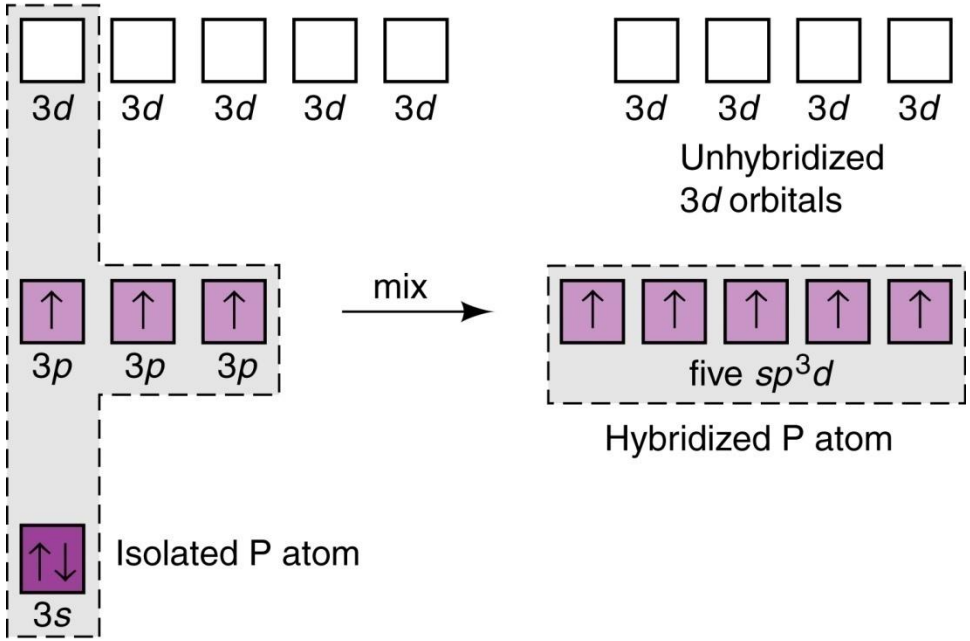
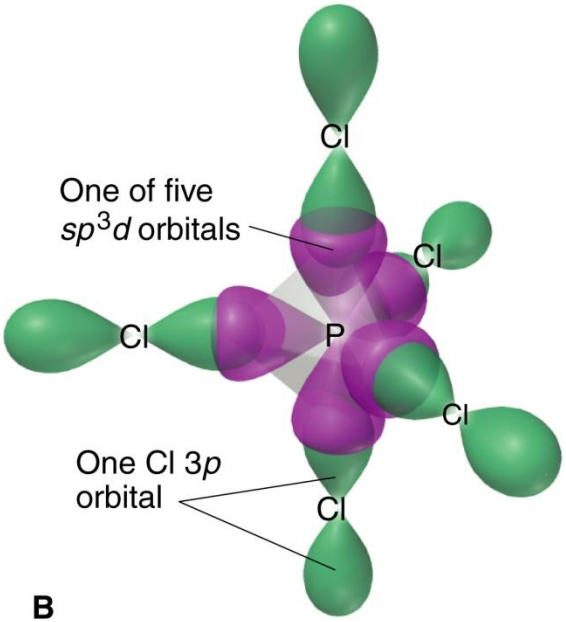


A

The formation of more than four bonding orbitals requires *d* orbital involvement in hybridization.



B

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Figure 11.7 The sp^3d^2 hybrid orbitals in SF_6.

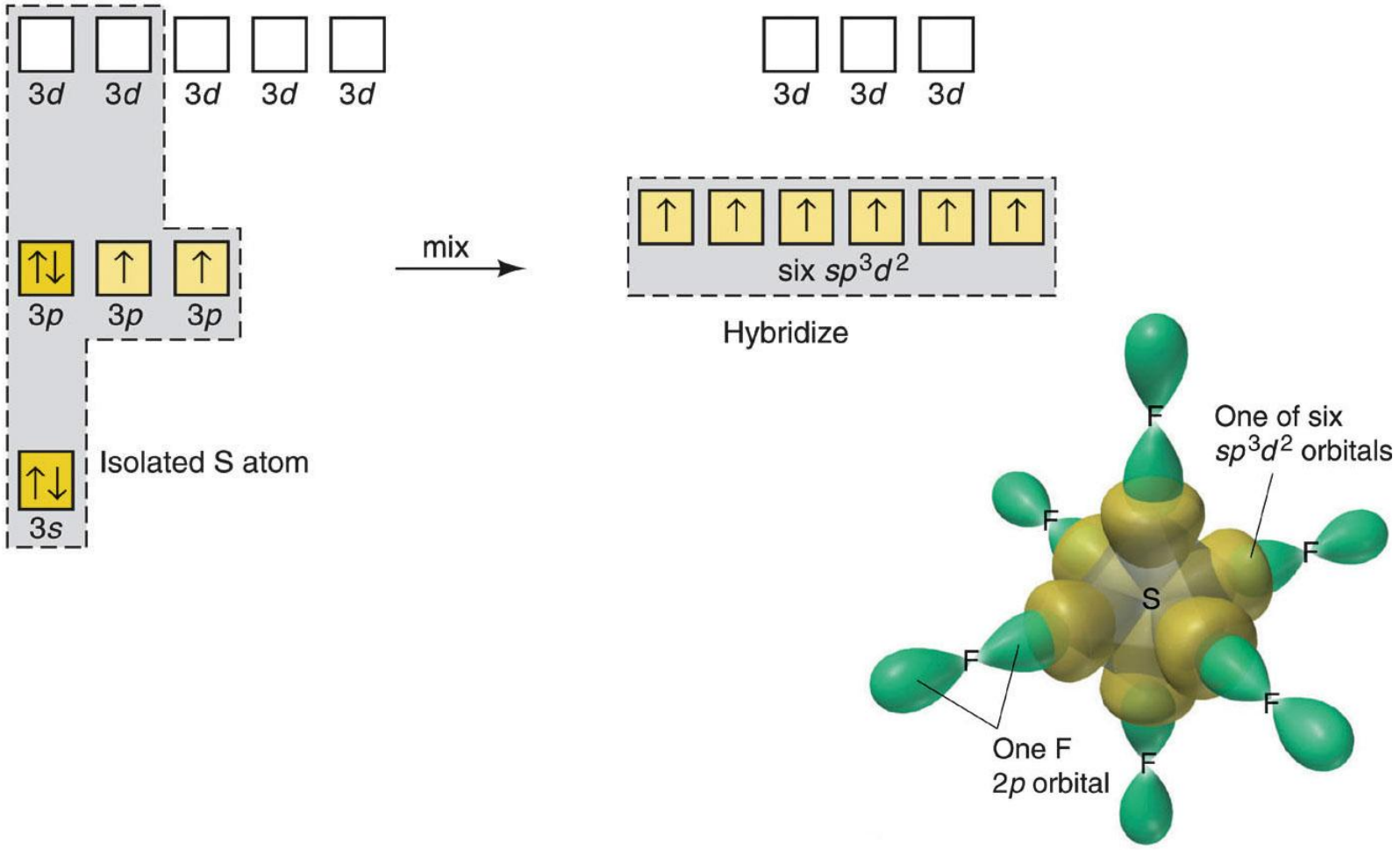

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Table 11.1 Composition and Orientation of Hybrid Orbitals.

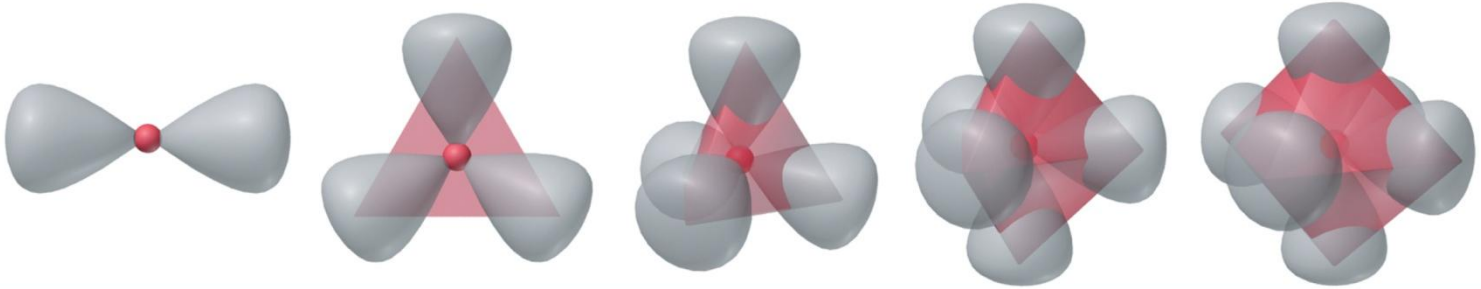
	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one *s* one *p*	one *s* two *p*	one *s* three *p*	one *s* three *p* one *d*	one *s* three *p* two *d*
Hybrid orbitals formed	two *p*	three sp^2	four sp^3	five sp^3d	six sp^3d^2
Unhybridized orbitals remaining	two *p*	one *p*	none	four *d*	three *d*
Orientation					

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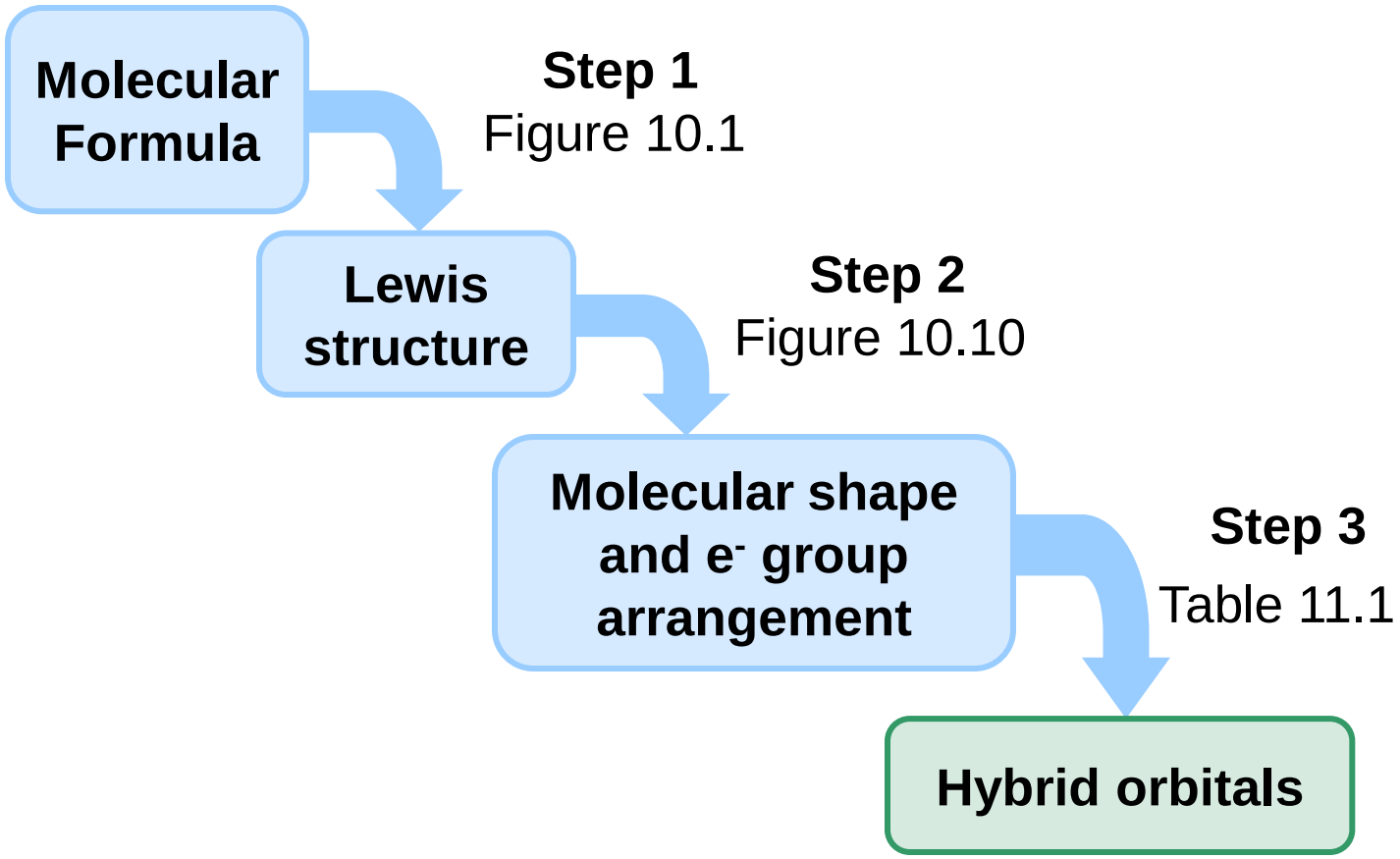
Figure 11.8 From molecular formula to hybrid orbitals.



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Sample Problem 11.1 Postulating Hybrid Orbitals in a Molecule

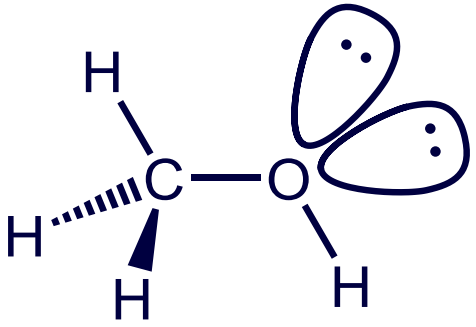
PROBLEM: Use partial orbital diagrams to describe how mixing of the atomic orbitals of the central atom(s) leads to hybrid orbitals in each of the following:

(a) Methanol, CH_3OH **(b)** Sulfur tetrafluoride, SF_4

PLAN: We use the molecular formula to draw the Lewis structure and determine the electron-group arrangement around each central atom. We then postulate the type of hybrid orbitals required and write a partial orbital diagram.

SOLUTION:

(a) CH_3OH



The electron-group arrangement is tetrahedral around both the C and the O atom.

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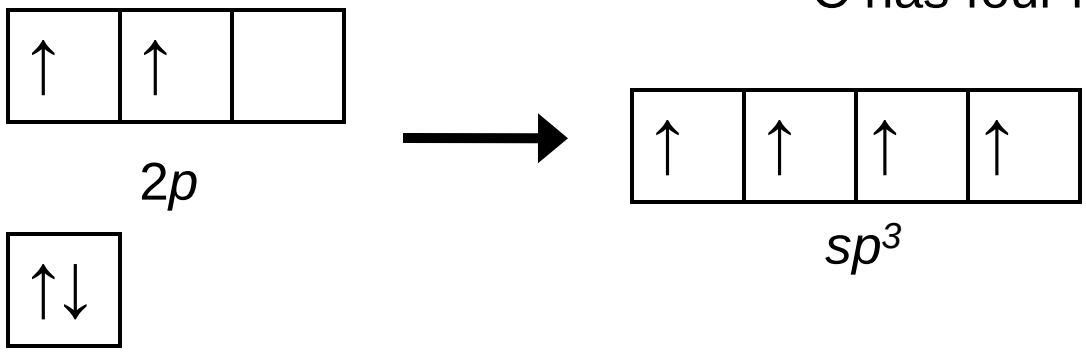
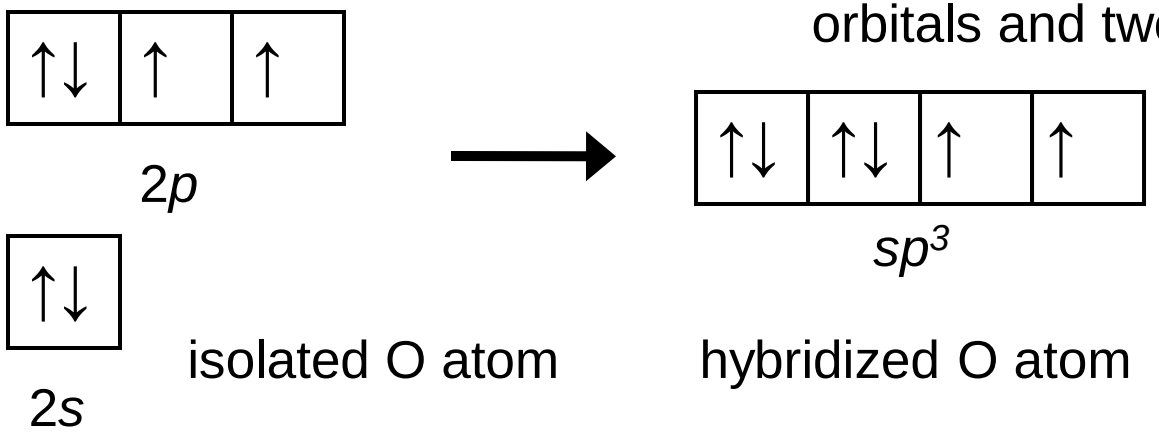
Sample Problem 11.1

C has four half-filled sp^3 orbitals.



The O atom has two half-filled sp^3 orbitals and two filled with lone pairs.



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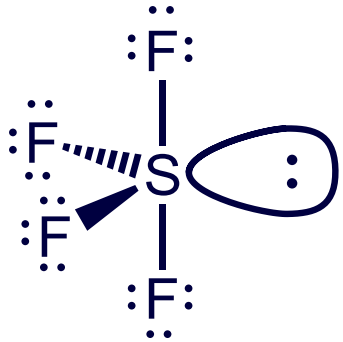
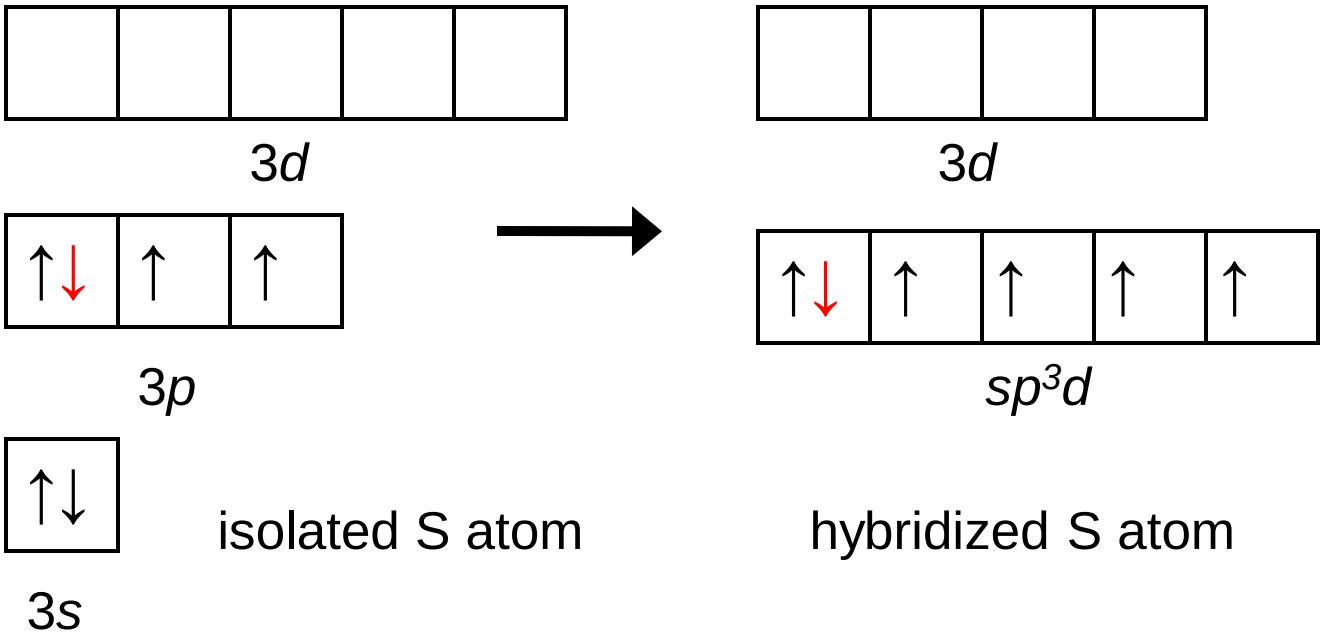
Sample Problem 11.1

(a) SF_4



The electron-group arrangement is trigonal bipyramidal, so the central S atom is sp^3d hybridized.



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Types of Covalent Bonds

A ***sigma*** (**σ**) bond is formed by ***end-to-end*** overlap of orbitals.

All single bonds are σ bonds.

A ***pi*** (π) bond is formed by ***sideways*** overlap of orbitals.

A π bond is weaker than a σ bond because sideways overlap is less effective than end-to-end overlap.

A double bond consists of one σ bond and one π bond

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Figure 11.9 The σ bonds in ethane (C_2H_6).

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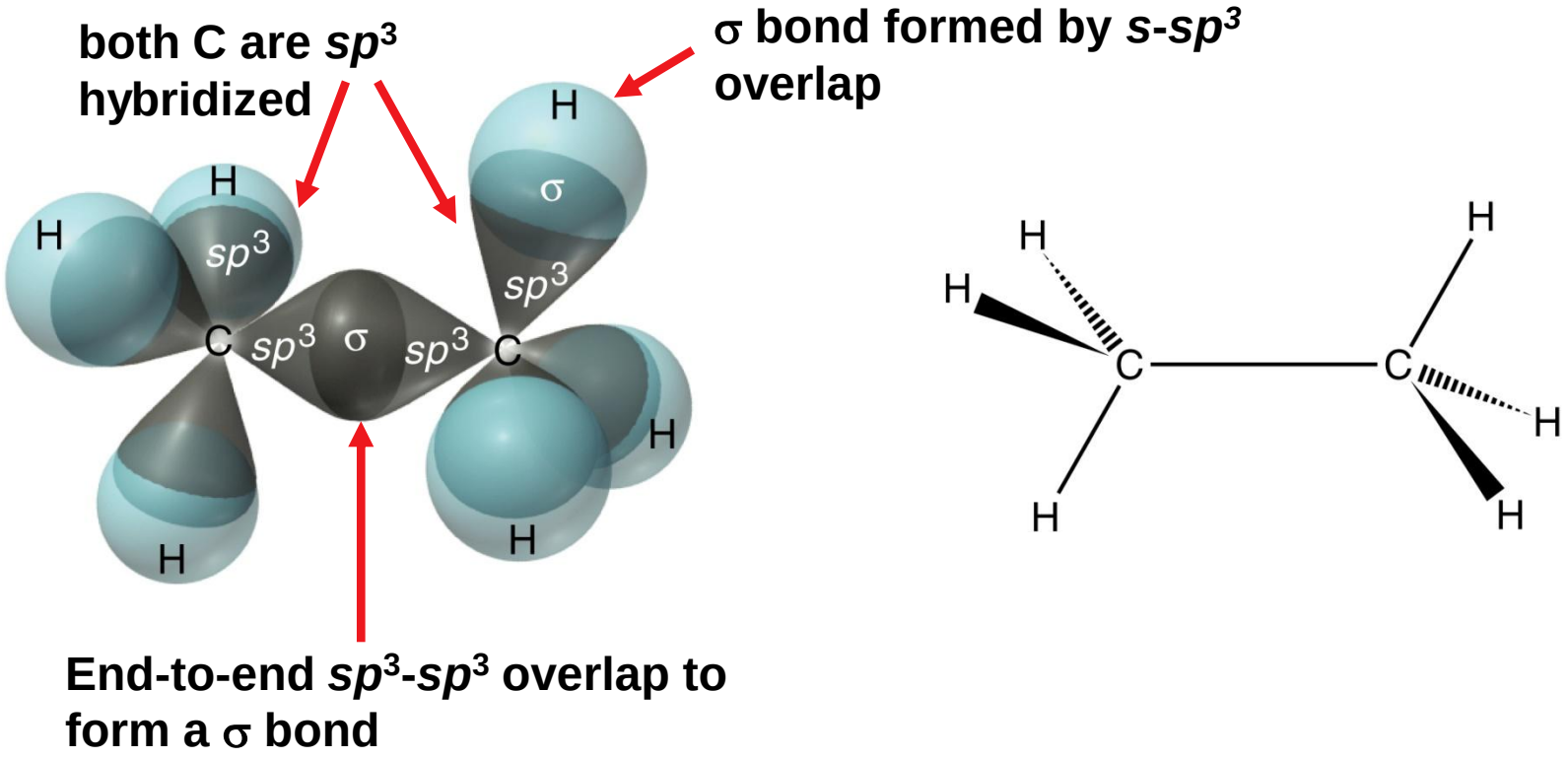

A σ bond is cylindrically symmetrical, with its highest electron density along the bond axis.

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Figure 11.9 continued

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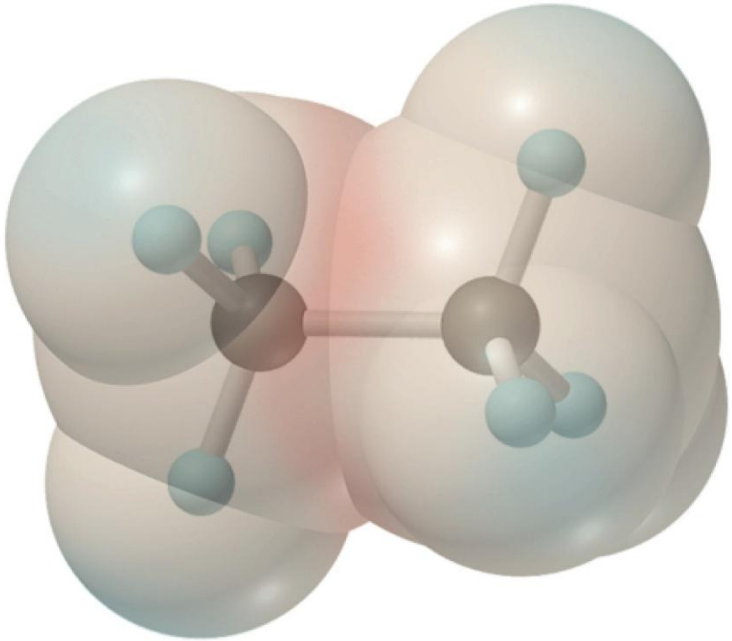

There is relatively even distribution of electron density over all σ bonds.

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Figure 11.10 The σ and π bonds in ethylene (C_2H_4).

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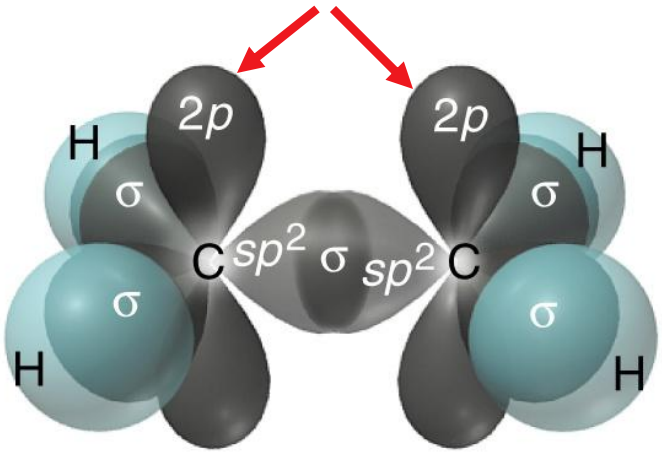
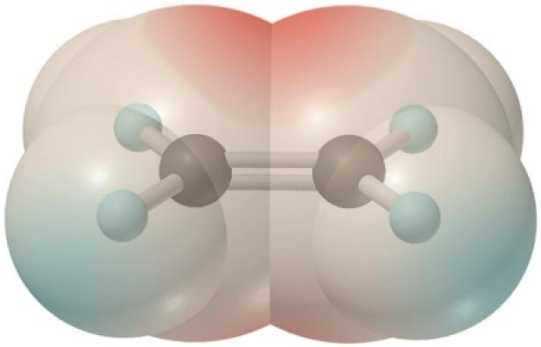
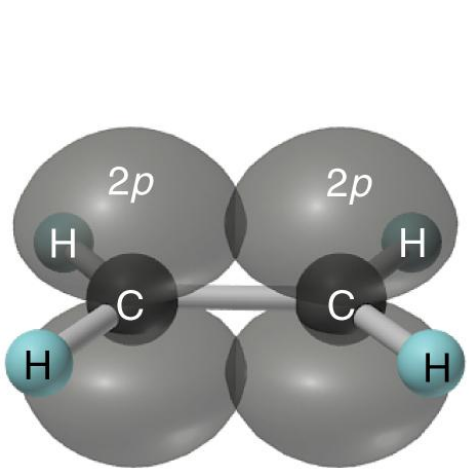
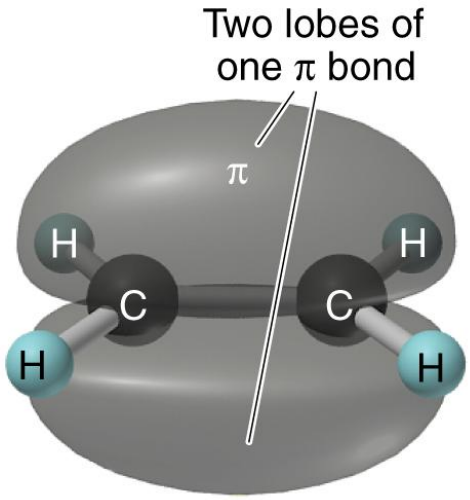
unhybridized *2p* orbitals





A π bond has two regions of electron density.





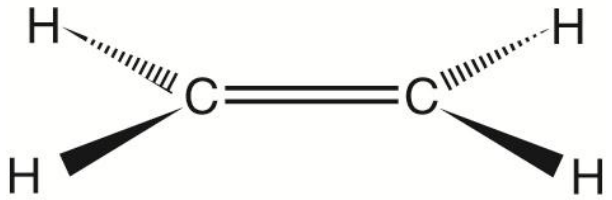


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Figure 11.11 The σ and π bonds in acetylene (C_2H_2).

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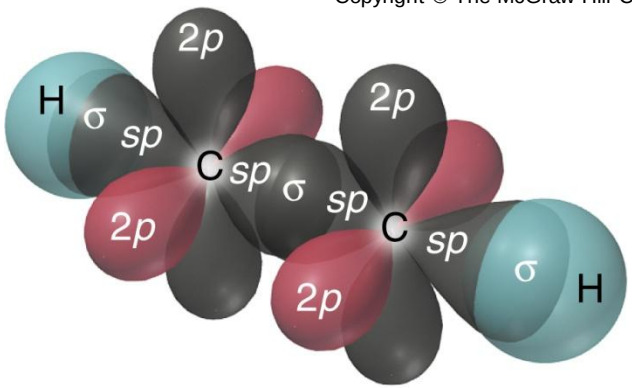
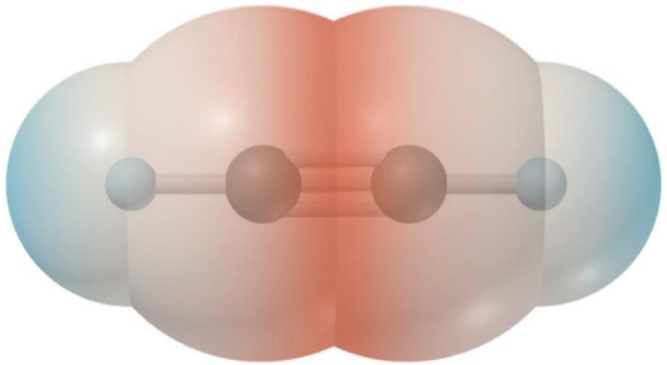
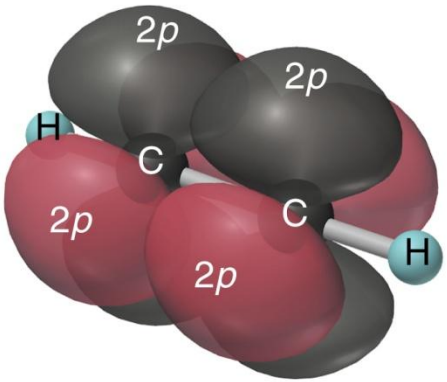
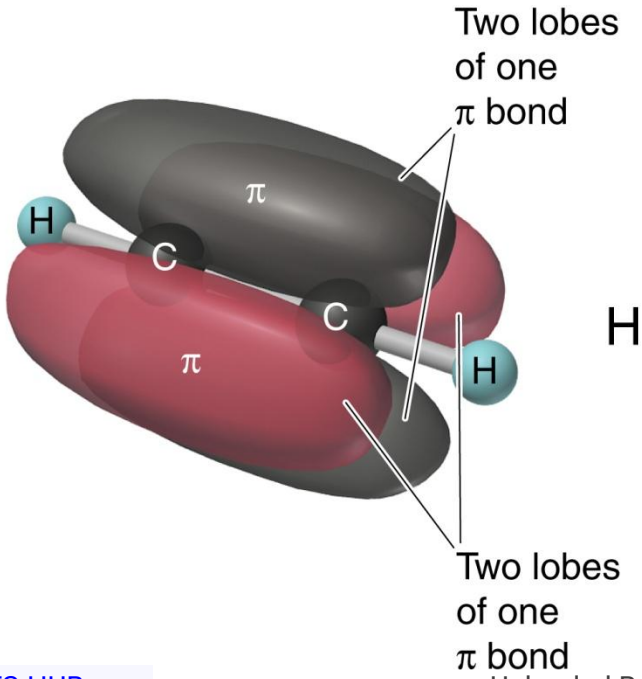




Each C is *sp* hybridized and has two unhybridized *p* orbitals.





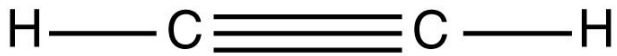


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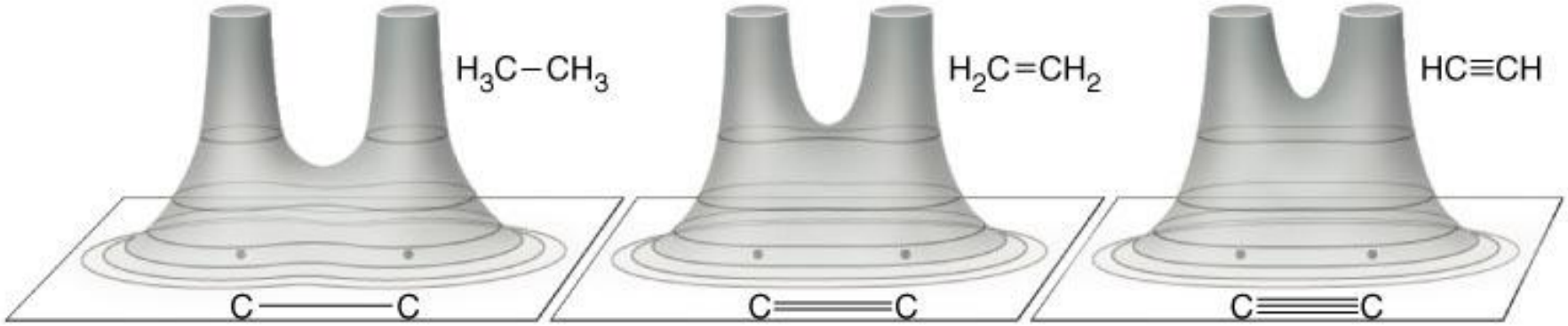
Figure 11.12 **Electron density and bond order in ethane, ethylene, and acetylene.**



A double bond is less than twice as strong as a single bond, because a π bond is weaker than a σ bond.

However, in terms of bond order, a single bond has BO = 1, a double bond has BO = 2, and a triple bond has BO = 3.

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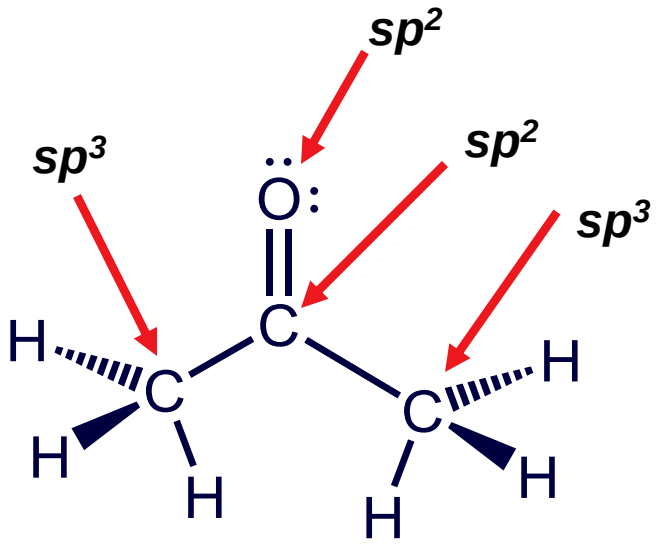
Sample Problem 11.2

Describing the Types of Bonds in Molecules

PROBLEM: Describe the types of bonds and orbitals in acetone, $(CH_3)_2CO$.

PLAN: We use the Lewis structures to determine the arrangement of groups and shape at each central atom. We postulate the hybrid orbitals, taking note of the multiple bonds present.

SOLUTION:



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Sample Problem 11.2

The sp^3 hybridized C atoms form σ bonds using sp^3 hybrid orbitals.

The sp^2 hybridized C and O atoms form σ bonds using sp^2 hybrid orbitals, and the π bond of the C=O double bond is formed using *p* orbitals.

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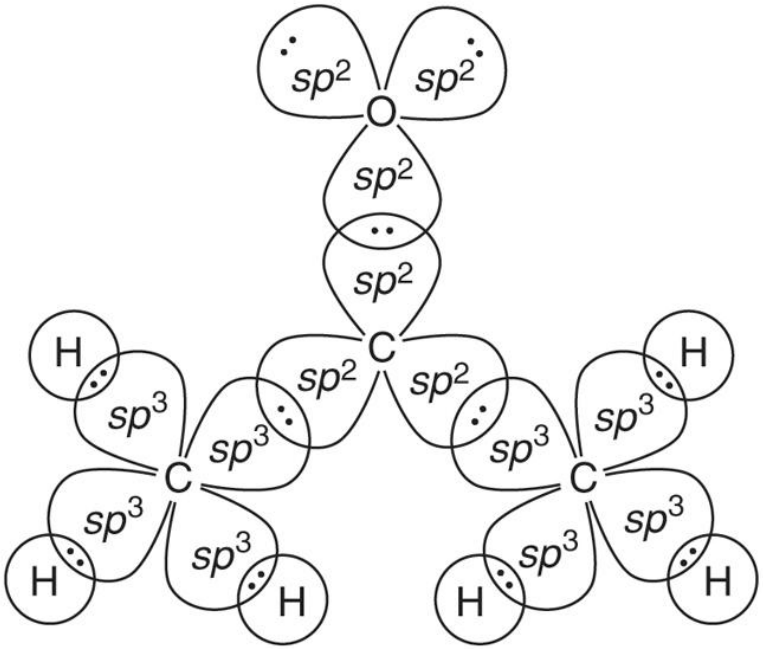
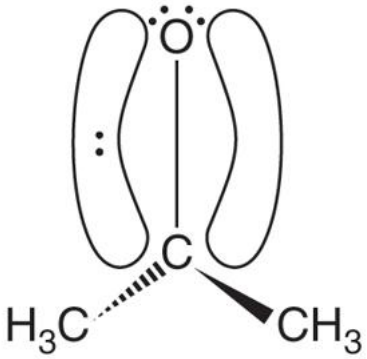


σ bonds



π bond (shown with molecule rotated 90°).

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Molecular Orbital (MO) Theory

The combination of orbitals to form bonds is viewed as the combination of ***wave functions***.

Atomic wave functions (AOs) combine to form ***molecular*** wave functions (MOs).

Addition of AOs forms a ***bonding MO***, which has a region of ***high*** electron density between the nuclei.

Subtraction of AOs forms an ***antibonding MO***, which has a ***node***, or region of ***zero*** electron density, between the nuclei.

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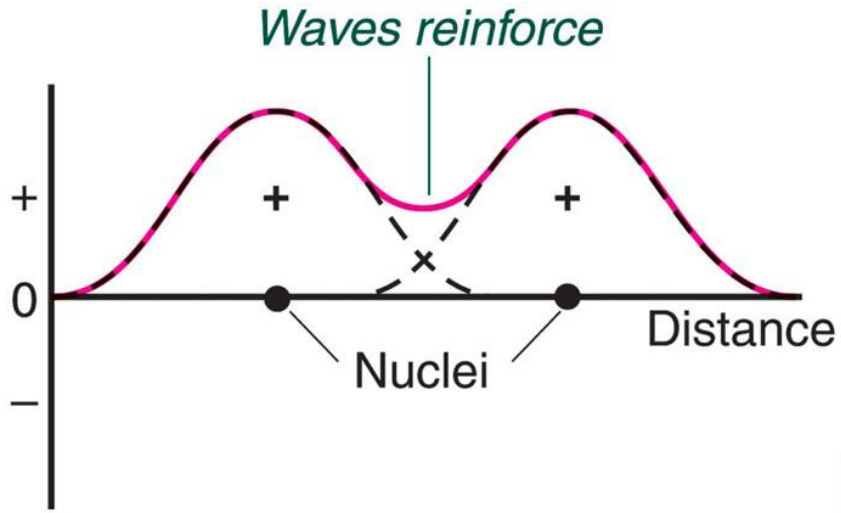
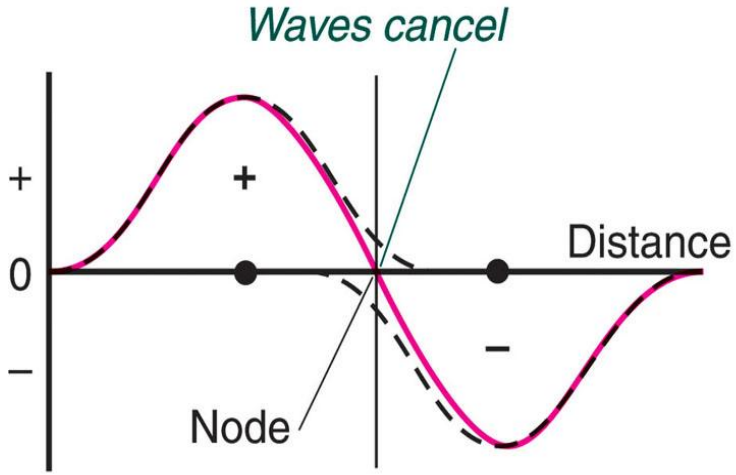
Figure 11.13

An analogy between light waves and atomic wave functions.



Amplitudes of wave functions added



Amplitudes of wave functions subtracted

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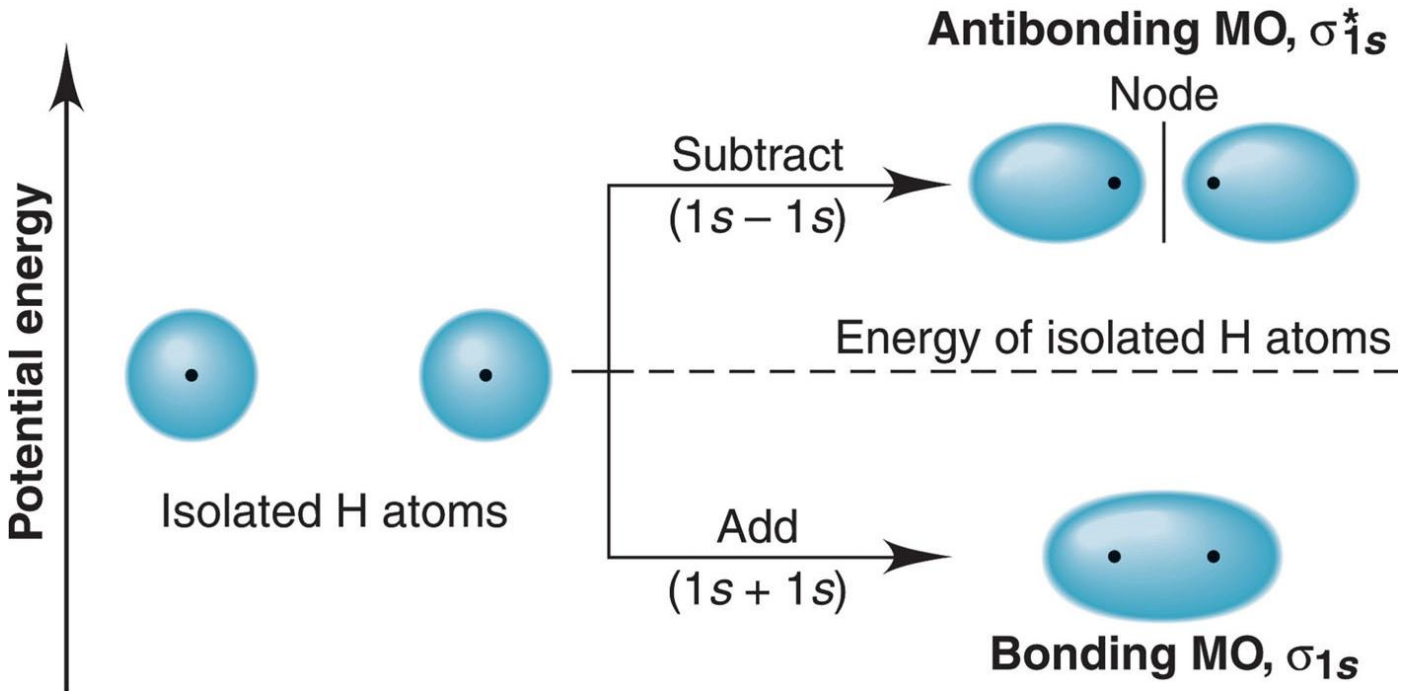
Figure 11.14 **Contours and energies of H_2 bonding and antibonding MOs.**



The bonding MO is lower in energy and the antibonding MO is higher in energy than the AOs that combined to form them.

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Molecular Orbital Diagrams

An ***MO diagram***, just like an atomic orbital diagram, shows the relative energy and number of electrons in each MO.

The MO diagram also shows the AOs from which each MO is formed.

Bond order is calculated as follows:

$\frac{1}{2}$[(# of e^- in bonding MO) – (# of e^- in antibonding MO)]

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Figure 11.15 MO diagram for H_2.

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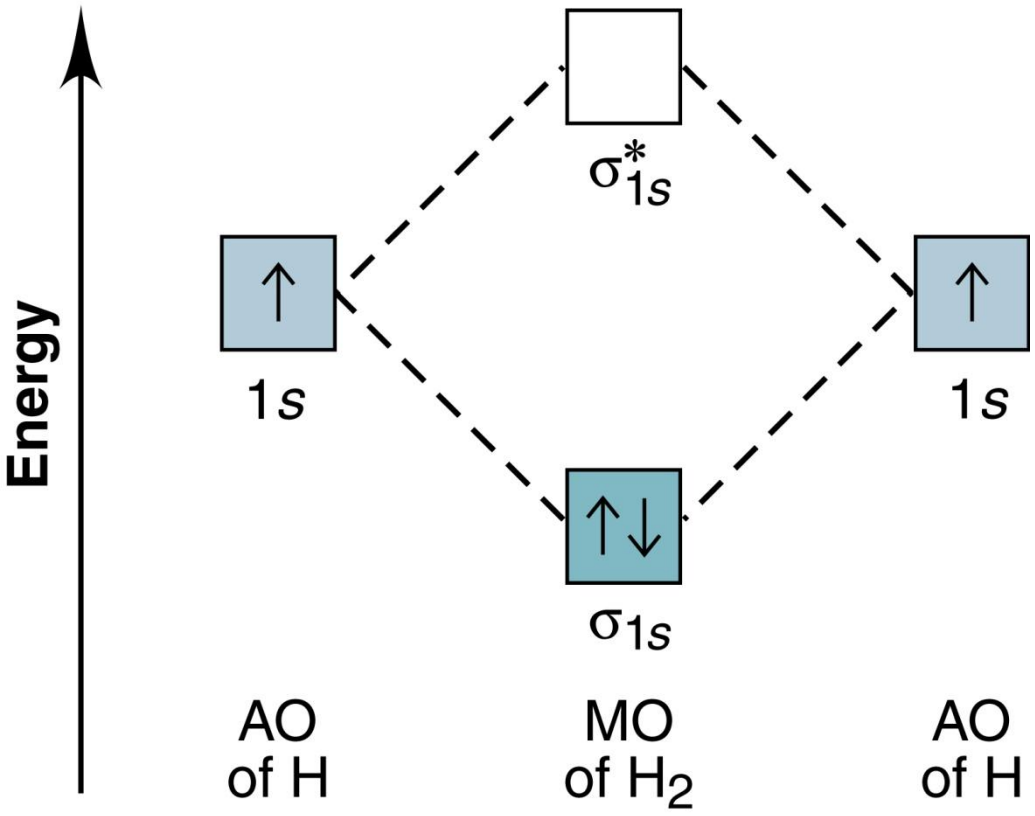

H_2 bond order = ½ (2 − 0) = 1

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Electrons in Molecular Orbitals

Electrons are placed in MOs just as they are in AOs.

- MOs are filled in order of increasing energy.
- An MO can hold a maximum of 2 e^- with opposite spins.
- Orbitals of equal energy are half-filled, with spins parallel, before pairing spins.

A molecular electron configuration shows the type of MO and the number of e^- each contains. For H_2 the configuration is $(\sigma_{1s})^2$.

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Figure 11.16 MO diagram for He_2^+ and He_2.

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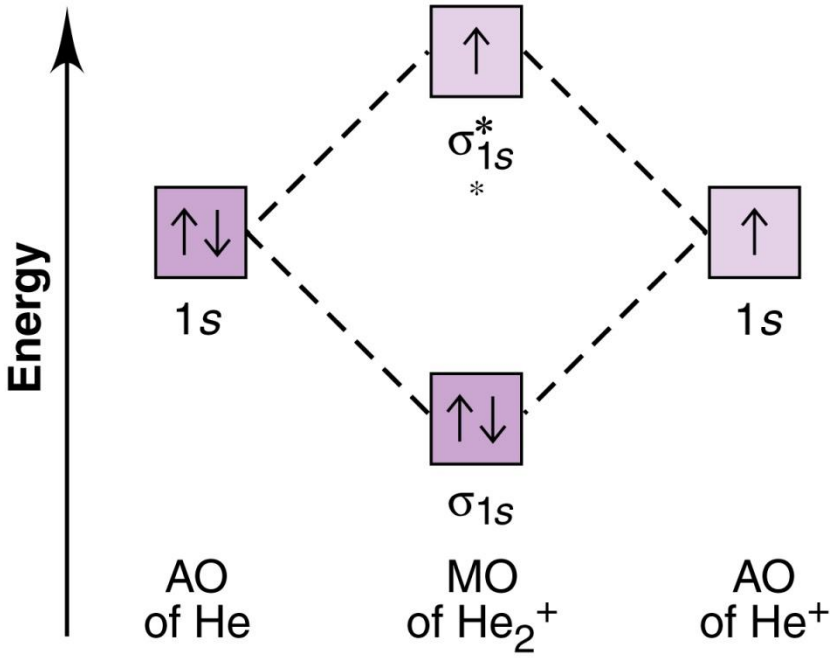

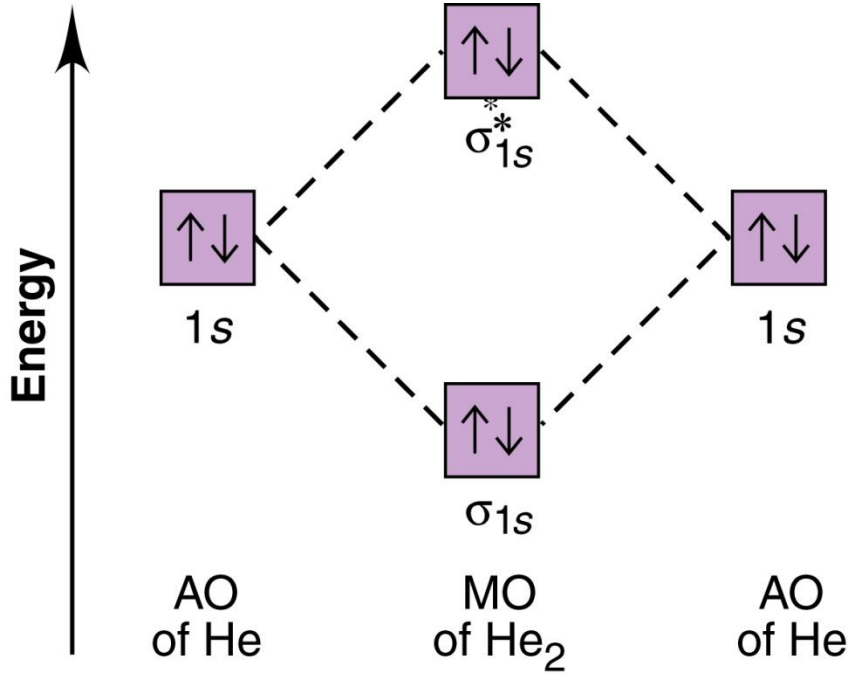

He_2^+ bond order = ½

$(\sigma_{1s})^2(\sigma^*_{1s})^1$

He_2 bond order = 0

$(\sigma_{1s})^2(\sigma^*_{1s})^2$

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Sample Problem 11.3 Predicting Stability of Species Using MO Diagrams

PROBLEM: Use MO diagrams to find bond orders and predict whether H_2^+ and H_2^- exist. If either exists, write its electron configuration.

PLAN: Since the 1*s* AOs form the MOs, the MO diagrams are similar to the one for H_2. We find the number of electrons in each species and distribute them one at a time to the MOs following the rules for orbital filling. We calculate the bond order and predict stability.

SOLUTION:

H_2^+ has one electron to place in its MOs while H_2^- has three electrons to place.

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Sample Problem 11.3

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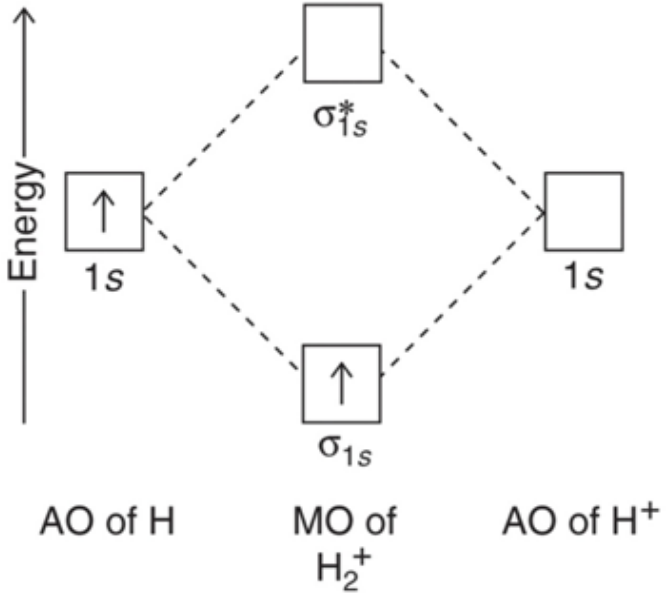

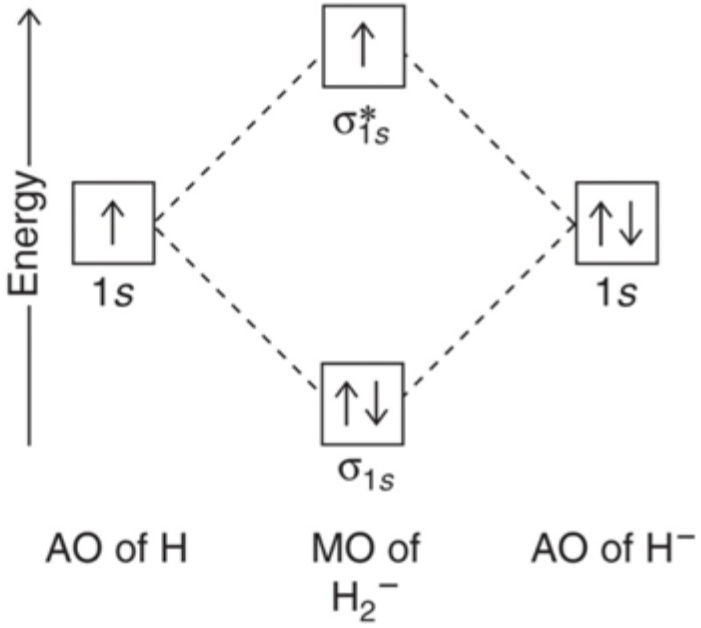

For H_2^+, the bond order is ½(1 – 0) = ½; so we predict that H_2^+ exists. The configuration is $(\sigma_{1s})^1$.

For H_2^-, the bond order is ½(2 – 1) = ½; so we predict that H_2^- exists. The configuration is $(\sigma_{1s})^2(\sigma^*_{1s})^1$

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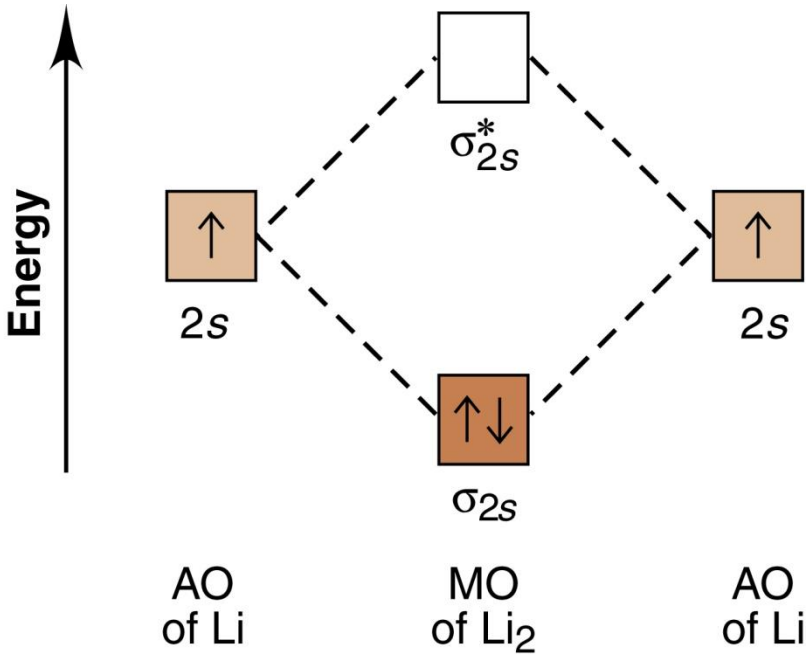
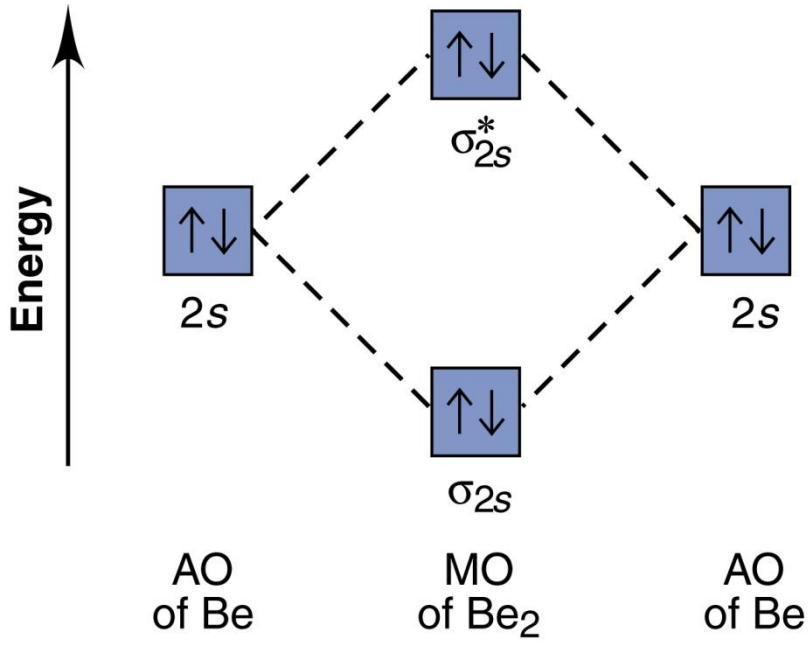
Figure 11.17 Bonding in *s*-block homonuclear diatomic molecules.



Li_2

Li_2 bond order = 1



Be_2

Be_2 bond order = 0

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Figure 11.18 Shapes and energies of σ and π MOs from combinations of 2*p* atomic orbitals.

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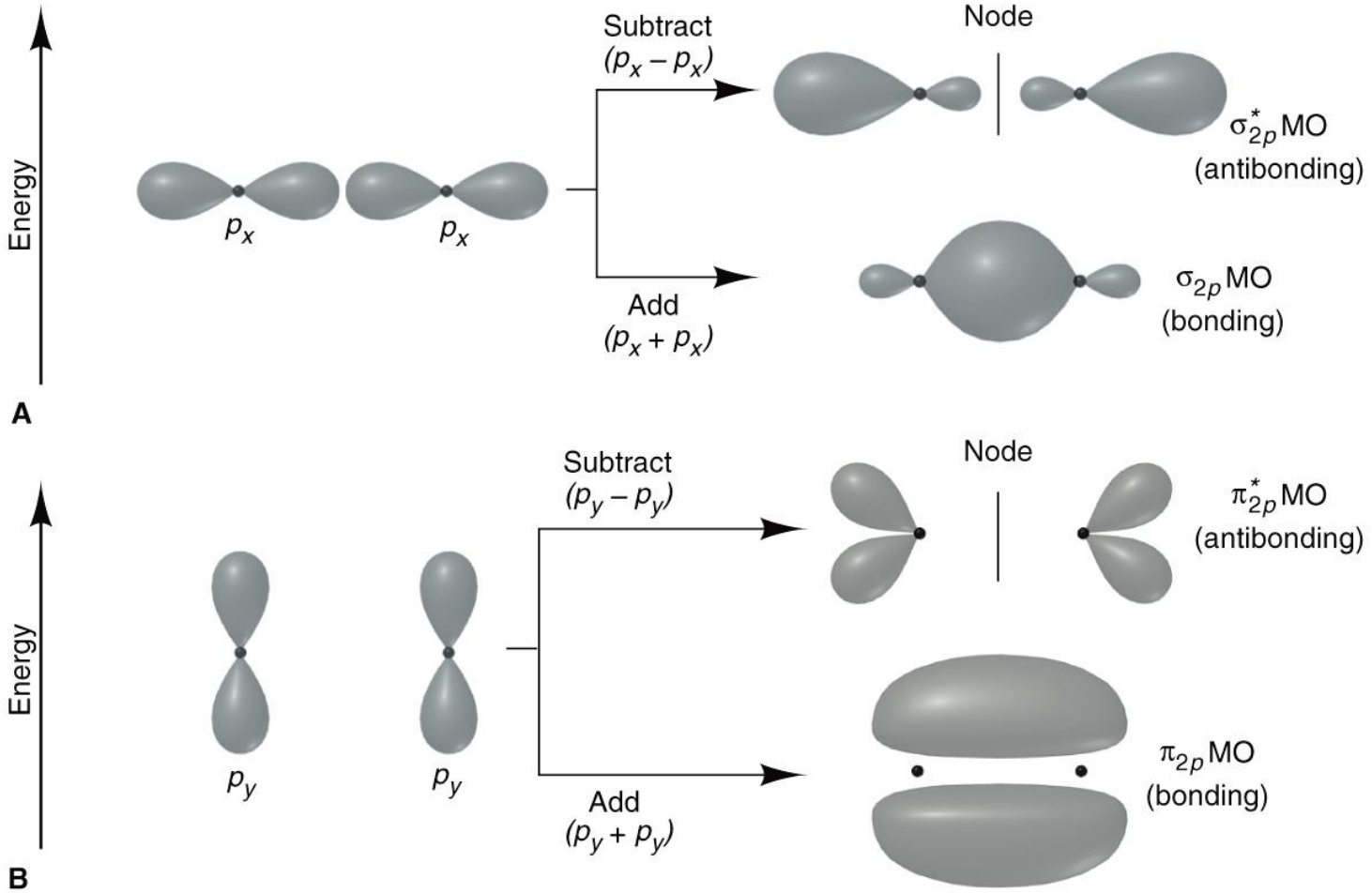

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Figure 11.19 Relative MO energy levels for Period 2 homonuclear diatomic molecules.

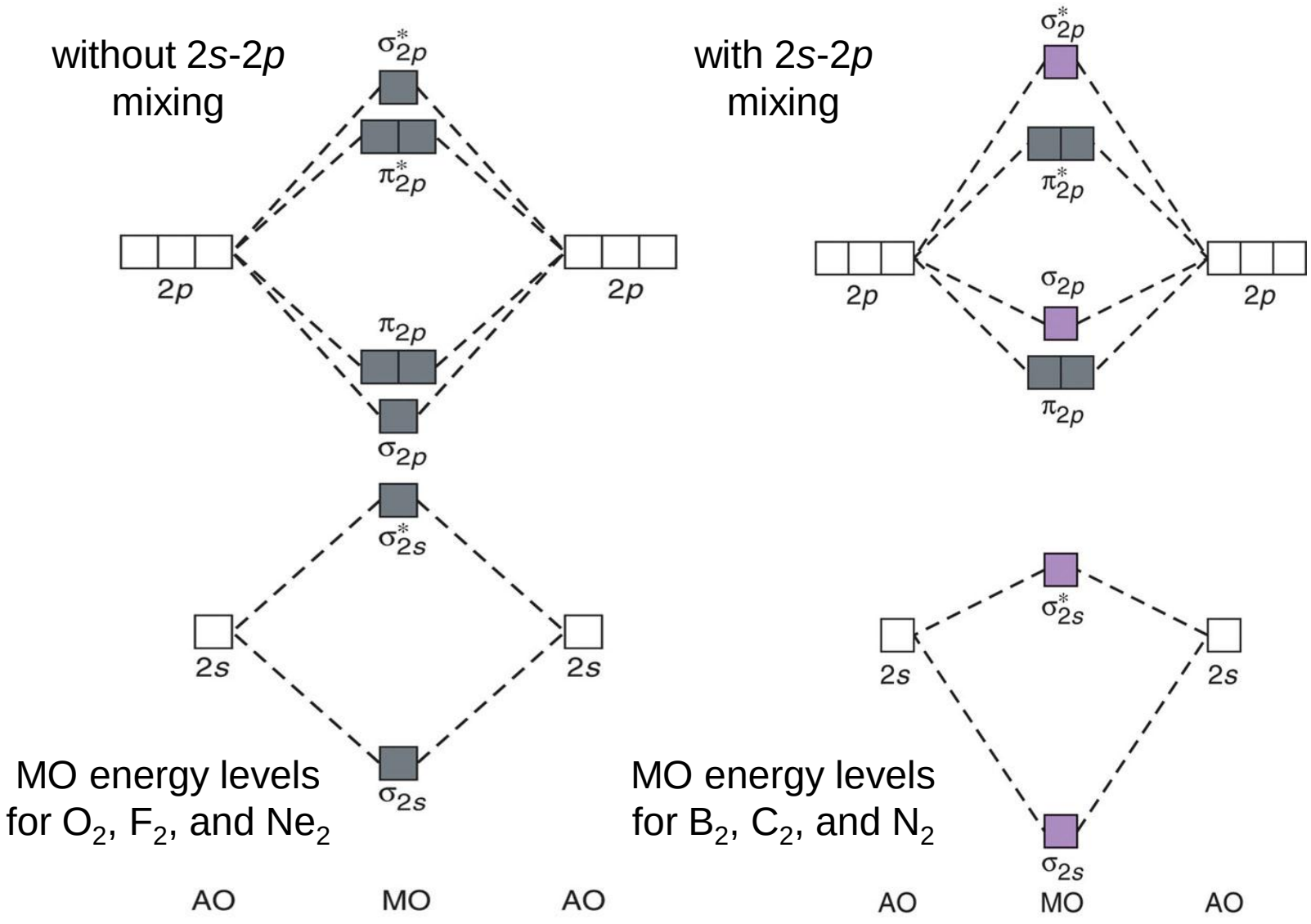

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Figure 11.20

MO occupancy and molecular properties for B_2 through Ne_2.

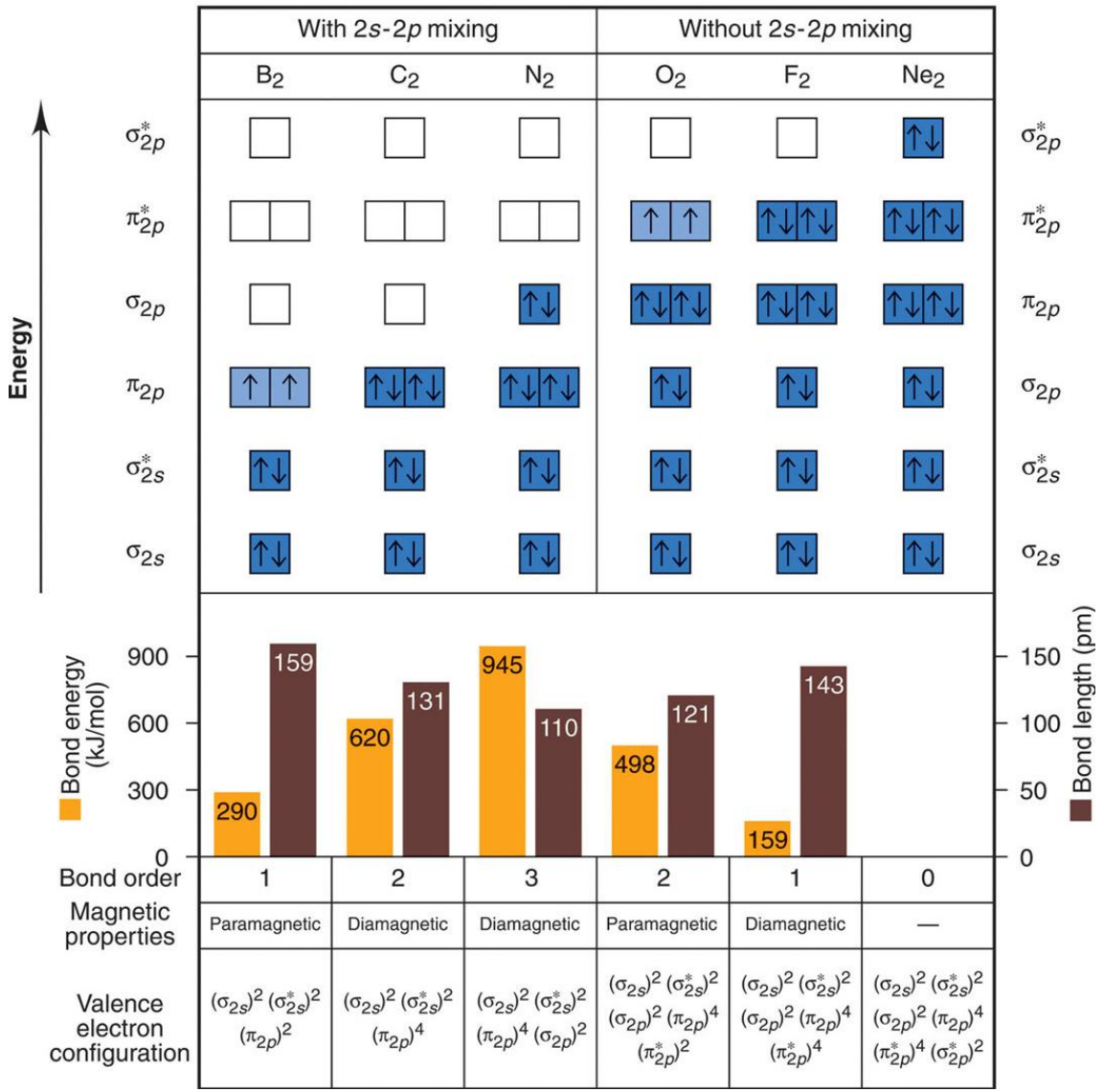

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Figure 11.21 The paramagnetic properties of O_2.

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Sample Problem 11.4 Using MO Theory to Explain Bond Properties

PROBLEM: Explain the following data with diagrams showing the occupancy of MOs:

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

PLAN: The data show that removing an electron from each parent molecule has opposite effects: N_2^+ has a weaker longer bond than N_2, but O_2^+ has a stronger, shorter bond than O_2. We determine the valence electrons in each species, draw the sequence of MO energy levels (showing orbital mixing in N_2 but not in O_2), and fill them with electrons. We then calculate bond orders, which relate directly to bond energy and inversely to bond length.

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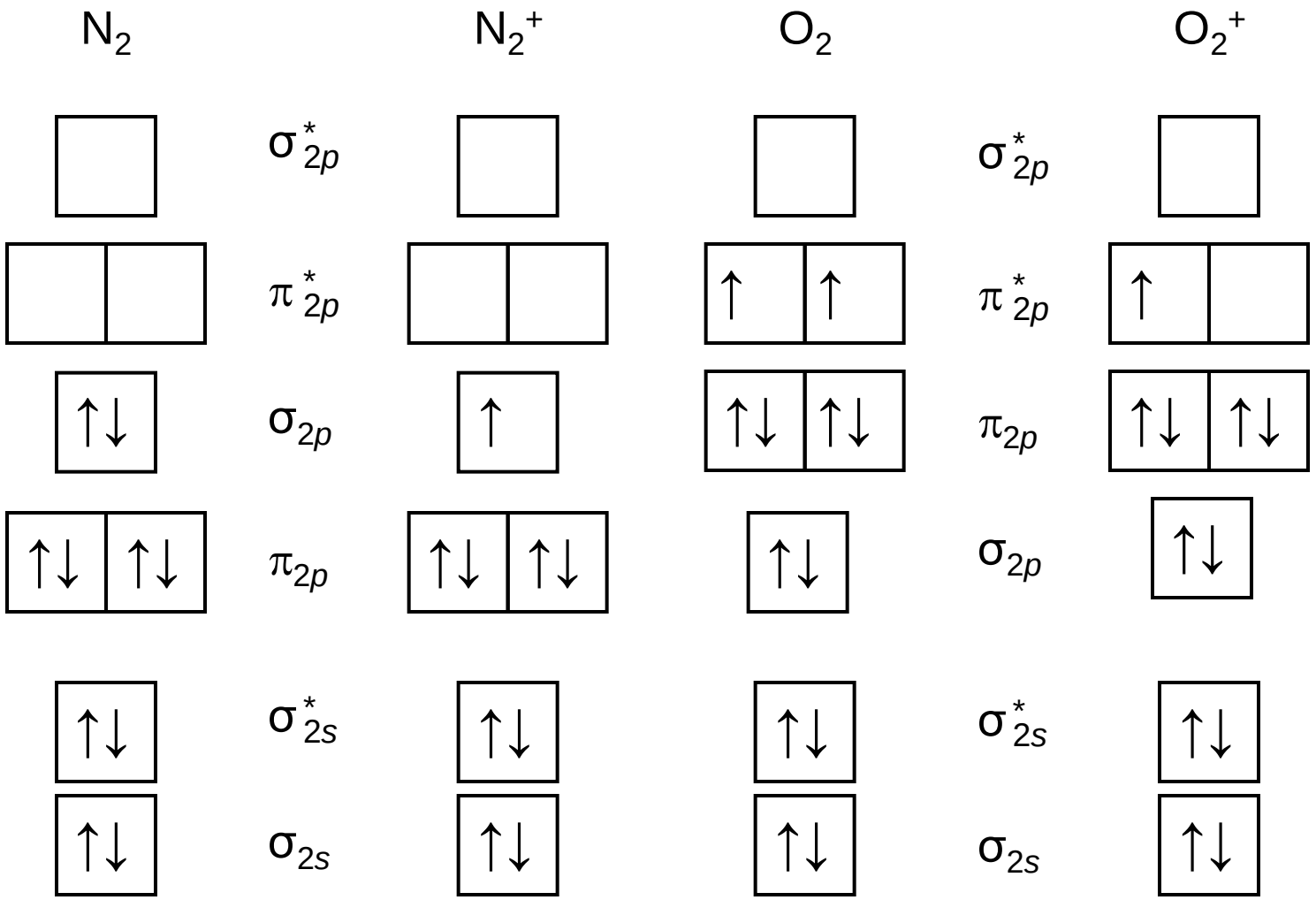
Sample Problem 11.4

SOLUTION:



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Sample Problem 11.4

Calculating bond orders:

For N_2 ½(8 – 2) = 3 For N_2^+ ½(7 – 2) = 2.5

N_2^+ has a longer, weaker bond than N_2 because to form N_2^+, a *bonding* electron is removed and the bond order decreases.

For O_2 ½(8 – 4) = 2 For O_2^+ ½(8 – 3) = 2.5

O_2^+ has a shorter, stronger bond than O_2 because to form O_2^+, an *antibonding* electron is removed and the bond order increases.

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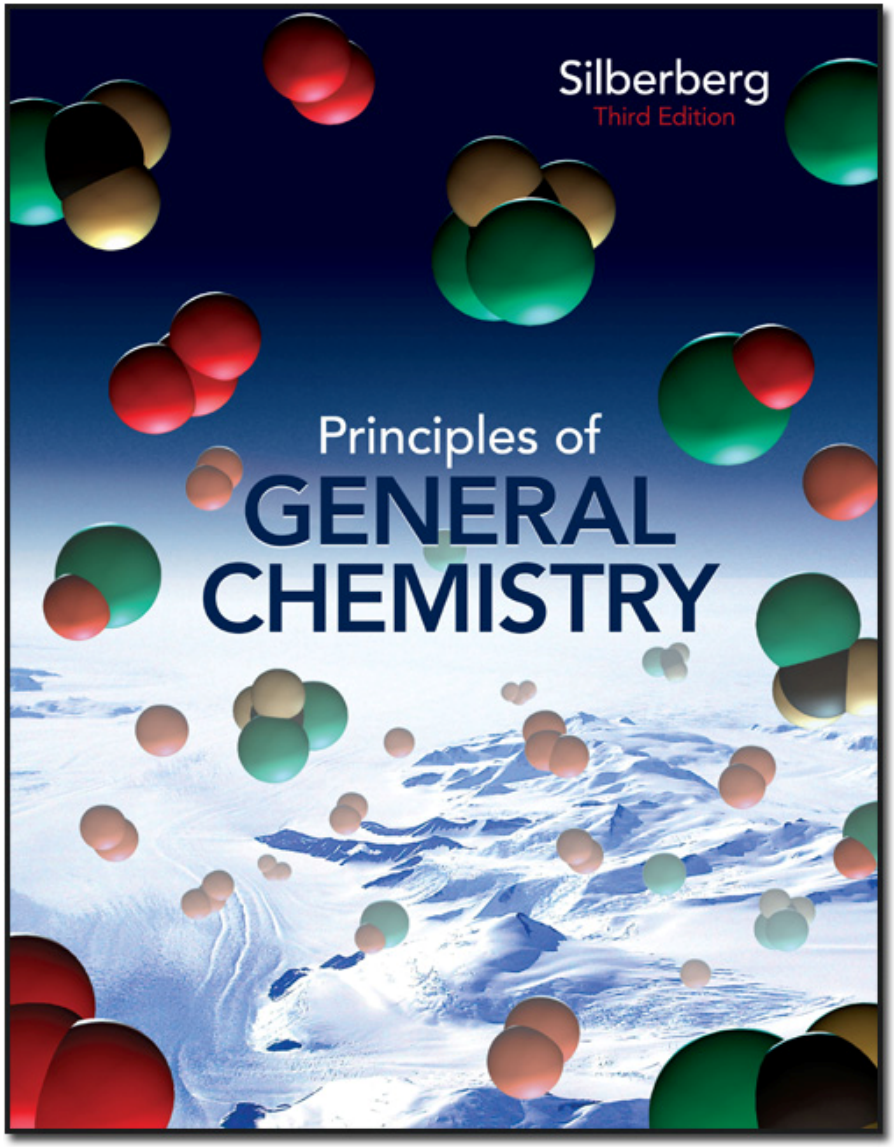

Chapter 12

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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Chapter 12

Intermolecular Forces:
Liquids, Solids, and Phase Changes

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Intermolecular Forces: Liquids, Solids, and Phase Changes

12.1 An Overview of Physical States and Phase Changes

12.2 Quantitative Aspects of Phase Changes

12.3 Types of Intermolecular Forces

12.4 Properties of the Liquid State

12.5 The Uniqueness of Water

12.6 The Solid State: Structure, Properties, and Bonding

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Phases of Matter

Each physical state of matter is a ***phase***, a physically distinct, homogeneous part of a system.

The properties of each phase are determined by the balance between the ***potential*** and ***kinetic*** energy of the particles.

The ***potential*** energy, in the form of ***attractive forces***, tends to draw particles together.

The ***kinetic*** energy associated with movement tends to disperse particles.

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Attractive Forces

Intramolecular or ***bonding*** forces are found ***within*** a molecule. The ***chemical*** behavior of each phase of matter is the same because the same basic particle is present in each case.

H_2O molecules are present whether the substance is in the solid, liquid, or gas phase.

Intermolecular or ***nonbonding*** forces are found ***between*** molecules. The ***physical*** behavior of each phase of matter is different because the ***strength*** of these forces differs from state to state.

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Table 12.1 A Macroscopic Comparison of Gases, Liquids, and Solids

State	Shape and Volume	Compressibility	Ability to Flow
Gas	Conforms to shape and volume of container	High	High
Liquid	Conforms to shape of container; volume limited by surface	Very low	Moderate
Solid	Maintains its own shape and volume	Almost none	Almost none

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Kinetic Molecular View of the Three States

	Attractive Forces vs. Kinetic Energy	Properties
Gas	Attractive forces are weak relative to kinetic energy.	Particles are far apart. A gas has no fixed shape or volume.
Liquid	Attractive forces are stronger because particles have less kinetic energy.	A liquid can flow and change shape, but has a fixed volume.
Solid	Attractions dominate motion. Particles are fixed in place relative to each other.	A solid has a fixed shape and volume.

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Phase Changes

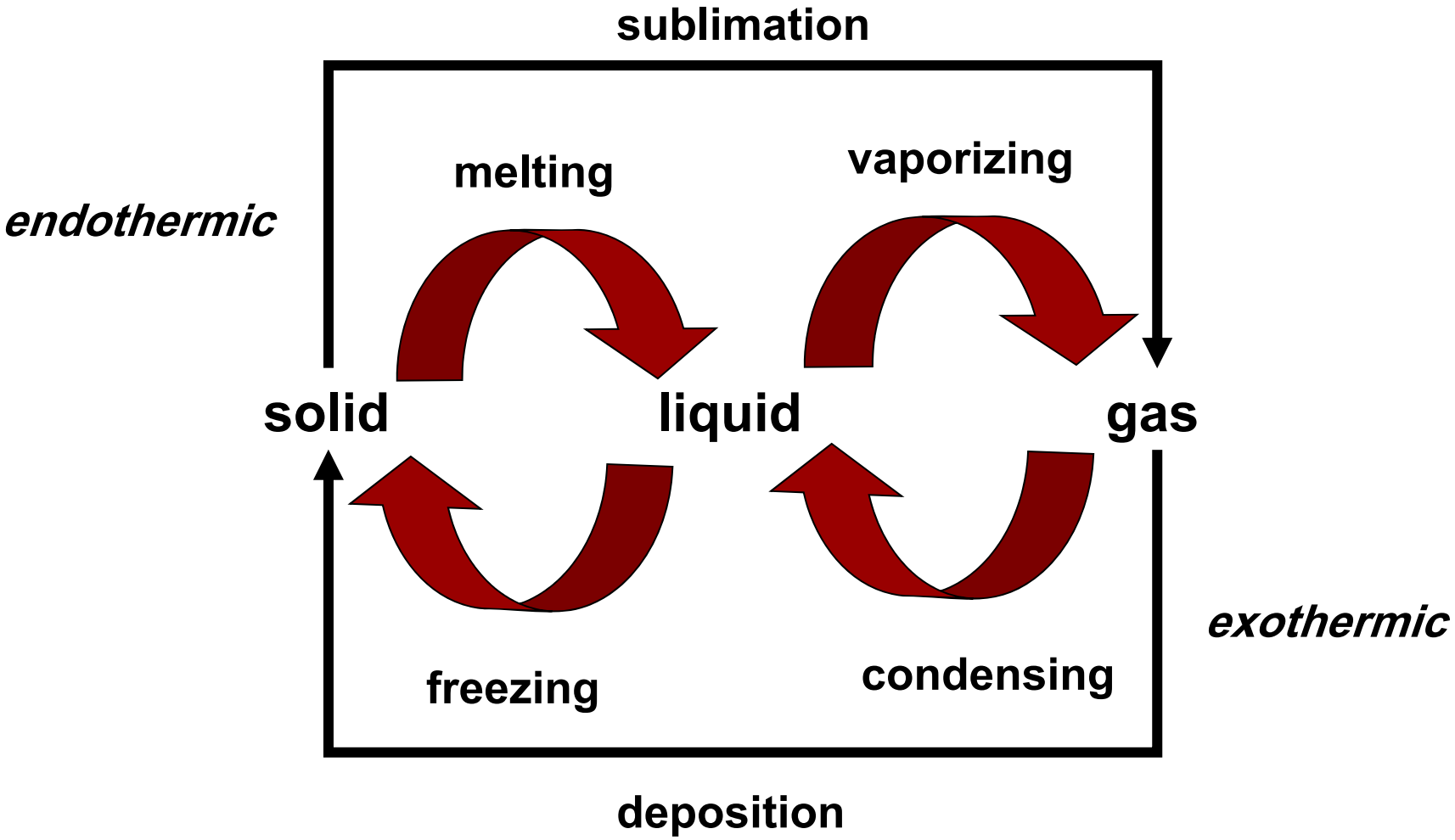

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Figure 12.1 Heats of vaporization and fusion for several common substances.

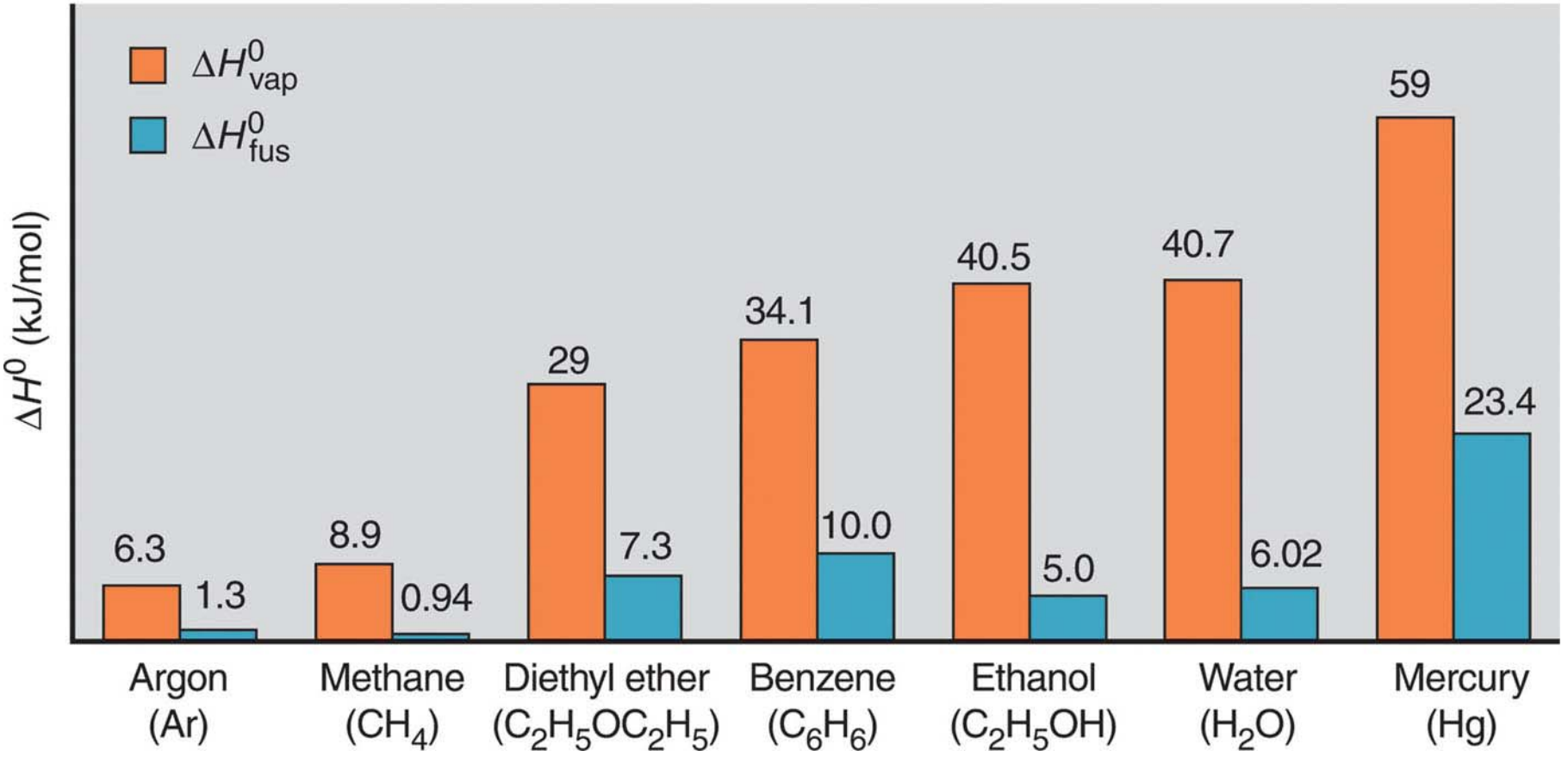

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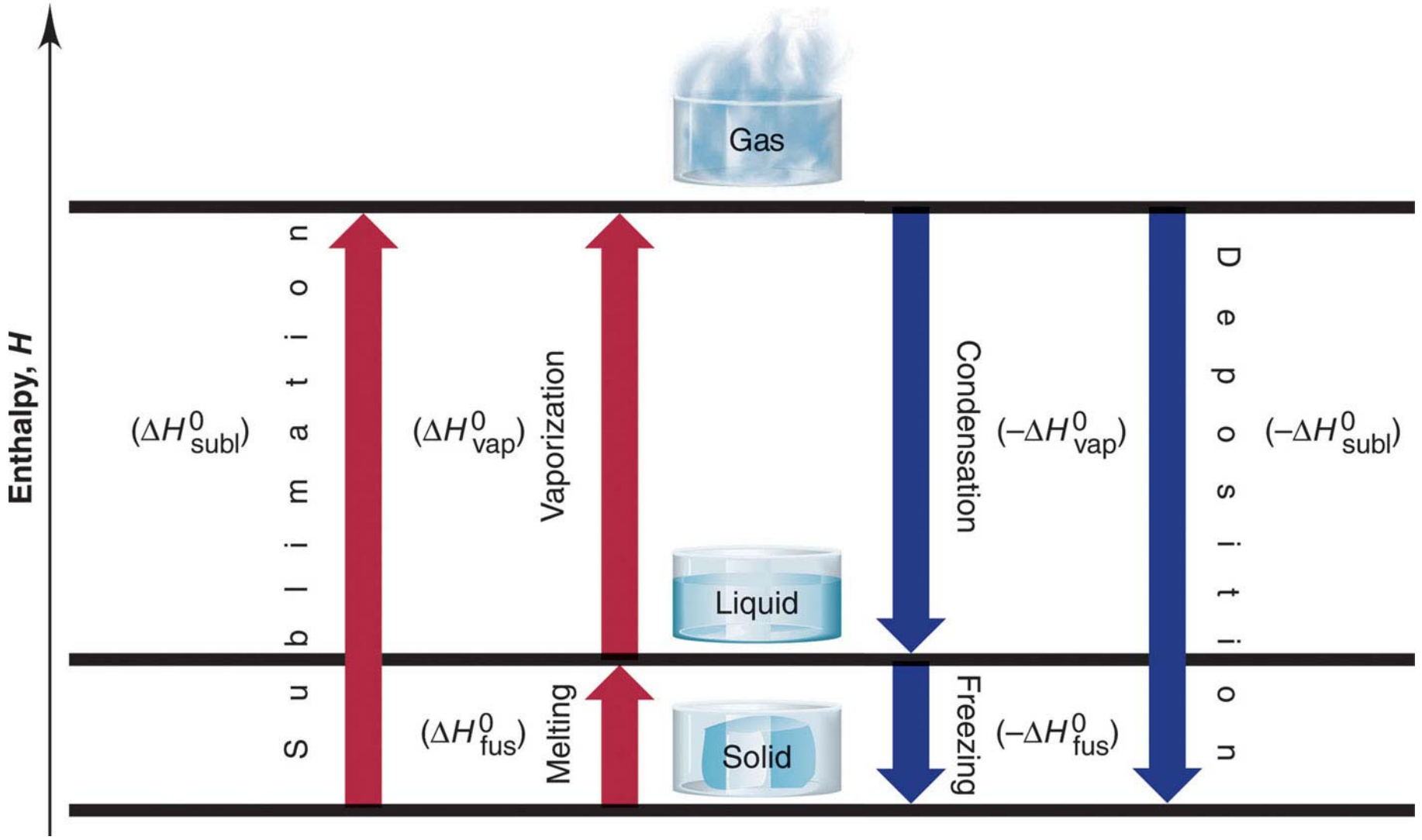
Figure 12.2 **Phase changes and their enthalpy changes.**



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Quantitative Aspects of Phase Changes

Within a phase, heat flow is accompanied by a ***change in temperature***, since the average E_k of the particles changes.

$$q = \text{(amount)} \times \text{(heat capacity)} \times \Delta T$$

During a phase change, heat flow occurs at ***constant temperature***, as the average distance between particles changes.

$$q = \text{(amount)}(\Delta H \text{ of phase change})$$

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Figure 12.3 A cooling curve for the conversion of gaseous water to ice.

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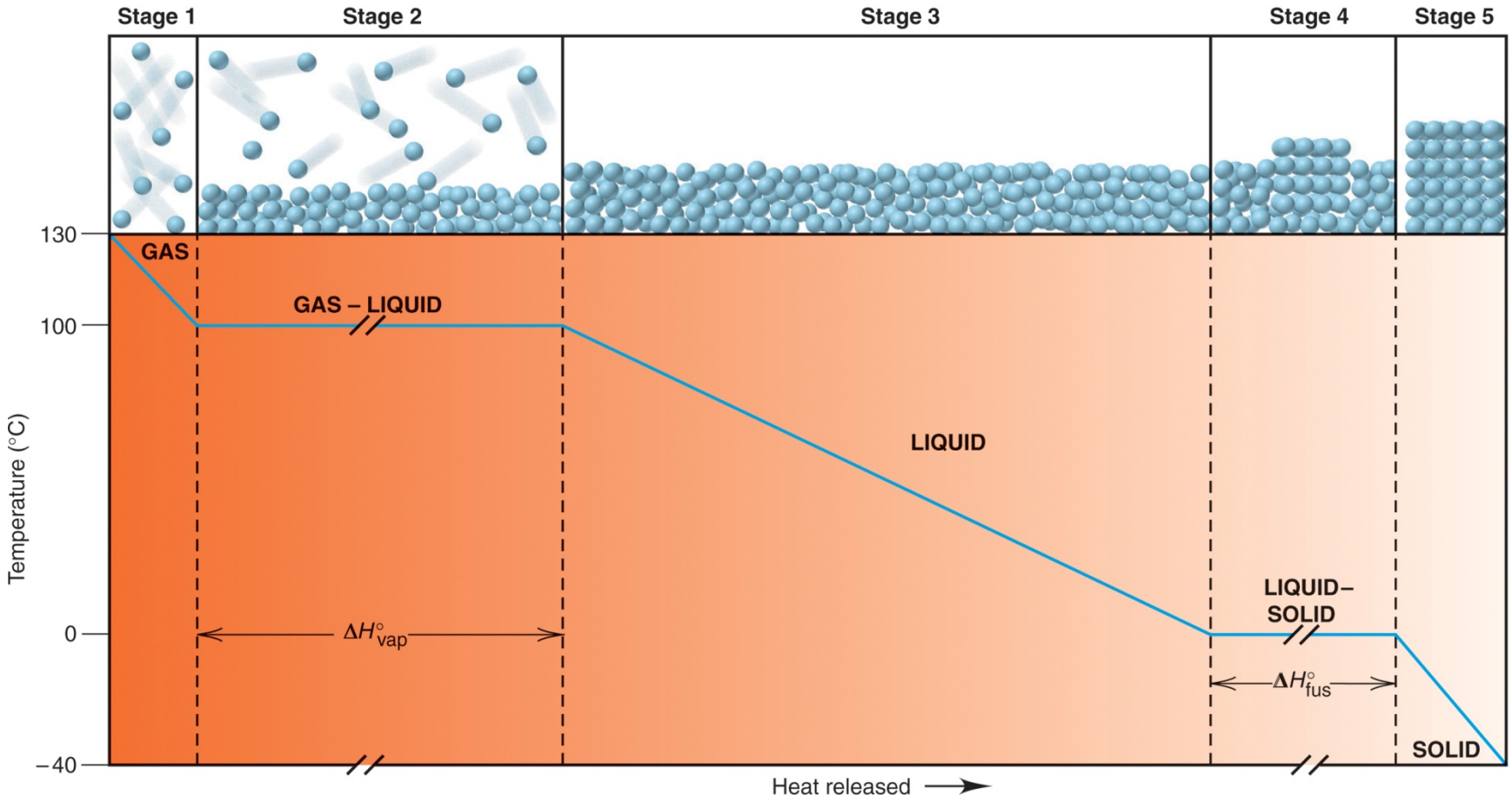

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Sample Problem 12.1 Finding the Heat of a Phase Change Depicted by Molecular Scenes

PROBLEM: The scenes below represent a phase change of water. Select data from the previous text discussion to find the heat (in kJ) released or absorbed when 24.3 g of H_2O undergoes this change.

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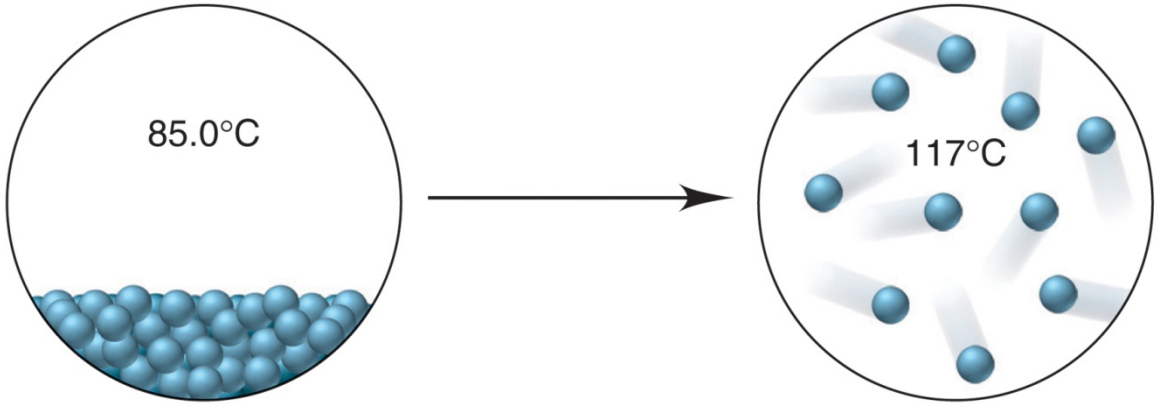

PLAN: The scenes show a disorderly, condensed phase at 85.0°C changing to separate particles at 117°C. A liquid is becoming a gas, so the scene shows vaporization. We must identify the number of stages in the process and calculate the heat absorbed in each.

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Sample Problem 12.1

SOLUTION:

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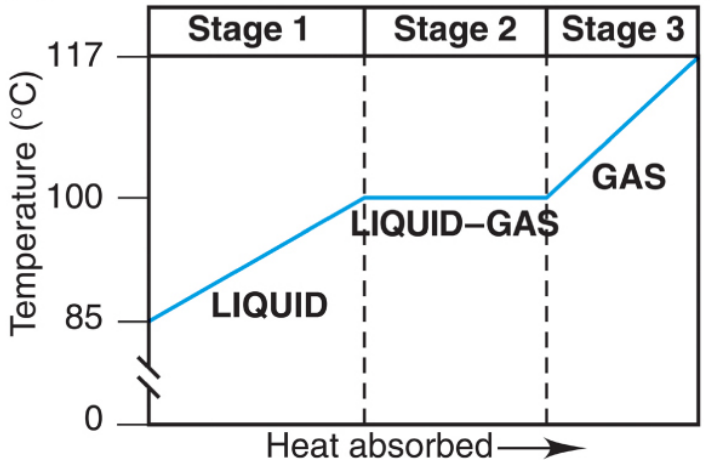

There are 3 stages involved in this process:

1) heating of the liquid to its boiling point
2) the phase change from liquid to gas
3) heating the gas to the final temperature

$$\text{mol } H_2O = 24.3 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 1.35 \text{ mol } H_2O$$

For Stage 1:

$q = n \times C_{water(l)} \times \Delta T$

Molar heat capacity (C) = q/moles x ΔT (J/mol·°C)

C of $H_2O(l)$ = 4.184 J/g.K x 18.02 g/mol = 75.40 J/mol.K

$q = n \times C_{water(l)} \times \Delta T$

= (1.35 mol)(75.4 J/mol·°C)(100. - 85.0°C)

= 1527 J = 1.53 kJ J/mol·°C

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Sample Problem 12.1

For Stage 2:

$q = n(\Delta H^{\circ}_{vap}) = (1.35\ mol)(40.7\ kJ/mol) = 54.9\ kJ$

For Stage 3:

$q = n \times C_{water(g)} \times \Delta T$

$= (1.35\ mol)(33.1\ J/mol{\cdot}°C)(117 - 100.°C)$

$= 759.6\ J = 0.760\ kJ$

C of $H_2O(g) = 1.843\ J/g.K$

$$\boldsymbol{q_{total} = 1.53 + 54.9 + 0.760\ kJ = 57.2\ kJ}$$

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Figure 12.4 Liquid-gas equilibrium.

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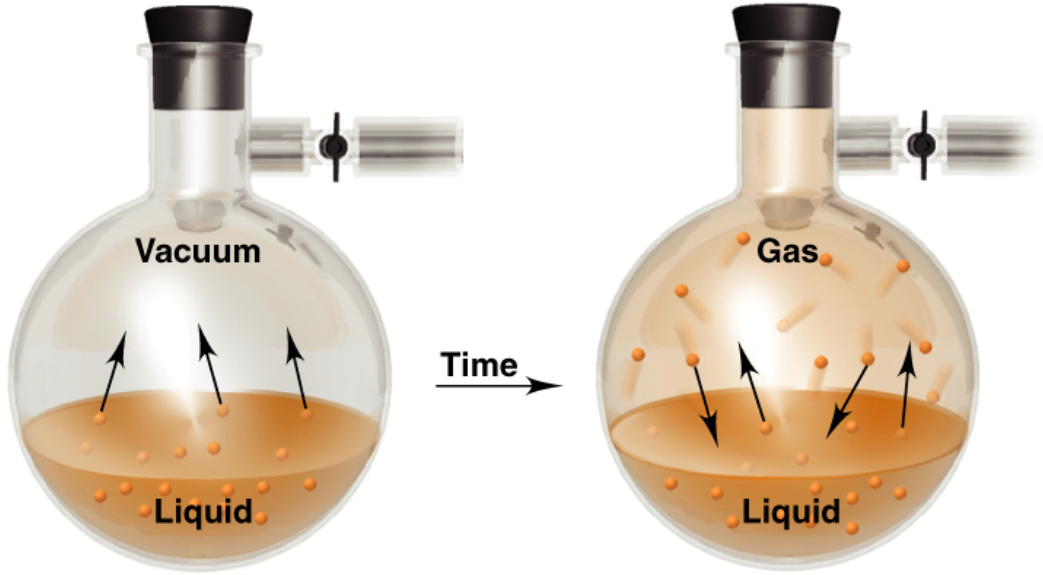

A Molecules in the liquid vaporize.

B Molecules vaporize and condense at the same rate.

In a closed flask, the system reaches a state of ***dynamic equilibrium***, where molecules are leaving and entering the liquid at the ***same rate***.

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Figure 12.4 continued

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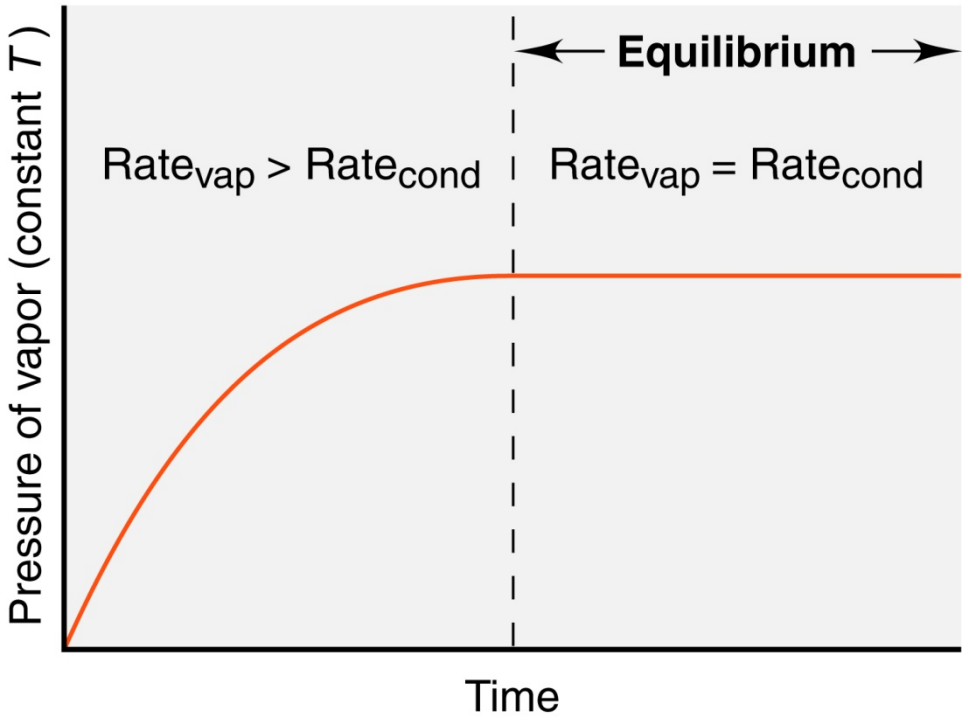

C Plot of pressure vs. time.

The ***vapor pressure*** is the pressure exerted by the vapor on the liquid. The pressure increases until equilibrium is reached; **at equilibrium the pressure is constant**.

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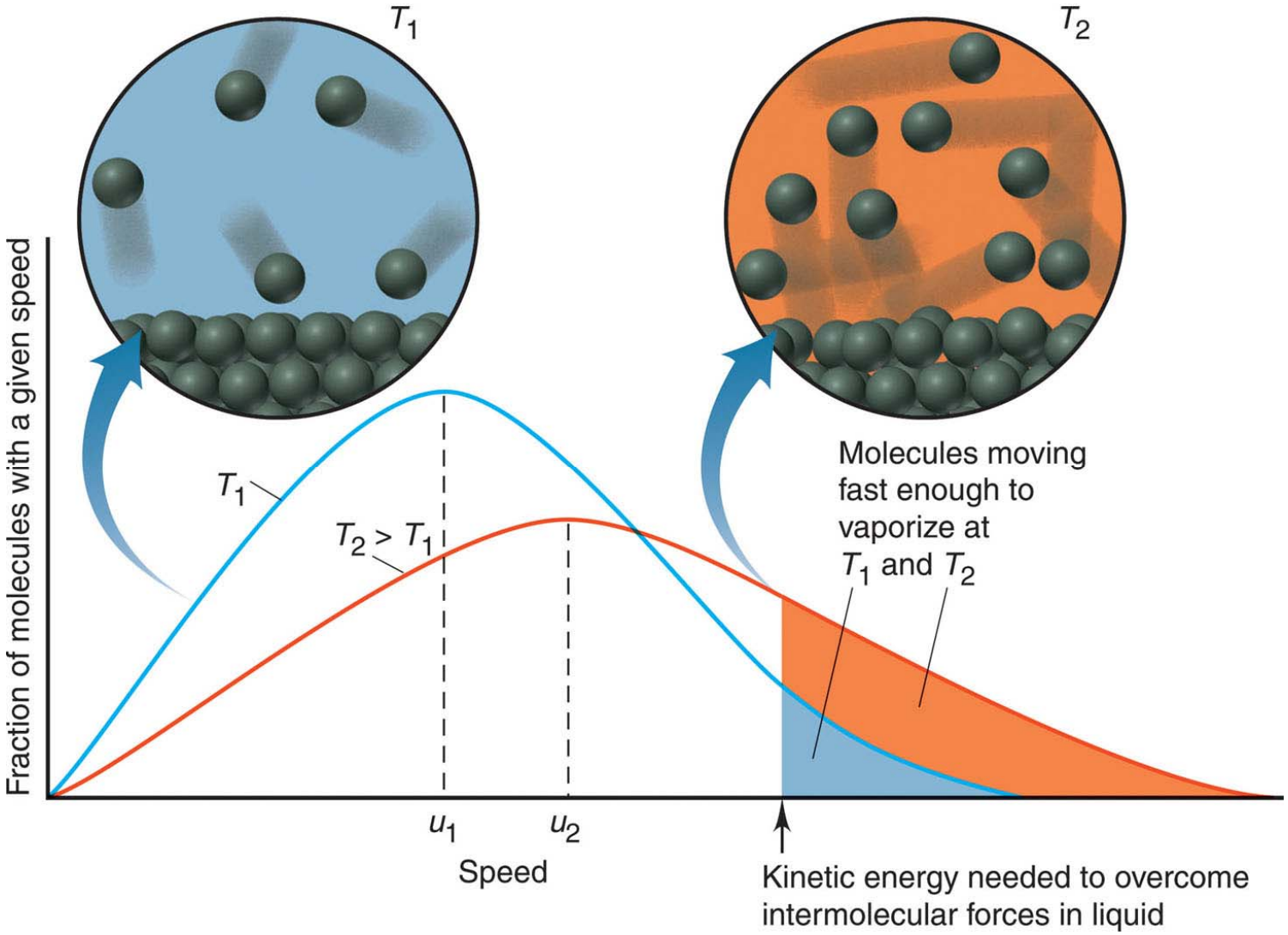
Figure 12.5 **The effect of temperature on the distribution of molecular speeds.**



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Factors affecting Vapor Pressure

As temperature ***increases***, the fraction of molecules with enough energy to enter the vapor phase ***increases***, and the vapor pressure ***increases***.

higher *T* ⟶ higher *P*

The ***weaker*** the intermolecular forces, the ***more*** easily particles enter the vapor phase, and the ***higher*** the vapor pressure.

weaker forces ⟶ higher *P*

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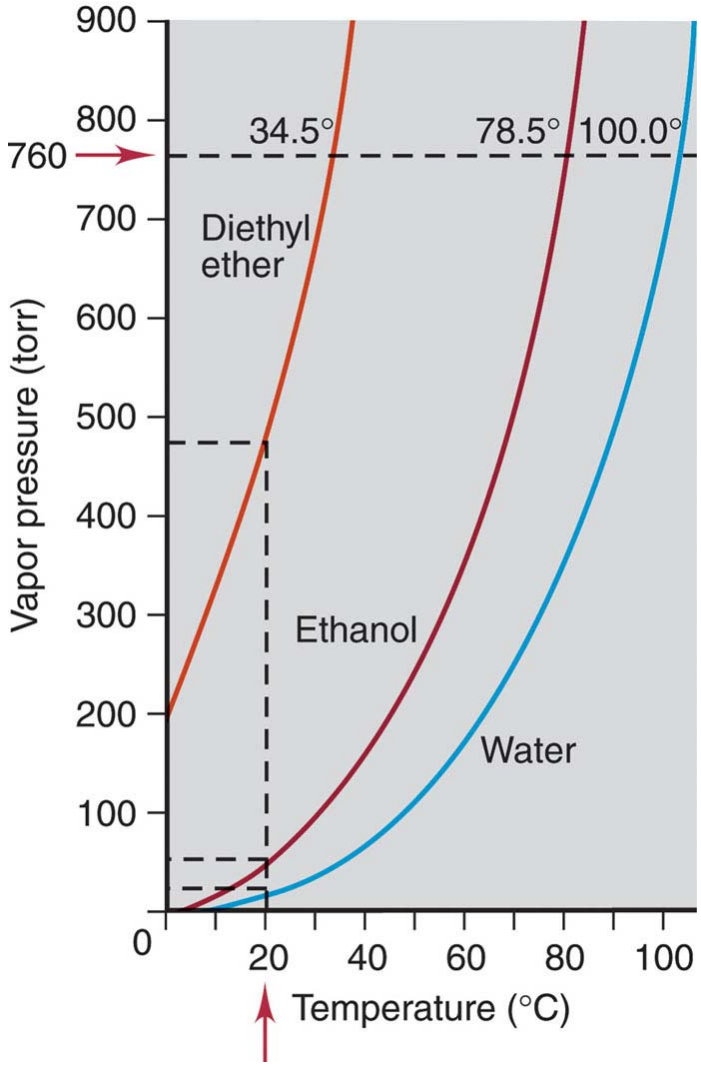
Figure 12.6 Vapor pressure as a function of temperature and intermolecular forces.



Vapor pressure ***increases*** as temperature ***increases***.

Vapor pressure ***decreases*** as the strength of the intermolecular forces ***increases***.

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The Clausius-Clapeyron Equation

This equation relates vapor pressure to temperature.

$$\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$

The two-point form is used when the vapor pressures at two different temperatures are known.

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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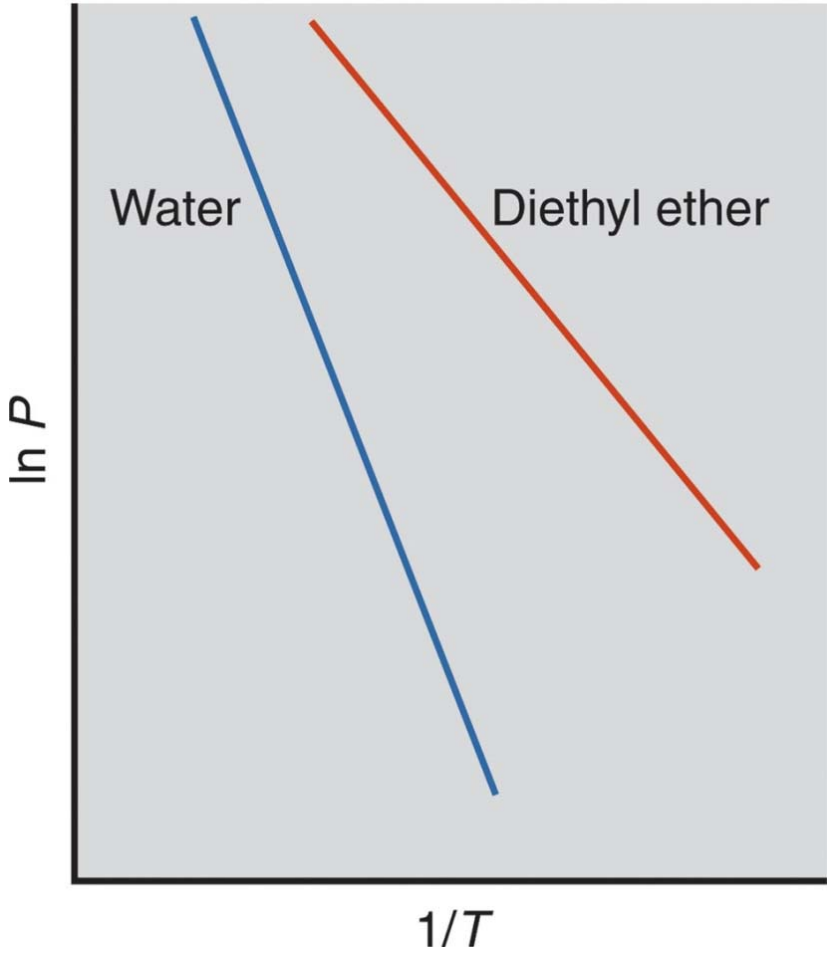
Figure 12.7 **Linear plots of the relationship between vapor pressure and temperature .**



$$\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$

$$\text{slope} = \frac{-\Delta H_{vap}}{R}$$

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Sample Problem 12.2 Applying the Clausius-Clapeyron Equation

PROBLEM: The vapor pressure of ethanol is 115 torr at 34.9°C. If ΔH_{vap} of ethanol is 40.5 kJ/mol, calculate the temperature (in °C) when the vapor pressure is 760 torr.

PLAN: We are given 4 of the 5 variables in the Clausius-Clapeyron equation, so we substitute these into the equation and solve for T_2. T values must be converted to K.

SOLUTION:

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$T_1 = 34.9°C + 273.15 = 308.0\ K$

$$\ln \frac{760\ torr}{115\ torr} = -\frac{40.5 \times 10^3\ J/mol}{8.314\ J/mol \cdot K}\left(\frac{1}{T_2} - \frac{1}{308.0\ K}\right)$$

$$T_2 = 350.\ K - 273.15 = 77°C$$

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Vapor Pressure and Boiling Point

The ***boiling point*** of a liquid is the temperature at which the vapor pressure equals the external pressure.

The ***normal boiling point*** of a substance is observed at standard atmospheric pressure or 760 torr.

As the external pressure on a liquid ***increases***, the boiling point ***increases***.

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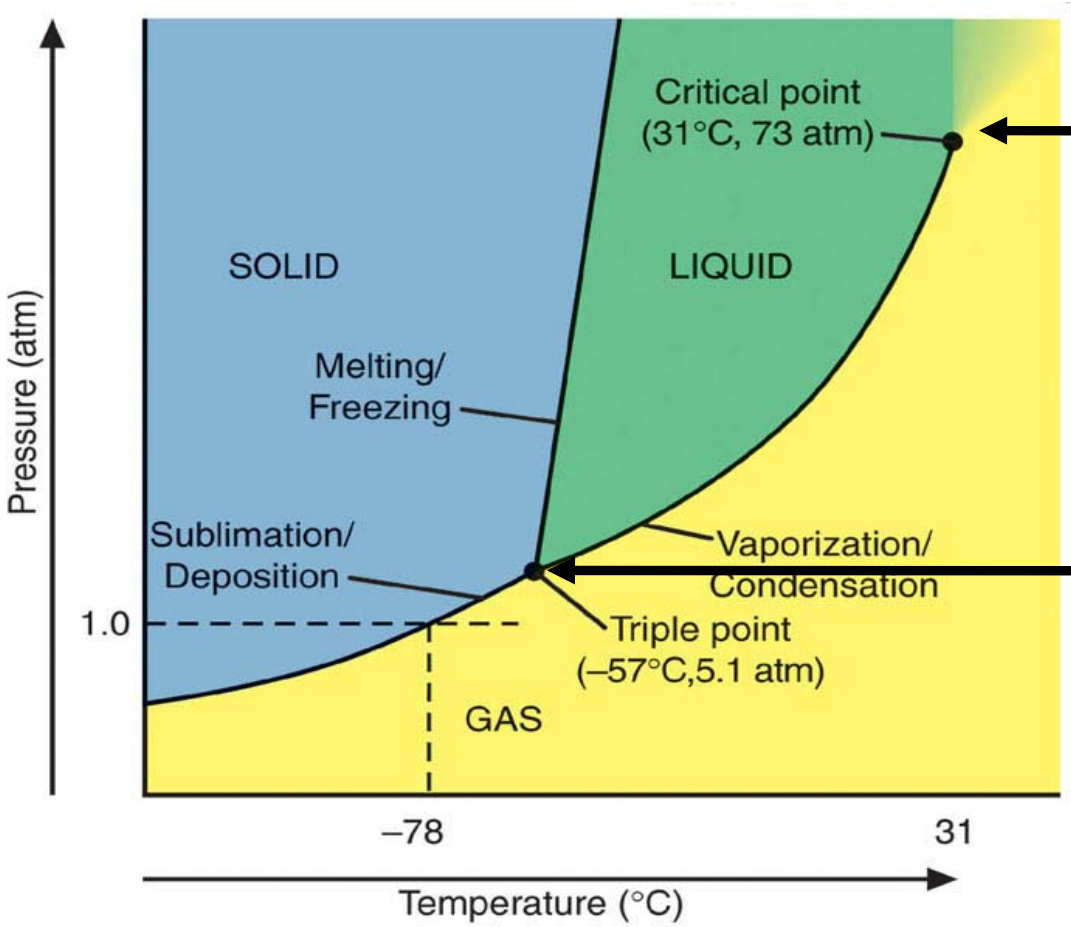
Figure 12.8 Phase diagram for CO_2.



At the critical point, the densities of the liquid and gas phases become equal.

At the triple point, all three phases are in equilibrium.

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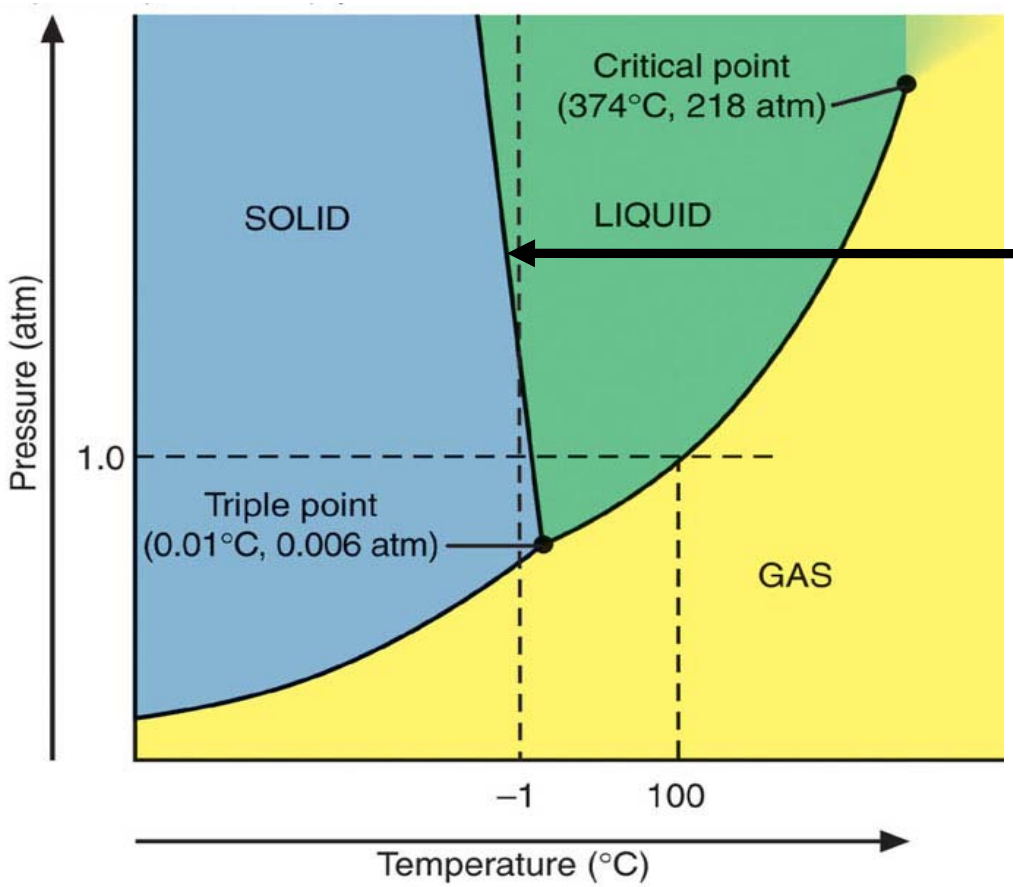
Figure 12.8 Phase diagram for H_2O.



The solid-liquid line slants to the *left* for H_2O, because the solid is *less* dense than the liquid. Water expands on freezing.

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The Nature of Intermolecular Forces

Intermolecular forces arise from the attraction between molecules with partial charges, or between ions and molecules.

Intermolecular forces are relatively ***weak*** compared to bonding forces because they involve smaller charges that are farther apart.

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Figure 12.9A Covalent and van der Waals radii.

The van der Waals ***distance*** is the distance between two ***nonbonded*** atoms in ***adjacent*** molecules.

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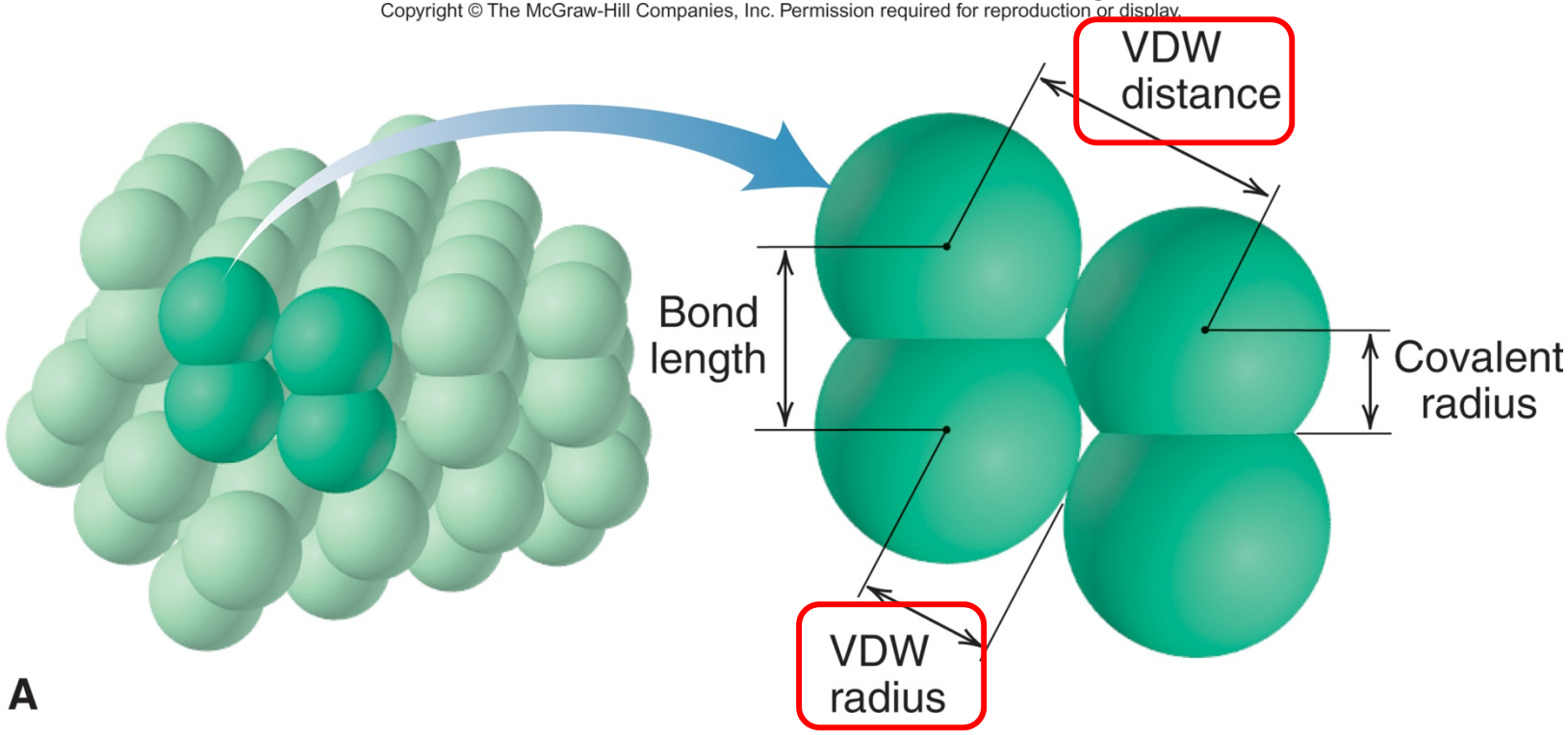

The van der Waals ***radius*** is one-half the closest distance between the nuclei of two ***nonbonded*** atoms. The VDW radius is ***always larger*** than the covalent radius.

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Figure 12.9B Periodic trends in covalent and van der Waals radii.

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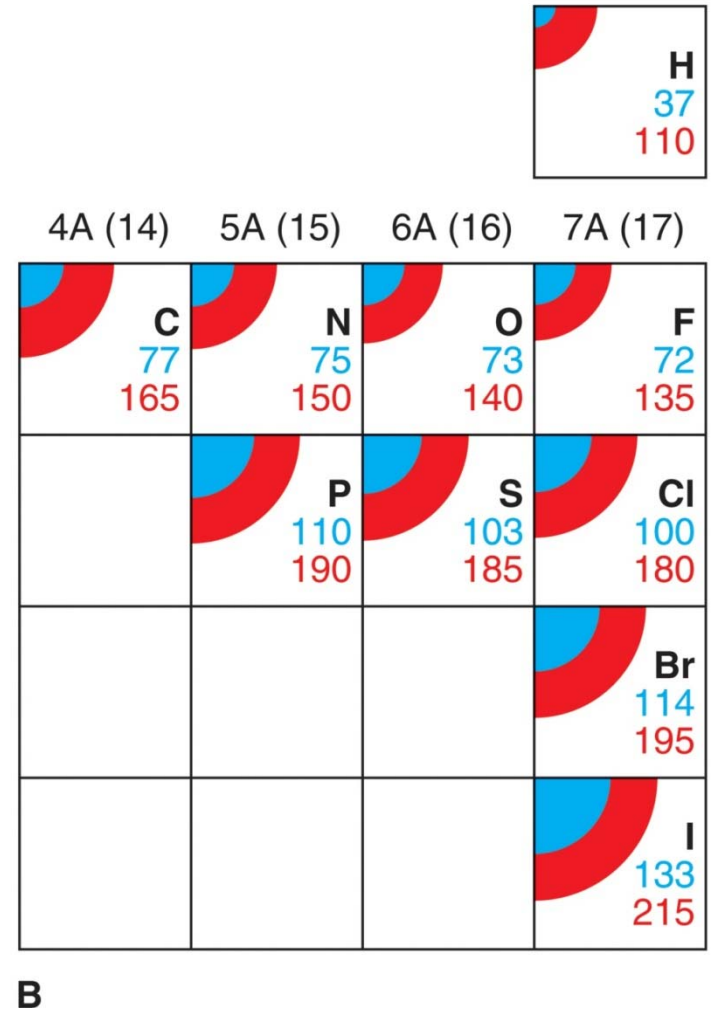

B

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Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

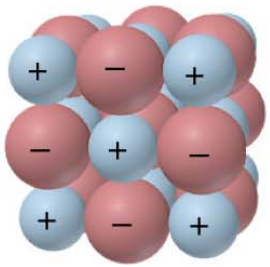
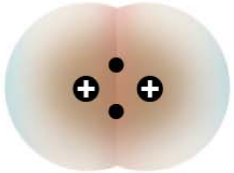
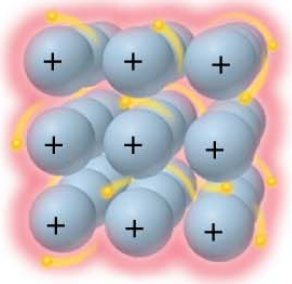
Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

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Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces (continued)

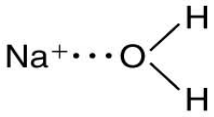
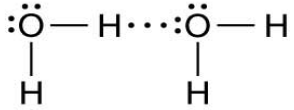
Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	
H bond		Polar bond to H–dipole charge (high EN of N, O, F)	10–40	
Dipole-dipole		Dipole charges	5–25	
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	
Dispersion (London)		Polarizable e^- clouds	0.05–40	

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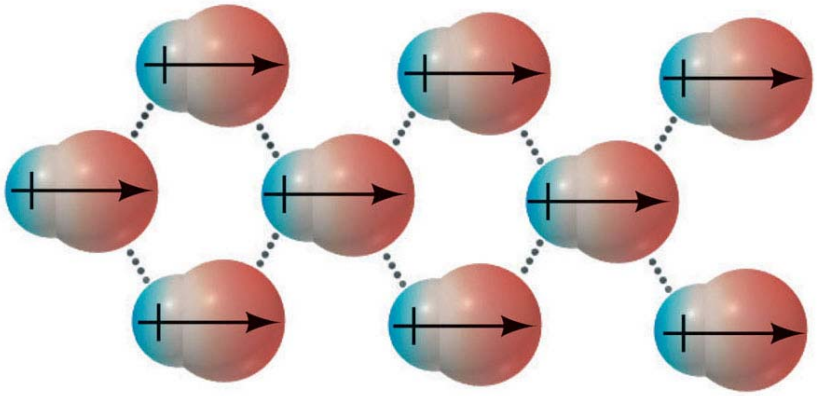
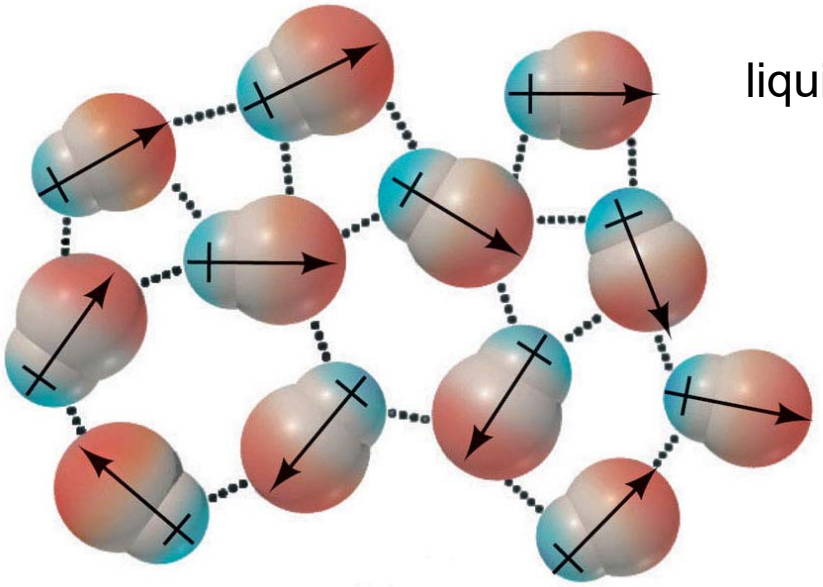
Figure 12.10 Polar molecules and dipole-dipole forces.



solid



liquid

The positive pole of one polar molecule attracts the negative pole of another.

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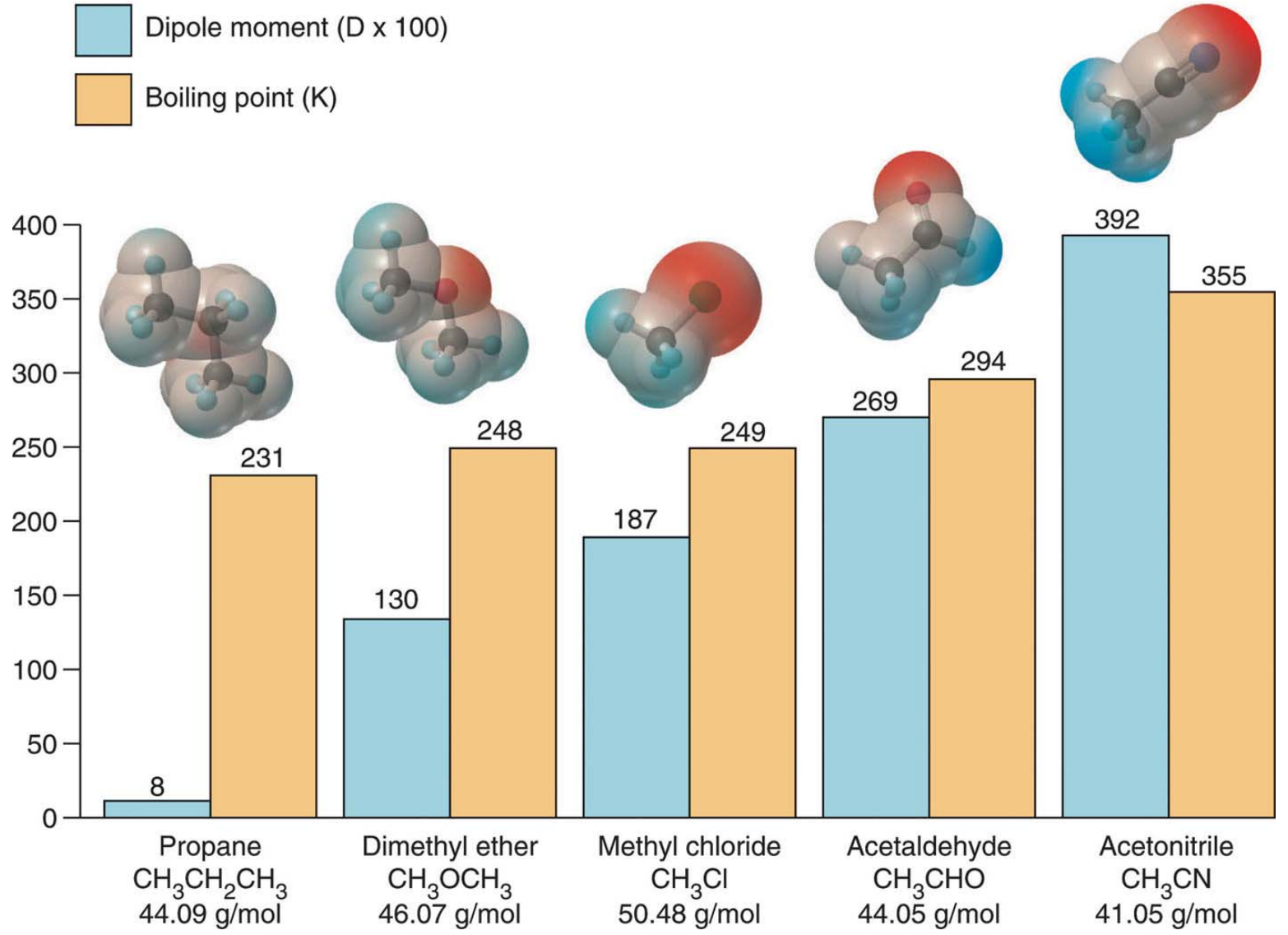
Figure 12.11 Dipole moment and boiling point.



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The Hydrogen Bond

Hydrogen bonding is possible for molecules that have a ***hydrogen atom*** covalently bonded to a small, highly electronegative atom with ***lone electron pairs***, specifically ***N, O, or F***.

An intermolecular ***hydrogen bond*** is the attraction between the ***H atom*** of one molecule and a ***lone pair of the N, O, or F atom*** of another molecule.

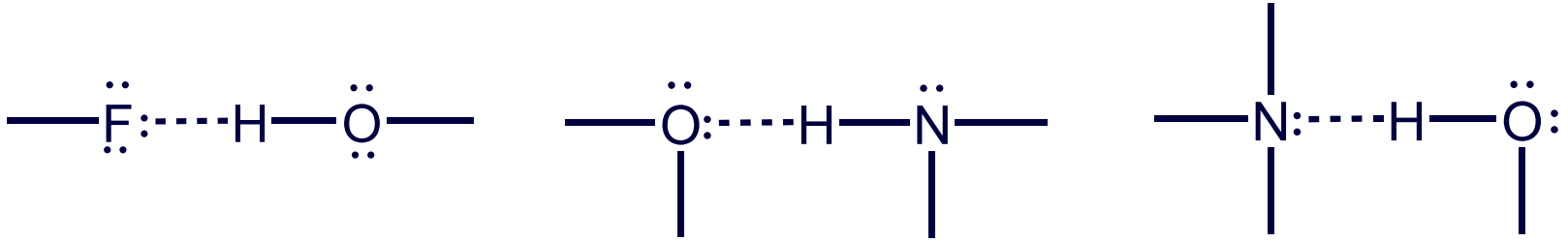

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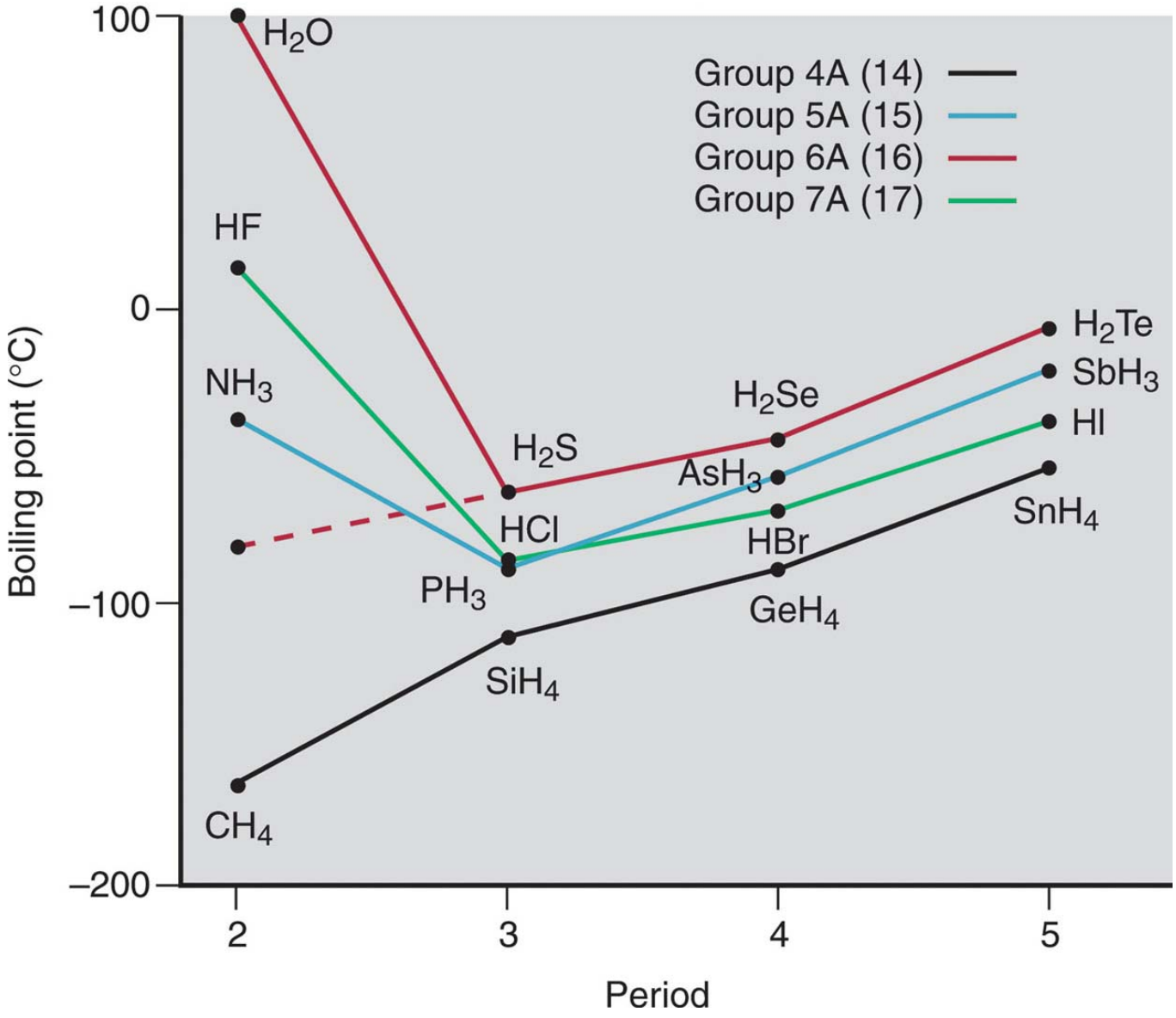
Figure 12.12 Hydrogen bonding and boiling point.



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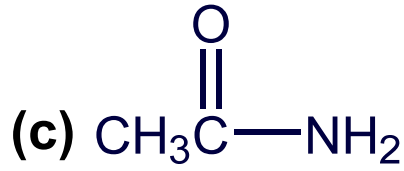
Sample Problem 12.3 **Drawing Hydrogen Bonds Between Molecules of a Substance**

PROBLEM: Which of the following substances exhibits H bonding? For any that do, draw the H bonds between two of its molecules.

(a) C_2H_6 **(b)** CH_3OH **(c)** 

PLAN: If the molecule does not contain N, O, or F it cannot form H bonds. If it contains any of these atoms covalently bonded to H, we draw two molecules in the pattern –B:----H–A.

SOLUTION:

(a) C_2H_6 has no N, O, or F, so **no H-bonds can form**.

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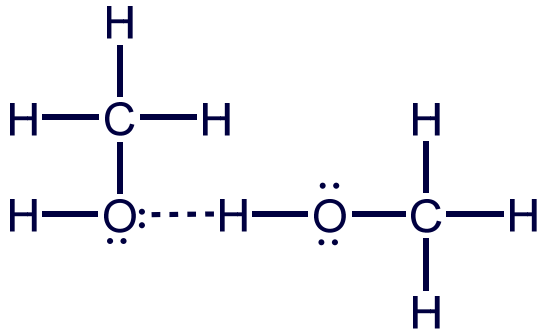
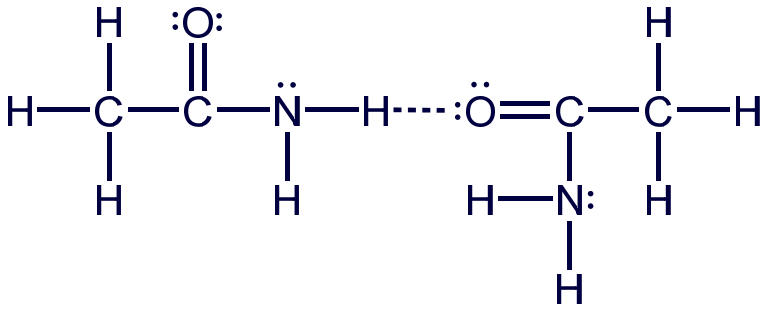
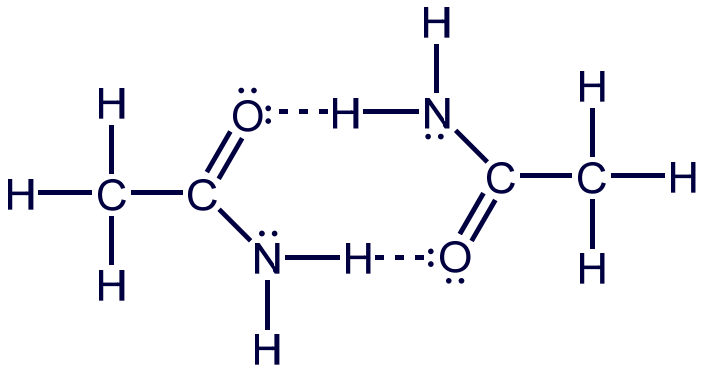
Sample Problem 12.3

(b) CH_3OH contains a covalent bond between O and H. It can form H bonds between its molecules:



(c) $CH_3C(=O)NH_2$ can form H bonds at two sites:





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Polarizability and Induced Dipoles

A nearby electric field can ***induce*** a distortion in the electron cloud of an atom, ion, or molecule.

- For a ***nonpolar*** molecule, this induces a ***temporary dipole moment***.
- For a ***polar*** molecule, the field ***enhances*** the existing dipole moment.

The ***polarizability*** of a particle is the ease with which its electron cloud is distorted.

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Trends in Polarizability

Smaller particles are ***less polarizable*** than larger ones because their electrons are held more tightly.

Polarizability ***increases down a group*** because atomic size increases and larger electron clouds distort more easily.

Polarizability ***decreases across a period*** because of increasing Z_{eff}.

Cations are smaller than their parent atoms and less polarizable; anions show the opposite trend.

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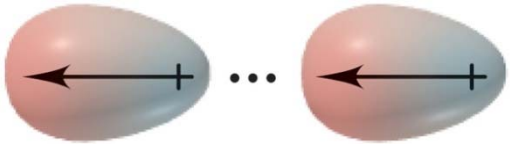
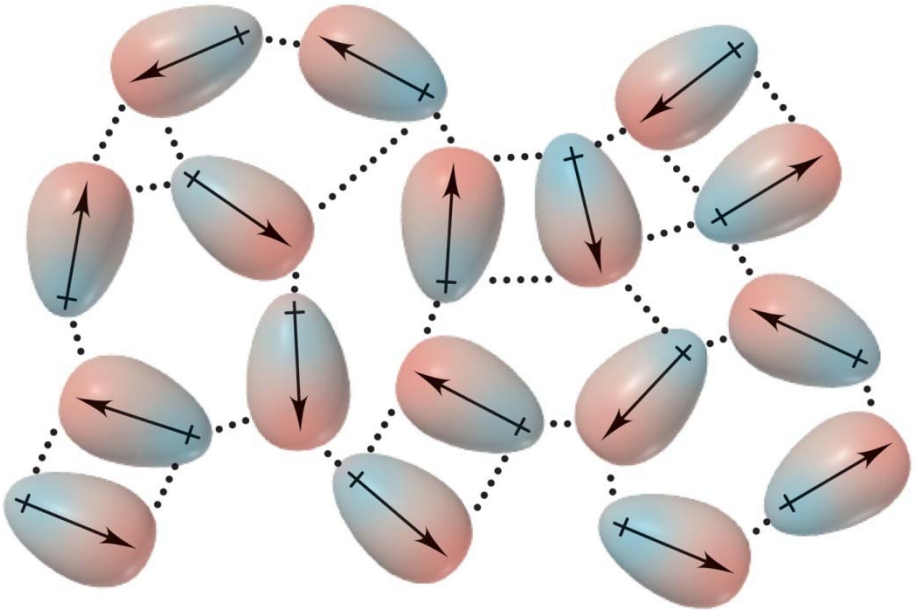
Figure 12.13 Dispersion forces among nonpolar particles.

A. When atoms are far apart they do not influence one other.



B. When atoms are close together, the instantaneous dipole in one atom induces a dipole in the other.



C. The process occurs throughout the sample.

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Dispersion (London) Forces

Dispersion forces or ***London forces*** arises when an ***instantaneous dipole*** in one particle ***induces*** a dipole in another, resulting in an attraction between them.

Dispersion forces exist between ***all particles***, increasing the energy of attraction in all matter.

Dispersion forces are ***stronger*** for ***more polarizable*** particles.

In general, larger particles experience stronger dispersion forces than smaller ones.

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Figure 12.14 Molar mass and trends in boiling point.

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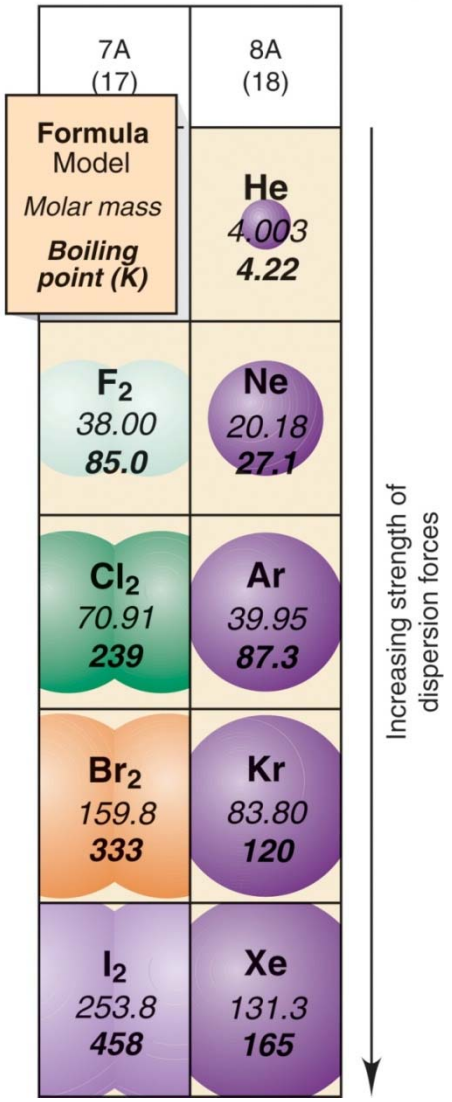

Dispersion forces are stronger for larger, more polarizable particles.

Polarizability correlates closely with molar mass for similar particles.

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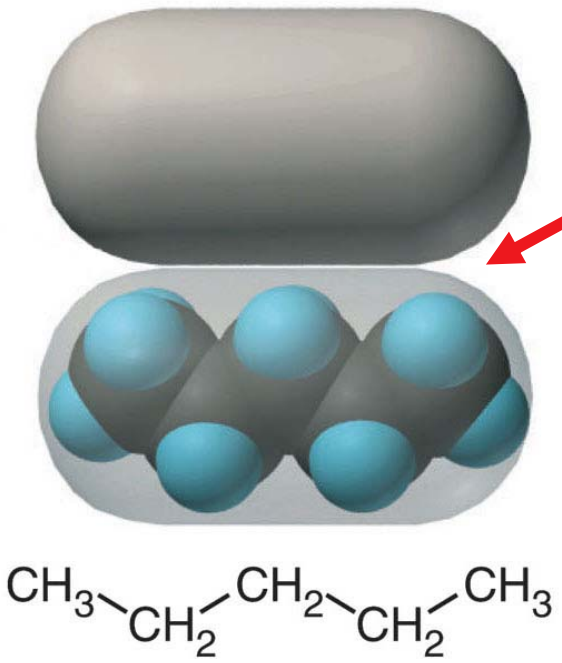
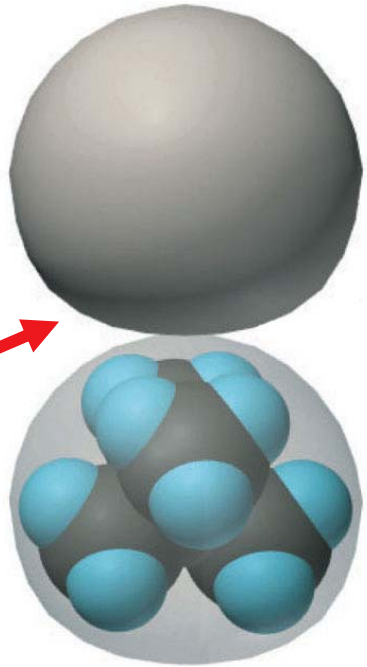
Figure 12.15 **Molecular shape, intermolecular contact, and boiling point.**

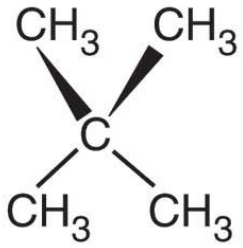


There are more points at which dispersion forces act.

n-Pentane, bp = 36.1°C

There are fewer points at which dispersion forces act.





Neopentane, bp = 9.5°C

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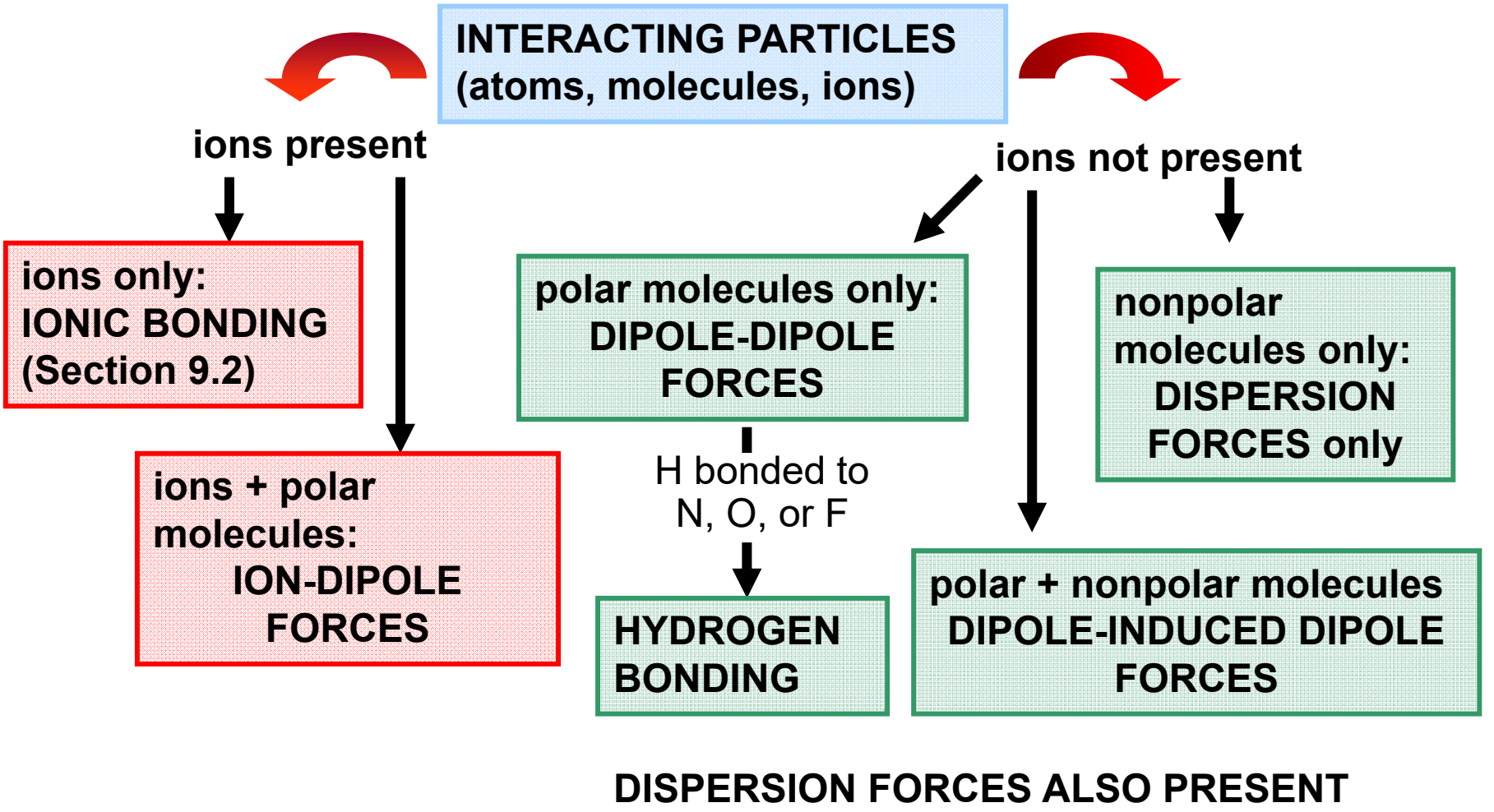
Figure 12.16 Determining the intermolecular forces in a sample.



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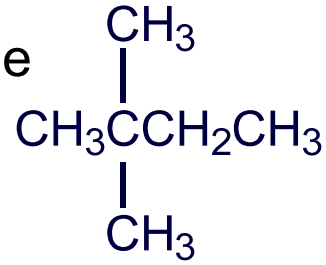
Sample Problem 12.4 Predicting the Types of Intermolecular Forces

PROBLEM: For each pair of substances, identify the key bonding and/or intermolecular force(s), and predict which one of the pair has the higher boiling point:

(a) $MgCl_2$ or PCl_3 **(b)** CH_3NH_2 or CH_3F **(c)** CH_3OH or CH_3CH_2OH

(d) Hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) or 2,2-dimethylbutane



PLAN: We examine the formulas and structures for key differences between the members of each pair: Are ions present? Are molecules polar or nonpolar? Is N, O, or F bonded to H? Do molecular compounds have different masses or shapes?

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Sample Problem 12.4

Remember that:

- Bonding forces are stronger than nonbonding (intermolecular) forces.
- Hydrogen bonding is a strong type of dipole-dipole force.
- Dispersion forces are decisive when the difference is molar mass or molecular shape.

SOLUTION:

(a) $MgCl_2$ consists of Mg^{2+} and Cl^- ions held together by **ionic bonding forces**; PCl_3 consists of polar molecules, so intermolecular **dipole-dipole** forces are present. The ionic bonding forces in $MgCl_2$ are stronger than the dipole-dipole forces in PCl_3.

$MgCl_2$ has a higher boiling point than PCl_3.

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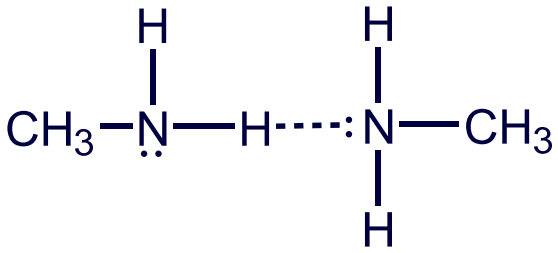
Sample Problem 12.4

(b) CH_3NH_2 and CH_3F both consist of **polar molecules** of about the same molar mass. CH_3NH_2 has covalent N-H bonds, so it can form **H bonds** between its molecules. CH_3F contains a C-F bond but no H-F bond, so **dipole-dipole** forces occur but not H bonds.



CH_3NH_2 has a higher boiling point than CH_3F.

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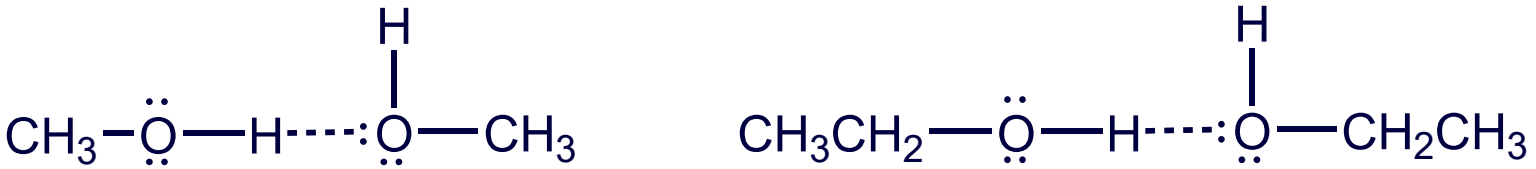
Sample Problem 12.4

(c) CH_3OH and CH_3CH_2OH are both **polar molecules** and both contain a covalent O-H bond. Both can therefore form **H bonds**.



CH_3CH_2OH has a larger molar mass than CH_3OH and its **dispersion forces** are therefore stronger.

CH_3CH_2OH has a higher boiling point than CH_3OH.

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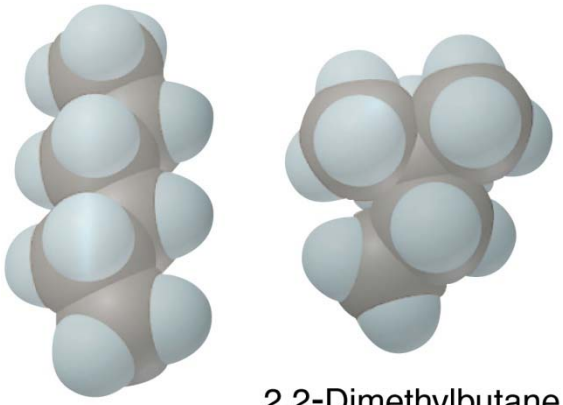
Sample Problem 12.4

(d) Hexane and 2,2-dimethylbutane are both **nonpolar molecules** and therefore experience **dispersion forces** as their only intermolecular force. They have equal molar masses but different molecular shapes.



Hexane

2,2-Dimethylbutane

Cylindrical hexane molecules make more intermolecular contact than the more compact 2,2-dimethylbutane molecules.

Hexane has a higher boiling point than 2,2-dimethylbutane.

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Sample Problem 12.4

CHECK:

The actual boiling points show our predictions are correct:

(a) $MgCl_2$ (1412°C) and PCl_3 (76°C)
(b) CH_3NH_2 (-6.3°C) and CH_3F (-78.4°C)
(c) CH_3OH (64,7°C) and CH_3CH_2OH (78.5°C)
(d) Hexane (69°C) and 2,2-dimethylbutane (49.7°C)

Remember that ***dispersion forces are always present***, but in (a) and (b) they are much less significant than the other forces that occur.

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Figure 12.17 The molecular basis of surface tension.

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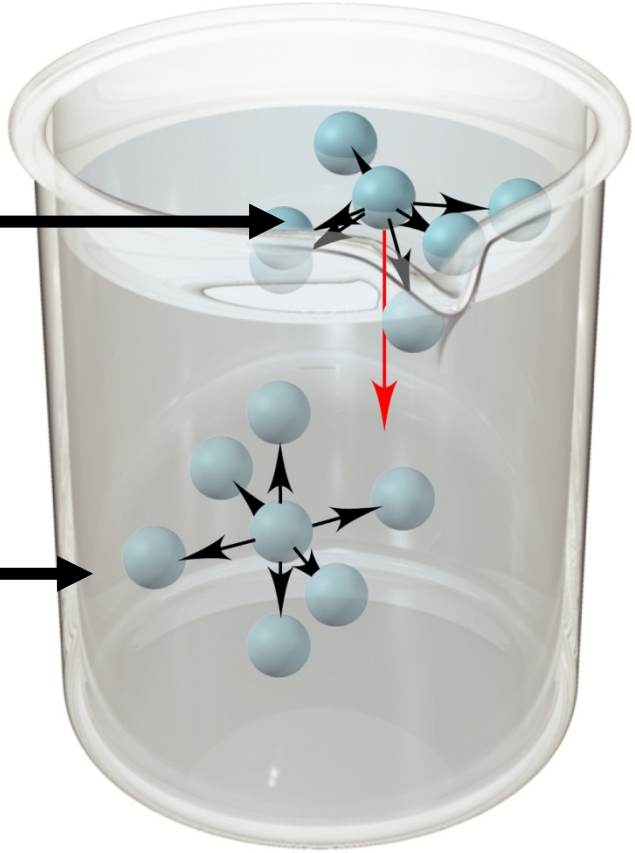
A surface molecule experiences a *net attraction downward*. This causes a liquid surface to have the smallest area possible.

An interior molecule is attracted by others on all sides.



Surface tension is the energy required to increase the surface area of a liquid. The ***stronger*** the forces between the particles the ***higher*** the surface tension.

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Table 12.3 Surface Tension and Forces Between Particles

Substance	Formula	Surface Tension (J/m^2) at 20^0C	Major Force(s)
Diethyl ether	$CH_3CH_2OCH_2CH_3$	$1.7x10^{-2}$	Dipole-dipole; dispersion
Ethanol	CH_3CH_2OH	$2.3x10^{-2}$	H bonding
Butanol	$CH_3CH_2CH_2CH_2OH$	$2.5x10^{-2}$	H bonding; dispersion
Water	H_2O	$7.3x10^{-2}$	H bonding
Mercury	Hg	$48x10^{-2}$	Metallic bonding

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Figure 12.18 Capillary action and the shape of the water or mercury meniscus in glass.

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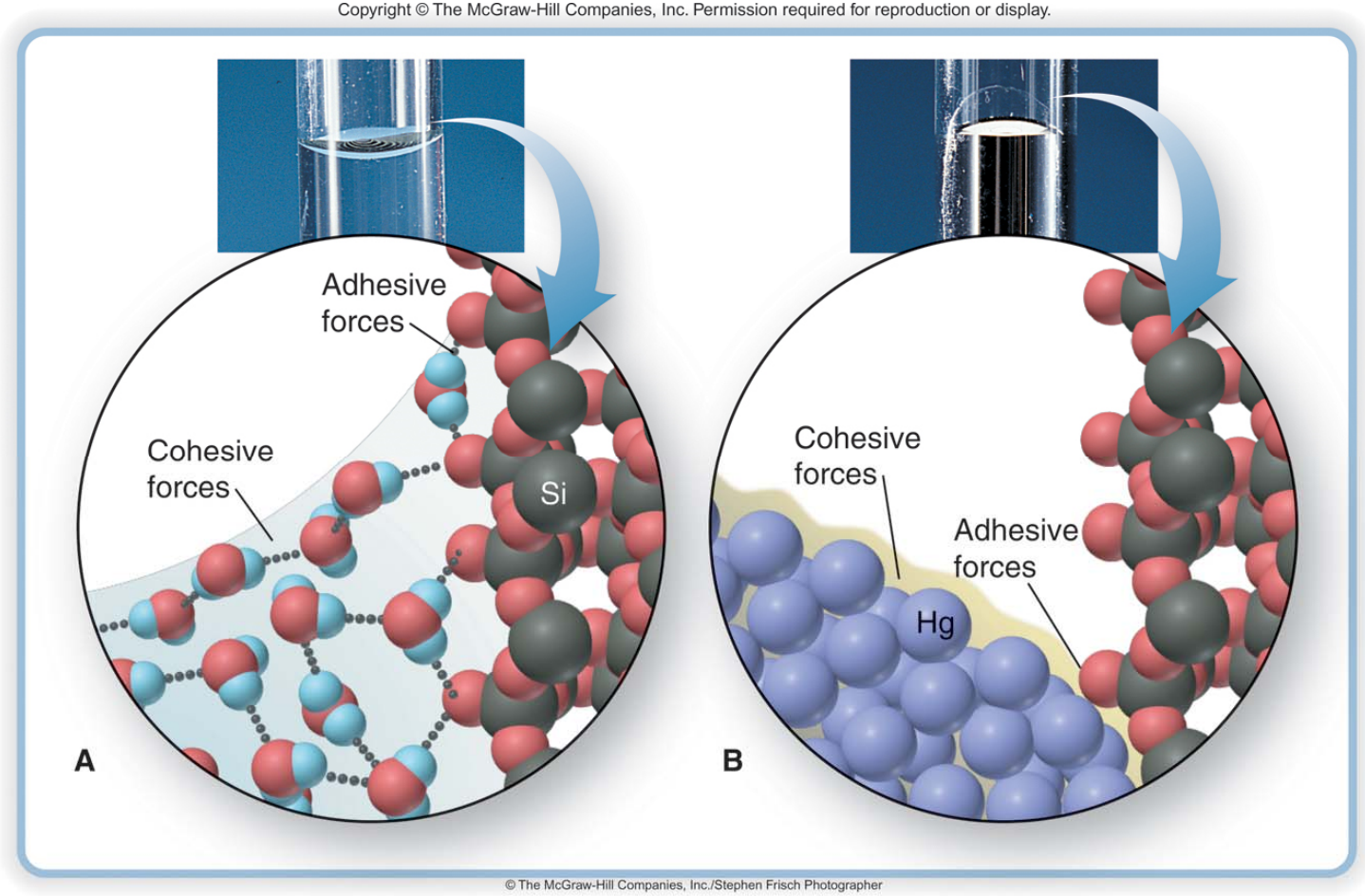

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A. Water displays a concave meniscus.

B. Mercury displays a convex meniscus.

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Table 12.4 Viscosity of Water at Several Temperatures

Viscosity is resistance of a fluid to flow.

Temperature (°C)	Viscosity ($N \cdot s/m^2$)*
20	1.00×10^{-3}
40	0.65×10^{-3}
60	0.47×10^{-3}
80	0.35×10^{-3}

*The units of viscosity are Newton-seconds per square meter.

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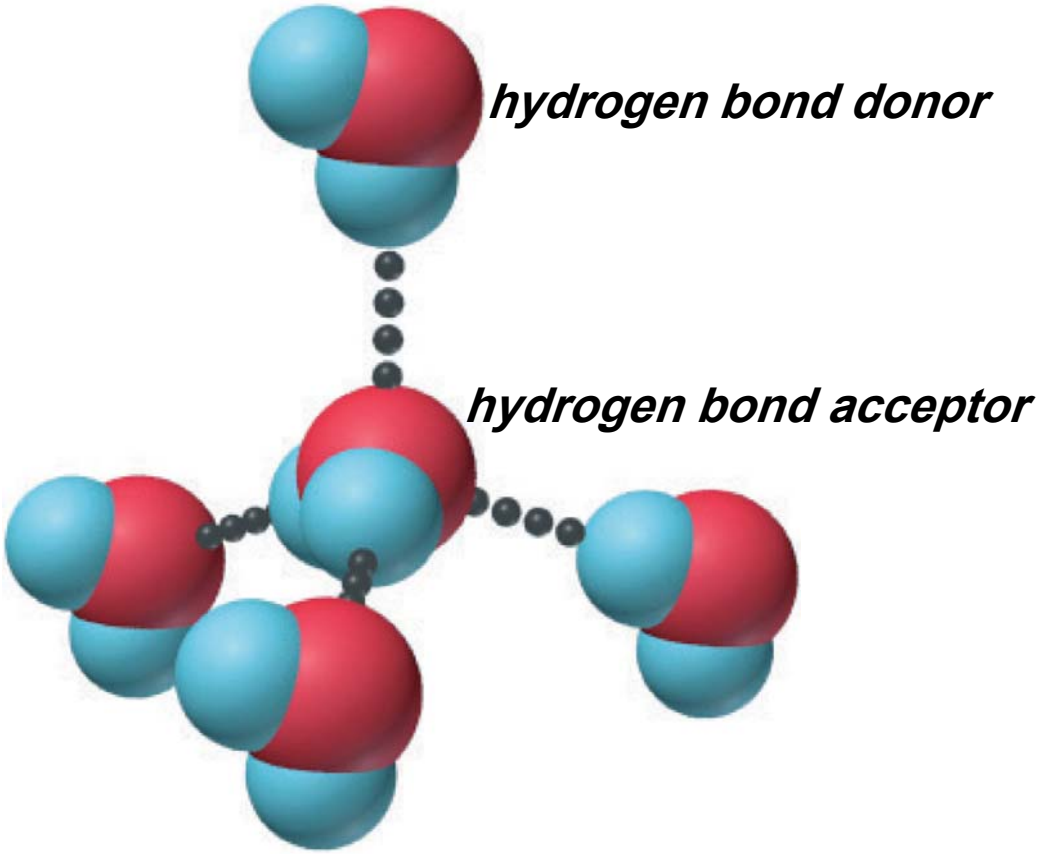
Figure 12.19 H-bonding ability of water.



Each H_2O molecule can form ***four*** H bonds to other molecules, resulting in a tetrahedral arrangement.

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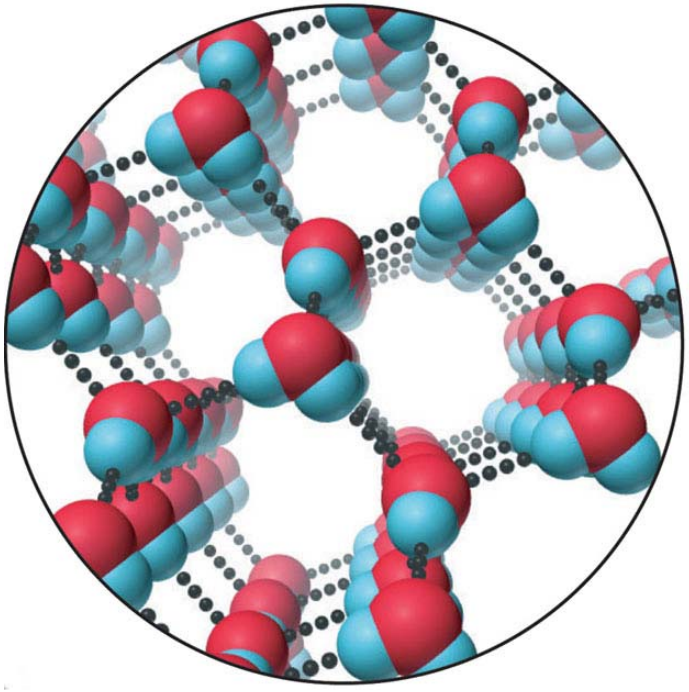
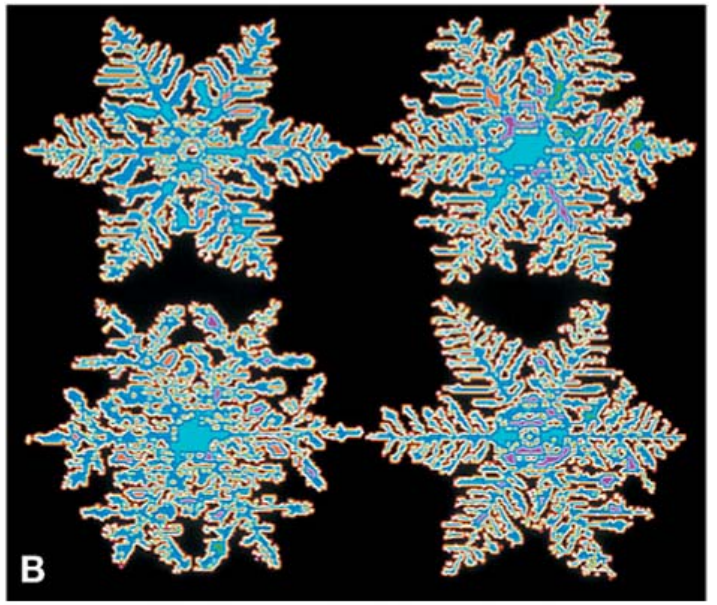
Figure 12.20 The hexagonal structure of ice.





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Ice has an open structure due to H bonding. Ice is therefore ***less dense*** than liquid water.

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The Solid State

Solids are divided into two categories:

Crystalline solids have well defined shapes due to the orderly arrangement of their particles.

Amorphous solids lack orderly arrangement and have poorly defined shapes.

A ***crystal*** is composed of particles packed in an orderly three-dimensional array called the ***crystal lattice***.

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Figure 12.21 The beauty of crystalline solids.

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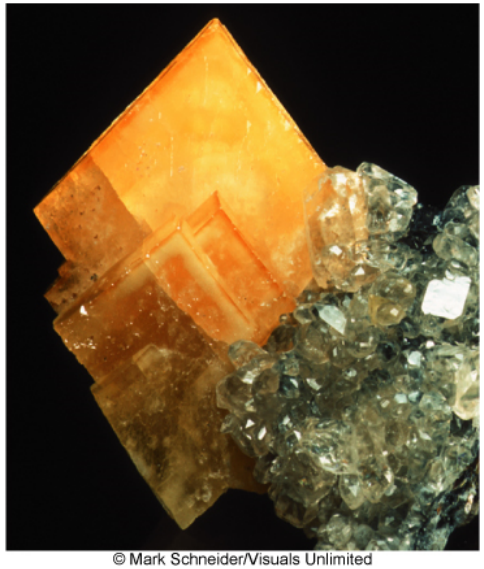

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Figure 12.22 The crystal lattice and the unit cell.

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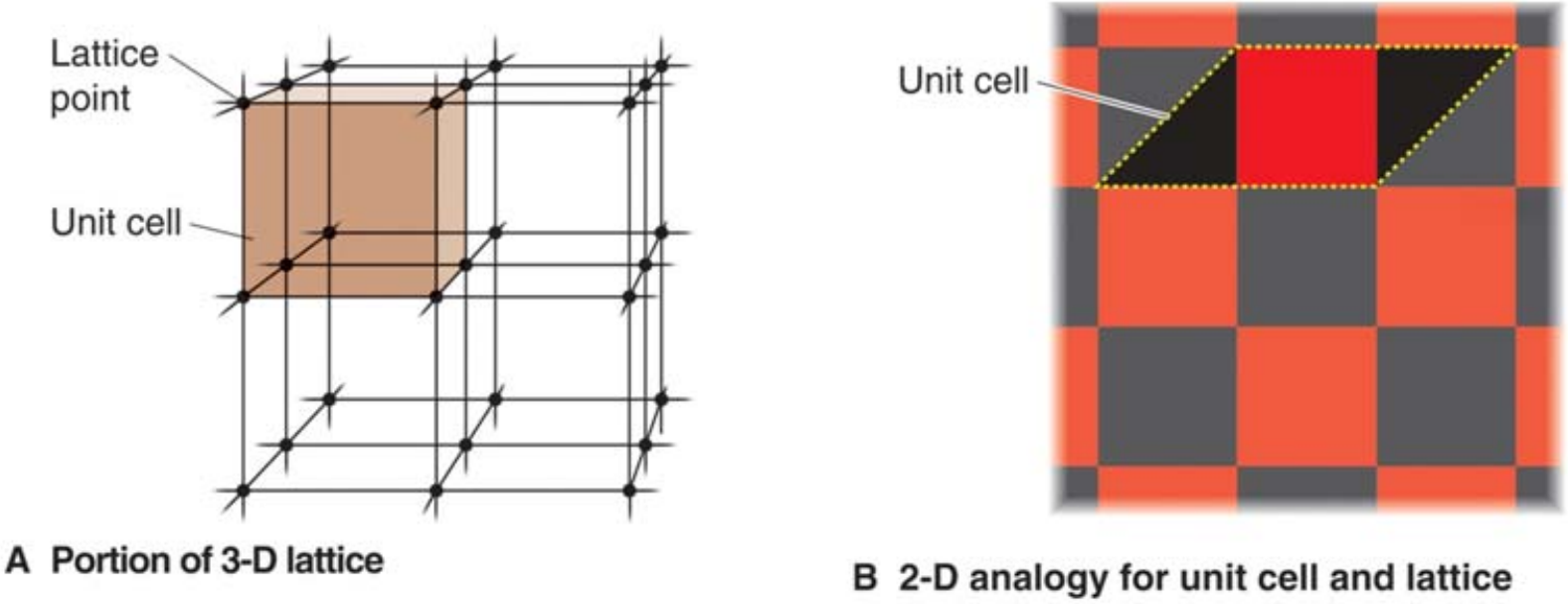

A Portion of 3-D lattice

B 2-D analogy for unit cell and lattice

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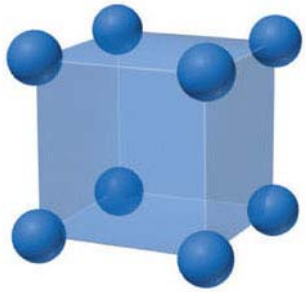
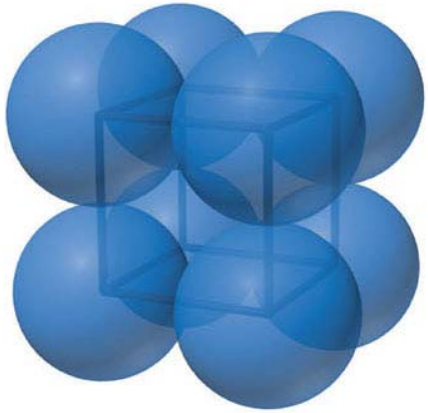
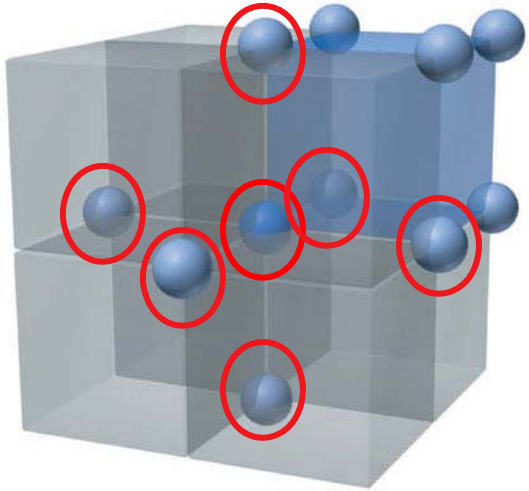
Figure 12.23A **Simple cubic unit cell.**



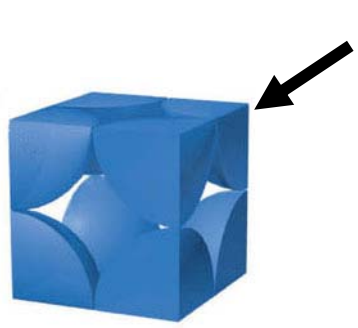
Expanded view.



Space-filling view.



Coordination number = 6



Atoms/unit cell = (⅛ x 8) = 1

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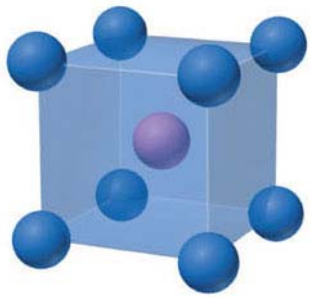
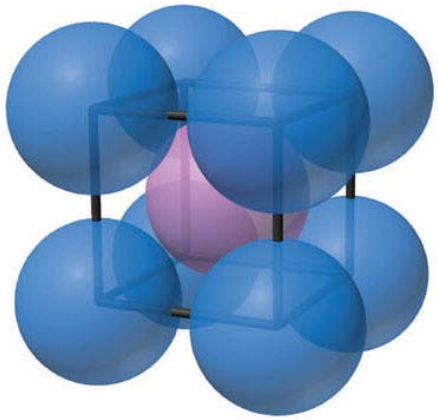
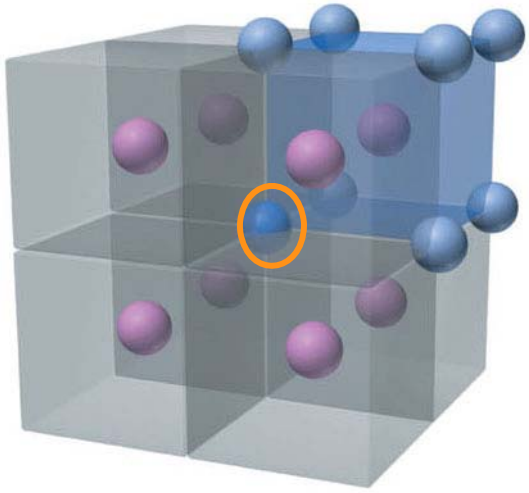
Figure 12.23B Body-centered cubic unit cell.







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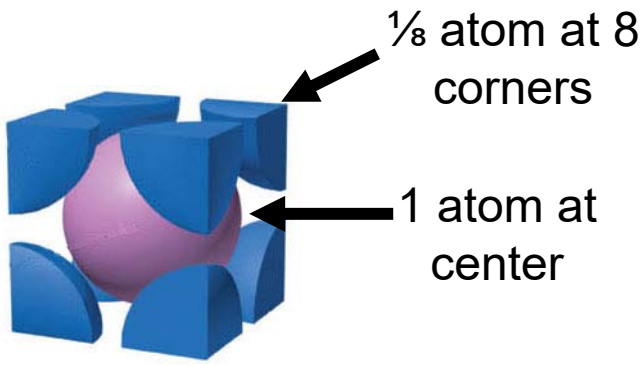

Atoms/unit cell = (⅛ x 8) + 1 = 2

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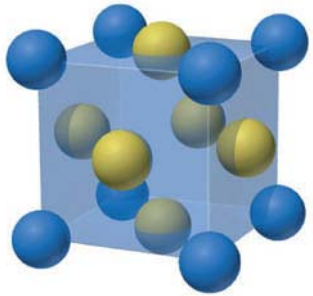
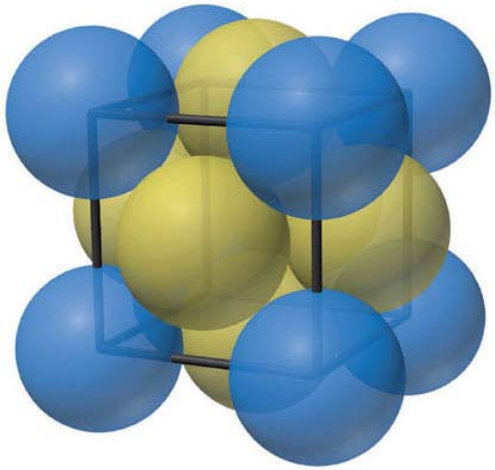
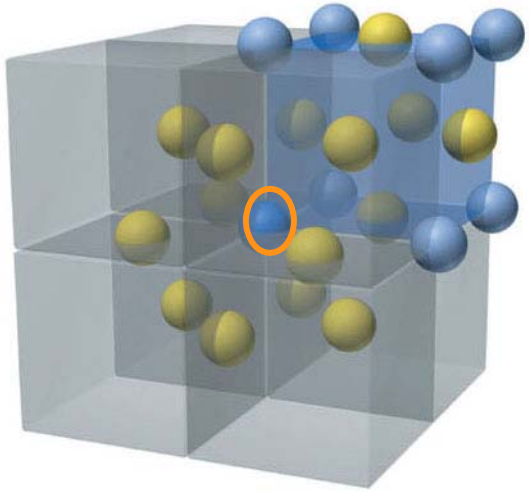
Figure 12.23C **The face-centered cubic cell.**







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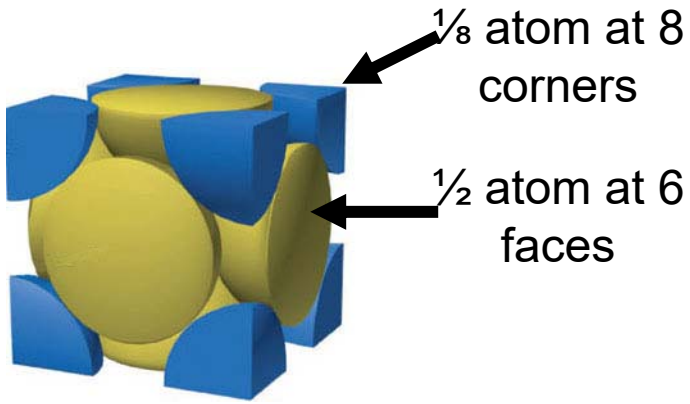

Atoms/unit cell = (⅛ x 8) + (½ x 6) = 4

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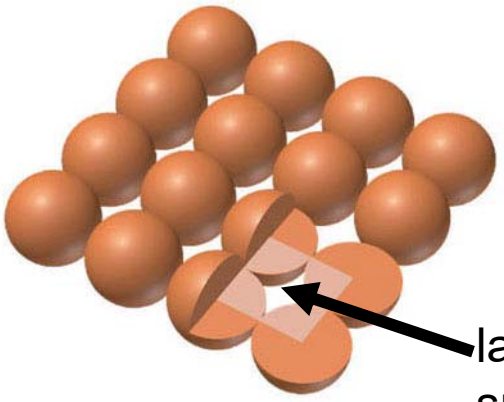
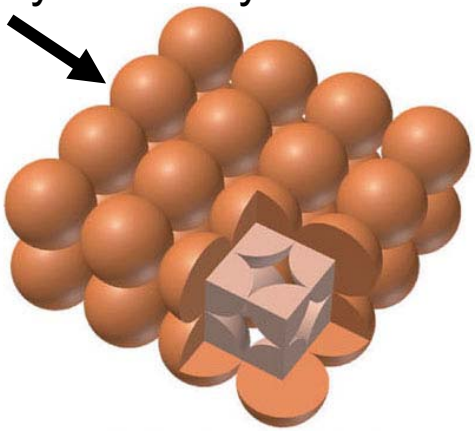
Figure 12.24 **Packing spheres to obtain three cubic and hexagonal cells.**



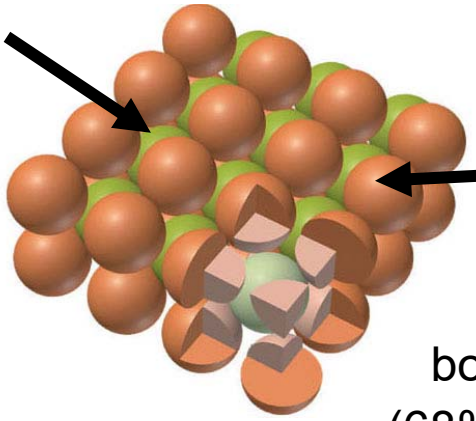
large diamond space

2nd layer directly over 1st



simple cubic
(52% packing efficiency)

2nd layer over diamond spaces in 1st



3rd layer over diamond spaces in 2nd

body-centered cubic
(68% packing efficiency)

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Figure 12.24 continued

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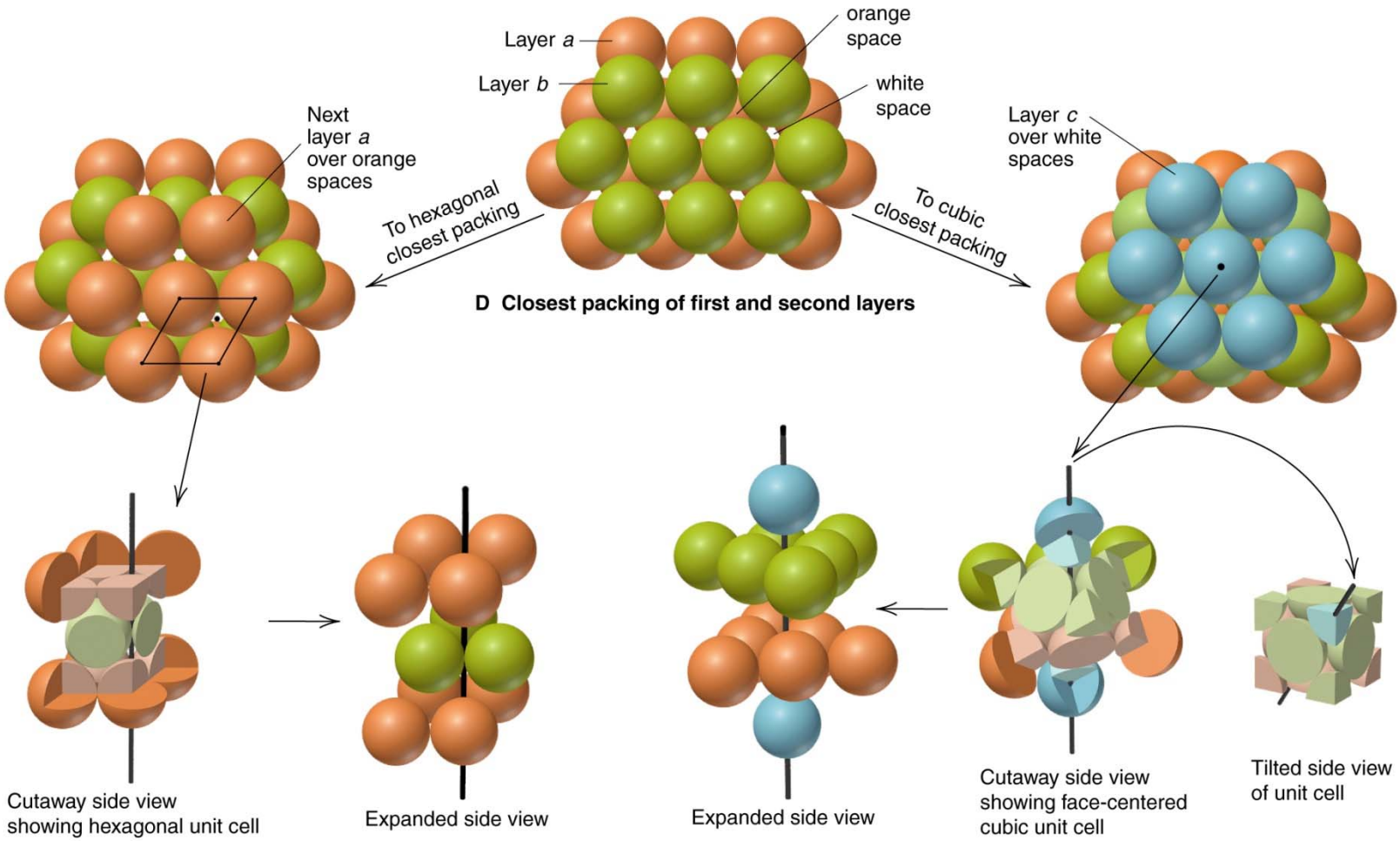

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Figure 12.26 **Edge length and atomic (ionic) radius in the three cubic unit cells.**

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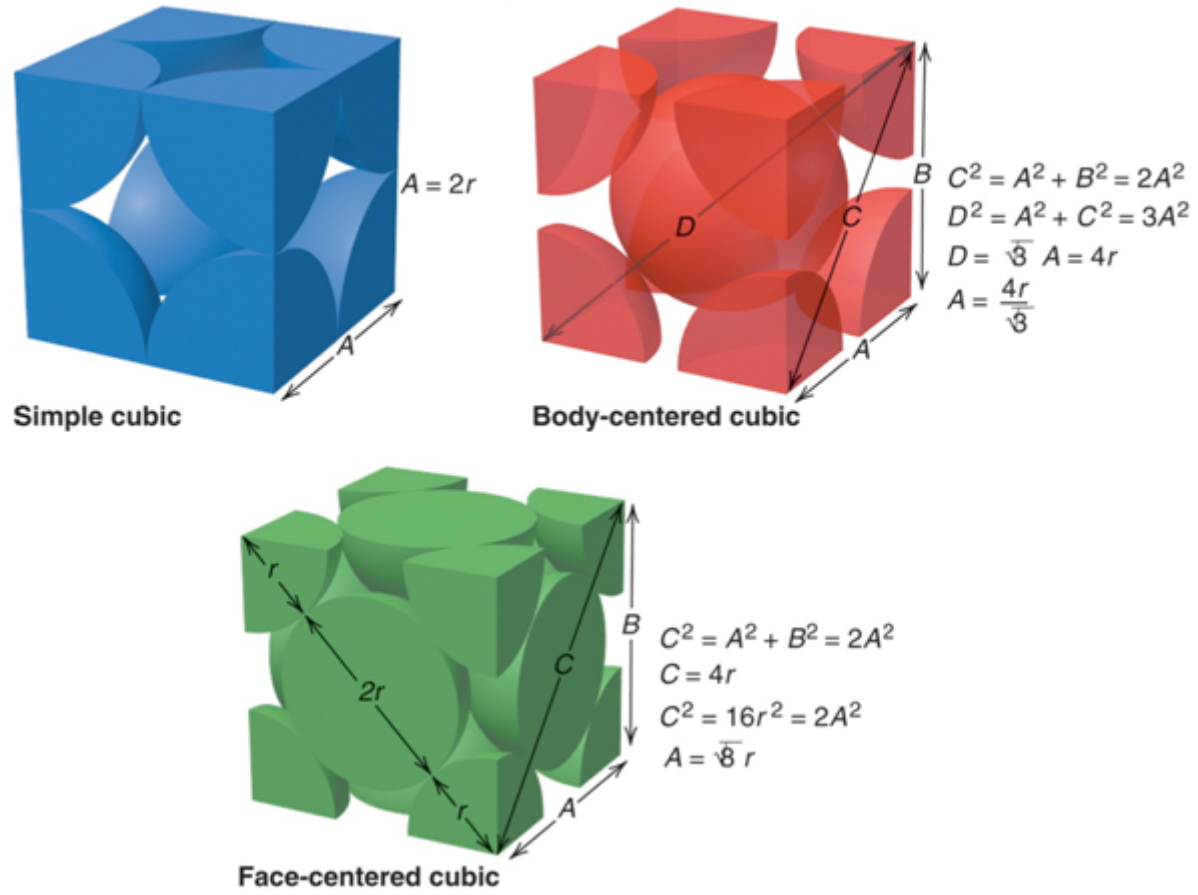

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Sample Problem 12.5 **Determining Atomic Radius from the Unit Cell**

PROBLEM: Copper adopts cubic closest packing, and the edge length of the unit cell is 361.5 pm. What is the atomic radius of copper?

PLAN: Cubic closest packing has a face-centered cubic unit cell, and we know the edge length. With Figure 12.26 and A = 361.5 pm, we solve for r.

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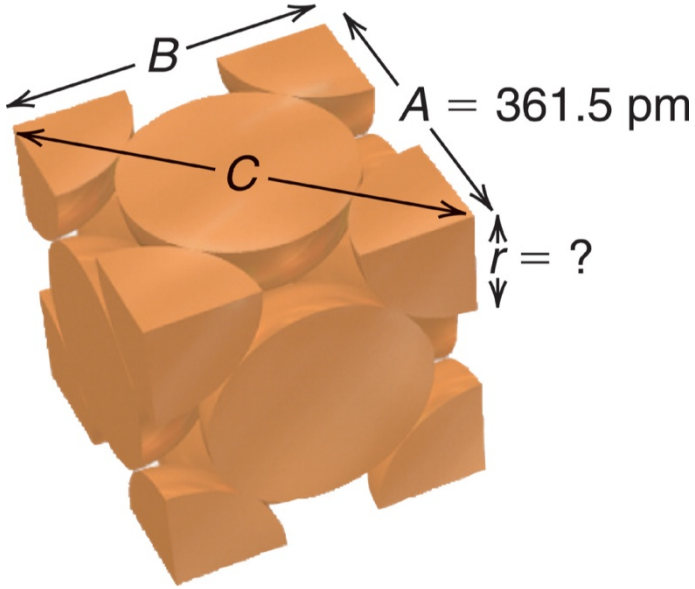

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Sample Problem 12.5

SOLUTION:

Using the Pythagorean theorem to find C, the diagonal of the cell's face:

$$C = \sqrt{A^2 + B^2}$$

The unit cell is a cube, so $A = B$, Therefore

$$C = \sqrt{2A^2} = \sqrt{2(361.5 \text{ pm})^2} = 511.2 \text{ pm}$$

$$C = 4r, \text{ so } r = \frac{511.2 \text{ pm}}{4} \quad \boxed{= 127.8 \text{ pm}}$$

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Types of Crystalline Solids

Atomic solids consist of individual atoms held together only by dispersion forces.

Molecular solids consist of individual molecules held together by various combinations of intermolecular forces.

Ionic solids consist of a regular array of cations and anions.

Metallic solids exhibit an organized crystal structure.

Network Covalent solids consist of atoms covalently bonded together in a three-dimensional network.

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Figure 12.27

Cubic closest packing of frozen argon (face-centered cubic cell).

Figure 12.28

Cubic closest packing (face-centered unit cell) of frozen CH_4.

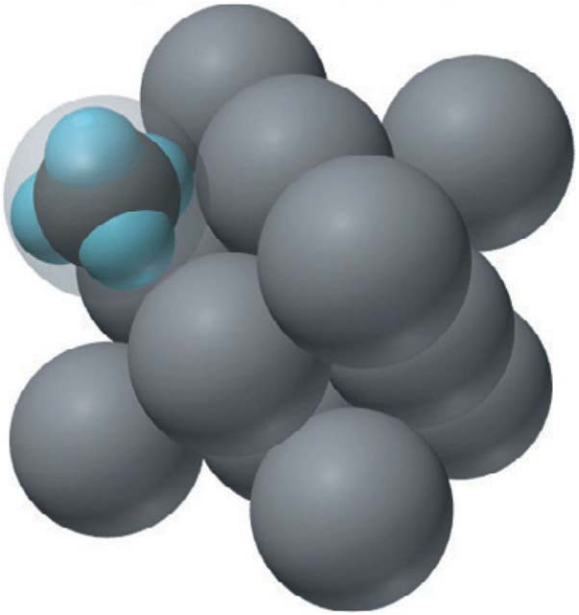

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Table 12.5 Characteristics of the Major Types of Crystalline Solids

Type	Particle(s)	Interparticle Forces	Physical Properties	Examples [mp, °C]
Atomic	Atoms	Dispersion	Soft, very low mp, poor thermal and electrical conductors	Group 8A(18) (Ne [-249) to Rn [-71])
Molecular	Molecules	Dispersion, dipole-dipole, H bonds	Fairly soft, low to moderate mp, poor thermal and electrical conductors	*Nonpolar** O_2 [-219], C_4H_{10} [-138] Cl_2 [-101], C_6H_{14} [-95] P_4 [44.1] *Polar* SO_2 [-73], $CHCl_3$ [-64] HNO_3 [-42], H_2O [0.0] CH_3COOH [17]

*Nonpolar molecular solids are arranged in order of increasing molar mass. Note the correlation with increasing melting point (mp).

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Table 12.5 Characteristics of the Major Types of Crystalline Solids (continued)

Type	Particle(s)	Interparticle Forces	Physical Properties	Examples [mp, °C]
Ionic	Positive and negative ions	Ion-ion attraction	Hard and brittle, high mp, good thermal and electrical conductors when molten	NaCl [801] CaF_2 [1423] MgO [2852]
Metallic	Atoms	Metallic bond	Soft to hard, low to very high mp, excellent thermal and electrical conductors, malleable and ductile	Na [97.8] Zn [420] Fe [1535]
Network covalent	Atoms	Covalent bond	Very hard, very high mp, usually poor thermal and electrical conductors	SiO_2 (quartz) [1610] C (diamond) [~4000]

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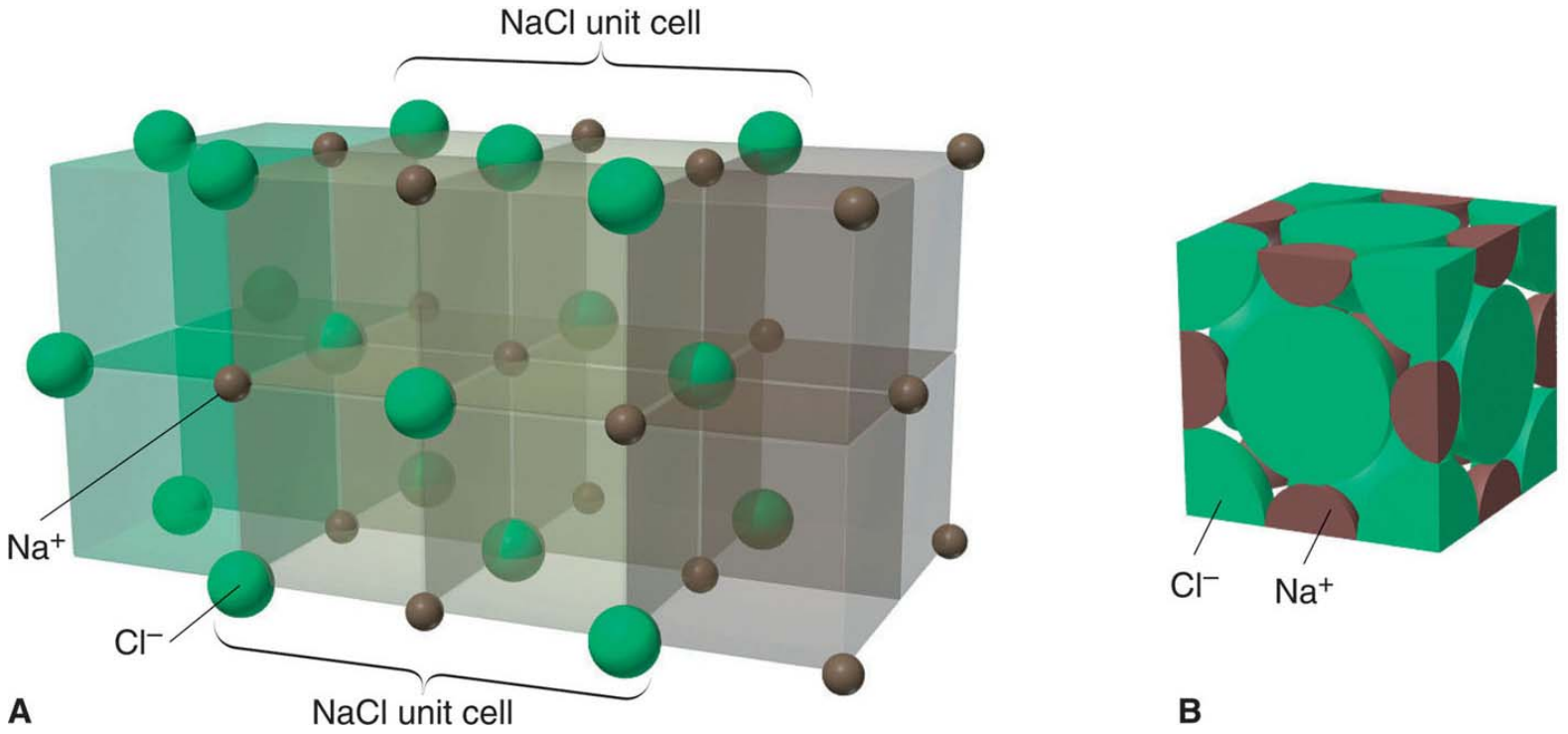
Figure 12.29 **The sodium chloride structure.**



Expanded view.

Space-filling model.

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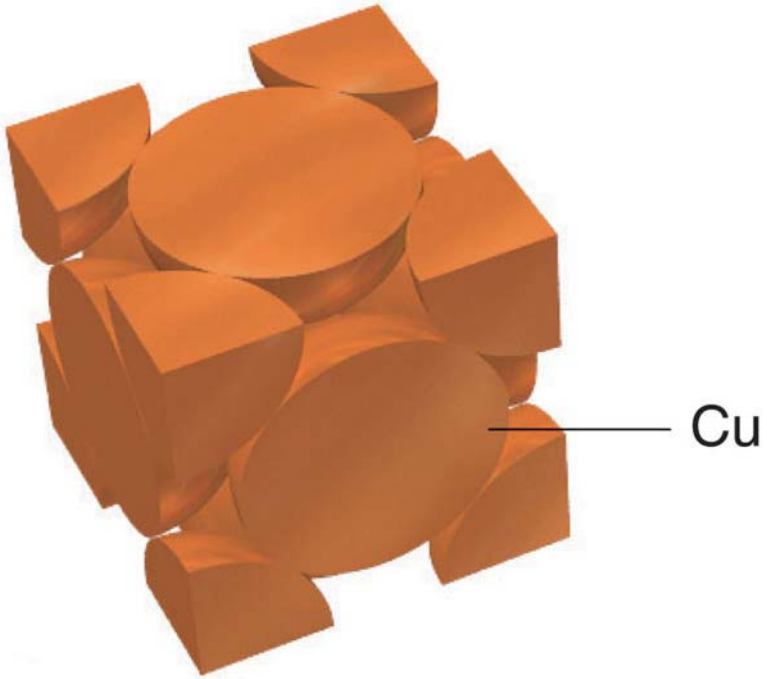
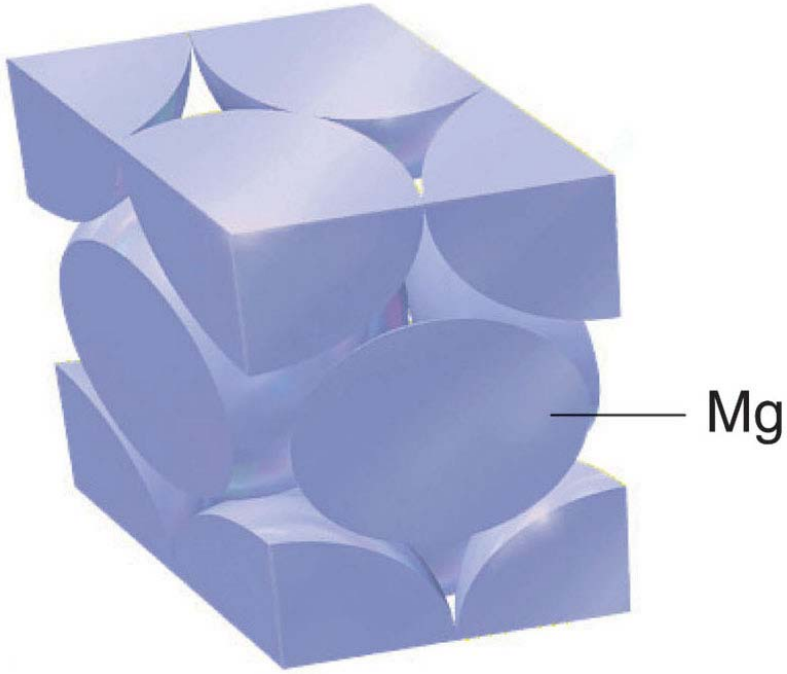
Figure 12.30 Crystal structures of metals.



A. Copper adopts cubic closest packing.



B. Magnesium adopts hexagonal closest packing.

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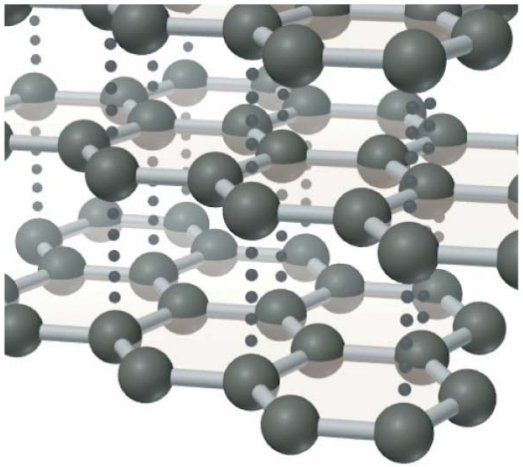
Table 12.6 Comparison of the Properties of Diamond and Graphite.

Property	Graphite	Diamond
Density (g/cm^3)	2.27	3.51
Hardness	< 1 (very soft)	10 (hardest)
Melting point (K)	4100	4100
Color	Shiny black	Colorless transparent
Electrical Conductivity	High (along sheet)	None
ΔH_{rxn} for combustion (kJ/mol)	-393.5	-395.4
ΔH°_f (kJ/mol)	0 (standard state)	1.90



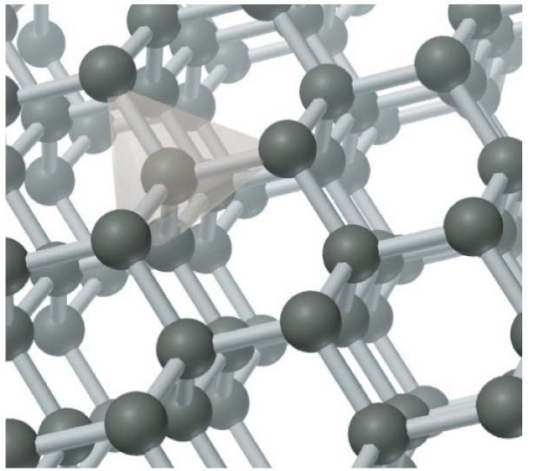


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Figure 12.32 The band of molecular orbitals in lithium metal.

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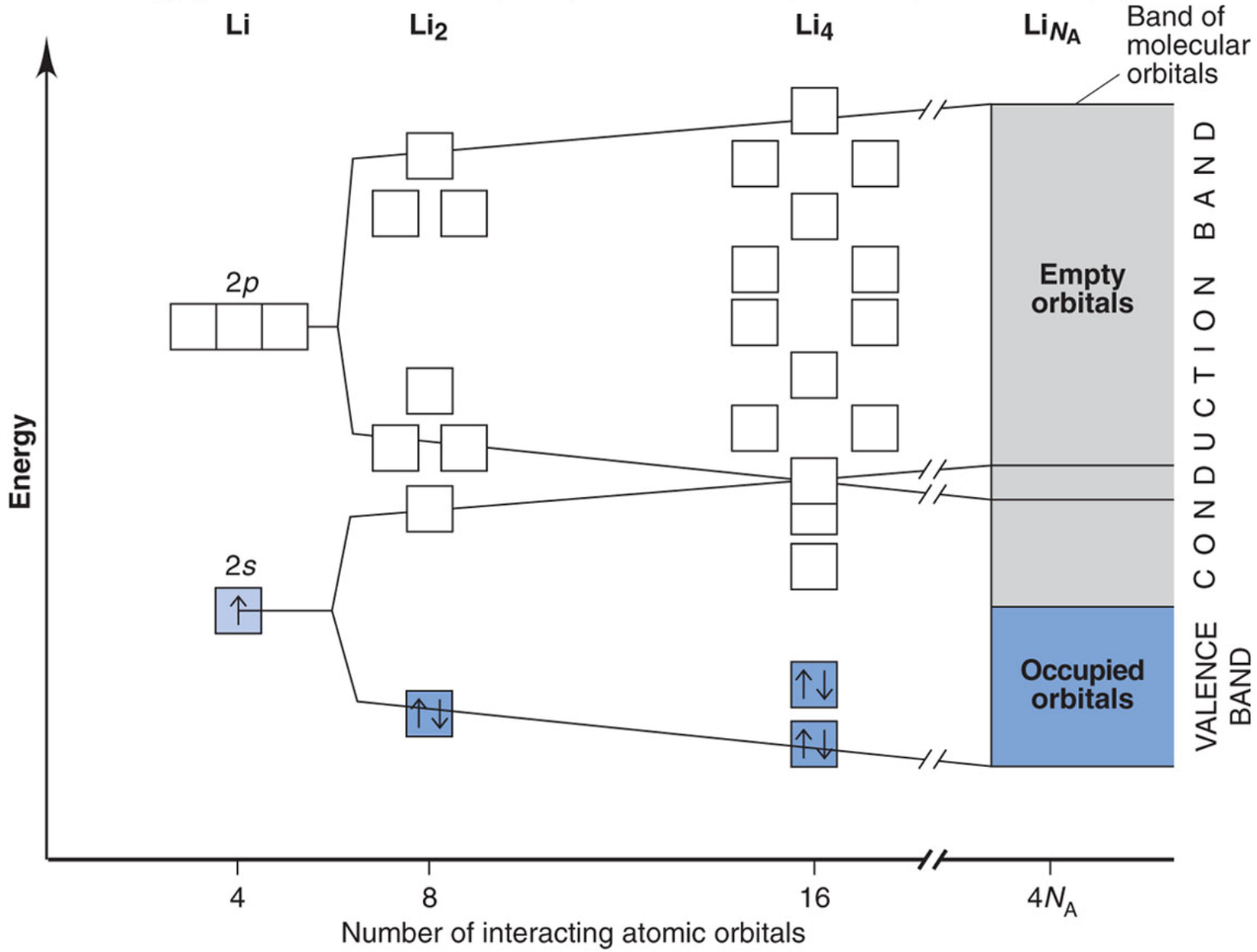

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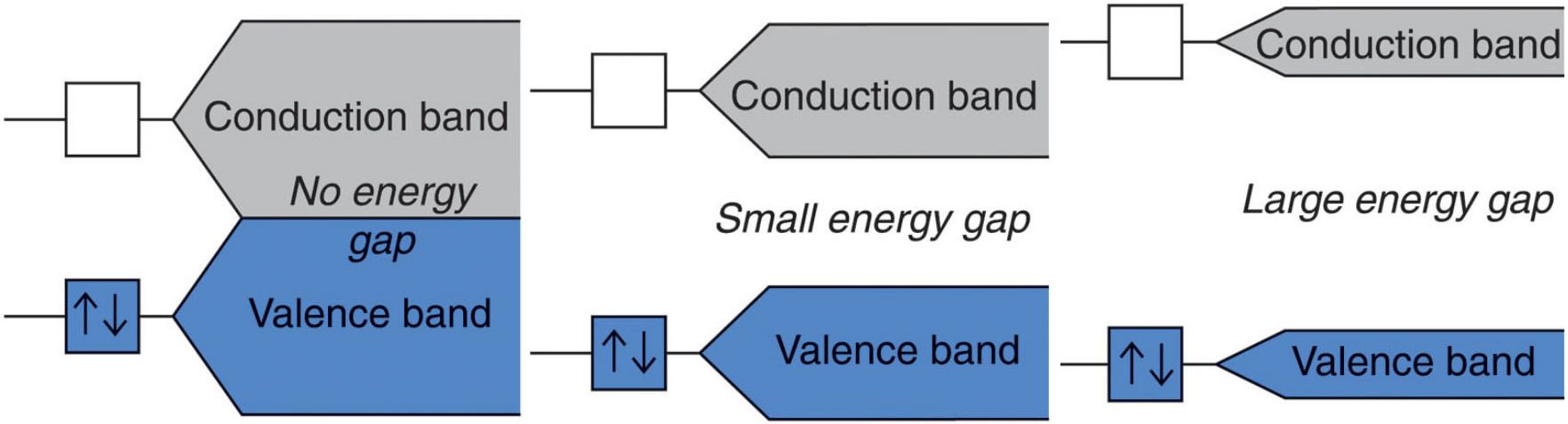
Figure 12.33 Electrical conductivity in a conductor, semiconductor, and insulator.



conductor semiconductor insulator

The conducting properties of a substance are determined by the energy gap between the valence and conduction bands of MOs.

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