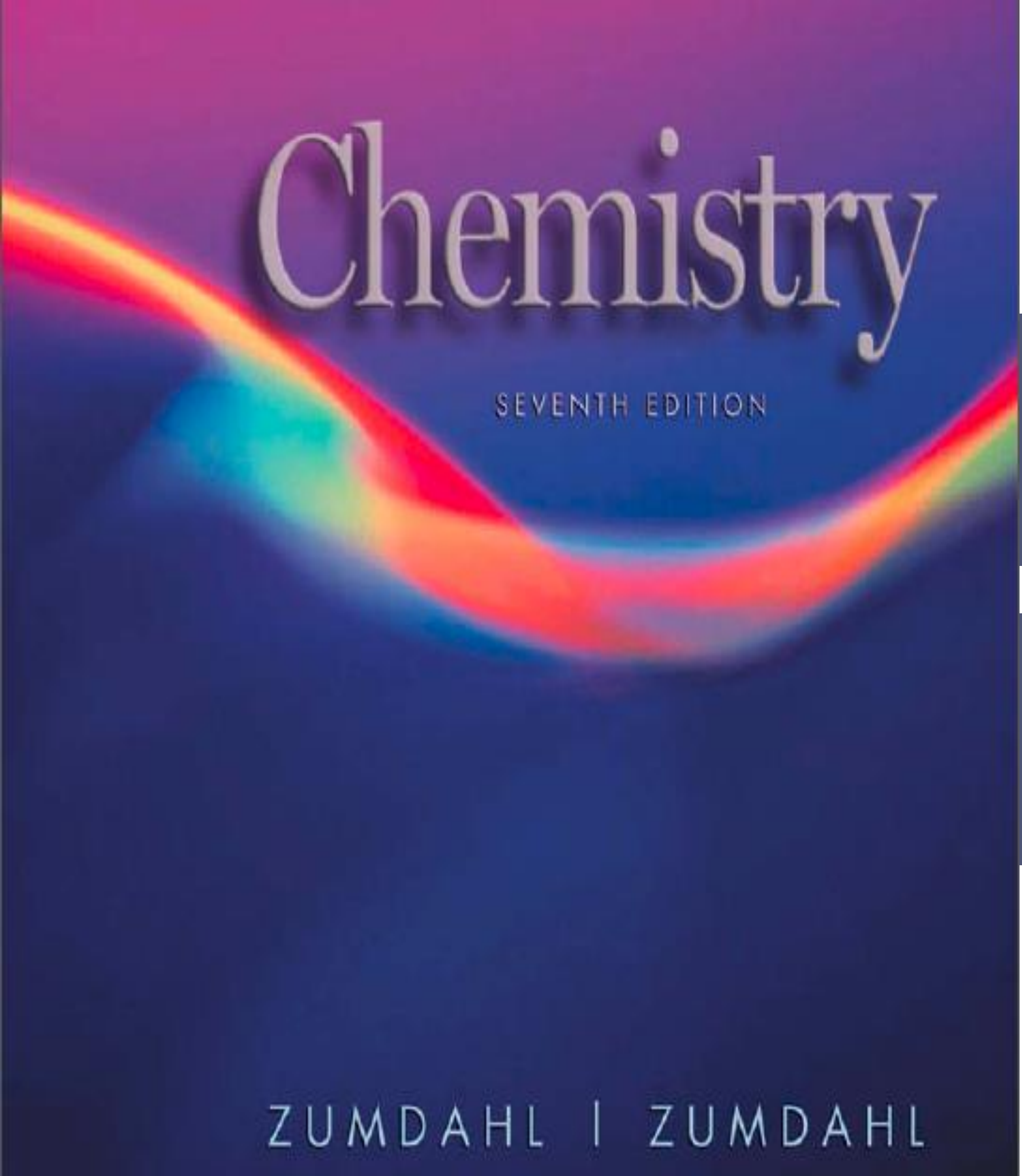


Chapter 5

Gases

A Gas

- Uniformly fills any container.
- Easily compressed.
- Mixes completely with any other gas.
- Exerts pressure on its surroundings

Pressure

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

- SI units = Newton/meter^2 = 1 Pascal (Pa)
- 1 standard atmosphere = 101,325 Pa
- 1 standard atmosphere = 1 atm = 760 mm Hg = 760 torr

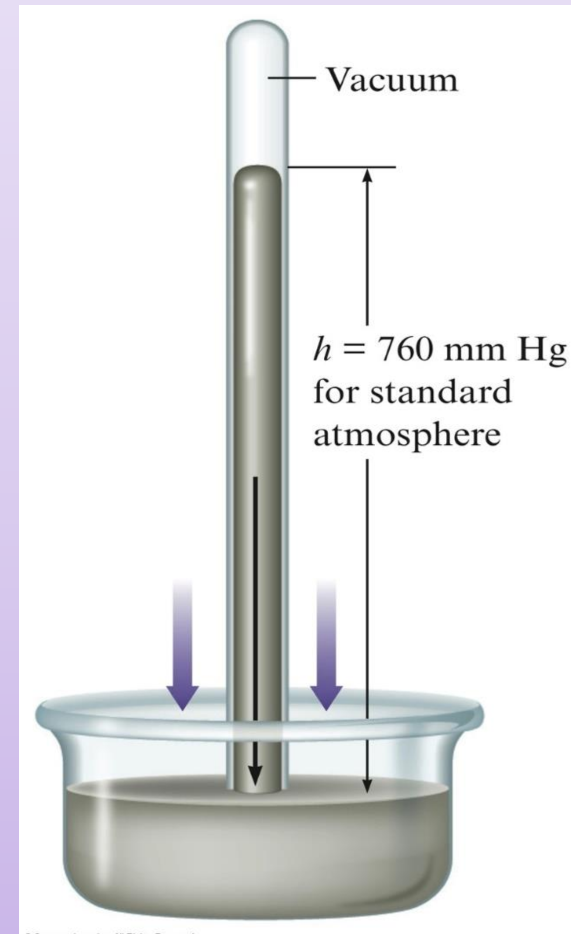
$$\begin{aligned} 1\ \text{atm} &= 760\ \text{mm Hg} \\ &= 760\ \text{torr} \\ &= 101{,}325\ \text{Pa} \\ &= 29.92\ \text{in Hg} \\ &= 14.7\ \text{lb/in}^2 \end{aligned}$$

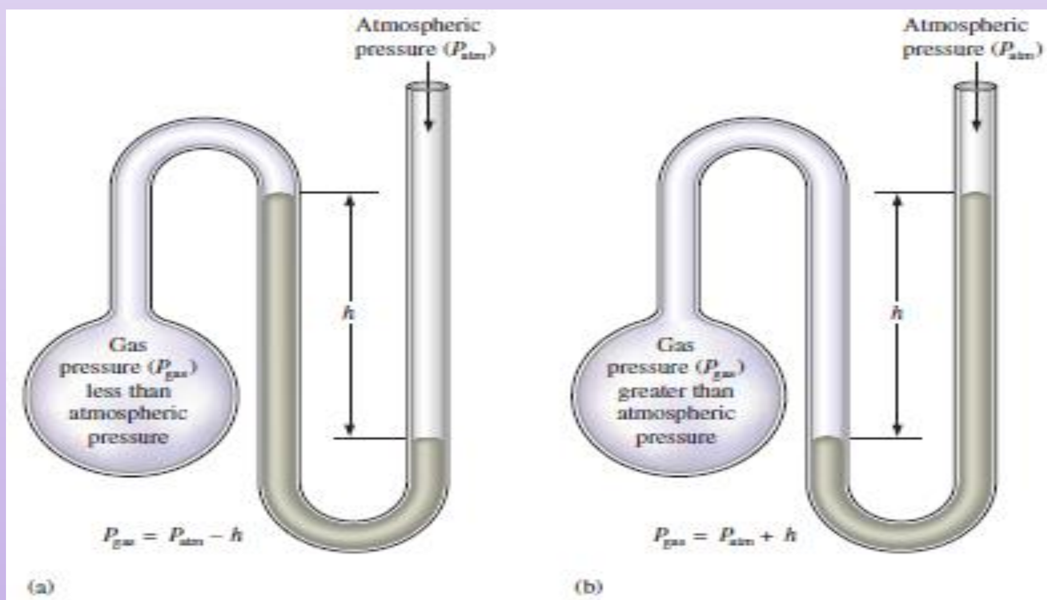
- Barometer

- Device used to measure atmospheric pressure. was invented in 1643 by an Italian scientist named Evangelista Torricelli (1608–1647)

- Manometer

- Device used for measuring the pressure of a gas in a container.





Sample Exercise 5.1

- The pressure of a gas is measured as 49 torr. Represent this pressure in both atmospheres and pascals.

- ***Solution***
- ***a- torr to atm***
- $\frac{49\ torr}{760\ atm}$ = 6.4 x 10-2 atm
- ***b-atm to pascals***
- 6.4 x10 $^{-2}$ x 101,325 = 6.5 x 10 ^{3} pa

- Boyle's law
- Boyle studied the relationship between the pressure of the gas and its volume.
- Pressure and volume are inversely related (constant T, temperature, and n, # of moles of gas).

$$V = \frac{k}{P} = k\frac{1}{P}$$

- PV = k (k is a constant for a given sample of air at a specific temperature)

$$P_1 \times V_1 = P_2 \times V_2$$

- A gas that strictly obeys Boyle's law is called an ideal gas

Sample Exercise 5.2

Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53-L sample of gaseous SO_2 at a pressure of 5.6×10^3 Pa. If the pressure is changed to 1.5×10^4 Pa at a constant temperature, what will be the new volume of the gas?

Solution

$$PV = k \qquad \text{or} \qquad P_1V_1 = P_2V_2$$

$$P_1 = 5.6 \times 10^3 \text{ Pa} \qquad P_2 = 1.5 \times 10^4 \text{ Pa}$$

$$V_1 = 1.53 \text{ L} \qquad V_2 = ?$$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{5.6 \times 10^3 \cancel{\text{Pa}} \times 1.53 \text{ L}}{1.5 \times 10^4 \cancel{\text{Pa}}} = 0.57 \text{ L}$$

The new volume will be 0.57 L.

❑Charles's law

- ❑ Volume and Temperature (in Kelvin) are directly related (constant P and n).

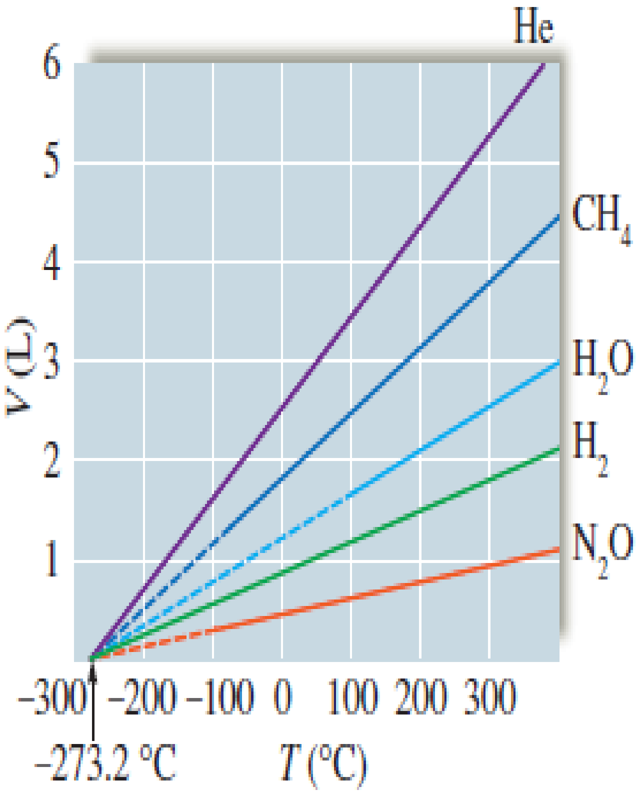
- ❑ the volume of a gas at constant pressure increases linearly with the temperature of the gas.

- ❑ $\boxed{V=bT}$ (b is a proportionality constant)

- ❑ K = °C + 273

- ❑ 0 K is called absolute zero.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



Sample Exercise 5.3

A sample of gas at 15ºC and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38ºC and 1 atm?

Solution

$$\frac{V}{T} = b \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$T_1 = 15°C + 273 = 288\ K$ $\qquad T_2 = 38°C + 273 = 311\ K$

$V_1 = 2.58\ L$ $\qquad V_2 = ?$

$$V_2 = \left(\frac{T_2}{T_1}\right)V_1 = \left(\frac{311\ K}{288\ K}\right)2.58\ L = 2.79\ L$$

Reality Check: The new volume is greater than the initial volume

Avogadro's Law

- Volume and number of moles are directly related (constant T and P).
- $V = an$ (a is a proportionality constant)

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Sample Exercise 5.4

Suppose we have a 12.2-L sample containing 0.50 mol oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25 °C. If all this O_2 were converted to ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone?

- ***Solution***
- The balanced equation for the reaction is

$$3O_2(g) \longrightarrow 2O_3(g)$$

- To calculate the moles of O3 produced

$$0.50\ \cancel{\text{mol } O_2} \times \frac{2 \text{ mol } O_3}{3\ \cancel{\text{mol } O_2}} = 0.33 \text{ mol } O_3$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$n_1 = 0.50 \text{ mol} \qquad n_2 = 0.33 \text{ mol}$$

$$V_1 = 12.2 \text{ L} \qquad V_2 = ?$$

$$V_2 = \left(\frac{n_2}{n_1}\right) V_1 = \left(\frac{0.33\ \cancel{\text{mol}}}{0.50\ \cancel{\text{mol}}}\right) 12.2 \text{ L} = 8.1 \text{ L}$$

- ***Reality Check***: Note that the volume decreases

❑ The Ideal Gas Law

- We can bring all of these laws together into one comprehensive law:
  - $V = bT$ (constant P and n)
  - $V = an$ (constant T and P)
  - $V = \dfrac{k}{P}$ (constant T and n)

PV = nRT (ideal gas law)

where R = 0.08206 L·atm/mol·K, the universal gas constant)

Sample Exercise 5.5

A sample of hydrogen gas (H_2) has a volume of 8.56 L at a temperature of ^{0}C and a pressure of 1.5 atm. Calculate the moles of H_2 molecules present in this gas sample.

- ***Solution***
- Solving the ideal gas law for *n* gives

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

In this case $P = 1.5$ atm, $V = 8.56$ L, $T = 0°\text{C} + 273 = 273$ K, and $R = 0.08206$ L · atm/K · mol. Thus

$$n = \frac{(1.5\ \cancel{\text{atm}})(8.56\ \cancel{\text{L}})}{\left(0.08206\,\frac{\cancel{\text{L}}\cdot\cancel{\text{atm}}}{\text{K}\cdot\text{mol}}\right)(273\ \cancel{\text{K}})} = 0.57\ \text{mol}$$

Gas Stoichiometry

- Molar Volume of an Ideal Gas
- For 1 mole of an ideal gas at 0° C and 1 atm, the volume of the gas is 22.42 L.

$$V = \frac{nRT}{P} = \frac{(1.000\ \cancel{\text{mol}})(0.08206\ \text{L}\cdot\cancel{\text{atm}}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(273.2\ \cancel{\text{K}})}{1.000\ \cancel{\text{atm}}} = 22.42\ \text{L}$$

- *STP* = standard temperature and pressure
  - 0° C and 1 atm
  - Therefore, <u>the molar volume</u> is 22.42 L at STP.

Sample Exercise 5.6

- A sample of nitrogen gas has a volume of 1.75 L at STP. How many moles of N_2 are present? $\therefore n_2 =$

- ***Solution***
- ***At STP***

$n_1 = 1 mol \qquad V_1 = 22.4 L$

$n_2 = ? \qquad V_2 = 1.75 L$

$$\therefore n_2 = 1.75 \cancel{L\ N_2} \times \frac{1 \text{ mol } N_2}{22.42 \cancel{L\ N_2}} = 7.81 \times 10^{-2} \text{ mol } N_2$$

Sample Exercise 5.7

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate ($CaCO_3$). Calculate the volume of CO_2 at STP produced from the decomposition of 152 g $CaCO_3$ by the reaction

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

Solution

moles of $CaCO_3$ $=\frac{152}{100}$ =1.52 mol

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

1 mol 1mol

1.52 mol will give $\longrightarrow$ 1.52 mol

At STP $\longrightarrow$ 1mol 22.4L

$\therefore$ 1.52 mol ?

Volume of CO_2 produced from 152g $CaCO_3$ $=\frac{22.4\ mol x\ 1.52L}{1\ mol}$=34.1L CO_2

Molar Mass of a Gas

$$\boxed{\text{Molar mass} = \frac{dRT}{P}} = \frac{\left(\frac{\text{g}}{\cancel{\text{L}}}\right)\left(\frac{\cancel{\text{L}}\cdot\cancel{\text{atm}}}{\text{mol}\cdot\cancel{\text{K}}}\right)(\cancel{\text{K}})}{(\cancel{\text{atm}})} = \frac{\text{g}}{\text{mol}}$$

- d = density of gas
- T = temperature in Kelvin
- P = pressure of gas
- R = universal gas constant

Sample Exercise 5.8

The density of a gas was measured at 1.50 atm and 27 °C and found to be 1.95 g/L. Calculate the molar mass of the gas

- ***Solution***

- Molar mass$=\frac{dRT}{P}=\frac{1.95\text{g/L}\text{x}0.082\text{x}300\text{K}}{1.5\text{atm}}$= 32g/mol

Dalton's Law of Partial Pressure

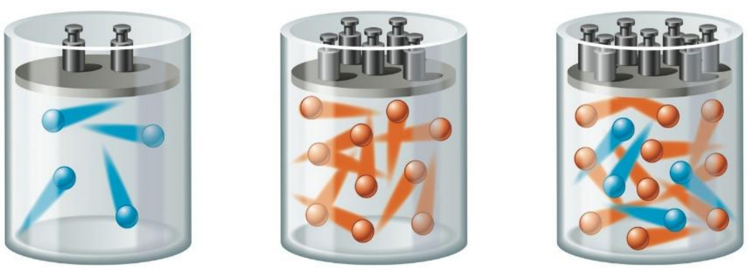
- For a mixture of gases in a container,

$$P_{Total} = P_1 + P_2 + P_3 + \ldots$$

- The total pressure exerted is the sum of the pressures that each gas would exert if it were alone.

$$P_1 = \frac{n_1RT}{V}, \qquad P_2 = \frac{n_2RT}{V}, \qquad P_3 = \frac{n_3RT}{V},$$

$$\begin{aligned} P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \cdots &= \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \cdots \\ &= (n_1 + n_2 + n_3 + \cdots)\left(\frac{RT}{V}\right) \\ &= n_{\text{TOTAL}}\left(\frac{RT}{V}\right) \end{aligned}$$



Sample Exercise 5.9

- Mixtures of helium and oxygen can be used in scuba diving tanks to help prevent "the bends." For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O_2 at 25C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.
- ***Solution***

The first step is to calculate the number of moles of each gas using the ideal gas law in the form: $n = \frac{PV}{RT}$

$$n_{He} = \frac{(1.0\ \cancel{atm})(46\ \cancel{L})}{(0.08206\ \cancel{L} \cdot \cancel{atm}/K \cdot mol)(298\ \cancel{K})} = 1.9\ mol$$

$$n_{O_2} = \frac{(1.0\ \cancel{atm})(12\ \cancel{L})}{(0.08206\ \cancel{L} \cdot \cancel{atm}/K \cdot mol)(298\ \cancel{K})} = 0.49\ mol$$

- the partial pressure of each gas

$$P = \frac{nRT}{V}$$

$$P_{He} = \frac{(1.9\ \cancel{mol})(0.08206\ \cancel{L} \cdot atm/\cancel{K} \cdot \cancel{mol})(298\ \cancel{K})}{5.0\ \cancel{L}} = 9.3\ atm$$

$$P_{O_2} = \frac{(0.49\ \cancel{mol})(0.08206\ \cancel{L} \cdot atm/\cancel{K} \cdot \cancel{mol})(298\ \cancel{K})}{5.0\ \cancel{L}} = 2.4\ atm$$

$$P_{TOTAL} = P_{He} + P_{O_2} = 9.3\ atm + 2.4\ atm = 11.7\ atm$$

❑ Mole Fraction

- the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

$$\chi_1 = \frac{n_1}{n_{\mathrm{TOTAL}}} = \frac{n_1}{n_1 + n_2 + n_3 + \cdots}$$

❑ Postulates of the Kinetic Molecular Theory

1) The particles are so small compared with the distances between them that *the volume of the individual particles can be assumed to be negligible (zero).*

2) The particles are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.
3) The particles are assumed to exert no forces on each other; they are assumed neither to attract nor to repel each other.
4) The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.

❑ The Meaning of Temperature

- The exact relationship between temperature and average kinetic energy can be obtained by combining the equations:

$$\frac{PV}{n} = RT = \frac{2}{3}(\mathrm{KE})_{\mathrm{avg}}$$

- which yields the expression
- $$(KE)_{avg} = \frac{3}{2} RT$$

❑ Root Mean Square Velocity

$$\sqrt{\overline{u^2}} = u_{\mathrm{rms}} = \sqrt{\frac{3RT}{N_A m}} \qquad u_{rms} = \sqrt{\frac{3RT}{M}}$$

R = 8.3145 J/K·mol

(J = joule = kg·m^2/s^2)

T = temperature of gas (in K)

M = mass of a mole of gas in kg (N_A x m)

- Final units are in m/s.

Sample Exercise 5.10

- Calculate the root mean square velocity for the atoms in a sample of helium gas at 25^0C. [atomic mass of He = 4g/mol]
- ***Solution***

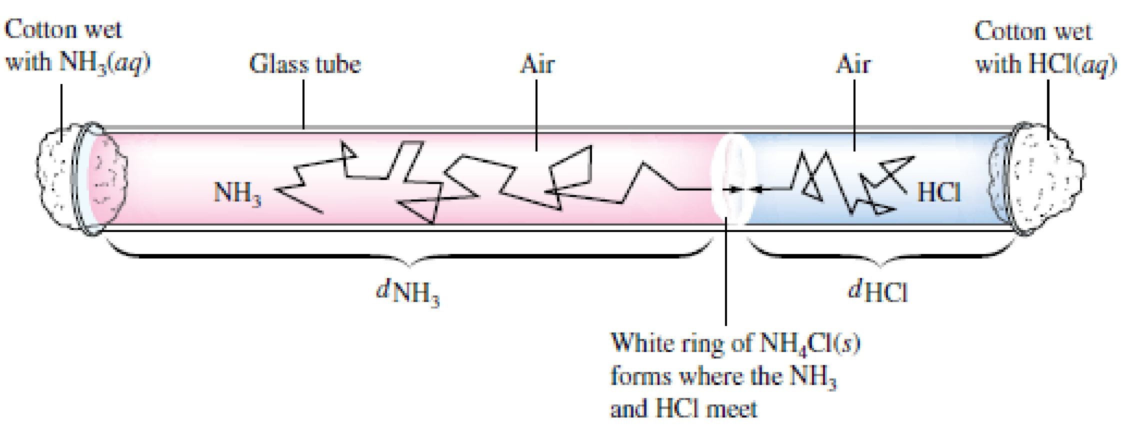
$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

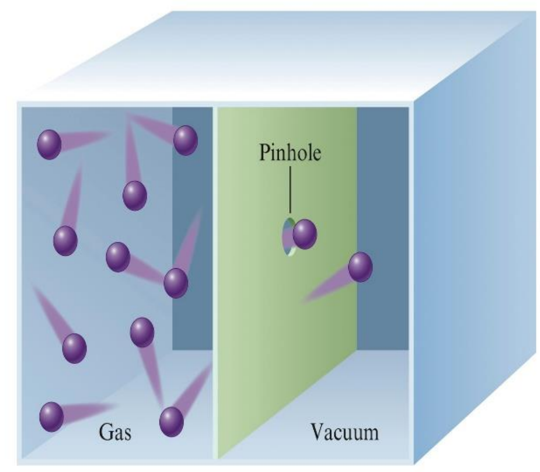
$$M = 4.00\frac{\text{g}}{\text{mol}} \times \frac{1\text{ kg}}{1000\text{ g}} = 4.00 \times 10^{-3}\text{ kg/mol}$$

$$u_{rms} = \sqrt{\frac{3\left(8.3145\frac{\text{J}}{\text{K}\cdot\cancel{\text{mol}}}\right)(298\ \cancel{\text{K}})}{4.00 \times 10^{-3}\frac{\text{kg}}{\cancel{\text{mol}}}}} = 1.36 \times 10^{3}\text{ m/s}$$

Effusion and Diffusion

- Diffusion – the mixing of gases.
- Effusion – describes the passage of a gas through a tiny orifice into an evacuated chamber.
  - Rate of effusion measures the speed at which the gas is transferred into the chamber.





- Graham's Law of Effusion

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

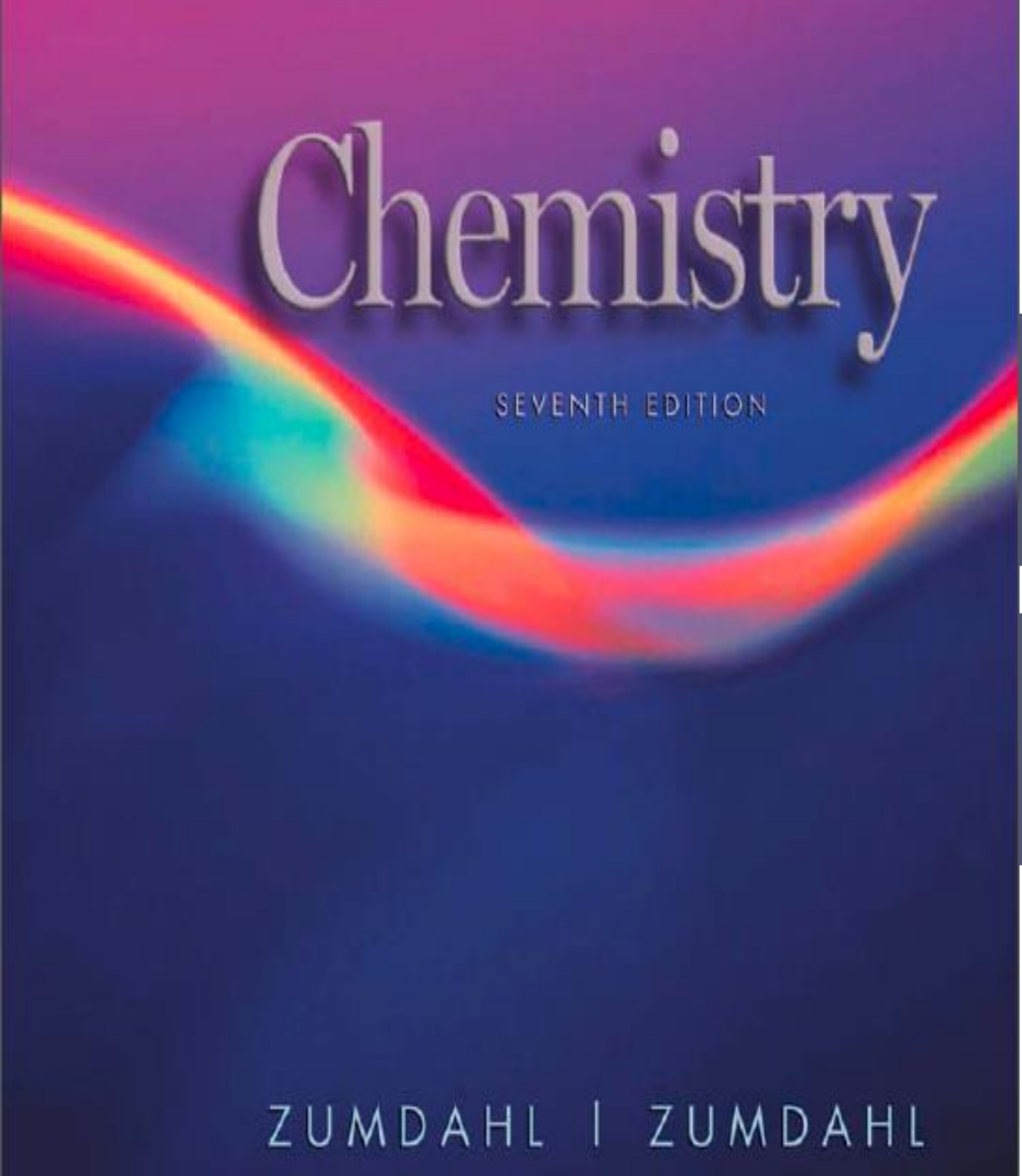
- M_1 and M_2 represent the molar masses of the gases.

Real Gases

- An ideal gas is a hypothetical concept. No gas exactly follows the ideal gas law.
- We must correct for non-ideal gas behavior when:
  - Pressure of the gas is high.
  - Temperature is low.
- Under these conditions:
  - Concentration of gas particles is high.
  - Attractive forces become important.

Real Gases (van der Waals Equation)

$$\underbrace{\underbrace{\left[P_{\text{obs}} + a\left(\frac{n}{V}\right)^2\right]}_{\text{Corrected pressure}}}_{P_{\text{ideal}}} \times \underbrace{\underbrace{(V - nb)}_{\text{Corrected volume}}}_{V_{\text{ideal}}} = nRT$$



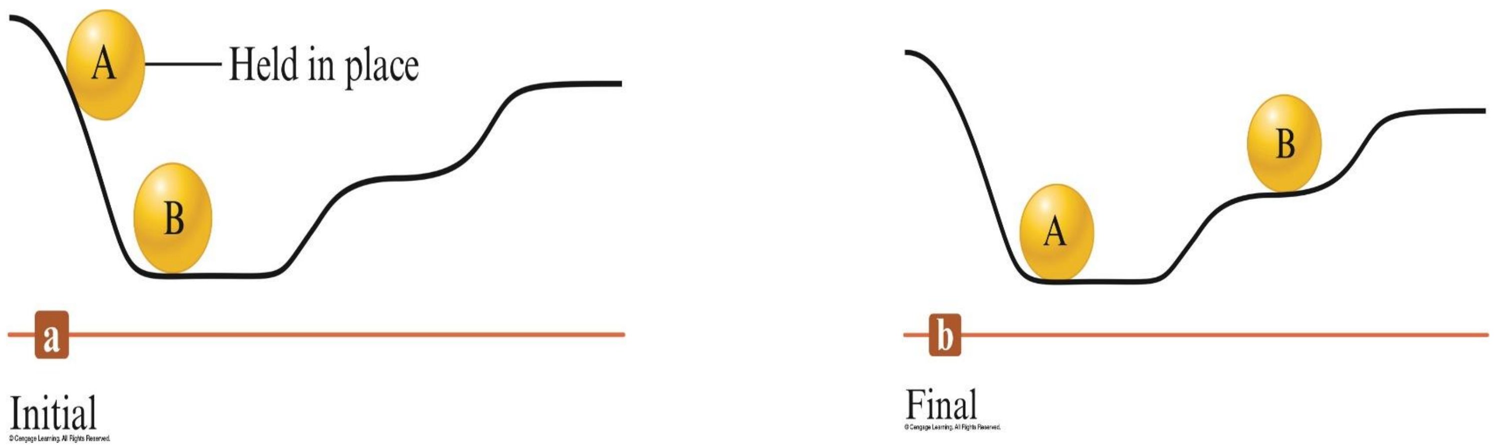
Chapter 6

Thermochemistry

Energy

- **Energy** Capacity to do work or to produce heat.
- **Law of conservation of energy** – energy can be converted from one form to another but can be neither created nor destroyed.
  - **The total energy** content of the universe is constant.
- **Potential energy** – energy due to position or composition.
- **Kinetic energy** – energy due to motion of the object and depends on the mass of the object and its velocity

- Initial Position
- In the initial position, ball A has a higher potential energy than ball B



- Final Position
- After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.

Chemical Energy

- System – part of the universe on which we wish to focus attention.
- Surroundings – include everything else in the universe.
- Endothermic Reaction:
  - Heat flow is into a system.
  - Absorb energy from the surroundings.
- Exothermic Reaction:
  - Energy flows out of the system.
- Energy gained by the surroundings must be equal to the energy lost by the system

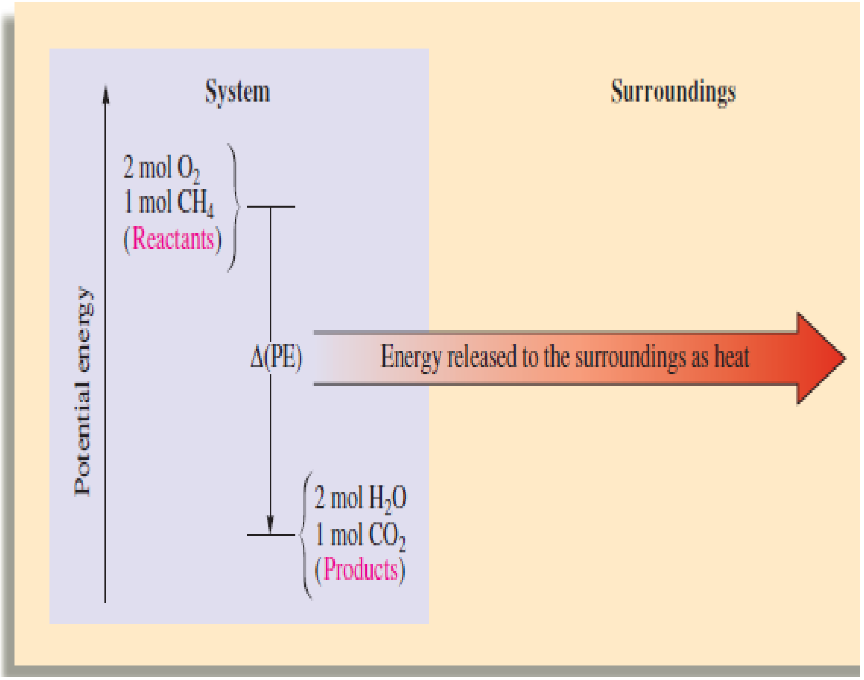


FIGURE 6.2
The combustion of methane releases the quantity of energy Δ(PE) to the surroundings via heat flow. This is an exothermic process.

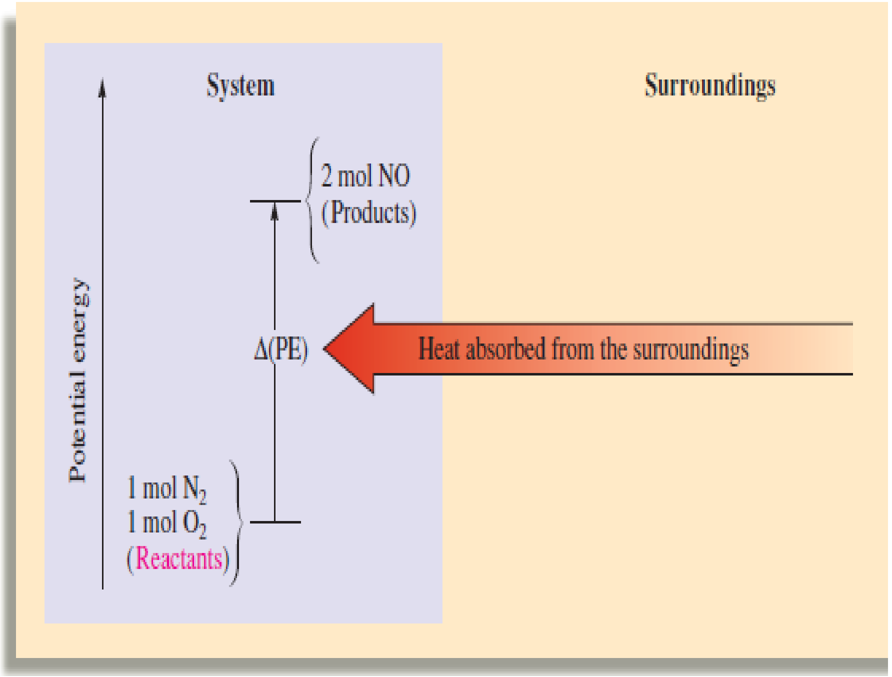


FIGURE 6.3
The energy diagram for the reaction of nitrogen and oxygen to form nitric oxide. This is an endothermic process: Heat [equal in magnitude to Δ(PE)] flows into the system from the surroundings.

Thermodynamics

- The study of energy and its interconversions is called thermodynamics.

- Law of conservation of energy is often called the first law of thermodynamics. and is stated as follows: The energy of the universe is constant.

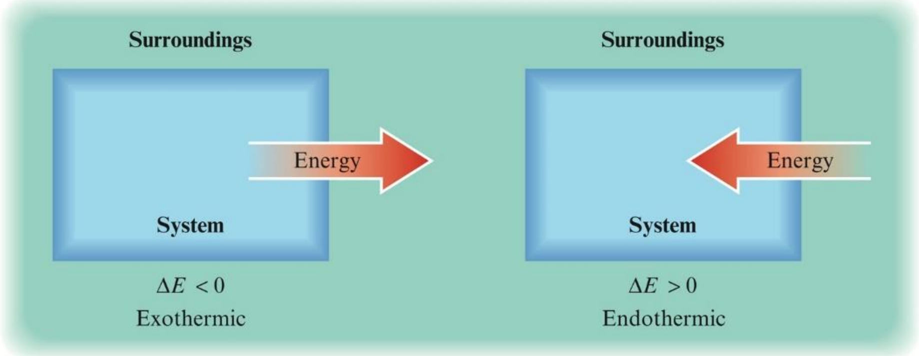
- Internal Energy

- Internal energy E of a system is the sum of the kinetic and potential energies of all the "particles" in the system.
- To change the internal energy of a system:
- $\Delta E = q + w$

q represents heat w represents work

Internal Energy

- Sign reflects the system's point of view.
- Endothermic Process:
  - q is positive
- Exothermic Process:
  - q is negative



- Sign reflects the system's point of view.
- System does work on surroundings:
  - w is negative
- Surroundings do work on the system:
  - w is positive

Sample Exercise 6.1

- Calculate E for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system
- ***Solution***
- We use the equation
- where q=+15.6 kJ(endothermic), and w=+ 1.4 kJ (work is done on the system). Thus

$$\Delta E = q + w$$

$$\Delta E = 15.6\,\text{kJ} + 1.4\,\text{kJ} = 17.0\,\text{kJ}$$

Change in Enthalpy

- Enthalpy H, which is defined as

$$H = E + PV$$

- where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system
- State function

$$q_p = \Delta H = \Delta E + P \Delta V$$

- $\Delta H = q$ at constant pressure(q_p)
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$

Calorimetry

- Science of measuring heat

The device used experimentally to determine the heat associated with a chemical reaction is called a **calorimeter.**

- Specific heat capacity:

The energy required to raise the temperature of one gram of a substance by one degree Celsius. and it

has the units J/^{0}C .g or J/K. g

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

- Molar heat capacity:
  - The energy required to raise the temperature of one mole of substance by one degree Celsius. and it has the units J/^{0}C. mol or J/K. mol

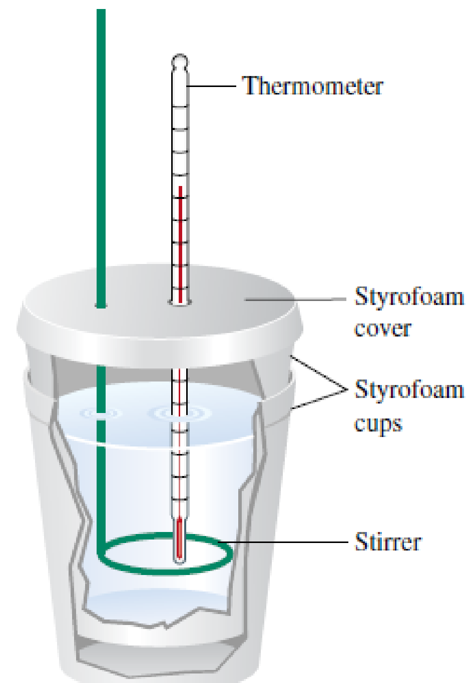


FIGURE 6.5
A coffee-cup calorimeter made of two Styrofoam cups.

- Hess's Law
- In going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.
- Characteristics of Enthalpy Changes
- 1-If a reaction is reversed, the sign of ΔH is also reversed.

$$Xe(g) + 2F_2(g) \longrightarrow XeF_4(s) \qquad \Delta H = -251 \text{ kJ}$$

$$XeF_4(s) \longrightarrow Xe(g) + 2F_2(g) \qquad \Delta H = +251 \text{ KJ}$$

- 2-The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

$$Xe(g) + 2F_2(g) \longrightarrow XeF_4(s) \qquad \Delta H = -251 \text{ kJ}$$

$$2Xe(g) + 4F_2(g) \longrightarrow 2XeF_4(s) \qquad \Delta H = 2(-251)=(-502)$$

Sample Exercise 6.2

- Two forms of carbon are graphite, the soft, black, slippery material used in "lead" pencils and as a lubricant for locks, and diamond, the brilliant, hard gemstone. Using the enthalpies of combustion for graphite (394 kJ/mol) and diamond (396 kJ/mol), calculate H for the conversion of graphite to diamond:
- ***Solution*** $C_{graphite}(s) \longrightarrow C_{diamond}(s)$
- The combustion reactions are

$$C_{graphite}(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -394 \text{ kJ}$$
$$C_{diamond}(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -396 \text{ kJ}$$

- Reverse the second reaction, then sum two reactions

$$\begin{array}{llll} C_{graphite}(s) + O_2(g) & \longrightarrow & CO_2(g) & \Delta H = -394 \text{ kJ} \\ CO_2(g) & \longrightarrow & C_{diamond}(s) + O_2(g) & \Delta H = -(-396 \text{ kJ}) \\ \hline C_{graphite}(s) & \longrightarrow & C_{diamond}(s) & \Delta H = 2 \text{ kJ} \end{array}$$

- Thus 2 kJ of energy is required to change 1 mol graphite to diamond

Standard Enthalpy of Formation (ΔH_f°)

- Change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.

- ## Conventional Definitions of Standard States
- For a Compound
  - For a gas, pressure is exactly 1 atm.
  - For a solution, concentration is exactly 1 *M*.
  - Pure substance (pure liquid or solid)
- For an Element
  - The form [$N_2(g)$, K(*s*)] in which it exists at 1 atm and 25° C.

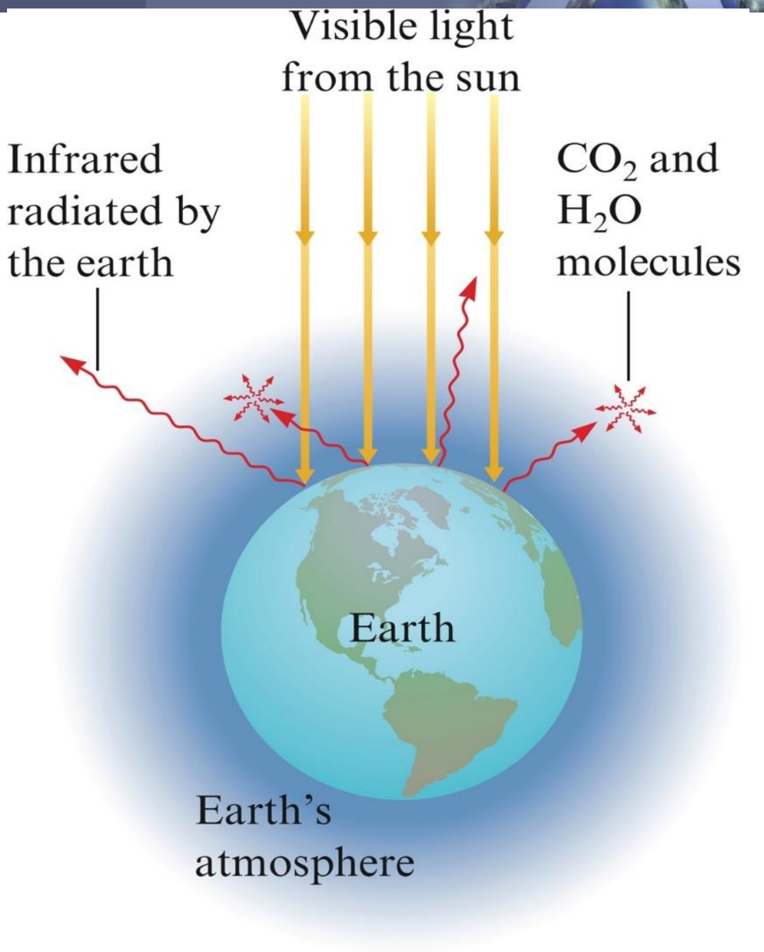
- Present Sources of Energy
- Fossil Fuels: Plants store energy that can be claimed by burning the plants themselves or the decay products that have been converted over millions of years to fossil fuels

- Petroleum : is a thick, dark liquid composed mostly of compounds called hydrocarbons that contain carbon and hydrogen

- Natural gas: usually associated with petroleum deposits, consists mostly of methane, but it also contains significant amounts of ethane, propane, and butane.

The Earth's Atmosphere

- Transparent to visible light from the sun. Visible light strikes the Earth, and part of it is changed to infrared radiation. Infrared radiation from Earth's surface is strongly absorbed by CO_2, H_2O, and other molecules present in smaller amounts in atmosphere.



Atmosphere traps some of the energy and keeps the Earth warmer than it would otherwise be. This is called greenhouse effect.