Chapter 10. Gases.

10.1 Characteristics of Gases.

All substances have three phases; solid, liquid and gas.
Substances that are liquids or solids under ordinary conditions may also exist as gases.
    These are often referred to as **vapors.**
Many of the properties of gases differ from those of solids and liquids.
    Gases are highly compressible and occupy the full volume of their containers.
    When a gas is subjected to pressure, its volume decreases
    Gases always form homogeneous mixtures with other gases.
Gases only occupy a small fraction of the volume of their containers.
    As a result, each molecule of gas behaves largely as though other molecules were absent.

10.2 Pressure.
Pressure is the force acting on an object per unit area: $P = F / A$
        Standard atmospheric pressure is the pressure required to support 760 mm of Hg in a column.
            Important non-SI units used to express gas pressure include:
                Atmospheres (atm)
                Millimeter of mercury (mm Hg) or **Torr.**
                1 atm = 760 mm Hg = 760 torr = 1.01325×10^5 Pa = 101.325 kPa.

10.3 The Gas Laws.

| The Gas Laws			
Boyle's Law	$PV = k$	constant n, T	$P_1 V_1 = P_2 V_2$
Charle's Law	$V = k \times T$	constant n, P	$V_1/T_1 = V_2/T_2$
Avogadro's Law	$V = k \times n$	constant P, T	$V_1/n_1 = V_2/n_2$
Combined	$PV/T = n$	constant n	$P_1 V_1/T_1 = P_2 V_2/T_2$
Ideal Gas Law	$PV = nRT$		
Density (d)	$PM = d\,RT$		
Molar Mass (M)	$d = PM/RT \quad or \quad M = dRT/P$		
Volume (V)	V (1mole, 6.022×10^{23} molecules) = 22.4 liters at STP		

The equations that express the relationships among T (temperature), P (pressure), V (volume), and n (number of moles) are known as *gas laws*.

R = **gas constant** = 0.08206 L.atm/mol.K

Define **STP (standard temperature and pressure)** = 0°C, 273.15 K, 1 atm.

The molar volume of a mol of an ideal gas at STP is 22.4 L.

A gas that strictly obeys Boyle's law is called an ideal gas.
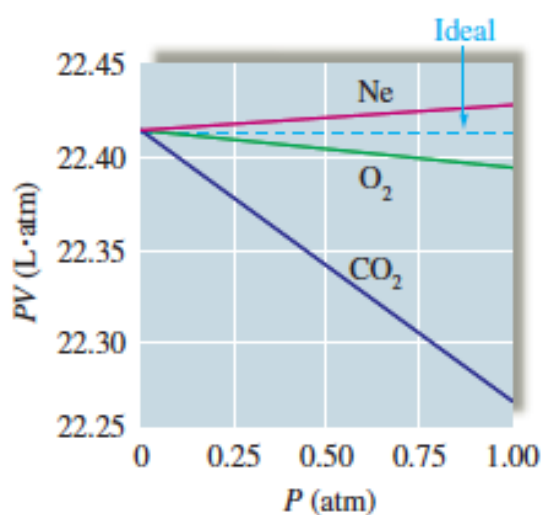
Volumes of Gases in Chemical Reactions
The ideal-gas equation relates P, V, and T to number of moles of gas.
The n can be used in stoichiometric calculations.

The Pressure-Volume Relationship: Boyle's Law

Boyle's law: the volume of a fixed quantity of gas, at constant temperature, is inversely proportional to its pressure. (n and T are constant)
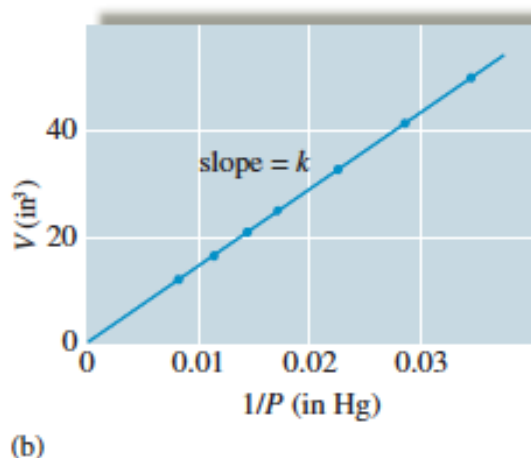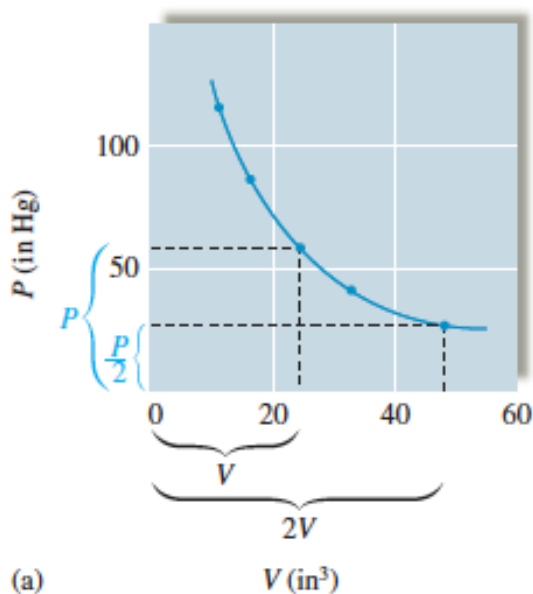
Boyle's Law
$V = k$ x $1/P$ or $PV = k$ *(constant)*

Example:

TABLE 5.1   Actual Data from Boyle's Experiment

| Volume (in³)	Pressure (in Hg)	Pressure × Volume (in Hg × in³)
117.5	12.0	14.1×10^2
87.2	16.0	14.0×10^2
70.7	20.0	14.1×10^2
58.8	24.0	14.1×10^2
44.2	32.0	14.1×10^2
35.3	40.0	14.1×10^2
29.1	48.0	14.0×10^2

(a)

(b)

A plot of V versus P is a hyperbola
Similarly, a plot of V versus $1/P$ must be a straight line passing through the origin with a slope = k.

The Temperature-Volume Relationship: Charles's Law

Charles's law: The volume of a fixed quantity of gas at constant pressure is directly proportional to its absolute temperature. (n and P are constant)

Charle's Law
$V = k \times T$ or $V/T = k$
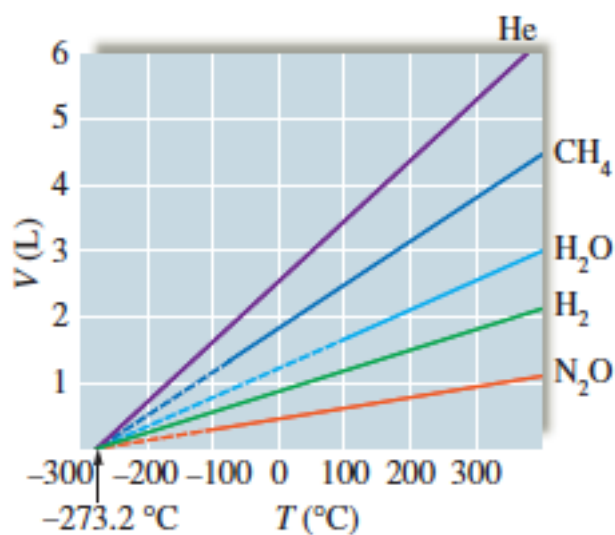
A plot of V versus T is a straight line.
When T is measured in ºC, the intercept on the temperature axis is –273.15ºC.
We define absolute zero, 0 K = -273.15ºC.

The Quantity-Volume Relationship: Avogadro's Law

Avogadro's hypothesis: Equal volumes of gases at the same temperature and pressure contain the same number of molecules.

Avogadro's law: The volume of gas at a given temperature and pressure is directly proportional to the number of moles of gas.

Avogadro's Law
$V = k$ x n or $V/n = k$

We can show that 22.4 L of any gas at $0^{o}C$ and 1 atmosphere contains 6.02×10^{23} gas molecules.

10.3 Gas Mixtures and Partial Pressures.

Since gas molecules are so gar apart, we can assume that they behave independently. Dalton observed:

The total pressure of a mixture of gases equals the sum of the pressures that each would exert if present alone (partial pressure).

Partial pressure is the pressure exerted by a particular component of a gas mixture.

Dalton's law of partial pressures:

In a gas mixture the total pressure is given by the sum of partial pressures of each gas component (sum of the pressures that each gas would exert if it were alone) and no matter what they are. The identity or composition of the involved gas particles is not important.

| Dalton's Law of Partial Pressures	
Total pressure of gas (1, 2, 3, ..) mixture = sum of partial pressures of each gas.	$P_t = P_1 + P_2 + P_3 + \ldots\ldots$
Total moles of gas mixture = Sum of each gas (1,2, 3,..) moles	$n_t = n_1 + n_2 + n_3 + \ldots\ldots$
Total pressure and ideal gas equation	$P_t = (\, n_1 + n_2 + n_3 + \quad)\, RT/V = n_t\, RT/V$
Mole fraction of a gas (1) in a mixture	$X_1 = n_1/n_t$
Partial pressure of a gas (1) in a mixture	$P_1 = X_1 P_t$

Note that a mole fraction is a dimensionless number.

Collecting Gases over Water

It is common to synthesize gases and collect them by displacing a volume of water. To calculate the amount of gas produced, we need to correct for partial pressure of the water:

Gases over Water
$P_{total} = P_{gas} + P_{water}$
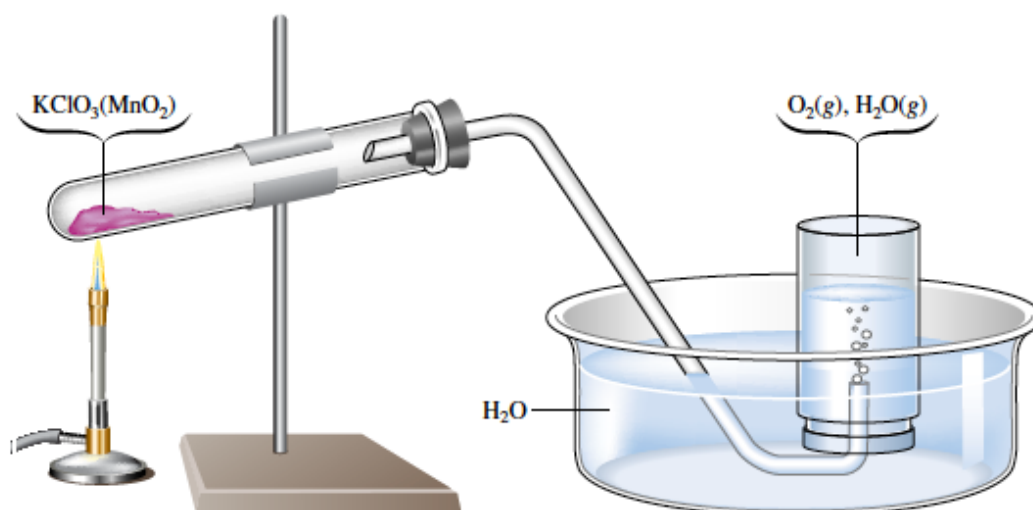
The vapor pressure of water varies with temperature.
Values can be found in Appendix B.

10.4 Kinetic-Molecular theory
The kinetic molecular theory was developed to *explain* gas behavior.

Summary
1) Gases consist of a large number of molecules in constant random motion.
2) The volume of individual molecules is negligible compared with the volume of the container.
3) The intermolecular forces (forces between gas molecules) are negligible.
4) The collisions are perfectly elastic. (No energy is lost)
5) The average kinetic energy of the gas molecules is proportional to the absolute temperature.
5) Kinetic molecular theory gives us an *understanding* of pressure and temperature on the molecular level.
6) The pressure of a gas results from the collisions with the walls of the container.
7) The magnitude of the pressure is determined by how often and how hard the molecules strike.
8) The absolute temperature of a gas is a measure of the average kinetic energy.
9) As the temperature increases, the average kinetic energy of the gas molecules increases.
10) As kinetic energy increases, the velocity of the gas molecules increases.

Average kinetic energy (KE $_{(Ave)}$) is related to rms speed (*u in meter/second)*;

Kinetic-Molecular Theory
$KE_{(Ave)} = 1/2\ mu^2$
If *V* increases and **T is constant**: **KE remains constant**: *u* remains constant, pressure decreases.   if **T increases** and *V* is constant: **KE increases**: **u increases**, pressure increases.

Root-mean-square (rms) speed, *u*, is the speed of a gas molecules having average kinetic energy. *m* is the mass of the molecule.

The average kinetic energy of a gas depends only on the absolute temperature, not on the identity of the gas.

Application to the Gas-Laws
We can understand empirical observations of gas properties with the framework of the kinetic-molecular theory.

Effect of an increase in volume (at constant temperature)
As volume increases at constant temperatures, the average kinetic of gas remains constant. Therefore, u is constant.
However, volume increases, so the gas molecules have to travel further to hit the walls of the container. Therefore, pressure decreases.

Effect of an increase in temperature (at constant volume)
If t**emperature increases** at constant volume, the average kinetic of the gas molecules increases. There are no more collisions with the container walls. Therefore, **u increases**.
The change in momentum in each collision increases (molecules strike harder). Therefore, **pressure increases.**

<u>The velocity depends on the temperature as shown below: The velocity increases with temperature at constant volume.</u>
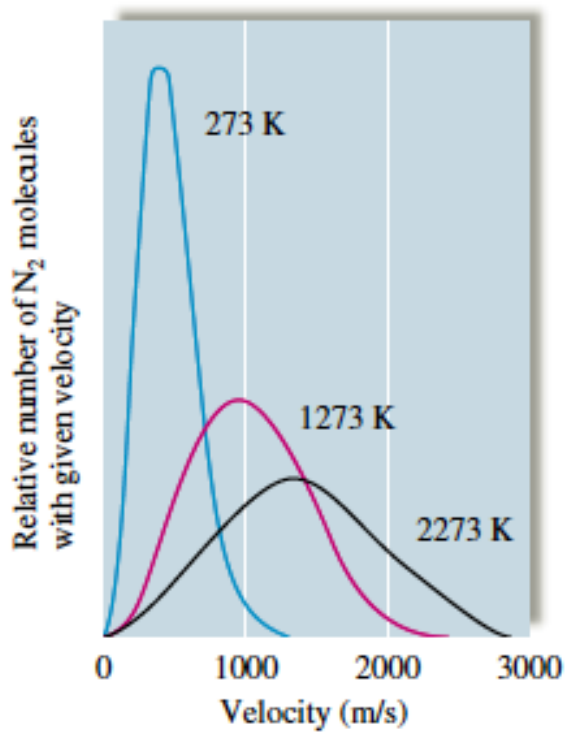
10.5 Molecular Effusion and Diffusion

Consider two gases at the same temperature; the lighter gas has a higher rms speed (u *in meter/second*) than the heavier gas.
Mathematically;

Molecular Effusion and Diffusion
$u^2 = 3RT/M$ so $u = \sqrt{3RT/M} = sort\ 3RT/M$
$u_1 / u_2 = \sqrt{M_1} / \sqrt{M_2}$

The lower the molar mass, M, the higher the rms speed (u) for that gas at a constant temperature.

Molecular speed depends on mass as shown below: The lighter gas travels faster at a constant temperature.
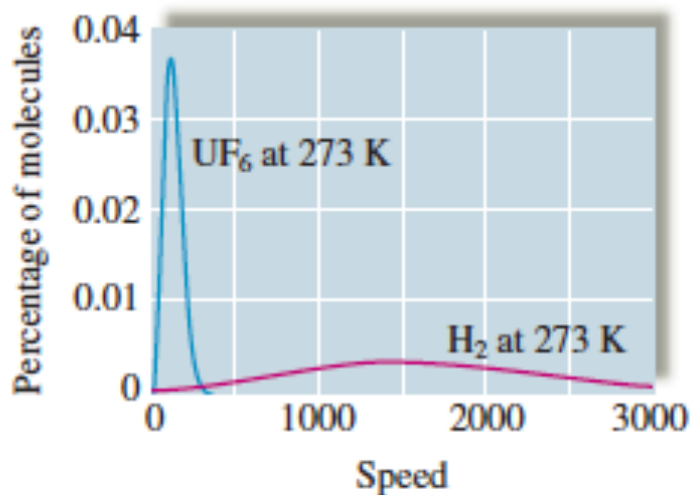
Two consequences of the dependence of molecular speeds on mass are:

Effusion is the escape of gas molecules through a tiny hole into an evacuated space.

Diffusion is the spread of one substance throughout a space or throughout a second substance.

10.6 Graham's Law of Effusion

The rate of effusion can be quantified.
Consider two gases with molar masses M_1 and M_2 with effusion rates, r_1 and r_2, respectively;

Graham's Law of Effusion
rate of effusion gas 1/rate of effusion of gas 2 =
$r_1 / r_2 = \sqrt{M_1} / \sqrt{M_2}$
$r_1 / r_2 = u_1 / u_2 = \sqrt{M_1} / \sqrt{M_2}$

The relative rate of effusion is given by **Graham's law**;
Therefore, the higher the rms speed the more likely that a gas molecule will hit the hole.

<u>Only those molecules which hit the small hole will escape through it.</u>
The rate of effusion will increase with temperature.
For gases at the same temperature, the gas with the lower molar mass will effuse first.

10.7 Deviation from Ideal behavior:

At low temperature and/or high pressure, gases behave in a less-than-ideal manner.

Under these conditions gas molecules are packed too tightly together. Two things happen:
1) the volume of the gas molecules becomes significant.
2) Gas molecules attract one another and stick together. The strong intermolecular forces (IMFs) will lead to more deviation.
Example H_2O with hydrogen bonding between the molecules (IMF) will deviate more than CH_4.