AP Chemistry
A. Allan

Chapter 5 - Gases

5.1 Pressure

- A. Properties of gases
  - 1. Gases uniformly fill any container
  - 2. Gases are easily compressed
  - 3. Gases mix completely with any other gas
  - 4. Gases exert pressure on their surroundings
    - a. Pressure = force/area
- B. Measuring barometric pressure
  - 1. The barometer
    - a. Inventor - Evangelista Torricelli (1643)
  - 2. Units
    - a. mm Hg (torr)
      - (1) 760 torr = Standard pressure
    - b. newtons/meter^2 = pascal (Pa)
      - (1) 101,325 Pa = Standard pressure
    - c. atmospheres
      - (1) 1 atmosphere = Standard pressure

5.2 The Gas Laws of Boyle, Charles, and Avogadro

- A. Boyle's Law (Robert Boyle, 1627 - 1691)
  - 1. the product of pressure times volume is a constant, provided the temperature remains the same

$$PV = k$$

    - a. P is inversely related to V
    - b. The graph of P versus V is hyperbolic
    - c. Volume increases linearly as the pressure decreases ($1/P$)
  - 2. At constant temperature, Boyle's law can be used to find a new volumes or a new pressure
    - a. $P_1V_1 = k = P_2V_2 \quad \therefore$

$$P_1V_1 = P_2V_2 \qquad \text{or} \qquad \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

  - 3. Boyle's law works best at low pressures
  - 4. Gases that obey Boyle's law are called <u>Ideal gases</u>
- B. Charles' Law (Jacques Charles, 1746 - 1823)
  - 1. The volume of a gas increase linearly with temperature provided the pressure remains constant
    - a. $V = bT \quad V/T = b$
      - (1) $V_1/T_1 = b = V_2/T_2$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{V_1}{V_2} = \frac{T_1}{T_2}$$

        - b. Temperature **<u>must</u>** be measured in degrees Kelvin
            - (1) K = °C + 273
            - (2) 0 K is "absolute zero"
- C. Avogadro's Law (Amedeo Avogadro, 1811)
    - 1. For a gas at constant temperature and pressure, the volume is directly proportional to the number of moles, n
        - a. $V = an$ $V/n = a$
            - (1) $V_1/n_1 = a = V_2/n_2 \therefore$

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

5.3 The Ideal Gas Law

- A. Derivation from existing laws
    - 1. $V = k/P$ $V = bT$ $V = an$

$$V = (k)(b)(a)\left(\frac{Tn}{P}\right)$$

    - 2. Constants <u>*k, b, a*</u> are combined into universal gas constant, R

$$V = \frac{nRT}{P} \quad \text{or} \quad PV = nRT$$

$$R = 0.08206\frac{L * atm}{K * mol}$$

- B. Limitations of the Ideal Gas Law
    - 1. Works well at low pressures and high temperatures
    - 2. Most gases do not behave ideally above 1 atm pressure
    - 3. Does not work well near the condensation conditions of a gas
- C. Solving for new volumes, temp or pressure (*n* remaining constant)
    - 1. Combined law (from general chem)
    - 2.

$$\frac{P_1V_1}{T_1} = n\,R = \frac{P_2V_2}{T_2} \quad \text{or} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$$

5.4 Gas Stiochiometry

A. Standard temperature and pressure (STP)
   1. 0 °C, 273 K
   2. 760 torr, 1 atm

B. Molar volume
   1. One mole of an ideal gas occupies 22.42 liters of volume at STP

C. Things to remember

$$Density = \frac{mass}{volume} \qquad n = \frac{grams \quad of \quad subs\tan ce}{molar \quad mass}$$

5.5 Dalton's Law of Partial Pressures (John Dalton, 1803)

A. Statement of law
   1. "For a mixture of gases in a container, the total pressure exerted is the sum of the pressures each gas would exert if it were alone"
   2. It is the total number of moles of particles that is important, not the identity or composition of the gas particles

B. Derivation
   1. $P_{TOTAL} = P_1 + P_2 + P_3 + \ldots$
   2. $P_1 = \frac{n_1 R\,T}{V} \quad P_2 = \frac{n_2 R\,T}{V} \quad P_3 = \frac{n_3 R\,T}{V} \quad \cdots$
   3. $P_{TOTAL} = \frac{n_1 R\,T}{V} + \frac{n_2 R\,T}{V} + \frac{n_3 R\,T}{V}$
   4. $P_{TOTAL} = (n_1 + n_2 + n_3 + \ldots)\left(\frac{R\,T}{V}\right)$
   5. $P_{TOTAL} = n_{TOTAL}\left(\frac{R\,T}{V}\right)$

C. Mole Fraction
   1. The ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture
   2. For an ideal gas, the mole fraction (***x***):

$$x_1 = \frac{n_1}{n_{TOTAL}} = \frac{P_1}{P_{TOTAL}}$$

5.6 The Kinetic Molecular Theory of Gases (KMT)

- A. Postulates of the KMT Related to <u>Ideal</u> Gases
  1. The particles are so small compared with the distances between them that the volume of the individual particles can be assumed to be zero
  2. The particles are in constant motion. Collisions of the particles with the walls of the container cause pressure
  3. Assume that the particles exert no forces on 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
- B. Explaining Observed Behavior with KMT
  1. *P* and *V* (*T* = constant)
     - a. As *V* is decreased, *P* increases:

       V decrease causes a decrease in the surface area. Since *P* is force/area, the decrease in *V* causes the area to decrease, increasing the *P*
  2. *P* and *T* (*V* = constant)
     - a. As *T* increase, *P* increases

       The increase in *T* causes an increase in average kinetic energy. Molecules moving faster collide with the walls of the container more frequently, and with greater force
  3. *V* and *T* (*P* = constant)
     - a. As *T* increases, *V* also increases

       Increased *T* creates more frequent, more forceful collisions. *V* must increase proportionally to increase the surface area, and maintain *P*
  4. *V* and *n* (*T* and *P* constant)
     - a. As n increases, V must increase

       Increasing the number of particles increases the number of collisions. This can be balanced by an increase in *V* to maintain constant *P*
  5. Dalton's law of partial pressures
     - a. *P* is independent of the type of gas molecule

       KMT states that particles are independent, and *V* is assumed to be zero. The identity of the molecule is therefore unimportant
- C. Root Mean Square Velocity
  1. Velocity of a gas is dependent on mass and temperature.
  2. Velocity of gases is determined as an average
     - a. *M* = mass of one mole of gas particles in kg
     - b. *R* = 8.3145 J/K•mol
       - *(1) joule* = kg•m^2/s^2

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

- D. Mean Free Path
  1. Average distance a molecule travels between collisions
     - a. 1 x 10^{-7} m for O_2 at STP

5.7 Effusion and Diffusion

A. Effusion
  1. Movement of a gas through a small opening into an evacuated container (vacuum)
  2. Graham's law of effusion

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

B. Diffusion
  1. The mixing of gases
  2. Diffusion is complicated to describe theoretically and mathematically

5.8 Real Gases and van der Waals Equation (Johannes van der Waals, 1873)

A. Volume
  1. Real gas molecules <u>do</u> have volume
  2. Volume available is not 100% of the container volume
     a. *n* = number of moles
     b. *b* = is an empirical constant, derived from experimental results

<u>Ideal</u>	<u>Real</u>
$P = \frac{nRT}{V}$	$P' = \frac{nRT}{V - nb}$

B. Pressure
  1. Molecules of real gases do experience attractive forces
     a. *a* = proportionality constant determined by observation of the gas

$$P_{obs} = P' - a\left(\frac{n}{V}\right)^2$$

C. Combining to derive van der Waal's eqn

$$P_{obs} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

and then rearranging…

$$\left[P_{obs} + a\left(\frac{n}{V}\right)^2\right] \times (V - nb) = nRT$$

5.9 Characteristics of Several Real Gases

A. Intermolecular Forces of Attraction

1. Larger intermolecular forces of attraction increase deviation from ideal behavior
2. For these molecules, the increase in van der Waals forces predicts this increase in deviation from ideal behavior

$$H_2 < N_2 < CH_4 < CO_2$$

5.10 Chemistry in the Atmosphere

A. Composition of the Troposphere

Composition of dry air (sea level	
Component	**Mole Fraction**
Nitrogen	0.78084
Oxygen	0.20948
Argon	0.00934
Carbon dioxide	0.000345
Neon	0.00001818
Helium	0.00000524
Methane	0.00000168

B. Photochemical Smog - the problem of nitrogen oxides (NO_x)

1. Auto exhaust contains small amounts of NO, which is quickly oxidized

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

2. Radiant energy causes NO_2 to decompose

$$NO_2(g) \rightarrow NO(g) + O(g)$$

3. Free oxygen atoms combine with oxygen molecules to form ozone

$$O(g) + O_2(g) \rightarrow O_3(g)$$

4. Ozone may absorb light energy and decompose to excited oxygen atoms and excited oxygen molecules

$$O_3(g) \rightarrow O_2^* + O^*$$

5. Excited oxygen atoms react with water to form the hydroxyl radical

$$O^* + H_2O \rightarrow 2OH$$

6. Hydroxyl can react with NO_2 to form nitric acid

$$OH + NO_2 \rightarrow HNO_3$$

C. Coal and acid rain

1. Most coal, especially cheap coal, contains sulfer

$$S \text{ (in coal)} + O_2 (g) \rightarrow SO_2 (g)$$

2. Sulfur dioxide is oxidized in air

$$2SO_2 (g) + O_2(g) \rightarrow 2SO_3 (g)$$

3. Acid rain forms at the SO3 combines with water in the air

$$SO_3 (g) + H_2O (l) \rightarrow H_2SO_4 (aq)$$