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 for homogeneous mixtures with other gases.
- Gases occupy only a small fraction of the volume of their containers.
  - As a result, each molecule of a gas behaves largely as though other molecules were absent.

10.2 Pressure

Atmospheric Pressure and the Barometer

- **Pressure** is the force acting on an object per unit of area:

$$P = \frac{F}{A}$$

- The SI unit of pressure is the **pascal**.
- Gravity exerts a force on the Earth's atmosphere.
- A column of air 1 m^2 in cross section extending to the top of the atmosphere exerts a force of 10^5 N.
  - Thus, the pressure of a 1 m^2 column of air extending to the top of the atmosphere is 100 kPa.
- Atmospheric pressure is measured with a barometer.
- If a tube if completely filled with mercury and then inverted into a container of mercury open to the atmosphere, the mercury will rise until the pressure due to the mass of the mercury column is the same as atmospheric pressure.
  -
  - Standard atmospheric pressure is the pressure required to support 760 mm of Hg in a column.
  - Units: 1 atm = 760 mm Hg = 760 torr = 1.01325 x 10^5 Pa = 101.325 kPa
- Atmospheric pressure is sometimes reported using a related unit, the **bar**.
  - 1 bar = 10^5 Pa

Pressures of Enclosed Gases and Manometers

- In the laboratory the pressures of gases not open to the atmosphere are measured using manometers.
- A manometer consists of a bulb of gas attached to a U-tube containing Hg.
- If the U-tube is closed, then the pressure of the gas is the difference in height of the liquid (usually Hg).
- If the U-tube is open to the atmosphere, a correction term needs to be added:
  - If $P_{gas} < P_{atm}$, then $P_{gas} + P_h = P_{atm}$
  - If $P_{gas} > P_{atm}$, then $P_{gas} = P_{atm} + P_h$
  - Big = Small + height

10.3 The Gas Laws

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

The Pressure-Volume Relationship: Boyle's Law

- Weather balloons are used as a practical application of the relationship between pressure and volume of a gas.
  - As the weather balloon ascends, the volume increases.
  - As the weather balloon gets farther from Earth's surface, the atmospheric pressure decreases.
- **Boyle's law**: The volume of a fixed quantity of gas, at constant temperature, is inversely proportional to its pressure.
- Mathematically:

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

- A plot of *V* versus *P* is a hyperbola.
  - Similarly, a plot of *V* versus 1/*P* is a straight line passing through the origin.
- The process of breathing illustrates Boyle's law:
  - As we breathe in, the diaphragm moves down, and the ribs expand. Therefore, the volume of the lungs increases.
  - According to Boyle's law, when the volume of the lungs increases, the pressure decreases. Therefore, the pressure inside the lungs is less than atmospheric pressure.
  - Atmospheric pressure then forces air into the lungs until the pressure once again equals atmospheric pressure.
  - As we breathe out, the diaphragm moves up and the ribs contract. Therefore, the volume of the lungs decreases.
  - By Boyle's law, the pressure increases and air is forced out.

The Temperature-Volume Relationship: Charles's Law

- We know that hot-air balloons expand when they are heated.
- **Charles's law**: The volume of a fixed quantity of gas at constant pressure is directly proportional to its absolute temperature.
- Mathematically:

$$V = constant \times T \text{ or } \frac{V}{T} = constant$$

- Note that the value of the constant depends on the pressure and number of moles of gas.
  - A plot of *V* versus *T* is a straight line.
  - When *T* is measures in ^{o}C, the intercept on the temperature axis is –273.15 ^{o}C
  - We define absolute zero, 0 K = -273.15 ^{o}C

The Quantity-Volume Relationship: Avagadro's Law

- Gay-Lussac's law of combining volumes: At a given temperature and pressure the volumes of gases that react with one another are ratios of small whole numbers.
- **Avagadro's hypothesis**: Equal volumes of gases at the same temperature and pressure contain the same number of molecules.
- **Avagadro's law**: The volume of a gas at a given temperature and pressure is directly proportional to the number of moles of gas.
  - Mathematically

$$V = constant \times n$$

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

10.4 The Ideal-Gas Equation

- Summarizing the gas laws:
  - Boyle: $V \propto \frac{1}{P}$ *(constant n, T)*
  - Charles: $V \propto T$ *(constant n, P)*
  - Avogadro: $V \propto n$ *(constant P, T)*
  - Combined: $V \propto \frac{nT}{P}$
- Ideal-gas equation: $P V = n R T$
  - Where R = **gas constant** = 0.08206 L·atm/mol·K
  - An **ideal gas** is a hypothetical gas whose *P*, *V*, and *T* behavior is completely described by the ideal-gas equation.
- Define **STP (standard temperature and pressure**) = 0^oC, 273.15 K, 1 atm
  - Volume of 1 mol of gas at STP is 22.4 L

Relating the Ideal-Gas Equations and the Gas Laws

- If $PV = nRT$ and *n* and *T* are constant, then *PV* = constant, and we have Boyle's law.
  - Other laws can be generated similarly.
- In general, if we have a gas under two sets of conditions, then

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

- We often have a situation in which *P, V,* and *T* all change for a fixed number of moles of gas.
- For this set of circumstances,

$$\frac{PV}{T} = nR = constant$$

10.5 Further Applications of the Ideal-Gas Equation

Gas Densities and Molar Masses

- Density has units of mass over volume.
- Rearranging the ideal-gas equation with *M* as molar mass we get:

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{nM}{V} = \frac{PM}{RT}$$

$$\therefore d = \frac{PM}{RT}$$

- The molar mass of a gas can be determined as follows:

$$M = \frac{dRT}{P}$$

Volumes of Gases in Chemical Reactions

- The ideal-gas equation relates *P, V,* and *T* to the number of moles of gas (*n*).
- The *n* can then be used in stoichiometric calculations.

10.6 Gas Mixtures and Partial Pressures

- Since gas molecules are so far 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** is the pressure exerted by a particular component of a gas mixture.
- **Dalton's law of partial pressure**: In a gas mixture the total pressure is given by the sum of partial pressures of each component:

$$P_t = P_1 + P_2 + P_3 + \ldots + P_n$$

- Each gas obeys the ideal-gas equation.
- Thus,

$$P_t = (n_1 + n_2 + n_3 + \ldots)\frac{RT}{V} = n_1\frac{RT}{V}$$

Partial Pressures and Mole Fractions

- Let n_1 be the number of moles of gas 1 exerting a partial pressure P_1, then

$$P_1 = X_1 P_1$$

  - Where X_1 is the **mole fraction** (n_1/n_t).

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 the partial pressure of the water:

$$P_{total} = P_{gas} + P_{water}$$

- The vapor pressure of water varies with temperature.
  - Values can be found in Appendix B.

10.7 Kinetic-Molecular Theory

- The **kinetic molecular theory** was developed to *explain* gas behavior.
  - Theory of moving molecules.
- Summary:
  - Gases consist of individual molecules in constant random motion.
  - The volume of individual molecules is negligible compared with the volume of the container.
  - Intermolecular forces (forces between gas molecules) are negligible.
  - Energy can be transferred between molecules during collisions, but the average kinetic energy is constant at constant temperature.
    - The collisions are perfectly elastic.
  - The average kinetic energy of the gas molecules is proportional to the absolute temperature.
- Kinetic-molecular theory gives us an *understanding* of pressure and temperature on the molecular level.
  - The pressure of a gas results from collisions of the molecules with the walls of the container.
  - The magnitude of the pressure is determined by how often and how hard the molecules strike.
- The absolute temperature of a gas is a measure of the average kinetic energy.
  - Some molecules will have less kinetic energy or more kinetic energy than the average (distribution).
  - There is a spread of individual energies of gas molecules in any sample of gas.
  - As the temperature increases, the average kinetic energy of the gas molecules increases.
- As kinetic energy increases, the velocity of the gas molecules increases.
  - **Root-mean-square (rms) speed**, *u*, is the speed of a gas molecule having average kinetic energy.
  - Average kinetic energy, ε, is related to rms speed:

    $$\varepsilon = 1/2\, mu^2$$

    Where *m* = mass of the molecule.

Application to the Gas Laws

- We can understand empirical observations of gas properties within the framework of the kinetic molecular theory.
- Effect of an increase in volume (at constant temperature):
  - As volume increases at constant temperature, the average kinetic energy of the gas remains constant.
  - Therefore, *u*, is constant.
  - However, volume increases, so the gas molecules have to travel farther to hit the wall of the container.
  - Therefore, pressure decreases.
- Effect of an increase in temperature (at constant volume):
  - If temperature increases at constant volume, the average kinetic energy of the gas molecules increases.
  - There are more collisions with the container walls.
  - The change in momentum in each collision increases (molecules strike harder).
  - Therefore, pressure increases.

10.8 Molecular Effusion and Diffusion

- The average kinetic energy of a gas is related to its mass:

$$\varepsilon = 1/2\,mu^2$$

- Consider two gases at the same temperature: the lighter gas has a higher rms speed than the heavier gas.
  - Mathematically:

$$u = \sqrt{\frac{3RT}{M}}$$

- The lower the molar mass, M, the higher the rms speed for that gas 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.

Graham's Law of Effusion

- The rate of effusion can be quantified.
- For two gases with molar masses M_1 and M_2. The relative rate of effusion is given by **Graham's law:**

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

- Only those molecules that hit the small hole will escape through it.
  - Therefore, the higher the rms speed the more likely that a gas molecules will hit the hole.
  - We can show

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \sqrt{\frac{M_2}{M_1}}$$

Diffusion and Mean Free Path

- Diffusion is faster for light gas molecules.
- Diffusion is significantly slower than the rms speed.
  - Diffusion is slowed by collisions of gas molecules with one another.
  - Consider someone opening a perfume bottle: It takes a while to detect the odor, but the average speed of the molecules at 25^{o}C is about 515 m/s!
- The average distance traveled by a gas molecule between collisions is called the **mean free path**.
- At sea level, the mean free path for air molecules is about 6×10^{-6} cm.

10.9 Real Gases: Deviations from Ideal Behavior

- From the ideal gas equation:

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

- For 1 mole of an ideal gas, $PV = nRT = 1$ for all pressures.
  - In a real gas, $PV = nRT$ varies from 1 significantly.
  - The higher the pressure the more the deviation from ideal behavior.

- For 1 mole of an ideal gas, $PV = nRT = 1$ for all temperatures.
  - In a real gas, $PV = nRT$ varies from 1 significantly.
  - As temperature increases, the gases behave more ideally.

- The assumptions in the kinetic-molecular theory show where ideal-gas behavior breaks down:
  - The molecules of a gas *have* finite volume.
  - Molecules of a gas *do* attract each other.

- As the pressure on a gas increases, the molecules are forced closer together.
  - As the molecules get closer together, the volume of the container gets smaller.
  - The smaller the container, the more of the total space the gas molecules occupy.
  - Therefore, the higher the pressure, the less the gas resembles an ideal gas.
  - The smaller the distance between gas molecules, the more likely that attractive forces will develop between the molecules.
  - Therefore, the less the gas resembles an ideal gas.

- As temperature increases, the gas molecules move faster and farther apart.
  - Also, higher temperatures mean that more energy is available to break intermolecular forces.
  - As temperature increases, the negative departure from ideal-gas behavior disappears.

The van der Waals Equation

- We add two terms to the ideal-gas equation to correct for
  - The volume of molecules: $(V - nb)$
  - Molecular attractions:

$$\left(\frac{n^2a}{V^2}\right)$$

  - The correction terms generate the **van der Waals equation:**

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

    - Where *a* and *b* are empirical constants.

  - To understand the effect of intermolecular forces on pressure, consider a molecule that is about to strike the wall of the container.
    - The striking molecule is attracted by neighboring molecules.
    - Therefore, the impact on the wall is lessened