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:

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

Atmospheric Pressure and the Barometer

- The SI unit of force is the *newton* (N).
  - $1\ N = 1\ kg\text{-}m/s^2$
- The SI unit of pressure is the **pascal** (Pa).
  - $1\ Pa = 1\ N/m^2$
  - A related unit is the **bar,** which is equal to 10^5 Pa.
  - Another pressure unit is pounds per square inch (psi, lbs/in^2).
- Gravity exerts a force on the Earth's atmosphere.
  - A column of air 1 m^2 in cross section extending to the upper atmosphere exerts a force of 10^5 N.
  - Thus, the pressure of a 1 m^2 column of air extending to the upper atmosphere is 100 kPa.
    - Atmospheric pressure at sea level is about 100 kPa or 1 bar or 14.7 psi.
    - The actual atmospheric pressure at a specific location depends on the altitude and weather conditions.
- Atmospheric pressure is measured with a *barometer*.
  - If a tube is completely filled with mercury and then inverted into a container of mercury open to the atmosphere, the mercury will rise 760 mm up the tube.
  - **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 = 1.01325 bar.
- The pressure of enclosed gases is measured with a *manometer*.

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 further 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:

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

- A plot of V versus P is a hyperbola.
- A plot of V versus $1/P$ must be a straight line passing through the origin.
- The working of the lungs 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:

- 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 $\quad V = \text{constant} \times T \text{ or } \dfrac{V}{T} = \text{constant} \quad$ measured in °C, the intercept on the temperature axis is – 273.15 °C.
- We define *absolute zero*, 0 K = –273.15 °C.

The Quantity-Volume Relationship: Avogadro'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.
- **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.
  - Mathematically:

$$V = \text{constant} \times n$$

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

10.4 The Ideal-Gas Equation

- Summarizing the gas laws:
  - Boyle: $V \propto 1/P$ (constant n, T)
  - Charles: $V \propto T$ (constant n, P)
  - Avogadro: $V \propto n$ (constant P, T)
  - Combined: $V \propto nT/P$
- **Ideal-gas equation** or **ideal-gas law**: $PV = nRT$
  - An **ideal gas** is a hypothetical gas whose P, V, and T behavior is completely described by the ideal-gas equation.
  - R = **gas constant** = 0.08206 L-atm/mol-K
    - Other numerical values of R in various units are given in Table 10.2.
- Define **STP** (**standard temperature and pressure**) = 0 °C, 273.15 K, 1 atm.

- The molar volume of 1 mol of an ideal gas at STP is 22.41 L.

Relating the Ideal-Gas Equation and the Gas Laws

- If $PV = nRT$ and n and T are constant, then PV is 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

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

- 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,

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

  - Which gives the *combined gas law*.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

10.5 Further Applications of the Ideal-Gas Equation

Gas Densities and Molar Mass

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

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

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

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

- 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 number of moles of gas.
- 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 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 pressures**: In a gas mixture the total pressure is given by the sum of partial pressures of each component:
$$P_t = P_1 + P_2 + P_3 + \ldots$$

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

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

Partial Pressures and Mole Fractions

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

$$P_1 = X_1 P_t$$

  - Where X_1 is the **mole fraction** (n_1/n_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 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 of Gases

- The **kinetic molecular theory of gases** was developed to *explain* gas behavior.
  - It is a theory of moving molecules.
- Summary:
  - 1. Gases consist of a large number of molecules in constant random motion.
  - 2. The combined volume of all the molecules is negligible compared with the volume of the container.
  - 3. 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.
  - 4. Energy can be transferred between molecules during collisions but, as long as the temperature remains constant, the *average* kinetic energy of the molecules does not change with time (the collisions are perfectly elastic.
  - 5. 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 the collisions 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.

Distributions of Molecular Speed

- As kinetic energy increases, the velocity of the gas molecules increases.
  - **Root-mean-square (rms) speed**, u_{rms}, is the speed of a gas molecule having average kinetic energy.
- Average kinetic energy, ε, is related to rms speed:

$$\varepsilon = \tfrac{1}{2}\,mu^2$$

  - where m = mass of the molecule.

Application of Kinetic-Molecular Theory 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 of the 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 temperature increases at constant volume, the average kinetic energy of the gas molecules increases.
  - There are more collisions with the container walls.
  - Therefore, u increases.
  - 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:
$$\varepsilon = \tfrac{1}{2}\,mu^2$$
- Consider two gases at the same temperature: the lighter gas has a higher rms speed than the heavier gas.
  - Mathematically:
$$u_{rms} = \sqrt{\frac{3RT}{M}}$$
  - 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.
- Consider two gases with molar masses M_1 and M_2, with effusion rates, r_1 and r_2, respectively:
  - 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 molecule will hit the hole.

- We can show that:
$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \sqrt{\frac{3RT/M_1}{3RT/M_2}} = \sqrt{\frac{M_2}{M_1}}$$

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 awhile to detect the odor, but the average speed of the molecules at 25 °C is about 515 m/s (1150 mi/hr).
- 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 mol of an ideal gas, $PV/RT = 1$ for all pressures.
    - In a real gas, PV/RT varies from 1 significantly.
    - The higher the pressure, the more the deviation from ideal behavior.
  - For 1 mol of an ideal gas, $PV/RT = 1$ for all temperatures.
    - 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 free space in which the molecules can move 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.
  - As the gas molecules get closer together, the intermolecular distances decrease.
  - 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 further apart.
  - Also, higher temperatures mean more energy 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: $(V - nb)$

  - For molecular attractions:

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

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

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

    - where a and b are empirical constants (van der Waals constants) that differ for each gas.
    - van der Waals constants for some common gases can be found in Table 10.3.
- 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.

Selected Problems: 28, 30, 32, 33, 35, 36, 39, 41, 43, 53, 54, 57, 58, 56, 63, 65, 66, 69, 70, 71, 74, 75.