

Chapter 10. Gases

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.

Pressure

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

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

Lung demo

Atmospheric Pressure and the Barometer

- The SI unit of force is the *newton* (N).
 - $1 \text{ N} = 1 \text{ kg}\cdot\text{m}/\text{s}^2$
- The SI unit of pressure is the **pascal** (Pa).
 - $1 \text{ Pa} = 1 \text{ N}/\text{m}^2 = 1 \text{ kg}\cdot\text{m}/\text{s}^2\text{m}^2 = 1 \text{ kg}/\text{s}^2\text{m}$
 - A related unit is the **bar**, which is equal to 10^5 Pa.
- 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.
 - The actual atmospheric pressure at a specific location depends on the altitude and weather conditions.

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- Atmospheric pressure is measured with a *barometer*.

DEMO tube with water and food coloring. Level example.

Now 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**
 - $1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa}$.

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*.

Show Demo of gas immersed in liquid N_2

Gas simulation demos

$$P = k(n)$$

$$P = kT$$

$$P \propto 1/V$$

Notice that gas properties are related to the number and energy of gas molecules.
Speed is related to temperature. Pressure is related to n and V .

10.4 The Ideal-Gas Equation

- **Ideal gas equation:** $PV = nRT$
 - An **ideal gas** is a hypothetical gas whose P , V , and T behavior is completely described by the ideal-gas equation.
 - $R = \text{gas constant} = 0.08206 \text{ L-atm/mol-K}$
- 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 .

Do some example calculations using $PV=nRT$

What is the volume of gas produced when 0.01 moles of NaHCO_3 is reacted with 100 ml of $0.2 \text{ M CH}_3\text{COOH (aq)}$?

- a) Balance

- b) Limiting reagent – compute moles of gas
- c) $PV = nRT$
- d) $0.01 * 0.08206 * 298 / 1 = V \text{ (L)} = 0.245 \text{ L}$

WHAT WOULD THE VOLUME BE IF THE PRESSURE WERE 0.8 ATM?

- 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

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

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

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

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

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

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

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

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:

$$P_t = P_1 + P_2 + P_3 + \dots$$

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

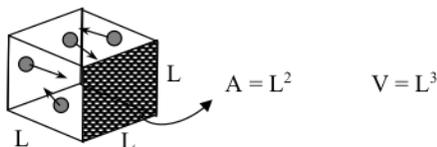
$$P_t = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = n_t \frac{RT}{V}$$

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.

Kinetic Molecular Theory

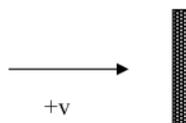
$$P = \frac{f}{A}$$



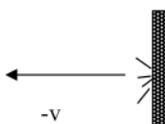
force = (force per collision)(collisions per sec per molecule)(molecules moving in the correct direction)

force per collision:

before collision:



after collision:



$$f = m a = m \frac{\Delta v}{\Delta t}$$

$$\Delta v = (+v) - (-v) = 2v$$

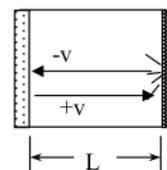
$$f = 2mv$$

collisions per sec

Taking a trip, want to stop periodically:

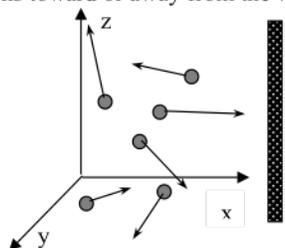
$$\text{stops per hour} = \frac{\text{speed}}{\text{distance between stops}} = \frac{60 \text{ mi/hr}}{60 \text{ mi}} = 1 \text{ stop/hour}$$

$$\text{collisions per second} = \frac{\text{speed}}{\text{distance between collisions}} = \frac{v}{2L}$$



molecules moving in the correct direction

Molecules moving in all directions, x, y, and z. On average only 1/3 are moving along the correct axis toward or away from the wall; only 1/3 are poised to strike the wall:



On average: 1/3 are moving along the x-axis \longleftrightarrow
 1/3 are moving along the y axis
 1/3 are moving along the z axis

for 1 mole total: $\frac{N_A}{3}$ are moving in the correct direction

$$f = (2mv) \left(\frac{v}{2L} \right) \left(\frac{N_A}{3} \right) = \frac{N_A m v^2}{3L}$$

average over all the molecules: $f = \frac{N_A m \overline{v^2}}{3L}$

$$P = \frac{f}{A} = \frac{N_A m \overline{v^2}}{3L^3} = \frac{N_A m \overline{v^2}}{3V}$$

root mean squared speed = $u = (\overline{v^2})^{1/2}$ $u^2 = \overline{v^2}$

$$PV = \frac{1}{3} N_A m u^2 \quad k\epsilon = \frac{1}{2} m u^2$$

$$PV = \frac{2}{3} N_A k\epsilon = RT \quad k\epsilon = \frac{3}{2} RT/N_A$$

10.8 Molecular Effusion and Diffusion

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

$$\varepsilon = \frac{1}{2} mu^2$$
- 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.
- Consider two gases with molar masses, M_1 and M_2 , and 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 which 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

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

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 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.
 - Similar molar mass related issues (e.g., passing of particles of solute through semipermeable membranes) for solutions will be discussed in Ch. 13 (section 13.5).

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 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.