

CHEM 20B Week 1

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Gases

- Eleven elements are gases under normal conditions
- Lower *molar mass* compounds such as carbon dioxide, hydrogen chloride
- A remarkable characteristics of gases is that many of their physical properties are very similar, particularly at low pressures, regardless of the identity of the gas.

Characteristics of Gases

1. **Compressibility:** Gases are more compressible than solids and liquids; suggests that there is a lot of space between the molecules of gases
2. **Motion:** Gas expands rapidly to fill the space available to it. Because balloons are spherical, we can infer that the motion of the molecules is chaotic, not favoring any single direction.

Our first primitive picture of a gas could be that gases are a collection of widely spaced molecules in ceaseless rapid chaotic motion.

Energy and Units

- Energy of atoms is made of two parts:
 1. **Kinetic Energy:** relating to how fast each atom moves.

$$\text{K.E.} = \frac{1}{2}mv^2$$

2. **Potential Energy:** energy that can turn into Kinetic Energy

Energy is measured in Joules ($1 \text{ J} = 1 \text{ kg m}^2/\text{sec}^2$)

Force

- $F = \text{Force} = \text{Energy}/\text{distance}$
- Force is measured in $J/m = \text{kg} \cdot \frac{m}{s^2}$, or Newtons (N).

Pressure

- Pressure is $\frac{\text{force}}{\text{area}}$, or $P = \frac{F}{A}$.
- Colliding gases exert a pressure on the sides of the container walls.
- The more vigorous the motion, the stronger the force and hence the higher the pressure.

- Pressure is measured in atm, bars, mmHg, and Pascals (Energy/Volume).
 - Pascal (Pa) = $\frac{J}{m^3} = \frac{N}{m^2}$
 - 1 atm = 1.01325×10^5 Pa
 - 1 bar = 1×10^5 Pa
 - 1 atm = 760 torr (any temperature)
 - 1 atm = 760 mm Hg (at 0°C)

PV=nRT, the Ideal Gas Law

- P = pressure
- V = volume
- T = temperature
- n = number of moles
- R = "gas constant" = $\frac{8.3J}{K \times mol}$

Pressure and Boyle's Law

- T fixed.
- The more mercury he added, the more the trapped air was compressed
- PV will be proportional to the amount of material
- $P \cdot V$ is unchanged if the amount of material is unchanged, and T is fixed.

Moles and Avogadro's Law

- For the same T and P, the ratios of the volumes between 2 different gases = ratio of the numbers of moles
- $H_2O \rightarrow H_2 + 1/2O_2$
- Under fixed P and T, $V_{H_2} = 2 \cdot V_{O_2}$ by experimental observation.
 - This implies that

$$\frac{PV_{H_2}}{n_{H_2}} = \frac{PV_{O_2}}{n_{O_2}}$$

$$PV = n f(T)$$

where $f(T)$ is universal.

- T is defined as T in Kelvin
- The numerical value of R was adjusted so that the difference in Kelvin("K") between boiling point of water and freezing point, when measured at the pressure near sea level, will be 100 (i.e., 100K), just like it is in Celsius

Defining the Temperature in Kelvin

- Fahrenheit and Celsius scale completely arbitrary designations
- We need a temperature that is based on a physical law.
- The simplest way to do that is to use the gas law.

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

Temperature and Charles' Law

Charles observed that all gases expand by the same relative amount between the same initial and final temperature under sufficient low pressure.

$$t = C \left(\frac{V}{V_0} - 1 \right)$$

- V_0 is the volume of the freezing point of water
- C is a constant that is the same for all gases.

Experimentally: put a container (with a movable plug) with air in boiling water, at $P = 1$ bar, and find that V is, say, 50.000 L. When the same container is then put into ice water, we'll find that $V = 36.601$ L.

$$\begin{aligned} \frac{PV(\text{at } T_{\text{boil}})}{PV(\text{at } T_{\text{freeze}})} &= \frac{1\text{bar} \cdot 50.000\text{L}}{1\text{bar} \cdot 36.601\text{L}} = 1.36609 \\ \frac{nRT_{\text{boil}}}{nRT_{\text{freeze}}} &= \frac{T_{\text{boil}}}{T_{\text{freeze}}} = 1.36609 \\ T_{\text{freeze}} &= \frac{100\text{K}}{0.36609} \end{aligned}$$

$$\therefore T_{\text{freeze}} = 273.16\text{K} \sim 273\text{K}, T_{\text{boil}} = 373.16\text{K}$$

In the same experiment, suppose $n = 1.61$ mol.

$$R = \frac{PV}{nT} = \frac{1\text{bar} \cdot 50.00\text{L}}{1.61\text{mol} \cdot 373.16\text{K}} = \frac{0.0831\text{bar} \cdot \text{L}}{\text{mol} \cdot \text{K}}$$

Simplifying,

$$R = 8.3 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

- For a fixed amount of gas under constant pressure, volume is directly proportional to temperature.

$$V = V_0 \left(1 + \frac{t}{273.15^\circ\text{C}} \right)$$

- T (Kelvin) = t ($^\circ\text{C}$) + 273.15 (fixed pressure and fixed amount of gas)

The Ideal Gas Law

Combining all of the following:

- Boyle's Law:

$$V \propto \frac{1}{p} \text{ (at constant temperature, fixed amount of gas)}$$

- Charles' Law:

$$V \propto T \text{ (at constant pressure, fixed amount of gas)}$$

- Avogadro's Law:

$$V \propto n \text{ (at constant temperature and pressure)}$$

We get...

$$\boxed{PV = nRT}$$

$$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

Dalton's Law: Mixture of Gases

- Dalton's Law holds under the same conditions as the ideal gas law.
- It is approximate at moderate pressures and becomes increasingly more accurate as the pressure is lowered.
- For a gas mixture at low pressure, the partial pressure of one component, A, is its concentration compared to the other gases present.

$$P_A = n_A \cdot \frac{RT}{V}$$

- Total pressure is the sum of the partial pressures.

$$P_{total} = P_A + P_B + \dots$$

$$P_A = \frac{n_A}{n_{tot}} \cdot P_{tot}$$

Kinetic Theory of Gases

Assumptions:

1. A gas consists of a collection of molecules in ceaseless random motion.
2. Gas molecules are infinitesimally small points.
3. The molecules move in straight lines until they collide.
4. The molecules do not influence one another except during collisions.
5. The collisions are elastic. No energy is lost during a collision.

$$\text{Root-mean-square speed } v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}}$$

$$T = \frac{Mv_{rms}^2}{3R}$$

Physical Derivation of the Ideal Gas Law

Gases always expand to fill all of the space they are given. As a result, the pressure is the force exerted from gas particles hitting the walls of the container.

Suppose that all the gas particles in a rectangular chamber (with side lengths l_x , l_y , and l_z) are identical, and have mass m . The pressure exerted on the walls is

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

where P represents pressure, F is the force exerted on the walls by particles, and A is the surface area of the wall.

For one gas molecule,

$$F = ma = m \cdot \frac{\Delta v}{\Delta t} = \frac{\Delta(mv)}{\Delta t} = \frac{\Delta p}{\Delta t}$$

Recall, Δp is the change in momentum of a particle.

The change in momentum can be calculated by

$$\Delta p = p_{\text{final}} - p_{\text{initial}}$$

A particle heading to a wall with momentum $-mv_x$ would bounce off with momentum mv_x . Therefore, the absolute change in momentum, $\Delta p = 2 \cdot mv_x$.

By definition of velocity,

$$v = \frac{d}{t}$$

where v represents velocity, d represents distance, and t represents time.

Thus, if the particle travels from one wall of the rectangular box to the other, bounces off, and returns to its starting point, then $d = 2 \cdot l_x$ and $v = v_x$. Solving for time, $t = 2 \cdot \frac{l_x}{v_x}$.

$$\therefore F = \frac{\Delta p}{\Delta t} = \frac{2 \cdot mv_x}{2 \cdot \frac{l_x}{v_x}} = \frac{mv_x^2}{l_x}$$

This is the force for one particle. Since all of the particles have the same mass, then the total force would be

$$F_{\text{total}} = F_1 + F_2 + F_3 + \dots + F_n$$

where F_i represents the contribution of force from the i -th particle.

There are N gas particles in the container. Therefore, the average square of x-component of velocity for all the particles will be:

$$v_x^2 = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N}$$

The total force is then:

$$F = \frac{m}{l_x} \cdot N \cdot \bar{v}_x^2$$

Since there are three dimensions to the cubic container, and the particles have random direction, it can be assumed that for an average particle, $\bar{v}_x = \bar{v}_y = \bar{v}_z$. Therefore, the mean square speed $\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 = 3\bar{v}_x^2$

$$\begin{aligned} P &= \frac{F}{A} = \frac{m \cdot N \cdot \frac{1}{3} \bar{v}_x^2}{l_x \cdot l_y \cdot l_z} \\ &= \frac{m \cdot N \cdot \bar{v}^2}{3V} \end{aligned}$$

Rearranging,

$$PV = \frac{1}{3} \cdot N \cdot m \cdot \bar{v}^2$$

On the side, find the energy of N_A molecules.

$$\bar{E} = N_A \cdot \frac{1}{2} m \bar{v}^2$$

N_A is equal to $\frac{N}{n}$ Average kinetic energy for 1 molecule is then $\frac{\bar{E}}{N_A} = \bar{\epsilon} = \frac{3RT}{2N_A}$. Simplifying,

$$\bar{\epsilon} = \frac{3}{2} K_B T$$

where $K_B = \frac{R}{N_A}$.

Additionally, $N_A \cdot m = M$, so $\bar{E} = \frac{1}{2} M \bar{v}^2 = \frac{3}{2} RT$. Solving for velocity,

$$\begin{aligned} \frac{1}{2} M \bar{v}^2 &= \frac{3}{2} RT \\ M \bar{v}^2 &= 3RT \\ \bar{v}^2 &= \frac{3RT}{M} \end{aligned}$$

Substituting into the PV equation from earlier,

$$PV = \frac{1}{3} \cdot N \cdot m \cdot \left(\frac{3RT}{M} \right)$$

Simplifying,

$$PV = N \cdot m \cdot \frac{RT}{M}$$

By definition earlier, $N_A \cdot n = N$. Therefore,

$$PV = N_A \cdot n \cdot m \cdot \frac{RT}{M}$$

Also, $N_A \cdot m = M$, so

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

Simplifying,

$$\boxed{PV = nRT}$$

Real Gases: Intermolecular Forces

There are many differences between ideal and real gases, since the assumptions made when defining an ideal gas do not apply to real gases.

Compressibility factor

$$z = \frac{PV}{nRT}$$

Remember that in this case, $PV \neq nRT$!

The van der Waals Equation of State

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

Rearranging,

$$P = \frac{nRT}{V - nb} - a \cdot \frac{n^2}{V^2}$$

This equation takes into account the intermolecular forces between the molecules.

The attractive forces are represented by:

$$P + a \cdot \frac{n^2}{V^2}$$

while the repulsive forces are represented by:

$$V_{\text{effective}} = V - nb$$

- Attractive forces hold molecules together, which means there are fewer independent molecules, which in turn reduces the rate of collisions with the wall. Therefore, $P_{\text{real}} < P_{\text{ideal}}$.
- Repulsive forces decreases the available space for a molecule, which increases the rate of collision with the wall. Therefore, $P_{\text{real}} > P_{\text{ideal}}$.

Molecule-Wall collisions

Rate of collisions of gas molecules with a section of wall of area A:

$$Z_w \propto \frac{N}{V} \cdot \bar{v} \cdot A$$

$$Z_w \propto \frac{1}{4} \cdot \frac{N}{V} \cdot \bar{v} \cdot A = \frac{1}{4} \cdot \frac{N}{V} \cdot \sqrt{\frac{8RT}{\pi M}} \cdot A$$

- The rate of effusion is represented by Z_w .
- M represents molarity.