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Kinetic Theory of Gases

Kinetic Theory of Ideal gases

Kinetic theory of gases explains the behavior of gases, it correlates the macroscopic properties of gases *e.g.*, Pressure, temperature etc., to the microscopic properties like speed, momentum, kinetic energy etc.

Assumptions of Kinetic Theory of Gases

(i) Every gas consists of extremely small particles known as molecules. The molecules of a given gas are all identical but are different from those of another gas.

(ii) The molecules of a gas are identical spherical, rigid and perfectly elastic point masses.

(iii) Their molecular size is negligible in comparison to intermolecular distance (10^{-9} m).

(iv) The speed of gas molecules lies between zero and infinity (very high speed).

(v) The distance covered by the molecules between two successive collisions is known as **free path** and mean of all free path is known as **mean free path**.

(vi) The number of collisions per unit volume in a gas remains constant.

(vii) No attractive or repulsive force acts between gas molecules.

(viii) Gravitational attraction among the molecules is ineffective due to extremely small masses and very high speed of molecules.

(ix) The density of gas is constant at all points of the vessel.

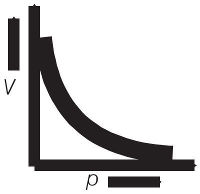
(x) The molecules of a gas keep on moving randomly in all possible directions with all possible velocities.

Gas Laws

Through experiments, it was established that gases irrespective of their nature obey the following laws

Boyle's Law

At constant temperature, the volume (V) of given mass of a gas is inversely proportional to its pressure (p), *i.e.*



$$V \propto \frac{1}{p} \quad \Rightarrow \quad pV = \text{constant}$$

For a given gas, $p_1V_1 = p_2V_2$

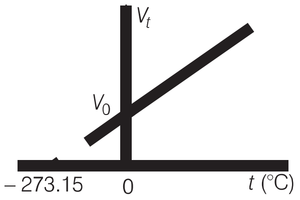
Charles' Law

At constant pressure, the volume (V) of a given mass of gas is directly proportional to its absolute temperature (T), *i.e.*

$$V \propto T \quad \Rightarrow \quad \frac{V}{T} = \text{constant}$$

For a given gas, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

At constant pressure, the volume (V) of a given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its volume at 0°C for each 1°C rise or fall in temperature.



Volume of the gas at t°C, $V_t = V_0\left(1 + \frac{t}{273.15}\right)$

where, V_0 is the volume of gas at 0°C.

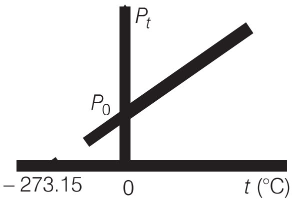
Gay Lussac's or Regnault's Law

At constant volume, the pressure p of a given mass of gas is directly proportional to its absolute temperature T, *i.e.*

$$p \propto T \quad \Rightarrow \quad \frac{p}{T} = \text{constant}$$

For a given gas, $\frac{p_1}{T_1} = \frac{p_2}{T_2}$

At constant volume, the pressure p of a given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its pressure at 0°C for each 1°C rise or fall in temperature.



Volume of the gas at t°C, $p_t = p_0 \left(1 + \frac{t}{273.15}\right)$

where, p_0 is the pressure of gas at 0°C.

Avogadro's Law

Avogadro stated that equal volume of all the gases under similar conditions of temperature and pressure contain equal number of molecules. This statement is called Avogadro's hypothesis. According to Avogadro's law $N_1 = N_2$, where N_1 and N_2 are number of molecules in two gases respectively.

(i) **Avogadro's number** The number of molecules present in 1g mole of a gas is defined as **Avogadro's number**.

$$N_A = 6.023 \times 10^{23} \text{ per gram mole}$$

(ii) At STP or NTP ($T = 273$ K and $p = 1$ atm), 22.4 L of each gas has 6.023×10^{23} molecules.

(iii) One mole of any gas at STP occupies 22.4 L of volume.

Dalton's Law of Partial Pressure

It states that the total pressure of a mixture of non-interacting ideal gases is the sum of partial pressures exerted by individual gases in the mixture. i.e. $p = p_1 + p_2 + p_3 + \ldots\ldots$

Ideal or Perfect Gas Equation

Gases which obey all gas laws in all conditions of pressure and temperature are called perfect gases.

Equation of perfect gas

$$pV = nRT$$

where, p = pressure, V = volume, T = absolute temperature,
R = universal gas constant and n = number of moles of a gas.

Universal gas constant, $R = 8.31\ \text{J mol}^{-1}\text{K}^{-1}$.

Real Gases

Real gases deviate slightly from ideal gas laws because

(i) Real gas molecules attract one another.
(ii) Real gas molecules occupy a finite volume.

Real or van der Waals' Gas Equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

where, a and b are called van der Waals' constants.

Dimension $[a] = [\text{ML}^5\text{T}^{-2}]$ and $[b] = [\text{L}^3]$

Units $a = \text{N-m}^4$ and $b = \text{m}^3$.

Note Real gases obey this equation at high pressure and low temperature

Pressure of a gas

Pressure due to an ideal gas is given by

$$p = \frac{1}{3}\frac{mn}{V}v^2 = \frac{1}{3}\rho\bar{v}^2$$

For one mole of an ideal gas,

$$p = \frac{1}{3}\frac{M}{V}\bar{v}^2$$

where, m = mass of one molecule, n = number of molecules,

V = volume of gas, $\bar{v} = \sqrt{\frac{\bar{v}_1^2 + \bar{v}_2^2 + \ldots + \bar{v}_n^2}{n}}$,

is called root mean square (rms) velocity of the gas molecules and M = molecular weight of the gas.

If p is the pressure of the gas and E is the kinetic energy per unit volume is E, then

$$p = \frac{2}{3} E$$

Note Effect of mass, volume and temperature on pressure

- when volume and temperature of a gas are constant, then pressure ∝ mass of gas.
- when mass and temperature of a gas are constant, then pressure $\propto \frac{1}{\text{volume}}$.
- when mass and volume of gas are constant, then pressure ∝ temperature $\propto c^2$.

Kinetic Energy of a Gas and Speed of Gas Molecules

(i) Average kinetic energy of translation per molecule of a gas is given by

$$E = \frac{3}{2} kT$$

where, k = Boltzmann's constant.

(ii) Average kinetic energy of translation per mole of a gas is given by

$$E = \frac{3}{2} RT$$

where, R = universal gas constant.

(iii) For a given gas kinetic energy

$$E \propto T$$

$$\Rightarrow \qquad \frac{E_1}{E_2} = \frac{T_1}{T_2}$$

(iv) Root mean square (rms) velocity of the gas molecules is given by

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3p}{\rho}}$$

(v) For a given gas, $v \propto \sqrt{T}$

(vi) For different gases, $v \propto \frac{1}{\sqrt{M}}$

(vii) Boltzmann's constant, $k = \frac{R}{N}$

where, R is an ideal gas constant and N = Avogadro number.

Value of Boltzmann's constant is 1.38×10^{-28} J/K.

(viii) The average speed of molecules of a gas is given by

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

(ix) The most probable speed of molecules v_{mp} of a gas is given by

$$v_{\text{mp}} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} \Rightarrow v_{\text{rms}} > \bar{v} > v_{\text{mp}}$$

(x) With rise in temperature rms speed of gas molecules increases as

$$v_{\text{rms}} \propto \sqrt{T}$$

(xi) With the increase in molecular weight rms speed of gas molecule decrease as

$$v_{\text{rms}} \propto \frac{1}{\sqrt{M}}$$

(xii) Rms speed of gas molecules is of the order of km/s, *e.g.* at NTP for hydrogen gas

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 273}{2 \times 10^3}} = 1.84$$

(xiii) Rms speed of gas molecules does not depend on the pressure of gas (if temperature remains constant) because $p \propto \rho$ (Boyle's law). If pressure is increased n times, then density will also increase by n times but v_{rms} remains constant.

Degree of Freedom

The degree of freedom for a dynamic system is the number of directions in which a particle can move freely or the total number of coordinates required to describe completely the position and configuration of the system.

It is denoted by f or N.

Degree of freedom of a system is given by

$$f \text{ or } N = 3A - R$$

where, A = number of particles in the system and R = number of independent relations between the particles.

Degree of freedom for different atomic particles are given below.

(i) For monoatomic gas = 3 (all translational).

(ii) For diatomic gas = 5 (3 translational, 2 rotational)

(iii) For non-linear triatomic gas = 6 (3 translational, 3 rotational)

(iv) For linear triatomic gas = 7 (3 translational,3 rotational and 1 vibrational)

Specific heat of a gas

(a) At constant volume, $C_V = \frac{f}{2}R$.

(b) At constant pressure, $C_p = \left(\frac{f}{2}+1\right)R$.

(c) Ratio of specific heats of a gas at constant pressure and at constant volume is given by $\gamma = 1 + \frac{2}{f}$.

Specific heat of solids, $C = 3R \Rightarrow C = 24\cdot 93\ \mathrm{J\,mol^{-1}\,K^{-1}}$.

Specific heat of water, $C = 9R \Rightarrow C = 74\cdot 97\ \mathrm{J\,mol^{-1}\,K^{-1}}$.

Nature of gas	$U = \frac{f}{2}RT$	$C_V = \frac{dU}{dT} = \frac{f}{2}R$	$C_p = C_V + R$	$\gamma = \frac{C_p}{C_V} = 1 + \frac{2}{f}$
Monoatomic	$\frac{3}{2}RT$	$\frac{3}{2}R$	$\frac{5}{2}R$	1.67
Dia and linear polyatomic	$\frac{5}{2}RT$	$\frac{5}{2}R$	$\frac{7}{2}R$	1.4
Non-linear polyatomic	$3RT$	$3R$	$4R$	1.33

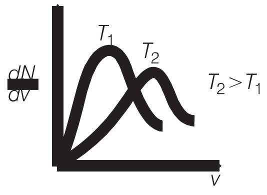
Maxwell's Law or the Distribution of Molecular Speeds

It derives an equation giving the distribution of molecules at different speeds

$$dN = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\left(\frac{mv^2}{2kT}\right)} .dv$$

where, dN is number of molecules with speed between v and $v + dv$.

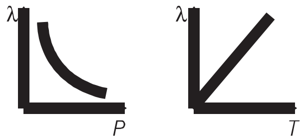
The $\frac{dN}{dv}$ *versus* v curve is shown below



Law of Equipartition of Energy

This law states that, for a dynamic system in thermal equilibrium, the total energy is distributed equally amongst all the degree of freedom and the energy associated with each molecule per degree of freedom is $\frac{1}{2} k_B T$. where, $k_B = 1.38 \times 10^{-23}$ JK^{-1} is Boltzmann constant and T is absolute temperature of system on the kelvin scale.

Mean Free Path



The average distance travelled by a molecule between two successive collisions is called mean free path (λ).

Mean free path is given by $\lambda = \frac{kT}{\sqrt{2}\,\pi\,\sigma^2\, p}$

where, σ = diameter of the molecule, p = pressure of the gas,

T = temperature and k = Botlzmann's constant.

Mean free path, $\lambda \propto T$ and $\lambda \propto \frac{1}{p}$

Brownian Motion

The continuous random motion of the particles of microscopic size suspended in air or any liquid is called Brownian motion.

Brownian motion is observed with many kind of small particles suspended in both liquids and gases.

Brownian motion is due to the unequal bombardment of the suspended particles by the molecules of the surrounding medium.

Critical Temperature, Pressure and Volume

Gases can't be liquified above a temperature called critical temperature (T_C) however large the pressure may be.

The pressure required to liquify the gas at critical temperature is called critical pressure (p_C) and the volume of the gas at critical temperature and pressure is called critical volume (V_C). Value of critical constants in terms of van der Waals' constants a and b are as under

$$V_C = 3b, \quad p_C = \frac{a}{27b^2} \quad \text{and} \quad T_C = \frac{8a}{27Rb}$$

Further, $\frac{RT_C}{p_C V_C} = \frac{8}{3}$ is called critical coefficient and is same for all gases.