Chapter One

KINETIC THEORY OF GASES

1.2 Gas Law for Ideal Gases

Boyle's Law

At constant temperature (T), the pressure (P) of a given mass a gas is inversely proportional to its volume (V)

$$P \propto \frac{1}{V}$$

Charle's Law

At constant pressure (P) the volume of a given mass of a gas is proportional to its temperature (T)

$$V \propto T$$

Avogadro's Law

At the same temperature and pressure, equal volume of all gases contain equal number of molecules (N).

$$N_1 = N_2$$

Graham's Law of Diffusion

When two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion (r) at each gas is inversely proportional to square root at density of gas (ρ)

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Dalton's Law of Partial Pressure: The sum of pressure exerted (P) by each gas occupying the same volume as that of the mixture (P_1, P_2, P_3,....)

$$P = P_1 + P_2 + P_3 + ...$$

Ideal Gas Equation:

Consider a sample of an Ideal gas at pressure P, volume V and temperature T the gas follows the equation

$$PV = nRT$$

Where n is number of molecules and R is proportionality constant known as gas constant

$$R = 8.314 \text{ J/mol/K}$$

Boltzmann constant K is ratio between R to Avogadro number N_A, $k_B = \frac{R}{N_A} = \frac{8.314}{6.03\times 10^{23}}$

$$k_B = 1.3\times 10^{-23} J/K$$

Example: Find the maximum attainable temperature of ideal gas in each process given by $p = p_0 - \alpha V^2$; where p_0, α and β are positive constants, and V is the volume of one mole of gas.

Solution: $$P = P_0 - \alpha V^2 \qquad \text{(i)}$$

Number of mole of gas = 1

We know $PV = nRT \quad \Rightarrow P = \frac{RT}{V}$ put in (i)

$$\frac{RT}{V} = P_0 - \alpha V^2 \quad \Rightarrow T = \frac{P_0 V}{R} - \frac{\alpha V^3}{R} \qquad \text{(ii)}$$

For T maximum, $\frac{dT}{dV} = 0 \quad \Rightarrow \frac{P_0}{R} - \frac{3\alpha V^2}{R} = 0$

$V = \sqrt{\frac{P_0}{3\alpha}}$ put in (ii) one will get $T_{\max} = \frac{2}{3} P_0 \sqrt{\frac{P_0}{3\alpha}}$

Example: Two thermally insulated vessel 1 and 2 are filled with air. They are connected by a short tube with a value. The volume of vessels and the pressure and temperate of air in them are (V_1, P_1, T_1) and (V_2, P_2, T_2) respectively. Calculate the air temperate and pressure established after opening of value if air follow Ideal gas equation.

Solution: For vessel (1) $P_1V_1 = n_1RT_1$ $\qquad n_1 = \frac{P_1V_1}{RT_1}$

For vessel (2) $P_2V_2 = n_2RT_2$ $\qquad n_2 = \frac{P_2V_2}{RT_2}$

After opening the value let pressure volume and temperature is P, V, T

$$PV = nRT$$

$$V = V_1 + V_2$$

$$n = n_1 + n_2 = \frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2}$$

Hence system is isolated then

Energy of (1) + energy of (2) = energy of composite

$$\frac{3}{2}n_1KT_1 + \frac{3}{2}n_2KT_2 = \frac{3}{2}(n_1 + n_2)KT$$

$$n_1T_1 + n_2T_2 = (n_1 + n_2)/T.$$

$$T = \frac{n_1T_1 + n_2T_2}{n_1 + n_2}$$

$$= \frac{\frac{P_1V_1}{RT_1}T_1 + \frac{(P_2V_2)}{RT_2}T_2}{\frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2}} \Rightarrow T = T_1T_2\frac{(P_1V_1 + P_2V_2)}{P_1V_1T_2 + P_2V_2T_1}$$

$$PV = nRT \qquad P = \frac{nRT}{V} \qquad P = \frac{P_1V_1 + P_2V_2}{V_1 + V_2}$$

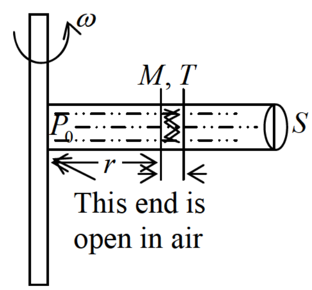
Example: A horizontal cylinder closed from one end is rotated with a constant angular velocity ω about a vertical axis passing through the open end of the cylinder. The outside air pressure is equal to p_0, the temperature to T, and the molar mass of air to M. Find the air pressure as a function of the distance r from the rotation axis. The molar mass is assumed to be independent of r.

Solution: Force equation of dr element.

$$dF = (dm)r\omega^2 \quad \text{if } S \text{ is cross section area then}$$

$$dP = \frac{dF}{S} = \left(\frac{dm}{S}\right)r\omega^2 \qquad dm = \left(\frac{S}{r\omega^2}\right)dP$$

Also we know $P(Sdr) = \left(\frac{dm}{M}\right)RT$



$$PS(dr) = \frac{RT}{M}\left(\frac{S}{r\omega^2}\right)dP$$

$$M\omega^2\int_0^r rdr = RT\int_{P_0}^{P}\frac{dP}{P}$$

$$\frac{M\omega^2 r^2}{2} = RT\ln\frac{P}{P_0}$$

$$P = P_0 e^{\frac{M\omega^2 r^2}{2RT}}$$

Example: Prove that $PA = \frac{1}{2}mN\langle v^2\rangle$ and $\langle E\rangle = \frac{2}{2}k_BT = k_BT$ in two dimension.

Solution: A molecule moving in the x direction will have momentum mv_{ix} normal to face of the cube before collision

$$\Delta P_{ix} = mv_{ix} - (-mv_{ix}) = 2mv_{ix}$$

Force acting on the wall by molecule is $f_{ix} = \frac{n_i 2mv_{ix}}{\Delta t} = \frac{n_i 2mv_{ix}^2}{2L} == \frac{n_i mv_{ix}^2}{L}$

Pressure exert on the wall of container by molecule $P_{ix} = \frac{mn_i v_{ix}^2}{L^3}$

So that pressure in the *x* direction expected by all group

$$P_x = \sum P_{ix} = \frac{m}{L^3}\sum n_i v_{ix}^2$$

Average value of v^2 is given by

$$\langle v_x^2\rangle = \frac{\sum_i n_i v_{ix}^2}{\sum n_i} = \frac{\sum_{i=1} n_i v_{ix}^2}{n}$$

For two dimensional system $\langle v_x^2\rangle + \langle v_y^2\rangle = \langle v^2\rangle$ and $\langle v_x^2\rangle = \langle v_y^2\rangle = \frac{\langle v^2\rangle}{2}$

So P_x can be written as

$$P_x = \frac{m}{L^2} n\langle v_x^2\rangle \text{ , } P = P_x = \frac{1}{2}\frac{m}{L^2} n\langle v^2\rangle \quad P = \frac{1}{2}\frac{mn\langle v^2\rangle}{A}$$

$$PA = \frac{1}{2} mN\langle v^2\rangle$$

1.3 Kinetic Interpretation of Temperature

According to assumption of Kinetic theory of gases, there is only translation motion of the molecule and there is not any potential acting between them, so

Average energy $\langle E\rangle$ of gases are equivalent to Average translation energy of a molecule $\langle E\rangle = \frac{1}{2} m\langle v^2\rangle$

Pressure at P as $P = \frac{1}{3} mn\langle v^2\rangle = \frac{2}{3} n\left(\frac{1}{2} m\langle v^2\rangle\right) = \frac{2}{3} n\langle E\rangle$

$$PV = \frac{2}{3} Vn\langle E\rangle \quad PV = \frac{2}{3} N\langle E\rangle \text{ where } n = \frac{N}{V} \text{ number density}$$

$$\langle E\rangle = \frac{3}{2}\frac{RT}{N_A} \text{ and } \langle E\rangle = \frac{3}{2}\left(\frac{R}{N_A}\right)T$$

$$\langle E\rangle = \frac{3}{2} K_B T \text{ where } k_B \text{ is Boltzman constant}$$

So average kinetic energy is given by

$$\langle E\rangle = \frac{3}{2} k_B T \text{ where T is absolute temperature.}$$

Example: It is possible to treat electromagnetic radiation in container whose wall is mirrors, as a gas of particle (photons) with a constant speed c and whose energy is related to their momentum p which is directed parallel to their velocity by $E = pc$. Show that if container is full of radiation the equation of state is $PV = \frac{1}{3}E$

Solution: Pressure $P = \frac{1}{3} nm\langle v^2\rangle = \frac{1}{3} n\langle mv \cdot v\rangle = \frac{1}{3} n\langle \vec{p}\cdot\vec{v}\rangle$

For Photon $v = c$ and velocity is parallel to momentum, so

$$P = \frac{1}{3} n\langle Pc\rangle \Rightarrow P = \frac{1}{3}\frac{N}{V}\langle pc\rangle$$

$$PV = \frac{1}{3}\langle Npc\rangle \Rightarrow PV = \frac{1}{3}E$$