The Gaseous state

Kinetic Molecular Theory of gases :-

The kinetic molecular theory of gases is based on following postulates:-

1. A gas consists of a large number of minute particles called molecules. The molecules are so small that their actual valuone is negligible as compared to the total volume (space) occupied by them.

2. The molecules are in state of constant rapid motion in all possible directions, colliding in a random manner. with one another and with the walls of vessel.

3. The molecular collisions are perfectly elastic so that there is no net loss of energy when gas molecules collide with one another or against the walls of the vessel. The kinetic energy may be transferred from one molecules to another but it is not converted into any other form of energy such as heat.

4. There are no attractive forces between molecules or between molecules and the walls of the container. The molecules move completely independent of each other.

5. The pressure of gas is due to the bombardment of the molecules in the walls of ~~oth~~ the containing vessel.

6. The laws of classical mechanics are applicable for motion of gaseous state molecules.

Pressure of an ideal gas:-

The postulates of kinetic theory are applicable for the derivation of pressure of a gas.

Let us consider N molecules of a gas, each having mass m, enclosed in a cubical vessel of volume V, each side of cube being l.

The motion of the molecules at any instant is considered to be totally random.

Velocity of one molecule of gas is 'c'.

The volume can be resolved into three components U, V, W along the three axes, x, y, z. Since the volume components are perpendicular to the wall of the container. Therefore

$$\boxed{c^2 = V^2 + U^2 + W^2} \quad \text{--- (1)}$$

Consider the motion of molecule along x-axis to be elastic and the walls remain stationary, on rebounding, only the sign component of velocity changes.

The resulting change of momentum in the x-direction (Δp_x) is given by

$$\boxed{\Delta p_x = m\{U - (-U)\} = 2mu} \quad \text{--- (2)}$$

Immediately after the collision, the molecule takes time equal to l/u to collide with the opposite wall (and time equal to $2l/u$ to strike against the same wall).

Hence the frequency of collision on the two opposite walls is given by u/l and the change in momentum is given by

$$\boxed{\frac{\Delta p_x}{\Delta t} = \frac{2mu}{l} \cdot u = \frac{2mu^2}{l}} \quad \text{——} \ (3)$$

The total change in momentum is given by (single molecule per unit time arising from collisions on all six walls):

$$\frac{\Delta p}{\Delta t} = \frac{2mu^2}{l} + \frac{2mv^2}{l} + \frac{2mw^2}{l}$$

$$= \frac{2m}{l}(u^2 + v^2 + w^2)$$

$$\boxed{\frac{\Delta p}{\Delta t} = \frac{2mc^2}{l}} \ \text{——} \ (4)$$

The total change in momentum of a single molecule per unit time arising from collisions on all the six walls is as given above.

However the total change in momentum per unit time for all the N molecules of container is obtained by summing the contributions of all the molecules. Thus

$$\boxed{\frac{\Delta p_{total}}{\Delta t} = \sum_{i=1}^{N} \frac{2mc_i^2}{l} = \frac{2m}{l} \sum_{i=1}^{N} c_i^2} \ \text{——} \ (5)$$

Defining mean square velocity as:-

$$\boxed{\langle c^2 \rangle = \frac{\sum c_i^2}{N}} \quad \text{——} \ (6)$$

Hence we get

$$\boxed{\frac{\Delta P_{total}}{\Delta t} = \frac{2mN}{l} \langle c^2 \rangle} \quad — (7)$$

According to Newton's second law of motion
force = rate of change of momentum

$$= \frac{\Delta P_{total}}{\Delta t}$$

and pressure is force per unit area.
In this respect surface area of cubical vessel $= 6l^2 = A$ and volume is V.
Hence the pressure exerted by N molecules of gas on the walls of the ~~wall~~ vessel is given as

$$\boxed{P = \frac{f}{A} = \frac{2mN}{6l^3} \langle c^2 \rangle = \frac{1}{3V} mN \langle c^2 \rangle} \quad — (8)$$

Root mean square velocity $= \langle c^2 \rangle^{1/2}$

$$= (\Sigma c_i^2/N)^{1/2}$$

$$= c$$

Therefore

$$\boxed{P = \frac{1}{3V} mNc^2} \quad — (9)$$

The equation can be rearranged as

$$\boxed{PV = \frac{1}{3} mNc^2} \rightarrow (10)$$

The equation is known as Kinetic gas equation.

Derivation of gas laws:-

① Boyle's law:-

Molecular velocities increases with rising temperature. Since KE $\propto c^2$, the ~~the~~ temperature can be defined in terms of KE (Kinetic energy). Thus according to kinetic theory, the absolute temperature T of a gas is proportional to the mean kinetic energy $\frac{1}{2}mc^2$ per molecule.

Thus at constant temperature, $\frac{1}{2}mc^2$ i.e. mean kinetic energy per molecule remains constant

Thus, $$\boxed{PV = \frac{2}{3} \times \frac{1}{2} mNc^2} \quad \text{—— ①}$$

For a definite mass of gas under consideration the number of molecules N of gas, must be constant. Thus PV = constant for a given mass of gas at constant temperature.

For, constant PV at a constant temperature the law is known as Boyle's law.

② Charles law:-

For a constant N, or definite quantity of gas at constant pressure

$$PV = \frac{2}{3} \times \frac{1}{2} mNc^2$$

$$V \propto \frac{1}{2} mc^2$$

where $\frac{1}{2}mc^2$ is kinetic energy of the molecule

Hence $V \propto T$ (at constant pressure) as T is related to kinetic energy as $K.E \propto T$

Therefore $V \propto (T)$ at constant P is the charles law.

(3) Avogadro's law:-

For two different gases

$$P_1V_1 = \frac{2}{3} \times \frac{1}{2} m_1 c_1^2 N_1 \quad \text{---} (1)$$

and

$$P_2V_2 = \frac{2}{3} \times \frac{1}{2} m_2 c_2^2 N_2 \quad \text{---} (2)$$

If the $P_1 = P_2$ and $V_1 = V_2$ then

$$\frac{1}{2} m_1 c_1^2 N_1 = \frac{1}{2} m_2 c_2^2 N_2 \quad \text{---} (3)$$

For ~~constant~~ same temperature

$$\frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2$$

Hence $N_1 = N_2$

Thus Avogadro's law states that equal volume of gases at similar temperature and pressure contains equal number of molecules.

From Avogadro's law it is shown that molar volume i.e. volume occupied by one mole of each substance in gaseous state (which is numerically equal to 22.414 dm^3 at N.T.P) would contains same number of molecules. This number is called <u>Avogadro's number</u> = 6.022×10^{23} mol^{-1}

Ideal gas equation:

Combining the three gas laws:-
① Boyle's law
② Charle's law
③ Avogadro's law as

For constant n, $V \propto \frac{1}{P}$ (at constant n, T) Boyle's law

$V \propto T$ (at constant P, n) Charle's law

$V \propto n$ (at constant P and T) Avogadro's law.

i.e. V is proportional to the product of these three terms

$$V \propto \frac{nT}{P} = \frac{RnT}{P}$$

or $\boxed{PV = nRT}$

This equation is termed as ideal gas equation and R is defined as proportionality constant, gas constant.

At N.T.P, volume occupied by ideal gas = 22.414 dm^3

$$R = \frac{PV}{nT} = \frac{(1\ atm)(22.414)dm^3}{(1\ mol)(273.15)K}$$

$$= 0.08202\ dm^3\ atm\ K^{-1}\ mol^{-1}$$

In SI units $1\ atm = 1.01325 \times 10^5\ N\ m^{-2}$

Hence $\boxed{R = 8.314\ J\ K^{-1}\ mol^{-1}}$

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