GASEOUS STATE

PART- I

Brotati Chakraborty
Department of Chemistry
Bejoy Narayan Mahavidyalaya, Itachuna, Hooghly

Sem I Honours (CC – 2)

- Three states of matter, viz., solid, liquid and gas
- Difference between the three states of matter
- A system is in a definite state when its mass, P, V and T have definite values.
- The relationship which connects the above four variables is known as equation of state of the system.

POSTULATES OF KINETIC THEORY

1. A gas consists of a large number of very small spherical particles which may be identified with the molecules. The molecules of a given gas are completely identical in size, shape and mass, but these differ from gas to gas.

2. The volume occupied by the molecules is negligible in comparison to the total volume of the gas.

3. The molecules are in rapid motion which is completely random. During their motion, they collide with one another and with the sides of the vessel. The normal pressure of the gas is due to the collision of molecules with the sides of the vessel.

4. The molecular collisions are perfectly elastic, i.e. there occurs no loss of energy when they collide with one another and with the sides of the vessel.

5. The laws of classical mechanics, in particular Newton’s second law of motion, are applicable to the molecules in motion.

6. There is no force of attraction or repulsion, amongst the molecules, i.e., they are moving independent of one another.

7. At any instant, a given molecule can have energy ranging from a small value to a very large value, but the average K.E. remains constant for a given temperature i.e. the average K.E. is proportional to the absolute temperature of the gas.

DERIVATION OF KINETIC GAS EQUATION

- Let us consider a volume of gas present in a cubical box of edge length ***l***.

- No. of gas molecules = ***N***
- Mass of each gas molecule = ***m***

- Molecules are moving in all directions, with speed covering a range of values.

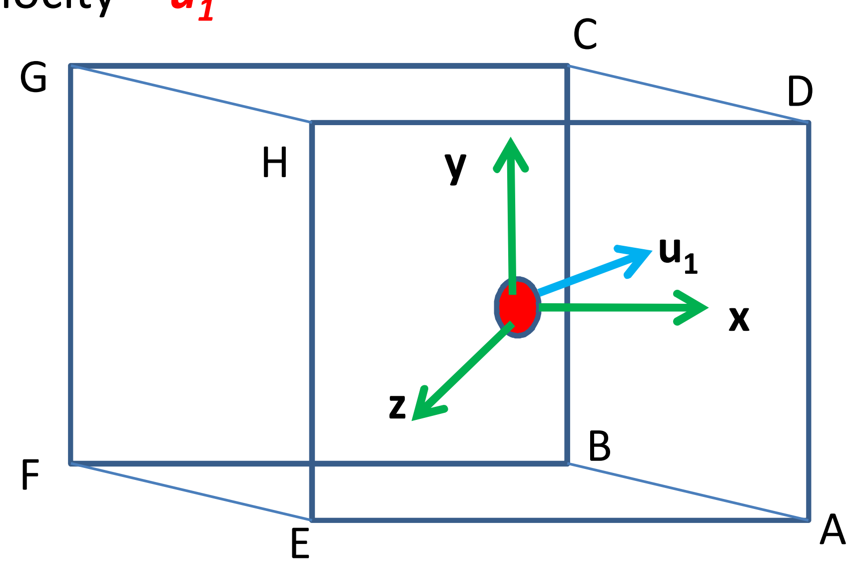
- Suppose for a particular molecule, velocity = u_1
- Its velocity along x-axis = u_x

  y-axis = u_y

  z-axis = u_z

  They are related as,

$$u_1^2 = u_x^2 + u_y^2 + u_z^2$$

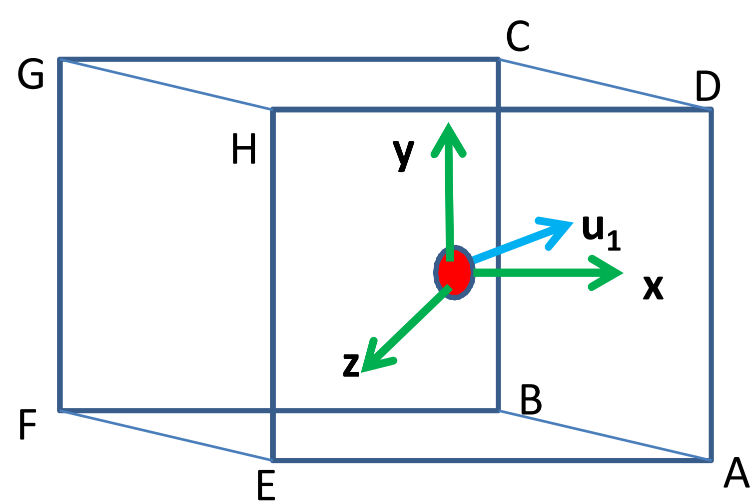


- Momentum of the molecule when it strikes the wall ABCD = mu_x
- Momentum of the molecules when it rebounds from wall ABCD = - mu_x
- Change in momentum of the molecule in a single collision with wall ABCD = $|2\ mu_x|$

- Total number of collisions the molecules makes on two opposite walls i.e. ABCD and EFGH ($\perp$ to x-axis) per second = $\frac{u_x}{l}$

- Total change in momentum per second due to such collisions with two opposite walls $\perp$ to x-axis = $2mu_x \frac{u_x}{l}$

$$= 2m\frac{u_x^2}{l}$$

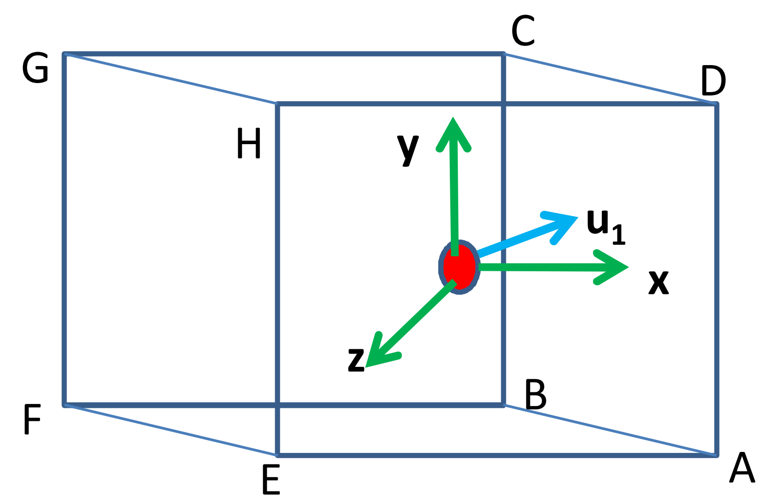


- Similarly, rate of change of momentum accompanying the impact of a single molecule with walls ⊥ to y-axis = $2m\frac{u_y^2}{l}$

- Similarly, rate of change of momentum accompanying the impact of a single molecule with walls ⊥ to z-axis = $2m\frac{u_z^2}{l}$

- Thus, total rate of change of momentum for impact of a single molecule with all the six walls of the cube = $\frac{2m}{l}\left(u_x^2 + u_y^2 + u_z^2\right)$

$$= \frac{2mu_1^2}{l}$$



- Now, according to Newton's second law of motion,

$$Force = mass \times acceleration$$
$$= mass \times \frac{d}{dt}(velocity)$$
$$= \frac{d}{dt}(mass \times velocity)$$
$$= rate\ of\ change\ of\ momentum$$

- Thus, total force exerted by a single molecule on the six walls of the cubic vessel = $\frac{2mu_1^2}{l}$

- Thus, total force exerted by *N* molecules on the six walls of the cubic vessel = $\frac{2m}{l}(u_1^2 + u_2^2 + ...u_N^2) \quad = \frac{2m}{l}N\overline{u^2}$

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + ... + u_N^2}{N}$$

mean square velocity

$$P = \frac{Force}{Area}$$

$$= \frac{2m}{l} N\overline{u^2} \times \frac{1}{6l^2}$$

$$= \frac{1}{3} \frac{mN\overline{u^2}}{l^3}$$

$$= \frac{1}{3} \frac{mN\overline{u^2}}{V}$$

$$\boxed{PV = \frac{1}{3} mN\overline{u^2}}$$

Kinetic gas equation

SOME DERIVATIONS FROM KINETIC EQUATION

According to kinetic gas theory, average energy of a molecule is proportional to the absolute temperature of a gas.

$$\therefore \frac{1}{2}m\overline{u^2} \propto T$$

$$\Rightarrow \frac{1}{2}m\overline{u^2} = KT$$

K is proportionality constant

Now,

$$PV = \frac{1}{3}mN\overline{u^2}$$

$$PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{u^2}\right) = \frac{2}{3}NKT$$

Proof of Boyle's law

- At constant temperature the volume of a given mass of gas is inversely proportional to its pressure.

- Thus, [i] T should remain constant

  [ii] Mass of gas is fixed $\Rightarrow$ N is constant

$$PV = \frac{2}{3} NKT = const \quad \Rightarrow \quad PV = const$$

$$\Rightarrow \quad \boxed{P \propto \frac{1}{V}}$$

const

const

Proof of Charles' law

- At constant pressure, the volume of a given mass of gas is directly proportional to its absolute temperature.

- Thus, [i] P should remain constant

  [ii] Mass of gas is fixed $\Rightarrow$ N is constant

const

$$PV = \frac{2}{3} NKT \qquad \Rightarrow \qquad V = \frac{2}{3} \frac{NK}{P} T$$

$$\Rightarrow \quad \boxed{V \propto T}$$

Proof of Avogadro's law

- Under similar conditions of pressure and temperature, equal volumes of all gases contains equal number of molecules.

- Let us consider two gases,

$$P_1V_1 = \frac{2}{3}N_1KT_1 \quad \text{and} \quad P_2V_2 = \frac{2}{3}N_2KT_2$$

As, $P_1 = P_2$ and $T_1 = T_2$, $\quad \therefore \dfrac{P_1V_1}{P_2V_2} = \dfrac{N_1KT_1}{N_2KT_2} \quad \Rightarrow \dfrac{V_1}{V_2} = \dfrac{N_1}{N_2}$

$$\boxed{\text{If, } V_1 = V_2 \text{ then, } N_1 = N_2}$$

Proof of Graham's law of diffusion

- At a given temperature and pressure, the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its density or molar mass.

- Now, rate of diffusion can be assumed to be directly proportional to the square root of mean square speed.

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{\overline{u_1^2}}{\overline{u_2^2}}}$$

- Now, $PV = \frac{1}{3} mN\overline{u^2} \qquad \Rightarrow \overline{u^2} = \frac{3PV}{mN}$

- For 1 mole of a gas, $PV = RT$ and $N = N_A$, $\therefore \quad \overline{u^2} = \frac{3RT}{M} \qquad M \rightarrow$ *molar mass*

- Thus, $\boxed{\frac{r_1}{r_2} = \sqrt{\frac{\overline{u_1^2}}{\overline{u_2^2}}} = \sqrt{\frac{M_2}{M_1}}}$

Average Kinetic Energy

$$\overline{KE} = \frac{1}{2}m\overline{u^2} = \frac{3}{2}\frac{PV}{N}$$

- For 1 mole of a gas, $PV = RT$ and $N = N_A$

$$\therefore \overline{KE} = \frac{3}{2}\frac{RT}{N_A} = \frac{3}{2}kT \qquad k \rightarrow \text{Boltzman constant}$$

- Total KE for 1 mole of a gas $= N_A\ \overline{KE}$

$$= N_A \cdot \frac{3}{2}kT$$

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

- $k = \dfrac{R}{N_A} = \dfrac{8.314 JK^{-1}mol^{-1}}{6.023\times 10^{23} mol^{-1}} = 1.38\times 10^{-23} JK^{-1}$