Graham's law of diffusion and effusion.

(1) **Diffusion** is the process of spontaneous spreading and intermixing of gases to form homogenous mixture irrespective of force of gravity. While **Effusion** is the escape of gas molecules through a tiny hole such as pinhole in a balloon.

- All gases spontaneously diffuse into one another when they are brought into contact.
- Diffusion into a vacuum will take place much more rapidly than diffusion into another place.
- Both the rate of diffusion of a gas and its rate of effusion depend on its molar mass. Lighter gases diffuses faster than heavier gases. The gas with highest rate of diffusion is hydrogen.

(2) According to this law, "At constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its vapor density."

Thus, rate of diffusion $(r) \propto \frac{1}{\sqrt{d}}$ (T and P constant)

For two or more gases at constant pressure and temperature,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Note: Always remember that vapor density is different from absolute density. The farmer is independent of temperature and has no unit while the latter depends upon temperature and expressed in gm^{-1}.

(3) Graham's law can be modified in a number of ways as,

(i) Since, 2 ×vapor density (V.D.) = Molecular weight

Then, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{d_2 \times 2}{d_1 \times 2}} = \sqrt{\frac{M_2}{M_1}}$

Where, M_1 and M_2 are the molecular weights of the two gases.

(ii) Since, rate of diffusion $(r) = \frac{\text{Volume of a gas diffused}}{\text{Time taken for diffusion}}$

Then, $\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{d_2}{d_1}}$

(a) When equal volume of the two gases diffuse, i.e. $V_1 = V_2$

Then, $\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}}$

(b) When volumes of the two gases diffuse in the same time , i.e. $t_1 = t_2$

Then, $\frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}}$

(iii) Since, $r \propto p$ (when p is not constant)

Then, $\frac{r_1}{r_2} = \frac{P_1}{P_2} = \sqrt{\frac{M_2}{M_1}} \quad \left(\because r \propto \frac{1}{\sqrt{M}} \right)$

Note: It should be noted that this law is true only for gases diffusing under low pressure gradient.

$CO_2 > SO_2 > SO_3 > PCl_3$ is order of rates of diffusion.

(4) Rate of diffusion and effusion can be determined as,

(i) Rate of diffusion is equal to distance travelled by gas per unit time through a tube of uniform cross-section.

(ii) Number of moles effusing per unit time is also called rate of diffusion.

(iii) Decrease in pressure of a cylinder per unit time is called rate of effusion of gas.

(iv) The volume of gas effused through a given surface per unit time is also called rate of effusion.

(5) **Applications:**Graham's law has been used as follows:

(i) To determine vapor densities and molecular weights of gases.

(ii) To prepare Ausell's marsh gas indicator, used in mines.

(iii) **Autolysis:**The process of separation of two gases on the basis of their different rates of diffusion due to difference in their densities is called atmolysis. It has been applied with success for the separation of isotopes and other gaseous mixtures. Example, this process was used for the large-scale separation of gaseous $^{235}UF_6$ and $^{238}UF_6$ during the second world war.