GRAHAM'S LAW OF DIFFUSION AND EFFUSION

Diffusion

The phenomenon of gases intermixing through the random movement of molecules is referred to as diffusion.

Effusion

When a gas is contained in a vessel at a higher pressure than the surrounding atmosphere, it will escape through a small opening in the container until the pressures inside and outside are balanced. This process is known as effusion.

The distinction between diffusion and effusion lies in the fact that, in diffusion, the gas spontaneously permeates through a porous barrier, while in effusion, the gas is expelled through a small orifice or hole by applying external pressure.

Graham's law of diffusion asserts that "under identical conditions of temperature and pressure, the rates of diffusion for different gases are inversely proportional to the square roots of their molecular masses or densities."

$$\text{Mathematically, } r \propto \sqrt{\frac{1}{M}} \text{ or } \sqrt{\frac{1}{d}} \text{ or. } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

Where, r_1 and r_2 are the rates of diffusion of gases 1 and 2.

M_1 and M_2 are their molecular masses.

d_1 and d_2 are their densities.

Effect of Volume on Rate of Diffusion

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

or

$$r = \frac{V}{t}$$

Let V_1 be the volume of gas 1 and V_2 be the volume of gas 2, then

$$r_1 = \frac{V_1}{t_1} \qquad r_2 = \frac{V_2}{t_2}$$

$$\therefore \qquad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \frac{V_1 t_2}{V_2 t_1}$$

(i) Comparison of Times Taken for the Same Volume of Two Gases

Let the times of diffusion for the same volume of two gases be t_1 and t_2 respectively. Then,

$$\frac{r_1}{r_2} = \frac{V/t_1}{V/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \text{ or } \frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(ii) Comparison of the Volumes of the Gases that Diffuse in Same Time

Let V_1 and V_2 be the volume of two gases that diffuse in same time t. Then,

$$\frac{r_1}{r_2} = \frac{v_1/t}{v_2/t} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \text{ or } \frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(iii) Effect of Pressure on Rate of Diffusion

Rate of diffusion is proportional to the pressure of the gas in the container.

$$r \propto P\text{ ; again, } r \propto \frac{1}{\sqrt{M}}$$

$$\text{or} \quad r \propto \frac{P}{\sqrt{M}} \quad \text{or} \quad \frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

Application of Graham's Law of Diffusion in Enrichment of Isotopes

Enrichment of Light Component

When a mixture of a heavier gas, denoted as B, and a lighter gas, denoted as A, is in contact with a porous barrier, the gas that passes through will have an increased concentration of the lighter component by a factor of $\sqrt{\frac{M_B}{M_A}}$, known as the enrichment factor. This is due to the more rapid effusion of lighter molecules compared to heavier ones. The remaining gas on the other side of the barrier will be enriched in the heavier component. Each passage through a porous barrier result in an enrichment factor equal to $\sqrt{\frac{M_B}{M_A}}$, and as a result, numerous successive barriers are necessary to achieve a significant enrichment of the heavier component.

Thus, enrichment factor for first barrier or operation $f_1 = \sqrt{\frac{M_B}{M_A}}$

$\therefore$ overall separation or enrichment factor $f = \frac{n'_A/n'_B}{n_A/n_B}$

In the context where n_A, n_B, n_A, and n'_B represent the concentrations of two isotopically distinct components before and after processing, if the desired enrichment of gas A is achieved in the x-operation, then...

$$(f_1)^x = \frac{n'_A/n'_B}{n_A/n_B} = f$$

or $$x \log f_1 = \log\left[\frac{n'_A/n'_B}{n_A/n_B}\right]$$

or $$x \log\left[\frac{M_B}{M_A}\right]^{1/2} = \log\left[\frac{n'_A/n'_B}{n_A/n_B}\right]$$

or $$\frac{x}{2}\log\left[\frac{M_B}{M_A}\right] = \log\left[\frac{n'_A/n'_B}{n_A/n_B}\right]$$

or $$x = \frac{2\log\left(\frac{n'_A/n'_B}{n_A/n_B}\right)}{\log\left(\frac{M_B}{M_A}\right)}$$