D. B. College (Jaynagar) Lect - 26
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Ex. 4 For the reaction, A + ⟶ C, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is 1 10^{-4} mol litre^{-1} minute^{-1}. In second experiment when the initial concentrations of (A) and (B) are 0.1 M and trations of both A and B are 0.3 M, the initial rate is 3.0 10^{-4} mol litre minute^{-1}. In the third experiment when the initial concentrations of both A and B are 0.3 M, the initial rate is 2.7 10^{-3} mol litre^{-1} minute^{-1}.

(a) Write rate law for this reactions

(b) Calculate the value of specific rate constant for this reactions.

Soln. Let, Rate $= K[A]^x [B]^y$

$r_1 = 1 \quad 10^{-4} = K(0.1)^x (0.1)^y$ --- (1)

$r_2 = 3 \; 10^{-4} = K(0.1)^x (0.3)^y$ ---- (2)

$r_3 = 2.7 \; 10^{-3} = k(0.3)^x (0.3)^y$ ---- (3)

By Eqs. (1 and 2) $\frac{r_1}{r_2} = \frac{1 \times 10^{-4}}{3 \times 10^{-4}} = \left(\frac{1}{3}\right)^y \therefore y = 1$

By Eqs. (2) and (3),

$\frac{r_2}{r_3} = \frac{3 \times 10^{-4}}{27 \times 10^{-4}} = \left(\frac{1}{3}\right) \therefore x = 2$

$\therefore$ Rate $= k[A]^2 [B]^1$

Also, $1 = 10^{-4} = k(0.1)^2 (0.1)^1$

$\therefore k = 10^{-1} = 0.1 \; L^2 \, mol^{-1} \, min^{-1}$

Ex. 5 The chemical reaction, $2O_3 \rightarrow 3O_2$ proceeds as follows:

$O_3 \rightleftharpoons O_2 + O$ -- (Fast)

$O + O_3 \rightarrow 2O_2$ -- (Slow)

The rate law expression should be

[A] $r = K[O_3]^2$ [B] $r = k[O_3]^2 [O_2]^{-1}$ [C] $r = k[O_3][O_2]$

[D] Unpredictable

Sol^n Rate of reaction $(r) = K[O][O_3]$

The rate of formation of $[O]$ depends on first step

$\therefore$ Since $K_{eq} = \frac{[O_2][O]}{[O_3]}$

$\therefore$ $[O] = K_{eq} \frac{[O_3]}{[O_2]}$

Or

$$r = k K_{eq} \frac{[O_3][O_3]}{[O_2]} = k \cdot [O_3]^2 [O_2]^{-1}$$

Ex. 6 Disintegration of radium takes place at an average rate of 1.42 10^{13} α-Particles per minute. Each α-Particle takes up 2 electrons from the air and becomes a neutral helium atom. After 420 days, the He gas Collected was 0.5 10^{-3} L measured at 300K and 750 mm of mercury Pressure, from the above data, Calculate Avogadro's number.

Soln No. of α-Particles (or) He formed = 1.42 10^{13} min^{-1}

$\therefore$ No of He particles formed in 420 days =

1.42 10^{13} 420 1440 = 8.588 10^{18}

Also at 27 C and 750 mm ; He = 0.5 mL

~~Using at 27 C and 750 mm ; He = 0.5 mL~~

using PV = nRT

$$\frac{750}{760} \cdot \frac{0.5}{1000} = n \quad 0.0821 \quad 300 \Rightarrow n = 2.0\ 10^{-5} \text{ moles}$$

2.0 10^{-5} moles of He = 8.588 10^{18} particles of He

$\Rightarrow$ 1 mole of He $= \frac{8.588 \times 10^{18}}{2.0 \times 10^{-5}}$ $\Rightarrow$ 4.294 10^{22} particles

$\therefore$ Avogadro's number = 4.294 10^{22} particles/mol