D.B. College (Jaynagar) Lect-29
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Ex.16 Calculate the order of reaction for which rate becomes half if volume of container having same amount of reactant is doubled (Assume gaseous phase reaction)

Soln.

$$Rate = k[a]^n$$

For case I: ~~let~~ a mole of reactant in vessel of V litre

$$\therefore \quad r_1 = k\left[\frac{a}{V}\right]^n \text{ ——— (1)}$$

For case II: ~~let~~ The volume is doubled, rate becomes half

$$\therefore \quad \frac{r_1}{2} = k\left[\frac{a}{2V}\right]^n \text{ ——— (2)}$$

$\therefore$ By Eqs. (1) and (2),

or $\quad 2 = (2)^n$

$\therefore \quad n = 1$

Ex.17 Rate constant of a first order reaction $A \longrightarrow B$, is $0.0693\ min^{-1}$. Calculate rate (i) at start and (ii) after 20 minutes. Initial Concentration of A is 1.0 M.

Sol^n $K_1 = 0.0693\ min^{-1}$

$$t_{\frac{1}{2}} = \frac{0.693}{K_1} = \frac{0.693}{0.0693} = 10\ min.$$

Since $C = C_0\left(\frac{1}{2}\right)^n \quad \left(n = \frac{t}{t_{1/2}}\right)$

$n = \frac{20}{10} = 2 \qquad C_0 = 1M$

$\therefore C = 1\left(\frac{1}{2}\right)^2 = \frac{1}{4}M$

Rate of the reaction at the start of reaction $= K_1\ C_0$

$= 10\ \ 0.0693\ 1 = 0.893\ M\ min^{-1}$

Rate after 30 min. $= K_1 C = 0.0693\ \frac{1}{4} = 17.33$

Ex. 18 Two reactants A and B separately $10^{-3} M\ min^{-1}$ Chemical reactions. Both reactions show two with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half-lives, Compare their at the start of reactions.

Sol^n. For A: rate $= K_A[A]$ ——— (i)

$t_{\frac{1}{2}(A)} = \frac{0.693}{K_A}$ ——— (ii)

for B : rate $= K_B[B]^2$ ——— (iii)

$$t_{1/2(B)} = \frac{1}{k_B \times a} \quad \text{———— (IV)}$$

Initial rate of A $\quad r_A = k_A\ a$

Initial rate of B $\quad r_B = k_B\ a^2$

$$\therefore \frac{r_A}{r_B} = \frac{k_A \times a}{k_B \times a^2} = \frac{k_A}{k_B \times a} \quad \text{———— (V)}$$

If $t_{1/2(A)} = t_{1/2(B)}$, then $\frac{0.693}{k_A} = \frac{1}{k_B \times a}$

$$\therefore \frac{k_A}{k_B} = 0.693\ a$$

$$\therefore \frac{r_A}{r_B} = \frac{0.693 \times a}{a} = 0.693$$