Chemical Kinetics

Chemical Kinetics is the branch of chem which deals with the study of speed or the rates of chemical reaⁿ.

Rate of reaction:- The rate of reaⁿ means the speed with which the reaⁿ takesplace. This is expressed either in terms of decrease in concⁿ of reactant per unit time or increase in concⁿ of product per unit time. Hence the rate of reaⁿ may be defined as the rate of reaⁿ is the change in the concⁿ of any one of the reactants or products per unit time.

i.e Rate of reaⁿ = $\frac{\text{Decrease in conc}^n \text{ of reactants}}{\text{Time interval}}$

or Rate of reaⁿ = $\frac{\text{Increase in conc}^n \text{ of product}}{\text{Time interval}}$

In general reaⁿ $A + B \longrightarrow C + D$

Rate of reaⁿ = $-\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$

It should be remembered that rate of reaⁿ is always positive. The minus sign in front of reactant term only indicates that, its concⁿ is decreasing with the progress of reaⁿ while plus sign in front of product term indicates that its concⁿ is increasing

with the progress of reaⁿ.

Unit of rate of reaⁿ :- The unit of rate of reaⁿ is mol/lit/sec or mol $L^{-1}s^{-1}$ or mol $L^{-1}min^{-1}$

Rate constant :- Rate const may be defined as the rate of reaⁿ when the concⁿ of each reactant is taken as unity.

Rate of reaⁿ = K[R]

If we assume that concⁿ are equal to unity

∴ Rate of reaⁿ = K

Order of reaⁿ :- The sum of concⁿ terms on which the rate of reaⁿ actually depends as observed experimentally is called order of reaⁿ.

Rate = $K[A]^{\alpha}[B]^{\beta}$ then order = $\alpha+\beta$

Thus order of reaⁿ may also be defined as the sum of powers to which the concⁿ terms in the rate law eqⁿ are raised.

Third order reaⁿ with equal concⁿ of all reactants :-

Third and higher order reaⁿ are rare because probability of collision betⁿ three or more mole

Defn:- In a third order reaction, the rate of reaction is proportional to the concn of three reactants or When the rate of reaction is directly proportional to product of concn raised to powers unity of three diff reactants or to the cube of concn of one of the reactants, the reaction is said to be of third order.

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with sufficient energy is very small in comparison with bimolecular collisions.

eg: $A + B + C \longrightarrow$ product

consider all that all the reactants are at the same initial concn 'a' the third order rate law can be written as

$$\frac{dx}{dt} \propto [A][B][C]$$

$$\frac{dx}{dt} \propto (a-x)(a-x)(a-x)$$

$$\frac{dx}{dt} \propto (a-x)^3$$

$$\frac{dx}{dt} = k_3 (a-x)^3$$

$$\frac{dx}{(a-x)^3} = k_3 dt$$

Taking integration

$$\frac{1}{2(a-x)^2} = k_3 t + C \quad \text{---} (1)$$

where C is integration constant

Applying initial condition i.e when $t = 0$, $x =$

$$\therefore \frac{1}{2(a)^2} = k_3 (0) + C$$

$$C = \frac{1}{2a^2} \quad \text{---} (2)$$

Putting eqn (2) in (1)

$$\frac{1}{2(a-x)^2} = k_3 t + \frac{1}{2a^2}$$

$$\frac{1}{2(a-x)^2} - \frac{1}{2a^2} = k_3 t$$

$$\frac{1}{2}\left(\frac{1}{a-x^2} - \frac{1}{a2}\right) = k_3 t$$

$$k_3 = \frac{1}{2t}\left(\frac{1}{a-x^2} - \frac{1}{a^2}\right)$$

$$k_3 = \frac{1}{2t}\left[\frac{a^2 - (a-x)^2}{a^2(a-x)^2}\right]$$

$$= \frac{1}{2t}\left[\frac{a^2 - (a^2 - 2ax + x^2)}{a^2(a^2 - 2ax + x^2)}\right]$$

$$= \frac{1}{2t}\left[\frac{a^2 - a^2 + 2ax - x^2}{a2(a-x)2}\right]$$

$$= \frac{1}{2t}\frac{x(2a-x)}{a^2(a-x)^2} = \frac{1}{2ta^2}\left[\frac{x(2a-x)}{(a-x)^2}\right]$$

eg: ① $2NO + H_2 \rightarrow N_2O + H_2O$

② $2NO + Cl_2 \rightarrow 2NOCl$

③ $2NO + Br_2 \rightarrow 2NOBr$

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Characteristics:

① The unit of third order reaⁿ is expressed as

$$\frac{1}{\text{sec.}(\text{mol/lit})^2} \left[\frac{\text{mole/lit}\ (\text{mole/lit})}{(\text{mole/lit})^2}\right]$$

$$= \frac{1}{\text{sec}\ (\text{mol/lit})^2} = \frac{1}{\text{sec}\ \frac{\text{mol}^2}{\text{lit}^2}}$$

$$= \text{sec}^{-1}\ \text{Lit}^{+2}\ .\ \text{mol}^{-2}$$

② The half life period for a third order reaⁿ is given as

$$t_{1/2} = \frac{1}{2ka^2}\left[\frac{x(2a-x)}{(a-x)^2}\right]$$

at half life period, $t = t_{1/2}$ & $x = a/2$

$$\therefore t_{1/2} = \frac{1}{2ka^2}\left(\frac{a/2\ (2a - a/2)}{(a - a/2)^2}\right)$$

$$= \frac{1}{2ka^2}\left(\frac{a/2\ \left(\frac{4a-a}{2}\right)}{\left(\frac{2a-a}{2}\right)^2}\right)$$

$$= \frac{1}{2ka^2}\left(\frac{a/2\ .\ \frac{3a}{2}}{\left(\frac{a}{2}\right)^2}\right)$$

$$= \frac{1}{2ka^2}\left(\frac{3\ (a/2)^2}{(a/2)^2}\right) = \frac{3}{2ka^2}$$

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$t_{1/2} \propto \frac{1}{a^2}$

Thus for third order reaⁿ $t_{1/2}$ is inversely proportional to a^2. initial conⁿ of reactant 'a' i.e a^2. square of

Kinetics of photochemical reqns.

Photochemical reqns are those which occurs by absorption of light. The light radiations of visible & ultraviolet regions lying betn 800 nm & 200 nm wave lengths bring such reqns.

1. Hydrogen chlorine reqn :-

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{k} 2HCl_{(g)}$$

Mech :

(1) $Cl_2 + h\nu \xrightarrow{k_1} 2Cl$

(2) $Cl + H_2 \xrightarrow{k_2} HCl + H$

③ $H + Cl_2 \xrightarrow{K_3} HCl + Cl$

④ Cl (at the walls) $\xrightarrow{K_4} \frac{1}{2} Cl_2$

Applying steady state eqn

$$\therefore \frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2] \quad \text{— ①}$$

$$\frac{d[Cl]}{dt} = k_1 I_a - k_2[Cl][H_2] + k_3[H][Cl_2] - k_4[Cl] = 0 \quad \text{— ②}$$

where I_a is the intensity of absorbed light

$$\frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2] = 0 \quad \text{— ③}$$

Adding eqn ② & ③

$$k_1 I_a - k_2[Cl][H_2] + k_3[H][Cl_2] - k_4[Cl] + k_2[Cl][H_2] - k_3[H][Cl_2] = 0$$

$$k_1 I_a - k_4[Cl] = 0$$

$$[Cl] = \frac{k_1 I_a}{k_4} \quad \text{— ④}$$

Putting eqn ④ in ③

$$k_2 \frac{k_1 I_a}{k_4}[H_2] - k_3[H][Cl_2] = 0$$

$$[H] = \frac{k_1 k_2 I_a [H_2]}{k_3 k_4 [Cl_2]} \quad \text{— ⑤}$$

putting eqns ④ & ⑤ in eqn ①

$$= \frac{k_2 k_1 I_a [H_2]}{k_4} + \frac{k_3 k_1 k_2 I_a [H_2] [Cl_2]}{k_3 k_4 [Cl_2]}$$

$$= \frac{k_1 k_2 I_a [H_2]}{k_4} + \frac{k_1 k_2 I_a [H_2]}{k_4}$$

$$= \frac{2 k_1 k_2 I_a [H_2]}{2 k_4}$$

$$= 2 \frac{k_1 k_2 I_a [H_2]}{k_4}$$

$$= K I_a [H_2]$$

where $K = \frac{2 k_1 k_2}{k_4}$

From above eqn rate is directly proportional to the intensity I_a of the absorbed radiation.