

Chemical Kinetics

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

Rate of reaction:- The rate of reaction means the speed with which the reaction takes place. 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 reaction may be defined as the rate of reaction is the change in the concⁿ of any one of the reactants or products per unit time.

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

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

In general reaction $A + B \rightarrow C + D$

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

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

with the progress of reaction.

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

Rate constant :- Rate constant may be defined as the rate of reaction when the concentration of each reactant is taken as unity.

$$\text{Rate of reaction} = k[R]$$

If we assume that concentrations are equal to unity

$$\therefore \text{Rate of reaction} = k$$

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

$\text{Rate} = k[A]^{\alpha}[B]^{\beta}$ then $\text{order} = \alpha + \beta$
Thus order of reaction may also be defined as the sum of powers to which the concentration terms in the rate law equation are raised.

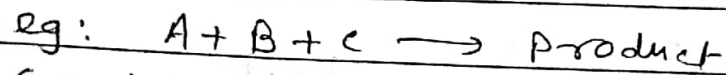
Third order reaction with equal concentration of all reactants :-

Third and higher order reactions are rare because probability of collision between three or more molecules

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

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concn raised to power three of three diff reactants or to the cube of one of the reactants, with sufficient energy is very small in comparison with bimolecular collisions.



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

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

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

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

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

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

order. 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 $t=0$, $x=0$

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

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

Putting eqn (2) in (1)

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

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

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

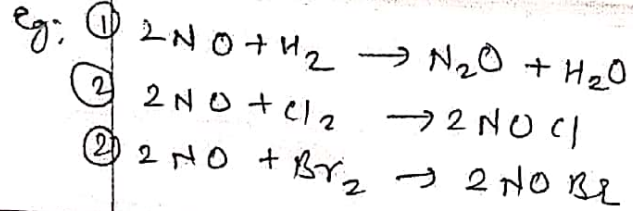
$$k_3 = \frac{1}{2t} \left(\frac{1}{a-x^2} - \frac{1}{a^2} \right)$$

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

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

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

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



Characteristics:

① The unit of third order reaction is expressed as

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

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

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

② The half life period for third order reaction is given as

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

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

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

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

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

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

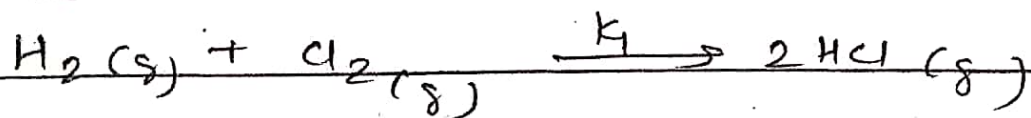
$$t_{1/2} \propto \frac{1}{a^2}$$

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

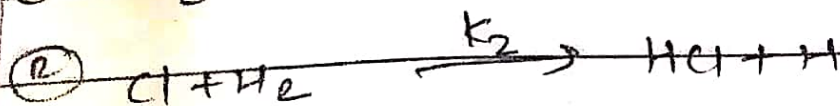
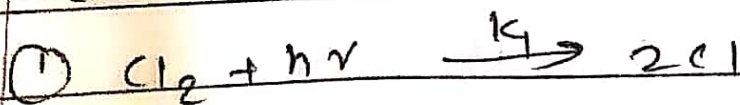
Kinetics of photochemical reactions.

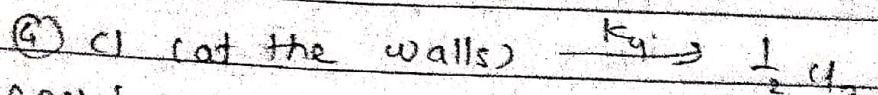
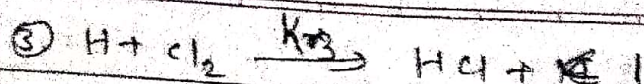
Photochemical reactions are those which occurs by absorption of light. The light radiations of visible & ultraviolet regions lying between 800 nm & 200 nm wave lengths bring such reactions.

1. Hydrogen chlorine reaction -



Mech:





Applying steady state eqn

$$\therefore \frac{d[Cl]}{dt} = k_2 [Cl] [H_2] + k_3 [H] [Cl_2] - ①$$

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

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

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

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

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

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

$$= K I_a [H_2]$$

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.