CHEMICAL KINETICS

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The branch of physical chemistry which deals with the rates of chemical reaction, the mechanism by which the chemical reactions take place and the effects of various factors (such as concentration, temperature, pressure, catalyst etc) on reaction rates is called chemical kinetics.

Types of Chemical reactions (On the basis of their rates)

1. Very fast or instantaneous reactions: These reactions occur at a very fast rate. Generally these reactions involve ionic species and known as ionic reaction.

   e.g. $AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3$

2. Moderate reaction : These reactions proceed with a measurable rates at normal temperature and it is these reactions that are studied in chemical kinetics. Mostly these reactions are molecular in nature. e.g. (a) Hydrolysis of ester (b) Decomposition of N_2O_5

3. Very slow reactions: These reactions are extremely slow.

   e.g. Rusting of iron : $Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3 . xH_2O}$

Rate of a reaction : It is defined as the change in concentration of reactant or product per unit time.

$$\frac{\Delta x}{\Delta t} \text{ or } \frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1}\right)$$

$\Rightarrow$ The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate and

$$\text{Instantaneous rate} = (\text{Average rate})_{\Delta t \to 0}$$

$$\Rightarrow A + B \to C + D,\ r = \frac{-d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$$

and for the reaction aA + bB = cC + dD

$$r = \frac{1}{a}\left\{-\frac{d[A]}{dt}\right\} = \frac{1}{b}\left\{-\frac{d[B]}{dt}\right\} = \frac{1}{c}\left\{+\frac{d[C]}{dt}\right\} = \frac{1}{d}\left\{+\frac{d[D]}{dt}\right\}$$

$\Rightarrow$ The rate of reaction is always positive.

$\Rightarrow$ $\text{Unit for rate of reaction} = \frac{\text{Unit of conc.}}{\text{Unit of time}} = \text{mole } L^{-1}\text{time}^{-1}$.

For gaseous reaction, the unit is atm time^{-1}

Factors affecting rate of a reaction

The rate of a chemical reaction depends on the following factors

1. Nature of reactants

(i) Physical state of reactants:
(ii) Physical size of the reactants:
(iii) Chemical nature of the reactants.

2. Temperature:

The rate of chemical reaction generally increases on increasing the temperature. The rate of a reaction becomes almost doubled or tripled for every 10°C rise in temperature.

Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differed by 10° (generally 25°C and 35°C).

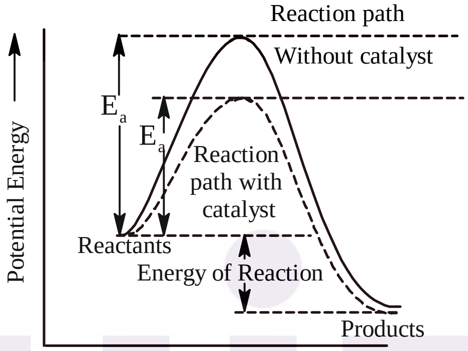
$$\text{Temperature coefficient} = \frac{\text{K at}(t+10^{o}\text{C})}{\text{K at }t^{o}\text{C}} = \frac{k_{35^{o}\text{C}}}{k_{25^{o}\text{C}}}$$

3. Concentration of reactants :

The rate of a chemical reaction depends upon the concentration of the reactants.

4. Presence of catalyst :

Rate of reaction depends on presence of catalyst. Positive catalyst decreases the value of Ea and increases the value of K (rate constant) and hence increases the rate of reaction.



A catalyst changes the reaction path

5. Effect of sunlight (For photochemical reaction):

Rate equation

It is mathematical equation which corelates rate of reaction with concentration (activity) of reactants.

For $aA + bB \to \text{Product}$,

$r = K a_A^m a_B^n$, where $m \le a$ & $n \le b$

Rate constant :

It is equal to rate of reaction when concentration fo each reactant is unity. It is a constant for a particular reaction at a given temperature and also known as specific rate cosntant or specific reaction rate (because rate constant is equal to rate of reaction under specific condition when concentration of each reactant is unity).

Consider a general reaction

$$aA + bB \longrightarrow \text{products}$$

$$\frac{dx}{dt} = k[A]^m[B]^n \text{ where } m \le a \ \& \ n \le b$$

when $C_A = C_B = 1$

then $\frac{dx}{dt} = k$

Unit of rate constant

Unit of rate constant depends on order of reaction.

∴ Unit of K is Litre^{n-1} mol^{1-n} time^{-1} where n = order of reaction

Molecularity	Order of Reaction
1. It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction	1. It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction.
2. It is always a whole number	2. It may be a whole number, zero, fractional, positive or negative
3. .It is theoritical concept	3. .It is experimentally determined.
4. It is meaningful only for simple reaction or individual steps of a complex reaction. It is meaningless for overall complex reaction	4. It is meant for the reaction and not for its individual steps.

Table: Rate constant and other parameters of different order reactions

Order	Rate constant constant	Unit of rate constant	Effect on rate by changing conc. to m times	Half-life period ($t_{1/2}$)
0	$k_0 = \frac{x}{t}$	conc. time^{-1} (mol L^{-1}s^{-1})	No change	$\frac{a}{2k_0}$
1	$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$, $C = C_0e^{-k_1t} \quad N = N_0e^{-k_1t}$, $k_1 = \frac{2.303}{(t_2-t_1)}\log_{10}\left(\frac{a-x_1}{a-x_2}\right)$	time^{-1}(s^{-1})	m times	$\frac{0.693}{k_1}$
2.	$k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{x}{ta(a-x)}$ (for the case when each reactant has equal concentration) $k_2 = \frac{2.303}{t(a-b)}\log_{10}\left[\frac{b(a-x)}{a(b-x)}\right]$ (for the case when both reactants have different concentration)	conc^{-1} time^{-1} (mol L^{-1})$^{-1}$ s^{-1}, L mol^{-1} s^{-1}	m^2 times	$\frac{1}{k_2a}$
3.	$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$	conc^{-2} time^{-1} (mol L^{-1})$^{-2}$ s^{-1}, L^2 mol^{-2} s^{-1}	m^3 times	$\frac{3}{2k_3a^2}$

n $n \geq 2$	$k_n = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{(a)^{n-1}}\right]$;	$conc^{(1-n)}time^{-1}$ $(mol\,L^{-1})^{(1-n)}s^{-1}$,	m^n times $L^{(n-1)}mol^{(1-n)}s^{-1}$	$\frac{2^{n-1}-1}{(n-1)k_n(a)^{n-1}}$ $n \geq 2$

For a reaction of general type: $nA \longrightarrow$ products, to be of:

Zero order:

$$k_0 = \frac{x}{nt} \text{ and } t_{1/2} = \frac{a}{2nk_0}$$

First Order

$$k_1 = \frac{2.303}{nt}\log\frac{a}{(a-x)} \text{ and } t_{1/2} = \frac{0.6932}{nk_1}$$

Second order

$$k_2 = \frac{1}{nt}\left\{\frac{x}{a(a-x)}\right\} \text{ and } t_{1/2} = \frac{1}{nak_2}$$

Third order

$$k_3 = \frac{1}{2nt}\left\{\frac{x(2a-x)}{a^2(a-x)^2}\right\} \text{ and } t_{1/2} = \frac{3}{2nk}$$

Relation between '$t_{1/2}$' and initial concentration 'a' for nth order reaction

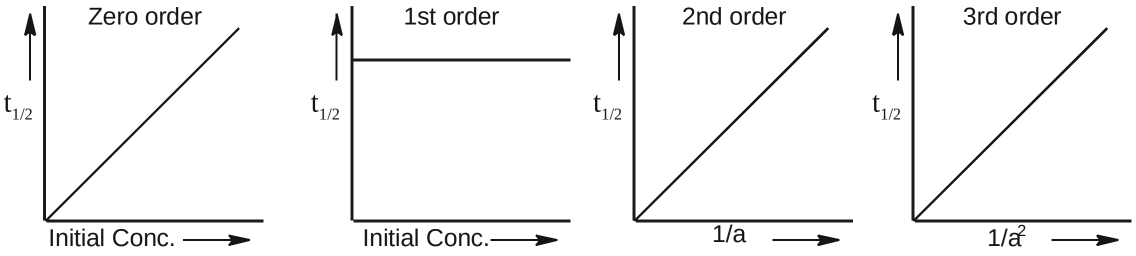
$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}};\ (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}};\ \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)[\log_{10} a_2 - \log_{10} a_1]$$

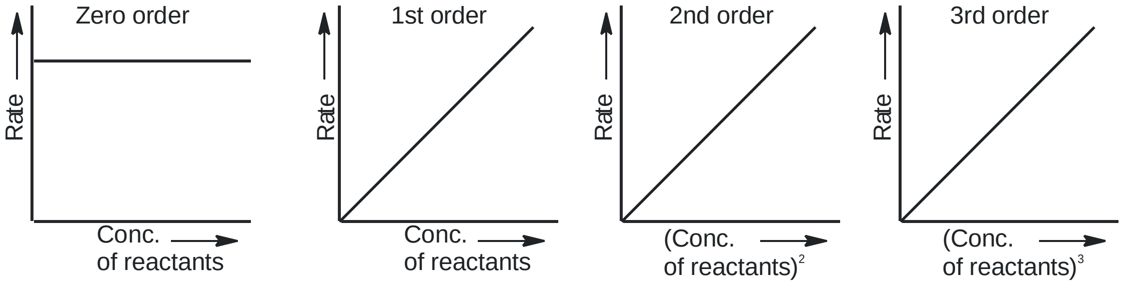
$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}$$

Important Graphs

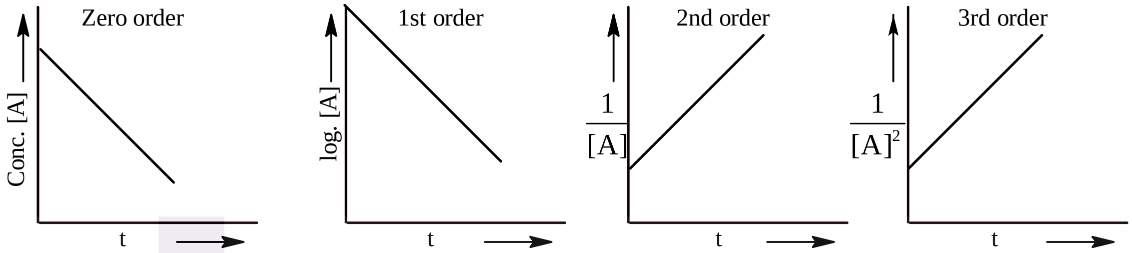
(a) Plots of half-lives Vs initial concentrations (a)



(b) Plots of rate Vs concentrations [Rate = k(conc.)^n]



(c) Plots from integrated rate equations



⇒ Activation energy

The minimum amount of energy which must be absorbed by the reactants to undergo chemical reactions is called activation energy (E_a).

Activation energy = Threshold energy – Average kinetic energy of reacting molecules.

$$E_a = E_{(\text{Threshold energy})} - E_{(\text{Reactants})}$$

Arrhenius equation

Arrhenius proposed a quantitative relationship between rate contatnt and temperature as,

$$K = Ae^{-E_a/RT} \qquad \dots \text{(i)}$$

This equation is called Arrhenius equation.

In which A is known as frequency factor or Arrhenius constant. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and R is the gas constant

Both A and E_a are collectively known as Arrhenius parameters.

Taking logarithm equation (i) may be written as,

$$\ln K = \ln A - Ea/RT$$

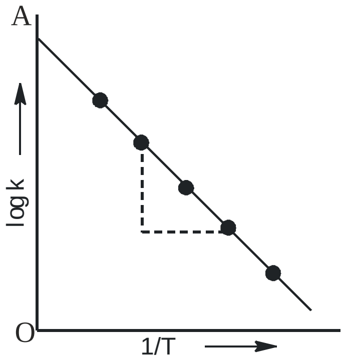
$$\log K = \log A - \frac{E_a}{2.303RT}$$

$$\log K = \left(-\frac{Ea}{2.303R}\right) \times \frac{1}{T} + \log A \qquad \text{(ii)}$$

$$(y \quad = \quad mx + c)$$

(As the value of activation energy (E_a) increases, the value of k decreases and therefore, the reaction rate decreases.)

When log K is plotted against 1/T, we get a straight line.



Intercept = OA = log A

Slope = $\tan\theta = \frac{-Ea}{2.303R}$

From equation (ii)

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right](\text{where } T_2 > T_1) \qquad \dots \text{(iii)}$$

where k_1 and k_2 are rate constant at temperatures T_1 and T_2

Photochemical reaction

The chemical reactions, which are initiated as a result of absorption of light, are known as photochemical reactions.

Characteristics of photochemical reactions

(i) Each molecule taking part in a photo chemical process absorbs only one photon of radiant energy thereby increasing its energy level by hv or $\frac{hc}{\lambda}$

(ii) Photochemical reactions do not occur in dark.

(iii) Each photochemical reaction requires a definite amount of energy which is characteristic of a particular wavelength of photon.

(iv) The rate of photochemical reactions depend upon the intensity of radiation's absorbed.

(v) The ΔG values for light initiated reactions may or may not be negative.

Quantum yield (or quantum efficiency):

The quantum efficency or quantum yield (ϕ) of a photochemical reaction is expressed as,

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photon absorbed}}$$