Chemical Kinetics

Prepared by
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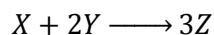**Silapathar College**

Introduction

Chemical kinetics is the study of rated of reactions, factors affecting the rate of reaction and mechanism of the reaction.

Rate of Reaction

Rate of reaction is the speed at which reactants are converted into products. *It may be defined as the change in concentration of reactant (or product) within a particular time interval.*

- Units of rate of reaction are mol L^{-1} $time^{-1}$.
- As the reaction progresses, rate of reaction decreases with time due to decrease in concentration of reactants. It reaches the value of zero as the reaction approaches completion.
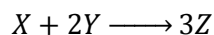- There are two ways of expressing rate of reaction.
    - (i) **Average rate of reaction,** which is defined as the rate of change of concentration of reactant or product per unit time. For example,
      $$X + 2Y \longrightarrow 3Z$$
      Average Rate = $-\dfrac{\Delta[X]}{\Delta t} = -\dfrac{1}{2}\dfrac{\Delta[Y]}{\Delta t} = +\dfrac{1}{3}\dfrac{\Delta[Z]}{\Delta t}$
      Where [X] and [Y] are concentration of reactant and [Z] is the concentration of product. Here, the negative sign shows that concentration of reactants is decreasing with time.
    - (ii) **Instantaneous rate of reaction,** which is calculated for any given instant of time. It may be defined as the rate of change of concentration of any of the reactants or products at a specific instant of time. For example,
      $$X + 2Y \longrightarrow 3Z$$
      Instantaneous rate,
      $$\dfrac{dx}{dt} = -\dfrac{d[X]}{dt} = -\dfrac{1}{2}\dfrac{d[Y]}{dt} = +\dfrac{1}{3}\dfrac{d[Z]}{dt}$$
      Here, $dx =$ corresponding change in concentration and $dt =$ small time interval.
      Here also the negative sign shows that concentration of reactants is decreasing with time.

Factors Affecting Rate of Reaction

The rate of reaction is affected by following factors

- **(i)** **Concentration of reactants** The rate of reaction increases with increase in concentration of reactants.
- **(ii)** **Temperature** For every 10 degree rise in temperature the rate of reaction almost doubled.
- **(iii)** **Nature of reactants** Some reactants are so reactive that their reactions are explosive while the other are almost inert.
- **(iv)** **Surface area of reactants** Larger the surface area of reactants more will be the rate of reaction.

Surface area $\propto$ the rate of reaction.

(v) **Addition of catalyst** Alters the rate of reaction.

(vi) **Exposure to radiations** Photochemical reactions take place only in presence of light.

Law of Mass Action

(Given by Gulberg and Waage) Rate of reaction depends only on the concentration of reactants.

For hypothetical reaction; $aA + bB \longrightarrow$ products

Rate $= k[A]^a[B]^b$

Here, $k = $ rate constant or velocity constant or specific reaction rate. Thus, rate constant may be defined as the rate of reaction when the concentration is reactant in the reaction is unity.

- Rate constant of a reaction increases with increase in temperature.
- Units of rate constant (k)

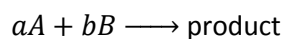 Rate $= dx/dt = k(\text{conc})^n$

  $$\therefore k = \frac{dx}{dt} \times \frac{1}{(\text{conc.})^n} = \frac{\text{conc.}}{\text{time}} \times \frac{1}{(\text{conc.})^n}$$

  $$= \frac{1}{\text{time}} \times \frac{1}{(\text{conc.})^{n-1}} \qquad K = (\text{mol L}^{-1})^{1-n} S^{-1}$$

  When n is order of the reaction.

Rate Law and Order of Reaction

Rate law is the expression, which expresses the observed rate of reaction in terms of concentration of reacting species. Let's consider the following reaction

$aA + bB \longrightarrow$ product

For this reaction, rate $= k[A]^\alpha[B]^\beta$ (Here, α and β may or may not be equal to a and b). This mathematical expression, which is used to give rate is called rate law and order with respect to A is α and with respect to B is β. (α and β may or may not be equal to a and b).

Order of reaction $= \alpha + \beta$

- Order of reaction is the sum of exponents of the concentration terms as expressed in the observed rate of reaction.
- Order of reaction can be zero, first, second or even in fractions. Reactions of higher order are rare because probability of collision of many molecules at one time is very less.
- The units of rate constant depend on the order of the reaction.

Order of reaction	Units of k
Zero ($n = 0$)	mol L^{-1}time^{-1}

First ($n = 1$)   time^{-1}
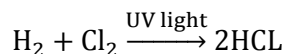
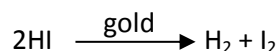Second ($n = 2$)   L mol^{-1} time^{-1}

(i) Zero order reactions are those reactions for which the rate of reaction remains constant throughout the reaction i.e. the rate does not change with concentration of reactants (because the rate of change of concentration of reactants does not change with time)

Rate = k [Reactant]$^\circ$

For example,
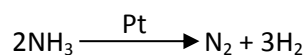
$$H_2 + Cl_2 \xrightarrow{\text{UV light}} 2HCL$$ Where $r = k[H_2]^0[Cl_2]^0$

$$2HI \xrightarrow{\text{gold}} H_2 + I_2$$ Where $r = k\,[HI]^0$

$$2NH_3 \xrightarrow{\text{Pt}} N_2 + 3H_2$$ Where $r = k[NH_3]^0$

For a hypothetical reaction

R $\rightarrow$ P

Rate = $-\dfrac{d[R]}{dt} = k[R]^0$

As any quantity raised to power zero is unity

Rate = $-\dfrac{d[R]}{dt} = k \times 1$

d[R] = $-k$ dt

integrating both sides

[R] = $-kt + I$ (1)

Where, I is the constant of integration.

At t = 0, the concentration of the reactant R = $[R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation

$[R]_0 = -k \times 0 + I$

$[R]_0 = I$

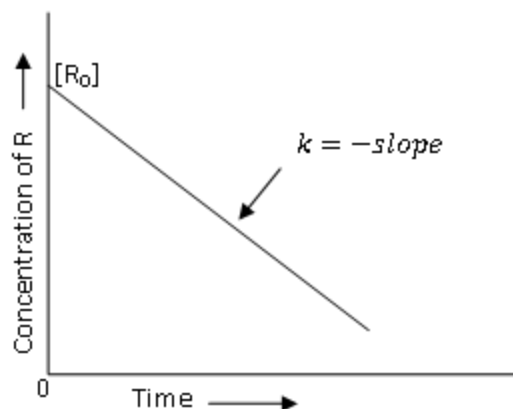Substituting the value of I in the equation (1)

[R] = $-kt + [R]_0$ (2)

Comparing (2) with equation of a straight line, y = mx + c, if we plot [R] against t, we get a straight line in shown fig. with slope = $-k$ and intercept equal to $[R]_0$.

Further simplifying equation (2), we get the rate constant, k as

$k = \dfrac{[R]_0 - [R]}{t}$ (3)

Variation in the concentration vs time plot for a zero order reaction

Characteristics of Zero Order Reaction:

1. All zero order reactions have constant rate.

2. The half life of such reactions is directly proportional to initial concentration and inversely proportional to the rate constant.

3. The unit of rate constant is mol litre^{-1}s^{-1}.

(ii) First order reactions are those reactions in which the rate of reaction is directly proportional to the first power of the concentration of the recanting substance. For example

R → P

Rate = $-\frac{d[R]}{dt} = k[R]$ or

$\frac{d[R]}{dt} = -kdt$

$k = \frac{2.303}{t} \log \left[\frac{A_0}{A}\right]$ OR $k = \frac{2.303}{t} log \frac{a}{a-x}$

Where, k = rate constant, a = initial concentration of reactant,

x = concentration of products after time t

A_0 = initial concentration

A = concentration after time t

Derivation of expression for integrated rate law for Ist order reaction. Let the reaction be R → P.

Rate=$-\frac{d[R]}{dt} \propto [R]$

$-\frac{d[R]}{dt} = k[R] \Rightarrow \frac{-d[R]}{[R]} = k\,dt$

Integrating both sides, we get

-ln [R] = $kt + I$ .....(1)   where I is integration constant

When t = 0, [R] = [R$_0$]

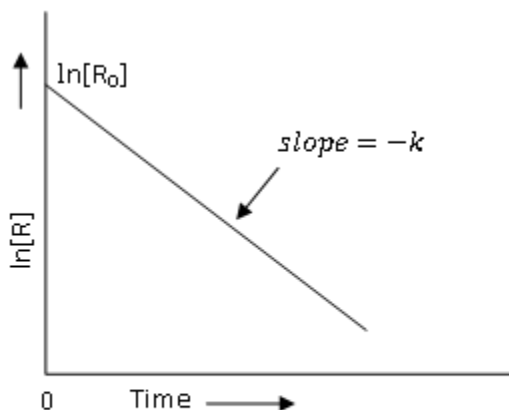-ln [R$_0$] = 0 + I

Substituting the value of I in (1) we get
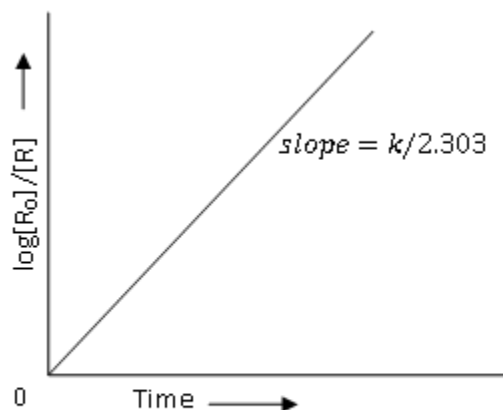
-ln [R] = $kt - ln$ [R$_0$]

$$ln[R] = -kt + ln[R]$$
$$ln\,[R_0] - ln\,[R] = kt$$
$$ln[R] = -kt + ln[R_0] \qquad\qquad (y = mx + c)$$
$$kt = ln\frac{[R_0]}{[R]}, \qquad kt = 2.303\,log\frac{[R_0]}{[R]} \qquad t = \frac{2.303}{k}\,log\frac{[R_0]}{[R]}$$
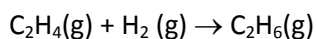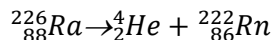

A plot between ln [R] and t for a first order reaction

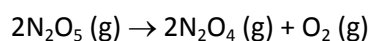*A plot between log[R_0]/[R] vs time for a first order reaction*

Example of first order reaction;

$C_2H_4(g) + H_2\,(g) \rightarrow C_2H_6(g)$ where   Rate $= k[C_2H_4]$

$^{226}_{88}Ra \rightarrow ^{4}_{2}He + ^{222}_{86}Rn$ where   Rate $= k[Ra]$

$2N_2O_5\,(g) \rightarrow 2N_2O_4\,(g) + O_2\,(g)$ where   Rate $= k[N_2O_5]$

(i) **Pseudo first order reactions** are which bimolecular or polymolecular but show first order kinetics under certain conditions (not truly first order ones) are called pseudo first order reaction. For example, the inversion of cane sugar is a bimolecular reaction but it is a first order reaction because the rate law says that the velocity depends only on the concentration of cane sugar.
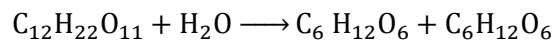
$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6\,H_{12}O_6 + C_6H_{12}O_6$$
 Cane sugar   water   glucose   fructose

Rate $= \dfrac{dx}{dt} = k\,[C_{12}H_{22}O_{11}]$

This reaction is Pseudo first order reaction.

Reaction	Order	Rate Law Equation	Expression for Rate Constant	Half-life Period
A $\longrightarrow$ product	0	Rate $= k$		$t_{1/2} = \dfrac{[A^0]}{2k}$

A ⟶ product	1	Rate $= k\,[A]$	$k = \dfrac{[A^0]-[A]}{t}$ $k = \dfrac{2.303}{t}\log\left[\dfrac{A^0}{A}\right]$	$t_{1/2} = \dfrac{0.693}{k}$
2A ⟶ product	2	Rate $= k\,[A]^2$	$k = \dfrac{1}{t}\left[\dfrac{1}{A}-\dfrac{1}{A^0}\right]$	$t_{1/2} \propto \dfrac{1}{[A^0]}$

Where, k = rate constant

A_0 = initial concentration

A = concentration after time t

Rate Determine Step: If a reaction is completed in more than one steps, it is the slowest step that always determines the rate of reaction. For example:
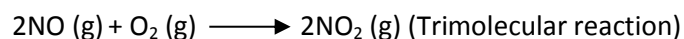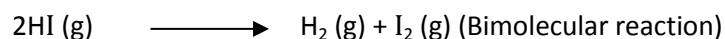
$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

1st step $H_2O_2 \longrightarrow H_2O + \dfrac{1}{2}O_2$ slow

2nd step $\dfrac{1}{2}O_2 + \dfrac{1}{2}O_2 \longrightarrow O_2$ fast
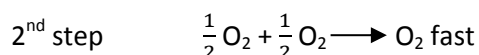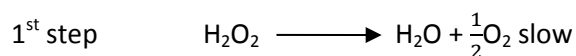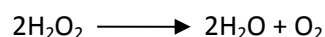
The 1st step is slow, therefore the order of the reaction is 1 since it involves only one molecule of H_2O_2. The molecularity is 2. This is also an example of pseudounimolecular reaction or pseudo first order reaction.

Initial Rate: The rate at the beginning of the reaction when concentrations have not changed appreciably is called initial rate of reaction.

Molecularity

Molecularity of reaction is defined as the number of reactant species, which must collide simultaneously in a step leading to chemical reaction. Usually reactions have a molecularity of one or two.

Reactions are classified as unimolecular, bimolecular or trimolecular for molecularity 1, 2 or 3.

Examples: $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Unimolecular reaction)

$2HI\ (g) \longrightarrow H_2\ (g) + I_2\ (g)$ (Bimolecular reaction)

$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$ (Trimolecular reaction)

Half Life Period of Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero order reaction

$$k = \frac{[R]_0 - [R]}{t}$$

At $t = t_{1/2}$, $[R] = \frac{1}{2}[R]_0$

$$\therefore k = \frac{[R]_0 - \frac{1}{2}[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that for zero order reaction

$$t_{1/2} \propto [R]_0 \qquad \text{and} \qquad t_{1/2} \propto \frac{1}{k}$$

For the first order reaction,

$$K = \frac{2.303}{t} \log\frac{[R]_0}{[R]}$$

at $t_{1/2}$ $[R] = \frac{[R]_0}{2}$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_0/2}$$

or $t_{1/2} = \frac{2.303}{k} \log 2$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k}$$

Since no concentration term is involved $t_{1/2}$ for a first order reaction is independent of initial concentration.

Note: General expression for half life period of nth order

$$t_{1/2} = [R]_0^{1-n}$$

Order	Molecularity
1. Order is the sum of the powers of the concentration terms in the rate law expression.	1. Molecularity is the number of reacting species undergoing simultaneous collisions in the elementary or simple reaction.
2. Order of a reaction is determined experimentally.	2. Molecularity is a theoretical concept.
3. Order of a reaction need not be a whole number, i.e., it can have fractional values also.	3. Molecularity has whole number values only, i.e., 1, 2, 3, etc.
4. Order of a reaction can be zero.	4. Molecularity of a reaction cannot be zero.
5. It is defined for simple as well as complex reactions.	5. It is defined only for simple reactions.

Difference between Rate of reaction and reaction rate constant

Rate of reaction	Reaction rate constant
1. It is the speed with which reactants are converted into products. It is measured as the rate of decrease of concentration of reactants or rate of increase of concentration of products with time.	1. It is the proportionality constant in the rate law and is defined as the rate of reaction when the concentration of the reactants is unity.
2. It depends upon the initial concentration of the reactants.	2. It is independent of the initial concentration of the reactants.
3. It changes with the change in time.	3. It remains constant through out the reaction.

Temperature Coefficient: It is the ratio of constant at temperature 308 K to the rate constant at temperature 298 K. Temperature coefficient $= \dfrac{k_{308}}{k_{298}} = 2 \text{ or } 3$

Arrhenius Equation of Reaction Rate: This is an equation which relates rate constant with temperature in the following way:

$$k = Ae^{-E_a/RT}$$

where A is frequency factor, E_a is the energy of activation

$$\ln k = \ln A - \frac{E_a}{RT}$$

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

A plot of log k vs. 1/T is a straight line whose slope is $-\dfrac{E_a}{2.303\,RT}$ and interception is log A.

If k_1 and k_2 are the rate constants at two temperatures T_1 and T_2, we have

$$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1} \qquad \text{-------- (i)}$$

$$\log k_2 = \log A - \frac{E_a}{2.303\,RT_2} \qquad \text{-------- (ii)}$$

subtracting (i) from (ii), we get,

$$\log k_2 - \log k_1 = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Threshold Energy: *The minimum energy that the reacting molecules must possess in order to undergo effective collisions to form the product is called* **threshold energy.**

Activation Energy: *It is the difference between the threshold energy and the average energy possessed by the reacting molecules.*

Activation energy (E_a) = Threshold energy – Average energy possessed by reacting molecules.

Activated Complex: *It is defined as intermediate formed between reacting molecules which is highly unstable and readily decomposes to yield product(s).For a hypothetical reaction* $\qquad$ A + B $\longrightarrow$ C + D
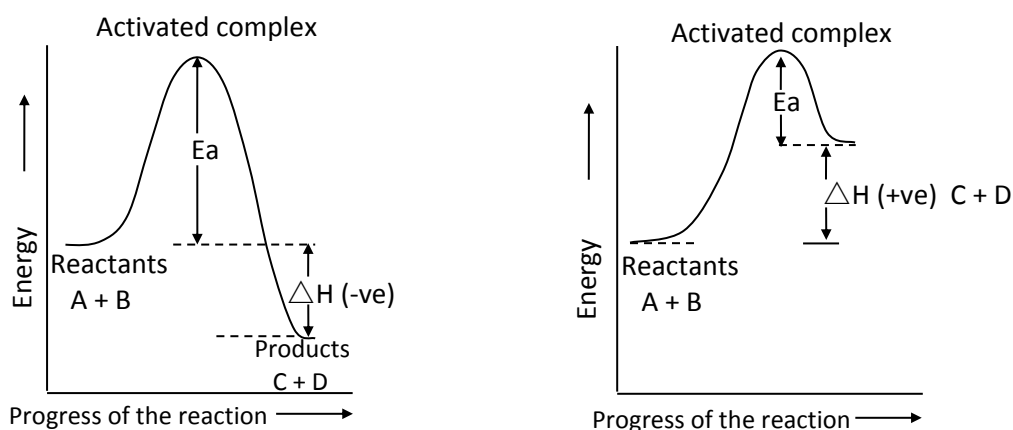

Concept of Activation Energy

Effective Collisions (f): All collisions between reacting molecules do not necessarily result in the formation of products. Only those collisions which lead to the formation of product molecules are called **effective collisions.**

Rate of reaction = $f \times z$, where z is collision frequency and 'f' is fraction of collisions, which are effective.

Collision Frequency (z): *It is defined as total number of collisions per unit volume per unit time.* $z = \sqrt{2\pi}\ \bar{v}\sigma^2 n^2$, where $\bar{v}$ is average velocity, σ is molecular diameter in cm, n is nu

Catalyst: A catalyst increases the rate of reaction by lowering down the activation energy by providing an alternative path to the reaction. Catalyst takes part in chemical reaction, forms an unstable intermediate and change into product and finally gets

regenerated, e.g., A → AC →   B + C. It cannot start a reaction which is thermodynamically not feasible, i.e., in which ΔG = +ve. It does not affect ΔH, ΔG and ΔS. It increases the rate of forward as well as backward reaction equally by lowering down their activation energies in a reversible reaction. Hence it does not disturb the equilibrium.

Effect of catalyst on activation energy
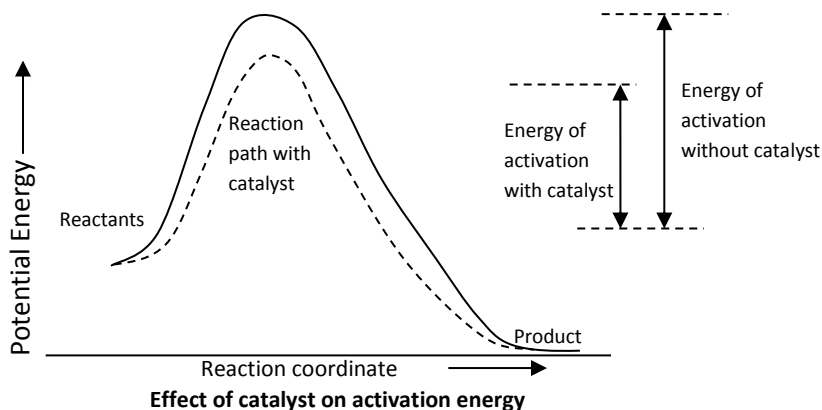
Collision Theory

(i) No reaction can take place without collision between molecules. In order to collide, the reacting molecules must possess certain minimum amount of energy. This minimum energy which a colliding molecule must possess is called as **threshold energy**.

(ii) Collision frequency (z) is defined as the total no. of collisions taking place per second per unit volume. Its value is directly proportional square root of temperature.

(iii) All the collisions which lead to formation of products are called effective collisions. Rate of reaction increases with increase in number of effective collisions.

(iv) According to collision theory the rate of reaction depends on collision frequency and effective collisions.

(v) For a molecule to undergo effective collision, it is essential for molecule to have proper orientation and sufficient energy.

(vi) It is observed that rate of reaction becomes 2-3 times for every 10° rise in temperature.

Activated Complex Theory

(i) Activation energy is the excess energy which is required by reactant molecule to undergo chemical reaction.

Activation energy = threshold energy – average kinetic energy of colliding molecule.

(ii) According to this theory first activated complex is formed by reaction between reactant molecules which possess energy equal to activation energy. The activated complex is unstable because its energy is more than that of the reactant molecules. This complex dissociates to from products which are more stable and have lesser energy.

Photochemical Reactions

   (i)   All such reactions take place only in presence of light but not in the dark.
   (ii) Rate of photochemical reaction is affected by the intensity of light absorbed.
   (iii) **Photosensitiser** is a substance which starts a photochemical reaction without itself undergoing any change.
   (iv) Quantum yield or Quantum efficiency (ϕ) of photochemical reaction can be calculated as follows.

$$\phi = \frac{\text{Number of molecules reacting in given time}}{\text{Number of quanta of light absorbed in the same time}}$$

Free energy change (ΔG_e) of a photochemical reaction may be positive (because during the reaction a part of light energy absorbed by reactants is converted into free energy by products).