CHAPTER-3

CHEMICAL KINETICS

Rate of Chemical Reaction and Factors Affecting Topic-1 Rate of Reaction

Concepts covered: Rate of reaction; Factors affecting rate; Rate law; Molecularity Order

Revision Notes

- **Chemical kinetics** is the branch of physical chemistry, which deals with the study of the rate of chemical reaction and mechanism of the reaction.
- Classification of Reactions on the Basis of Rate of Reaction:
 - Fast (Instantaneous) reaction: The reaction proceeds so rapidly, that the determination of rate of reaction is difficult. It occurs within few seconds.

Example: ionic reactions, organic substitution reactions.

- Slow reaction: The reaction proceeds extremely slow and may take several months for completion. Example: Rusting of iron.
- Moderate (Molecular) reaction: The reaction proceeds between very fast and very slow reaction and their rate can be measured conveniently.

Example: Hydrolysis of esters.

- Elementary reaction: The reaction in which one or more of the chemical species react directly to form
 products in a single reaction step and with a single transition step.
- Rate of reaction: The rate of reaction is the change of concentration of any reactant or product, with time for a reaction.

For reaction, $A + B \rightarrow C$ Rate of reaction, $A = \frac{\text{Decrease in concentration of } A}{\text{Time taken}} = \frac{-\Delta A}{\Delta t}$

Similarly for reaction, $B = \frac{-\Delta B}{\Delta t}$ and for product $C = \frac{\Delta C}{\Delta t}$

Unit : mol $L^{-1} s^{-1}$ or atm s^{-1} .

Instantaneous Rate of Reaction: Instantaneous rate is defined as the rate of change in concentration of any one of the reactant or product at a particular time. Instantaneous rate,



Average Rate of Reaction: The rate of reaction measured over a long time interval is called average rate of a reaction.

Average rate $=\frac{\Delta x}{\Delta t}$, where, $\Delta x =$ change in concentration in given time and $\Delta t =$ time taken.

- > Factors affecting the rate of a chemical reaction:
 - (i) Effect of concentration: Rate of reaction is directly proportional to the concentration of the reactants. Thus, to increase the rate of a reaction, the concentration of the reactants has to be increased.
 - (ii) **Temperature of the reaction:** The rate of a reaction increases with the increase in temperature. Increase in temperature increases the kinetic energy of the molecules which results in the increase in rate of reaction.
 - (iii) **Pressure of the reaction:** Pressure affects the rate of only gaseous reactions. Increase in pressure decreases volume and increases concentration. Increase in concentration increases the rate of reaction.
 - (iv) **Presence of catalyst:** In the presence of a catalyst, the activation energy of a reaction decreases due to which the reaction proceeds at a faster rate.
 - (v) Nature of the reactants: In a chemical reaction, some bonds are broken while some new bonds are formed. Thus, if the molecules are simpler, then less bonds will rupture and the rate of reaction becomes faster while in complex molecules more bonds will rupture and the velocity of the reaction decreases.
 - (vi) Surface area of the reactants: In some heterogeneous reactions, the reaction takes place at the surface of the reactant. Thus in such reactions, the reaction rate is greatly affected by the surface area. Marble powder reacts faster than marble chips.
 - (vii) Effect of radiations: Those reactions which are initiated by the radiations of particular wavelengths are termed as photochemical reactions. These reactions generally proceed at a faster rate than normal thermal reactions.
 - (viii) Effect of physical state: Rate of reaction depends upon physical state of the reactant, e.g., I₂(*g*) reacts faster than I₂(*s*), AgNO₃(*aq*) reacts with NaCl but AgNO₃(*s*) does not react with NaCl.



Law of Mass Action: "At constant temperature, the rate of a chemical reaction is directly proportional to the product of active masses of reacting species with each active mass term raised to the power equal to the stoichiometric coefficient of that species in the chemical reaction."

$$aA + bB \longrightarrow Products$$

Here, Rate of reaction [A]^{*a*}[B]^{*b*}, where [A] and [B] are active masses of the reactants A and B respectively.

- > Active mass of a substance in the solution or gas phase is equal to its molar concentration.
- Rate Law: The rate law states that the rate of reaction is directly proportional to the product of molar concentration of reactants and each concentration is raised to some power which may or may not be equal to stoichiometry coefficients of reacting species

Rate =
$$k[A]^m[B]^n$$

- Rate Constant: Rate constant is also called specific reaction rate. When concentration of both the reactants are unity (one), then the rate of reaction is known as rate constant. It is denoted by 'k'.
- Molecularity: Total number of atoms, ions or molecules of the reactants Participate in the reaction is termed as molecularity. It is always in whole number. It is never more than three. It cannot be zero. Example:

 $\begin{array}{l} NH_4NO_2 \longrightarrow N_2 + 2H_2O \mbox{ (Unimolecular reaction)} \\ 2HI \longrightarrow H_2 + I_2 \mbox{ (Bimolecular reaction)} \\ 2NO + O_2 \longrightarrow 2NO_2 \mbox{ (Trimolecular reaction)} \end{array}$

For a complex reaction, generally, molecularity of the slowest step is same as the order of the overall reaction.

- > Rate determining step: The slowest step in the reaction mechanism is called as the rate determining step.
- Initial rate of reaction: The rate at the beginning of the reaction when the concentrations have not changed appreciably is called as the initial rate of reaction.
- > Order of a reaction: It is the power to which concentration term of a particular reactant in the rate law is raised.

$$aA + bB + cC \longrightarrow Products$$

$$Rate = k[A]^p[B]^q[C]^r$$

where *p*, *q* and *r* represents the order of reaction with respect to A, B and C respectively. Overall order of reaction = p + q + r

- Pseudo first order reaction: It is the reaction which seems to be of higher order but behave as first order under certain conditions.
- This reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substance. In this reaction, water is taken as excess,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

So, rate = $k [C_{12}H_{22}O_{11}]$

O---- Key Formulae

> Rate of reaction of a reactant = $\frac{\text{Decrease in concentration of reactant}}{\text{Time taken}}$

> Instantaneous rate of reaction =
$$\frac{dx}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{-d[C]}{dt}$$

Average rate $=\frac{\Delta x}{\Delta t}$ where Δx = change in concentration in given time and Δt = time taken

O-w Key Terms

Catalyst: A substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change at the end of the reaction.

Order of a Reaction, Integrated Rate Equations and Half-Life of a Reaction

Concept covered: Order of reaction, Half life of reaction



Revision Notes

- Order of reaction: Order is defined as the sum of powers of concentration of the reactants in the rate equation or rate law. Order of reaction is experimentally determined and is not written from the balanced chemical equation. Order of reaction can be whole number, zero or fractional.
- > Zero order reaction: The rate of reaction does not change with the concentration of the reactants.

i.e.,

Rate =
$$k[A]_0$$

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

where, 'k' is rate constant and unit of the rate constant k is mol $L^{-1}s^{-1}$.

This reaction will be zero order reaction.

Photosynthesis of HCl(g) is an example of zero order reaction.

Graphical representation of a zero order reaction:



First order reaction: The rate of reaction is directly proportional to the concentration of reacting substance. In reaction, A → Products

 \Rightarrow

$$\frac{-d[A]}{dt} = k[A]$$
$$\frac{-d[A]}{[A]} = kdt$$
$$\int \frac{-d[A]}{[A]} = \int kdt$$

Rate ∝ [A]

On integration,

 $-\log_{e}[A] = kt + C$ [where, C is the constant of integration]

...(1)

At initial, t = 0, $[A] = [A]_0$

$$-\log_e[A]_0 = C$$

Therefore, equation (1) becomes, $-\log [A] =$

$$bg_e[A] = kt - \log_e[A]_0$$
$$k = -\frac{1}{t}\log_e\frac{[A]}{[A]_0}$$

or

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

Unit of rate constant is s⁻¹.

Decomposition of NH_4NO_2 is an example for first order reaction. Graphical representation of a first order reaction:





> Second order reaction: The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2.

$$\frac{dx}{dt} = k[\mathbf{A}]^{1}[\mathbf{B}]^{1}$$

Unit of rate constant is mol⁻¹ L s⁻¹ or M⁻¹s⁻¹, where M is molarity.

Reaction	Order	Unit of rate constant	Example		
Zero order	0	$mol L^{-1} s^{-1}$	$H_2 + Cl_2 \xrightarrow{Sunlight} 2HCl$		
First order	1	s ⁻¹	$2N_2O_5 \rightarrow 4NO_2 + O_2$		
Pseudo first order 1		s ⁻¹	$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$		
Second order 2		mol ⁻¹ L s ⁻¹	$H_2 + I_2 \Longrightarrow 2HI$		

Equation for typical first order gas phase reaction: $A(g) \rightarrow B(g) + C(g)$ ۶

$$k = \frac{2.303}{t} \log \frac{p_i}{p_A}$$
$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

or

:.

- where p_i is the initial pressure of A at time, t = 0 and p_i is the total pressure at time t.
- > Half-life of a reaction: The time taken for a reaction when half of the starting material has reacted is called half-life of a reaction. $t_{1/2} = \frac{[A]_0}{2k}$

For zero order reaction,

Where, $[A]_0$ is the initial and last concentration of reactant it means there is no change in concentration and 'k' is rate constant.

For 1st order reaction,
$$t_{1/2} = \frac{0.693}{k}$$

 n^{th} Order reaction: In general for n^{th} order reaction of the type ۶

$$A \rightarrow \text{products, where, } \frac{dx}{dt} = k[A]^n$$
$$k_n = \frac{1}{t(n-1)} \left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

Where, $[A]_0$ is initial concentration, [A] is final concentration after time t and n can have all the values except 1.

> Half-life of a reaction of n^{th} order:

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

$$t_{1/2} \propto [A] \text{ for zero order}$$

$$t_{1/2} \text{ is independent of [A] for 1^{st} order}$$

$$t_{1/2} \propto \frac{1}{[A]} \text{ for 2^{nd} order}$$

$$t_{1/2} \propto \frac{1}{[A]^2} \text{ for 3^{rd} order}$$

Amount of substance left after *n* half-lives $=\frac{[A]_0}{2^n}$

> Integrated rate laws for the reactions of zero and first order:

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half life	Units of k
0	$A \rightarrow P$	$\frac{d[\mathbf{A}]}{dt} = -k$	$kt = [\mathbf{A}]_0 - [\mathbf{A}]$	[A] Vs. <i>t</i>	$\frac{[A]_0}{2k}$	conc. time ⁻¹
1	$A \rightarrow P$	$\frac{d[\mathbf{A}]}{dt} = -k[\mathbf{A}]$	$[A] = [A]_0 e^{-kt}$ $kt = \frac{\ln[A]_0}{[A]}$	ln[A] Vs. t	$\ln \frac{2}{k}$	time ⁻¹

> Lifetime: The time in which 98% of the reaction is completed is called lifetime.

Mnemonics

Concept: Order of reaction. Mnemonics: Find Owl that keeps its eye Clean. Interpretation: First order reaction rate is dependent on concentration of reaction. Concept: Zero order reaction Mnemonics: Zebra cannot keep its eye Clean. Interpretation: Zero order reaction rate is not dependent on concentration of reaction.

©=ϖ Key Formulαe

> Zero order reaction:
$$k = \frac{[A]_0 - [A]}{t}$$

$$t_{1/2} = \frac{\left[A\right]_0}{2k}$$

k

First order reaction:
$$k = \frac{2.303}{t} \log \frac{[A_0]}{A}$$

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

o=**∞ Key Terms**

- Photochemical reactions: The chemical reaction whose rate is influenced by radiations, particularly from ultraviolet and visible light is known as photochemical reactions.
- > Intermediate: Species formed in one step and consumed in another.

Topic-3Concept of Energy, Collision Theory and Arrhenius
Equation

Concept covered: Activation energy, Collision theory, Arrhenius equation

≻

Revision Notes

Temperature Coefficient: The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient.

Temperature coefficient = $\frac{\text{Rate constant at 308 K}}{\text{Rate constant at 298 K}}$

It is observed that for a chemical reaction, with rise in temperature by 10°, the rate constant is nearly doubled.

Activation energy: It is an extra energy which must be possessed by reactant molecules so that the collision between reactant molecules is effective and leads to the formation of product molecules.
 Activation energy (E_a) for a reaction cannot be zero. It is not possible that every collision between molecules will be effective. E_a cannot have negative value.



Fig. 5

- Threshold energy: The minimum energy that the reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.
- > 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 the fraction of collisions, which are effective.

The number of collisions that take place per second per unit volume of the reaction mixture is called collision frequency. It is represented by 'Z'.

'Z' should be above effective collisions.

- Activated complex is defined as an unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product.
- Collision theory: According to the collision theory, rate of reaction depends on the collision frequency and effective collisions.

Rate =
$$Z_{AB}e^{-E_a/RT}$$

where Z_{AB} represents the collision frequency of reactants A and B. $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

According to the Collision theory, another factor P which is called steric factor refers to the orientation of molecules which collide, is important and contributes to effective collision.

$$K = PZ_{AB}e^{-E_a/RT}$$

Arrhenius equation: Activated complex is defined as an unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product. Arrhenius equation gives the relation between rate of reaction and temperature.

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

where k = Rate constant

- A = Frequency factor (Arrhenius factor)
- E_a = Activation energy

R = Gas constant

T = Temperature in Kelvin

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

 $\frac{1}{T} \rightarrow$ Fig. 6

Intercept = $\ln A$

Slope =

A plot of log k vs 1/T gives a straight line with slope $=\frac{E_a}{2.303R}$

If k_2 and k_1 are rate constants at temperature T_2 and T_1 respectively, then

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

O-ur Key Formulae

- > Temperature coefficient = $\frac{\text{Rate constant at}(T+10)^0}{\text{Rate constant at }T^0}$
- > Rate of reaction = $f \times Z$
- Arrhenius equation : $k = Ae^{-E_a/RT}$
- \succ k = PZ_{AB}e^{-E_a/RT}