

Revision Notes on Chemical Kinetics:

Rate of Reaction:

- Rate of change of extent of reaction is the rate of reaction.
- Rate of reaction is positive for product and negative for reactant.
- For reaction $aA \rightarrow bB$
 $\text{Rate} = 1/b(\Delta[B]/\Delta t) = -1/a(\Delta[A]/\Delta t)$
- It goes on decreasing as the reaction progress due to decrease in the concentration(s) of the reactant(s).

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- Unit of rate of reaction : $\text{mol L}^{-1} \text{s}^{-1}$
- 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.
- In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentration of the reactants decreases, i.e., products are produced.
- The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.

Order of Reaction

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For reaction $aA + bB + \dots \rightarrow cC + \dots$

$$R \propto [A]^m [B]^n \text{ or } R = k[A]^m [B]^n \dots$$

Where m and n may or may not be equal to a & b.

m is order of reaction with respect to A and n is the order of reaction with respect to B.

$m + n + \dots$ is the overall order of the reaction.

Elementary Reaction:

- It is the reaction which completes in a single step.
- A reaction may involve more than one elementary reactions or steps also.
- Overall rate of reaction depends on the slowest elementary step and thus it is known as rate determining step.

Molecularity of Reaction:

- Number of molecules taking part in an elementary step is known as its molecularity.
- Order of an elementary reaction is always equal to its molecularity.
- Elementary reactions with molecularity greater than three are not known because collisions in which more than three particles come together simultaneously are rare.

Chemical Reaction	Molecularity
$\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$	Unimolecular
$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	Bimolecular
$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$	Trimolecular
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	Bimolecular
$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	Trimolecular
$2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{SnCl}_2 + 2\text{FeCl}_2$	Trimolecular

Differential and Integrated Rate Laws:

Zero Order Reactions:

For Reaction: $\text{A} \rightarrow \text{Product}$

$$[\text{A}]_0 - [\text{A}]_t = k_0 t$$

Where,

$[\text{A}]_0$ = Initial concentration of A

$[\text{A}]_t$ = Concentration of A at time t.

k_0 = Rate constant for zero order reaction.

Half Life:

$$t_{1/2} = [\text{A}]_0 / 2k$$

Unit of rate constant = $\text{mol dm}^{-3} \text{s}^{-1}$

Examples:

- Enzyme catalyzed reactions are zero order with respect to substrate concentration.
- Decomposition of gases on the surface of metallic catalysts like decomposition of HI on gold surface.

First Order Reactions:



$$(\Delta [A] / \Delta t) = -k_1 \Delta t$$

$$\text{or } k_1 = (2.303 / t) \log ([A]_0 / [A]_t)$$

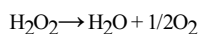
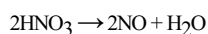
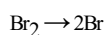
Half Life:

$$t_{1/2} = 0.693 / k_1$$

Half life is independent of the initial concentration of the reactant for a first order reaction.

$$\text{Units of } k_1 = \text{s}^{-1}$$

Examples:



Pseudo First Order Reactions:

These are the reactions in which more than one species is involved in the rate determining step but still the order of reaction is one.

Examples:

- **Acid hydrolysis of ester:** $\text{CH}_3\text{COOEt} + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{EtOH}$
- **Inversion of cane sugar:**
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- Decomposition of benzenediazonium halides $\text{C}_6\text{H}_5\text{N}=\text{NCl} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$

Half – Life of a nth Order Reaction:

$$k t_{1/2} = (2^{n-1} - 1) / (n - 1) [A_0]^{n-1}$$

Where, n = order of reaction $\neq 1$

Parallel Reactions:

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.

If we assume that both of them are first order, we get.

$$k_1 = \text{fractional yield of B} \times k_{av}$$

$$k_2 = \text{fractional yield of C} \times k_{av}$$

If $k_1 > k_2$ then

$A \rightarrow B$ main and

$A \rightarrow C$ is side reaction

Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

i.e

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2 .

Sequential Reactions:

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

$A \rightarrow B \rightarrow C$ and so on

.....(i).....(ii).....(iii)

Integrating equation (i), we get

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Arrhenius Equation:

$$k = A \exp(-E_a/RT)$$

Where, k = Rate constant

A = pre-exponential factor

E_a = Activation energy

Temperature Coefficient:

The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperature differing by 10°C.

$$\mu = \text{Temperature coefficient} = k_{(t+10)}/k_t$$

Let temperature coefficient of a reaction be ' μ ' when temperature is raised from T_1 to T_2 ; then the ratio of rate constants or rate may be calculated as

Its value lies generally between 2 and 3.

Collision Theory of Reaction Rate

- A chemical reaction takes place due to collision among reactant molecules.
- The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
- The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.
- Every collision does not bring a chemical change.
- The collisions that actually produce the products are effective collisions.
- The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and
- disperse in different directions with different velocities.
- For a collision to be effective, the following two barriers are to be cleared.
 1. Energy Barrier
 2. Orientation Barrier

Radioactivity:

All radioactive decay follow 1st order kinetics

For radioactive decay $A \rightarrow B$

$$-(dN_A/dt) = \lambda N_A$$

Where, λ = decay constant of reaction

N_A = number of nuclei of the radioactive substance at the time when rate is calculated.

Arrhenius equation is not valid for radioactive decay.

Integrated Rate Law: $N_t = N_0 e^{-\lambda t}$

Half Life: $t_{1/2} = 0.693/\lambda$

Average life time: Life time of a single isolated nucleus, $t_{av} = 1/\lambda$

Activity: Rate of decay

$$A = dN_A/dt, \text{ Also, } A_t = A_0 e^{-\lambda t}$$

Specific Activity: activity per unit mass of the sample.

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Units: dps or Becquerel