UNIT-I :Chemical Kinetics-I

SYLLABUS

The concept of reaction rates. Effect of temperature, pressure, catalyst and other factors on reaction rates. Order and molecularity of a reaction, Derivation of integrated rate equations for zero, first and second order reactions (similar and different reactants). Half–life of a reaction.General methods for determination of order of a reaction.

The rate of reaction refers to the speed at which the products are formed from the reactants in a chemical reaction. It gives some insight into the time frame under which a reaction can be completed. For example, the reaction rate of the combustion of cellulose in fire is very high and the reaction is completed in less than a second.

What is the Reaction Rate?

Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reactions occur.

Rate of reaction: The rate of reaction is the amount of chemical change occurring per unit time. The rate is generally expressed as the decrease in concentration of the reactant or as the increase in concentration of a product per unit time.

Consider a reaction $A \rightarrow P$, and if C_A is the concentration of reactant and C_P is the concentration of product at time t ,*then*

$$Rate = \frac{-\,dC_A}{dt} = \frac{+dC_p}{dt}$$

Consider a reaction of the type $aA + bB \rightarrow cC + dD$

$$Rate = \frac{1}{a}\frac{-\,dC_A}{dt} = \frac{1}{b}\frac{-dC_B}{dt} = \frac{1}{c}\frac{+\,dC_C}{dt} = \frac{1}{d}\frac{+\,dC_D}{dt}$$

Rate constant: the rate of a reaction $A \rightarrow Product$ is experimentally found to be given by $r=kCA$ where k is the rate constant.

For a reaction $aA+bB \rightarrow Product$ $r= k[A]^a[B]^b$

Unit of rate constant:

(1) For zero order reaction : zero order reaction means rate does not depend on the concentration of the reactants $A \rightarrow P$

$$rate=-\ \frac{-d[A]}{dt} = k[A]^0 = k\ \ (mol/L)\ S^{-1} = k\ So\ unit\ of\ k = (mol/L)\ S^{-1}$$

(2) First order reaction: For a general first order reaction $A \rightarrow P$

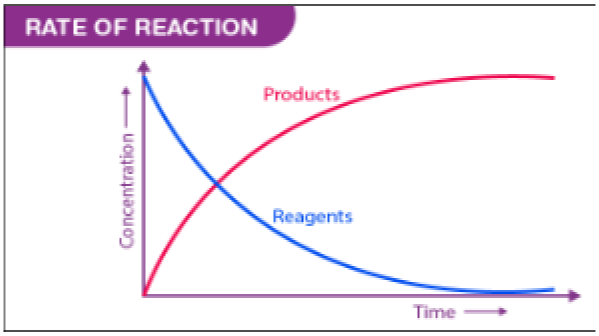
$$rate = \frac{-d[A]}{dt} = k[A]\ (mol/L)^{-1} / \ (mol/L)^{-1}\quad S^{-1} = k\ S^{-1}$$

Unit of k = s^{-1}

(3) Second order reaction:

$A+B\rightarrow P$ $rate = \frac{-dx}{dt} = k[A][B]$ = k$(mol/L)^{-1}$ s^{-1}

Unit of k = $(mol/L)^{-1}$ s^{-1}



Order of a reaction (n):

It is the sum of the exponents of the concentration terms in the rate equation.

By stating the order of a reaction, the quantitative dependence of its rate on the concentration of a reacting substance can be indicated.

For a reaction , α A+ β B+ γ C→ Product, $rate = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{-d[C]}{dt}$

or, rate can also be written as $rate = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$

Order of a reaction, n=α+β+γ

eg.: $2HI = H_2 + I_2$

$rate = k[HI]^2$, here n =2 .If n=1, reaction is said to be first order reaction if n=2, it is second order reaction and n=0, it is zero order reaction
As per the general definition, the speed with which a reaction takes place is referred to as the rate of a reaction.
For example, wood combustion has a high reaction rate since the process is fast and rusting of iron has a low reaction rate as the process is slow.

Molecularity of a reaction (n):

Molecularity of a reaction is defined as: "The number of reacting species (atoms, ions, or molecules) that come together simultaneously to collide and bring about a chemical reaction in an elementary step." It is a theoretical concept that applies only to elementary reactions, not to overall complex reactions.Molecularity is always a whole number (1, 2, or 3).

- It is never zero or fractional.
- It refers to one step (elementary reaction) only.

- It is not the same as order of reaction (which is determined experimentally).

1. Unimolecular Reaction (Molecularity = 1)Only one species is involved in the rate-determining step.

Example:
2N2O5→N2O4+ ½ O2 Here, only one molecule of N_2O_5 decomposes on its own.

2. Bimolecular Reaction (Molecularity = 2) Two species collide simultaneously.

Example:
$2NO+O3 \rightarrow NO2+O2$ One molecule of NO and one molecule of O_3 collide and react.

3. Termolecular Reaction (Molecularity = 3).Three species must collide simultaneously (rare due to low probability of three-body collisions).

Example:
$2NO+O2 \rightarrow 2NO2$ Two molecules of NO and one molecule of O_2 react.

Difference between Order and Molecularity

Aspect	**Order**	**Molecularity**
Definition	Derived from the rate law expression and can be fractional or whole.	The count of molecules in an elementary step is always a whole number.
Determination	Determined experimentally.	Determined from the reaction mechanism.
Applicability	Applies to both elementary and complex reactions.	Applies only to elementary reactions.
Values	Can be zero, fractional, or a whole number.	Always a positive whole number.

Factors Affecting the Rate of Reaction

The various factions that can affect the rate of a chemical reaction are listed in this subsection.

Nature of the reaction

- The rate of reaction highly depends on the type and nature of the reaction. As mentioned earlier, few reactions are naturally faster than others while some reactions are very slow.
- The physical state of reactants, number of reactants, complexity of reaction and other factors highly influence the reaction rate as well.
- The rate of reaction is generally slower in liquids when compared to gases and slower in solids when compared to liquids. Size of the reactant also matters a lot. The smaller the size of reactant, the faster the reaction.

Nature of the reactants

- The **nature of reactants** plays a crucial role in determining the **rate of a chemical reaction**.
- Reactions involving **ionic compounds**, **gases or solutions**, and **highly reactive or polar substances** tend to proceed **faster** due to easier bond breaking, increased molecular interactions, and favorable reaction pathways.
- In contrast, reactions involving **covalent compounds**, **solids**, or **bulky molecules** are generally slower.

- Understanding these differences is essential for predicting and controlling reaction rates in both academic and industrial chemistry.

Effect of concentration on reaction rate

- According to the collision theory, the rate of reaction increases with the increase in the concentration of the reactants.
- As per the law of mass action, the chemical reaction rate is directly proportional to the concentration of reactants.
- This implies that the chemical reaction rate increases with the increase in concentration and decreases with the decrease in the concentration of reactants.
- Time plays a major role in changing the concentration of reactants and products. Therefore, even time is a vital factor affecting the reaction rate.

Pressure factor

- Pressure increases the concentration of gases which in turn results in the increase of the rate of reaction. The reaction rate increases in the direction of less gaseous molecules and decreases in the reverse direction.
- Thus, it can be understood that pressure and concentration are interlinked and that they both affect the rate of reaction.

Effect of temperature

- According to collision theory, a chemical reaction that takes place at a higher temperature generates more energy than a reaction at a lower temperature.
- This is because colliding particles will have the required activation energy at high temperature and more successful collisions will take place.
- There are some reactions that are independent of temperature. Reactions without an activation barrier are examples of chemical reactions that are independent of temperature.

Effect of Solvent

- The rate of reaction also depends on the type of solvent. Properties of solvent and ionic strength highly affect the reaction rate.

Effect of Catalyst

- A catalyst is a substance that increases the rate of a chemical reaction without being consumed in the process.
- Lowers activation energy (Ea).Provides an alternative reaction pathway.Remains chemically unchanged.Does not alter equilibrium or thermodynamics.Highly specific in function

Integrated rate Equation of Zero Order Reaction

For a zero-order reaction, the rate of reaction is independent of the concentration of the reactant. The general form of such a reaction is:

The reaction can be represented as A → Products.

$$\text{Rate} = \frac{-d[A]}{dt} = k$$

$$d[A] = dt$$

where [A] is the concentration of the reactant at time t, and k is the rate constant.

Now, integrating both sides with proper limits, the left-hand side is integrated from the initial concentration $[A]_0$ to [A] at time t, and the right-hand side is integrated from 0 to t. Where $[A]_0$ is the initial concentration of the reactants and [A] is the concentration of the reactants at time t

$$\int_{[A]0}^{[A]} d[A] = \int_{0}^{t} -k\, dt$$

$$[A]_{[A]_0}^{[A]} = -\ k[t]_0^i$$

$$[[A]-[A_0] = -k\ [t-0]$$

$$[A]-[A_0\ ]= -k\ t$$

Assume If concentration $[A]_0$ at a time t_0 is equal to "a" and concentration [A] at the time t is equal to "a-x" then the above equation becomes

$$(a-x)-a = -k\ t$$

$$x = kt$$

$$k = \frac{1}{t} x$$

Units of rate constant for Zero order reaction are : **(mol/lit) sec $^{-1}$**

Integrated rate Equation of First Order Reaction

For a first-order reaction where a single reactant A is converted into products, the rate of reaction is directly proportional to the concentration of the reactant at any time.

The reaction can be represented as A → Products.

The rate law for a first-order reaction is given by

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]$$

where [A] is the concentration of the reactant at time t, and k is the rate constant. To derive the integrated rate law, we rearrange the rate equation and separate the variables:

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

Now, integrating both sides with proper limits, the left-hand side is integrated from the initial concentration $[A]_0$ to [A] at time t, and the right-hand side is integrated from 0 to t. Where $[A]_0$ is the initial concentration of the reactants and [A] is the concentration of the reactants at time t

$$\int_{[A]0}^{[A]} \frac{d[A]}{[A]} = \int_{0}^{t} -k\,dt$$

. Using logarithmic rules, this can be simplified to

$$\ln(\frac{[A]}{[A]_0} = -kt.$$

$$\textbf{OR}\ \ln\frac{[A]_0}{[A]} = kt.$$

$$k.=\frac{1}{t}\ \ln\frac{[A]_0}{[A]}$$

this expression can also be written using base-10 logarithms

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

This is the integrated rate law for a first-order reaction. It shows how the concentration of the reactant decreases exponentially over time.

Assume If concentration $[A]_0$ at a time t_0 is equal to "a" and concentration [A] at the time t is equal to "a-x" then the above equation becomes

$$k.=\frac{2.303}{t}\log(\frac{a}{a-x})$$

Units of rate constant for First order reaction are : **sec** $^{-1}$

A plot of ln[A] versus time (t) gives a straight line with a negative slope equal to –k and a y-intercept equal to $\ln[A]_0$, confirming that the reaction follows first-order kinetics.

One of the key characteristics of a first-order reaction is that its half-life ($t_{1/2}$), the time required for the concentration of the reactant to reduce to half of its initial value, is constant and independent of the initial concentration.

The half-life is given by $t_{1/2} = 0.693/k$. This constancy of half-life is a distinguishing feature of first-order reactions and is used in identifying the order of a reaction experimentally.

Integrated rate Equation of Second Order Reaction involving one reactant

For a second-order reaction involving **only one reactant**, the general form of the reaction is:

A → Products

The **rate law** for a second-order reaction with respect to the same reactant is:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2$$

To derive the integrated rate equation, we rearrange the rate law and separate the variables:

$$\frac{d[A]}{dt} = - k[A]^2$$

$$\frac{d[A]}{[A]2} = -k\,dt$$

Now, we integrate both sides. The left side is integrated from the initial concentration $[A]_0$ to final concentration [A] , and the right side is from time 0 to time t:

$$\int_{[A]0}^{[A]} \frac{d[A]}{[A]2} = \int_0^t -k\,dt$$

$$\left[-\frac{1}{[A]}\right]_{A_0}^{A} = -k\,[t]_0^t \qquad (\,Because \int \frac{1}{x^2}\,dx = \frac{-1}{x}\ \&$$

$$\int 1\,dt = t\ )$$

By substituting the limits in the above expression

$$-[\frac{1}{[A]} - \frac{1}{[A]_0}] = - k\,[t\text{-}0]$$

$$-[\frac{1}{[A]} - \frac{1}{[A]_0}] = - kt$$

$$[\frac{1}{[A]} - \frac{1}{[A]_0}] = kt$$

$$k = \frac{1}{t}\,[\frac{1}{[A]} - \frac{1}{[A]_0}]$$

Assume If concentration $[A]_0$ at a time t_0 is equal to "a" and concentration [A] at the time t is equal to "a-x" then the above equation becomes

$$k = \frac{1}{t}\,[\frac{1}{(a-x)} - \frac{1}{a}]$$

$$k = \frac{1}{t}\,[\frac{x}{a(a-x)}]$$

Units of rate constant for Second order reaction are : **$(mol/lit)^{-1}$ sec^{-1}**

Integrated rate Equation of Second Order Reaction involving two reactants

For a **second-order reaction involving two different reactants**, the reaction is typically of the type:

$$A+B \rightarrow Products$$

Assuming the reaction is second order overall and **first order with respect to each reactant**, the **rate law** is:

The **rate law** for a second-order reaction with respect to the same reactant is:

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = k[A]\,[B]$$

Case 1: When $[A]_0 \neq [B]_0$ (initial concentrations of A and B are different)

Let the initial concentrations be $[A]_0$ and $[B]_0$ let X be the amount of A (and amount of B) reacted at time t. Then the concentrations at time t are:

$$[A]=[A]_0-X, [B]=[B]_0-X$$

Substitute into the rate law:

$$\frac{dx}{dt} = k\,([A]_0-X)\,([B]_0-X)$$

This is a separable differential equation, and its integration leads to the **integrated rate law**:

$$kt = \frac{1}{[B]_0-[A]_0} \ln\left[\frac{[B]\ [A]_0}{[A]\ [B]_0}\right]$$

$$k = \frac{1}{t}\ \frac{1}{[B]_0-[A]_0} \ln\left[\frac{[B]\ [A]_0}{[A]\ [B]_0}\right]$$

Assume If concentration $[A]_0$ at a time t_0 is equal to "a" concentration $[B]_0$ at a time t_0 is equal to "b" and concentration [A] at the time t is equal to "a-x" and concentration [B] at the time t is equal to "b-x"then the above equation becomes

$$k = \frac{1}{t}\ \frac{1}{(b-a)} \ln\left[\frac{a(b-x)}{b(a-x)}\right]$$

This is the **integrated rate law for a second-order reaction with two reactants having different initial concentrations**.

Units of rate constant for Second order reaction are : **$(\text{mol/lit})^{-1}$ sec^{-1}**

Case 2: When $[A]_0 = [B]_0$ **(equal initial concentrations)**

If the initial concentrations of A and B are the same, i.e., $[A]_0 = [B]_0 = a$, then the reaction behaves like a second-order reaction with respect to a single reactant:

A+A→Products Then, the integrated rate law becomes:

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

This is the same as the integrated rate law for a second-order reaction with one reactant, because both reactants are consumed in equal amounts.

Note:Units of rate constant for "n th "order reaction are : **$(mol/lit)^{1-n}$ .sec $^{-1}$**

Half-Life of a Reaction

Definition :

The **half-life** of a reaction, denoted by $t_{\frac{1}{2}}$, is the **time required for the concentration of a reactant to decrease to half of its initial value**.

In other words, if a reaction starts with an initial concentration $[A]_0$, the half-life is the time it takes for the concentration to become $\frac{[A]_0}{2}$

It is a useful measure of the **speed of a reaction** and varies depending on the **order of the reaction**:

★ For **zero-order reactions**, the half-life is directly proportional to the initial concentration:

Integrated Rate equation for Zero order reaction is : k = $\frac{1}{t}\ x$

If t = $t_{\frac{1}{2}}$ then x = $\frac{[A]_0}{2}$ (As per the definition of Half-life)

Substitute these values in Integrated Rate equation for Zero order reaction the equation becomes

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

★ For **first-order reactions**, the half-life is constant and independent of the initial concentration:

Integrated Rate equation for First order reaction is :k.= $\frac{2.303}{t}$ log($\frac{a}{a-x}$)

If t = $t_{\frac{1}{2}}$ then x = $\frac{a}{2}$ (As per the definition of Half-life)

Substitute these values in Integrated Rate equation for First order reaction the equation become

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

★ For **second-order reactions**, the half-life depends on the initial concentration:

Integrated Rate equation for Second order reaction is :k = $\frac{1}{t}\ [\frac{x}{a(a-x)}\ ]$

If t = $t_{\frac{1}{2}}$ then x = $\frac{a}{2}$ (As per the definition of Half-life)

Substitute these values in Integrated Rate equation for Second order reaction the equation become

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

Half-life is especially useful in studying the kinetics of radioactive decay and chemical reactions.

Experimental Determination of Order of a Reaction

(1) Graphical method

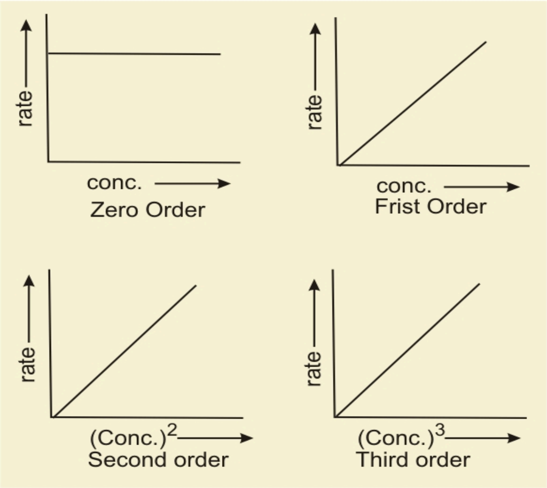
This method is used when there is only one reactant. It involves the following steps:

1) The concentrations of the reactants are measured by some suitable method.

2) A graph is plotted between concentration and time.

3) The instantaneous rates of the reaction at different times are calculated by finding out the slopes of the tangents corresponding to different times.

4) The rate of reaction is plotted versus concentration,[A] or (concentration)^2, $[A]^2$ and so on.



(a) If rate of reaction remains constant in rate versus concentration graph, it means that the rate is independent of the concentration of the reactant, i.e.

Rate = k $[A]^0$ = k Therefore, the reaction is of zero order.

(b) If a straight line is obtained in rate versus concentration graph, it means that the rate is directly proportional to concentration of the reactant i.e.

Rate = k [A] Therefore, the reaction is of first order.

(c) If a straight line is obtained in rate versus (concentration)2 graph, it means that

Rate = k $[A]^2$ Therefore, the order of the reaction is two.

(d) Similarly, if we get straight line in rate versus (concentration)3 graph, then

Rate = k$[A]^3$ and the order of reaction is 3

If we get straight line by plotting graph of rate versus (concentration)n, where n =1, 2, 3…. so on, then

Rate = k$[A]^n$ and the order of reaction is n.

(2) Use of integrated rate equation

The kinetic data is fitted to different integrated rate equations. Wherever the data fit with the equation for the correct order of the reaction, it will give a constant value of rate constant for all data points (concentrations at different times).

For a general reaction:A — — —> Products

the integrated rate equation for zero, first and second order reactions are below given:

For Zero Order Reaction $k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$

For First Order Reaction $k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$

For Second Order Reaction $k = \frac{1}{t}\,\frac{1}{(b-a)}\ln\left[\frac{a(b-x)}{b(a-x)}\right]$

(3) Initial Rate Method

The graphical methods cannot be applied for the reaction which involve more than one reactant.The rates of such reactions can be determined by the initial rate method.

a) The initial rate of the reaction i.e. the rate at the beginning of the reaction is measured.The rate over an initial time interval that is short enough so that concentration of the reactants do not change appreciably from their initial values.This corresponds to slope of the tangent to the concentration versus time graph at t=0.

b) The initial concentration of only one reactant is changed and the rate is determined again.From this order with respect to that particular reactant is calculated.

c) The procedure is repeated with respect to each reactant until the overall rate law is fully determined.

d) The sum of the individual orders with respect to each reactant gives the order of the reaction.

Consider a reaction

aA + bB + c C ➡ Products

The general form of the rate law may be written as :

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

Then initial rate of the reaction may be given as :

r_0 = Rate = $k\,[A]_0^p\,[B]_0^q\,[C]_0^r$

If [B] and [C] are kept constant, then

$r_0 = k_0\,[A]_0^p \quad where\ k_0 = k\ [B]_0^q\,[C]_0^r$

The value of p can be determined by inspecting the rate at different values of [A].If we know the initial rates at two different concentrations of A.

$(r_0)_1 = k_0\,[A_0]_1^p$

$(r_0)_2 = k_0\,[A_0]_2^p$

where $(r_0)_1$ and $(r_0)_2$ are initial rates of reactions when the initial concentration of A are $[Ao]_1$ and $[Ao]_2$ n= p+ q+ c

(4) Ostwald Isolation Method

The total order of the reaction is then equal to the sum of the orders of reaction for individual reactants.This method is based on the principle that if the concentration of all but one reactant are taken in excess , then during the course of the reaction, the concentration of those reactants taken in excess will remain almost constant and hence variation in rate will correspond to the concentration of that reactant whose concentration is small.This process is repeated one by one and order with respect to each reactant is determined.

The overall order will be the sum of all these orders.

$$aA + bB + c\,C \text{ — — —> Products}$$

Suppose we isolate A by taking B and C in large excess and get order of reaction with respect to A.Similarly , we isolate B by taking A and C in B and and C.

$$\text{Overall order of reaction } n= p+ q+ r$$

(5)Van't Hoff's Differential Method

The **Van't Hoff Differential Method** is a classical technique used to determine the **order of a chemical reaction** by measuring the **initial rate** of reaction at **different initial concentrations** of the reactant.

Consider a reaction: A→Products

The **rate law** can be written as: Rate = $\frac{-d[A]}{dt}$ =k$[A]^n$

Where: A = concentration of the reactant k = rate constant n = order of the reaction (to be determined)

Procedure:

1. Measure the **initial concentration** $[A]_1$ and the corresponding **initial rate** R_1
2. Change the initial concentration to $[A]_2$ and measure the new rate R_2
3. Use the rate law: $R_1 = k[A]_1^n$ and $R_2 = k[A]_2^n$
4. Divide the two equations:

$$\frac{R_2}{R_1} = \frac{k[A]_2^n}{k[A]_1^n} \Rightarrow \frac{R_2}{R_1} = \left(\frac{[A]_2}{[A]_1}\right)^n$$

5. Take logarithms:

$$\log\frac{R_2}{R_1} = n\,log\frac{[A]_2}{[A]_1}$$

6. Solve for n: $n = \dfrac{log\frac{R_2}{R_1}}{log\frac{[A]_2}{[A]_1}}$