



CHEMICAL KINETICS



- * Reaction Rates
- * Theory of Reaction Rates
- * Rate Law
- * Molecularity and Order

REACTION RATES

Chemistry, by its very nature, is concerned with change. Reactant substances are converted by chemical reactions into product substances. The properties of the substances change in a reaction.

The feasibility of a reaction can be predicted by thermodynamics. Along with feasibility, the extent of reaction can be determined from chemical equilibrium. It is equally important to know the speed at which a reaction is occurring. This is called kinetic feasibility of a reaction.

3.1.1

Types of reactions

*Ionic reactions
are fast and
instantaneous*

The branch of chemistry which deals with the study of reaction rates and their mechanisms is called chemical kinetics or reaction kinetics. The word kinetics is derived from the Greek word 'kinesis' meaning movement.

Based on the speed, chemical reactions are broadly classified into two types : Fast reactions are those in which the time required for the completion of the reaction is very less. Reactions between ionic substances are fast and are called instantaneous. Slow reactions are those in which the time required for the completion of the reaction is very high. Generally reactions between covalent substances are slow and time consuming.

Kinetics in practice is studied and useful for all reactions except very fast, very slow and explosive reactions.

How fast or how slow the reactions occur is dependent on the nature of reactants, the nature of the reaction and experimental conditions of the reaction. The relative speeds of some chemical reactions are listed in Table 3.1.

Table 3.1 Some chemical reactions and their speeds

Equation of the chemical reaction	Approximate time required for almost completion	Speed of the reaction
$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$	Few years	Very slow
$\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \xrightarrow{\text{H}^+} \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$	Few hours	Slow
$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	Few minutes	Not so fast
$\text{HCl}(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{KCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	Very much less than a milli sec	Very fast

3.1.2

Rate of a reaction


**Rate of reaction
is change in
concentration
per unit time**


The speed of an automobile is expressed in terms of change in the position or distance by it in a certain period of time. Similarly the rate of a reaction, also called the speed of the reaction, is expressed in terms of change in the concentration in a certain period of time.

The rate of a reaction is defined as the change in molar concentration of a reactant or a product per unit time. To be more specific, rate can be expressed as the rate of decrease in concentration of a reactant or the rate of increase in concentration of a product.

Let us consider a hypothetical reaction, where one mole of reactant 'R' is converted to one mole of product 'P' assuming that the volume of the system remains constant. If the concentrations of reactant and product at time t_1 , are $[R]_1$ and $[P]_1$, respectively and at time t_2 , the concentrations are $[R]_2$ and $[P]_2$, then

Change in time, $\Delta t = t_2 - t_1$ = time taken

Change in the concentration of reactant, $\Delta[R] = [R]_2 - [R]_1$

Change in the concentration of product, $\Delta[P] = [P]_2 - [P]_1$

Here, the square brackets are used to express molar concentrations. Molar concentration of a solution is also termed as active mass.

$$\text{Rate of disappearance of R} = \frac{\text{decrease in concentration of R}}{\text{time taken}} = \frac{\Delta[R]}{\Delta t}$$

$$\text{Rate of appearance of P} = \frac{\text{increase in concentration of P}}{\text{time taken}} = \frac{\Delta[P]}{\Delta t}$$

Rate of a reaction is mathematically given as

$$\text{Rate} = \frac{\Delta C}{\Delta t} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$$

Negative sign is to denote that the reactant concentration decreases and positive sign is to denote that the product concentration increases in the reaction.

The rates can be determined with respect to any reactant or any product present in a given chemical reaction. But in arriving at the rate of reaction, the stoichiometric coefficients of the reactants or the products are to be taken into account.

For the reaction of forming nitric oxide from its elements, $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$

The rate measured with respect to N_2 is $-\frac{\Delta[\text{N}_2]}{\Delta t}$, with respect to O_2 is $-\frac{\Delta[\text{O}_2]}{\Delta t}$ and with respect to NO is $+\frac{\Delta[\text{NO}]}{\Delta t}$.

The rate of the reaction, expressed in terms of each substance, can be different. For example in the above reaction, the rate of formation of NO is twice the rate of removal of either N_2 or O_2 . To express a common rate equation for any reaction, stoichiometric coefficients of different participant substances are written in denominators, to relate the rates measured.

$$-\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{\Delta[\text{NO}]}{2\Delta t}$$

In general for a reaction, $x\text{A} + y\text{B} \rightarrow m\text{P} + n\text{Q}$, the rates measured, with respect to reactants A or B and products P and Q are equated as,

$$-\frac{1}{x} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{y} \frac{\Delta[\text{B}]}{\Delta t} = +\frac{1}{m} \frac{\Delta[\text{P}]}{\Delta t} = +\frac{1}{n} \frac{\Delta[\text{Q}]}{\Delta t}$$

3.1.3**Instant rate**

Rate of reaction at a specified time is called instantaneous rate

The rate of a reaction is not maintained constant throughout the reaction. The rates obtained over an interval of time are called average rates of the reaction. Average rate depends upon the change in concentration of a substance and time taken for that change to occur.

The rate of a reaction at a specified time is called instant rate. It is also called instantaneous rate. The rate of a chemical reaction at any instant is the decrease in the concentration of reactant or increase in the concentration of product at that specified time during the process of the reaction. Average and instant rates of a reaction are shown graphically in Fig 3.1.

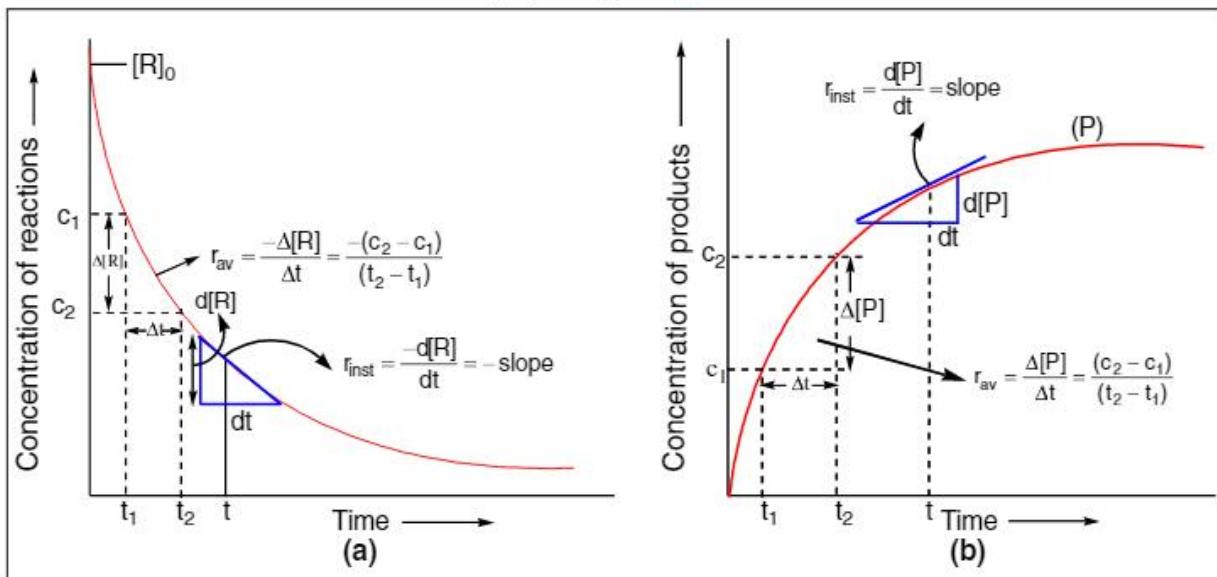


Fig 3.1 Average rate and instantaneous rate of a chemical reaction

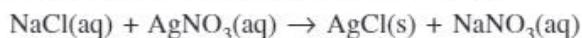
Units of reaction rate are mol L⁻¹ s⁻¹

Instant rate can be determined graphically by drawing a tangent at time 't' on either of the curves for concentration of reactant and concentration of product versus time and calculating its slope.

The units of rate are: concentration time⁻¹. If concentration is in mol L⁻¹ and the time is given in seconds, the units of rate are mol L⁻¹ s⁻¹ or mol dm⁻³ s⁻¹. For gaseous reactions, partial pressures of the substances are given. The units of rate will be atm s⁻¹ or Pa s⁻¹. The units of rate are also given as g L⁻¹s⁻¹ or in SI system as kg m⁻³ s⁻¹.

3.1.4**Factors influencing reaction rates**

Nature of reactants : Reactions between ionic substances are instantaneous as the forces operate between the oppositely charged ions are strong electrostatic attractions. A white precipitate of silver chloride is obtained immediately by mixing solutions of sodium chloride and silver nitrate.



Reactants between covalent substances are slow and time consuming. These reactions involve bond breaking and bond making. The more the number of bonds transformed, the more is the time required. Formation of ammonia between the elements nitrogen and hydrogen is very slow.

**Rate of reaction
is directly
proportional to
concentration of
reactants**

Concentration of reactants : At a given temperature, the rate of reaction depends on the concentration of the reactants. The effect of concentration on the rate of the reaction is known from the law of mass action. The rate of a reaction at any instant of time is directly proportional to the concentration of reactants taking part in the reaction at that instant.

In case of gaseous reactions, partial pressures are measured for the substances. The rate of the reaction is proportional to the partial pressure each of the reactants involved in the reaction.

Temperature : The rate of reaction increases with an increase in the temperature of the reaction. 50% of nitrogen pentoxide decomposes in 10 days at 0°C , in 5 hours at 25°C and in 12 minutes at 50°C .

The temperature dependence of the rate of a chemical reaction is explained by Arrhenius equation, which was originally called the Van't Hoff's proposal.

$$k = A e^{-E_a/RT}$$

Here A is the Arrhenius factor, also called frequency factor or pre-exponential factor. It is a constant for a given reaction. k is the rate constant, R is the molar gas constant and E_a is the energy of activation.

Taking logarithms on both side of the Arrhenius equation, we get

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (\text{or}) \quad \log k = -\frac{E_a}{2.303RT} + \log A$$

A plot of $\ln k$ versus T^{-1} is a straight line as shown in Fig 3.2, with a negative slope. The slope is given as $-E_a/R$.

Activation energy
 $E_a = -R \times \text{slope}$

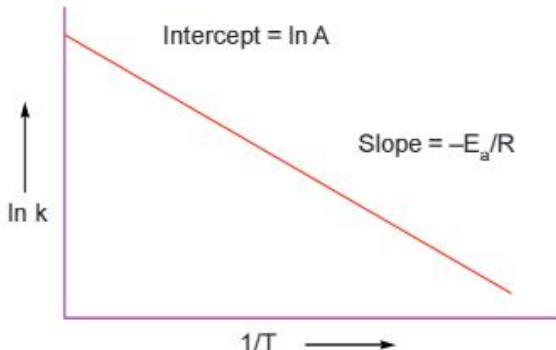


Fig 3.2 A plot of $\ln k$ and inverse of temperature

**Rate of reaction
is generally
doubled for
every 10°C rise
in temperature**

It has been found that for a chemical reaction, the specific rate is approximately doubled for every 10°C rise of temperature for many reactions. The ratio of two specific rates measured at temperatures that differ by 10°C is called the temperature coefficient of the reaction. The temperature coefficient is normally 2. It approaches a value of 3 in some reactions.

$$\text{Temperature coefficient} = \frac{k_{(t+10)^{\circ}\text{C}}}{k_{t^{\circ}\text{C}}} = \frac{k_{35^{\circ}\text{C}}}{k_{25^{\circ}\text{C}}} = 2$$

If k_1 and k_2 are the rate constants of a given chemical reaction at two different temperatures, T_1 and T_2 , and assuming the free exponential factors are same at different temperatures.

Catalyst increases the rate by lowering of energy of activation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (\text{or})$$

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

Catalyst : A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent change. Catalyst increases the rate of reaction by changing the path of the reaction. In the presence of a catalyst, the reaction takes place through a different path of lower activation energy as shown in Fig 3.3.

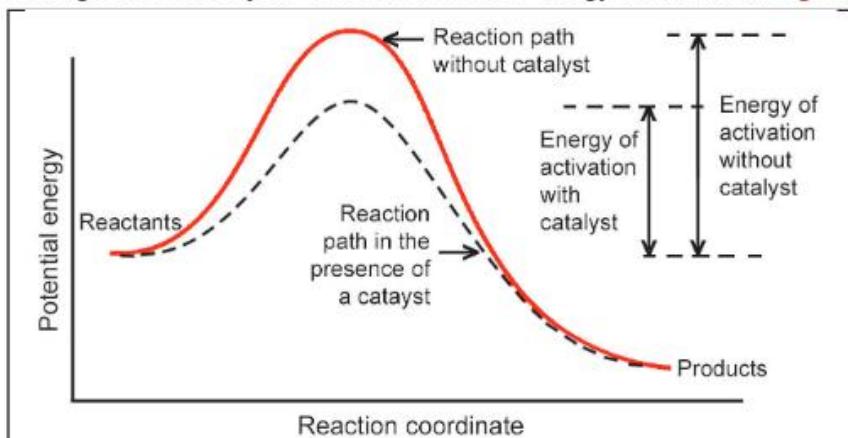


Fig 3.3 Path of uncatalysed and catalysed reaction

It may be noted that photochemical reactions are fast, because of the production of highly reactive intermediates obtained with the help of light. It is also to be noted that smaller the particle size of the solid reactants, greater is the surface area and higher is the rate of reaction.



P.3.1 Formation of water from its elements is spontaneous, but is slow. Comment.

Solution Free energy decreases during the formation of water from its elements. Hence, thermodynamically the reaction is spontaneous. Criterion of spontaneity should not be correlated with time. Spontaneous reaction means that it will take place but how long it will take, thermodynamics does not tell.

At room temperature, without using a catalyst, about 1% of the reaction is complete in one year. The reaction is slow. It is kinetically non-spontaneous.



P.3.2 Express the rate of the reaction between bromide and bromate ions in acid medium.

Solution The reaction between bromide and bromate ions in acid medium is given by the equation,



The rate of the reaction is expressed as,

$$\text{Rate} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t}.$$



P.3.3 $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$. The rate of disappearance of nitrogen is $0.02 \text{ mol L}^{-1} \text{s}^{-1}$. What is the rate of appearance of ammonia?

$$\text{Solution} \quad \frac{\Delta[\text{N}_2]}{\Delta t} = 0.02 \text{ mol L}^{-1} \text{s}^{-1} = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

The rate of appearance of ammonia = $0.04 \text{ mol L}^{-1} \text{s}^{-1}$. It is also given as $0.68 \text{ g L}^{-1} \text{s}^{-1}$.

CHEMISTRY IID



P.3.4 $2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$; $2\text{NO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$. Which is relatively faster ? Why ?

Solution $2\text{NO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{NO(g)}$ is relatively faster. In both the reactions, the stoichiometry is same and number of bonds transformed is also same. The number of electrons shared in CO molecule is 6 and in NO molecule is 5. Breaking bond in NO molecule is relatively easy than that in CO molecule. Further NO has unpaired electron and thus more reactive.



P.3.5 Decolourisation of acidified permanganate is fast by Mohr's salt, but is slow by oxalate. Explain.

Solution Oxalate, OOC-COO^- , on oxidation gives CO_2 . It involves breaking of C–C bond, which requires energy. Hence decolourisation of MnO_4^- by $\text{C}_2\text{O}_4^{2-}$ is slow. On the other hand Mohr's salt is a complex salt containing Fe^{2+} ions.



P.3.6 At 27°C and 37°C , the rates of a reaction are given as $1.6 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$. Calculate the energy of activation for the given reaction.

Solution The ratio of specific rates at two different temperatures are given as,

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

Substituting the values k_1 , k_2 , T_1 , T_2 and molar gas constant R

$$0.301 = \frac{E_a \times 1000}{2.303 \times 8.314} \times \frac{10}{300 \times 310}$$

$$\text{Energy of activation} = E_a = 53 \text{ kJ mol}^{-1}$$



P.3.7 The temperature coefficient of a reaction is 2 and the rate of the reaction at 25°C is $3 \text{ mol L}^{-1} \text{ min}^{-1}$. Calculate the rate at 75°C .

Solution According to Arrhenius, for every 10°C rise in the temperature, the rate of reaction is doubled.

Rise in the temperature = $75^\circ\text{C} - 25^\circ\text{C} = 50^\circ\text{C} = 5 \times 10^\circ\text{C}$

The increase in the rate of the reaction = $2^5 = 32$ times

The rate of reaction $75^\circ\text{C} = 3 \times 32 = 94 \text{ mol L}^{-1} \text{ min}^{-1}$.



P.3.8 Pre-exponential factor for a reaction is $8.4 \times 10^{21} \text{ mol L}^{-1} \text{ s}^{-1}$. What will be the specific rate at a temperature of one million degree?

Solution Arrhenius equation for the specific rate, $k = A e^{-E_a/RT}$

Since temperature T is very large, T^{-1} tends to zero and e^0 becomes equal to 1.

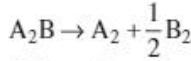
Specific rate of the reaction, $k = A = 8.4 \times 10^{21} \text{ mol L}^{-1} \text{ s}^{-1}$.



P.3.9 A_2B is an ideal gas, which decomposes according to the equation: $\text{A}_2\text{B} \rightarrow \text{A}_2 + \frac{1}{2}\text{B}_2$.

At start, the initial pressure is 100 mm Hg and after 5 minutes, the pressure is 120 mm Hg . What is the average rate of decomposition of A_2B ? Assume T and V are constant.

Solution The decomposition reaction of gaseous A_2B is given as



100 0 0 at start of the reaction

100-2x 2x x after the reaction

$$100 - 2x + 2x + x = 100 + x = 120 \text{ mm}$$

$$x = 20 \text{ mm or } 2x = 40 \text{ mm}$$

The decrease in pressure of reactant substance, A_2B in 5 min is 40 mm.

$$\begin{aligned} \text{The rate of decomposition of } \text{A}_2\text{B} &= \frac{40}{5} = 8 \text{ mm min}^{-1} \\ &= 0.133 \text{ mm s}^{-1} \end{aligned}$$

EXERCISE - 3.1.1

- Mention different types of reactions based on their speeds. Give examples.
- What are average rate and instant rate? How is rate determined graphically?
- How nature and concentration of reactants influence the rate of a reaction.
- Discuss the effect of temperature on the rate of a reaction.
- What is catalyst? How does it influences the rate?
- Define rates with respect to substances and rate of the reaction for Haber's process, $N_2 + 3H_2 \rightarrow 2NH_3$.
- In a reaction, $2A \rightarrow$ Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?
(Ans : $0.005\text{ mol L}^{-1}\text{ min}^{-1}$)
- For the reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction.
(Ans : $6.66 \times 10^{-6}\text{ Ms}^{-1}$)
- The first order rate constant for the decomposition of ethyl iodide by the reaction $C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$, at 600 K is $1.60 \times 10^{-5}\text{ s}^{-1}$. Its energy of activation is 209 kJ/mol . Calculate the rate constant of the reaction at 700K . (Ans : $6.4 \times 10^{-4}\text{s}^{-1}$)

RATE LAW**3.2.1****Rate equation**

Butyl chloride on hydrolysis gives butyl alcohol. At different intervals of time, the concentration change and the average rates are listed in Table 3.2.

Table 3.2 Average rates of hydrolysis of butyl chloride

Completion of C_4H_9Cl , mol L^{-1}	Time, sec	Average rate of the reaction, $\text{mol L}^{-1}\text{s}^{-1}$
0.1000	0	—
0.0905	50	1.90×10^{-4}
0.0820	100	1.71×10^{-4}
0.0741	150	1.58×10^{-4}
0.0671	200	1.40×10^{-4}
0.0549	300	1.22×10^{-4}
0.0355	500	1.07×10^{-4}
0.0171	800	0.55×10^{-4}

The results show that the rate of reaction decreases with time as the concentration of the reactants decrease. Conversely rate of reaction increases when reactant concentration increases. The dependence of rate with concentration was proposed by Guldberg and Waage in the form of law of mass action. The rate at which the reaction proceeds is directly proportional to the product of concentrations of reactants.

The dependence of the rate of the reaction on the concentration of each of the reactants is established from the experimental results. The results so obtained are presented in the form of a mathematical equation, which is known as rate law or rate equation. Rate equation is an experimentally established equation.


Equation giving rate in terms of concentration of reactants is called rate law


The equation that describes mathematically the dependence of the rate of a reaction on the concentration terms of the reactants is known as rate law. If no complexities are present in the mechanism the reaction are called elementary reactions. The rate equation can be written using the stoichiometric equation of the chemical reaction. In case of complex reactions, rate equation can not be written using stoichiometric equation of the chemical reaction.

The formation of nitrogen dioxide by the oxidation of nitric oxide is given as, $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$.

The rate of this reaction can be measured as a function of initial concentrations, either by keeping the concentration of one of the reactants constant and changing that of the other reactant or by changing the concentrations of both reactants. The experimental results are presented in Table 3.3.

Table 3.3 Initial rate of formation of nitrogen dioxide

Experiment	Initial concentrations		Initial rate, mol L ⁻¹ s ⁻¹
	NO, mol L ⁻¹	O ₂ , mol L ⁻¹	
A	0.3	0.3	0.096
B	0.3	0.6	0.193
C	0.6	0.3	0.384
D	0.6	0.6	0.767

When the concentration of O₂ is doubled, keeping the concentration of NO constant, the rate is doubled. When the concentration of NO is doubled, keeping the concentration of O₂ constant, the rate increases by a factor of four. Hence the rate depends on the concentration of O₂ to the first power and concentration of NO to the second power. The rate equation for the reaction is given as,

$$\text{Rate} \propto [\text{NO}]^2 [\text{O}_2]$$

3.2.2

Rate constant

For an elementary reaction,
 $x\text{A} + y\text{B} \rightarrow \text{Products}$.

The rate equation is given as,

$$\text{Rate} \propto [\text{A}]^x [\text{B}]^y \quad (\text{or}) \quad \text{Rate} = k [\text{A}]^x [\text{B}]^y,$$

Here k is the proportionality constant called rate constant.

If the rate equation is given as, Rate = k[C]ⁿ, then the rate constant (k)
 $k = \text{Rate} / [\text{C}]^n$.

Here 'n' depends upon the nature of reaction. It may be any integer or zero or a fraction.

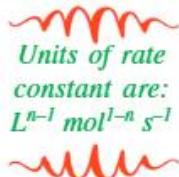
If the concentration of each reactant is taken as one mol L⁻¹, the rate of the reaction is equal to rate constant and the rate constant is called specific rate constant. Specific rate constant is independent of the concentration of reactant. It depends, for a given reaction, only on temperature. The main differences between rate and rate constant of a reaction are given in Table 3.4.


Specific rate is independent on concentration


Table 3.4 Differences between rate of reaction and rate constant

Rate of reaction	Rate constant
1. Rate is the speed with which reactants are converted into products.	1. Rate constant is a proportionality constant.
2. It is the change in concentration of a reactant or a product per unit time.	2. It is equal to the reaction rate at unit concentration of reactants.
3. It is dependent on the concentration of reactants.	3. It is independent on concentration of reactants.
4. It can be given as average rate or instant rate for a given reaction.	4. It can be given only in a single fashion for a given reaction.
5. It is dependent on the reaction temperature and catalyst.	5. It is also dependent on the reaction temperature and catalyst.
6. Units of reaction rate are : mol L ⁻¹ s ⁻¹	6. Units of rate constant are: mol ⁽¹⁻ⁿ⁾ s ⁻¹ , when n is the order of reaction.

Rate constant or specific rate is defined as the rate of reaction corresponding to unit concentration of all the reactants in a reaction.


Units of rate constant are:
 $L^{n-1} \text{ mol}^{1-n} \text{ s}^{-1}$

$$\text{Units of rate constant} = \frac{\text{units of rate}}{[\text{units of concentration}]^n}$$

In general, units for rate constant are: $L^{(n-1)} \text{ mol}^{(1-n)} \text{ s}^{-1}$.

Some examples of rate law and units of rate constant are given in Table 3.5. In few reactions, the rate law is not reflected by the stoichiometric coefficients of chemical equation.

Table 3.5 Rate law and units of rate constant of same chemical reactions

Chemical reaction	Experiment rate law	Units of rate constant
$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	Rate = $k[\text{H}_2\text{O}_2]$	s^{-1}
$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	Rate = $k[\text{NO}]^2 [\text{O}_2]$	$\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$
$2\text{NH}_3 + \text{Cl}_2 \xrightarrow{\text{Pt, 1130K}} \text{N}_2 + 3\text{H}_2$	Rate = k	$\text{mol L}^{-1} \text{ s}^{-1}$
$\text{C}_2\text{H}_4 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6$	Rate = $k [\text{C}_2\text{H}_4]$	s^{-1}
$\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$	Rate = $k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$	$\text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$
$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	Rate = $k [\text{CH}_3\text{COOC}_2\text{H}_5]$	s^{-1}



P.3.10 Rate of a chemical reaction depends on concentration of reactants, but the rate constant is independent on concentration. Why?

Solution According to law of mass action rate of a reaction is proportional to the concentration of each reactant involved in the reaction.

Rate constant is the rate of reaction at unit concentration of each reactant. Hence rate constant is independent of concentrations of reactants.

Therefore rate is dependent and rate constant is independent on the concentration.



P.3.11 For a reaction, $aA \rightarrow \text{Products}$, the units of rate constant are given as $\text{L mol}^{-1} \text{ s}^{-1}$. Write the rate expression.

Solution Units of rate constant of the reaction = $\frac{\text{units of rate}}{(\text{concentration})^n}$
 $\text{L mol}^{-1} \text{ s}^{-1} = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^n}$

Therefore the value of n is equal to 2.

Rate equation for the reaction is given as, rate = $k [A]^2$.



P.3.12 Rate expressions for two reactions are : (a) rate_a = $k_a[A]$ and (b) rate_b = $k_b[B]^2$.

When $[A] = [B] = 1 \text{ mol L}^{-1}$, $k_a = k_b \text{ mol L}^{-1}$. If $[A] = [B] = 2 \text{ mol L}^{-1}$, write the relation between rate_a and rate_b.

Solution Rate_a = $k_a [2 \text{ mol L}^{-1}]$

$$\text{Rate}_b = k_b [2 \text{ mol L}^{-1}]^2 = k_a [2 \text{ mol L}^{-1}]^2$$

The ratio of the rates of two reactions (a) and (b) is given as,

$$\frac{\text{Rate}_a}{\text{Rate}_b} = \frac{k_a [2 \text{ mol L}^{-1}]}{k_a [2 \text{ mol L}^{-1}]^2} = \frac{1}{2}$$

The ratio of the rates = 1 : 2.



P.3.13 Units of rate constant is the same for the elementary reactions :

Reaction (1), $A + B + C \rightarrow \text{products}$;

Reaction (2), $A + 2B \rightarrow \text{products}$;

Reaction (3), $3A \rightarrow \text{products}$. Substantiate.

Solution $A + B + C \rightarrow \text{products}$; rate = $k [A] [B] [C]$

$A + 2B \rightarrow \text{products}$; rate = $k [A] [2B]^2$

$3A \rightarrow \text{products}$; rate = $k [A]^3$

Since the number of concentration terms is the same for all the rate laws, the units of rate constant are also same.

The units of rate constant of any of these reactions are $\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$.



P.3.14 The decomposition of nitrogen pentoxide is given as $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. The rates of reaction

$$\text{are } \frac{[\text{N}_2\text{O}_5]}{\Delta t} = k_1 [\text{N}_2\text{O}_5]; \frac{\Delta[\text{NO}_2]}{\Delta t} = k_2 [\text{N}_2\text{O}_5] \text{ and } \frac{\Delta[\text{O}_2]}{\Delta t} = k_3 [\text{N}_2\text{O}_5].$$

Relate the rate constants, k_1 , k_2 and k_3 .

Solution The rate of the reaction is given as $-\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = +\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = +\frac{1}{1} \frac{\Delta[\text{O}_2]}{\Delta t}$

Substituting the given values of rate in the above expression ,

$$\frac{1}{2} k_1 [\text{N}_2\text{O}_5] = \frac{1}{4} k_2 [\text{N}_2\text{O}_5] = \frac{1}{1} k_3 [\text{N}_2\text{O}_5]$$

Therefore, the rate constants k_1 , k_2 and k_3 are related as,

$$2k_1 = k_2 = 4k_3.$$

EXERCISE - 3.1.2

- Define rate law. How is it related to the stoichiometric equation and experimental results?
- What are (a) rate constant and (b) specific rate? Write the units of rate constant.
- Write four main differences between reaction rate and reaction rate constant.

4. The initial concentration of N_2O_5 in the following first order reaction $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$ was 1.24×10^{-2} mol L⁻¹ (Ans : 0.03 min^{-1})
5. Write the rate law and units of rate constant for the following elementary reactions.
 (a) A + B → Products, (b) 2A → Products, (c) 2A + B → Products and
 (d) A + 2B → Products.
6. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P (mm of Hg)
0	35.0
360	54.0
720	63.0

(Ans : $2.2 \times 10^{-3} \text{ min}^{-1}$)

THEORY OF REACTION RATES

3.3.1

Arrhenius theory

The rate constant of a reaction is given in terms of frequency factor (A), energy of activation (E_a) and absolute temperature (T) as,

$$k = Ae^{-E_a/RT} \quad (\text{or}) \quad \ln k = \ln A - \frac{E_a}{RT}$$

Arrhenius provided the physical justification for the rate of reaction. He interpreted that the main factor on which the rate of a chemical reaction depends is energy of activation (E_a).

Consider the formation of hydrogen iodide on heating gaseous hydrogen and iodine. According to Arrhenius, this reaction take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate as shown in Fig 3.4. The intermediate is called transition state, as it exists for a very short period of time. It breaks up to form finally product molecules.

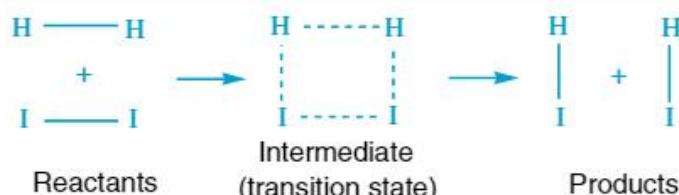


Fig 3.4 Formation of hydrogen iodide from elements through transition state

The central idea of transition state is that bond breaking and bond making must occur in a reaction continuously or simultaneously.

The energy required to form this activated complex intermediate is called activation energy. Activated complex has more energy compared to reactants as well as products. Hence its stability is very less. Formation of transition state is slow, but its transformation is fast. The formation of transition state can be detected these days as the sophistication highly sensitive instruments are available to detect these short lived species (10^{-10} – 10^{-15} s). Before the invention of these instruments, existence of transition state was proposed to explain the Arrhenius equation and reaction mechanism.

Intermediate formed between reactants and products is called transition state

Energy required to form activated complex is called activation energy

All the molecules of reacting substances do not have the same kinetic energy. In the Maxwell's curve of the distribution of molecular velocities of gases, the peak position corresponds to most probable kinetic energy. With an increase in the temperature, fraction of molecules with lower kinetic energy decreases and that with higher kinetic energy increases as shown in Fig 3.5. It is clear that at $(t + 10)$, the molecule having energy greater than activation energy get doubled, leading to doubling the rate of the reaction.

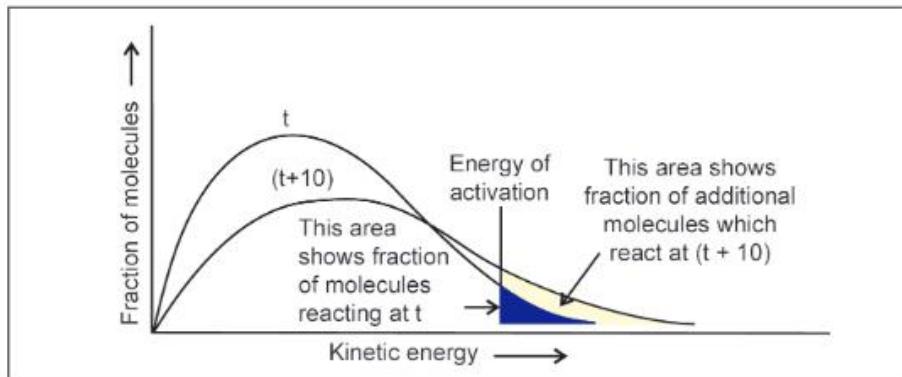


Fig 3.5 Maxwell distribution curve showing dependence of kinetic energy on temperature

3.3.2

Collision theory

Reaction occurs when molecules collide with each other

Molecular collision theory of reaction rates was developed by Trautz and Lewis. It is based on kinetic theory of gases. It provides a better insight into the energetic and mechanistic aspects of chemical reaction. According to simpler molecular collision theory, the reactant molecules are assumed to be hard spheres. The reaction is postulated to occur when molecules collide with each other.

The main points of collision theory are:

1. The reactant molecules must collide together, if they are to react with each other.
2. The number of collisions per sec per unit volume of the reaction mixture is generally high and is known as collision frequency.
3. All collisions do not lead to chemical reactions. Only those collisions give rise to chemical reaction in which the molecules acquire energy level greater than or equal to threshold energy.

Energy of colliding molecular is more than that of product molecules in an exothermic reaction.

Energy of colliding molecules is less than that of product molecules in an endothermic reaction.

The energy barrier diagram is given in Fig 3.6 for both exothermic and endothermic reactions

The change in enthalpy (ΔH) is negative in an exothermic reaction and is positive in an endothermic reaction

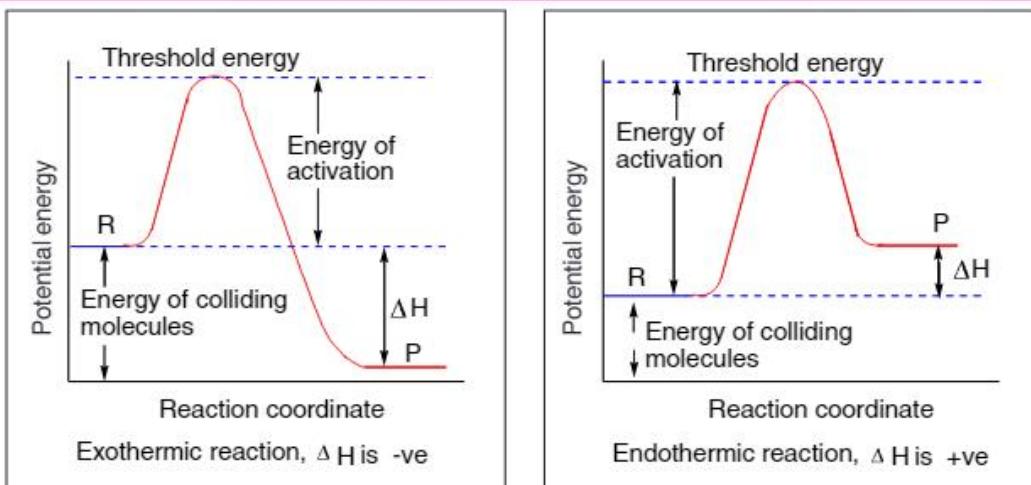


Fig 3.6 Energy profile diagrams

Fraction of fruitful collisions is given as

$$\frac{k}{A} = e^{-E_a/RT}$$

Collisions having threshold energy are called effective collisions

- Collisions possessing a minimum of threshold energy are called effective collisions. These are also called fruitful or productive collisions. The fraction of fruitful collisions is given as $\frac{k}{A} = e^{-E_a/RT}$.
- Collisions among molecules possessing energy less than threshold energy do not result in the formation of products. They are called normal collisions. They are to be provided with excess energy.
- The additional energy required by reacting molecules to attain threshold energy is called activation energy.

Activation energy = Threshold energy – Energy of colliding molecules.

- In addition to the requirement that the reactant species collide with sufficient energy for the rearrangement of bonds, an orientational requirement also exists. Proper orientation of reactant molecules lead to bond formation as shown in Fig 3.7. Improper orientation makes them simply bounce back and no products are formed.

If P is the orientation factor and Z is the collision factor, $k = PZ e^{-E_a/RT}$.

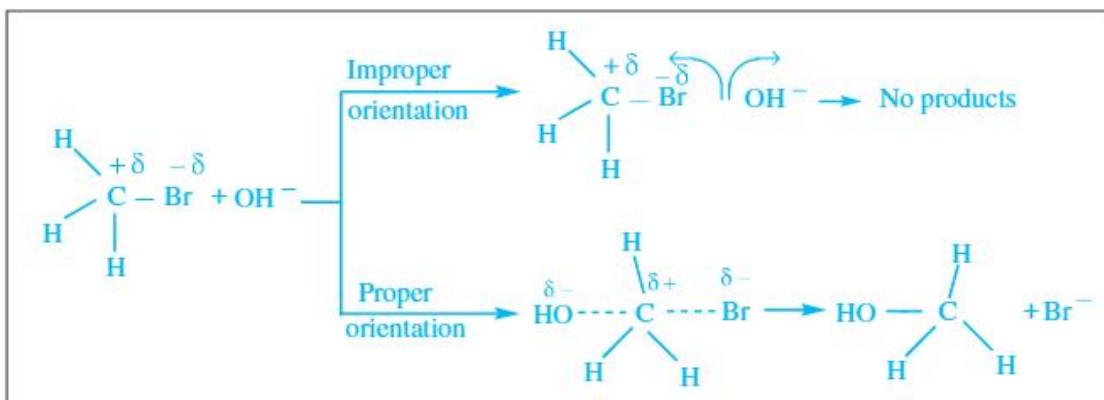
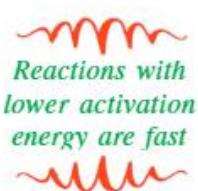


Fig 3.7 Proper and improper orientation of molecules

For a molecule of AB, σ is collision diameter and μ is reduced mass. k is the Boltzmann constant and T is the temperature in kelvin.

Thus in collision theory activation energy and proper orientation of molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Energy of activation is a factor characteristic of reactants. It is independent of concentration and pressure, but to the first approximation, independent of temperature also. If activation energy of forward reaction (E_{af}) is less than that of the backward reaction (E_{ab}), the reaction is exothermic.



The heat of the reaction, $\Delta H = E_{af} - E_{ab}$

Reactions with lower activation energy are fast and with higher activation energy are slow. For ionic reactions, the energy of activation is negligibly small and hence they are instantaneous. For covalent reactions, the energy of activation is high and the reactions are time consuming. Introduction of a catalyst alters the path, with a newer path of low activation energy, the time required for a covalent reaction is also low.



P.3.15

An increase in temperature by 10° , can increase the number of collisions only by 2%, but the rate of reaction increases by 100%. Why?

Solution

Temperature is directly proportional to kinetic energy. Number of collisions is proportional to velocity or square root of temperature.

However, in the Arrhenius rate expression, rate increases exponentially but not linearly, with a change in temperature. The number of molecules exceeding the activation energy approximately doubles by a 10° rise in temperature. Hence rate increases by 100%.



P.3.16

What is the difference between activated complex and unstable intermediate?

Solution

An unstable intermediate is an actual chemical species. It has normal bond orders. It may be stabilised under different reaction conditions. Activated complex is postulated species, which has maximum energy during the conversion from reactants to products. No matter which way the bond lengths and bond strengths vary, stabilisation does not result.



P.3.17

At 25°C the activation energy for a catalysed reaction is 162 kJ mol^{-1} and for uncatalysed reaction is 350 kJ mol^{-1} . How many times the rate is increased in the presence of catalyst?

Solution

According to Arrhenius equation, the specific rates (k) of a reaction with different activation energies (E_a) are given as

$$\log \frac{k_1}{k_2} = \frac{1}{2.303RT} [E_{a_2} - E_{a_1}] = \frac{(350 - 162)1000}{2.303 \times 8.314 \times 298}$$

Therefore the ratio of rates, $k_1/k_2 = 8.9 \times 10^{32}$.

In the presence of a catalyst rate is increased by 8.9×10^{32} times.



P.3.18

Energy of activation and orientation of molecule together determine the criteria for effective collision. Explain.

Solution

In the molecular collision theory of reaction rates,

Rate constant, $k = PZ e^{-E_a/RT}$

Here P is the orientation factor and Z is the collision factor.

The product of P and Z is the pre-exponential factor, A in the Arrhenius theory.

Rate constant, $k = A e^{-E_a/RT}$.

EXERCISE - 3.1.3

- What is activated complex? Discuss its formation and transformation.
- Write the main points of collision theory of reaction rates.
- Distinguish between a proper and an improper collision.
- How is the reaction rate influenced by energy of activation?
- The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298 K. Calculate E_a .
(Ans : 52.9 kJ mol⁻¹)
- The activation energy for the reaction $2\text{HI(g)} \rightarrow \text{H}_2 + \text{I}_2(\text{g})$ is 209.5 kJ mol⁻¹ at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?
(Ans : 1.47×10^{-19})

MOLECULARITY AND ORDER**3.4.1****Molecularity of reaction**

Majority of chemical reactions known are complex reactions. Only few reactions are elementary reactions. An elementary reaction is that in which the reactants are directly converted into final products in a single step. In a complex reaction, reactants are converted into final products through different elementary steps.

A sequential representation of elementary steps in an overall chemical reaction is known as reaction mechanism. For example, the reaction $\text{A} \rightarrow \text{Z}$, may take place in the elementary steps as : $\text{A} \rightarrow 2\text{B}$; $2\text{B} \rightarrow \text{I}$ and $\text{I} \rightarrow \text{Z}$, where B and I are intermediates.

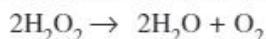
The number of atoms or molecules or ions participating in an elementary step which must collide simultaneously to bring about a chemical reaction is called molecularity. In a chemical reaction, every elementary step has a molecularity of its own. Elementary reactions take place one after another with different rates.

The slowest among different elementary steps of a reaction, limits the rate of the reaction and is called rate determining step. The rate of overall reaction is controlled by the rate limiting step. The number of atoms or molecules or ions participating in the rate determining step of the reaction is called overall molecularity of the reaction.

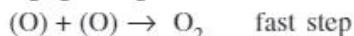
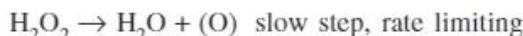
The reaction can be unimolecular when one reacting species is involved. Decomposition of ammonium nitrite to give nitrogen is an example of unimolecular reaction. Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide into elements. Trimolecular reactions involve simultaneous collision between three reacting species. Trimolecular reactions are also called termolecular reactions. Molecularity of the oxidation of colourless nitric oxide to coloured nitrogen dioxide is three.

The probability that four or more molecules collide simultaneously to give product is very small. Hence molecularity greater than three is rare. Molecularity is never zero and it can not be fractional.

The decomposition of hydrogen peroxide is unimolecular, though the stoichiometric equation for the decomposition of hydrogen peroxide is given as,

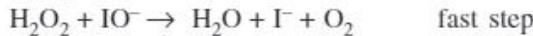


The mechanism of the decomposition of hydrogen peroxide has two steps:



$$\text{Rate of the reaction} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2].$$

The decomposition of hydrogen peroxide, catalysed by iodide ion in alkaline medium is bimolecular. The mechanism has two steps:



$$\text{Rate of the reaction} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2][\text{I}^-].$$

3.4.2

Order of reaction



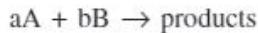
*Sum of powers
of concentration
terms in rate law
is called order*



The rate of a given chemical reaction at constant temperature depends on the product of the concentration terms of the reactants. The equation representing the rate of reaction is called rate law. The sum of the powers of the concentration terms in the rate equation is called order of the reaction.

In the rate equation, rate = $k [C]^n$, the order of the reaction is ‘n’.

For a general reaction,



The rate equation is given as, Rate = $k [\text{A}]^x [\text{B}]^y$.

The order with respect to reactant A is ‘x’, with respect to reactant B is ‘y’ and the overall order of the reaction is $(x+y)$. Here the stoichiometric coefficients of the reactants ‘a’ and ‘b’ may or may not be equal to ‘x’ and ‘y’.

Unlike molecularity, order of the reaction may be zero, a finite number or fractional. Accordingly reactions are classified as zero, first, second, third, etc., or in general n^{th} order reaction.

The mass differences between molecularity and order of chemical reactions are summarised in **Table 3.6**.

Table 3.6 Differences between molecularity and order of reaction

Molecularity of reaction	Order of reaction
1. Molecularity is the number of atoms or molecules or ions participating the rate limiting step of a reaction	1. Order is the sum of powers of concentrations terms in rate equation
2. It is obtained from the reaction mechanism	2. It is obtained from the experimentally derived rate law
3. Molecularity may be 1,2 or 3	3. Order may be 1,2 or 3
4. Molecularity is neither zero nor fractional	4. Order may be zero or it may be fractional
5. It is defined for every step, called	5. It is defined for whole reaction elementary reaction

3.4.3**Integrated rate equations**

Differential rate equation upon integration gives a relation between directly measured experimental concentrations at different times and rate constant. The integrated rate equations are different for the reactions of different orders.

Reaction in which rate of the reaction is independent of the concentration of the reaction substances is called zero order reaction. Starting from an initial concentration of reactant is $[R]_0 = 'a'$, if ' x ' is the concentration transformed in a time interval of ' t ', the concentration of the reactant after time ' t ' is $[R]_t = '(a - x)'$.

Rate is dependent on single concentration term in a first order reaction
Rate constant of first order reaction is
 $k = \frac{1}{t} \ln \frac{a}{a-x}$

$$\text{Rate} = -\frac{-dC}{dt} = \frac{d(a-x)}{dt} = k(a-x)^0 = k.$$

$$\int dx = K \int dt \quad (\text{or}) \quad x = Kt \quad (\text{or}) \quad \text{specific rate, } K = x/t$$

Reaction in which rate of the reaction is directly proportional to the single concentration term of the reacting substance is called first order reaction.

$$\text{Rate} = -\frac{-dC}{dt} = \frac{d(a-x)}{dt} = \frac{dx}{dt} = k(a-x)$$

$$\int \frac{dx}{a-x} = \int k dt \quad (\text{or}) \quad -\ln(a-x) = kt + c$$

$$\text{When } t = 0, x = 0, -\ln(a-0) = k \times 0 + c \quad (\text{or}) \quad -\ln a = c$$

$$\text{Hence, } -\ln(a-x) = kt - \ln a$$

$$kt = \ln \frac{a}{(a-x)} \quad (\text{or}) \quad k = \frac{1}{t} \ln \frac{a}{(a-x)} \quad (\text{or})$$

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

If p_i is initial pressure and p_t is total pressure at time t

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

A plot of $\ln(a-x)$ against time ' t ' for a first order reaction is a straight line with a slope of $-k$ and intercept of $\ln a$. A plot of $\ln a/(a-x)$ against time is also a straight line with a slope k as shown in Fig 3.8.

For a zero order reaction the graphs are different as shown in Fig 3.9. The rate of a zero order reaction is constant throughout the course of the reaction and is equal to the rate constant of the reaction.

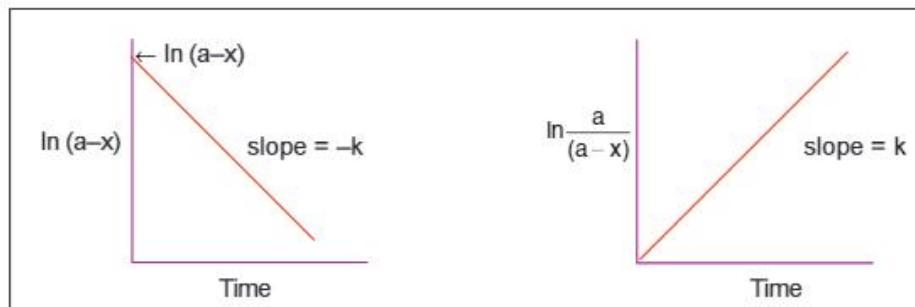


Fig 3.8 First order reactions graphs


*Rate of a zero
order reaction is
equal to its rate
constant*

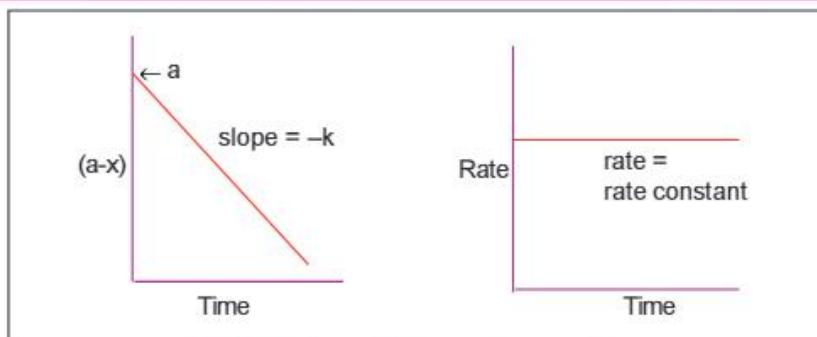



Fig 3.9 Zero order reaction graphs

Half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

Half-life is represented as $t_{0.5}$ or $t_{1/2}$.

The time 't' will be ' $t_{1/2}$ ' when $(a - x) = a/2$.

For a zero order reaction, the rate constant (k) is

$$k = \frac{x}{t} \quad (\text{or}) \quad t = \frac{x}{k}$$

The half-life is given as, $t_{1/2} = \frac{a}{2k}$

Half-life of a zero order reaction is directly proportional to the initial concentration of reactants and inversely proportional to the specific rate.

For a first order reaction, the rate constant (k) is

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad (\text{or})$$

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

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a/2} = \frac{2.303 \log 2}{k} \quad (\text{or})$$

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

Half-life of a first order reaction is a constant. It is independent of the initial concentration of reactant. It is only dependent on nature of the substances and temperature.

The relation between initial amount of the substance and substance left unreacted following first order kinetics after 'n' half-lives is given as,

$$\text{Amount left unreacted} = \frac{\text{Initial amount taken}}{2^n}$$

Integrated rate laws, units of rate constants and half-life expressions for some reactions are listed in Table 3.7.

Examples of different orders of chemical reactions are given in Table 3.8.

Table 3.7 Differential and integrated rate laws of some reactions

Order of reaction	Differential rate law	Integrated rate law	Units of rate constant	Half-life
Zero order	$-\frac{dc}{dt} = k$	$k = \frac{x}{t}$	$\text{mol L}^{-1} \text{ s}^{-1}$	$t_{1/2} = \frac{a}{2k}$
First order	$-\frac{dc}{dt} = k(a-x)$	$k = \frac{2.303}{t} \log \frac{a}{a-x}$	s^{-1}	$t_{1/2} = \frac{\ln 2}{k}$
Second order	$-\frac{dc}{dt} = k(a-x)^2$	$k = \frac{1}{t} \frac{x}{a(a-x)}$	$\text{L mol}^{-1} \text{ s}^{-1}$	$t_{1/2} = \frac{1}{ka}$

Table 3.8 Examples of different orders of chemical reactions

Order	Example of the chemical reaction and equation	Rate law
Zero	Decomposition of ammonia gas on hot platinum surface $2\text{NH}_3(\text{g}) \xrightarrow{\text{Pt}} \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	Rate = $k[\text{NH}_3]^0$ (or) Rate = k
First	Thermal decomposition of nitrogen pentoxide $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$	Rate = $k[\text{N}_2\text{O}_5]$
First	Decomposition of aqueous hydrogen peroxide $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$	Rate = $k[\text{H}_2\text{O}]$
First	Decomposition of ammonium nitrite $\text{NH}_4\text{NO}_2(\text{s}) \xrightarrow{\Delta} 2\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$	Rate = $k[\text{NH}_4\text{O}_2]$
First	Thermal decomposition of gaseous sulphuryl chloride $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$	Rate = $k[\text{SO}_2\text{Cl}_2]$
Second	Decomposition of chlorine monoxide $2\text{Cl}_2\text{O}(\text{g}) \rightarrow 2\text{Cl}_2(\text{g}) + \text{O}_2(\text{g})$	Rate = $k[\text{Cl}_2\text{O}]^2$
Second	Thermal decomposition of nitrous oxide $2\text{N}_2\text{O}(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$	Rate = $k[\text{N}_2\text{O}]^2$
Second	Alkaline hydrolysis of ethyl acetate $\text{AcC}_2\text{H}_5(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaAc}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{l})$	Rate = $k[\text{Ac C}_2\text{H}_5][\text{OH}^-]$
Third	Oxidation of nitric oxide to nitrogen dioxide $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$	Rate = $k[\text{NO}]^2 [\text{O}_2]$
Third	Formation of nitrosyl chloride from nitric oxide $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NOCl}(\text{g})$	Rate = $k[\text{NO}]^2 [\text{Cl}_2]$
Third	Reduction of ferric chloride by stannous chloride $\text{SnCl}_2(\text{aq}) + 2\text{FeCl}_3(\text{aq}) \rightarrow \text{SnCl}_4(\text{aq}) + 2\text{FeCl}_2(\text{aq})$	Rate = $k[\text{Sn}^{2+}][\text{Fe}^{3+}]^2$

3.4.4

Determination of order of reaction

Starting from initial concentration 'a' if the change in concentration in time 't' is 'x' the rate equation in terms of order of the reaction 'n' is given as,

$$\text{Rate of reaction} = \frac{dx}{dt} = k(a-x)^n$$

The order of a reaction is determined using integrated equation method, half-life method, van't Hoff's differential method and Ostwald's isolation method.

Integrated form of rate equation method : It is also called trial and error method. The kinetic data is substituted in one of the integrated rate laws (Table 3.8) and the specific rates are calculated. If the same value of 'k' is obtained from the data of a reaction, the trial of choosing the rate law is successful and the corresponding order is obtained.

Alternately, the order can also be ascertained graphically interpreting the results in terms of integrated rate law. As shown in Fig 3.10, x vs time is a straight line parallel to time axis denotes zero order. $\log [a/(a-x)]$ vs time is a straight line with a positive slope passing through origin denotes first order. $[x/a(a-x)]$ vs time is a straight line with a positive slope passing through origin denotes second order.

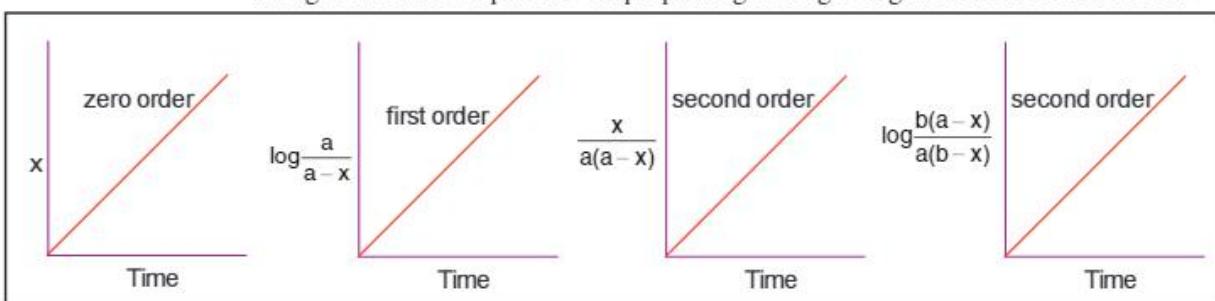
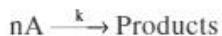


Fig 3.10 Graphical methods to determine the order of reaction

If 'n' is the order of a reaction,
 $t_{1/2} \propto a^{1-n}$

Half-time method : The time required for the initial concentration (a) of the reactant to become one-half of its value ($a/2$) during the progress of the reaction is called half-time ($t_{1/2}$) of the reaction. Half-time, also known as half-life is inversely proportional to $a^{(n-1)}$, where n is the order of the reaction of the type,



$$t_{1/2} \propto \frac{1}{a^{n-1}} \text{ (or) } t_{1/2} \propto a^{1-n}$$

Say a given reaction is started separately with two initial concentrations ' a_1 ', and ' a_2 '. The half - time values ($t_{1/2}$)₁ and ($t_{1/2}$)₂ are determined experimentally and the order is established from the equation.

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

Differential method : The rate of a reaction of order 'n' is given for two initial concentrations, C_1 and C_2 as

$$-\frac{dC_1}{dt} = kC_1^n \text{ and } -\frac{dC_2}{dt} = kC_2^n$$

$$\log\left(\frac{-dC_1}{dt}\right) = \log k + n \log C_1 \quad \text{and} \quad \log\left(\frac{-dC_2}{dt}\right) = \log k + n \log C_2$$

$$\log\left(-\frac{dC_1}{dt}\right) - \log\left(\frac{dC_2}{dt}\right) = n (\log C_1 - \log C_2)$$

$$\text{Hence, order of the reaction, } n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right)}{\log C_1 - \log C_2}$$

This is called van't Hoff's equation.

Determining the rates of a reaction from the concentration time graphs of Fig 3.11, for two different initial concentration, order can be determined by substituting the rates in van't Hoff's equation

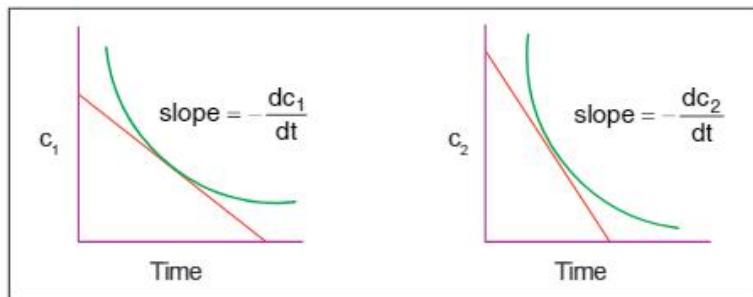
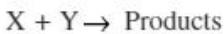


Fig 3.11 Rates of reactions from the slopes

Order with respect to each reactant is obtained using isolaton method



Ostwald's isolation method : The isolation method is useful for the determination of order with respect to each of the reactant separately.



By applying Ostwald's method, the order n_x with respect to the reactant X and n_y with respect to reactant Y are separately determined.

For the purpose of determining orders, two experiments are conducted. In one experiment, concentration of Y is taken in large excess compared to that of X. Order, n_x is determined by varying the concentration of X in one of the three methods described above. In the second experiment concentration of X is taken in large excess. Order, n_y is determined.

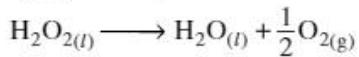
The total order of the reaction is $(n_x + n_y)$.

3.4.5

Some applications of first order reactions

Decomposition of H_2O_2

H_2O_2 Decomposes in solution obeying first order kinetics.



H_2O_2 being reducing agent the progress of reaction is determined by titrating against standard KMnO_4 solution and volume of KMnO_4 is proportional to the concentration of H_2O_2 . If V_0 and V_t be the volume of standard KMnO_4 solution required for complete oxidation of H_2O_2 at zero time and time 't'.

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

	$H_2O_2(l) \longrightarrow H_2O(l) + 1/2O_2(g)$
initial mol L ⁻¹	a 0 0
at time = t, mol L ⁻¹	a-x x x/2

$V_0 \propto a$ and $V_t \propto (a - x)$

$$\text{So, } k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Decomposition of N_2O_5 in CCl_4 i.e., liquid phase

It follows first order kinetics N_2O_5 in CCl_4 solvent decomposes to evolve O_2 , gas. Unreacted N_2O_5 and formed NO_2 remains dissolves in CCl_4 .



initially moles	a	0	0
moles at time = t	a-x	2x	x/2
moles at time = ∞	a-a	2a	a/2

If V_∞ and V_t is the volume of O_2 at $t = \infty$ and at time t, then $\frac{a}{2} \propto V_\infty \Rightarrow a \propto 2V_\infty$

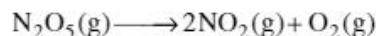
$$\text{similarly } \frac{x}{2} \propto V_t$$

$$\therefore x \propto 2V_t \quad \therefore a - x \propto 2(V_\infty - V_t)$$

$$\frac{a}{a-x} = \frac{V_\infty}{V_\infty - V_t}$$

$$kt = \ln \frac{a}{a-x} = \ln \frac{V_\infty}{V_\infty - V_t} \quad (\text{or}) \quad k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

Decomposition of N_2O_5 in gaseous phase



initial pressure	P_0	0	0
Partial pressure at time = t	$P_0 - x$	2x	x/2
Partial pressure at time = ∞	$P^0 - P^0$	$2P^0$	$\frac{P^0}{2}$

If total pressure P_∞ at infinite time or after the completion of reaction is given as well as P_T i.e., total pressure at time

= t is given then

$$\therefore 2P_0 + \frac{P_0}{2} = P_\infty \quad \text{or} \quad P_0 = \frac{2}{5}P_\infty$$

Now $P_0 - x + 2x + \frac{x}{2} = P_T$ or $x = \frac{2}{3}(P_T - P_0)$ putting the values of P_0 in terms of P_∞ and

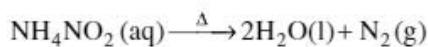
$\therefore x$ in terms of P_T and P_∞ , we get

$$\frac{P^0}{P^0 - x} = \frac{3P_\infty}{P_\infty - 5P_T}$$

$$kt = \ln \frac{P^0}{P^0 - x} = \ln \frac{3P_\infty}{5P_\infty - 5P_T}$$

$$k = \frac{1}{t} \ln \frac{3P_\infty}{10(P_\infty - P_T)}$$

Decomposition of NH_4NO_2



initial moles	a	0	0
moles at time = t	a - x	2x	x
moles at t = ∞	a - a	2a	a

The progress of the reaction can be known by measuring the volume of N_2 (g) evolved. If V_∞ and V_t be the volume of N_2 gas evolved at time t and at the completion of reaction then

$$k = \frac{1}{t} \ln \frac{V_\infty}{V_\infty - V_t}$$

3.4.6

Pseudo first order reactions

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between cane sugar and water. The reaction is called hydrolysis of sucrose and some times inversion of cane sugar. In practice the reaction is performed in the presence of large excess of water. During the hydrolysis of 0.01 mol of sucrose with 10 mol of water, amounts of various constituents of the beginning and completion of the reaction are given under.

$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	+ $\text{H}_2\text{O} \xrightarrow{\text{H}^+}$	$\text{C}_6\text{H}_{12}\text{O}_6$	+ $\text{C}_6\text{H}_{12}\text{O}_6$
Sucrose	Water	Glucose	Fructose
Initial	0.1 mol	10 mol	0 mol
After completion	0 mol	9.9 mol	0.1 mol

In this hydrolysis reaction sucrose is isolated by taking large excess of water. The concentration of water does not get altered much during the course of reaction.

The rate of the reaction is given as,

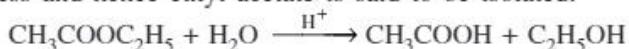
$$\text{Rate} = k' [\text{C}_{12}\text{H}_{22}\text{O}_{11}] [\text{H}_2\text{O}]$$

The term $[\text{H}_2\text{O}]$ can be taken as constant. The concentration of water is 55.5 mol L⁻¹, which is assumed constant. The equation thus becomes,

$$\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}], \text{ where rate constant, } k = k' [\text{H}_2\text{O}]$$

The reaction behaves as first order reaction in isolated conditions. Such reactions are called pseudo first order reactions or pseudo unimolecular reactions.

Base hydrolysis of ester is a second order reaction. Acid catalysed hydrolysis of ethyl acetate is a pseudo first order reaction, because water is taken large in excess and hence ethyl acetate is said to be isolated.



$$\text{Rate of the reaction, rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

The progress of reaction will be followed by standard alkali solution. If V_0 , V_t and V_∞ be the volumes of alkali needed to neutralise the given volume of the reaction mixture at time t = 0, t = t and t = ∞ . V_0 will be used to neutralise acid i.e., H^+

There by,

$$V_0 \propto [\text{H}^+]$$

$$V_t \alpha [H^+] + [CH_3COOH]_t \\ \text{or } V_t \alpha [H^+] + x \text{ or } V_t \alpha v_0 + x \Rightarrow x \alpha V_t - V_0$$

$$V_\infty [H^+] + [CH_3COOH]_\infty$$

$$\text{Similarly } V_\infty \alpha [H^+] + a \Rightarrow a \alpha V_\infty - V_0$$

$$a - x \alpha (V_\infty - V_0) = (V_t - V_0)$$

$$\text{or } a - x \alpha V_\infty - V_t$$

$$\text{So, } kt = \ln \frac{a}{a-x} = \ln \frac{V_\infty - V_0}{V_\infty - V_t}$$

In such a pseudo unimolecular reaction, the molecularity is 2, but the order of reaction is taken as 1.



- P.3.19** The rate constant of a reaction is $2.5 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$. Calculate the initial rate with concentration 0.2 mol L^{-1} .

Solution From the units of rate constant, order of the reaction is 2.

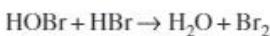
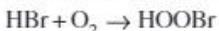
For a second order reaction, rate = $k [\text{concentration}]^2$

$$\text{Initial rate of the reaction} = 2.5 \times 10^{-2} (0.2)^2 = 1 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$



- P.3.20** $4\text{HBr} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2$. The molecularity of the reaction appears as 5, but experimentally, it is 2. Explain.

Solution The mechanism of oxidation reaction of HBr is given in three steps.



Molecularity of each step is 2. The overall molecularity of the slowest step (1st) is 2



- P.3.21** The experimental data for the reaction $2\text{A} + \text{B}_2 \rightarrow 2\text{AB}$ is given below. Based on the data write the rate equation.

[A], mol L ⁻¹	[B ₂], mol L ⁻¹	Rate, mol L ⁻¹ s ⁻¹
0.5	0.5	1.6×10^{-4}
0.5	1.0	3.2×10^{-4}
1.0	1.0	3.2×10^{-4}

Solution Keeping [A] constant, doubling [B₂], the rate is doubled. Hence, order with respect to 'B₂' is 1. Keeping [B₂] constant, doubling [A], there is no change in the rate. Hence, order with respect to 'A' is zero.

The rate equation is, rate = $K[A]^0[B_2]^1$ (or) rate = $K[B_2]$.



- P.3.22** 75% of a first order reaction is complete in 30 min. Calculate (a) half life, (b) rate constant and (c) time required for 99.9% completion of the reaction.

Solution Time required for 75% completion is 2 half-lives = 30 min.

$$(a) \text{Half-life } (t_{1/2}) = 15 \text{ min}$$

$$(b) \text{Rate constant, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{15} = 0.046 \text{ min}^{-1} \text{ (or) } 7.7 \times 10^{-4} \text{ s}^{-1}$$

$$(c) \text{Time required for 99.9\% of the reaction (t)}$$

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{0.046} \log \frac{100}{0.1} = 149 \text{ min}$$



P.3.23 For the reaction $X \rightarrow Y + Z$, if the initial concentration of X was reduced from 2M to 1M in 20 min and from 1M to 0.25M in 40min, find the order.

Solution Half-life, $(t_{1/2}) \propto a^{1-n}$.

Here, half-life is independent on the initial concentration.

The order of the reaction is 1.



P.3.24 A first order reaction is 20% complete in 10 min. How long it takes to complete 80%?

Solution Applying first order integral rate equation, rate constant K is given as,

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

$$k = \frac{2.303}{10} \log \frac{100}{100-20} = 0.0223 \text{ min}^{-1}$$

Time required for 80% completion of the first order reaction, $t_{0.8}$

$$t_{0.8} = \frac{2.303}{k} \log \frac{100}{100-80} = \frac{2.303}{0.0223} \log \frac{100}{20} = 72.2 \text{ min.}$$



P.3.25 $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$, The reaction, follows third order kinetics.

Write (a) rate law and (b) units of rate constant.

What happens to the rate if the volume of vessel is reduce to one - half at constant temperature ?

Solution (a) Rate law is given as, rate $= k [\text{NO}]^2 [\text{H}_2]$

(b) Units of rate constant $= \text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$

If volume of the vessel is halved, concentration of each reactant is doubled. The rate will be
Rate $= k [2\text{NO}]^2 [2\text{H}_2] = 8 k[\text{NO}]^2 [\text{H}_2]$

Rate will be 8 times more than the original rate of the reaction.



P.3.26 The initial concentration of ethyl acetate is 0.85 mol L^{-1} . Following the acid catalysed hydrolysis, the concentrations of ester after 30 min and 60 min of the reaction are respectively 0.8 and 0.754 mol L^{-1} . Calculate the rate constant and pseudo rate constant.

Solution Acid catalysed ester follows pseudo first order kinetics.

The rate constant k is given as

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

$$k = \frac{2.303}{30} \log \frac{0.85}{0.05} = 2.020 \times 10^{-3} \text{ min}^{-1} \quad (\text{or})$$

$$k = \frac{2.303}{30} \log \frac{0.80}{0.046} = 1.997 \times 10^{-3} \text{ min}^{-1}$$

The rate constant (k) is the product of pseudo first order rate constant (k').

Concentration of water, taken as constant as 55.5 mol L^{-1}

$$k = k'[\text{H}_2\text{O}] . \text{ Substituting the values, } 1.997 \times 10^{-3} = k'[55.5]$$

$$\text{Pseudo rate constant } = k' = 3.6 \times 10^{-5} \text{ L mol}^{-1} \text{ min}^{-1}.$$



P.3.27 At 193°C , the rate law for the reaction $2\text{Cl}_2\text{O} \rightarrow 2\text{Cl}_2 + \text{O}_2$ is, rate = $k [\text{Cl}_2\text{O}]^2$.

- How the rate changes if $[\text{Cl}_2\text{O}]$ is raised to threefold of the original?
- How should $[\text{Cl}_2\text{O}]$ be changed in order to double the rate?

Solution Original rate is given as, rate = $k [\text{Cl}_2\text{O}]^2$

(a) Rate with threefold concentration of Cl_2O is $k [3 \text{Cl}_2\text{O}]^2$.

This is nine times to the original rate.

(b) With $[\text{Cl}_2\text{O}]$ the rate is $r = k [\text{Cl}_2\text{O}]^2$.

Requirement is that 'r' should be doubled at concentration of, Cl_2O as x .

$$\frac{2r}{r} = \frac{kx^2}{k[\text{Cl}_2\text{O}]^2} \text{ (or) } x = \sqrt{2}[\text{Cl}_2\text{O}]$$

The concentration of Cl_2O should be increased by 1.414 times.



P.3.28 The rate of a reaction is given as, rate = $k[X]^{3/2} [Y]^{-1/2}$.

What is the order of the reaction? If Y is taken large in excess, write the rate equation.

Solution Rate law of the reaction is given as, rate = $k [X]^{3/2}[Y]^{-1/2}$.

Order with respect to X is 3/2

Order with respect to Y is -1/2

Over all order of the reaction = $3/2 - 1/2 = 1$

If Y is taken large in excess, the rate is independent of its concentration, as [Y] is taken as constant during the course of reaction.

The rate equation where X is isolated is, rate = $k[X]^{3/2}$.



P.3.29 A and B are two radioactive substances with half lives 20 min and 30 min respectively. Starting from equal number of moles of A and B, after 1hr, what is the (a) ratio of moles of A and B and (b) ratio of activity of A and B?

Solution The given time, 1 hour is $3 t_{1/2}$ for substance A and $2 t_{1/2}$ for substance B

The fraction of A left after $3 t_{1/2} = 1/2^3 = 1/8$

The fraction of B left after $2 t_{1/2} = 1/2^2 = 1/4$

(a) The ratio of moles left = $1/8 : 1/4 = 1 : 2$.

$$(b) \text{The ratio of activities} = \frac{\lambda_A N_A}{\lambda_B N_B} = \frac{N_A(t_{1/2})_B}{N_B(t_{1/2})_A} = \frac{(1/8) \times 30}{(1/4) \times 20} = 3 : 4.$$



P.3.30 Half-life of ^{210}Pb is 22 years. 2 grams of lead is allowed to decay for 11 years. (a) How much lead is left? and (b) What is the percentage decay?

Solution Number of half-lives (n) = $\frac{\text{Total time}}{\text{Half-life}} = \frac{11\text{y}}{22\text{y}} = \frac{1}{2} = 0.5$.

$$(a) \text{Amount of lead left undecayed} = \frac{\text{Amount of lead taken}}{2^n} = \frac{2}{\sqrt{2}} = 1.414 \text{ g}$$

(b) Amount of lead decayed = Amount taken - left amount

$$= 2 - 1.414 = 0.586 \text{ g}$$

$$\text{Percentage of lead decayed} = \frac{0.586 \times 100}{2} = 29.3\%.$$



- P.3.31** 20% of a radioactive substance undergoes decay in 20 min. What is the percentage decay in 1 hour?

Solution Radioactive decay follows first order kinetics.

Starting from 100, decay in 20 min is 20 and left undecayed is 80

Starting from 80, decay in 20 min is 16 and left undecayed is 64

Starting from 64, decay in 20 min is 12.8 and left undecayed is 51.2

In one hour, percentage decay is, $100 - 51.2 = 48.8\%$.

EXERCISE - 3.1.4

1. Write the difference between elementary and complex reactions. What is rate limiting step?
2. What are the main differences between order and molecularity?
3. Define half-life. How is it related to the rate constant of zero and first order rate constants?
4. Derive an expression for the integral rate constant of a first order reaction.
5. Discuss the methods of determining the order of reaction.
6. A first order reaction has rate constant $1.15 \times 10^{-1}\text{s}^{-1}$. How long will 10 grams of this reactant take to reduce 6 grams? (Ans : 444s)
7. Half life of a first order reaction is $2.1 \times 10^{12}\text{s}^{-1}$. Calculate the rate constant of the reaction. (Ans : $5.5 \times 10^{14}\text{s}^{-1}$)
8. $\text{N}_2\text{O}_5(\text{g})$ is at a pressure of 0.5 atm. After 100 s the pressure of the decomposition mixture is 0.512 atm. Calculate the rate constant. (Ans : $4.98 \times 10^{-4}\text{s}^{-1}$)
9. A first order reaction has a rate constant $1.15 \times 10^{-3}\text{s}^{-1}$. How long will 5 g of this reactant take to reduce to 3 g? (Ans : 7.4 min)
10. Rate constant for a reaction, $\text{X} \rightarrow \text{Y}$, is $4.5 \times 10^{-3}\text{min}^{-1}$. If the initial concentration of X is 1 mol L^{-1} , what is the rate of reaction after one hour? (Ans : $3.44 \times 10^{-3}\text{ mol L}^{-1}\text{m}^{-1}$)
11. Time required to decompose SO_2Cl_2 to half its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction. (Ans : $1.9 \times 10^{-4}\text{s}^{-1}$)



1. Reactions which consume more time are called slow reactions and which do not consume time are called instantaneous reactions.
2. Rate of a reaction is defined as change in the concentration of reactant or product in unit time.
3. Reactions between ionic substances are fast, but between covalent substances are slow.

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4. The rate of a reaction is directly proportional to the product of the concentrations of the reactants taking part in the reaction.
5. The ratio of two specific rates measured at temperatures that differ by 10°C is called temperature coefficient.
6. Arrhenius equation for specific rate (k) is given in terms of activation energy (E_a), temperature, (T) and frequency factor (A) as, $A e^{-E_a/RT}$ or $\ln k = \ln A - E_a/RT$.
7. For every 10° rise in temperature, the rate is approximately doubled or tripled.
8. Catalyst increases the rate by changing the path of a reaction, in which the new path has lower energy of activation.
9. Equation that describes mathematically the dependence of the rate of a reaction on concentration terms of reactants is called rate equation or rate law.
10. Units of rate of reaction are $\text{mol L}^{-1}\text{s}^{-1}$ and units of rate constant are $\text{L}^{n-1}\text{mol}^{1-n}\text{s}^{-1}$.
11. Reacting molecules should undergo collision for any reaction to occur.
12. Colliding molecules shall have to possess a minimum energy to give products. This minimum energy is called threshold energy.
13. Difference between threshold energy and energy of reacting molecules in the normal state is called activation energy.
14. Only a fraction of collisions are productive. This fraction is called fruitful or effective collisions.
15. A complex chemical reaction may proceed in two or more steps, each is called an elementary step. Simple reactions have only one elementary step.
16. The slowest of different elementary steps is called rate limiting or rate determining step.
17. The number of atoms or molecules or ions participating in an elementary step, which collide simultaneously to bring about a reaction is called molecularity.
18. Molecularity may be 1 or 2 or 3. It is never zero and it can not be fractional.
19. Order of the reaction is the sum of the powers of the concentration terms in the rate law.
20. Order of a reaction is experimentally determined. It is obtained from the rate equation and not from stoichiometry equation.
21. Order of reaction can have any value including zero and fractional.
22. Half-life ($t_{1/2}$) is the time required for 50% completion of the concentration of reactants to products. Half-life of a first order reaction is independent on initial concentration of reactants.
23. The integral rate equation for zero order, first order and second order reactions are respectively.
$$k = \frac{x}{t}; k = \frac{1}{t} \ln \frac{a}{a-x} \text{ and } k = \frac{1}{t} \frac{x}{a(a-x)}$$
24. The order of the reaction can be determined by integrated rate equation method, half-life method, van't Hoff's differential method and Ostwald's isolation method.

EXERCISE - 3.2

- Discuss on the kinetic spontaneity of a chemical reaction. Is a slow reaction spontaneous?
- Why the reactions involving covalent substances are slow? How they can be made rapid?
- How are rate and rate constant related to a free radical reaction?
- What is the role played by catalyst to alter the rate of reaction? Explain diagrammatically.
- Time required for 99% completion of a first order reaction is twice to that required for 90% completion of the same reaction. Explain.
- A collision that attains threshold energy level need not be successful. Explain.
- Decomposition of ozone to oxygen proceeds in two steps : Step 1 (fast), $O_3 \rightleftharpoons O_2 + (O)$ and Step 2 (slow), $O_3 + (O) \rightleftharpoons 2O_2$. The rate law is, rate = $k [O_3]^2 [O_2]^{-1}$. Explain.
- $A \rightarrow$ products. The concentration of A changes from 0.2 to 0.15 mol L⁻¹ in 10 min. Calculate the average rate.
(Ans : 8.33×10^{-4} mol L⁻¹ mol s⁻¹)
- $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$, was carried out in water. Initial concentration of iodide ion was 0.25 mol L⁻¹ and the concentration after 10 min was 0.23 mol L⁻¹. Calculate the rate of appearance of iodine.
(Ans : 1×10^{-3} mol L⁻¹ min⁻¹)
- What is activated complex? How is it formed and transformed into product?
- Discuss the energy barrier diagram for reaction rates. When the reaction becomes exothermic and when it will be endothermic?
- The rate of a reaction triples when temperature changes from 20°C to 50°C. Calculate the energy of activation.
(Ans : 28.8 KJ mol⁻¹)
- The rate constant at 0°C is 7.87×10^{-7} s⁻¹ for a reaction whose energy of activation is 103 kJ mol⁻¹. Calculate the rate constant at 20°C.
(Ans : 1.75×10^{-5} s⁻¹)
- Decomposition of X and Y obey first order with half lives 54 and 18 min, respectively. Starting with $[X]/[Y] = 1$, calculate the time required for the ratio 4 : 1.
(Ans : 54 min)
- In the chemical reaction, $3A + B \longrightarrow 2C + 3D$, the rate of appearance of C is reported as 1 mol L⁻¹ s⁻¹. What is the rate of disappearance of A?
(Ans : 1.5 mol L⁻¹ s⁻¹)
- Decay constant of a nuclear reaction is temperature independent. Why?
- At 380°C, the half life of decomposition of hydrogen peroxide is 6 hr and activation energy is 200 KJ mol⁻¹. Calculate the times required for 50% and 75% decomposition at 450°C.
(Ans : 10.2 min; 20.4 min)
- The rate constant of a first order reaction at 500 K is 2.35×10^{-5} s⁻¹. At what temperature, the half-life of the reaction is 256 min?
(Ans : 513 K)
- With 100 kJ mol⁻¹ activation energy for an uncatalysed reaction at 20°C, the catalyst lowers the energy of activation by 75%. What will be the effective rate if other conditions are same?
(Ans : 2.34×10^{13} times)
- Write the rate equation, integral rate constant and half life dependence with initial concentration for zero order and second order reactions.
- Comment on the temperature dependence of half-life of a first order reaction.
- When rate is plotted vs $(a - x^n)$, a straight line is obtained with positive slope, passing through origin. Draw the graphs and discuss.

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23. The order of the reaction $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$ is 1.5. Substantiate.
24. What is a pseudo-order reaction? Why is it so called?
25. If a second order reaction is 75% complete in 1 hr, calculate the rate constant.
(Ans : $3 \text{ L mol}^{-1} \text{ hr}^{-1}$)
26. For a reaction, the reactant concentration decreases 20% in 1 hr and 40% in 2hr. What are the units of rate constant?
(Ans : $\text{L}^{-1} \text{mol hr}^{-1}$)
27. The rate of a first order reaction is $0.04 \text{ mol L}^{-1} \text{s}^{-1}$ after 10 s. and $0.03 \text{ mol L}^{-1} \text{s}^{-1}$ after 20 s of starting the reaction. Calculate the half-life of the reaction.
(Ans : 24 s)
28. A reaction proceeds 5 times more at 60°C , as it does at 30°C . Calculate the energy of activation.
(Ans : 45 KJ mol^{-1})
29. Rate constant of a reaction is 10^{-3} s^{-1} . Calculate the percentage completion of the reaction in 200 s.
(Ans : 18.12%)
30. Time required for 50% completion of the first order reaction is one hr. What is the time required for 99% completion of the same reaction?
(Ans : 6.67 hr)
31. A first order reaction is 50% complete in 30 min at 27°C and 10 min at 47°C . Calculate the rate constant and activation energy at 27°C .
(Ans : $E_a = 43.86 \text{ kJ mol}^{-1}$)
32. The concentrations of N_2O_5 decomposing in first order kinetics after 800 s is 1.45 mol L^{-1} and after 1600 s is 0.88 mol L^{-1} . Calculate the rate constant.
(Ans : $6.2 \times 10^{-4} \text{ s}^{-1}$)
33. For the catalytic decomposition of a substance, half-lives are given below. Find order
- | Pressure (pascal) | 6667 | 13333 | 26666 |
|-------------------|------|-------|-------|
| Half life (Hours) | 3.52 | 1.92 | 1.0 |
- (Ans : 2)
34. A drop of solution (0.05 mL) contains $2 \times 10^{-6} \text{ mol}$ of H^+ . How long it takes for this H^+ to disappear, if the rate constant is $10^7 \text{ mol L}^{-1} \text{ s}^{-1}$?
(Ans : $4 \times 10^{-9} \text{ s}^{-1}$)
35. Half-life period of ^{14}C is 5770 years. If an old wooden toy has 0.25% of activity of ^{14}C . Calculate the age of toy. Fresh wood has 2% activity of ^{14}C .
(Ans : 17310 y)
36. Ten gram atoms of an alpha active element disintegrated in a sealed container in one hour. If the gas collected is 11.2 cc at STP, calculate the half-life of the radioactive element.
(Ans : 13860 hr)
37. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.
(Ans : 77.7 min)
38. Acid catalysed hydrolysis of ethylacetate can be considered as an example of pseudo first order reaction. Explain.
39. Rate of decomposition of a substance increases by a factor 2.25 for 1.5 times increase in concentration at constant temperature. Calculate the order of reaction.
(Ans : 2)
40. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
(Ans : 77.7 min)

