# CHEMICAL KINETICS & NUCLEAR CHEMISTRY

## CLASSIFICATION OF REACTIONS : [IN TERMS OF RATES]

**(i)** There are certain reactions which are too slow e.g. rusting of iron, weathering of rocks.

**(ii)** Instantaneous reactions i.e. too fast e.g. Detonation of explosives, acid-base neutralization, precipitation of AgCl by NaCl and $AgNO_3$.

**(iii)** Neither too fast nor too slow e.g. combination of $H_2$ and $Cl_2$ in presence of light, hydrolysis of ethyl acetate catalysed by acid, decomposition of azomethane

### RATE OF REACTION :

The change in concentration of either reactant or product per unit time.

Formula : $v = \pm \frac{dc}{dt}$

dc = change in concentration in a small interval dt.

[–] sign is used when we refer to reactant concentration.

[+] sign is used when we refer to product concentration.

**Ex.** $N_2 + 3H_2 \rightarrow 2NH_3$

**(i)** Rate of formation of ammonia $= +\frac{d[NH_3]}{dt}$

**(ii)** Rate of disappearance of nitrogen $= -\frac{d[N_2]}{dt}$

**(iii)** Rate of disappearance of hydrogen $= -\frac{d[H_2]}{dt}$

$$\text{Rate of reaction} = +\frac{1}{2}\frac{d[NH_3]}{dt} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$$

Thus, $\text{Rate of reaction} = -\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

or rate of formation of ammonia = Twice the rate of disappearance of nitrogen

i.e. $\frac{d[NH_3]}{dt} = \frac{2}{3}\left[-\frac{d[H_2]}{dt}\right]$

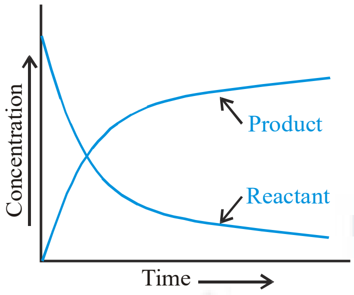
### AVERAGE VELOCITY OF REACTION :

Change in the concentration of reactants or products per unit time is called average reaction velocity. If Δc is the change in the concentration of reactants and product in Δt time, then

$$\text{Average velocity} = \pm\frac{\Delta c}{\Delta t}$$

or $$\text{Average velocity} = \frac{(-)\text{Change in the concentration of reactants}}{\text{Time}}$$

$$\frac{(+)\text{Change in the concentration of products}}{\text{Time}}$$



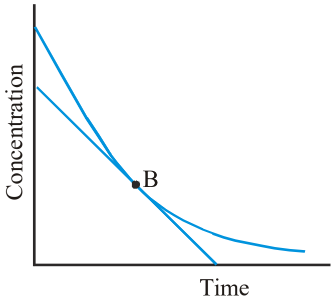
$$\text{Unit of average velocity} = \frac{\text{Unit of concentration}}{\text{Unit of time}} = \frac{\text{gram mole}}{\text{litre} \times \text{Second}} = \text{gram mole litre}^{-1}\ \text{second}^{-1}$$

## INSTANTANEOUS RATE OF THE REACTION :

The rate of reaction determined at specified concentration or specified time is called **instantaneous rate**.

The instantaneous rate of the reaction can be determined by measuring concentration of reactant or product at a instant of time and plotting concentration versus time.

The instantaneous rate at any time is determined by the slope of the tangent at a point on the time-concentration curve corresponding to the specified time.



The slope of the tangent at a point is the limiting value of $\frac{\Delta c}{\Delta t}$.

$$\lim_{\Delta t \to 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt}$$

In terms of the concentration of reactant, the rate of the reaction $= -\frac{dc}{dt}$. The –sign indicates that the concentration of reactant decreases with time.

In terms of the concentration of product, the rate of the reaction $= +\frac{dc}{dt}$. The +sign indicates that the concentration of product increases with time. In the reaction if at a time t the concentration of product is x and at time t + dt, the concentration becomes x + dx then the reaction rate $= \frac{dx}{dt}$.

**For example the rate of reaction :** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

in terms of the concentrations of $N_2$, $H_2$ and $NH_3$ can be expressed as :

$$-\frac{d[N_2]}{dt}, -\frac{1}{3}\frac{d[H_2]}{dt}, +\frac{1}{2}\frac{d[NH_3]}{dt}$$

**Ex.** From the concentrations of R at different times given below, calculate the average rate of the reaction: $R \rightarrow P$ during different intervals of time.

| t/s | 0 | 5 | 10 | 20 | 30 |
|---|---|---|---|---|---|
| $10^3 \times [R]/\text{mol L}^{-1}$ | 160 | 80 | 40 | 10 | 2.5 |

**Sol.** We can determine the difference in concentration over different intervals of time and thus determine the rate by dividing Δ[R] by Δt.

| $\dfrac{[R]_1 \times 10^3}{\text{mol L}^{-1}}$ | $\dfrac{[R]_2 \times 10^3}{\text{mol L}^{-1}}$ | $\dfrac{t_2}{s}$ | $\dfrac{t_1}{s}$ | $\dfrac{r_{av} \times 10^3}{\text{mol L}^{-1}\text{s}^{-1}} = \dfrac{-[R_2 - R_1] \times 10^3}{[t_2 - t_1]}$ |
|---|---|---|---|---|
| 160 | 80 | 5 | 0 | **16** |
| 80 | 40 | 10 | 5 | **8** |
| 40 | 10 | 20 | 10 | **3** |
| 10 | 2.5 | 30 | 20 | **0.75** |

**Ex.** What should be **(a)** the rate of disappearance of B and **(b)** the rate of formation of C, if the rate of disappearance of A for the reaction $A + B \rightarrow 2C$ is $10^{-2}$ mole/litre/second at a particular temperature ?

**Sol.** **(a)** Rate of disappearance of A = Rate of disappearance of B

$= 10^{-2}$ mole/litre/second

**(b)** Rate of disappearance of A = $\dfrac{1}{2} \times$ Rate of formation of C

Rate of formation of C = 2 × Rate of disappearance of A

$= 2 \times 10^{-2}$ mole/litre/second

**Ex.** A gaseous reaction : $2A(g) + B(g) \rightarrow 2C(g)$,

Show a decrease in pressure from 120 mm to 100 mm in 10 minutes. The rate of appearance of C is -

**[A]** 2 mm/min **[B]** 4 mm/min **[C]** 10 mm/min **[D]** 12 mm/min. **Ans. [B]**

**Sol.** Suppose 2p is the pressure of C after 10 min.

Fall in pressure of A = 2p ; Fall in pressure of B = p

Total fall in pressure = (2p + p) – 2p = p = 20 mm

Pressure of C = 2p = 40 mm

Rate of appearance of C = 40/10 = 4 mm/min

**Ex.** The term $\dfrac{dx}{dt}$ in the rate expression refers to the -

**[A]** concentration of the reactants **[B]** increase in concentration of the reactants

**[C]** instantaneous rate of the reaction **[D]** average rate of the reaction **Ans. [C]**

**Sol.** It is expression for instantaneous rate

**Ex.** Which of the following expression can be used to describe the instantaneous rate of the reaction ?

$2A + B \rightarrow A_2B$

**[A]** $-\dfrac{1}{2}\dfrac{d[A]}{dt}$ **[B]** $-\dfrac{d[A]}{dt}$ **[C]** $\dfrac{1}{2}\dfrac{d[A_2B]}{dt}$ **[D]** $-\dfrac{1}{2}\dfrac{d[A]}{dt}.\dfrac{d[B]}{dt}$ **Ans. [A]**

**Sol.** The instantaneous rate of the reaction can be expressed by any of the following expressions

$$-\frac{1}{2}\frac{d[A]}{dt} \text{ or } -\frac{d[B]}{dt} \text{ or } \frac{d[A_2B]}{dt}$$

**Ex.** Which of the following will react at the highest rate ?

**[A]** 1 mol of A and 1 mol of B in a 1 L vessel **[B]** 2 mol of A and 2 mol of B in a 2 L vessel

**[C]** 3 mol of A and 3 mol of B in a 3 L vessel **[D]** All would react at the same rate **Ans. [D]**

**Sol.** Since all have same conc. of reactants, all would react at same rate.

### FACTORS AFFECTING THE RATE OF REACTION :

**(i) Concentration :** Law of mass action enunciates that greater is the conc. of the reactants, the more rapidly the reaction proceeds.

**(ii) Pressure (Gaseous reaction) :** On increasing the pressure, volume decreases and conc. increases and hence the rate increases.

**(iii) Temperature :** It is generally observed that rise in temperature increases the reaction rate.

**(iv) Nature of the reactants :** The rate depends upon specific bonds involved and hence on the nature of reactants.

$$\boxed{g > l > s}$$

**(v) Surface area of the reactants :** In heterogeneous reactions, more powdered is the form of reactants, more is the velocity. [as more active centres are provided]

**(vi) Catalyst :** Affects the rate immensely.

**Ex.** For the reaction :

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Given : $\frac{d[NO]}{dt} = 3.6 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$

Calculate : **(i)** rate of disappearance of ammonia

**(ii)** rate of formation of water

**Sol.** From the eqn. it is clear that

$$\text{Rate} = -\frac{1}{4}\frac{d[NH_3]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt} \qquad \text{Thus :} \quad -\frac{1}{4}\frac{d[NH_3]}{dt} = \frac{1}{4}\frac{d[NO]}{dt}$$

$$\text{or} \quad -\frac{d[NH_3]}{dt} = \frac{d[NO]}{dt} = 3.6 \times 10^{-3} \text{ mol } L^{-1} s^{-1} \qquad \text{Also} \quad \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$$

$$\frac{3}{2}\frac{d[NO]}{dt} = \frac{d[H_2O]}{dt}$$

$$\frac{3}{2} \times 3.6 \times 10^{-3} = \frac{d[H_2O]}{dt}$$

$$\frac{d[H_2O]}{dt} = 5.4 \times 10^{-3} \text{ mol } L^{-1} s^{-1}$$

**Ex.** The following reaction was studied in a closed vessel.

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

It was found that concentration of $NO_2$ increases by $4.0 \times 10^{-2}$ mol $L^{-1}$ in five seconds, calculate

**(a)** the rate of reaction

**(b)** the rate of change of concentration $N_2O_5$.

**Sol.** **(a)** Rate $= \frac{1}{4}\frac{d[NO_2]}{dt}$

But $\frac{d[NO_2]}{dt} = \frac{4.0\times10^{-2}\,mol\,L^{-1}}{5sec} = 8 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$

∴ Rate of reaction $= \frac{1}{4} \times 8 \times 10^{-3}\ mol\ L^{-1}\ s^{-1} = 2 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$

**(b)** Rate of change of conc. of $N_2O_5$

$= \frac{-d[N_2O_5]}{dt} = -\frac{1}{2} \times$ Rate of formation of $NO_2$

$= -\frac{1}{2}\frac{[d[N_2O_5]]}{dt} = -\frac{1}{2} \times 8 \times 10^{-3} = 4 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$

**Ex.** The rate of change in concentration of R in the reaction, $2P + Q \longrightarrow 2R + 3S$, was reported as $1.0\ mol\ L^{-1}\ sec^{-1}$. Calculate the reaction rate as well as rate of change of concentration of P, Q and S.

**Sol.** $\frac{-1}{2}\frac{d[P]}{dt} = -\frac{d[Q]}{dt} = \frac{1}{2}\frac{d[R]}{dt} = \frac{1}{3}\frac{d[S]}{dt} =$ Rate of reaction

✈ $\frac{d[R]}{dt} = 1.0\ molL^{-1}\ s^{-1}$

∴ $-\frac{d[P]}{dt} = \frac{d[R]}{dt} = 1.0\ mol\ L^{-1}\ s^{-1}$

$\frac{-d[Q]}{dt} = \frac{1}{2}\frac{d[R]}{dt} = \frac{1}{2} = 0.5\ molL^{-1}\ s^{-1}$

$\frac{-d[S]}{dt} = \frac{3}{2}\frac{d[R]}{dt} = \frac{3}{2} \times 1 = 1.5\ molL^{-1}\ s^{-1}$

Rate of reaction $= \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2} \times 1 = 0.5\ mol\ L^{-1}s^{-1}$

## SPECIFIC REACTION RATE :

Applying law of mass action to the reaction :

$$m_1A + m_2B \rightarrow n_1C + n_2D$$

$$\text{Rate} \propto [A]^{m_1}\ [B]^{m_2}$$

or $$v = k\,[A]^{m_1}\ [B]^{m_2}$$

This equation is known as rate law. Where k is the proportionality constant and is called

**(i)** Velocity constant or **(ii)** Velocity coefficient or **(iii)** Specific reaction rate.

On putting [A] = [B] = 1, where have : v = k

Hence specific reaction rate is the rate of the reaction when the concentration of each reactant is taken as unit.

### Unit of Specific Reaction Rate

$v = k\,[A]^{m_1} . [B]^{m_2}$

$$\frac{\text{conc.}}{\text{time}} = k[\text{conc.}]^{m_1+m_2}$$

$$[\text{conc.}]^{[1-(m_1+m_2)]} \times [\text{time}]^{-1} = k \qquad \text{or} \qquad k = \left[\frac{\text{mole}}{\text{litre}}\right]^{[1-(m_1+m_2)]} . [\text{second}^{-1}]$$

## DISTINCTION BETWEEN UNIT OF RATE AND RATE CONSTANT :

**Rate of a reaction :** Its units are always mole litre$^{-1}$ time$^{-1}$.

**Rate constant :** Its unit depends upon the order of reaction.

### RATE LAW :

**(a)** It may also not depend upon the concentration of each reactant or product of the reaction.

Suppose, $mA + nB \rightarrow \text{Product}$

$$\boxed{R \propto [A]^m[B]^n}$$

**(b)** Rate of a chemical reaction is directly proportional to the product of the concentration of reactants raise to the power of their stoichiometric coefficient.

**(c)** The rate law represents the experimentally observed rate of reaction which depends upon the slowest step of the reaction.

**(d)** Rate law cannot be deduce from the equation for a given reaction. It can be find by experiments only.

**(e)** The rate law may not bear a simple relationship of the stoichiometric equation.

**Ex.** In the reaction, $A + 2B \rightarrow 6C + 2D$, if the initial rate $-\frac{d[A]}{dt}$ at $t = 0$ is $2.6 \times 10^{-2}$ M sec$^{-1}$, what will be the value of $-\frac{d[B]}{dt}$ at $t = 0$ ?

**[A]** $8.5 \times 10^{-2}$ M sec$^{-1}$ **[B]** $2.5 \times 10^{-2}$ M sec$^{-1}$

**[C]** $5.2 \times 10^{-2}$ M sec$^{-1}$ **[D]** $7.5 \times 10^{-2}$ M sec$^{-1}$ **Ans. [C]**

**Sol.** From the reaction it is evident that when a mole of A is reacting, 2 moles of B must react. Hence the decrease in the concentration of B must be twice that of A

$$\therefore \quad -\frac{d[B]}{dt} = 2\left[-\frac{d[A]}{dt}\right]$$

$$= 2 \times 2.6 \times 10^{-2} = 5.2 \times 10^{-2}\ \text{M sec}^{-1}$$

**Ex.** The dimensions of rate constant of a second order reaction involves :

**[A]** time and concentration **[B]** neither time nor concentration

**[C]** time only **[D]** concentration only **Ans. [A]**

**Sol.** $k = \frac{\text{Rate}}{[A]^2} = \frac{\text{mol L}^{-1}\text{ s}^{-1}}{(\text{mol L}^{-1})^2} = \frac{\text{s}^{-1}}{\text{mol L}^{-1}} = (\text{mol L}^{-1})^{-1}\text{ s}^{-1}$

**Ex.** The rate constant of a reaction has same units as the rate of reaction. The reaction is of

**[A]** zero order **[B]** first order **[C]** second order **[D]** none of these **Ans. [A]**

**Sol.** For a zero order reaction, r = k$[A]^\circ$. Thus the units of k are the same as that of rate of reaction.

**Ex.** The rate constant of n$^{th}$ order reaction has units :

**[A]** $\text{litre}^{1-n}\text{mol}^{1-n}\text{sec}^{-1}$ **[B]** $\text{mol}^{1-n}\text{litre}^{1-n}\text{sec}$

**[C]** $\text{mol}^{1-n^2}\ \text{litre}^{n^2}\ \text{sec}^{-1}$ **[D]** $\text{mol}^{1-n}\text{litre}^{n-1}\text{sec}^{-1}$ **Ans. [D]**

**Sol.** For an n$^{th}$ order reaction : rate = k [conc.]$^n$

$$k = \frac{\text{rate}}{[\text{conc.}]^n}$$

$$\text{Units of k} = \frac{\text{mol L}^{-1}\ \text{s}^{-1}}{(\text{mol L}^{-1})^{-}} = \text{mol}^{1-n}\,\text{L}^{n-1}\,\text{s}^{-1}$$

**Ex.** On which of the following factors, the rate constant does not depend ?

**[A]** Temperature **[B]** Concentration

**[C]** Presence of catalyst **[D]** Nature of reactants **Ans. [B]**

**Sol.** Rate constant is independent of the conc. of the reactants.

## ORDER OF REACTION :

The sum of the power of the concentration terms on which the rate of reaction actually depends as observed experimentally is called the order of the reaction. For example,

Order of reaction = x + y

Thus, the order of reaction may also be defined as the sum of the exponents (powers) to which the concentration terms in the rate law equation are raised in order to express the observed rate of the reaction.

Thus, reaction is said to be of the first order if its rate is given by the expression of the type,

$r = k_1C_A$

Second order if the rate is given by the expression of the type,

$r = k_2{C^2}_A$

or $r = k_2C_AC_B$

third order if the rate is given by the expression of the type

$r = k_3{C_A}^3$ or $r = k_3C_A^2C_B$ or $r = k_3C_A{C_B}^2$ or $k_3C_AC_BC_C$ and so on

For zero order reaction, the rate equation is written as $R = k_0$. It is to be noted that the order of reaction is essentially an experimental quantity.

**Note:** **Order may be zero, fractional, integer or negative.**

### Examples showing different values of order of reactions :

| | Reaction | Rate law | Order |
|---|---|---|---|
| **(i)** | $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ | $R = K\,[N_2O_5]^1$ | 1 |
| **(ii)** | $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(\bullet) + 3H_2O(\bullet)$ | $R = K\,[Br^-]\,[BrO_3^-]\,[H^+]^2$ | 1 + 1 + 2 = 4 |
| **(iii)** | $H_2\text{(Para)} \longrightarrow H_2\text{(ortho)}$ | $R = K\,[H_{2\,(\text{Para})}]^{3/2}$ | 3/2 |

| | | | |
|---|---|---|---|
| **(iv)** | $NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2(g)$ | $R = K\,[NO_2]^2\,[CO]^o$ | $2 + 0 = 2$ |
| **(v)** | $2O_3\,(g) \longrightarrow 3O_2\,(g)$ | $R = K\,[O_3]^2\,[O_2]^{-1}$ | $2 - 1 = 1$ |
| **(vi)** | $H_2 + Cl_2 \xrightarrow{hv} 2\,HCl$ | $R = K\,[H_2]^0[Cl_2]^0$ | $0 + 0 = 0$ |

The reaction **(ii)** does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called **complex reaction** and takes places in a sequence of a number of **elementary reactions**. For an elementary reaction the sum of stoichiometric coefficients = order of the reactions. But for complex reactions order is to be experimentally calculated.

**Ex** The rate of a certain reaction depends on concentration according to the equation : $\frac{-dC}{dt} = \frac{K_1C}{1+K_2C}$.

What will be the order of reaction, when concentration **(C)** is :

**(a)** very-very high, **(b)** very-very low.

**Sol.** **(a)**
$$\frac{-dC}{dt} = \frac{K_1C}{1+K_2C} = \frac{K_1}{\frac{1}{C}+K_2}$$

if C is very-very high then $\frac{1}{C}$ being small may be neglected.

$$\therefore \quad \frac{-dC}{dt} = \frac{K_1}{K_2} = \text{constant, i.e., zero order reaction.}$$

**(b)** If C is very-very low $1 + K_2C \approx K'$

$$\therefore \quad \frac{-dC}{dt} = \frac{K_1C}{K'} = \left(\frac{K_1}{K'}\right) \times \text{concentration}$$

i.e., I order reaction.

**Ex. :**

| **Reaction** | **Experimental rate equation** | **order** |
|---|---|---|
| $H_2 + Cl_2 \rightarrow 2HCl$ | $v = k$ | zero |
| $H_2 + Br_2 \rightarrow 2HBr$ | $v = k\,[H_2]\,[Br_2]^{1/2}$ | one and half |
| $H_2 + I_2 \rightarrow 2HI$ | $v = k\,[H_2]\,[I_2]$ | two |

**Examples of fractional order reaction**

**Reaction :** $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$

$v = k\,[CO]^2\,[Cl_2]^{1/2}$, order $= 2.5$

**Reaction :** $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$

$v = k\,[COCl_2]^{3/2}$, order $= 1.5$

**Ex.** For the chemical reaction,

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

Rate $= k\,[HBr]\,[O_2]$

What is the probable mechanism of the reaction ?

**Sol.** $HBr + O_2 \longrightarrow HOOBr$ (slow)

$HOOBr + HBr \longrightarrow 2HOBr$ (fast)

$HOBr + HBr \longrightarrow H_2O + [Br_2] \times 2$ (fast)

**Ex.** Nitric oxide (NO) reacts with oxygen to produce nitrogen dioxide :

$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2(g)$

What is the predicted rate law, if the mechanism is :-

$NO\,(g) + O_2\,(g) \xrightleftharpoons{k} NO_3\,(g)$ (fast)

$NO_3\,(g) + NO\,(g) \xrightarrow{k_1} 2NO_2\,(g)$ (slow)

**Sol.** From the slow step,

Rate = $k_1\,[NO_3]\,[NO]$ ..........**(i)**

From fast step :

Equilibrium constant (K) = $\dfrac{[NO_3]}{[NO][O_2]}$ ..........**(ii)**

Substituting the value of $[NO_3]$ from equation **(ii)** into equation **(i)**, we get

Rate= $k'[NO]^2\,[O_2]$

## MOLECULARITY OF A REACTION :

"Molecularity is defined as the number of molecules, atoms, or radicals that must collide simultaneously in order for the reaction to take place." It is always a whole number and cannot be negative.

In the elementary processes :

| **Participating species** | | **Molecularity** |
|---|---|---|
| One species participates | ..... | unimolecular, 1 |
| Two species participates | ..... | bimolecular, 2 |
| Three species participates | ..... | trimolecular, 3 |

**Ex.**

| | | |
|---|---|---|
| $N_2O_4 \rightarrow 2NO_2$ | ...... | unimolecular |
| $H_2 + I_2 \rightarrow 2HI$ | ...... | bimolecular |
| $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ | ...... | trimolecular |

**Note :** If the reaction takes place in two or more steps then the overall molecularity of the reaction is monitored by the slow or rate determining step.

### DIFFERENCE BETWEEN MOLECULARITY AND ORDER OF REACTION :

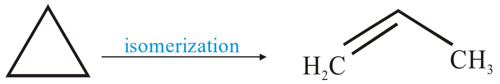
| S.No. | Molecularity | Order of Reaction |
|---|---|---|
| 1 | Molecularity can neither be zero nor fractional | Order of a reaction can be zero, fractional or integer |
| 2 | It is the number of molecules of reactants concentration terms taking part in elementary step of a reaction. | It is sum of power raised or the rate expression. |
| 3 | It can not have negative value. | Order of a reaction may have negative value. |
| 4 | Molecularity is a theoretical property. | Order is an experimental property. |
| 5 | Molecularity concerns with mechanism. | Order concerns with kinetic (rate law). |

**Ex.**

| Reaction | Rate law | Order |
|---|---|---|
| $CH_3CHO \longrightarrow CH_4 + CO$ | Rate $\propto [CH_3CHO]^{3/2}$ | 1.5 |
| $NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$ | Rate $\propto [NH_3]^0$ | 0 |
| $2HI \longrightarrow H_2 + I_2$ | Rate $\propto [HI]^0$, i.e. Rate = k | 0 |

Order may change with change in experimental conditions while molecularity can't.

**Ex.**



This reaction follows first order kinetics at high pressure and 2nd order kinetics at low pressure of cyclopropane.

## PSEUDO UNIMOLECULAR REACTION

Consider the reaction : $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Since water is present in large excess, its concentration hardly changes during the course of the reaction. And as such rate depends only on the concentration of ester. The order is one but the molecularity is two. Such reactions are called **pseudo unimolecular reaction**.

**Ex.** For a chemical reaction, A → products, the rate of reaction doubles when the concentration of A is increased by 4 times. The order of reaction is

**[A]** 4 **[B]** 0 **[C]** 1/2 **[D]** 1 **Ans. [C]**

**Ans.** $r = k[A]^n$ ........ **(i)** ; $2r = k[4A]^n$ .......... **(ii)**

Dividing **(ii)** by **(i)** $\frac{2r}{r} = \frac{k}{k}\left[\frac{4A}{A}\right]^n$

or $2 = 2^{2n}$ or $2n = 1$ or $n = 1/2$

**Ex** For a hypothetical reaction

A + B → products, the rate law is, $r = k[B][A]^\circ$, the order of reaction is :

**[A]** 0 **[B]** 1 **[C]** 2 **[D]** 3 **Ans. [B]**

**Sol.** $1 + 0 = 1$

**Ex.** The slowest step of a particular reaction is found to be

$$\frac{1}{2}X_2 + Y_2 \rightarrow XY_2$$

The order of the reaction is

**[A]** 2 **[B]** 3 **[C]** 3.5 **[D]** 1.5 **Ans. [D]**

**Sol.** $r = k[X_2]^{1/2}[Y_2]^1$ $\therefore$ Order = 0.5 + 1 = 1.5

**Ex.** The rate of certain hypothetical reaction A + B + C → products, is given by

$$r = \frac{dA}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$$

The order of a reaction is given by

**[A]** 1 **[B]** 1/2 **[C]** 2 **[D]** 13/12 **Ans. [D]**

**Sol.** Order of reaction $= \frac{1}{2} + \frac{1}{3} + \frac{1}{4} = \frac{6+4+3}{12} = \frac{13}{12}$

## ZERO ORDER REACTION

Reaction whose rate is not affected by concentration said to be of zero order reaction.

**Ex. :**

**(i)** Reaction between Acetone and Bromine

**(ii)** Dissociation of HI on gold surface

### (A) Unit of Rate Constant :

$\boxed{k = mol\ L^{-1} sec^{-1}}$ Unit of rate of reaction = Unit of rate constant.

### (B) Rate Constant of Zero Order Reaction :

$\boxed{x = kt}$

The rate of reaction is independent of the concentration of the reaction substance.

### (C) Determination of Half life Period of Zero Order Reaction :

At $t = t_{½}$ ; $x = \frac{a}{2}$

$\boxed{t_{1/2} = \frac{a}{2k}}$ or $\boxed{t_{1/2} \propto a}$

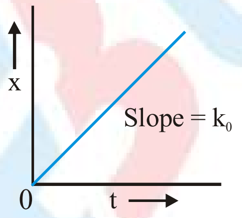
The half life period is directly proportional to the initial concentration of the reactants.

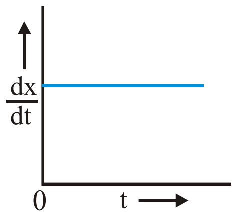
**Ex.** The rate equation of a reaction is $k[A]^{1/2}[B]^{1/2}[C]^{-1}$. What should be the order of the reaction ?

**Sol.** $n = \frac{1}{2} + \frac{1}{2} - 1 = 0$

$\therefore$ Order of the reaction is zero.

**Graphical representation**





**Ex. :**

- Photochemical reactions, like $H_2 + Cl_2 \longrightarrow 2HCl$, are zero order reaction.
- Decomposition of $NH_3$ on platinum surface is also zero order reaction.

## FIRST ORDER REACTION :

When the rate of reaction depends only on one concentration term of reactant.

A first order reaction is one whose rate varies as first power of the concentration of the reactant, i.e. the rate increases as number of times as the concentration of reactant is increased.

Let us, consider a unimolecular first order reaction represented by the general equation,

| | A $\longrightarrow$ | Product |
|---|---|---|
| At t = 0 | a | 0 |
| At t = t | a – x | x |

The initial concentration of A is a mole $L^{-1}$ and its concentration after time t is (a – x) mole $L^{-1}$. This means during the time interval t, x mole $L^{-1}$ of A has reacted.

The rate of reaction at any time t is given by the following first order kinetics.

$$\frac{d(a-x)}{dt} \propto (a-x)$$

or $\quad \frac{d(x)}{dt} \propto (a-x) \quad$ or $\quad \frac{dx}{dt} = k\,(a-x)$

where k is the rate constant of the reaction.

$$\frac{dx}{a-x} = kdt$$

This is differential rate equation and can be solved by integration.

$$\int \frac{dx}{a-x} = k\int dt$$

or $\quad -\ln(a-x) = k.t + C$ ...............**(1)**

where C is integration constant.

The constant C can be evaluated by applying the initial condition of the reaction i.e. when t = 0, x = 0. Putting these in equation **(1)**, we get

$C = -\ln a$

Putting the value of C in equation **(1)**, we get

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

or $\quad k = \frac{1}{t}\ln\frac{a}{a-x} = \frac{2.303}{t}\log\frac{a}{a-x}$ ................**(2)**

Also, $k = \frac{2.303}{(t_2 - t_1)}\log\frac{(a-x_1)}{(a-x_2)}$

and $k = \frac{2.303}{(t_2 - t_1)}\log\frac{R_1}{R_2}$

where $(a - x_1)$ is concentration at time $t_1$ and $(a - x_2)$ is concentration after time $t_2$ and $R_1$ is rate at time $t_1$ and $R_2$ is rate at time $t_2$.

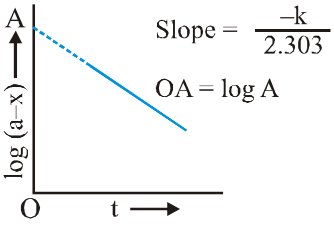
If $[A]_0$ and [A] be the concentrations of reactant at zero time and time t respectively, then Eq. **(2)** may be put as

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

Also, $\quad [A] = [A]_0\, e^{-kt}$

This is the integrated rate expression for first order reaction.

As, $k = \frac{1}{t}\ln\frac{a}{a-x} \Rightarrow \log(a-x) = \log(a) - \frac{kt}{2.303}$



$kt = \ln a - \ln(a-x)$

Also, $(a-x) = ae^{-kt}$

$x = a(1 - e^{-kt})$

∴ Degree of dissociation $\left(\frac{x}{a}\right) = (1 - e^{-kt})$

### Unit of Rate constant

The differential rate expression for n$^{th}$ order reaction is as follows :

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

or
$$k = \frac{dx}{(a-x)^n\,dt} = \frac{(\text{concentration})}{(\text{concentration})^n\,\text{time}} = (\text{conc.})^{1-n}\,\text{time}^{-1}$$

If concentration be expressed in mole L$^{-1}$ and time in minutes, then

$k = (\text{mole L}^{-1})^{1-n}\,\text{min}^{-1}$

For zero order reaction, n = 0 and hence, k = mole L$^{-1}$ min$^{-1}$

For first order reaction, n = 1 and hence,

$k = (\text{mole L}^{-1})^{0}\,\text{min}^{-1} = \text{min}^{-1}$

For second order reaction, n = 2 and hence,

$k = (\text{mole L}^{-1})^{-1}\,\text{min}^{-1} = \text{mole}^{-1}\,\text{L min}^{-1}$

The rate constant of a first order reaction has only time in its unit. It has no concentration term in the unit. This means the numerical value of k for a first order reaction is independent of the unit in which concentration is expressed. If concentration unit is changed, the numerical value of k for a first order reaction will not change. However, it would change with change in time. Say, k is $6.0 \times 10^{-3}$ min then it may also be written as $1 \times 10^{-4}\,s^{-1}$, i.e., numerical value of k will decrease 60 times if time unit is changed from hour to minute or from minute to second.

### Half - time or half - life period of a first order reaction :

The half - time of a reaction is defined as the time required to reduce the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus,

When $x = \frac{a}{2}$, $t = t_{1/2}$

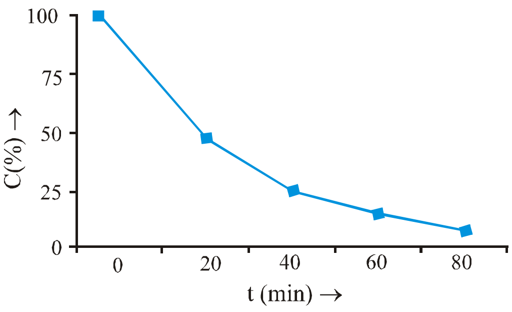
Putting these values in Eq. (2), we get

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303}{t_{1/2}} \times 0.30103$$

$(\because \log 2 = 0.30103)$

$$t_{1/2} = \frac{0.693}{k} \qquad \text{.............(3)}$$

Since k is a constant for a given reaction at a given temperature and the expression lacks any concentration term so from Eq. (3) it is evident that half-time of a first order reaction is a constant independent of initial concentration of reactant. This means if we start with 4 moles L$^{-1}$ of a reactant reacting by first order kinetics, then after 20 minutes it is reduced to 2 moles L$^{-1}$. That is, after 20 minutes from the start of reaction the concentration of the reactant will be 2 moles L$^{-1}$ after 40 minutes from the start of reaction, the concentration is 1 mole L$^{-1}$. After 60 minutes from the start of reaction, the concentration of the reactant will be reduced to 0.5 mol L$^{-1}$. In other words, if during 20 minutes 50% of the reaction completes, then in 40 minutes 75%, in 60 minutes 85.5% of the reaction and so on, will complete as shown in the figure above.



Thus, fraction left after n half-lives $= \left(\frac{1}{2}\right)^n$

Concentration left after n half-lives, $[A] = \left(\frac{1}{2}\right)^n [A]_0$

It is also to be noted that Eq. **(3)** helps to calculate $t_{1/2}$ or k.

A general expression for $t_{1/2}$ is as follows.

### Half - life of a nth order reaction

Let us find out $t_{1/2}$ for n^th^ order reaction where $n \neq 1$.

$$\therefore \quad \frac{-d[A]}{dt} = k_n[A]^n \Rightarrow \frac{-d[A]}{[A]^n} = kdt \qquad \Rightarrow -\int_{[A]_0}^{[A]_0/2} \frac{d[A]}{[A]^n} = k\int_0^{t_{1/2}} dt$$

$$\int_{[A]_0/2}^{[A]_0} [A]^{-n}\, d[A] = k_n t_{1/2} \qquad \left[\frac{[A]^{1-n}}{1-n}\right]_{[A]_{0/2}}^{[A]_0} = k_n t_{1/2}$$

$$\Rightarrow \quad \frac{1}{1-n}\left([A]_0^{1-n} - \left[\frac{[A]_0}{2}\right]^{1-n}\right) = k_n t_{1/2} \qquad \Rightarrow \frac{[A]_0^{1-n}}{1-n}\left[1-\left(\frac{1}{2}\right)^{1-n}\right] = k_n t_{1/2}$$

$$\Rightarrow \quad \frac{1}{(1-n)[A]_0^{n-1}}[1-2^{n-1}] = k_n t_{1/2} \qquad \Rightarrow \frac{(2^{n-1}-1)}{k_n(n-1)[A]_0} = t_{1/2} \; \textbf{(order } n \neq 1\textbf{)}$$

Therefore, for $n^{th}$ order reaction, the half-life is inversely related to the initial concentration raised to the power of (n – 1).

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where n = order of reaction.

**Ex.** **(i)** All radioactive reactions

**(ii)** $A \rightarrow$ Product

**(iii)** $2NO \rightleftharpoons 2N_2 + O_2$

**(iv)** $2Cl_2O_7 \rightarrow 2Cl_2 + 7O_2$

### (A) Unit of rate constant of first order reaction

$$K = (sec)^{-1} \qquad \Delta n = 1$$

### (B) Velocity constant for first order reaction

$$\boxed{k_1 = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}} \quad \Rightarrow \quad \boxed{t = \frac{2.303}{k_1}\log_{10}\frac{a}{(a-x)}}$$

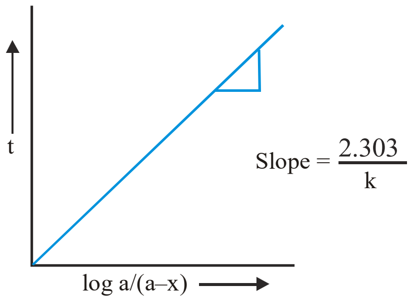
where t = time, a = initial concentration at t = 0

(a – x) = concentration after time t

K = Rate constant

### (C) Graphical Representation

Graph between t v/s $\log \frac{a}{(a-x)}$ is a straight line



**Ex.** Calculate $\frac{t_{0.75}}{t_{0.50}}$ for a 1st order reaction :

**Sol.** $k = \frac{2.303}{t_{3/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}} \quad \Rightarrow \quad \frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2\log 2}{\log 2} = 2$

**Ex.** At least how many half-lives should elapse for a 1st order reaction A $\longrightarrow$ products so that the reaction is at least 95% completed ? (log 2 = 0.3)

**(A)** 4 **(B)** 5 **(C)** 6 **(D)** 7

**Sol.** **(B)**

$$\underset{0\%}{100} \xrightarrow{t_{1/2}} \underset{50\%}{50} \xrightarrow{t_{1/2}} \underset{75\%}{25} \xrightarrow{t_{1/2}} \underset{87.5\%}{12.5} \xrightarrow{t_{1/2}} \underset{93.75\%}{6.25} \xrightarrow{t_{1/2}} \underset{96.875\%}{3.125}$$

**Ex.** A first order reaction gets 90% completed in 40 minute. Find out the half-life period of the reaction.

**Sol.** Suppose that the initial concentration of reactant **(a)** = 100 t = 40 minutes

90% of the reaction get completed in 40 minutes.

Therefore,

$$x = 90$$

$$k_1 = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$= \frac{2.303}{40} \log \frac{100}{100 - 90} \Rightarrow k_1 = \frac{2.303}{40} \log 10$$

$$= \frac{2.303}{40} \times 1 = 5.757 \times 10^{-2} \text{ minutes}^{-1}$$

$$t_{½} = \frac{0.693}{5.757 \times 10^{-2}} = 10.3 \text{ minutes}$$

**Ex.** Prove with the help of the following data that hydrolysis of $H_2O_2$ is a first order reaction. Initial concentration in the reaction 25.0.

**Sol.**

| **Time, t (in minutes)** | **10** | **20** | **30** |
|---|---|---|---|
| **V** | **20.0** | **15.7** | **12.5** |

For a first order reaction, $k_1 = \frac{2.303}{t} \log \frac{a}{a - x}$ ; Here, a = 25

$$k_1 \text{ at } t = 10 \text{ minutes} = \frac{2.303}{10} \log \frac{25}{20} = \frac{2.303}{10} \times 0.0969 = 2.23 \times 10^{-2}$$

$$k_1 \text{ at } t = 20 \text{ minutes} = \frac{2.303}{20} \log \frac{25}{15.7} = \frac{2.303}{20} \times 0.2020 = 2.32 \times 10^{-2}$$

$$k_1 \text{ at } t = 30 \text{ minutes} = \frac{2.303}{30} \log \frac{25}{12.5} = \frac{2.303}{30} \times 0.3010 = 2.31 \times 10^{-2}$$

Constant value of k shows that hydrolysis of $H_2O_2$ in aqueous medium is a first order reaction.

**Ex.** The rate constant for an isomerization reaction, $A \longrightarrow B$, is $2.5 \times 10^{-3}\ \text{min}^{-1}$. If the initial concentration of A is 1M, calculate the rate of reaction after 1 hr.

**Sol.** As, $k = \dfrac{2.303}{t} \log \dfrac{a}{(a-x)}$, for first order reaction

$$\Rightarrow \qquad 2.5 \times 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)}$$

$$\therefore \qquad (a-x) = 0.8607$$

The rate after 60 minutes $= k\,(a-x) = 2.5 \times 10^{-3} \times 0.8607 = 2.1518 \times 10^{-3}$

**Ex.** The rate of a first order reaction is 0.08 mol $L^{-1}$ at 20 min. and 0.06 mol $L^{-1}$ at 40 min. after start of reaction. Find the half-life of reaction.

**Sol.** As, rate = k[A]

$0.08 = k[A]_{10}$

$0.06 = k[A]_{20}$

$$\therefore \qquad \frac{[A]_{10}}{[A]_{20}} = \frac{0.08}{0.06} = \frac{4}{3}$$

For first order reaction :

$$t = 2.303 \log \frac{[A]_{10}}{[A]_{20}}$$

when t = (40 – 20) = 20 min.

$$\therefore \qquad 20 = \frac{2.303}{k} \log \frac{4}{3}$$

$$\therefore \qquad k = \frac{2.303}{20} \log \frac{4}{3} = 0.0144\ \text{min}^{-1}$$

$$\therefore \qquad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0144} = 48.13\ \text{min}$$

**Ex.** Radioactive decay of an atomic nucleus is a first order reaction. Half-life period of radium $[_{88}Ra^{226}]$ is 1590 years. Find out its decay constant.

**Sol.** $t_{½} = \dfrac{0.693}{k_1} = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{1590} = 4.358 \times 10^{-4}\ Y^{-1}$

## SECOND ORDER REACTION

$$A \quad + \quad A \quad \longrightarrow \quad \text{Product}$$

$$A \quad + \quad B \quad \longrightarrow \quad \text{Product}$$

| | | | |
|---|---|---|---|
| At t = 0 | a | a | 0 |
| At t = t | (a – x) | (a – x) | x |
| At $t = t_1$ | $(a - x_1)$ | $(a - x_1)$ | $x_1$ |
| At $t = t_2$ | $(a - x_2)$ | $(a - x_2)$ | $x_2$ |

**As per rate law,** $\dfrac{dx}{dt} = k_2[A]^n = k_2[A]^2 = k_2\,[A][B]$

$$\therefore \qquad \left(\frac{dx}{dt}\right) = k_2\,(a-x)^2$$

($k_2$ = rate constant for second order reaction)

Also, $k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{1}{t}\frac{a}{a(a-x)}$ or $k_2 = \frac{1}{(t_2-t_1)}\left[\frac{1}{(a-x_2)} - \frac{1}{(a-x_1)}\right]$

Where $(a - x_1)$ and $(a - x_2)$ are the concentration of the reactant A at time $t_1$ and $t_2$ respectively. If reactant A and B have different concentrations a and b, then $k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

when a >> b then $(a - b) \approx a$

$(a - x) \approx a$

Equation reduces to

$$k_2 = \frac{2.303}{t \times a} \log_{10} \frac{b}{a-x}$$

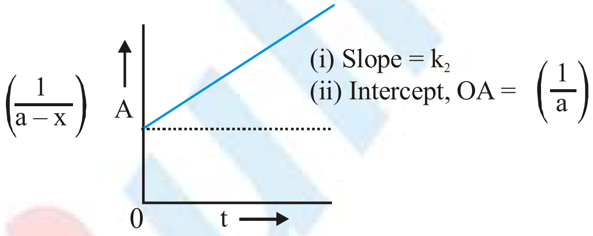
$\Rightarrow$ $k_2' = k_2 \times a = \frac{2.303}{t} \log_{10}\left(\frac{b}{b-x}\right)$ (equation for first order kinetics)

This is an example of pseudo first order reaction.

Equation for second order reaction can be rewritten as

$$\frac{a}{(a-x)} = k_2 t + \frac{1}{a}$$

**Graphical Representation**



In general for $n^{th}$ order reaction,

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

In general for $n^{th}$ order reaction,

$$t_{1/2(n)} = \frac{2^{n-1} - 1}{(n-1)k_n (a)^{n-1}} \; (n \geq 2)$$

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

$\Rightarrow$ $t_{1/2(n)} \propto a^{(1-n)}$

**Ex.** Initial concentrations of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 3000 seconds. How much time will be taken in 20% completion of the reaction ?

**Sol.** $k_2 = \frac{1}{t}\frac{x}{a(a-x)}$

Suppose, a = 1 $k_2 = \frac{1}{3000} \times \frac{0.6}{1(1-0.6)} = \frac{1}{3000} \times \frac{0.6}{0.4}$

Now, for 20% completion

$k_2 = \frac{1}{t}\frac{x}{a(1-x)}$

$$\frac{1}{3000}\times\frac{0.6}{0.4}=\frac{1}{t}\times\frac{(0.2)}{1(1-0.2)}$$

$$\frac{1}{3000}\times\frac{0.6}{0.4}=\frac{1}{t}\times\frac{1}{4}$$

$$t=\frac{3000}{0.6}\times\frac{0.4}{4}$$

t = 500 second

**Ex.** A second order reaction requires 70 minutes to change the concentration of reactants from 0.08 M to 0.01 M. How much time will it require to become 0.04 M.

**Sol.** For second order reaction

when, $(a-x)=0.01$

$$k_2=\frac{x}{t.a(a-x)}$$

$$k_2=\frac{0.07}{70\times 0.08\times(0.01)} \qquad ......\textbf{(1)}$$

$(a-x)=0.04$

$$k_2=\frac{0.04}{t\times 0.08\times(0.04)} \qquad .......\textbf{(2)}$$

From the equation **(1)** and **(2)**

$$\frac{0.07}{70\times 0.08\times(0.01)}=\frac{0.04}{t\times 0.08\times(0.04)}$$

t = 10 minutes

**Ex.** Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below :

| t/min | 0 | 30 | 60 | 90 |
|---|---|---|---|---|
| c/M | 0.8500 | 0.8004 | 0.7538 | 0.7096. |

Show that it follows a pseudo first order reaction as the concentration of $H_2O$ remains nearly constant (51.2 M) during the course of the reaction. What is the value of k in the equation?

rate = k $[CH_3COOCH_3]\,[H_2O]$

**Sol.** For pseudo first order reaction, the reaction should be first order with respect to the ester when $[H_2O]$ = constant. From the above data we note

| t | c | $k\{H_2O\}=\dfrac{\ln(c_0/c)}{t}$ min$^{-1}$ |
|---|---|---|
| 0 | 0.8500 | – |
| 30 | 0.8004 | $2.004\times10^{-3}$ |
| 60 | 0.7538 | $2.002\times10^{-3}$ |
| 90 | 0.7096 | $2.005\times10^{-3}$ |

It can be seen that k $[H_2O]$ is constant and equal to $2.004 \times 10^{-3}$ $min^{-1}$ and hence it is pseudo first order reaction. We can now determine k from

$$k\,[H_2O] = 2.004 \times 10^{-3}\ min^{-1}$$

$$k\,[51.2\ M] = 2.004 \times 10^{-3}\ min^{-1}$$

$$k = 3.914 \times 10^{-5}\ M^{-1}\ min^{-1}$$

It has the units of a second order reaction.

## THIRD ORDER REACTION

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

**(i)** $2NO + O_2 \rightleftharpoons 2NO_2$ **(ii)** $A + B + C \rightarrow \text{Product}$

**Rate constant of third order reaction**

$$\boxed{k_3 = \frac{1}{t}\cdot\frac{x(2a-x)}{2a^2(a-x)^2}}$$

**Half life period** $\boxed{t_{1/2} = \frac{3}{2ka^2}}$

Thus, half life is inversely proportional to the square of initial concentration.

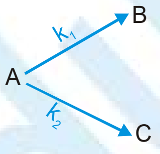
**nth order reaction :**

$A \rightarrow \text{Product}$

$$k_n t = \frac{1}{n-1}\left\{\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right\} \qquad [n \neq 1, n = \text{order}]$$

$$t_{1/2} = \frac{1}{k_n(n-1)}\cdot\left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$

**Side or concurrent reaction :**

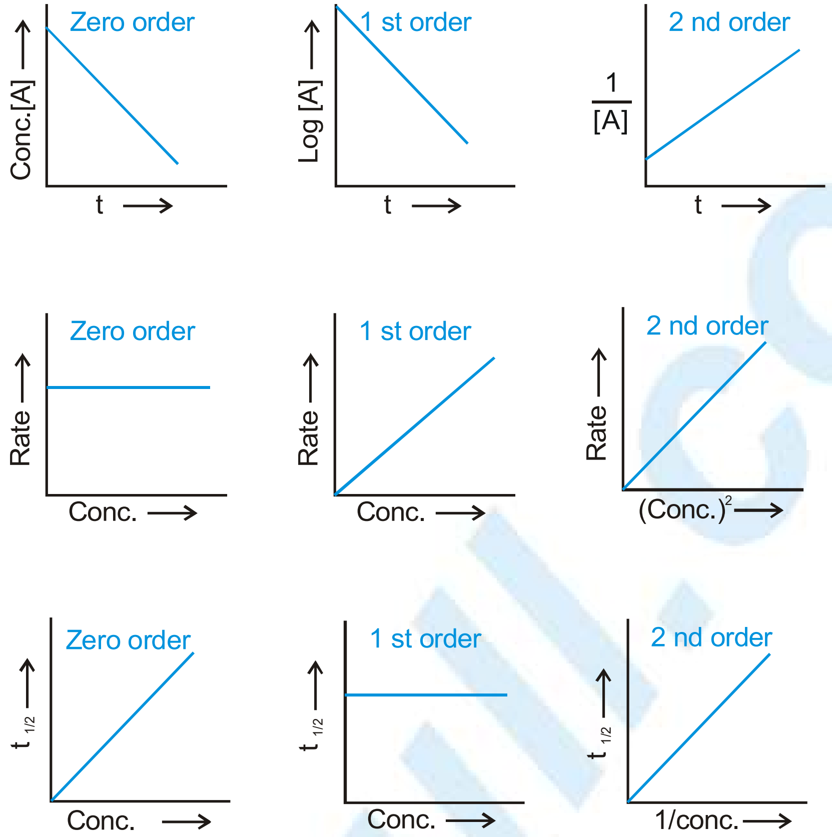


; $\ln\frac{[A]_0}{[A]_t} = (k_1 + k_2)\,t$ ; $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

**Consecutive reaction :**

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$ : $t_{max} = \frac{1}{k_1 - k_2}\ln\left(\frac{k_1}{k_2}\right)$ : $[B]_{max} = [A]_0\left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1-k_2}}$

## Graphical comparison of different orders



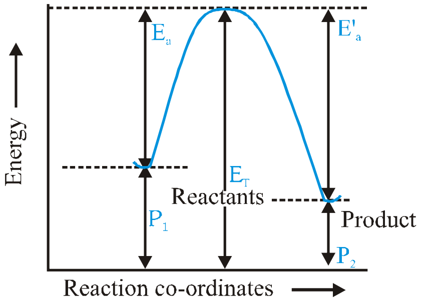
## THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must colloid together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy ($E_T$).

**Activation energy (Ea) :**

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.

$E_T$ = Threshold energy
$E_a$ = Activation energy of forward reaction
$E'_a$ = activation energy of backward reaction
$P_1$ = Potential energy of reactants
$P_2$ = Potential energy of products



## EFFECT OF CATALYST

A catalyst is a substance, which increases the rate of reaction without itself being consumed at the end of the reaction, and the phenomenon is called catalysis. There are some catalysts which decrease the rate of reaction and such catalysts are called negative catalyst. Obviously, the catalyst accelerating the rate will be positive catalyst. However, the term positive is seldom used and catalyst itself implies positive catalyst.

Catalysts are generally foreign substances but sometimes one of the product formed may act as a catalyst and such a catalyst is called "auto catalyst" and the phenomenon is called **auto catalysis.**

Thermal decomposition of $KClO_3$ is found to be accelerated by the presence of $MnO_2$. Here, $MnO_2$ (foreign substance) act as a catalyst $2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2\uparrow + [MnO_2]$

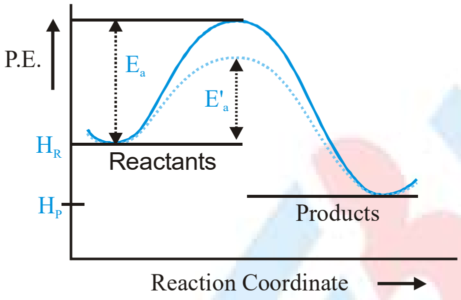
$MnO_2$ can be received in the same composition and mass at the end of the reaction.

In the permanganate titration of oxalic acid in the presence of bench $H_2SO_4$ (acid medium), it is found that there is slow discharge of the colour of permanganate solution in the beginning but after sometime the discharge of the colour becomes faster. This is due to the formation of $MnSO_4$ during the reaction which acts as a catalyst for the same reaction. Thus, $MnSO_4$ is an **"auto catalyst"** for this reaction. This is an example of auto catalyst.

$2KMnO_4 + 4H_2SO_4 + 5H_2C_2O_2 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2$

## GENERAL CHARACTERISTIC OF CATALYST

- A catalyst does not initiate the reaction, it simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence ΔG°. It simply lowers the time needed to attain equilibrium. This mean if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst also the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.
- A catalyst drives the reaction through a different route for which energy barrier is of shortest height and Hence, $E_a$ is of lower magnitude. That is, the function of the catalyst is to lower down the activation energy.



$E_a$ = Energy of activation in absence of catalyst.

$E'_a$ = Energy of activation in presence of catalyst.

$E_a - E'_a$ = Lowering of activation energy by catalyst.

If k and $k_{cat}$ be the rate constant of a reaction at a given temperature T, and $E_a$ and $E'_a$ are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'_a/RT}}{Ae^{-E_a/RT}}$$

$$\frac{k_{cat}}{k} = Ae^{(E_a - E'_a)/RT}$$

Since $E_a$, $E'_a$ is +ve, so $k_{cat} > k$. The ratio $\frac{k_{cat}}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature and this depends upon $E_a - E'_a$. Greater the value of $E_a - E'_a$, more number of times $k_{cat}$ is greater than k.

The rate of reaction in the presence of catalyst at any temperature $T_1$ may be made equal to the rate of reaction in absence of catalyst but we will have to raise the temperature. Let, this temperature be $T_2$, then

$$e^{-E'_a/RT_1} = e^{-E_a/RT_2}$$

or $$\frac{E'_a}{T_1} = \frac{E_a}{T_2}$$

**Ex.** A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of catalyst at the same rate, the temperature required is 400K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 40 kJ/mol.

**Sol.** Let, $E_a$ and $E'_a$ be the energy of activation in absence and presence of catalyst for hydrogenation reaction, as

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

$$k_1 = Ae^{-E_a/R\times500} \quad \text{(In absence of catalyst)}$$

$$k_2 = Ae^{-E'_a/R\times400} \quad \text{(In presence of catalyst)}$$

Given, $r_1 = r_2$ ; Hence $k_1 = k_2$

$$e^{-E_a/R\times500} = e^{-E'_a/R\times400}$$

$$\Rightarrow \quad \frac{E_a}{R\times500} = \frac{E'_a}{R\times400} \quad \text{or} \quad \frac{E_a}{500} = \frac{E_a - 40}{400} \quad (\text{As } E_a - E'_a = 40)$$

$$\therefore \quad E_a = 200 \text{ kJ/mol}^{-1}$$

## DETERMINATION OF ORDER OF REACTION

### Integration Method

In this method, value of k is determined by putting values of initial concentration of reactants and change in concentration with time in kinetic equation of first, second and third order reactions. The equation by which constant value of k is obtained is called order of that reaction.

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x} \quad \text{(For first order reaction)}$$

$$k_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \quad \text{(For second order reaction)}$$

$$k_3 = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] \quad \text{(For third order reaction)}$$

**Ex.** For a reaction, A → B, it has been found that the order of the reaction is zero with respect to A. Which of the following expression correctly describes the reaction ?

**[A]** $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$ **[B]** $[A]_0 - [A] = kt$ **[C]** $t_{1/2} = \frac{0.693}{k}$ **[D]** $t_{1/2} \propto \frac{1}{[A]_0}$ **Ans. [B]**

**Sol.** $-\frac{d[A]}{dt} = k[A]_0, -d[A] = kdt$

Integrating from $t = 0$ to $t = t$ $\quad [A]_0 - [A] = kt$

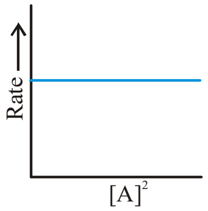
### Graphical Method

If a straight line is obtained on drawing a graph between log (a – x) and time then it is first order reaction.

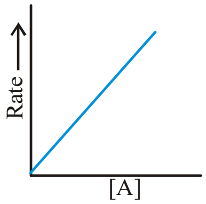
If a straight line is obtained on drawing a graph between $(a-x)^2$ and $\frac{dx}{dt}$, then it is second order reaction.

**Ex.** Which of the following graphs is for a second order reaction ?

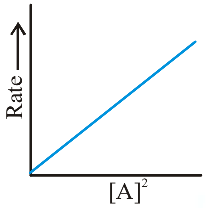
**[A]**



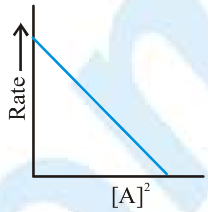
**[B]**



**[C]**



**[D]**



**Ans. [C]**

**Sol.** For second order reaction rate vs $[A]^2$ is a straight line with slope equal to k rate = $k[A]^2$

If a straight line is obtained on drawing a graph between $(a - x)^3$ and $\frac{dx}{dt}$, then it is third order reaction.

**Half-life Method**

Relation between half-life period of a reaction and initial concentration is as follows : $t^{1/2} \propto \frac{1}{a^{n-1}}$

| | |
|---|---|
| For first order reaction | (Half life $\propto a^0$) |
| For second order reaction | (Half life $\propto 1/a$) |
| For third order reaction | (Half life $\propto 1/a^2$) |

**Ex.** For a first order reaction, $t_{0.75}$ is 1386 seconds. Therefore, the specific rate constant is

**[A]** $10^{-1}\ s^{-1}$ **[B]** $10^{-3}\ s^{-1}$ **[C]** $10^{-2}\ s^{-1}$ **[D]** $10^{-4}\ s^{-1}$ **Ans. [B]**

**Sol.** $t_{0.75} = 1386\ s = 2 \times t_{0.5}$ ; $t_{0.5} = \frac{1386}{2} = 693\ s$ ; $k = \frac{0.693}{693\,s} = 1 \times 10^{-3}\ s^{-1}$

**Ex.** $t_{½}$ of first order reactions is given by $\frac{0.693}{k}$, $t_{3/4}$ would be equal to

**[A]** $\frac{0.693}{k}$ **[B]** $\frac{0.346}{k}$ **[C]** $\frac{1.386}{k}$ **[D]** $\frac{0.924}{k}$ **Ans. [C]**

**Sol.** $t_{3/4} = 2(t_{½}) = \frac{2 \times 0.693}{k} = \frac{1.386}{k}$

**Ex.** The $t_{½}$ of a first order reaction is found to be 2 minutes. The percentage of the reactant left after 360 seconds is :

**[A]** 12.5 **[B]** 25 **[C]** 15 **[D]** 7.5 **Ans. [A]**

**Sol.** 360 seconds = 6 min = 3 half-lives

$$100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5$$

**Ex.** The rate of decomposition of $N_2O_5$ in $CCl_4$ solution has been studied at 318 K and the following results have been obtained :

| t/min | 0 | 135 | 342 | 683 | 1693 |
|---|---|---|---|---|---|
| c/M | 2.08 | 1.91 | 1.67 | 1.35 | 0.57 |

Find the order of the reaction and calculate its rate constant. What is the half-life period?

**Sol.** It can be shown that these data will not satisfy the integrated rate law of zero order. We now try integrated first order equation i.e., $k = \frac{\ln(c_0 / c)}{t}$

| t/min | c/M | $k = \frac{\ln(c_0/c)}{t}\ \text{min}^{-1}$ |
|---|---|---|
| 0 | 2.08 | $6.32 \times 10^{-4}$ |
| 135 | 1.91 | $6.30 \times 10^{-4}$ |
| 342 | 1.67 | $6.32 \times 10^{-4}$ |
| 683 | 1.35 | $6.32 \times 10^{-4}$ |
| 1693 | 0.57 | $6.31 \times 10^{-4}$ |

It can be seen that the value of k is almost constant for all the experimental results and hence it is first order reaction with $k = 6.31 \times 10^{-4}\ \text{min}^{-1}$.

$$t_{1/2} = \frac{0.69}{6.31 \times 10^{-4}\ \text{min}^{-1}} = 1.094 \times 10^{3}\ \text{min}^{-1}$$

Graphical method : Alternatively, if we draw a graph between ln c against t, we obtain a straight line with slope = – k.

**Ex.** In the reduction of nitric gas with hydrogen, the reaction was found to be 50% complete in 210 seconds when the initial pressure of the mixture was 200 mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300 mm. Calculate the total order of the reaction.

**Sol.** For a nth order reaction (n ≠ 1), $t_{1/2} \propto \frac{1}{c_0^{n-1}}$

$$\frac{210}{140} = \left(\frac{300}{200}\right)^{n-1} \qquad n = 2$$

## OSTWALD ISOLATION METHOD

This method is used to find out the order of complex reactions. If nA, nB and nC molecules of substance A, B and C, respectively, are present in a reaction, then nA + nB + nC will be the order of reaction.
When B and C are in excess, the order of reaction will be nA.
When A and B are in excess, the order of reaction will be nC.
When A and C are in excess, the order of reaction will be nB.

**Ex.** When the initial concentration of a reaction was doubled, its half life become half, What should be the order of the reaction ?

**Sol.** Rate law for product of a reaction is as follows :

$$\text{Rate} = k[A]^n \qquad \text{and} \quad \frac{t_{0.5}}{t_{\frac{0.5}{2}}} = \left[\frac{2a}{a}\right]^{n-1}$$

$$2 = [2]^{n-1}; \qquad n - 1 = 2$$

$$n = 2$$

**Ex.** The reaction : $CH_3COF + H_2O \rightarrow CH_3COOH + HF$

has been studied under the following initial conditions :

**Case I**

$c^0_{H_2O} = 1.00\ M$

$c^0_{CH_3COF} = 0.01\ M$

**Case II**

$c^0_{H_2O} = 0.02\ M$

$c^0_{CH_3COF} = 0.80\ M$

Concentration were monitored as a function of time and are given below :

**Case I**

| t/min | $c_{CH_3COF}$ / M |
|---|---|
| 0 | 0.01000 |
| 10 | 0.00857 |
| 20 | 0.00735 |
| 40 | 0.00540 |

**Case II**

| t/min | $c_{H_2O}$ /M |
|---|---|
| 0 | 0.0200 |
| 10 | 0.0176 |
| 20 | 0.0156 |
| 40 | 0.0122 |

Determine the order of the reaction and the rate constant for the reaction.

**Sol.** Let rate = k $(c_{CH_3COF})^a (c_{H_2O})^b$

We shall use here Ostwald isolation method, as in one set of experimental conditions, $c^0_{H_2O} >> c^0_{CH_3COF}$ and in the second case, $c^0_{H_2O} << c^0_{CH_3COF}$. In the first case we determine the order of the reaction with respect to $CH_3COF$. We note that the reaction is not of zero order as rate of reaction changes with time. We now, apply first order equation and find,

| t/min | $c_{CH_3COF}$ / M | $\frac{k(c_{H_2O})^b}{min^{-1}} = \frac{\ln\left(\frac{c^0_{CH_3COF}}{c_{CH_3COF}}\right)}{t}$ |
|---|---|---|
| 0 | 0.01000 | – |
| 10 | 0.00857 | 0.0154 |
| 20 | 0.00735 | 0.0154 |
| 40 | 0.00540 | 0.0154 |

Therefore, $k(c_{H_2O}) = 0.0154\ min^{-1}$

and we know that the order of reaction with respect to $CH_3COF$ is 1. Now we determine the order of reaction with respect to water. Again we try for first order equation.

| t/min | $c_{H_2O}$ / M | $\frac{k(c_{CH_3COF})^b}{min^{-1}} = \frac{\ln\left(\frac{c^0_{H_2O}}{c_{H_2O}}\right)}{t}$ |
|---|---|---|
| 0 | 0.0200 | – |
| 10 | 0.0176 | 0.0128 |
| 20 | 0.0156 | 0.0124 |
| 40 | 0.0122 | 0.0124 |

average = $0.0125\ min^{-1}$

The reaction is first order in $H_2O$ and we have $k(c_{CH_3COF}) = 0.0125\ min^{-1}$

$$\text{Niw in case I, } k = \frac{0.0154 min^{-1}}{1.00} = 0.0.154\ M^{-1}\ min^{-1}$$

$$\text{and in case II} = \frac{0.0125}{0.800} = 0.0156\ M^{-1}\ min^{-1}.$$

## TEMPERATURE EFFECT

The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient which is a ratio of two rate constants differing by a temperature of 10°. Generally the temperature selected are 298K and 308K. It is mathematically expressed as,

$$\text{Temperature coefficient} = \frac{\text{rate constant at 308K}}{\text{rate constant at 298K}} = \frac{k_t + 10}{k_t}$$

**The value of temperature coefficient for most of the reactions lies between 2 to 3.**

**Ex.** For a reaction T.C. = 2, Calculate $\frac{k_{40°C}}{k_{25°C}}$ for this reaction.

**Sol.** $\frac{k_2}{k_1} = (T.C.)^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$

But the method of temperature coefficient was not exact and to explain the effect of temperature on reaction rate new theory was evolved

## ARRHENIUS EQUATION

Arrhenius derived a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression is

$$k = A.e^{-Ea/RT}$$

(Here, A = frequency factor; Ea = activation energy ; R = gas constant and T = temperature).

If $k_!$ and $k_2$ are rate constants at temperature $T_1$ and $T_2$ then

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\ \ R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

**Ex.** Ethylene oxide is decomposed into $CH_4$ and CO. Rate constant for this reaction may be described by the equation $\log k\ (s^{-1}) = 14.34 - \frac{1.25\times10^4}{T}$

**(i)** What will be the energy of activation of this reaction ?

**(ii)** What will be the value of k at 670 K ?

**(iii)** At what temperature will its half-life period be 25.6 minutes ?

**Sol.** **(i)** We know, $\log_{10}k = \log_{10}A - \frac{E_a}{2.303RT}$ .......**(i)**

Given, $\log k\ (s^{-1}) = 14.34 - \frac{1.25\times10^4}{T}$ .......**(ii)**

Comparing Eqs. **(i)** and **(ii)**, we get

$$\frac{E_a}{2.303R} = 1.25 \times 10^4$$

**(ii)** $E_a = 1.25 \times 10^4 \times 2.303 \times 8.314 \times 10^{-3}$

$\therefore$ $E_a = 239.339$ kJ/mol

Substituting the value of T (670 K) in Eq. **(ii)**,

$$\log k\,(s^{-1}) = 14.34 - \frac{1.25\times10^4}{670} = 4.3167$$

$\therefore$ $k = 4.82 \times 10^{-5}\ s^{-1}$

**(iii)** $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{256\times 60} = 0.000451\ \text{sec}^{-1}$

$\Rightarrow \log 0.000451\ \text{sec}^{-1}$

$= 14.34 - \dfrac{1.25\times10^4}{T}$ $\Rightarrow$ **T = 706.79 K**

**Ex.** Two I$^{st}$ order rxns. are initially having equal rate at a particular temprature. Temprature of both the reaction is increased by same amount. Calculate rate of which reaction will increase by greater amount ( reaction with low $E_a$ or high $E_a$)

**Sol.** ●n $\left(\dfrac{k_2}{k_1}\right) = \dfrac{E_a}{R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\}$ .....**(i)**

●n $\left(\dfrac{k_2'}{k_1}\right) = \dfrac{E_a'}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2'}\right]$ .....**(ii)**

Equation **(i)** – **(ii)**.

●n $\left(\dfrac{k_2}{k_2'}\right) = \dfrac{\Delta T}{R}\ (E_a - E_{a'})$

if $E_a > E_{a'}$, $k_2 > k_2'$

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

$$\frac{dk}{dT} = \frac{-\,EaA}{RT}\left(\frac{-1}{T^2}\right)A\,e^{-E_a/RT}$$

temprature coeff. of rate constant $\dfrac{1}{K}\dfrac{dk}{dT} = \dfrac{E_a}{RT^2}$

$\dfrac{\Delta k}{k.\Delta T}$ = fractional change / unit temp. rise

**Ex.** Explain on the basis of temprature coeff. of rate const. that equilibrium of endothermic reaction shifts in forward direction on increasing temprature while equilibriums of exothermic shift back.

●n $\left(\dfrac{K_{eq1}}{K_{eq2}}\right) = \dfrac{\Delta H}{R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\}$

**Sol.** $\Delta H = E_{af} - E_{ab} > 0$ (for endothermic)

$E_{af} > E_{ab}$

on increasing temp. $k_f \uparrow$ more than $k_b$

equilibrium will shift in forward direction.

**Ex.** The rate constant of forward reaction a reaction increases by 6% when the temperature of the reaction is increased from 300 to 301 K, whereas equilibrium constant increases by 2%. Calculate the activation energy for the forward as well as backward reaction.

**Sol.** According to Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{E_{a(f)}}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

If $k_1 = k$ at 300 K then at 301 K, $k_2 = k + k \times \frac{6}{100} = 1.06\ k$

$$\therefore \quad \log_{10}\frac{1.06\,k}{k} = \frac{E_{a_{(f)}}}{2.303 \times 8.314}\left[\frac{301 - 300}{300 \times 301}\right]$$

$$\therefore \quad E_{a_{(f)}} = \log(1.06) \times 2.303 \times 8.314 \times 300 \times 301 = 43753 \text{ J/mol} = 43.753 \text{ kJ/mol}$$

According to van't Hoff equation, $\log \frac{k_2}{k_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

If $k_1 = k$ at 300 k, $k_2 = k + \frac{2}{100} = 1.02\ k$

$$\log_{10}\frac{1.02\,k}{k} = \frac{\Delta H^\circ}{2.303 \times 8.314}\left(\frac{301 - 300}{300 \times 301}\right)$$

$$\therefore \quad \Delta H^\circ = (\log 1.02) \times 2.303 \times 8.314 \times 300 \times 301 \text{ J/mol}$$

$$= 14869 \text{ J mol}^{-1} = 14.87 \text{ kJ/mol}$$

Thus, reaction is endothermic.

For such a reaction, $\Delta H^\circ = E_{a(f)} - E_{a(b)}$

$$\therefore \quad E_{a(b)} = E_{a(f)} - \Delta H^\circ = 43.753 - 14.87 \text{ kJ/mol} = 28.883 \text{ kJ mol}^{-1}$$

**Ex.** Value of rate constant for a first order reaction at 500 K is $1.60 \times 10^{-5}$ second$^{-1}$, whereas at 600 K, it is $6.36 \times 10^{-3}$ second$^{-1}$. Find out the activation energy of the reaction.

**Sol.** $\log\left(\frac{k_1}{k_2}\right) = \frac{-E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$\log 1.60 \times 10^{-5} - \log 6.36 \times 10^{-3} = \frac{-E_a}{2.303 \times 8.314}\left[\frac{1}{500} - \frac{1}{600}\right]$$

$$5.241 - 3.8035 = \frac{E_a}{19.15} \times \frac{1}{3000} \qquad E_a = 2.5999 \times 19.15 \times 3000$$

$$E_a = 1.49 \times 10^5$$

**Ex.** An exothermic reaction, $X \rightarrow Y$, has an activation energy 30 kJ $mol^{-1}$. If energy change ($\Delta E$) during the reaction is – 20kJ, then the activation energy for the reverse reaction is

**[A]** –30kJ **[B]** 20 kJ **[C]** 50 kJ **[D]** 10 kJ **Ans. [C]**

**Sol.** $\Delta E = E_{a_{(f)}} - E_{a_{(b)}}$ ; $-20 = 30 - E_{a_{(b)}}$ ; $E_{a_{(b)}} = 50$ kJ

**Ex.** An endothermic reaction, $A \rightarrow B$, has an activation energy as x kJ $mol^{-1}$ of A. If energy change of the reaction is y kJ, the activation energy of reverse reaction is

**[A]** $-x$ **[B]** $x - y$ **[C]** $x + y$ **[D]** $y - x$

**Ans. [B]**

**Sol.** $\Delta E = E_{a_{(f)}} - E_{a_{(b)}}$ ; $y = x - E_{a_{(b)}}$ ; $E_{a_{(b)}} = x - y$

**Ex.** Which of the following relations is correct ?

**[A]** $k = A\,e^{Ea/RT}$ **[B]** $\ln k - \ln A = \frac{E_a}{RT}$ **[C]** $\ln A - \ln k = \frac{E_a}{RT}$ **[D]** $\ln A - \ln k = -\frac{E_a}{RT}$

**Ans. [C]**

**Sol.** $k = Ae^{-Ea/RT}$

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

**Ex.** Which of the following expression give the effect of temperature on the rate constant ?

**[A]** $\ln A = RT \ln E_a - \ln k$ **[B]** $\ln k = \ln A - E_a/RT$

**[C]** $k = AE_a/RT$ **[D]** None of these **Ans. [B]**

**Sol.** The effect of temperature on rate constant is quantitatively given by Arrhenius equation

$$k = Ae^{-Ea/RT} \text{ or } \ln k = \ln A - E_a/RT$$

**Ex.** The plot of log k vs $\frac{1}{T}$ helps to calculate

**[A]** Energy of activation **[B]** Rate constant of the reaction

**[C]** Order of the reaction **[D]** Energy of activations as well as the frequency factor

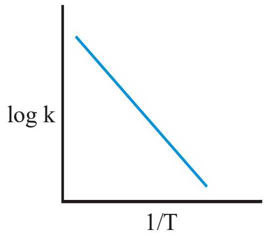
**Ans. [D]**

**Sol.** According to Arrhenius equation : $\log k = \log A - \frac{E_a}{2.303} \cdot \frac{1}{T}$

Plot of log k vs. $\frac{1}{T}$ is straight line

Slope $= -\frac{E_a}{2.303\,R}$

Intercept = log A



**Ex.** The progress of the reaction given below, consider the reaction given below,

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

the reaction can be followed by measuring the concentration of acid (HCl acid used as catalyst plus acetic acid formed during the reaction) by means of alkali titration. Calculate the volume of alkali (NaOH) needed for the end point that will increase with time.

**Sol.** $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

| | | | | |
|---|---|---|---|---|
| At t = 0 | a | excess | 0 | 0 |
| At t = t | a – x | | x | x |
| At t = ∞ | 0 | | a | a |

If $V_0$, $V_t$ and $V_\infty$ are the volumes of NaOH solution needed for the end point of titration of the reaction mixture at zero time, time t and at infinity, i.e. after completion of the reaction the condition being achieved by heating the reaction mixture for some time, then

$V_0 \propto$ [acid catalyst]

$V_t \propto$ [acid catalyst] + x

$V_\infty \propto$ [acid catalyst] + a

$\therefore \quad V_\infty - V_t \propto a - x$

$\quad V_\infty - V_0 \propto a$

(since concentration of HCl acid acting as catalyst will remain constant).

The above reaction which is of first order ( actually pseudo unimolecular) will, therefore, obey following equation.

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

**Ex.** $H_2O_2\,(aq.) \longrightarrow H_2O + \frac{1}{2}O_2\uparrow$

| | | | |
|---|---|---|---|
| At t = 0 | a | 0 | 0 |
| At t = t | a – x | x | x |

Since $H_2O_2$ acts as a reducing agent towards $KMnO_4$, so concentrations of $H_2O_2$ at various time intervals may be determined by the titration of the reaction mixture against standard $KMnO_4$ solution. The titre value will go on decreasing with time. If $V_0$ and $V_t$ be the titre values at zero time and any time t then $V_0 \propto a$ and $V_t \propto a - x$

The above reaction being first order, its rate constant may be expressed as

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

**Ex.** The reaction mentioned below is first order w.r.t. sucrose and zero order w.r.t. water, since water is in large excess as compared to sucrose. That is, it is an example of pseudo unimolecular reaction. Sucrose, glucose and fructose all are optically active substances. Therefore, the progress of the reaction can be followed by measuring angle of rotations of the reaction mixture at various time intervals.

During the reaction, angle of rotation goes on decreasing and after sometime there is reversal of the direction of rotation, i.e. from dextro to laevo and Hence, the reaction is called **"inversion of cane sugar"** or inversion of sucrose.

$$\underset{\text{d-Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{d-Glucose}}{C_6H_{12}O_6} + \underset{\bullet\text{-Fructose}}{C_6H_{12}O_6}$$

| | | | | |
|---|---|---|---|---|
| Initially | a | Excess | 0 | 0 |
| After time t | a – x | Constant | x | x |
| At infinity | 0 | Constant | a | a |

Angle of optical rotation is measured by means of an instrument called polarimeter. Optical rotation is mathematically expressed as,

$$R_{obs} = \bullet.C.\,[\alpha]_D^t$$

where

● = length of the polarimeter tube

C = concentration of test solution

$[\alpha]_D^t$ = specific rotation

For a given sample and polarimeter, ● and $[\alpha]_D^t$ are constant.

$R_{obs} \propto C$, or $R_{obs} = kC$,

If $r_0$, $r_t$ and $r_\infty$ be the observed angle of rotations of the sample at zero time, time t and infinity respectively, and $k_1$, $k_2$ and $k_3$ be proportionate in terms of sucrose, glucose and fructose, respectively.

Then,

$r_0 = k_1 a$

$r_t = k_1(a - x) + k_2 x + k_3 x$

$r_\infty = k_2 a + k_3 a$

From these equations it can be shown that

$$\frac{a}{a-x} = \frac{r_0 - r_\infty}{r_t - r_\infty}$$

So, the expression for the rate constant of this reaction in terms of the optical rotational data may be put as k

$$= \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

**Ex.**

| | $2N_2O_5 \longrightarrow$ | $4NO_2$ | $+ O_2$ |
|---|---|---|---|
| At t = 0 | $P_0$ | 0 | 0 |
| At t = t | $P_0 - 2x$ | 4x | x |
| At t = ∞ | 0 | $2P_0$ | ½ $P_0$ |

The progress of the reaction can be followed by measuring the pressure of the gaseous mixture in a closed vessel, i.e. at constant volume. The expression for the rate constant in terms of pressure data will be as given below.

$$k = \frac{2.303}{t} \log \frac{P_0}{P_t}, \text{ where } P_t = P_0 - 2x$$

If total pressure after any time t and at ∞ is given, then it is possible to find $P_0$ and x and hence, k may be calculated.

**Ex.** Consider a first order reaction,

$A \rightarrow B + C$

Assume that A, B and C are gases. The given data is

| Time | 0 | T |
|---|---|---|
| Partial pressure of A | $P_1$ | $P_2$ |

And we have to find the rate constant of the reaction.

**Sol.** Since A is a gas assuming it to be ideal, we can state that $P_A = [A]\,RT$ [From PV = nRT]

$\therefore$ At t = 0, $P_1 = [A]_0 RT$ and at t = t, $P_2 = [A]_t RT$. Thus, the ratio of the concentration of A at two different time intervals is equal to the ratio of its partial pressure at those same time intervals.

$$\therefore \quad \frac{[A]_0}{[A]_t} = \frac{P_1}{P_2}$$

$$\therefore \quad k = \frac{1}{t} \ln \frac{P_1}{P_2}$$

**Ex.** $A \rightarrow B + C$

| | | |
|---|---|---|
| Time | 0 | t |
| Total pressure of A + B + C | $P_1$ | $P_2$ |

Find k.

**Sol.** In this case, we are given total pressure of the system at these time intervals. The total pressure obviously includes the pressure of A, B and C. At t = 0, the system would only have A. Therefore, the total pressure at t = 0 would be the initial pressure of A.

$\therefore$ $P_1$ is the initial pressure of A. At time t, let us assume moles of A will decompose to give B and C because of which its pressure is reduced by an amount x while that of B and C is increased by x each. That is :

| | $A \longrightarrow$ | B + | C |
|---|---|---|---|
| Initial | $P_1$ | 0 | 0 |
| At time t | $P_1 - x$ | x | x |

$\therefore$ Total pressure at time t = $P_1 + x = P_2$

$\Rightarrow \quad x = P_2 - P_1$

Now the pressure of A at time t would be $P_1 - x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

$$\therefore \quad k = \ln\frac{[A]_0}{[A]_t} = \ln\frac{P_1}{(2P_1 - P_2)}$$

**Ex.** For the given following first order reaction,

$$A \longrightarrow B + C$$

| | | |
|---|---|---|
| Time | T | $\infty$ |
| Total pressure of A + B + C | $P_2$ | $P_3$ |

Calculate k.

**Sol.** Here $\infty$ means that the reaction is complete. Now, we have

| | A $\longrightarrow$ | B + | C |
|---|---|---|---|
| At t = 0 | $P_1$ | 0 | 0 |
| At t = t | $(P_1 - x)$ | x | x |
| At t = $\infty$ | 0 | $P_1$ | $P_1$ |

$\therefore \quad 2P_1 = P_3$

$$\Rightarrow \quad P_1 = \frac{P_3}{2}$$

At time t,

$P_1 + x = P_2$

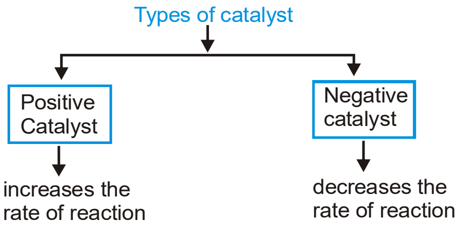
$$\Rightarrow \quad \frac{P_3}{2} + x = P_2 \Rightarrow x = P_2 - \frac{P_3}{2}$$

$$\Rightarrow \quad P_1 - x = \frac{P_3}{2} - (P_2 - \frac{P_3}{2}) = P_3 - P_2$$

$$k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{P_3/2}{(P_3 - P_2)} = \frac{1}{t}\ln\frac{P_3}{2(P_3 - P_2)}$$

## CATALYST AND CATALYSIS :

A **catalyst** is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called **catalysis**.



Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called **"auto catalyst"** and the phenomena is called **auto catalysis**.

**Examples of catalysis**

**(a)** Thermal decomposition of KClO$_3$ is found to be accelerated by the presence of MnO$_2$. Here MnO$_2$ acts as a catalysts.

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 \uparrow + [MnO_2]$$

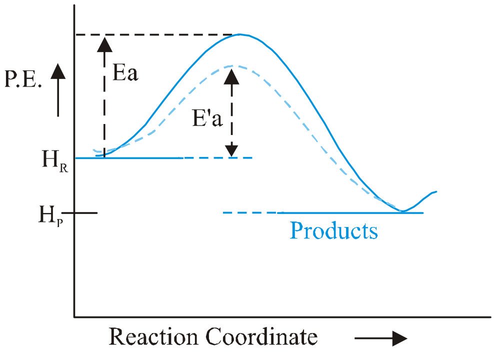
MnO$_2$ can be received in the same composition and mass at the end of the reaction.

**(b)** In the permanganate titration of oxalic acid initially there is slow discharge of the colour of permanganate solution but afterwards the discharge of the colour become faster. This is due to the formation of MnSO$_4$ during the reaction which acts as a catalyst for the same reaction. Thus, MnSO$_4$ is an **"auto catalyst"** for this reaction. This is an example of auto catalyst.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2 + 2MnSO_4$$

## General Characteristics of Catalyst

- A catalyst does not initiate the reaction. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence $\Delta G^o$. It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.
- A catalyst drives the reaction through a low energy path and hence E$_a$ is less. That is, the function of the catalyst is to lower down the activation energy.
  $E_a$ = Energy of activation in absence of catalyst.
  $E'_a$ = Energy of activation in presence of catalyst.
  $E_a - E'_a$ = lowering of activation energy by catalyst.



## Comparison of Rates of Reaction in Presence and Absence of Catalyst

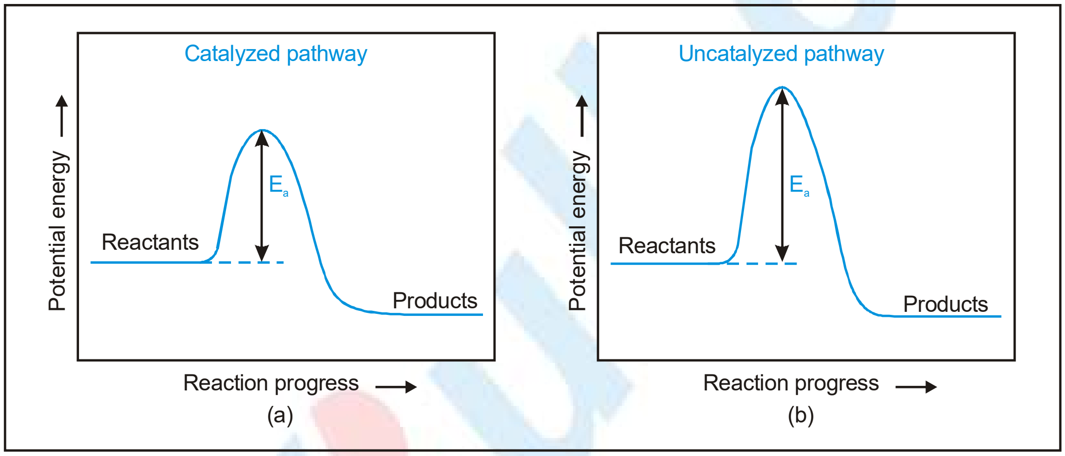
If k and $k_{cat}$ be the rate constant of a reaction at a given temperature T, and $E_a$ and $E'_a$ are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'a/RT}}{Ae^{-Ea/RT}} = Ae^{(E_a - E'_a)/RT}$$

Since $E_a - E'_a$ is positive so $k_{cat} > k$. the ratio $\frac{k_{cat}}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature

The rate of reaction in the presence of catalyst at any temperature $T_1$ may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature be

$$T_2 \;=\; e^{-E'_a/RT_1} = e^{-E_a/RT_2} \quad \text{or} \qquad \frac{E'_a}{T_1} = \frac{E_a}{T_2}$$



**Ex.** For the reaction $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ under the same concentration conditions of the reactants, the rate of the reaction at 250°C is 1500 times as fast as the same reaction at 150°C. Calculate the activation energy of the reaction. If the frequency factor is $2.0 \times 10^{10}\ M^{-1}\ sec^{-1}$, calculate the rate constant of the reaction at 150°C.

**Sol.** $$\log\frac{k_2}{k_1} = \frac{E}{2.303\ R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

$$\log 1500 = \frac{E}{2.303 \times 2} \times \frac{100}{523 \times 423}$$

$$E = \frac{3.1761 \times 2.303 \times 2 \times 523 \times 423}{100} = 32.36\ \text{kcal mol}^{-1}$$

$$\log k = \log A - \frac{E}{2.303\ RT} = \log(2.0 \times 10^{10}) - \frac{32360}{2.303 \times 2 \times 423} = 10.301 - 16.609 = -6.308$$

$$k = 4.92 \times 10^{-7}\ \text{litres mol}^{-1}\ \text{sec}^{-1}$$

**Ex.** The pyrolysis of an organic ester follows a first order process and its rate constant can be expressed as

$$\ln k = 78.09 - \frac{42075}{T}$$

where k is given in the $\text{min}^{-1}$. Calculate the time required for 25 percent reaction to complete at 227°C.

**Sol.** $\ln k = 78.09 - \dfrac{42075}{500} = -6.06$

$$\log k = -\frac{6.06}{2.303} = -2.63\ ;\ k = 2.344 \times 10–3\ \text{min}^{-1}$$

$$\text{when } x = 0.25\ ;\ k = \frac{2.303}{t_{1/4}} \log \frac{a}{0.75a}$$

$$t_{1/4} = \frac{2.303}{2.344 \times 10^{-3}} \log 1.333 = 123.06\ \text{min}$$

**Ex.** The slope of the plot of log k vs $\dfrac{1}{T}$ for a certain reaction was found to be $-5.4 \times 10^3$. Calculate the energy of activation of the reaction. If the rate constant of the reaction is $1.155 \times 10^{-2}\ \text{sec}^{-1}$ at 373 K, what is its frequency factor ?

**Sol.** **(a)** slope $= \dfrac{-E}{2.303\ R} = -5.4 \times 10^3$

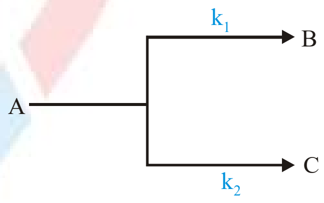
$$E = 5.4 \times 10^3 \times 2.303 \times 1.987 = 24.624\ \text{cal mol}^{-1}$$

**(b)** $E = Ae^{-E/RT}$ ; $\log 1.155 \times 10^{-2} = \log A - \dfrac{24.624}{2.303 \times 1.987 \times 373}$

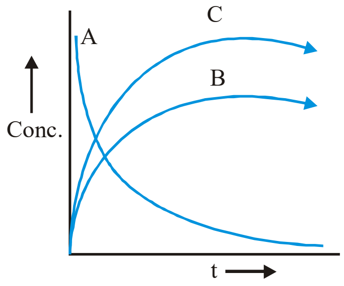
or $A = 1.764 \times 10^3\ \text{sec}^{-1}$

## PARALLEL REACTIONS

These are reactions in which reaction substances do not follow a particular path to give a particular set of products. It follows one or more paths to give different products, e.g.



The reactant A follows two different paths to form B and C as shown below :

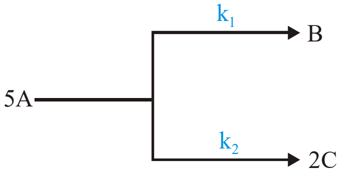


$$\text{Rate} = -\frac{d[A]}{dt} = k_1\mathbf{[A] + k_2[A]}$$

$$= k[A] \; [\text{As}, (k_1 + k_2) = k]$$

$$\% \text{ yield of B} = \frac{k_1}{k_1 + k_2} \times 100$$

**Ex.** A follows parallel path, first order reaction giving B and C as



If initial concentration of A is 0.25 M, calculate the concentration of C after 5 hours of reaction.
[Given : $k_1 = 1.5 \times 10^{-5}\ s^{-1}$, $k_2 = 5 \times 10^{-6}\ s^{-1}$]

**Sol.** $k = \frac{2.303}{t}\log\frac{[A]}{[A]_t}$ $\qquad (k = k_1 + k_2 = 1.5 \times 10^{-5} + 5 \times 10^{-6} = 2 \times 10^{-5}\ s^{-1})$

$$\Rightarrow \quad 2 \times 10^{-5} = \frac{2.303}{t}\log\frac{0.25}{[A]_t}$$

$$\therefore \quad [A]_t = 0.1744\ M$$

$$\therefore \quad [A]_{\text{decomposed}} = [A]_0 - [A]_t = 0.25 - 0.1744 = 0.0756\ M$$

$$\text{Fraction of C formed} = \frac{k_2}{(k_1 + k_2)} \times [A]_{\text{decomped}} \times \frac{2}{5} = \frac{5 \times 10^{-6}}{2 \times 10^{-5}} \times 0.0756 \times \frac{2}{5} = 7.56 \times 10^{-3}\ M$$

(5 moles of A are used to give 2 moles of C)

## SEQUENTIAL REACTIONS

These are reactions which proceed from reactants to product through one or more intermediate stages,

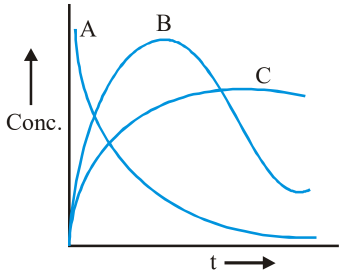
**Ex.** $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

### Graphical representation

$$\frac{-d[A]}{dt} = k_1[A] \qquad \text{.............(1)}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \text{.............(2)}$$

$$\frac{d[C]}{dt} = k_2[B] \qquad \text{.............(3)}$$



Integrating Eq. (1), we get

$$[A] = [A]_0\, e^{-k_1 t}$$

Now, we shall integrate Eq. (2) and find the concentration of B related to time t.

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \Rightarrow \qquad \frac{d[B]}{dt} + k_2[B] = k_1[A]$$

Substituting [A] as $[A]_0 e^{-k_1 t}$

$$\Rightarrow \qquad \frac{d[B]}{dt} + k_2[B] = k_1 [A]_0 e^{-k_1 t} \qquad \text{.............}(4)$$

Integration of the above equation is not possible as we are not able to separate the two variables, [B] and t. Therefore, we multiply Eq. (4) by integrating factor $e^{k_2 t}$, on both the sides of the equation.

$$\left(\frac{d[B]}{dt} + k_2[B]\right) e^{k_2 t} = k_1 [A]_0 e^{(k_2 - k_1)t}$$

We can see that the left hand side of the equation is a differential of $[B]\ e^{k_2 t}$.

$$\therefore \qquad \frac{d}{dt}([B]e^{k_2 t}) = k_1[A]_0 e^{(k_2 - k_1)t}$$

$$d([B]e^{k_2 t}) = k_1 [A]_0 e^{(k_2 - k_1)t} dt$$

Integrating within the limits 0 to t.

$$\int d([B]e^{k_2 t}) = k_1[A]_0 \int_0^t e^{(k_2 - k_1)t} dt \qquad \Rightarrow \qquad [B]e^{k_2 t} = k_1[A]_0 \left[\frac{e^{(k_2 - k_1)t}}{(k_2 - k_1)}\right]_0^t$$

$$\Rightarrow \qquad [B]e^{k_2 t} = \frac{k_1[A]_0}{(k_2 - k_1)}[e^{(k_2 - k_1)t} - 1] \qquad \Rightarrow \qquad [B] = \frac{k_1[A]_0}{(k_2 - k_1)} e^{-k_2 t}[e^{(k_2 - k_1)t} - 1]$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}] \qquad \text{.............}(5)$$

Now, in order to find [C], substitute Eq. (5) in Eq. (3), we get

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A]_0}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}]$$

$$\therefore \qquad d[C] = \frac{k_1 k_2 [A]_0}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}]dt$$

On integrating, we get

$$\int d[C] = \frac{k_1 k_2 [A]_0}{(k_2 - k_1)} \int_0^t [e^{-k_1 t} - e^{-k_2 t}]dt$$

$$\Rightarrow \qquad [C] = \frac{k_1 k_2 [A]_0}{(k_2 - k_1)}\left[\left(\frac{e^{-k_1 t}}{-k_1}\right)_0^t - \left(\frac{e^{-k_2 t}}{-k_2}\right)_0^t\right]$$

$$\Rightarrow \qquad [C] = \frac{k_1 k_2}{(k_2 - k_1)}[A]_0\left[\left(\frac{e^{-k_1 t} - 1}{-k_1}\right) - \left(\frac{e^{-k_2 t} - 1}{-k_2}\right)\right]$$

$$\Rightarrow \qquad [C]=\frac{k_1k_2}{k_2-k_1}[A]_0\left[\left(\frac{1-e^{-k_1t}}{k_1}\right)-\left(\frac{1-e^{-k_2t}}{k_2}\right)\right]$$

$$[C]=\frac{[A]_0}{k_2-k_1}[k_2(1-e^{-k_1t})(1-e^{-k_2t})]$$

$B_{max}$ and $t_{max}$ : We can also attempt to find the time when [B] becomes maximum. For this, we differentiate Eq. (5) and find $\frac{d[B]}{dt}$ and equate it to zero.

$$\therefore \qquad \frac{d[B]}{dt}=\frac{k_1[A]_0}{(k_2-k_1)}\left[e^{-k_1t}(-k_1)+e^{-k_2t}(k_2)\right]=0$$

$$\Rightarrow \qquad k_1e^{-k_1t}=k_2e^{-k_2t}$$

$\frac{k_1}{k_2}=e^{(k_1-k_2)t}$, taking log of both the sides

$$\therefore \qquad t_{max}=\frac{1}{k_1-k_2}\ln\frac{k_1}{k_2} \qquad \text{...........(6)}$$

Substituting Eq. (6) in Eq. (5)

$$\mathbf{Bmax}=[A]_0\left[\frac{k_2}{k_1}\right]^{k_2/k_1-k_2}$$

**Ex.** Starting from the equation for radioactive decay i.e. $-\frac{dN}{dt}=\lambda N$, derive the expression, mean life = $\frac{1}{\lambda}$.

**Sol.** (i) $-\frac{dN}{dt}=\lambda N$ . This on integration gives (with $N = N_0$ , at $t = 0$) ; $N = N_0e^{-\lambda t}$

$$\text{Mean life}=\left[\frac{\int_{t=0}^{\infty}tdN}{\int_{t=0}^{\infty}dN}\right]=\frac{\int_{t=0}^{\infty}t\frac{dN}{dt}dt}{\int_{t=0}^{\infty}\frac{dN}{dt}dt}=\frac{\int_{t=0}^{\infty}(-\lambda N_0)e^{-\lambda t}\,t\,dt}{\int_{t=0}^{\infty}(-\lambda N_0)e^{-\lambda t}dt}=\frac{1}{\lambda}. \qquad \therefore \text{Mean life}=\frac{1}{\lambda}$$

**Ex.** In the case of first order consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (Product), one may show that the concentration of B is given by

$$C_B=\frac{k_1C_A^0}{(k_2-k_1)}\left[e^{-k_1t}-e^{-k_2t}\right].$$

The usual assumptions are $C_A = C_A{}^0$ at $t = 0$ while $C_B = C_C = 0$ at $t = 0$. Show that $C_B$ has its maximum value at time $t=\left(\frac{2.303}{k_2-k_1}\right)\log\left(\frac{k_2}{k_1}\right)$.

**Sol.** $$\frac{dC_B}{dt} = \frac{k_1 C_A^{\circ}}{(k_2 - k_1)}\left[k_2 e^{-k_2 t} - k_1 e^{-k_1 t}\right]$$

equating this zero $\quad k_2\, e^{-k_2 t} = k_1\, e^{-k_1 t}$

$$\therefore \frac{k_2}{k_1} = e^{(k_2-k_1)t} \quad \therefore \ell n\left(\frac{k_2}{k_1}\right) = (k_2 - k_1)\,t \qquad \therefore \quad t = \left(\frac{2.303}{k_2 - k_1}\right)\log\left(\frac{k_2}{k_1}\right)$$

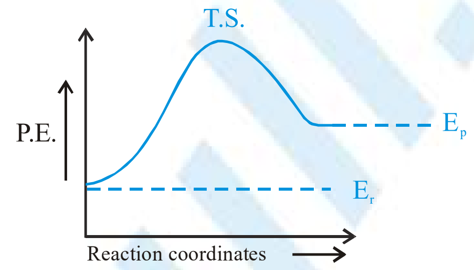
## MECHANISM OF A REACTION

Reactions can be divided into

- Elementary / simple / single step
- Complex / multi-step

### ELEMENTARY REACTION

- These reaction take place in single step without formation of any intermediate



- For elementary reaction we can define molecularity of the reaction which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy
- molecularity will always be a natural no

  1 = unimolecular one molecule gets excited (like radioactivity)
  2.= bimolecular
  3 = trimolecular
- Molecularly $\leq$ 3 because the probability of simultaneous collision between 4 or more molecules in proper orientation is very low
- For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity

  Order of elementary reaction w.r.t. reactant = stoichiometric co-efficient of the reactant

  $H_2 + I_2 \rightleftharpoons 2HI$ (Simple reaction)

  rate = $k\,[H_2]\,[I_2]$

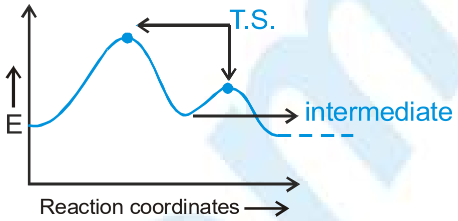
  $2H_2 + 2I_2 \rightleftharpoons 4HI$ ( not elementary )

reaction obtained by multiplying an elementary reaction with some no will not be of elementary nature

$H_2 + Cl_2 \rightleftharpoons 2HCl$

order = 0

### COMPLEX REACTION :



- Reaction which proceed in more than two steps. or having some mechanism. ( sequence of elementary reaction in which any complex reaction proceeds)
- For complex reaction each step of mechanism will be having its own molecularity but molecularity of net complex reaction will not be defined.
- Order of complex reaction can be zero fractions whole no, even negative w.r.t. some species.
- Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using Rate determine step (R.D.S) if given.
- Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.

The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.

The mechanism of most of the reaction will be calculated or predicted by using mainly the following approximations.

## CALCULATION OF RATE LAW/ ORDER

### (A) MECHANISM IN WHICH R.D.S. GIVEN

### (i) If R.D.S. involves only reactant, product or catalyst on reactant side

**rate law of R.D.S. = rate law of reaction**

**Ex.** Calculate order and rate law of reaction

$2NO_2 + F_2 \longrightarrow 2NO_2F$ with help of mechanism

I $NO_2 + F_2 \xrightarrow{k_1} NO_2F + F$ (slow)

II $NO_2 + F \xrightarrow{k_2} NO_2F$ (fast)

molecularity = 2 for both

According to RDS

Rate = $k_1 [NO_2] [F_2]$

**Ex.** Calculate rate law

$3ClO^- \rightarrow ClO_3^- + 2Cl^-$

$2ClO^- \xrightarrow{k_1} ClO_2^- + Cl^-$ (slow)

$ClO_2^- + ClO^- \xrightarrow{k_2} ClO_3^- + Cl^-$ (fast )

Rate = $k_1[ClO^-]^2$

### (ii) RDS is having intermediate on reactant side

To calculate order, we have to specify [ intermediate] in expression of rate law in terms of conc. of [R], [P] or catalyst with the help of same equilibrium step given in mechanism.

**Ex** $2O_3 \rightarrow 3O_2$

$O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ (fast eq. step)

(intermediate)

$O + O_3 \xrightarrow{k_3} 2O_2$ (slow)

From R.D.S., rate $= k_3 [O_3] [O]$

According to equilibrium step.

$$K_{eq.} = \frac{k_1}{k_2} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \left[\frac{k_1[O_3]}{k_2[O_2]}\right]$$

$$\text{Rate} = k_3[O_3][O] = k_3\,[O_3]\left[\frac{k_1[O_3]}{k_2[O_2]}\right].$$

$$\text{Rate} = \frac{k_1 k_3}{k_2}\,\frac{[O_3]^2}{[O_2]}$$

**Ex** $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br^-} C_6H_5N_2^+ + 2H_2O$

intermediate

$H^+ + HNO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2NO_2^+$ (fast) equilibrium step

intermediate

$H_2NO_2^+ + Br^- \xrightarrow{k_3} NOBr + H_2O$ (slow)

$NOBr^- + C_6H_5NH_2 \xrightarrow{k_4} C_6H_5N_2^+ + Br^- + H_2O$ (fast)

**Sol.** $r = k_3\,[Br^-][H_2NO_2^+]$

$$K_{eq} = \frac{k_1}{k_2} = \frac{[H_2NO_2^+]}{[H^+][HNO_2]}$$

$$[H_2NO_2^+] = \left[\frac{k_1}{k_2}\right][H^+]\,[HNO_2]$$

$$r = \frac{k_1 k_3}{k_2}[H^+]\,[HNO_2]\,[Br^-].$$

**Ex** $2O_3 \rightarrow 3O_2$

$O_3 \quad O_2 + O$

$O_2 + O \xrightarrow{k_2} O_3$

$O_3 + O \xrightarrow{k_3} 2O_2$

**Sol.** $$\text{rate} = \frac{-1}{2}\frac{d[O_3]}{dt} = \frac{1}{3}\frac{d[O_2]}{dt}$$

$$\frac{d[O_3]}{dt} = -k_1[O_3] + k_2[O_2][O] - k_3[O_3][O]$$

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_2[O_2][O] + k_3[O_3][O]$$

At steady state $\frac{d[O]}{dt} = 0$

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O_2][O] - k_3[O_3][O] = 0$$

$$[O] = \frac{k_1[O_3]}{k_2[O_2] + k_3[O_3]}$$

$$\frac{d[O_3]}{dt} = -k_1[O_3] + \frac{\{k_2[O_2]k_1[O_3]\}}{k_2[O_2] + k_3[O_3]} - \frac{k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$= -k_1[O_3] + \frac{k_1k_2[O_2][O_3] - k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$= \frac{k_1k_2[O_2][O_3] - k_1k_3[O_3]^2 + k_1k_2[O_2][O_3] - k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$= \frac{-2k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$\left[\frac{-1}{2}\frac{d}{dt}[O_3]\right] = \frac{k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$\text{Rate} = -\frac{1}{2}\frac{d}{dt}[O_3]$$

$$\text{So, Rate (r)} = \frac{k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

if 3rd step is RDS then $k_1 >> k_3$

$k_2 >> k_3$

$$r = \frac{k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

**Ex** $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br} C_6H_5N_2^+ + 2H_2O$

$H^+ + HNO_2 \xrightarrow{k_1} H_2NO_2^+$

$H_2NO_2^+ \xrightarrow{k_2} H^+ + HNO_2$

$HNO_2^+ + Br^- \xrightarrow{k_3} NOBr + H_2O.$

$NOBr + C_6H_5NH_2 \xrightarrow{k_4} C_6H_5N_2^+ + H_2O + Br^-$

**Sol.** $$\frac{d[H_2NO_2^+]}{dt} = k_1[H^+][HNO_2] - k_2[H_2NO_2^+] - k_3[H_2NO_2^+][Br^-] = 0$$

$$[H_2NO_2^+] = k_1 \frac{[H^+]]HNO_2]}{k_2 + k_3[Br^-]}$$

$$\text{rate} = \frac{d}{dt}[C_6H_5NH_2] = \frac{d}{dt}[HNO_2]$$

$$\frac{d}{dt}[C_6H_5NH_2] = k_4[ONBr][C_6H_5NH_2]$$

$$\frac{d}{dt}[NOBr] = -k_4[C_6H_5NH_2][NOBr] + k_3[Br^-][H_2NO_2^+] = 0$$

$$[NOBr] = \frac{k_3[Br^-][H_2NO_2^+]}{k_4[C_6H_5NH_2]}$$

$$r = \frac{k_4 k_3[Br^-][H_2NO_2^+]}{k_4[C_6H_5NH_2]}[C_6H_5NH_2]$$

$$r = \frac{k_1 k_3[Br^-][H^+][HNO_2]}{k_2 + k_3[Br^-]}$$

## HYPOTHESIS OF STEADY STATE

There are many reactions which involve multi steps and the intermediates (one or more) do not appear in the overall equation, e.g. $2NO + O_2 \longrightarrow 2NO_2$

Steps involved in the above reaction are

$$NO + O_2 \longrightarrow NO_3$$

$$NO + NO_3 \longrightarrow 2NO_2$$

---

$$2NO + O_2 \longrightarrow 2NO_2$$

In the above steps, $NO_3$ is an intermediate species and do not appear in the overall balanced equation. Usually these intermediates are very reactive and do not accumulate to any significant extent during the reaction.

For hypothetical reaction,

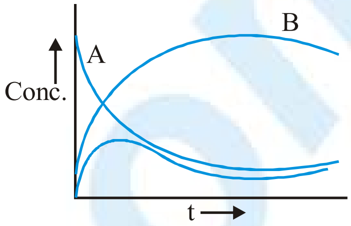
$$A \longrightarrow B$$

The reaction can proceeds in the following steps :

$$A \xrightarrow{k_1} I$$

$$I \xrightarrow{k_2} B$$

The concentration of the intermediate [I] is much less than the reactant [A] as well as the product [B]. Accordingly the formation of intermediate will start at zero, rises to maximum, and then fall back to zero. If the concentration of intermediate remains small during the reaction, then the curves of reactants, intermediate and product versus t will be given as below :



From the plot, it is clear that the slope of the curve for intermediate much less than those for reactants A and products B. It is, therefore good approximation to take $\frac{d[I]}{dt} = 0$, for each reaction intermediate.

**This is steady state (stationary state) approximation.**

## RADIOACTIVITY

All radioactive decay follows first order kinetics and this is where the similarity ends. This will be explained later in the chapter.

We have measured the rate of reaction in chemical kinetics based on the rate of change of concentration of reactants or products. But this procedure will not work for calculating the rate of a radioactive reaction. This is because most of the time the radioactive substance is a solid. Therefore, its concentration would be a constant with time (assuming it to be pure and that the product does not remain with the reactants). Therefore, the rate of radioactive reactions is measured by calculating the rate of change of number of nuclei of the radioactive substance.

For a radioactive decay A → B, the rate of reaction is calculated as

$$\frac{-dN_A}{dt} = \lambda N_A$$

where λ = decay constant of reaction.

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

As you can see, the above rate law is very much similar to the rate law of a first order chemical reaction, but all other similarities ceases here. For example unlike a chemical reaction the decay constant (λ) does not depend on temperature. Arrhenius equation is not valid for radioactive decay.

$$\frac{-dN_A}{dt} = \lambda N_A$$

Integrating the differential rate law, we get

$$-\int_{N_0}^{N_t} \frac{dN_A}{N_A} = \lambda \int_0^t dt$$

$$\log \frac{N_0}{N_t} = \lambda t$$

where

$N_0$ = number of nuclei of A, at t = 0

$N_t$ = number of nuclei of A, at t = t

λ = decay constant

The expression can be rearranged to give

$N_t = N_0 e^{-\lambda t}$ .............**(1)**

This suggest that the number of nuclei of radioactive substance A at any instant of time can be calculated, if we know the number of nuclei at t = 0, its decay constant and the time.

### Half-Life

Just like a first order reaction, the half-life of radioactive decay is given by

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

[Note : Let us start with 10 nuclei. If the half-life is 5 minutes, then at the end of first 5 minutes, number of nuclei would be 5. Now, what would be the number of nuclei after next 5 minutes ? Will it be 2.5 or 2 or 3 ? We can clearly see that it cannot be 2.5 and if it is 2 or 3 then it cannot be called as half-life. This dilemma can be overcome by understanding that all formula relating to kinetics are only valid when the sample size is very large and in such a large sample size, a small difference of 0.5 will be insignificant.

The fact that radioactive decay follows the exponential law implies that this phenomenon is statistical in nature. Every nucleus in a sample of a radionuclide has a certain probability of decaying, but there is no way to know in advance which nuclei will actually decay in a particular time span. If the sample is large enough, i.e. if many nuclei are present - the actual fraction of it that decays in a certain time span will be very close to the probability for any individual nucleus to decay. To say that, a certain radioisotope has a half-life of 5 hr. signifies that every nucleus of this isotope has a 50 percent chance of decaying in every 5 hr. period. This does not mean probability of 100 percent decaying is 10 hr. A nucleus does not have a memory, and its decay probability per unit time is constant until it actually does decay. A half-life of 5 hr. implies a 75 probability of decay in 10 hr., which increases to 87.5% in 15 hr., to 93.75% in 20 hr., and so on, because in every 5 hr. The probability of decay is 50 percent.

### Average–Life Time

Average life time is defined as the life time of a single isolated nucleus. Let us imagine, a single nucleus which decays in 1 second. Assuming 1 second time interval to be very small, the rate of change of nuclei would be 1/1 (because –dN = 1 and dt = 1). We can also see that since $\frac{-dN}{dt} = \lambda N$, for a single isolated nucleus N = 1, $\frac{-dN}{dt} = \lambda$. Therefore, in this present case, $\lambda = 1$.

Now, let us assume, the same nucleus decays in 2 seconds, we can see that $\frac{-dN}{dt}$, i.e. $\lambda$ is equal to ½ . You will also notice that in the 1st case the nucleus survived for 1 second and in the second case it survived for 2 seconds. Therefore, the life time of a single isolated nucleus is $\frac{1}{\lambda}$.

$$\therefore \qquad t_{av} = \frac{1}{\lambda}$$

### Activity

Activity is the rate of decay of a radioactive element. It is represented as 'A' and is equal to $\lambda N$. By no means should activity be confused with rate of change of radioactive nuclei represented by $\frac{-dN}{dt}$. This is because $\frac{-dN}{dt}$ talks about the overall change in the number of nuclei in a given instant of time while activity only talks about that change which is decay. For example, if you go to a market with Rs. 50 in your pocket and you spend Rs. 20 in 5 minutes then your rate of change of money in the wallet is Rs. 4/min and in fact the rate of spending the money is also Rs. 4/min. Here, you can see both are same. But if while spending Rs. 20 in 5 minutes, somebody keeps Rs. 10 in your wallet, then the rate of change of money in your wallet would become Rs. 2.5 /min while the rate of spending the money is Rs. 4/min. This implies that as long as the radioactive substance is only decaying the rate of change of nuclei and activity are same and Eq.(1) in terms activity of radioactive substance can be written as $A_t = A_0e^{-\lambda t}$. But if the radioactive substance is also being produced, then $\frac{dN}{dt}$ = rate of production – activity (of course it's a different matter that rate of production may or may not be a constant).

### Specific Activity

It is defined as per unit mass of the sample. Let, radioactive sample weighing w g have a decay constant λ. The number of nuclei in the w g would be $\frac{w}{M} \times N_0$, where M = molecular weight of the radioactive substance and $N_0$ = Avogadro's number.

$$\therefore \qquad \text{Specific activity} = \frac{\left(\lambda \times \frac{w}{M} \times N_0\right)}{w} = \frac{\lambda \times N_0}{M}$$

It should be remembered that if a radioactive sample is pure and the product does not remain with reactant, then specific activity is a constant.

### Units of Activity

The unit of radioactivity of a substance is measured as the rate at which it changes into daughter nucleus. It has been derived on the scale of disintegration of radium.

Let us consider, 1g of radium (atomic mass = 226 and $t_{1/2}$ = 1600 yrs) undergoes decay, then

Rate of decay of radium = λ × Number of nuclei of Ra in 1g

$$= \frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60} \times \frac{1 \times 6.023 \times 10^{23}}{226} = 3.7 \times 10^{10} \text{ dps} = 3.7 \times 10^{10} \text{ becquerel}$$

= 1 curie (✈ 1 Ci = $3.7 \times 10^{10}$ dps)

= $3.7 \times 10^4$ Rutherford (✈ 1Rd = $10^6$ dps)

The SI unit of activity is dps or Becquerel.

**Ex.** $^{210}_{84}Po$ decays with emission of α-particle to $^{206}_{82}Pb$ with a half-life period of 138.4 days. If 1g of $^{210}_{84}Po$ is placed in a sealed tube, how much helium will be accumulated in 69.2 days ? Express the answer in $cm^3$ at STP.

**Sol.** $^{210}_{84}Po \rightarrow ^{206}_{82}Po + ^{4}_{2}He$

Amount of $^{210}_{84}Po$ left after 69.2 days can be calculated by applying

$N = N_0\,(1/2)^n$

$n = t/t_{1/2} = \frac{69.2}{138.2} = \frac{1}{2}$

$$\therefore \qquad N = 1 \times \left(\frac{1}{2}\right)^{1/2} = 0.702 \text{ g}$$

Amount of polonium disintegrated = 1 – 0.7072 = 0.2928 g

Moles of polonium in 0.2928 g $= \frac{0.2928}{210}$

$$\text{Moles of helium atoms formed} = \frac{0.2928}{210}$$

$$\therefore \quad \text{Volume of helium collected} = \frac{0.2928}{210} \times 22400 = 31.23\ \text{cm}^3$$

## CARBON DATING

The cosmic ray generates neutrons in the atmosphere which bombards the nucleus of atmospheric nitrogen to form radioactive $^{14}C$ hence $^{14}C$ in the atmosphere has been remaining constant over thousands of years. In living materials, the ratio of $^{14}C$ to $^{12}C$ remains relatively constant. When the tissue in an animal or plant dies, assimilation of radioactive $^{14}C$ ceased to continue. Therefore, in the dead tissue the ratio of $^{14}C$ to $^{12}C$ would decrease depending on the age of the tissue.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}p$$

$$^{14}_{6}C + ^{14}_{7}N + ^{0}_{-1}e$$

A sample of dead tissue is burnt to give carbon dioxide and the carbon dioxide is analysed for the ratio of $^{14}C$ to $^{12}C$. From this data, age of dead tissue (plant or animal) can be determined.

$$\text{Age (t)} = \frac{2.303}{\lambda}\log\frac{N_0}{N}$$

$$\Rightarrow \text{Age} = \frac{2.303 \times t_{1/2}(^{14}C)}{0.693}\log\left(\frac{N_0}{N}\right)$$

$N_0$ = ratio of $^{14}C/^{12}C$ in living plant
N = ratio of $^{14}C/^{12}C$ in the wood

$$\text{Age} = \frac{2.303 \times t_{1/2}}{0.693}\log\left(\frac{A_0}{A}\right)$$

$A_0$ = Original activity
A = Final activity

$$\text{Also, } N = \left(\frac{1}{2}\right)^n N_0 \Rightarrow \text{where } n = \frac{t}{t_{1/2}}$$

## ROCK DATING

It is based on the kinetics of radioactive decay. It is assumed that no lead was originally present in the sample and whole of it came from uranium.

Initial no. of mole ($N_0$) = [U] + [Pb]

Final no. of mole (N) = [U]

$$\frac{N_0}{N} = \frac{[U]+[Pb]}{[U]} = 1 + \frac{[Pb]}{[U]}$$

$$t = \frac{2.303}{\lambda}\log\left[\frac{N_0}{N}\right]$$

$$\Rightarrow t = \frac{2.303}{\lambda}\log\left[1 + \frac{[Pb]}{[U]}\right]$$

$$\text{Also, } \left[1 + \frac{[Pb]}{[U]}\right] = (2)^n \qquad \left(n = \frac{t}{t_{1/2}}\right)$$

**Ex.** A sample of uranium mineral was found to contain $^{206}$Pb and $^{238}$U in the ratio of 0.008 : 1. Estimate the age of the mineral (half-life of $^{238}$U is 4.51 × $10^9$ years).

**Sol.** $t = \dfrac{2.303}{\lambda}\log\left[1+\dfrac{^{206}\text{Pb}}{^{238}\text{U}}\right]$

$$t = \frac{2.303}{0.693}\times t_{1/2}\times\log\left[1+\frac{^{206}\text{Pb}}{^{238}\text{U}}\right]$$

$\Rightarrow$ Ratio by mass $^{206}\text{Pb} : {}^{238}\text{U} = 0.008 : 1$

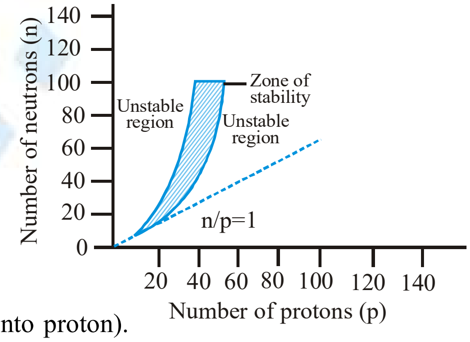
Ratio by moles $^{206}\text{Pb} : {}^{238}\text{U} = \dfrac{0.008}{206} : \dfrac{1}{238} = 0.0092$

$$\therefore\ t = \frac{2.303\times 4.51\times 10^9}{0.693}\log(1+0.0092)$$

$$= \frac{2.303\times 4.51\times 10^9}{0.693}\times 0.00397 = \frac{0.0412}{0.693}\times 10^9 = 5.945\times 10^7 \text{ years}$$

## STABILITY OF NUCLEI WITH RESPECT TO NEUTRON - PROTON RATIO :

If number of neutrons is plotted against the number of protons, the stable nuclei lie within well-defined region called zone of stability. All the nuclei falling outside this zone are invariably radioactive and unstable in nature. Nuclei that fall above the stability zone has an excess of neutrons while those lying below have more protons. These nuclei attain stability by making adjustment in n/p ratio.



### When (n/p) ratio is higher than that required for stability :

Such nuclei have tendency to emit β-rays (transforming a neutron into proton).

$$^1_0\text{n} \longrightarrow {}^1_1\text{p} + {}^0_{-1}\text{e} \ (\beta\text{-particle})$$

$$^{14}_{6}\text{U} \longrightarrow {}^{14}_{7}\text{N} + {}^0_{-1}\text{e}$$

$$\frac{n}{p} \qquad 1.33 \qquad 1$$

$$^{87}_{36}\text{Kr} \longrightarrow {}^{87}_{37}\text{Rb} + {}^0_{-1}\text{e}$$

$$\frac{n}{p} : \quad \frac{51}{36} \qquad \frac{50}{37}$$

### When (n/p) ratio is lower than that required for stability :

Such nuclei have tendency to increase n/p ratio by adopting any of the following three ways.

- By emission of an α-particle (natural radioactivity).

$$^{298}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^4_2\text{He} \ (\alpha\text{-particle})$$

$$\left(\frac{n}{P}\right) \quad \left(\frac{146}{92}\right) \quad \left(\frac{144}{90}\right)$$

$$=1.50 \qquad =1.60$$

- By emission of positron

$$^{13}_{7}\text{N} \longrightarrow {}^{13}_{6}\text{C} + {}^0_{+1}\text{e}$$

$$\frac{n}{p} \qquad \frac{6}{7} \qquad \frac{7}{6}$$

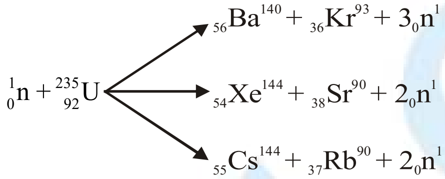
- By K-electron capture

$$\begin{array}{ccc} & {}^{194}_{79}\mathrm{Au} + e^{0}_{-1} & \longrightarrow {}^{194}_{78}\mathrm{Pt} \\ \left(\frac{n}{P}\right) & \frac{115}{79} & \frac{116}{78} \end{array}$$

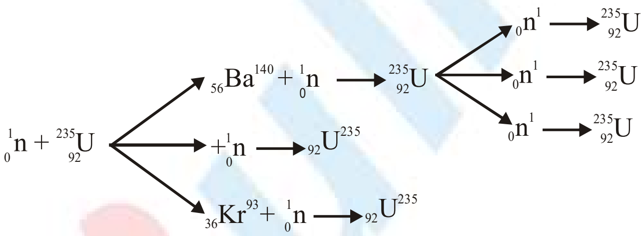
$\alpha$-emission is usually observed in natural radioactive isotopes while emission of positron or K-electron capture is observed in artificial radioactive isotopes. The unstable nuclei continue to emit $\alpha$ or $\beta$-particle until stable nucleus comes into existence.

## NUCLEAR FISSION

It is a nuclear reaction in which heavy nucleus splits into lighter nuclei of comparable masses with release of large amount of energy by bombardment with suitable sub-atomic particles, i.e.



If the neutrons from each nuclear fission are absorbed by other ${}_{92}U^{235}$ nuclei, these nuclei split and release even more neutrons. Thus, a chain reaction can occur. A nuclear chain reaction is a self sustaining series of nuclear fissions caused by the previous neutrons released from the previous nuclear reactions.



There should be critical amount of the fissionable material to maintain fission chain. This in turn requires, minimum critical mass of the fissionable material. It is the small mass of the fissionable material in which chain reaction can be sustained. If mass is larger than critical mass (supercritical mass), then the number of nuclei that split, multiplies rapidly. An atomic bomb is detonated with small amount of chemical explosive that push together two or more masses of fissionable material to get a supercritical mass.

A nuclear fission reactor is a device that permits a controlled chain nuclear fissions. Control rods made of elements such as boron and cadmium, absorb additional neutrons and can therefore, slow the chain reactions.

## NUCLEAR FUSION

It is a nuclear reaction in which two lighter nuclei are fused together to form a heavier nuclei. To achieve this, colliding nuclei must posses enough kinetic energy to overcome the initial force of repulsion between the positively charged core. At very high temperature of the order of $10^6$ to $10^7$ K, the nuclei may have the sufficient energy to overcome the repulsive forces and fuse. Such reactions are therefore also known as thermonuclear reactions.

$${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.8\,MeV$$

$${}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{4}_{2}He + 24.9\,MeV$$

$${}^{1}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + 20.0\,MeV$$

$${}^{7}_{3}Li + {}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 17.7\,MeV$$

The energy of fusion process is due to mass defect (converted into binding energy). The high temperature required to initiate such reaction may be attained initially through fission process.

Hydrogen bomb is based on the principle of fusion reactions. Energy released is so enormous that it is about 1000 times that of atomic bomb. In hydrogen bomb, a mixture of deuterium oxide ($D_2O$) and tritium oxide ($T_2O$) is enclosed in space surrounding an ordinary atomic bomb. The temperature produced by the explosion of the atomic bomb initiates the fusion reaction between ${}_{1}^{2}H$ and ${}_{1}^{3}H$ releasing huge amount of energy.

It is believed that the high temperature of stars including the sun is due to fusion reactions. E. Salt Peter in 1953, proposed a proton-proton chain reaction.

$${}_{1}^{1}H + {}_{1}^{1}H \longrightarrow {}_{1}^{2}H + {}_{+1}^{0}e + \gamma$$

$${}_{1}^{2}H + {}_{1}^{1}H \longrightarrow {}_{2}^{3}He + \gamma$$

$${}_{2}^{3}He + {}_{1}^{1}H \longrightarrow {}_{2}^{4}He + {}_{+1}^{0}e + \gamma$$

---

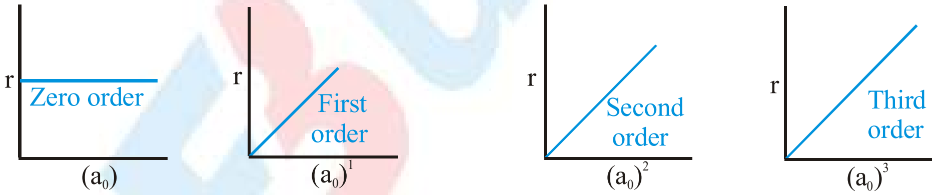
$$4{}_{1}^{1}H \longrightarrow {}_{2}^{4}He + 2{}_{+1}^{0}e + 24.7 MeV$$

**1.** Expression for rate constants for reaction of different orders

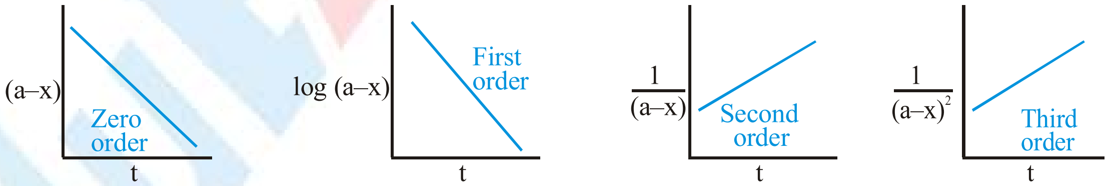
| Type of reaction | Integrated rate equation | Unit of rate constant | Half-life period | $t^{3/4}$ life period |
|---|---|---|---|---|
| Zero order reaction | $-\frac{d[A]}{dt} = k_0[A]^0$<br>Differentiation form $\frac{dx}{dt} = k$ | Concentration/time–1 | $t_{\frac{1}{2}} = \frac{a}{2k_0}$ | -- |
| First order reaction | $k_1 \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$ | $\text{time}^{-1}$ | $t_{\frac{1}{2}} = \frac{0.693}{K_1}$ | $t_{\frac{3}{4}} = 2 \times \frac{0.693}{k_1} = \frac{1.382}{k_1}$ |
| Second order reaction | $k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$<br>Differential form<br>$\frac{dx}{dt} = k(a-x)^2$ | $\text{Mole}^{-1}\,\text{litre time}^{-1}$ | $t_{\frac{1}{2}} = \frac{1}{k_2 a}$ | $t_{\frac{3}{4}} = \frac{3}{k_2 a}$ |
| Third order reaction | $k_3 = \frac{x \times (2a-x)}{t2a^2(a-x)^2}$<br>Differential form<br>$\frac{dx}{dt} = k(a-x)^3$ | $\text{Litre}^2\,\text{mole}^{-2}\,\text{time}^{-1}$ | $t_{\frac{1}{2}} = \frac{3}{2k_3 a^2}$ | -- |

**2.** Some typical linear plots for reactions of different orders :

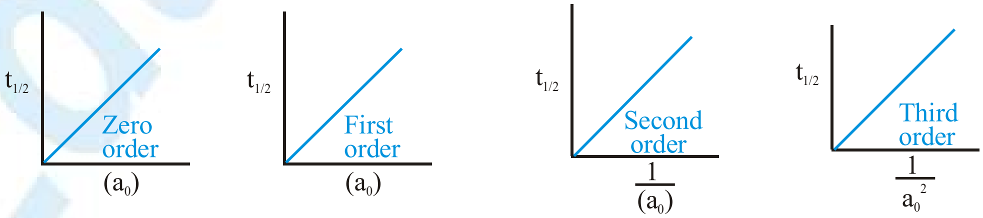
**(i)**



**(ii)**



**(iii)**



**3.** Amount left after n half-lives $= \left(\frac{1}{2}\right)^n [A]_0$

No. of half-lives $= \frac{\text{Total time}}{t_{1/2}}$

**4.** Exponential form of expression for rate constant for reaction of 1st order : $[A] = [A]_0 e^{-kt}$ or $C_t = C_0 e^{-kt}$

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

**6.** Arrhenius equation for effect of temperature on rate constant,

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

on $\log k = \log R - \frac{E_a}{2.303RT}$

Also, $\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$

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

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_1 - T_2}{T_1T_2}\right]$$

**7.** Examples of reactions of 1st order and their formula for rate constants

**(i)** $2N_2O_5 \rightarrow 4NO_2 + O_2$ ; $k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$

where $V_\infty$ = volume of $O_2$ gas collected at infinite time

$V_t$ = volume of $O_2$ gas collected at time t

**(ii)** $NH_4NO_2 \rightarrow 2H_2O + N_2$ ; $k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$

where $V_\infty$ and $V_t$ are volumes of $N_2$ gas collected after infinity time and after time t respectively.

**(iii)** $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$ ; $k = \frac{2.303}{t}\log\frac{V_D}{V_t}$

where $V_D$ and $V_t$ are the volumes of $KMnO_4$ solution used for titrating a definite volume of the reaction mixture at t = D and at time t respectively.

**(iv)** $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

$$k = \frac{2.303}{t}\log\frac{V_\infty - V_D}{V_\infty - V_t}$$

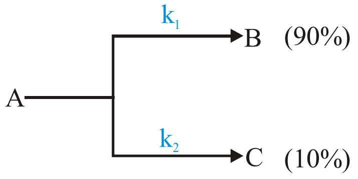
where $V_D$, $V_t$ and $V_\infty$ are the volume of NaOH solution used for titration mixture at zero time, after time t and after infinity respectively.

**(v)** $$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$k = \frac{2.303}{t}\log\frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$$

where $r_0$, $r_t$ and $r_\infty$ are the polarimetric reading at zero time, after time t and after infinity respectively.

**8.** Rate law equation for reactions involving parallel reaction



$$\text{Rate} = -\frac{d[A]}{[dt]} = k_1[A] + k_2[A] = [k_1 + k_2][A]$$

**9.** Degree of dissociation at any time t = $(1 - e^{-kt})$