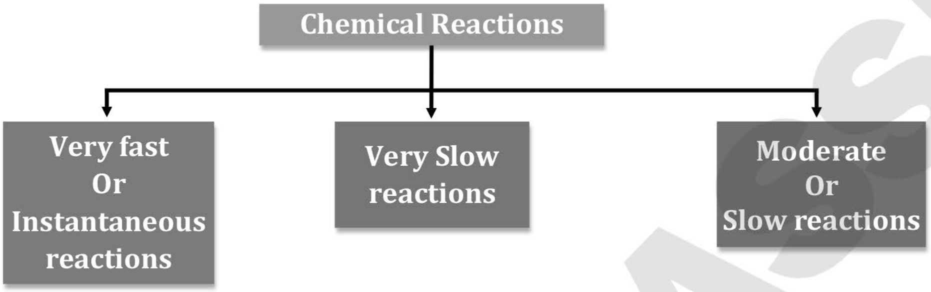
Introduction

Chemical Kinetics is the branch of physical chemistry which deals with the study of rate of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction.
On the basis of rate, chemical reaction are broadly divided into three categories:



(A) **Very fast or instantaneous reactions:** Generally these reactions involve ionic species and known as ionic reactions. These reactions take about 10^{-14} or 10^{-16} seconds for completion. So, it is almost impossible to determine the rate of these reactions.

Examples:

$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$
(white ppt)

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$
(white ppt)

$HCl + NaOH \rightarrow NaCl + H_2O$

(B) **Very slow reactions:** These reactions proceed very slowly, may take days or months to show any measurable change at room temperature.

Examples:

- Rusting of iron.
- Reaction between H_2 and O_2 to form H_2O at ordinary temperature in absence of catalyst.
- $CO + 2H_2 \xrightarrow{\text{at room temperature}} CH_3OH$

(C) **Moderate or slow reactions:** This type of reactions proceed with measurable rates at normal temperature and we can measure the rate of these reactions easily. Mostly these reactions are molecular in nature.

Examples:

- Decomposition of H_2O_2
  $2H_2O_2 \rightarrow 2H_2O + O_2$
- Decomposition of N_2O_5
  $2N_2O_5 \rightarrow 4NO_2 + O_2$
- Hydrolysis of ester
  $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$
- Inversion of cane sugar in aqueous solution
- Reaction of NO with chlorine
  $NO + Cl_2 \rightarrow NOCl_2$

Rate of Reaction

Rate of reaction is defined as the change in concentration or pressure of reactant or product per unit time. It is always a positive quantity.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant of product}}{\text{Time taken in change}} \qquad r = \pm\frac{\Delta C}{\Delta t}$$

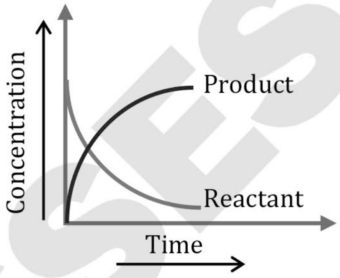
Where ΔC = change in concentration in a small interval Δt

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

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

For gaseous reactions $r = \pm\frac{\Delta P}{\Delta t}$ (unit of rate = pressure time^{-1})

and $r = \frac{1}{RT} \times \left[\pm\frac{\Delta P}{\Delta t}\right]$ (unit of rate = M time^{-1})



Types of Rate of Reactions:

Types of Rate of reactions

Average Rate of Reaction | **Instantaneous Rate of Reaction**

(A) Average Rate of Reaction

The rate of reaction over a certain measurable period of time during the course of reaction is called average rate of reaction. It is denoted by $\bar{r}$.

For a reaction $A \rightarrow B$

$$r_{\text{average}} = \left(\frac{[A]_2 - [A]_1}{t_2 - t_1}\right) = \frac{\Delta[A]}{\Delta t}$$

Where $[A]_1$ = Concentration of reactant A at time t_1,

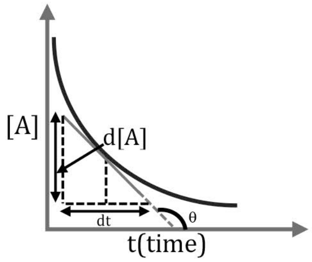
$[A]_2$ = Concentration of reactant A at time t_2.

(B) Instantaneous Rate of Reaction

The rate of reaction at any particular instant during the course of reaction is called instantaneous rate of reaction.

For a reaction $A \rightarrow B$

Mathematically ; Instantaneous rate = $\lim_{\Delta t \to 0}$ (Average rate)



$$r_{\text{inst}} = \lim_{\Delta t \to 0}\left(-\frac{\Delta[A]}{\Delta t}\right) = \lim_{\Delta t \to 0}\left(\frac{\Delta[B]}{\Delta t}\right)$$

or $$\boxed{\mathbf{r_{inst} = (-)\frac{d[A]}{dt} = (+)\frac{d(B)}{dt}}}$$

Hence, Slope of the tangent at time t in plot of concentration with time gives instantaneous rate of reaction.

Instantaneous rate of reaction = $\lim_{\Delta t \to 0}\left(\pm\frac{\Delta C}{\Delta t}\right) = \pm\frac{dC}{dt}$

Rate of Reaction in the Form of Stoichiometry of a Chemical Reaction

Let us consider a reaction: $m_1A + m_2B \rightarrow n_1P + n_2Q$

Where, Rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of disappearance of B = $-\frac{d[B]}{dt}$

Rate of appearance of P = $\frac{d[P]}{dt}$

Rate of appearance of Q = $\frac{d[Q]}{dt}$

$$\boxed{\text{Rate of Reaction} = \frac{1}{m_1}\left(-\frac{d[A]}{dt}\right) = \frac{1}{m_2}\left(-\frac{d/[B]}{dt}\right) = \frac{1}{n_1}\frac{d[P]}{dt} = \frac{1}{n_2}\frac{d[Q]}{dt}}$$

- Rate of reaction is always positive; negative sign represents decrease in concentration of reactant.

Units of Rate of Reaction

Unit of rate of reaction = mol L^{-1} $time^{-1}$ i.e. (mol L^{-1} s^{-1} or mol L^{-1} min^{-1} or mol L^{-1} h^{-1})

Illustration 1:

For the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$, if rate of appearance (ROA) of $NH_3 = 2\times10^{-4}$ mol L^{-1} s^{-1}

Then calculate rate of disappearance (ROD) of N_2 & H_2 and also calculate rate of the reaction ?

Solution:

$N_2 + 3H_2 \rightarrow 2NH_3$

ROR = 1 × ROD of N_2 = $\frac{1}{3}$ × ROD of H_2 = $\frac{1}{2}$ × ROA of NH_3

ROD of N_2 = $\frac{1}{2} \times 2 \times 10^{-4} = 10^{-4}$ ms^{-1}

ROD of H_2 = $\frac{3}{2} \times 2 \times 10^{-4} = 3 \times 10^{-4}$ ms^{-1}

ROR = $\frac{1}{2}$ × ROA of NH_3 = $\frac{1}{2} \times 2 \times 10^{-4} = 10^{-4}$ ms^{-1}

Illustration 2:

If the reaction $2NO_2 \rightarrow 2NO + O_2$, the rate of formation of NO is 6 g min^{-1}, calculate rate of disappearance of NO_2 in g min^{-1}.

Solution:

$2NO_2 \rightarrow 2NO + O_2$

ROR = $\frac{1}{2}$ × ROD of NO_2 = $\frac{1}{2}$ × ROF of NO = 1 × ROF of O_2

ROD of NO_2 = $\frac{2}{2}$ × ROF of NO

ROD of NO_2 = $1 \times \frac{6}{30}\frac{\text{mol}}{\text{min.}}$ = 0.2 mol min^{-1} (molar mass of NO = 30)

$(\text{ROD of } NO_2)_{g\,min^{-1}}$ = 0.2 × 46 = 9.2 g min^{-1} (molar mass of NO_2 = 46)

Illustration 3:

A gaseous hypothetical chemical equation $2A \rightleftharpoons B+C$ is carried out in a closed vessel. The concentration of B is found to increase by 5×10^{-3} mol L^{-1} in 10 second. The rate of appearance of B is :

Solution:

Increase in concentration of B = 5×10^{-3} mol L^{-1} Time = 10 sec

Rate of appearance of B = $\dfrac{\text{increase of conc. B}}{\text{Time taken}}$

$$= \frac{5\times10^{-3}\ \text{mol}\,L^{-1}}{10\ \text{sec}} = 5 \times 10^{-4}\ \text{mol}\ L^{-1}\ \text{sec}^{-1}$$

Rate Law

The experimental expression of rate of reaction in terms of concentration of reactants is known as rate law. In this expression the rate of a reaction is proportional to the product of molar concentration of reactants with each term raised to the power or exponent that has to be found experimentally.

In a chemical reaction: $aA + bB \rightarrow$ Product

The rate law is: $\textbf{Rate} \propto [A]^x [B]^y$

The values of exponents x and y are found experimentally which may or may not be same as stoichiometric coefficients.

Above relationship can be written as :-

$$\text{Rate} = k[A]^x[B]^y$$

Where k is a proportionality constant known as rate constant.

Rate constant:

In a chemical reaction –

$$n_1A + n_2B \rightarrow m_1C + m_2D$$

according to law of mass action

$$\text{Rate} = k[A]^{n_1}[B]^{n_2}$$

but according to rate law (experimental concept)

$$\text{Rate} = k[A]^x[B]^y$$

if $[A] = [B] = 1$ mol/L

then, Rate = k

Rate of reaction at unit concentration of reactants is called as rate constant or specific reaction rate. Rate constant does not depend on concentration of reactant but it depends on temperature and catalyst.

Order of Reaction

The sum of powers of concentration of reactants in rate law expression is known as order of reaction.

For the reaction $aA + bB \rightarrow$ Product

Rate law is Rate = $k[A]^x[B]^y$

Here x = order of reaction with respect to A

y = order of reaction with respect to B

$x + y = n$ (overall order of reaction)

Order of reaction may be zero, positive, negative or fractional.

Order of reaction is an experimental quantity.

Units of rate constant:

Rate = $k[A]^n$

$$k = \frac{r}{[A]^n} = \frac{\text{unit of rate}}{[\text{unit of concentration}]^n} = \frac{\frac{\text{mol}}{\text{L}} \times \text{time}^{-1}}{\left[\frac{\text{mol}}{\text{L}}\right]^n}$$

$$k = \left[\frac{\text{mol}}{\text{L}}\right]^{1-n} \times \text{time}^{-1}$$

For gaseous reaction unit of k may be = $(\text{atm})^{1-n} \times \text{time}^{-1}$

Illustration 4:

For a reaction rate law equation is $r = k(C)^{5/2}$. Then unit of rate constant will be:

Solution:

$r = k(C)^{5/2}$

$$\text{Unit of K} = \frac{\text{unit of r}}{(\text{unit of concentration})^{5/2}}$$

$$= \left(\frac{\text{mol}}{\text{L}}\right)^{1-5/2} \times \text{sec}^{-1} = \text{mol}^{-3/2}\,\text{L}^{3/2}\,\text{s}^{-1}$$

Illustration 5:

For a reaction the initial rate is given as: $R_0 = k[A]_0^2[B]_0$ by what factor, the initial rate of reaction will increase if initial concentration of A is 1.5 times and B is tripled?

(1) 4.5 (2) 2.25 (3) 6.75 (4) None of these

Solution:

$R_0 = K[A]_0^2[B]_0$

$[A]_1 \rightarrow [1.5A]_0$, $[B]_1 \rightarrow [3B]_0$

$[B]_1 \rightarrow [3B]_0$

$= K[1.5\ A]_0^2\ [3B]_0$

$= K \times 6.75\ [A]_0^2\ [B]_0$

$\Rightarrow R_1 = 6.75\ R_0$

Molecularity

Total number of molecules, atoms or ions (reacting species) participating in an elementary reaction is called as molecularity of reaction.

- Molecularity is a theoretical quantity.
- Molecularity can be an integer (1, 2 or 3) but it cannot be zero or negative or fractional.
- In elementary reaction molecularity is equal to its order.
- In complex reaction molecularity of each step of mechanism is defined separately.
- Total molecularity of complex reaction is meaningless.
- In complex reactions generally molecularity of slowest step is same as order of reaction which can be considered as molecularity of reaction. (Except when slowest step contain intermediate)
- Maximum value of molecularity or order is 3 because chances of effective collision of more than three molecules is very rare.

Mechanism of Reaction

(a) Elementary reactions:

Those reactions which completes in single step and which have exponents in rate law equal to stoichiometric coefficients of the reactants.

If $A + B \rightarrow$ Products; is an elementary reaction

then rate law will be – Rate = k[A][B]

Zero order reactions can never be elementary reactions.

For elementary reactions fractional order is not possible.

Mechanism of Reaction

(b) Complex reactions:

Those reactions which complete in multisteps. For these reactions a mechanism is proposed.

- For complex reactions the overall rate of reaction is controlled by the slowest step which is called as rate determining step (R.D.S.).
- In rate law expression rate of reaction depends on concentration of reactants of slowest step which must be free from intermediate.
- If R.D.S. contains intermediate, its value is solved using K_{eq} of fast step (assumed as reversible)

Example-1

$2NO_2Cl \rightarrow 2NO_2 + Cl_2$

Experimentally, the rate law is Rate = k$[NO_2Cl]$

The mechanism of the reaction is given as –

(i) $NO_2Cl \rightarrow NO_2 + Cl$ (slow step)

(ii) $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ (fast step)

So the rate law from slowest step Rate = k$[NO_2Cl]$

In this way the predicted rate law derived from two step mechanism agrees with experimental rate law.

Example-2

$2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$

experimentally the rate law is, Rate = k $[NO]^2[H_2]$

The mechanism of the reaction is given as –

(i) $2NO \underset{K_b}{\overset{K_f}{\rightleftharpoons}} N_2O_2$ (fast step)

(ii) $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow step)

(iii) $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast step)

The Rate law from slowest step is:

Rate = k$[N_2O_2]$ $[H_2]$

The rate law expression should be free from intermediate species N_2O_2.

From fast reversible step –

$k_f[NO]^2 = k_b[N_2O_2]$

$$\therefore \quad [N_2O_2] = \frac{k_f}{k_b}[NO]^2$$

and rate law becomes

$$\text{Rate} = k\left(\frac{k_f}{k_b}\right)[NO]^2\,[H_2]$$

Therefore, Rate = k'$[NO]^2[H_2]$

This derived rate law agrees with experimental rate law.

Pseudo First Order Reaction

A chemical reaction in which value of order of reaction is one but molecularity is more than one are known as pseudo unimolecular/pseudo first order reaction.

Example-1

Hydrolysis of ester in acidic medium.

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

Rate = k $[CH_3COOC_2H_5][H_2O]$

Water is in excess then its concentration remain constant during the reaction and $[H_2O]$ is taken as constant therefore,

Rate = k' $[CH_3COOC_2H_5]$ where k' = k $[H_2O]$

Example-2

Inversion of cane sugar.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate = k $[C_{12}H_{22}O_{11}][H_2O]$

Water is in excess then its concentration remain constant during the reaction and $[H_2O]$ is taken as constant therefore,

$$\text{Rate} = k' [C_{12}H_{22}O_{11}] \qquad \text{where } k' = k[H_2O]$$

Golden Key Points

- Reactant taken in excess can't affect order of reaction.
- In certain complex reaction product is also considered in order calculation.
- Order of reaction is determined experimentally.

Illustration 6:

For $A + 2B \rightarrow C$

Rate law: $r = k[A]\,[B]^2$; Find order of reaction if B is taken in excess

Solution:

For a reaction

$A + 2B \rightarrow C$

Rate law; $r = k[A][B]^2$

Since B is taken in excess

$r = K[A]$

(1st order reaction)

Half Life Time & Fractional Life Time

t_{fraction} or t_x: The time in which x fraction of initial amount of reactant is consumed; is called fractional life.

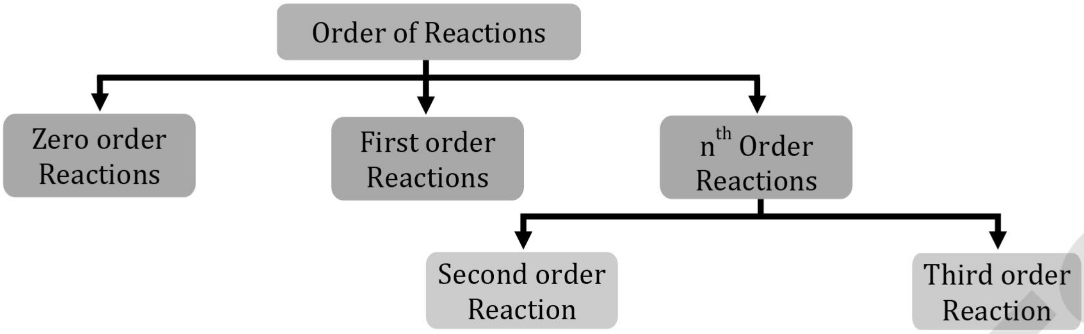
if, $x = \frac{a}{2}$; $t_{1/2}$ or $t_{50\%}$

$x = \frac{3a}{4}$; $t_{3/4}$ or $t_{75\%}$

$x = \frac{7a}{8}$; $t_{7/8}$ or $t_{87.5\%}$

$x = a$; $t_{\text{completion}} = t_{100\%}$

Study of Different Order Reactions



Zero order reactions

Reactions in which rate of reaction remains independent of concentration of the reactant are said to be zero order reactions.

- Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.

Example:

(a) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

(b) $2NH_3(g) \xrightarrow[\Delta]{Pt} N_2(g) + 3H_2(g)$

(c) Reaction between Acetone and Bromine.

(d) Dissociation of HI on gold surface.

(e) Adsorption of gases on metal surface: At low P, rate of adsorption is proportional to surface area covered which is proportional to P or concentration of gas hence order is 1 whereas at high P, complete surface gets covered by gas & rate becomes independent of P & concentration hence order is 0.

Differential Rate Equation

	A	→	**Product**
t = 0	a		0
t = t s	(a – x)		x

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

$$\boxed{\frac{dx}{dt} = k[A]^0}$$

Calculation of Rate Constant

Let us take the reaction

$A \rightarrow$ Product

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

$$-\int d[A] = \int k dt$$

$-[A]_t = kt + C$

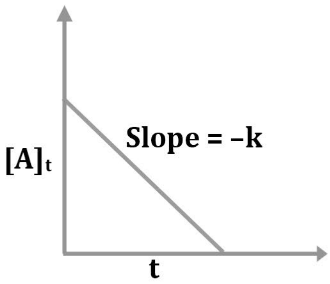
at t = 0 $[A]_t = [A]_0$

$-[A]_0 = k \times 0 + C$

$C = -[A]_0$

On substituting the value of C

$-[A]_t = kt - [A]_0$



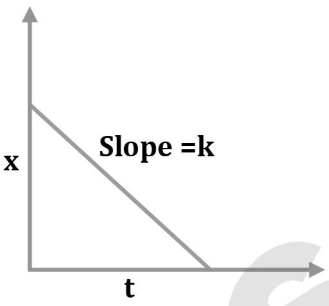
$[A]_t = [A]_0 - kt$ [Integrated rate equation]

$y = c - mx$

$[A]_0 - [A]_t = kt$

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

$x = kt$



x = Amount of reactant that will change in product.

- For zero order reaction, rate of reaction is equal to rate constant

Unit of rate constant

$k = \text{mol L}^{-1}\text{ s}^{-1}$ = unit of rate of reaction.

Half-life period – The time in which half of the initial amount of reactant is consumed.

At $t = t_{1/2}$, $[A]_t = \frac{[A]_0}{2}$

$$\therefore \quad k\,t_{1/2} = [A]_0 - \frac{[A]_0}{2} \quad \text{or} \quad t_{1/2} = \frac{[A]_0}{2k}$$

The half life period for a zero order reaction is directly proportional to the initial concentration of the reactants.

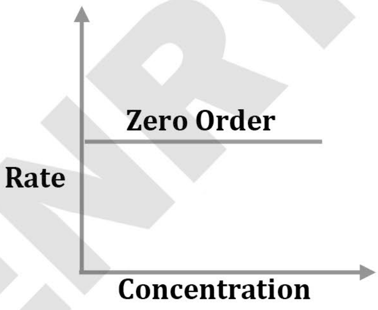
Time for completion of reaction

$[A]_t = [A]_0 - kt$

For competition $[A]_t = 0$

$$k = \frac{[A]_0}{t} \qquad t_{100\%} = \frac{[A]_0}{k}$$

Graphical representation



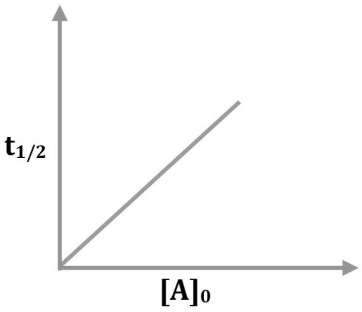


Illustration 7:

For a reaction concentration of reactant is 0.5 M after 30 s. Then, find out initial concentration of reactant ($k = 10^{-2}\text{ mol L}^{-1}\text{ s}^{-1}$)

Solution:

Since unit of $k = \text{mol L}^{-1}\text{s}^{-1}$ $\therefore$ Zero order reaction.

$[A]_t = [A]_0 - kt$

$0.5 = [A]_0 - 10^{-2} \times 30$

$[A]_0 = 0.5 + 0.3$

$[A]_0 = 0.8\text{ M}$

Illustration 8:

In a zero order reaction, if time for 87.5% completion is 5 min then $t_{50\%}$?

Solution:

$$t_{87.5} = \frac{7}{8}\frac{[A]_0}{K}$$

$$t_{50\%} = \frac{[A]_0}{2K}$$

$$\frac{t_{87.5\%}}{t_{50\%}} = \frac{7}{4}$$

$$t_{50\%} = \frac{4}{7}\ t_{87.5\%}$$

$$t_{50\%} = \frac{4}{7} \times 5 = \frac{20}{7}\ \text{min}$$

First order reactions

Reactions in which the rate of reaction is directly proportional to concentration of reactant.

Example :

(a) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

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

(d) $2H_2O_2 \longrightarrow 2H_2O + O_2$

(e) All radioactive decay

Differential rate equation

	A	**→**	**Product**
t = 0	a		0
t = t s	(a – x)		x

$$-\frac{d[A]}{dt} = k[A] \qquad \boxed{\frac{dx}{dt} = k(a-x)}$$

Calculation of rate constant

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

$-\ln[A]_t = kt + c$ ...(i)

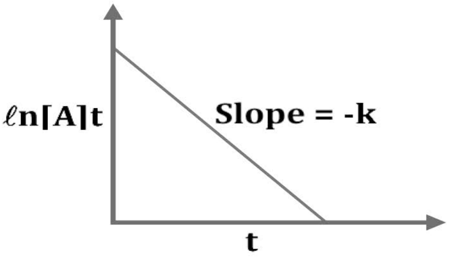
At $t = 0$; $[A]_t = [A]_0$ $\therefore$ $C = -\ln[A]_0$

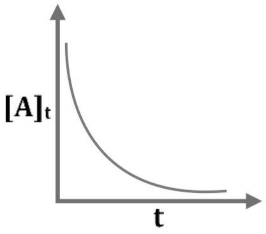
Putting the value of C in equation (i)

$-\ln[A]_t = kt - \ln[A]_0$

$$\ln[A]_t = \ln[A]_0 - kt$$

$y = c - mx$





$$\ln\frac{[A]_0}{[A]_t}=kt \qquad kt=\ln\left(\frac{a}{a-x}\right) \qquad ...(ii)$$

$$2.303\ \log_{10}\frac{[A]_0}{[A]_t}=kt$$

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

from equation(ii)

$$\frac{[A]_o}{[A]_t}=e^{kt}$$

$$\frac{[A]_t}{[A]_o}=e^{-kt}\Rightarrow\ [A]_t=[A]_0e^{-kt}$$ Wilhemy equation

Unit of rate constant [$k = \text{time}^{-1}$]

Half-life Period: The time in which half of the initial amount of reactant is consumed.

At $t = t_{1/2}$; $x = a/2$; $a-x = a/2$

$$t_{1/2}=\frac{1}{k}\ \ell n\left(\frac{a}{a/2}\right) \quad \text{or} \quad t_{1/2}=\frac{\ell n2}{k}=\frac{2.303}{k}(\log 2)\ \text{ or }\ t_{1/2}=\frac{0.693}{k}$$

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

Time for 3/4th of the Reaction ($t_{3/4}$): The time in which 3/4th of the initial amount of reactant is consumed.

At $t = t_{3/4}$; $x = 3a/4$; $a-x = a/4$

$$t_{3/4}=\frac{2.303}{k}(\log 4)=\frac{2.303}{k}\times 2\ \log 2=2\times t_{1/2}$$

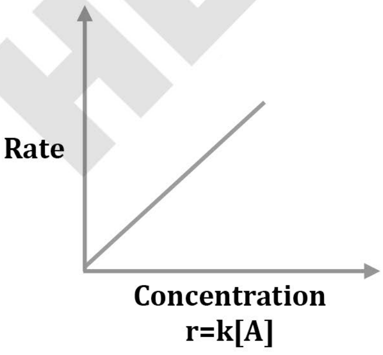
$t_{3/4}$ for first order reaction is independent of the initial concentration of reactant.

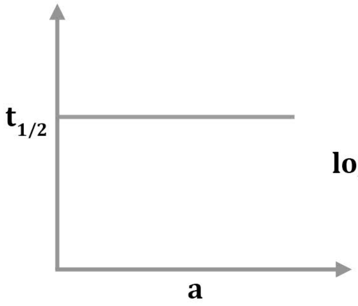
Interval Formula $$k=\frac{2.303}{t_2-t_1}\log\frac{a-x_1}{a-x_2}$$

where x_1 and x_2 are the amount consumed at time t_1 and t_2 respectively.

Time required for the completion of definite fraction of the first order reaction is independent of the initial concentration of the reactant.

Graphical Representation





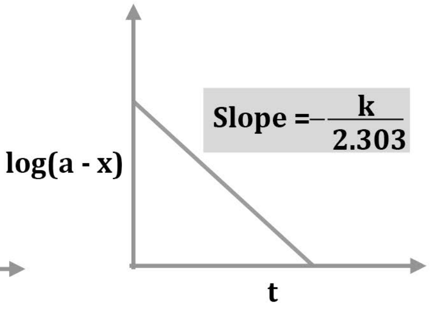


Illustration 9:

If $t_{1/2}$ of 1st order reaction is 30 min. then find ROR when concentration of reactant is 0.8 M?

Solution:

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

$$30 = \frac{0.693}{K}$$

$$K = \frac{0.693}{30}\ \text{min}^{-1}$$

$$r = K[A]^1 = \frac{0.693}{30} \times 0.8 = 0.018\ \text{mol L}^{-1}\text{min}^{-1}$$

Illustration 10:

In first order reaction, time for 90% completion is 15 min. then find time for $t_{99.9\%}$ completion?

Solution:

$$K_1 = \frac{2.303}{t_{90\%}} \log \frac{100}{100-90}$$

$$K_2 = \frac{2.303}{t_{99.9\%}} \log \frac{100}{100-99.9}$$

$K_1 = K_2$ = same

$$\frac{2.303}{t_{90\%}} \log 10 = \frac{2.303}{t_{99.9\%}} \log 1000$$

$t_{99\%} = 3t_{90\%} = 3 \times 15 = 45$ min

Illustration 11:

How much time is required for conversion of reactant from 20 g to 0.625 g in 1st order reaction (t_{12} is 5 min)?

Solution:

$$20 \xrightarrow[5]{} 10 \xrightarrow[5]{} 5 \xrightarrow[5]{} 2.5 \xrightarrow[5]{} 1.25 \xrightarrow[5]{} 0.625$$

Total time = 25 min

or $[A]_t = \dfrac{[A]_0}{(2)^n} \rightarrow (2)^n = \dfrac{20}{0.625}$

$(2)^n = 32 \rightarrow n = 5$

$$5 = \frac{\text{total time}}{5}$$

Total time = 25 min

First Order Kinetics in Terms of Volume

$$k = \frac{1}{t} \ell n \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right)$$

Where, V_∞ = volume at the end of the reaction.

V_t = volume at time t

V_0 = Volume at time t = 0

First Order Kinetics in Terms of Pressure

$$k = \frac{1}{t}\ell n\left(\frac{P_\infty - P_0}{P_\infty - P_t}\right)$$

Where, P_∞ = Pressure at the end of the reaction.

P_t = Pressure at time t

P_0 = Pressure at time t = 0

Illustration 12:

$2A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$ is a first order reaction with initial pressure P_0 and after time t pressure is P_t then calculate K ?

Solution:

$2A_{(g)}$	$\longrightarrow$	$2B_{(g)}$	$+$	$C_{(g)}$
P_0		0		0
$(P_0 - 2x)$		$2x$		x

$P_t = P_0 - 2x + 2x + x = P_0 + x$

$\Rightarrow x = P_t - P_0$

$$K = \frac{2.303}{t}\log\frac{P_0}{P_0 - 2x} = \frac{2.303}{t}\log\frac{P_0}{P_0 - 2(P_t - P_0)}$$

$$K = \frac{2.303}{t}\log\frac{P_0}{3P_0 - 2P_t}$$

Illustration 13:

$A_{(g)} \rightarrow 2B_{(g)} + C_{(s)}$ is a first order reaction with initial pressure P_0 and after time t pressure is P_t then calculate K ?

Solution:

$A_{(g)}$	$\longrightarrow$	$2B_{(g)}$	$+$	$C_{(s)}$
P_0		0		–
$(P_0 - x)$		$2x$		–

$P_t = P_0 - x + 2x = P_0 + x$

$\Rightarrow x = P_t - P_0$

$$K = \frac{2.303}{t}\log\frac{P_0}{P_0 - x} = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$

$$K = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$

General Integrated Rate Equation (n^th order kinetics)

$$kt = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] \quad [n \neq 1]$$

If $t = t_{1/2}$; $x = \frac{a}{2}$

Therefore $kt_{1/2} = \frac{1}{(n-1)}\left[\left(\frac{2}{a}\right)^{n-1} - \left(\frac{1}{a}\right)^{n-1}\right]$

$kt_{1/2} = \frac{1}{(n-1)}\left[\frac{2^{n-1}-1}{a^{n-1}}\right]$ $(n \neq 1)$; $t_{1/2} \propto \frac{1}{a^{n-1}}$

Second Order Reactions

Hydrolysis of ester by alkali (Saponification)

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

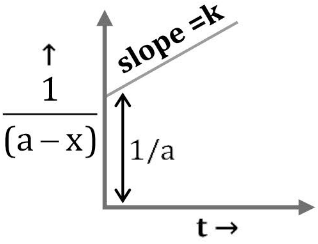
$H_2 + I_2 \rightarrow 2HI$ $2HI \rightarrow H_2 + I_2$

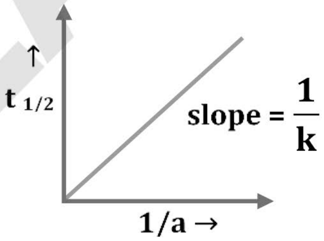
$2NO_2 \rightarrow 2NO + O_2$ $2NO_2 + F_2 \rightarrow 2NO_2F$

$NO + O_3 \rightarrow NO_2 + O_2$ $2Cl_2O \rightarrow 2Cl_2 + O_2$

For second order: n = 2 $kt = \frac{1}{(2-1)}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{1}{(a-x)} - \frac{1}{a}$

Half life $t_{1/2} = \frac{1}{ak}$





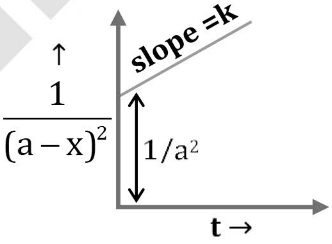
Third Order Reactions

$2NO + O_2 \rightarrow 2NO_2$ $2NO + Cl_2 \rightarrow 2NOCl$

$2NO + H_2 \rightarrow N_2O + H_2O$ $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

for third order n = 3 $kt = \frac{1}{(3-1)}\left[\frac{1}{(a-x^2)} - \frac{1}{a^2}\right] = \frac{1}{2}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$

Half life $t_{1/2} = \frac{3}{2a^2k}$



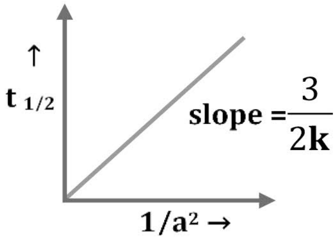


Illustration 14:

The rate constant for a second order reaction is $8 \times 10^{-5}\ M^{-1}\ min^{-1}$: How long will it take a 1M solution to be reduced to 0.5 M.

Solution:

$$\because \quad \frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$$

$$\frac{1}{0.5} = (8 \times 10^{-5})t + \frac{1}{1}$$

$$1 = (8 \times 10^{-5})t$$

$$t = \frac{1}{8 \times 10^{-5}} = 1.25 \times 10^{4}\ \text{min}$$

Collision Theory of Chemical Reactions

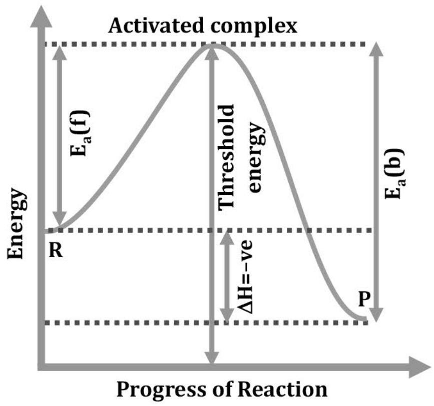
This theory was given by Max Trautz and William Lewis. According to it, for a reaction to occur there must be collisions in between reacting molecules. Total number of collisions per second in unit volume is called collision frequency(z). Generally its value is very high for gaseous reactions (10^{25} to 10^{28} collisions/sec-cm^3). But only a small fraction of these collisions are capable to convert reactant into product. These collisions are called as effective collisions.

For effective collision following two conditions must be satisfied at a time:

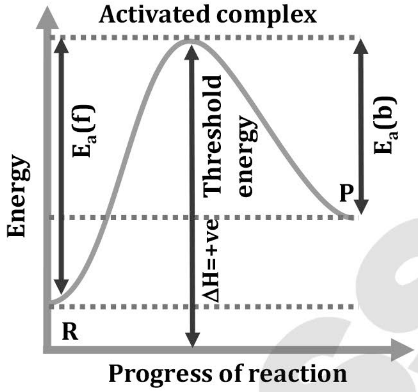
(a) Reacting molecules must posses a minimum amount of energy.

(b) Proper orientation of collision

- **Threshold energy**: The minimum energy which must be possessed by reacting molecules for a chemical reaction to occur.
- **Activation energy**: The minimum extra amount of energy required by reactant molecules for converting into products.



Exothermic reaction



Endothermic reaction

1. $E_a(f)$ = Activation energy for forward reaction
2. $E_a(b)$ = Activation energy for backward reaction

   If not specified in questions then consider E_a for forward reaction.

$$\boxed{\Delta H = E_{a(f)} - E_{a(b)}} \;;\; \boxed{\Delta H = H_p - H_R}$$

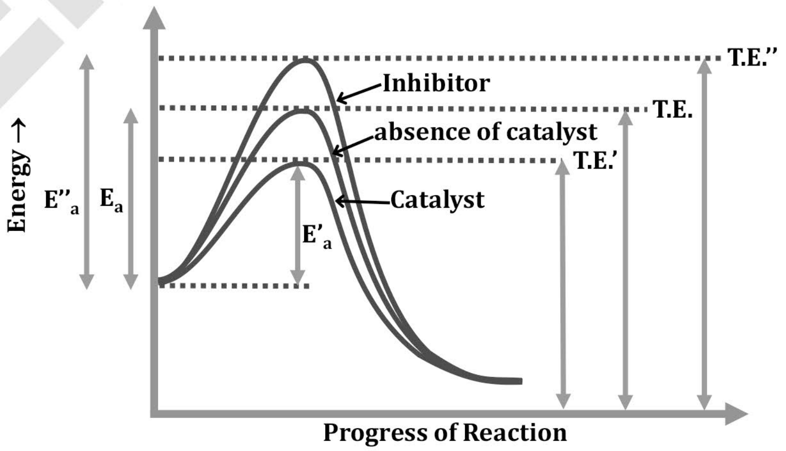
Activation Energy Mainly Depends Upon:

(i) **Nature of reactant**: For different reactants, number of bonds and bond energies are different, therefore activation energy will also be different.

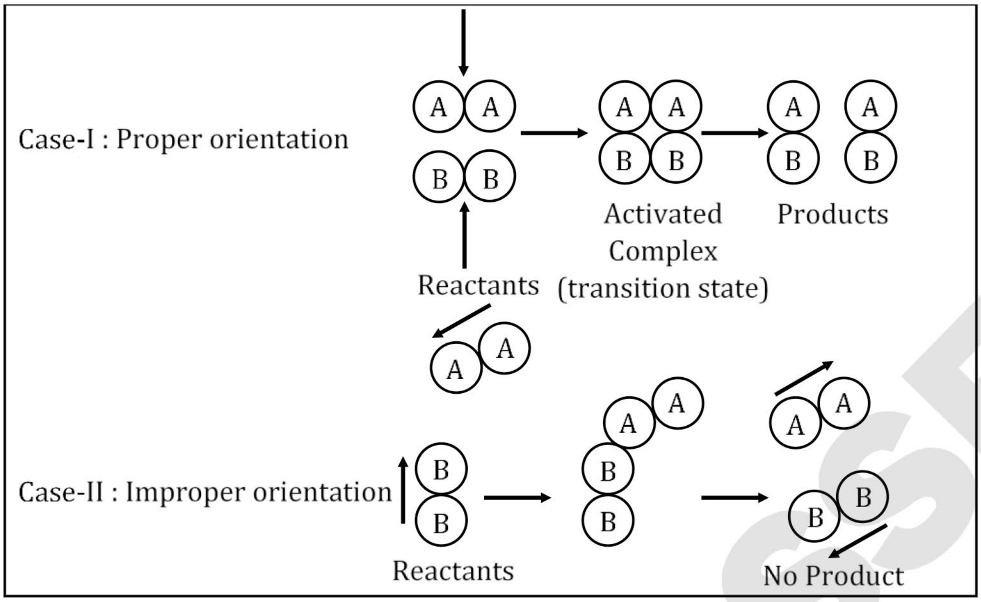
Reactions which have less E_a, take place at faster rate.

(ii) **Presence of catalyst**: Catalyst provide an alternative path of reaction mechanism for the reaction.

- In presence of catalyst threshold energy decreases, activation energy decreases and rate of reaction increases.
- In presence of negative catalyst (inhibitor) threshold energy increases, activation energy increases, rate of reaction decreases.



(b) Orientation:



- **Limitations:**

(i) This theory is mainly applicable for gaseous reactions and also for solutions in which reacting species are molecules.

(ii) This theory is mainly applicable for simple bimolecular reactions but fails for complex reactions.

(iii) It considers molecules to be hard sphere and ignore structural aspect of molecules.

★ Golden Key Points ★

- Activated complex is most unstable complex formed in the transition state with effective collision.
- On increasing temperature E_a for reaction does not decrease but number of active molecules which are crossing the energy barrier increases therefore rate of reaction increases.
- According to Arrhenius ; rate of reaction $\propto e^{-E_a/RT}$

E_a = Activation energy
R = Gas constant
T = Temperature (in K)

Illustration 15:

The E_a for an exothermic reaction $A \rightarrow B$ is 80 kJ mol^{-1}. Heat of reaction is 20 kJ mol^{-1}. E_a for the reaction $B \rightarrow A$ will be ?

Solution:

$\Delta H = E_{a(f)} - E_{a(b)} \quad \Rightarrow \quad -20 = 80 - E_{a(b)}$

$E_{a(b)} = 100$ kJ mol^{-1}

Illustration 16:

For the reaction $A + B \rightleftharpoons C + D$ the activation energy is 32 kJ mol^{-1}. For the reverse reaction the E_a is 58 kJ mol^{-1}. Determine

(i) Nature of reaction (ii) ΔH

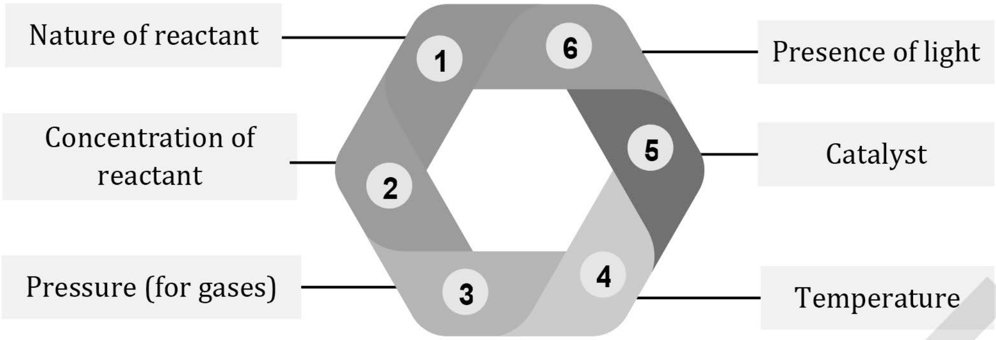
Solution:

$\Delta H = E_{a(f)} - E_{a(b)}$

$\Delta H = 32 - 58$

$\Delta H = -26$ kJ mol^{-1} (exothermic)

Factors Affecting Rate of Reaction



1. **Nature of reactant:**

   (a) Physical state of reactant:

   increasing order of rate of reaction – Solid < liquid < gas

   (Intermolecular attractive force decreases which provides more freedom for collisions)

   (b) Physical size of particles (if reactant is solid):

$$\boxed{\text{Rate of reaction} \propto \frac{1}{\text{physical size}} \propto \text{surface area}}$$

   (c) Chemical nature of reactant: For different reacting species number of bonds broken and their bond energies are different. Therefore requirement of activation energy is also different. Now reactions having less value of activation energy will take place at faster rate.

2. **Concentration of reactant:** Rate of reaction $\propto$ concentration of reactant

3. **Pressure:** Effect of pressure on Rate of reaction is negligible when reactants are solid or liquid. But if reactants are in gaseous state then rate of reaction increases on increasing pressure because number of effective collisions increases.

4. **Temperature: On increasing temperature rate of reaction increases whether the reaction is exothermic or endothermic.** When temperature increases KE of molecules increases, number of activated molecules increases thus rate of reaction increases.

   Relation between rate constant and Temperature:

   (a) Generally it is found that for every 10 °C rise in temperature Rate of reaction becomes 2 to 3 times.

   Temperature coefficient (μ): It is defined as ratio of rate constant of a reaction at two different temperatures which will be differ by 10 °C.

$$\boxed{\mu = \frac{k_{T+10}}{k_T} = 2 \text{ to } 3 \quad ; \quad \frac{r_2}{r_1} = \frac{k_2}{k_1} = \mu^{\Delta T/10}}$$

   If temperature of reaction is not specified then consider 25 °C.

   (If μ is not given consider it as minimum 2)

Maxwell And Boltzmann Energy Distribution Curve

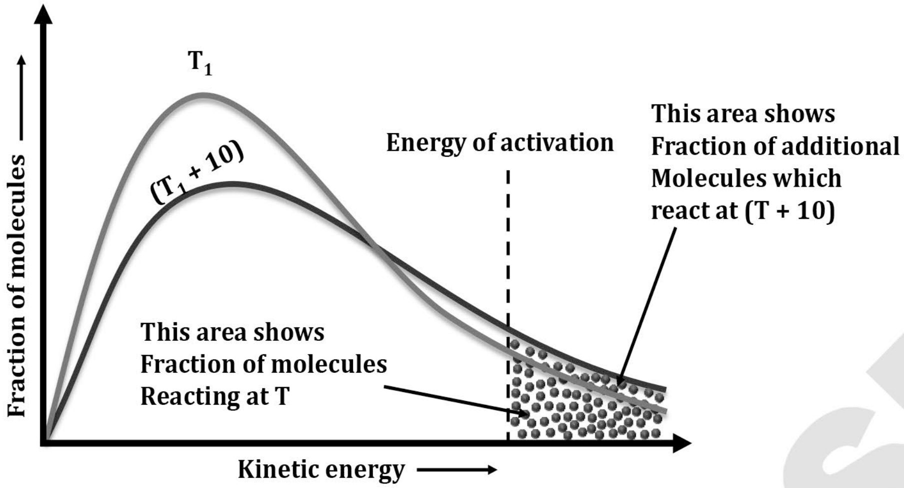


Illustration 17:

If temperature of a reaction is increased from t_1 to t_2 then rate of reaction becomes?

Solution:

$(\mu)^{t_2-t_1/10} \Rightarrow (\mu)^{\Delta T/10}$ times ; $r_{new} = r_{old} \times (\mu)^{\Delta T/10}$

Illustration 18:

If temperature of a reaction is increased from 10°C to 90°C then how many times rate of reaction will become?

Solution:

2^8 times

Illustration 19:

A reaction is carried out at 10°C. If temperature is increased by 50°C then how many times rate of reaction will become?

Solution:

32 times

(b) Arrhenius equation

$$K = Ae^{\frac{-E_a}{RT}} \qquad ...(1)$$

A = Arrhenius constant / pre-exponential factor / Frequency factor
E = Activation energy
R = gas constant
T = Temperature (kelvin)

- k increases with increase in temperature
  If T $\rightarrow \infty$; k = A

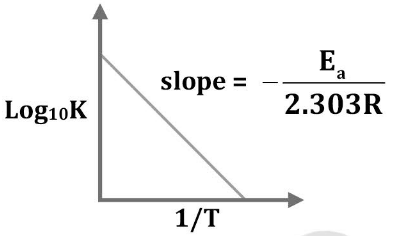
- $\frac{k}{A} = e^{-E_a/RT}$ = fraction of molecules having energy $\geq E_a$

  $e^{-E_a/RT}$ = Boltzman factor

  On taking logarithm for equation (1) on both sides.

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

  $2.303 \log_{10}k = 2.303 \log_{10}A - \frac{E_a}{RT}$



$$\boxed{\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}} \qquad ...(2)$$

$y = c - mx$

- E_a of reaction can be determined by measuring rate constant at two different temperatures

  At temperature T_1:

  $$\log_{10}k_1 = \log_{10} A - \frac{E_a}{2.303RT_1} \qquad ...(3)$$

  At temperature T_2

  $$\log_{10}k_2 = \log_{10}A - \frac{E_a}{2.303RT_2} \qquad ...(4)$$

  Equation (4) – Equation (3) gives -

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

  $$\boxed{\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)}$$

- From arrhenius equation - $k = Ae^{-E_a/RT}$

  $$\ell nk = \ell nA - \frac{E_a}{ER}$$

  $$\frac{d}{dT}(\ell nk) = \frac{d}{dT}(\ell nA) + \frac{d}{dT}\left(-\frac{E_a}{RT}\right)$$

  $$= 0 - \frac{E_a}{R}\frac{d}{dT}(T^{-1}) = \frac{E_a}{R}(T^{-2})$$

  $$\boxed{\frac{d}{dT}\ell nk = \frac{E_a}{RT^2}}$$ differential form of Arrhenius equation

5. **Presence of catalyst:** In presence of catalyst E_a of reaction decreases and rate of reaction increases.

6. **Exposure to radiation:** Rate of some reactions also increases when reaction are carried out in the presence of radiation. (only for photochemical reaction)

   e.g. formation of HCl

   $H_2 + Cl_2 \longrightarrow 2HCl$ (very slow reaction)

   $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ (explosive)

Illustration 20:

For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

Solution:

Let $T_1 = 25\ °C$, $T_2 = 35\ °C$

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

Given: Temperature coefficient = $\frac{k_2}{k_1} = 2$

$T_1 = 25 + 273 = 298$ k,

$T_2 = 35 + 273 = 308$ k, R = 8.314

$$\log 2 = \frac{E_a}{2.303\times8.314}\times\left(\frac{10}{298\times308}\right)$$

$E_a = 52.897$ kJ

Illustration 21:

An exothermic reaction A → B has an activation energy of 17 kJ mol^{-1} of A. The heat of the reaction is 40 kJ. Calculate the activation energy for the reverse reaction B → A.

Solution:

For the reaction A → B.

Activation energy $E_a = 17$ kJ

$\Delta H = -40$ kJ

$\Delta H = E_a(f) - E_a(b)$

$E_a(b) = 17 - (-40)$

= 57 kJ

Illustration 22:

For first order gaseous reaction log k when plotted against 1/T, gives a straight line with a slope of –8000. Calculate the activation energy of the reaction.

Solution:

Arrhenius equation $k = Ae^{-Ea/RT}$

$$\log k = \log A - \frac{E_a}{2.303R}\times\frac{1}{T}$$

when curve is plotted between log k and $\frac{1}{T}$, a straight line is obtained. Slope of this line $= -\frac{E_a}{2.303R}$

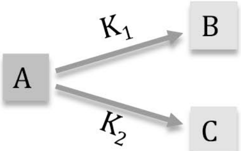
Then, $\frac{E_a}{2.303R} = 8000$

or $E_a = 8000 \times 2.303 \times 1.987$

= 36608 Cal

Parallel First Order Reaction

Reactant A converts into products B & C through parallel reactions of first order as following:



$K_{eff} = K_1 + K_2$

$$\boxed{\%\ \text{Yield of B} = \frac{K_1}{K_1 + K_2} \times 100}$$