Chemical Kinetics

Rate of a Chemical Reaction

- Expressed in terms of –
- Rate of decrease in concentration of any one of the reactants
- Rate of increase in concentration of any one of the products
- For a reaction R → P

One mole of R → One mole of P

- $[R]_1$ and $[P]_1$ are the concentrations of $[R]$ and $[P]$ respectively at time t_1

$[R]_2$ and $[P]_2$ are the concentrations of $[R]$ and $[P]$ respectively at time t_2

∴Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}}$$

$$= \frac{-\Delta[R]}{\Delta t} \qquad (1)$$

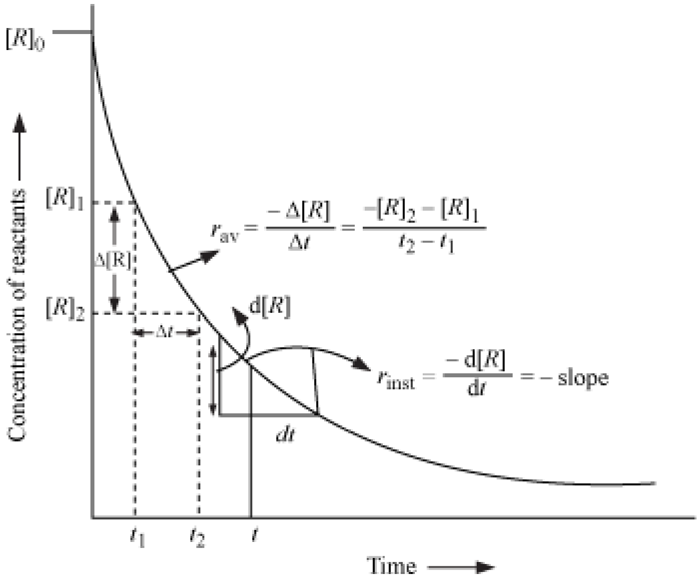
(Since $\Delta[R]$ is a negative quantity, it is multiplied by -1 to make the rate a positive quantity.)

And, rate of appearance of P

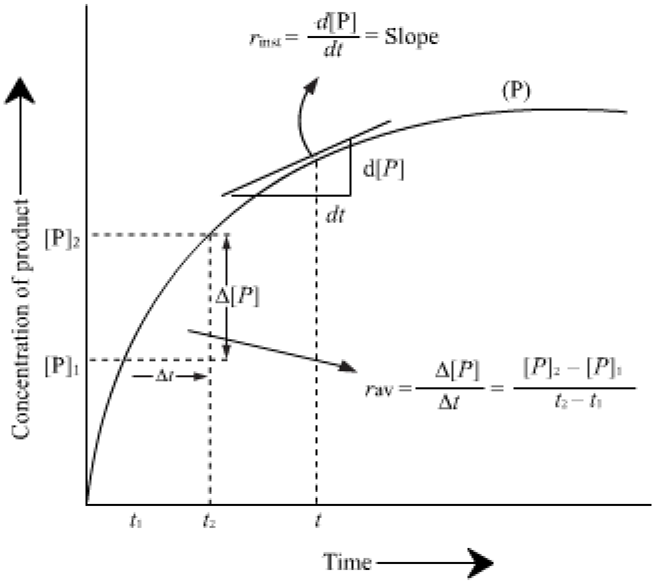
$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}}$$

$$= \frac{+\Delta[P]}{\Delta t} \qquad (2)$$

- Equations (1) and (2) represent the average rate of a reaction.
- The dependence of the average rate upon the change in the concentration of the reactants or products, and the time taken for that change to occur, is shown in the given figures.



(a)



- Instantaneous rate – The rate of a particular moment of time

- Obtained when the average rate at the smallest time interval, say *dt* (i.e., when Δ*t* approaches zero) is considered

- Mathematically, for an infinitesimaly small (*dt*), instantaneous rate is given by

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

As $\Delta t \rightarrow 0$

$$r_{\text{inst}} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$

- For the reactions –
- $Hg_{(l)} + Cl_{2(g)} \longrightarrow HgCl_{2(s)}$

  Rate of reaction $= -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$

- $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

  Rate of reaction $= -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$

  When the stoichiometric coefficients of the reactants or products are not equal to one, the rate of disappearance of any of the reactants or the rate of appearance of any of the products is divided by their respective coefficients.

- $5Br^-_{(aq)} + BrO^-_{3(aq)} + 6H^+_{(aq)} \longrightarrow 3Br_{2(aq)} + 3H_2O_{(l)}$

  $$\text{Rate} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

- For a gaseous reaction –
- At constant temperature, concentration is directly proportional to the partial pressure of a species
- Rate can be expressed as the rate of change in partial pressure of the reactants or the products

Factors Influencing Rate of a Reaction

- **Rate of a reaction depends upon**
- Concentration of reactants (pressure in case of gases)
- Temperature

- Catalyst

Dependence of Rate on Concentration

- At a given temperature, the rate may depend on the concentration of one or more reactants and products.
- **Rate law**
- Representation of the rate of reaction in terms of the concentration of the reactants
- Also known as **rate equation** or **rate expression**

Rate Expression and Rate Constant

- **For a general reaction**

$$aA + bB \longrightarrow cC + dD$$

Where, a, b, c, d = Stoichiometric coefficients of reactants and products

- Rate of reaction generally increases when reactant concentrations increase.

$$\therefore \text{Rate} \propto [A]^x [B]^y$$

x and y may or may not be equal to a and b.

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

$$\Rightarrow -\frac{d[R]}{dt} = k[A]^x [B]^y \qquad (1)$$

'k' is called rate constant

- Equation (1) is called rate law or rate expression.
- **Rate Law –** An expression in which the rate of reaction is given in terms of the molar concentration of the reactants, with each term raised to some power, which may or may not be the stoichiometric coefficient of the reacting species in a balanced chemical equation.
- Example: $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$

$\text{Rate} = k[NO]^2[O_2]$ (Experimentally determined)

Differential form of rate expression is

$$-\frac{d[R]}{dt} = k[NO]^2[O_2]$$

- For this reaction, the exponents of the concentration terms are the same as their stoichiometric coefficients in the balanced chemical equation.
- Some other examples −
- $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

$\text{Rate} = k[CHCl_3][Cl_2]^{\frac{1}{2}}$ (Experimentally determined)

- $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$ →

$\text{Rate} = k[CH_3COOC_2H_5]^1[H_2O]^0$ (Experimentally determined)

Here, the exponents of the concentration terms are not the same as their stoichiometric coefficients.

- Rate law cannot be predicted by looking at the balanced chemical equation. It must be determined experimentally.

Order of Reaction

- For a reaction with rate equation,

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

Overall order $= x + y$

- Can be 0, 1, 2, 3, and even a fraction
- Zero order reaction − Rate of reaction is independent of the concentration of the reactants

Unit of Rate Constant

- For a general reaction

$aA + bB \rightarrow cC + dD$

- Rate = $k\ [A]^x\ [B]^y$

- $x + y = n$ = Order of the reaction
- $k = \frac{[\text{Rate}]}{[\text{A}]^x [\text{B}]^y}$

  $= \frac{\text{Concentration}}{\text{Time}} \times \frac{1}{(\text{Concentration})^n}$

- SI units of concentration and time are mol L^{-1} and s respectively.
- Taking the SI units of concentration and time, the units of rate constant (k) for different reactions are listed in the given table.

Reaction	**Order**	**Units of rate constant**
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{ Ls}^{-1}$

Molecularity of Reaction

- Number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction
- Example:
- $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

  Molecularity = 1 (Unimolecular)

- $2HI \longrightarrow H_2 + I_2$

  Molecularity = 2 (Bimolecular)

- $2NO + O_2 \longrightarrow 2NO_2$

  Molecularity = 3 (Trimolecular)

- Complex reactions involving more than three molecules must take place in more than one step.
- The overall rate of the reaction is controlled by the slowest step in the reaction, called the rate-determining step.
- For example:

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

- The given decomposition reaction of H_2O_2 takes place in two steps:

$$H_2O_2 + I^- \longrightarrow H_2O + IO^-$$

$$H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$$

- The species IO^- is the intermediate.
- First step is slow and it is the rate-determining step.

  Thus, the rate of formation of the intermediate will determine the rate of this reaction.

Integrated Rate Equations for Zero and First Order Reactions

Integrated rate equations

- Concentration dependence of rate is called differential rate equation.
- Not convenient to determine the instantaneous rate; difficult to determine the rate law and hence, the order of reaction
- To avoid the difficulty, the differential rate equation is integrated to give a relation between concentrations at different times and rate constant, which is called integrated rate equation.

Zero order reactions

- Rate of reaction is proportional to zero order of the concentration of the reactant.
- **Derivation of rate equation**

  For the reaction, R → P

  $$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

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

  $$\Rightarrow -\frac{d[R]}{dt} = k \times 1$$

  $$\Rightarrow d[R] = -k[dt]$$

  Integrating both sides,

  $[R] = -kt + I$ …(i)

  I is the constant of integration.

  When $t = 0$, $[R] = [R]_0$

  $[R]_0$ = Initial concentration of the reactant

  Substituting $[R] = [R]_0$ in equation (i),

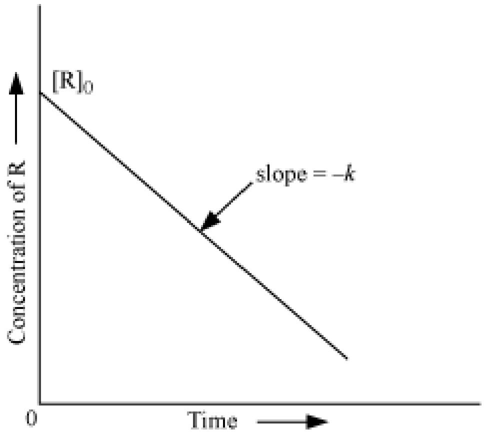
  $[R]_0 = -k \times 0 + I$

  Or, $[R]_0 = I$

  Substituting value of I in equation (i),

  $[R] = -kt + [R]_0$

  If [R] is plotted against time (t), a straight line is obtained as shown in the given figure.



Slope = $-k$

Intercept = $[R]_0$

Simplified rate equation for zero order reaction is

$$k = \frac{[R]_0 - [R]}{t}$$

- Examples:
- Some enzyme-catalysed reactions
- Some reactions which occur on metal surface

For example, decomposition of gaseous ammonia on hot platinum surface at high pressure: $2NH_{3(g)} \xrightarrow[\text{Pt catalyst}]{1130\text{ K}} N_{2(g)} + 3H_{2(g)}$

Rate = $k[NH_3]^0 = k$

- Thermal decomposition of HI on gold surface

First Order Reactions

- Rate of reaction is proportional to the first power of the concentration of the reactant R.
- **Derivation of rate equation**

For the reaction, R → P

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

$$\therefore \frac{d[R]}{[R]} = -k\,dt$$

Integrating this equation,

$\ln [R] = -kt + I$ …(ii)

I = Integration constant

When $t = 0$, $[R] = [R]_0$

$[R]_0$ = Initial concentration of the reactant

Substituting $[R] = [R]_0$ in equation (ii),

$\ln [R]_0 = -k \times 0 + I$

Or, $\ln [R]_0 = I$

Substituting the value of I in equation (ii),

$\ln [R] = -kt + \ln [R]_0$ …(iii)

$$\ln \frac{[R]}{[R]_0} = -kt$$

$$\Rightarrow \ln \frac{[R]_0}{[R]} = kt$$

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

From equation (iii),

At time t_1, $\ln [R]_1 = -kt_1 + \ln [R]_0$ …(iv)

At time t_2, $\ln [R]_2 = -kt_2 + \ln [R]_0$ …(v)

$[R]_1$ = Concentration of reactant at time t_1

$[R]_2$ = Concentration of reactant at time t_2

(iv) − (v) ⇒ $\ln [R]_1 - \ln [R]_2 = -kt_1 - (-kt_2)$

$$\Rightarrow \ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$\Rightarrow k = \frac{1}{t_2 - t_1} \ln \frac{[R]_1}{[R]_2}$$

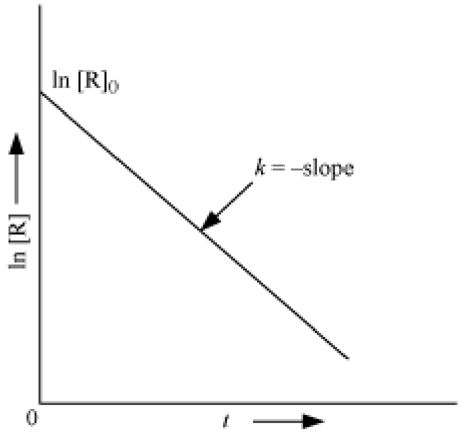
Equation (iii) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog on both sides,

$[R] = [R]_0 e^{-kt}$ ...(vii)

Plot of ln [R] against t is shown in the figure below.



Slope = $-k$

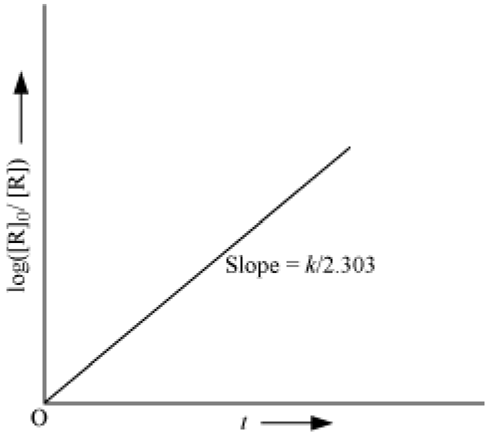
Intercept = ln $[R]_0$

- First order rate equation can also be written as

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

Plot of log $[R]_0$ / [R] vs. t is shown in the figure below.



$$\text{slope} = \frac{k}{2.303}$$

- Examples:
- Hydrogenation of ethene

$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$

Rate = k $[C_2H_4]$

- All natural and artificial radioactive decay of unstable nucleus

$${}^{226}_{88}\text{Ra} \rightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$

Rate = k [Ra]

- Decomposition of N_2O_5 and NO_2

First Order Gas Phase Reaction

$A_{(g)} \rightarrow B_{(g)} + C_{(g)}$

p_i = Initial pressure of A

p_t = Total pressure at time 't'

Total pressure, $p_t = p_A + p_B + p_C$

p_A , p_B, and p_C are the partial pressures of A, B, and C respectively.

If x atm is decrease in pressure of A at time t and one mole each of B and C is being formed, then the increase in pressure of B and C will also be x atm each.

$$\begin{array}{llll} & A_{(g)} \longrightarrow & B_{(g)} & + \quad C_{(g)} \\ \text{At } \ t=0 & p_i \text{ atm} & 0 \text{ atm} & 0 \text{ atm} \\ \text{At time } t & (p_i - x)\text{atm} & x\text{atm} & x\text{atm} \end{array}$$

Where, p_i is the initial pressure at t = 0

$p_t = (p_i - x) + x + x$

$\Rightarrow p_t = p_i + x$

$\Rightarrow x = p_t - p_i$

Where, $p_A = p_i - x = p_i - (p_t - p_i)$

$= 2\,p_i - p_t$

$$\therefore k = \frac{2.303}{t} \log \frac{p_i}{p_A}$$

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

Half-Life of a Reaction

- The time in which the concentration of a reactant is reduced to one half of its initial concentration
- Denoted by $t_{1/2}$

Half-Life for a Zero Order Reaction

- Rate constant for a zero order reaction is

$$k = \frac{[R]_0 - [R]}{t}$$

At $t = t_{1/2}$,

$$[R] = \frac{1}{2}[R]_0$$

Rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - \frac{1}{2}[R]_0}{t_{1/2}}$$
$$\Rightarrow t_{1/2} = \frac{[R]_0}{2k}$$

- $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants, i.e., $t_{1/2} \propto [R]_0$.

- $t_{1/2}$ for a zero order reaction is inversely proportional to the rate constant.

Half-Life for a First Order Reaction

- Rate constant for the first order reaction is

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

At $t_{1/2}$,

$$[R] = \frac{[R]_0}{2}$$

$$\text{Thus, } k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2}$$
$$\Rightarrow t_{1/2} = \frac{2.303}{k}\log 2$$
$$\Rightarrow t_{1/2} = \frac{0.693}{k}$$

- For a first order reaction, the half-life period is constant, i.e., $t_{1/2}$ is independent of $[R]_0$.

The given table summarises the mathematical features of integrated laws of zero and first order reactions.

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k

0	R → P	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	$[R]$ vs t	$[R]_0/2k$	conc time^{-1} or mol L^{-1}s^{-1}
1	R → P	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \{[R]_0/[R]\}$	ln $[R]$ vs t	ln $2/k$	time^{-1} or s^{-1}

What are Pseudo First Order Reactions?

- The order of the reactions can sometimes be altered. For example, consider a chemical reaction between two substances when one reactant is present in excess.

  Hydrolysis of ethyl acetate −

$$\begin{array}{llllllll} & CH_3COOC_2H_5 & + & H_2O & \xrightarrow{H^+} & CH_3COOH & + & C_2H_5OH \\ t = 0 & 0.01\text{ mol} & & 10\text{ mol} & & 0\text{ mol} & & 0\text{ mol} \\ t & 0\text{ mol} & & 9.99\text{ mol} & & 0.01\text{ mol} & & 0.01\text{ mol} \end{array}$$

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

  The concentration of water does not change much during the course of the reaction. Thus, the term $[H_2O]$ can be taken to be constant.

$$\therefore \text{Rate} = k[CH_3COOC_2H_5]$$
$$\text{Where, } k = k'[H_2O]$$

- Thus, the given reaction behaves as a first order reaction. Such reactions are called pseudo first order reactions.

  Another example: Inversion of cane sugar

$$\begin{array}{llllllll} C_{12}H_{22}O_{11} & + & H_2O & \xrightarrow{H^+} & C_6H_{12}O_6 & + & C_6H_{12}O_6 & \\ \text{Cane sugar} & & & & \text{Glucose} & & \text{Fructose} & \text{Rate} = k[C_{12}H_{22}O_{11}] \end{array}$$

Temperature Dependence of Rate of a Reaction & Effect of Catalyst

Temperature Dependence of Rate of a Reaction

- Increase in temperature accelerates the rate of reaction.
- With the rise in temperature by 10°, the rate constant of a chemical reaction is nearly doubled.
- The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.

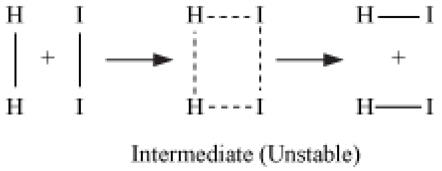
  $k = A e^{-E_a/RT}$

  A = Arrhenius factor or frequency factor or pre-exponential factor

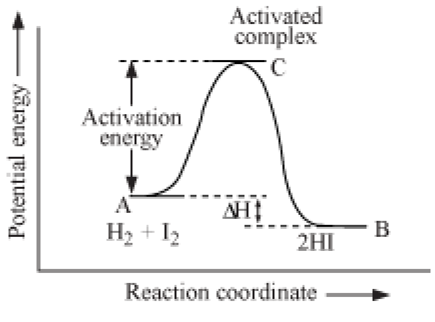
  R = Gas constant

  E_a = Activation energy (in J mol^{-1})

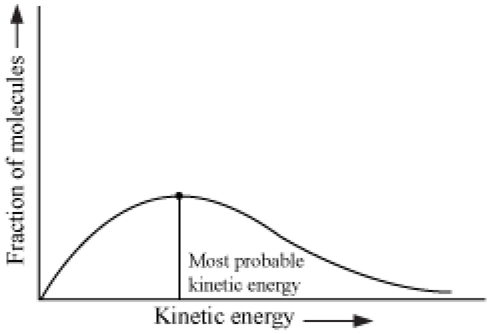
- Formation of HI through the intermediate in the reaction $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ is shown in the figure below.



- According to Arrhenius, the reaction can take place only when H_2 and I_2 molecules collide to form unstable intermediate.
- Energy required to form this unstable intermediate (called activated complex) is called activation energy.



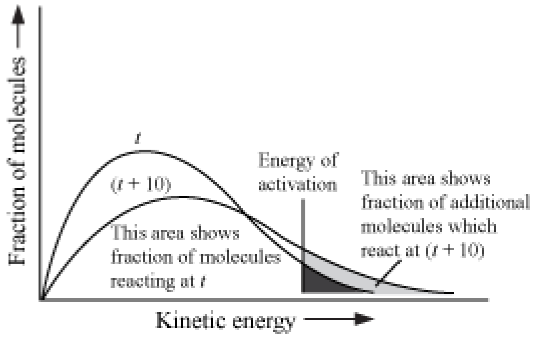
- Energy is released when the complex decomposes to form products (that is HI).
- Final heat of the reaction depends upon the nature of reactants and products.
- The distribution curve showing the energies of the molecules is shown in the figure below.



- The peak of the curve corresponds to the most probable kinetic energy.

  Most probable kinetic energy – Kinetic energy of maximum fraction of molecules

- When the temperature is raised, the maximum of the curve moves to a higher energy value.



- There is greater proportion of molecules with much higher energies.
- Increase in temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a.
- In the curve at $(t + 10)$, it is evident that the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled, leading to doubling the rate of a reaction.

  Arrhenius Equation

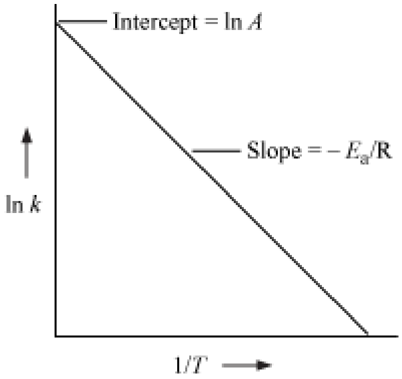
  $$k = Ae^{-E_a/RT} \qquad (1)$$

  Factor $e^{-E_a/RT}$ represents the fraction of molecules that have kinetic energy greater than E_a.

  Taking natural logarithm on both sides of equation (1), we obtain

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

Plot of $\ln k$ vs $\frac{1}{T}$ gives a straight line (shown in figure).



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

Intercept = ln *A*

- At temperature (T_1),

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

At temperature (T_2),

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

Now we obtain,

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

- Increase in temperature or decrease in activation energy will result in an increase in the rate of the reaction and this increase is exponential.

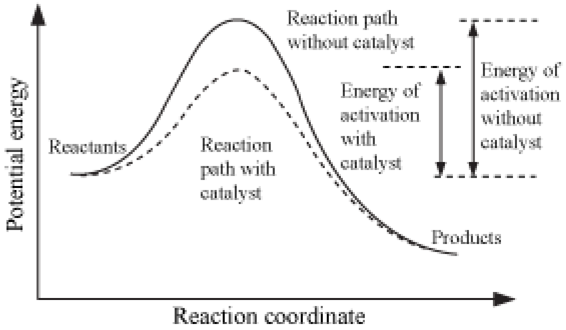
Effect of Catalyst

- Catalyst – Substance that alters the rate of a reaction without itself undergoing any permanent chemical change

- For the reaction – $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$,

  MnO_2 catalyses the reaction by increasing the rate

- Catalyst reduces the activation energy between the reactants and products and hence, lowers the potential energy barrier (shown in figure).



- Lower the value of activation energy, faster will be the rate of reaction.
- Catalyst does not alter Gibbs energy (ΔG) of the reaction.
- It catalyses spontaneous reactions, but not non-spontaneous reactions.
- In helps in attaining the equilibrium faster (that is, it catalyses forward as well as backward reactions to the same extent).

Collision Theory of Chemical Reactions

- Developed by Max Trautz and William Lewis in 1916-18
- Gives energetic and mechanistic aspects of reactions
- Based on kinetic theory of gases
- Assumptions – Reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.
- Factors which affect the rate of reactions:
- Collision frequency (Z) = Number of collisions per second per unit volume of the reaction mixture
- Activation energy
- For a bimolecular reaction,

$$A + B \longrightarrow \text{Products}$$

Rate of reaction = $Z_{AB}e^{-E_a/RT}$

Z_{AB} = Collision frequency of reactants (A and B)

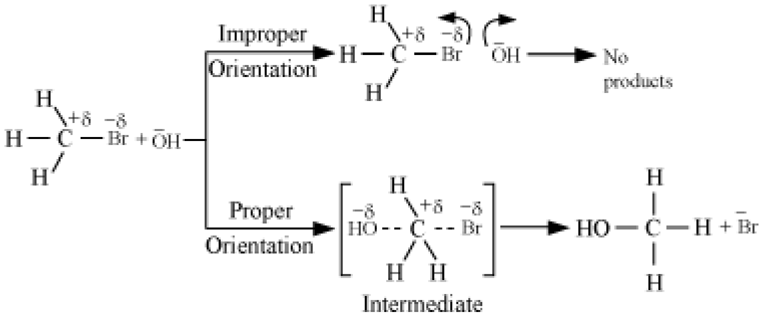
$e^{-E_a/RT}$ = Fraction of molecules with energies equal to or greater than E_a

- As compared with Arrhenius equation, A is related to collision frequency (Z).
- All collisions do not lead to the formation of products.
- Effective collisions:
- Collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products

Threshold energy = Activation energy + Energy possessed by reacting species

- Example − Formation of methanol from bromomethane requires proper orientation of reactant molecules.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$



- Proper orientation of reactant molecules − Bond formation
- Improper orientation of reactant molecules − No products are formed
- To account for effective collisions, another factor *P* is introduced.

Now, Rate = $PZ_{AB}e^{-E_a/RT}$

- *P* is called probability or steric factor.
- It takes into account the fact that in collision, molecules must be properly oriented.
- Thus, in collision theory, the factors that determine the criteria for effective collisions, and hence the rate of a chemical reaction, are:
- Activation energy
- Proper orientation of molecules
- Drawback – It considers atoms/molecules to be hard spheres and ignores their structural aspect.