CHEMICAL KINETICS

- Branch of chemistry which deals with the study of rates of chemical reactions, the factors which influence them and the mechanism by which the chemical reaction proceeds.
- The word kinetics is derived from the Greek word 'Kinesis' meaning movement.

Instantaneous Reactions

- Reactions which take place very fast are called Instantaneous Reactions.
- $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$
- $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$
- $HCl + NaOH \longrightarrow NaCl + H_2O$

Slow Reactions

- These are chemical reactions which take place at very slow rate.
- These reactions can take days, months or even years to complete.

Examples

- Rusting of Iron, Fermentation of Sugar, Transformation of carbon into diamond, Weathering of rocks

Examples for reactions studied under Chemical Kinetics

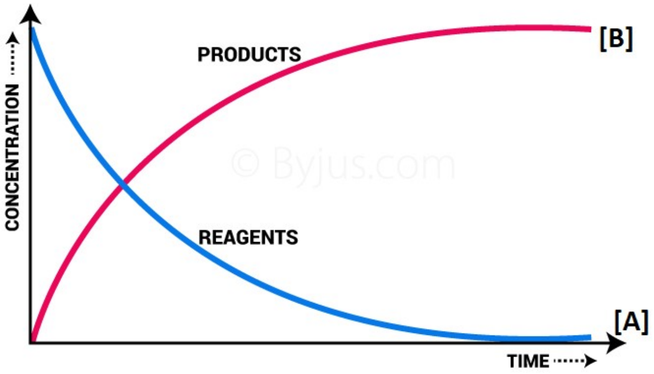
- Decomposition of hydrogen peroxide: $2H_2O_2 \longrightarrow 2H_2O + O_2$
- Decomposition of nitrogen pentoxide: $2N_2O_5 \longrightarrow 2N_2O_4 + O_2$
- Hydrolysis of an ester: $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
- Inversion of cane sugar in aqueous solution.
- $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
- Reaction between nitric oxide and chlorine: $NO + Cl_2 \longrightarrow NOCl_2$

RATE OF A CHEMICAL REACTION

- The rate of a reaction is defined as the change in concentration of the reactants or products per unit time.
- Consider a reaction, $A \longrightarrow B$

$$\text{i)Rate of a reaction} = \frac{\text{Decrease in concentration of A}}{\text{Time Taken}} = \frac{[A]_2 - [A]_1}{T_2 - T_1} = \frac{-\Delta[A]}{\Delta t}$$

$$\text{ii)Rate of a reaction} = \frac{\text{Increase in concentration of B}}{\text{Time Taken}} = \frac{[B]_2 - [B]_1}{T_2 - T_1} = \frac{\Delta[B]}{\Delta t}$$



- Consider a reaction $A + B \longrightarrow 2C$
- Here one mole of A reacts with one mole of B to form 2 moles of C.
- This means that the rate of disappearance of both A and B are same.
- But the rate of formation of C is twice the rate of disappearance of A and B.
- For obtaining the rate expression, we must divide the rate expression by the stoichiometric coefficient of the corresponding substance in the balanced equation.
- $\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-\Delta[B]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$

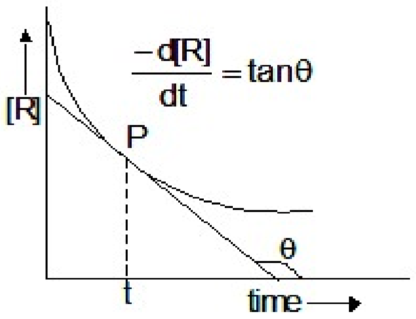
  Eg: $2N_2O_5 \longrightarrow 4NO_2 + O_2$
- $\text{rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$

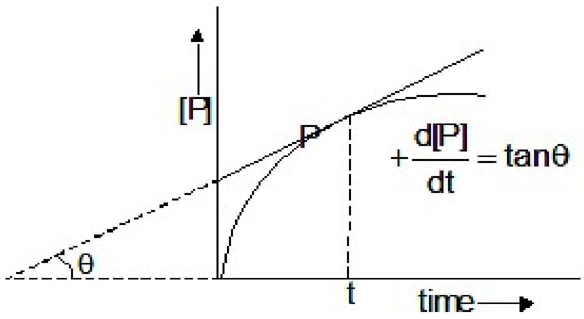
  Eg: $N_2 + 3H_2 \rightleftharpoons 2NH_3$
- $\text{rate} = \frac{-\Delta[N_2]}{\Delta t} = \frac{-1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

INSTANTANEOUS RATE OF A REACTION

- The rate of a reaction at a particular instant is known as instantaneous rate of a reaction.
- Instantaneous rate is the average rate of reaction at which the time interval Δt is as small as possible so that the rate of reaction remains almost constant at this time interval.
- Consider a reaction $A \longrightarrow B$
- $\text{rate} = \frac{-d[A]}{dt}$ or $\frac{d[B]}{dt}$
- where d[A] and d[B] are small changes in the concentrations of A and B in a small time ‘dt’.

- In order to determine the instantaneous rate of a reaction at any time ‘t’,
- A graph is plotted between concentration of reactant [R] or product [P] and time.
- A tangent is drawn to the curve at the point corresponding to time ‘t’.
- The slope of this tangent gives the instantaneous rate of the reaction at the time ‘t’.





- Consider the reaction, $A + B \longrightarrow 2C$
- Instantaneous rate $= \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$

Eg: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

- Instantaneous rate $= \frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

AVERAGE RATE OF A REACTION

- The rate measured over a long time interval is called average rate.
- For the reaction, $A \longrightarrow B$
- Average rate $= \frac{-\Delta[A]}{\Delta t}$ or $\frac{\Delta[B]}{\Delta t}$
- When Δt approaches zero, the average rate approaches instantaneous rate.

$$\text{Instantaneous rate} = \left[\frac{-\Delta[A]}{\Delta t}\right]_{\Delta t \to 0} = \frac{-d[A]}{dt}$$

$$\text{Instantaneous rate} = \left[\frac{\Delta[B]}{\Delta t}\right]_{\Delta t \to 0} = \frac{d[B]}{dt}$$

RATE LAW OR RATE EQUATION

- The law states that at constant temperature, the rate of a reaction is directly proportional to the product of the molar concentrations of the reactants with each concentration term raised to the power equal to the numerical coefficient of the species.
- Consider a general reaction, $aA + bB \longrightarrow \text{Products}$

$$r \propto [A]^a [B]^b$$

$$r = K [A]^a [B]^b$$

- where k is called rate constant. When [A] = [B] = 1, r = k.
- Rate constant of a reaction is the rate of the reaction when the molar concentration of each of the reactant is unity.

ORDER OF A REACTION

- Order of a reaction is defined as the sum of the powers of the concentration terms which is to express the rate of a reaction.
- For the reaction, $aA + bB \longrightarrow \text{Products}$
- Rate = $K[A]^a[B]^b$
- Then the order of the reaction = (a+b)
- Order of a reaction may be of different types.

1. ZERO ORDER REACTIONS

- The rate of the reaction is independent of the concentration of all the reactants.
- Eg: $2NH_3 \xrightarrow{\text{Pt/Surface}} N_2 + 3H_2$
- The rate of the reaction is independent of the concentration of all the reactants.
- Rate = $K[NH_3]^0$, Order = 0

2. FIRST ORDER REACTIONS

- The rate of the reaction depends upon one concentration term only.
- Eg: $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$ **Rate = K $[N_2O_5]^1$** **Order = 1**

  $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ **Rate = K $[H_2O_2]^1$** **Order = 1**

  $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ **Rate = K $[NH_4NO_2]^1$** **Order = 1**
- All natural and artificial Radioactive decay reactions are first order.

3. SECOND ORDER REACTIONS

- The rate of the reaction depends upon two concentration terms.
- Eg: $NO_2 + CO \longrightarrow CO_2 + NO$ **Rate = K $[NO_2]^1[CO]^1$** **Order = 2**

  $H_2 + I_2 \longrightarrow 2HI$ **Rate = K $[H_2]^1[I_2]^1$** **Order = 2**

  $2NO_2 \longrightarrow 2NO + O_2$ **Rate = K $[NO_2]^2$** **Order = 2**

4. THIRD ORDER REACTIONS

- The rate of the reaction depends upon three concentration terms.
- Eg: $2NO + Cl_2 \longrightarrow 2NOCl$ **Rate = K $[NO]^2[Cl_2]^1$** **Order = 3**

  $2NO + O_2 \longrightarrow 2NO_2$ **Rate = K $[NO]^2[O_2]^1$** **Order = 3**

ELEMENTARY REACTIONS:

- Chemical reactions which take place in a single step.
- All the molecules of the reactants undergo simultaneous collision, as in the balanced chemical equation
- Eg: $H_2 + I_2 \longrightarrow 2HI$

COMPLEX REACTIONS

- A reaction which takes place in a sequence of number of elementary reactions.
- Reaction between H_2 and Br_2 takes place in a number of steps involving both Br and H atoms.

EXAMPLES

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

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

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

RATE EXPRESSION FOR A ZERO ORDER REACTION

Consider a zero order reaction of the type

$$R \longrightarrow \text{Products}$$

The rate at any moment is given by the equation

$$\text{rate} = \frac{-d[R]}{dt} = K_0[R]^0 \quad \text{................ (1)}$$

$$\frac{-d[R]}{dt} = K_0 \quad \text{................. (2)}$$

$$\text{or } d[R] = -K_0 dt \quad \text{.................. (3)}$$

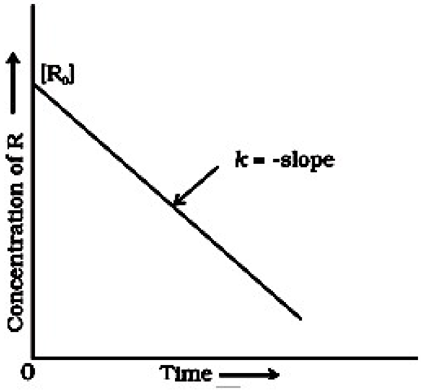
Integrating the above equation within the limit 0 to t,

$$\int_0^t d[R] = -K_0 \int_0^t dt \quad \text{.................. (4)}$$

$$[R] - [R]_0 = -K_0 t \quad \text{.................... (5)}$$

$$[R] = [R]_0 - K_0 t \quad \text{..................... (6)}$$

From equation (6), it is clear that if we plot [R] against 't', we get a straight line with slope = $-K_0$ and intercept = $[R]_0$.



Rearranging eqn (6) we get

$$K_0 = \frac{[R]_0 - [R]}{t}$$

RATE EXPRESSION FOR A FIRST ORDER REACTION

Consider a general first order reaction, $R \longrightarrow$ Product

Let $[R]_0$ be the initial concentration of 'R' and $[R]$ be the concentration of 'R' after a time 't'. Now the rate of the reaction at this moment is given by

$$\frac{-d[R]}{dt} = K[R] \quad \text{.............................} \quad (1)$$

Rearranging the equation

$$\frac{-d[R]}{[R]} = Kdt \quad \text{.............................} \quad (2)$$

Integrating the above equation

$$\int \frac{-d[R]}{[R]} = K\int dt \quad \text{.............................} \quad (3)$$

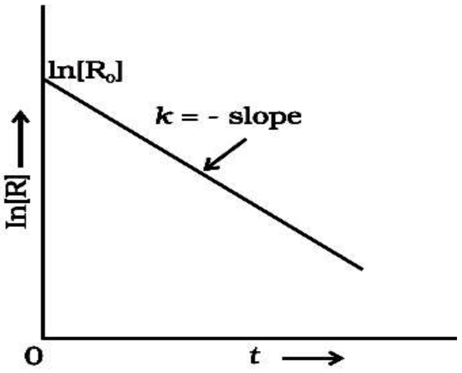
$$-\ln[R] = kt + C \quad \text{.......................} \quad (4)$$

To get the value of k, put the value of t = 0, in eqn (4)

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

$$-\ln[R]_0 = 0 + C$$

$$C = -\ln[R]_0$$



Substituting the value of C in eqn (4) we get

$$-\ln[R] = kt - \ln[R]_0$$

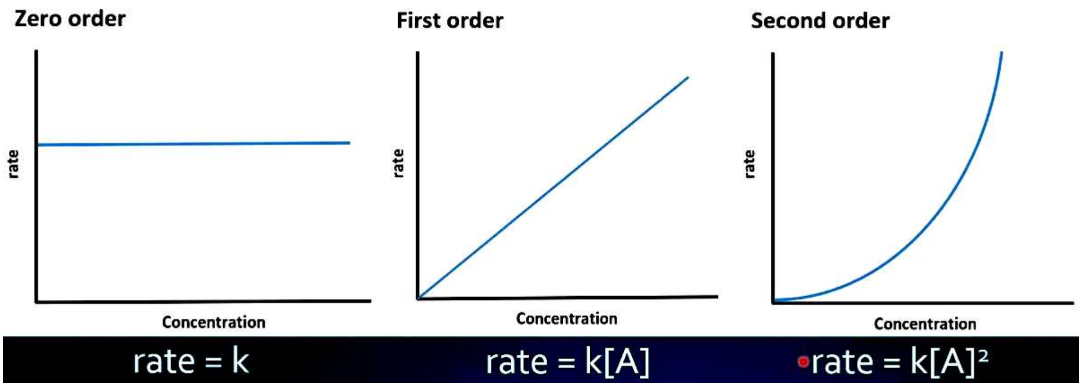
$$kt = \ln[R]_0 - \ln[R]$$

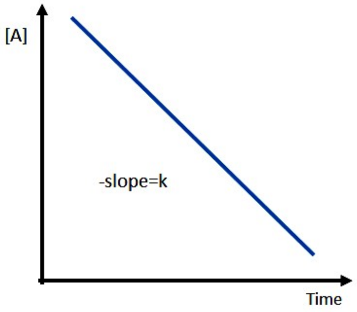
$$kt = \ln\frac{[R]_0}{[R]}$$

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

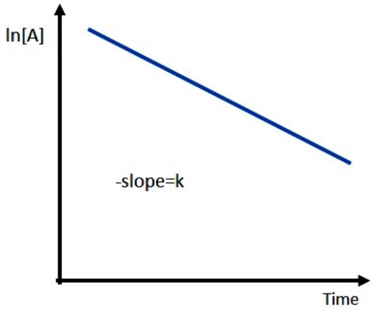
$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

PLOTS FOR INTEGRATED RATE EQUATIONS

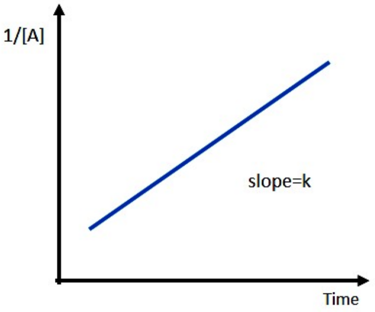




Zeroth-order Reaction



First-order Reaction



Second-order Reaction

QUESTIONS

1. The conversion of a molecule A to B follows second order kinetics.

a) Write the rate equation for the second order reaction.

Consider the reaction $2A \longrightarrow \text{Products}$

$$\text{Rate} = K[A]^2$$

b) If the concentration of A is increased to 4 times, how will it affect the formation of B.

$$r = K[A]^2$$

$$r = k\,[4A]^2$$

$$r = 16K[A]^2$$

i.e., Rate of the reaction is increased by 16 times.

c) Indicate the order and Molecularity of the reaction given below:

$$C_{12}H_{22}O_{11} \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Ans: Pseudo first order reaction and molecularity is 2.

2. Zero order reaction means that the rate of a reaction is independent of the concentration of the reactants.

i) Write an example for a zero order reaction.

Decomposition of NH_3 on a platinum surface

$$2NH_3 \xrightarrow{\text{Pt/Surface}} N_2 + 3H_2$$

ii) Write the integral rate expression for the zero order reaction.

$$K_0 = \frac{[A]_0 - [A]}{t}$$

UNITS OF RATE CONSTANT

- Rate constant has different units for reactions of different order.
- General rule for rate of reaction may be given as:
- $\text{Mol}^{1-n}\ \text{Litre}^{n-1}\ \text{Time}^{-1}$ where n = order of reaction

1. For a zero order reaction, the unit of rate constant is $\text{mol L}^{-1}\,\text{T}^{-1}$ or $(\text{mol L}^{-1}\,\text{S}^{-1})$.

2. For a first order reaction, unit of rate constant is Time^{-1} or (S^{-1}).

3. For a second order reaction, unit of rate constant is Litre mol^{-1} $Time^{-1}$

or (Litre mol^{-1} S^{-1}).

4. For a third order reaction, the unit of rate constant is $Litre^2$ mol^{-2} $Time^{-1}$

or ($Litre^2$ mol^{-2} S^{-1}).

QUESTION

1. Unit of rate constant (k) of a reaction depends on the order of the reaction. If concentration is expressed in mol L^{-1} and time in seconds (s), find the unit of k for zero, first and second order reaction.

a. For a zero order reaction, the unit of rate constant is mol L^{-1} T^{-1}.

b. For a first order reaction, unit of rate constant is $Time^{-1}$.

c. For a second order reaction, unit of rate constant is Litre mol^{-1} $Time^{-1}$.

2. Write the unit of rate constant of a 2nd order reaction if concentration is in mol L^{-1} and time in S.

Litre mol^{-1} $Time^{-1}$

3. The conversion of molecules A to B follows second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B?

$$2A \longrightarrow \text{Products}$$

$$\text{Rate} = K[A]^2$$

$$\text{Rate} = K[3A]^2$$

$$\text{Rate} = 9K[A]^2$$

4. Rate of a reaction is the change in concentration of any one of the reactants or any one of the products in unit time.

i) Express the rate of the following reaction in terms of reactants and products:

$$2HI \longrightarrow H_2 + I_2$$

$$\text{rate} = -\frac{1}{2}\frac{d[HI]}{dt} = +\frac{d[H_2]}{dt} = +\frac{d[I_2]}{dt}$$

ii) If the rate expression for the above reaction is rate = $k[HI]^2$, what is the order of the reaction?

Ans: Second Order

iii) Whether the Molecularity and order of the above reaction are the same? Give reason.

Ans: Yes the molecularity and the order of the reaction are same because both the reactants are involved in the rate determining step.

REACTION LIFE TIME

- It is defined as the time taken by a reaction to proceed to 98% of completion.
- The shorter the life time, the faster the reaction.

- Reaction life times are used to compare the various reaction.
- Reactions are also compared with half-life periods.

HALF LIFE PERIOD

- The half life period of a reaction is the time required to complete half of the reaction.
- The time required to reduce the concentration of a reactant to one half of its initial value.
- It is generally denoted by $t_{1/2}$.
- The shorter the half-life period, the faster is the reaction.

HALF LIFE PERIOD OF A ZERO ORDER REACTION

We have the relation $K_0 = \dfrac{[R]_0 - [R]}{t}$

$$\text{When } t = t_{1/2},\ R = \frac{[R]_0}{2}$$

$$K_0 = \frac{[R]_0 - \dfrac{[R]_0}{2}}{t_{1/2}}$$

$$K_0 = \frac{[R]_0}{2t_{1/2}}, \qquad t_{1/2} = \frac{[R]_0}{2K_0}$$

HALF LIFE PERIOD OF A FIRST ORDER REACTION

For a first order reaction, $K = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]}$

$$\text{When } t = t_{1/2},\ [R] = \frac{[R]_0}{2}$$

$$K = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{\dfrac{[R]_0}{2}}$$

$$K = \frac{2.303}{t_{1/2}}\log 2$$

$$K = \frac{2.303 \times 0.3010}{t_{1/2}},$$

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

QUESTIONS

1. An archeological substance contained wood had only 66.66% of the 14C found in a tree. Calculate the age of the sample if the half-life of 14C is 5730 years.

$t_{1/2}$ = 5730 years $\quad [A]_0 = 100 \quad [A] = 66.66$

$$K = \frac{0.693}{t_{1/2}}, \quad K = \frac{0.693}{5730} = 1.2 \times 10^{-4}, \quad t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}, \quad t = \frac{2.303}{1.2\times10^{-4}}\log\frac{100}{66.66}$$

t = 3353 years

2. Half-life period of a first order reaction is 20 seconds. How much time will it take to complete 90% of the reaction?

$t_{1/2} = 20$ s $\quad [A]_0 = 100 \quad [A] = 100 - 90 = 10$

$$K = \frac{0.693}{t_{1/2}}. \quad K = \frac{0.693}{20} = 0.03465\ S^{-1}, \qquad t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}, \qquad t = \frac{2.303}{0.03465}\log\frac{100}{10},$$

t = 66.46 s

3. a) The unit of rate constants of a reaction depends on the order of the reactions. Values of 'K' of two reactions are given below. Find the order of each reaction.

i) K = 3 x 10-2mol$L^{-1}S^{-1}$ ii) K = 5 x 10^{-3} mol^{-1}LS^{-1}

Answer: i) Zero Order ii) Second Order

b) i) Write the integrated rate equation for a first order reaction.

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

ii) Write the relation between half-life and rate constant of a first order reaction.

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

iii) Rate constant of a reaction is 5 x $10^{-2}S^{-1}$. Find the half-life of the reaction.

$$t_{1/2} = \frac{0.693}{K}, \qquad t_{1/2} = \frac{0.693}{5\times10^{-2}} = 13.86 \text{ sec}$$

PSEUDO FIRST ORDER REACTIONS

- Reactions which appear to be of higher order but actually follow first order kinetics are called pseudo first order reactions.
- Eg: Acid hydrolysis of ethyl acetate into ethyl alcohol and acetic acid.
- $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
- It is a bimolecular reaction but its order is 'one'.
- This is because during the reaction only the concentration of ester decreases with time.
- Usually a dilute aqueous solution of ester mixed with dilute aqueous acid, to conduct the acid hydrolysis
- The concentration of water in the reaction mixture being in large excess as compared to ester, does not decrease appreciably during the reaction.
- Therefore, the hydrolysis of ethyl acetate is pseudo first order reaction.

MOLECULARITY OF A REACTION

- Molecularity is the number of reacting species which collide simultaneously to bring about a chemical reaction.

UNIMOLECULAR REACTIONS

- If a reaction involves the decomposition of only a single species, the molecularity is one or it is called a unimolecular reaction.

- Eg: $H_2O_2 \longrightarrow H_2O + ½O_2$

BIMOLECULAR REACTIONS

- If a reaction involves the collision of two species, the molecularity is two or it is called a bimolecular reaction.
- Eg: $2HI \longrightarrow H_2 + I_2$

TRIMOLECULAR REACTIONS

- If a reaction involves the collision of three species, the molecularity is three or it is called a trimolecular reaction.
- Eg: $2NO + O_2 \longrightarrow 2NO_2$

DIFFERENCE BETWEEN ORDER AND MOLECULARITY OF A REACTION

	Order		Molecularity
1	Order is the sum of the powers of the concentration terms in the rate law.	1	It is the number of reacting species undergoing simultaneous collision.
2	It is determined experimentally.	2	It is a theoretical concept.
3	It can have fractional values.	3	It can have integral values only.
4	Order of a reaction can be zero.	4	Molecularity cannot be zero.

QUESTION

1. Consider a general reaction aA + bB → cC + dD. The rate expression for the reaction is $r = k[A]^x[b]^y$. Establish the significance of (a+b) and (x+y) in terms of order and molecularity.

(a+b) Indicates the molecularity of the reaction and (x+y) indicates the order of the reaction.

TEMPERATURE DEPENDENCE OF RATE CONSTANT

Arrhenius Equation

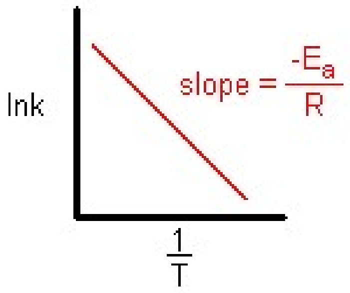
- When the temperature is increased, the kinetic energy of the reactant molecule increases.
- This will increase the number of collisions.
- Ultimately the rate of reaction will be enhanced.
- Arrhenius suggested an equation which describes rate constant, k as a function of temperature on the basis of the observations from a large number of experiments.
- The temperature dependence of the rate constant is expressed as

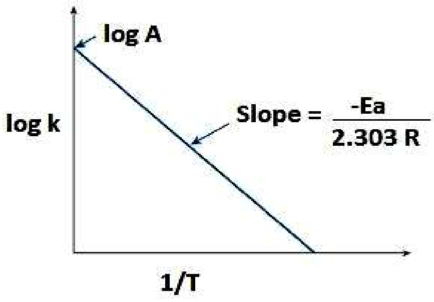
$$K = Ae^{-Ea/RT}$$

- where 'Ea' is the activation energy and 'A' is the frequency factor.
- The two quantities 'A' and 'Ea' are collectively called the Arrhenius Parameters.
- Taking Natural Logarithm on both sides,
- $\ln K = \ln A - \dfrac{Ea}{RT}$
- Taking common logarithm on both sides,
- $\log K = \log A - \dfrac{Ea}{2.303RT}$
- From the above equation, it is clear that a plot of log K against $1/T$ gives a straight line with slope equal to $-\dfrac{Ea}{2.303\,R}$ and the intercept equal to log A.

EVALUATION OF ACTIVATION ENERGY

- The activation energy can be evaluated by the graphical method.
- This is done by plotting a graph between log K against $1/T$.
- The plot gives a straight line having a slope equal to $\dfrac{-Ea}{2.303\,R}$.
- Thus by knowing the value of slope and gas constant R, the activation energy, Ea can be calculated.
- $Ea = -2.303\,R \times \text{Slope}$

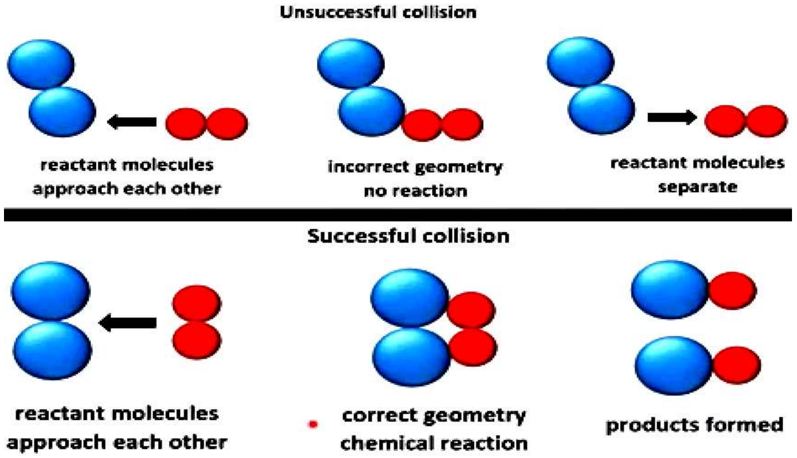




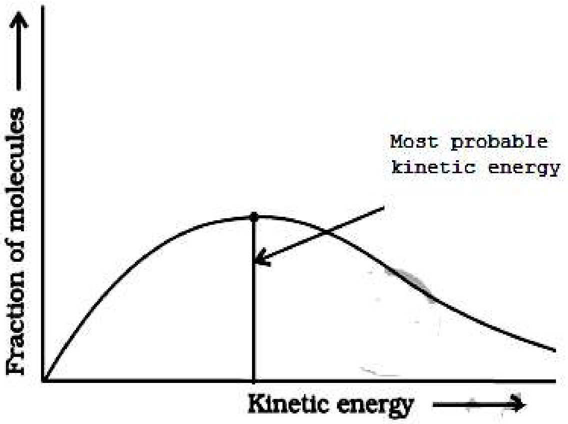
EFFECT OF TEMPERATURE ON REACTION RATE

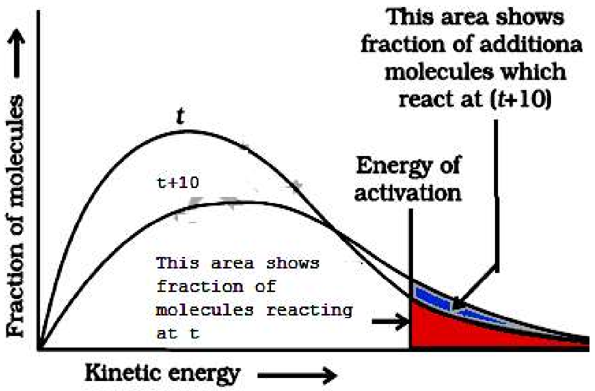
1. COLLISION THEORY

- According to collision theory, a chemical reaction takes place when the reactant molecules collide with one another.
- All collisions are however, not effective collisions.
- An effective collision which results into a chemical reaction.
- For effective collisions, the colliding molecules possess a certain minimum amount of energy called threshold energy.
- Colliding molecules must have proper orientation.



- **Threshold energy** may be defined as the minimum amount of energy which the colliding molecules must possess to make an effective collision.
- Collision of molecules which possess threshold energy or more, result in breaking up of bonds and it leads to chemical reaction.
- At lower temperature, there are only a few molecules which possess threshold energy.
- As the temperature increases, the kinetic energy of molecules increases and hence more and more molecules possess threshold energy.
- Thus rate of reaction increases sharply with increase of temperature.





- As the temperature is increased from ‘T’ Kelvin to (T+10) Kelvin, the curve shifts as shown in the figure.
- The shaded area beyond E_T now becomes double.
- This shows that the fraction of molecules possessing energy equal to or greater than the threshold energy becomes almost double.
- Hence the number of effective collisions increases and hence the rate of the reaction becomes double.

COLLISION FREQUENCY

- The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

TEMPERATURE COEFFICIENT

- Temperature co-efficient is the ratio of the rate constants of a reaction at two temperatures differing by 10^0.
- $$\text{Temperature Coefficient} = \frac{\text{Rate constant at } (T+10)\,K}{\text{Rate constant at 'T' } K}$$
- For every 10^0C rise in temperature, the rate of the reaction is nearly doubled**.**

ARRHENIUS EQUATION FOR THE REACTION AT TWO DIFFERENT TEMPERATURES

When the reaction is carried out at two different temperatures T_1 and T_2 with rate constants K_1 and K_2, then the Arrhenius Equation can be written as

$$\log K_1 = \log A - \frac{Ea}{2.303RT_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\log K_2 = \log A - \frac{Ea}{2.303\,RT_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Equation (2) — (1)

$$\log K_2 - \log K_1 = \frac{Ea}{2.303RT_1} - \frac{Ea}{2.303RT_2}$$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

QUESTIONS

1. The rate constants of a reaction at 1000K and 1060K are $0.01M^{-1}S^{-1}$ and $0.10M^{-1}S^{-1}$ respectively. Find the value of Ea.

$K_1 = 0.01M^{-1}\,S^{-1}$ $\quad$ $K_2 = 0.10\,M^{-1}\,S^{-1}$ $\quad$ $T_1 = 1000K$ $\quad$ $T_2 = 1060\,K$ $\quad$ $R = 8.314$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right], \quad Ea = \frac{\log\left(\frac{K_2}{K_1}\right) \times 2.303 \times R \times T_1T_2}{T_2 - T_1}$$

$$Ea = \frac{\log\left(\frac{0.10}{0.01}\right) \times 2.303 \times 8.314 \times 1000 \times 1060}{1060 - 1000}$$

2. The rate constants of a reaction at 600K and 900K are $0.02S^{-1}$ and $0.06S^{-1}$ respectively. Find the value of Ea.

$K_1 = 0.02\,S^{-1}$ $\quad$ $K_2 = 0.06\,S^{-1}$ $\quad$ $T_1 = 600K$ $\quad$ $T_2 = 900\,K$ $\quad$ $R = 8.314$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right], \qquad Ea = \frac{\log\left(\frac{K_2}{K_1}\right) \times 2.303 \times R \times T_1T_2}{T_2 - T_1}$$

$$Ea = \frac{\log\left(\frac{0.06}{0.02}\right) \times 2.303 \times 8.314 \times 600 \times 900}{900 - 600}$$

3. The temperature dependence of rate of a chemical reaction can be accurately explained by Arrhenius equation. With the help of Arrhenius equation, calculate the rate constant for the first order reaction $C_2H_5I \longrightarrow C_2H_4 + HI$ at 700K. Energy of activation (Ea) for the reaction is 209 kJ/mol and rate constant at 600 K is 1.6x10-5 s-1 (R = 8.314 J/K/mol).

$K_1 = 1.60 \times 10^{-5}\ S^{-1}$ $\quad K_2 = ?$ $\quad T_1 = 600K$ $\quad T_2 = 700\ K$ $\quad R = 8.314$

$Ea = 209 kJ/mol = 209 \times 10^3 J/mol$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad \log\left(\frac{K_2}{1.60 \times 10^{-5}}\right) = \frac{209 \times 10^3 J}{2.303 \times 8.314}\left[\frac{700-600}{600 \times 700}\right]$$

$$\log\left(\frac{K_2}{1.60 \times 10^{-5}}\right) = 2.6 \qquad \log K_2 - \log\left(1.60 \times 10^{-5}\right) = 2.6$$

$$\log K_2 - \log\left(1.60 \times 10^{-5}\right) = 2.6 \qquad \log K_2 = 2.6 + \log\left(1.60 \times 10^{-5}\right)$$

$\log K_2 = -2.195$ $\qquad$ So K_2 = Anti log(-2.195) = $6.38 \times 10^{-3}\ s^{-1}$

4. The rate of the reaction triples when temperature changes from 20^0C to 50^0C. Calculate the energy of activation for such a reaction. Given R = 8.314 $JK^{-1}mol^{-1}$.

$\left(\frac{K_2}{K_1}\right) = 3$, $T_1 = 293$ K, $T_2 = 323$ K, R = 8.314 $JK^{-1}mol^{-1}$.

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right], \qquad Ea = \frac{\log\left(\frac{K_2}{K_1}\right) \times 2.303 \times R \times T_1T_2}{T_2 - T_1}$$

$$Ea = \frac{\log 3 \times 2.303 \times 8.314 \times 293 \times 323}{323 - 293} = 2.82 \times 10^4 = 28.82\ kJmol^{-1}.$$

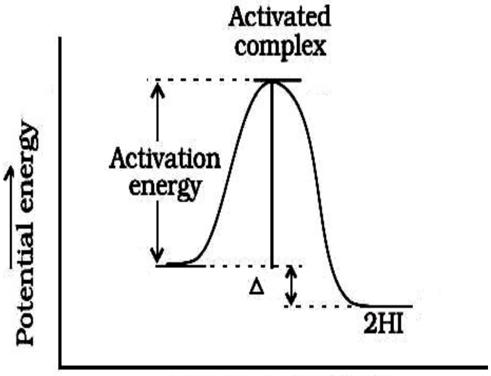
5. The rate of the reaction doubles when temperature changes from 20^0C to 37^0C. Calculate the energy of activation for such a reaction. Given R = 8.314 $JK^{-1}mol^{-1}$.

$\left(\frac{K_2}{K_1}\right) = 2$, $T_1 = 293$ K, $T_2 = 310$ K, R = 8.314 $JK^{-1}mol^{-1}$.

$$\log\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right], \qquad Ea = \frac{\log\left(\frac{K_2}{K_1}\right) \times 2.303 \times R \times T_1T_2}{T_2 - T_1}$$

$$Ea = \frac{\log 2 \times 2.303 \times 8.314 \times 293 \times 310}{310 - 293} = 5.36 \times 10^4 = 53.60 \text{ kJmol}^{-1}.$$

2. TRANSITION STATE THEORY

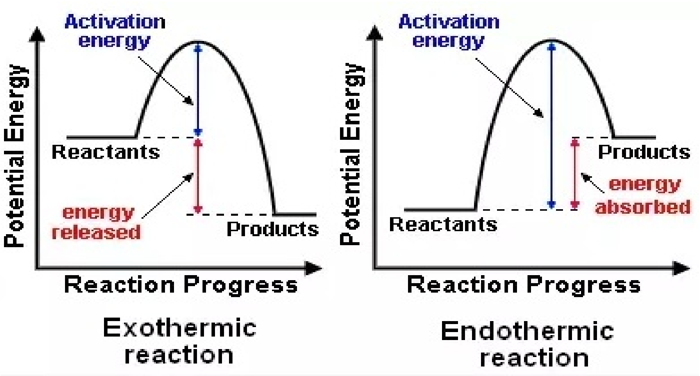


- In a chemical reaction, the reactant molecules must come together to form an activated complex.
- Its energy is higher than the reactant molecules
- i.e., the reactant molecules have to acquire a certain amount of energy before they react to form the products.
- The minimum extra energy which must be supplied to enable them to cross over the energy barrier between reactants and products is called Activation Energy.
- **Activation Energy = Threshold energy — Average PE of the reactants**

ENERGY BARRIER

- There is an energy barrier for each reaction.
- The reacting species must be provided with sufficient energy to cross the energy barrier.
- The minimum amount of energy required by reactant molecules to participate in a reaction is called **activation energy.**
- Activation energy = threshold energy – average kinetic energy of reacting molecules
- Threshold energy = initial potential energy of reactant molecules + activation energy.
- A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex.
- The life span of an activated complex is very small.
- Thus, the activated complex breaks either into reactants again or new substances, i.e., products.
- The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products.

- The energy changes during exothermic and endothermic reactions versus the progress of the reaction are shown in the figure.



Thus, every chemical reaction whether exothermic or endothermic has an energy barrier This has to be overcome before reactants can be transformed into products.

If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision

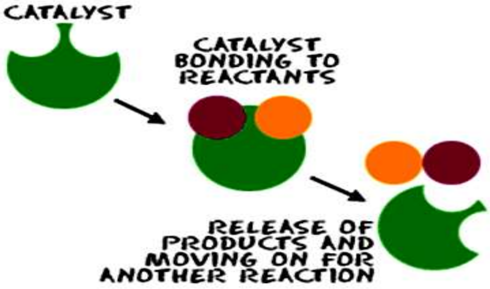
Then they can go to the right side of the slope and consequently change into products.

If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast.

If the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow.

EFFECT OF CATALYST ON REACTION RATE

- A catalyst is a substance which alters the rate of a chemical reaction without itself undergoing any permanent chemical change.
- The action of a catalyst can be explained by the intermediate complex formation theory.
- According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in the formation of an intermediate complex.
- This has a transitory existence and decomposes to yield products and the catalyst.



- Catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products.
- It lowers the potential energy barrier.
- From Arrhenius equation, it is seen that lower the value of activation energy faster will be the rate of a reaction. This is done by catalyst.
- A small amount of the catalyst can catalyze a large amount of reactants.
- A catalyst does not alter Gibbs energy, ΔG of a reaction.

- It catalyses the spontaneous reactions but does not catalyze non spontaneous reactions.
- A catalyst does not change the equilibrium constant of a reaction.