Chemical Kinetics

The branch of physical chemistry which deals with the study of rate of reaction, mechanism of reaction and the factors affecting the rate of reaction is called chemical kinetics.

Rate of reaction: The change in the rate of concentration of reactant or product with time is called rate of reaction.

Let us consider a reactant 'A' changes to product 'B'. At time 't_1', let the concentration of reactant 'A' be A_1 and the product 'B' be B_1. Similarly, at time $t = t_2$ let the concentration of reactant 'A' be A_2 and the product 'B' be B_2.

$$A \longrightarrow B$$

At time $t = t_1$	A_1	B_1
At time $t = t_2$	A_2	B_2

Now,

Change in concentration of reactant 'A' = $[A_1 - A_2]$

Change in time = $t_2 - t_1$

∴ Rate of reaction w.r.t. A = $\dfrac{\text{Change in concentration}}{\text{time}}$

$$= \frac{[A_1 - A_2]}{t_2 - t_1}$$

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

This -ve sign indicates that the concentration of reactant decreases with time

Similarly,

Rate of reaction w.r.t. B = $\frac{\text{Change in concentration}}{\text{time}}$

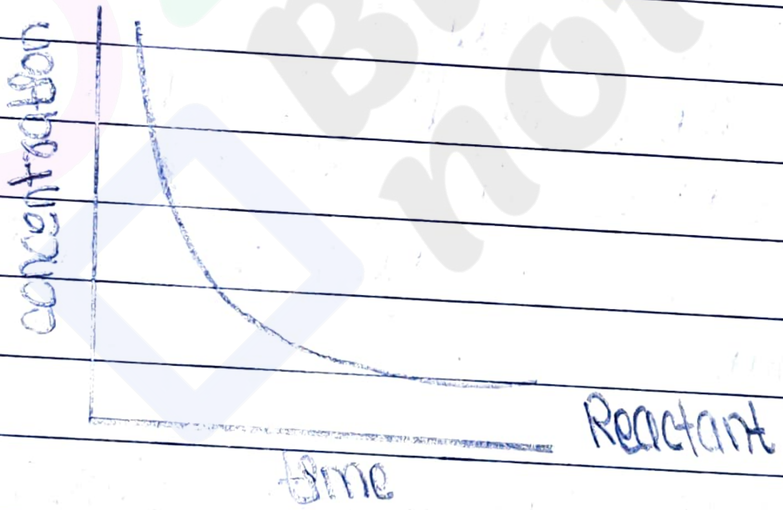
$$= \frac{[B_2 - B_1]}{t_2 - t_1}$$

$$= +\frac{d[B]}{dt}$$

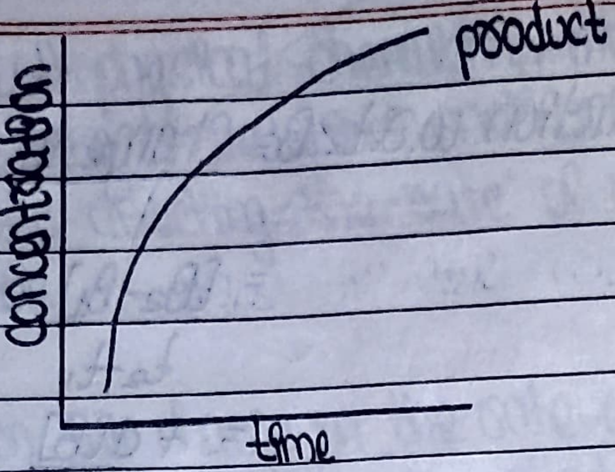
This +ve sign indicates that the concentration of product increases with time.

Rate of reaction = Rate of disappearance = Rate of appearance

$$\text{i.e., } -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$



Equivalent rate equation is the rate of reaction w.r.t. any species divided by its ~~surr~~ stoichiometry coefficient. The rate equation which is independent of the reactant or product is called equivalent rate expression.



Unit of Rate of reaction

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{time}}$$

$$= \frac{mol\ L^{-1}}{s}$$

$$= mol\ L^{-1} s^{-1}$$

Types of rate of reaction

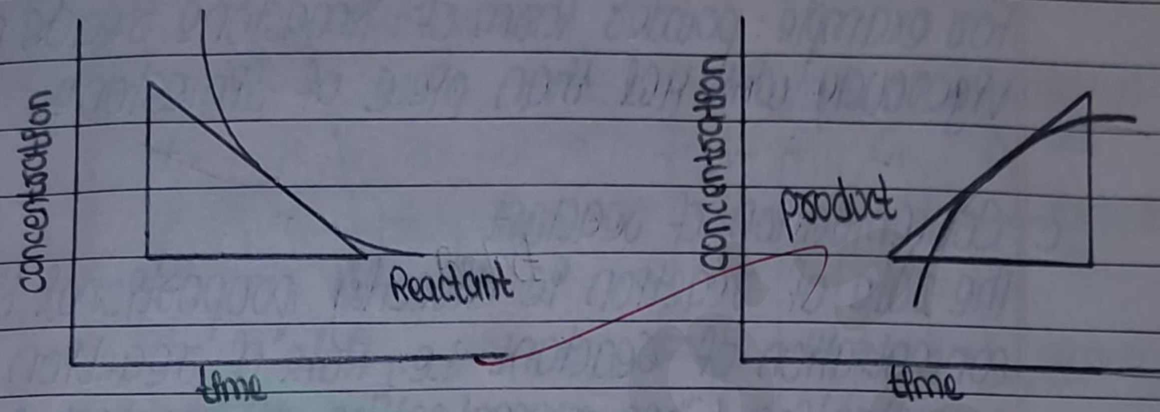
1. Average rate of reaction: The change in the concentration of reactant or product with certain interval of time period is called average rate of reaction. It can be measured.

2. Instantaneous rate of reaction: The rate of chemical reaction at any particular instant of time during chemical change. As time interval decreases, the average rate of reaction becomes instantaneous. It can be determined by knowing the slope of tangent drawn on concentration time curve at particular time

$$\text{Instantaneous rate} = \text{Average rate (when } \Delta t \longrightarrow 0)$$

$$= \frac{\Delta r}{\Delta t} \text{ (when } \Delta t \longrightarrow 0)$$

$$\text{Instantaneous rate of reaction} = \text{slope of tangent} = \frac{dy}{dx}$$



Factor affecting rate of reaction

Collisions between the reacting molecules is the primary requirement for the chemical reaction to occur but all the collisions may not cause chemical reaction. Those collisions which cause chemical reaction are called effective collision.

Besides collisions there are certain factors that affect the rate of chemical reaction. They are

a Nature of reactant

The rate of chemical reaction depends upon the nature of reactant. If the reactant is ionic compound then it shows ionic reaction which is very fast but if the reactant is covalent compound then it shows molecular reaction which is very slow.

b. Particle size of reactant

Rate of reaction increases with size of reactant molecules increases. When the surface area increases, the number of collisions will also increases and hence the reaction will be faster.

For example: powder form of limestone reacts more vigorously with HCl than piece of limestone.

c. Concentration of reactant

The rate of reaction is directly proportional to concentration of reactant i.e., Rate of reaction $\propto$ concentration. When concentration of reactant increases then the rate of reaction also increases. This is due to the increase in effective collision of reacting molecules.

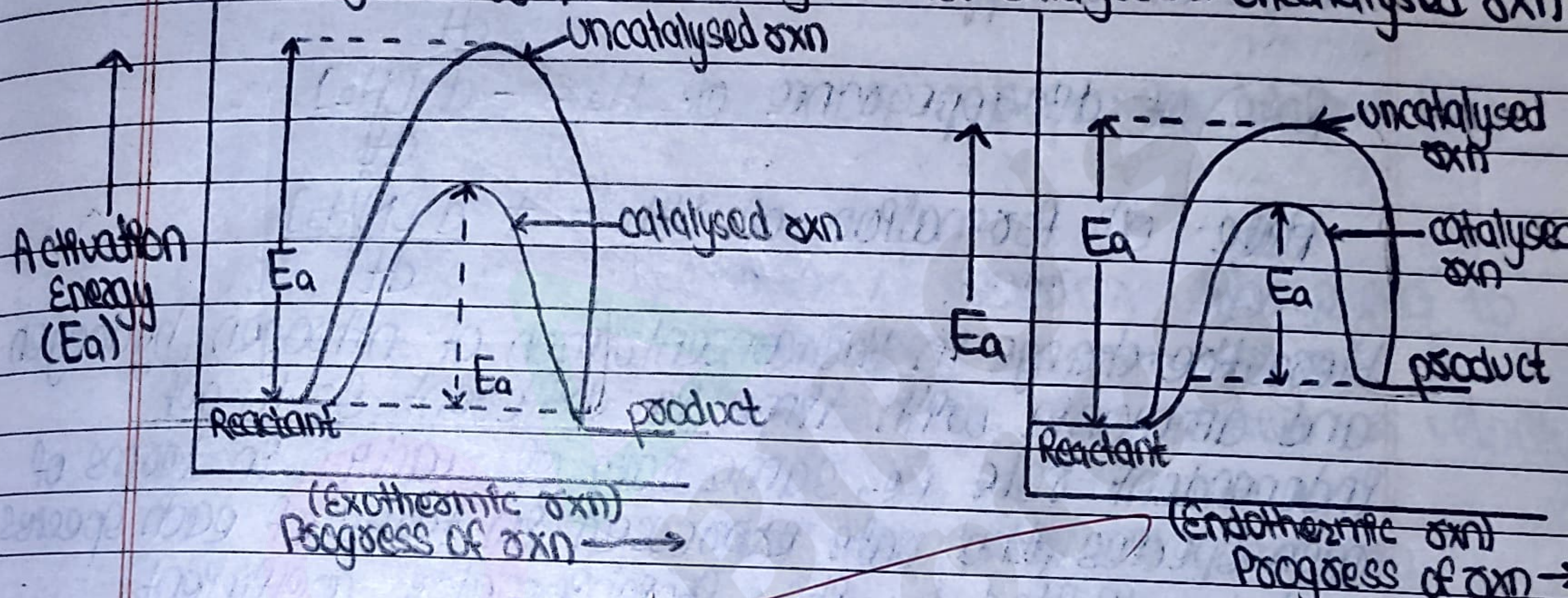
d. Temperature

Rate of reaction increases nearly by two or three times when the temperature is increased by 10°C. On increasing the temperature ~~the temperature~~ on reactant molecules, the average kinetic energy is increased so that the reactant is changed into product easily.

e. Catalyst

A catalyst itself donot take part in chemical reaction but changes the rate of reaction. By using the positive catalyst the rate of reaction is increased. catalyst decreases the activation energy (Ea) and provides new mechanism or path which ultimately increases the rate of reaction. But -ve catalyst decreases the rate of reaction.

Fig: Energy profile diagram for catalysed & uncatalysed rxn



f Light

The rate of photochemical reaction increases with the intensity of light because the light photons provides the essential energy of activation for the reaction.

Example: the rate of reaction between Hydrogen gas and chlorine gas increases with the intensity of light.

$$H_2(g) + Cl_2(g) \xrightarrow[h\nu]{\text{sunlight}} HCl(g)$$

Rate of reaction and stoichiometry

Let us consider a reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Now,

Rate of disappearance of $N_2 = -\frac{d[N_2]}{dt}$

Rate of disappearance of $H_2 = -\frac{d[H_2]}{dt}$

Rate of formation of $NH_3 = +\frac{d[NH_3]}{dt}$

Here, the change in the concentration of nitrogen, hydrogen and ammonia with time is different. So to get independent rate i.e., same rate of reaction in terms of each species, the rate expressed in terms of each species must be divided by its stoichiometric coefficient.

i.e.,

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

The mathematical expression that gives the true rate of rxn in terms of concentration which influences the rate of rxn is called rate law.

Rate law equation

Let us consider a general reaction,

$$aA + bB \longrightarrow \text{Product}$$

where, 'A' and 'B' are the reactants and 'a' and 'b' are their respectively stoichiometric coefficient in the balanced equation.

The rate of reaction is directly proportional ($\propto$) $[A]^p [B]^q$.

$$\text{Rate} = k\,[A]^p\,[B]^q \quad \ldots\ldots (i)$$

where, p and q are the order of reaction with respect to reactant 'A' and 'B' respectively.

The proportionality 'k' is known as rate constant or velocity constant or specific rate constant.

This eq^n (i) is called rate law equation or rate law.

If $[A] = [B] = 1\ \text{mol}\ l^{-1}$

Then, eq^n (i)

$$\text{Rate} = k$$

Therefore, rate constant (k) can be defined as the rate of reaction when the concentration of each reactant species is unit.

Characteristics of rate constant (k)

i. Rate constant is the measure of rate of reaction, higher the value of rate constant, higher will be the rate of reaction and vice versa.

ii. The value of rate constant is different for different reaction.

iii For a particular reaction the value of rate constant is different at different temperature.

Order of reaction

Consider a general reaction

$$aA + bB \longrightarrow \text{product}$$

The rate law eq^n is

$$R = k[A]^p[B]^q \quad \ldots(i)$$

where p and q are the order of reaction with respect to reactant A and B respectively.

The overall order of reaction $(n) = p+q$

Order of reaction is defined as the sum of powers of concentration terms raised in the rate law equation. It is experimentally determine value and may be zero or have fractional value or whole number.

If $n = p+q = 0$, then the reaction is zero order reaction.

If $n = p+q = 1$, then the reaction is first order reaction.

If $n = p+q = 2$, then the reaction is second order reaction.

Types of order of reaction

1. Zero order reaction

The reaction in which the rate of reaction is independent on initial concentration of reactant is called zero order reaction.

Let us consider a zero order reaction.

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

The rate law equation for zero order reaction is

$$R = k_0[A]^0 \text{ ......(i)}$$

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

At time $t=0$,	a mol l^{-1}	0
At time $t=t$,	$(a-x)$ mol l^{-1}	x

where, a = initial concentration of reactant
x = the amount of product formed after time t

The rate law equation for zero order reaction is

$R = k_0[A]^0$ (where k_0 = rate constant for zero order reaction

$$-\frac{d[A]}{dt} = k_0$$

$$-\frac{d(a-x)}{dt} = k_0$$

$$-\frac{da}{dt} + \frac{dx}{dt} = k_0$$

$$\frac{dx}{dt} = k_0 \text{ .....(ii)}$$

This eqn (ii) is the differential rate law equation for zero order reaction

Unit of k_0

$R = k_0[A]^0$

$R = k_0$

$k_0 = mol\,L^{-1}\,s^{-1}$

∴ The unit of rate constant for zero order (k_0) = $mol\,L^{-1}\,s^{-1}$

2. First order reaction

The reaction whose rate depends on the first power of concentration of reactant is called first order reaction.

Consider a general first order reaction.

$A \longrightarrow$ Product

At time t=0 a mol L^{-1} 0

At time t=t (a−x) mol L^{-1} x

where, a = initial concentration of reactant

x = the amount of product formed after time t

The rate law equation for first order reaction is

$$R = k_1[A]^1$$

$$-\frac{d[A]}{dt} = k_1[A_1]$$ where, k_1 = rate constant for 1st order

$$-\frac{d(a-x)}{dt} = k_1(a-x)$$

$$-\frac{d(a)}{dt} + \frac{d(x)}{dt} = k_1(a-x)$$

$$\frac{d(x)}{dt} = k_1(a-x) \ldots\ldots (ii)$$

This equation (ii) is the differential rate law equation for first order reaction.

On arranging equation (ii)

i.e., $\frac{dx}{(a-x)} = k_1 dt$

On integrating

$\int \frac{dx}{(a-x)} = k_1 \int dt$

$-\ln(a-x) = k_1 t + I$ ......(iii) (where, I = integration constan

When t=0, then x=0

Putting the value of 't' and x in eqn (iii), we get $I = -\ln a$

$-\ln(a-x) = k_1 t - \ln a$ → Now, putting the value of I in equation (iii), we get

$\ln a - \ln(a-x) = k_1 t$

$k_1 t = \ln \frac{a}{a-x}$

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

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

This is the differential integrated rate law equation for first order reaction.

Unit of rate constant (k_1)

The rate law equation for first order reaction is

$R = k_1 [A]^1$

$k = \frac{R}{[A]^1}$

$= \frac{mol\ L^{-1} s^{-1}}{mol\ L^{-1}}$

$= s^{-1}$ The unit for rate constant for 1st order rxn is s^{-1} or $time^{-1}$

Half life period ($T_{1/2}$ or $T_{0.5}$)

The time period required to consume the half of the initial concentration of reactant is called half life period. It is denoted by ~~half life~~. $T_{1/2}$ or $T_{0.5}$.

The rate law equation for first order reaction is

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

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

When $t = t_{1/2}$

Then $x = \frac{a}{2}$

$$\text{Now, } t_{1/2} = \frac{2.303}{k} \log \frac{a}{(a-a/2)}$$

$$= \frac{2.303}{k} \log 2$$

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

Therefore, the half life period of reaction is independent of initial concentration of reactant but depends on the rate constant.

The example of first order reaction are

1. Hydrolysis of ester in the presence of dilute HCl.

$$\underset{\text{(Ethylethonate)}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{(Ethanoic acid)}}{CH_3COOH} + \underset{\text{(Ethanal)}}{C_2H_5OH}$$

2. Decomposition of hydrogen peroxide

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2} O_2$$

3. Second order reaction

The reaction in which rate depends on second power of concentration of reactant is known as second order reaction. If the concentration of reactant is double then rate of reaction increases by four times.

Consider a general second order reaction

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

At $t=0$ $\quad a \text{ mol } l^{-1} \quad 0$

At $t=t$ $\quad (a-x) \text{ mol } l^{-1} \quad x$

The rate law equation for second order reaction is

$$R = k_2[A]^2$$

$$\frac{-d[A]}{dt} = k_2[A]^2$$

$$\frac{-d(a-x)}{dt} = k_2(a-x)^2$$

$$\frac{dx}{dt} = k_2(a-x)^2$$

This is the differential rate law eqn for second order rxn.

Unit of rate constant (k_2)

The rate law eqn for second order reaction is

$$R = k_2[A]^2$$

$$k_2 = \frac{R}{[A]^2}$$

$$= \frac{\text{mol } l^{-1} s^{-1}}{\text{mol}^2 l^{-2}}$$

$$= \text{mol}^{-1} l \, s^{-1}$$

The unit of rate constant (k_2) for second order reaction is $mol^{-1}\, l\, s^{-1}$.

The example of second order reaction are

1. Decomposition of ozone into oxygen

$$2O_3 \longrightarrow 3O_2$$

2. Hydrolysis of ester in presence of alkali

$$\underset{\text{(Ethyl ethanoate)}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{(Sod. acetate)}}{CH_3COONa} + C_2H_5OH$$

4. Third order reaction

The reaction in which rate depends on third power of concentration of reactant is known as third order reaction. If the concentration of reactant is double then the rate of reaction increases by eight time.

Consider a general third order reaction.

$$A \longrightarrow Product$$

At $t=0$, $a\ mol\ l^{-1}$ $\qquad 0$

At $t=t$, $(a-x)\ mol\ l^{-1}$ $\qquad x$

The rate law equation for third order reaction is

$$R = k_3[A]^3$$

$$\frac{-d[A]}{dt} = k_3[A]^3$$

$$\frac{-d(a-x)}{dt} = k_3(a-x)^3$$

$$\frac{dx}{dt} = k_3(a-x)^3$$

This is the differential rate law eqⁿ for third order rxn.

Unit of rate constant (k_3)

The rate law equation for third order reaction is

$$R = k_3[A]^3$$

$$\text{or, } k_3 = \frac{R}{[A]^3}$$

$$= \frac{mol\ l^{-1}\ s^{-1}}{mol^3\ l^{-3}}$$

$$= mol^{-2}\ l^2\ s^{-1}$$

∴ The unit of rate constant (k_3) for third order reaction is $mol^{-2}\ l^2\ s^{-1}$.

At $t=0$ $\quad a\ mol\ l^{-1}$ $\quad 0$

At $t=t$ $\quad (a-x)\ mol\ l^{-1}$ $\quad x$

The rate law eqn for third order reaction is

$$R = k_3[A]^3$$

$$-\frac{d[A]}{dt} = k_3[A]^3$$

$$-\frac{d(a-x)}{dt} = k_3(a-x)^3$$

$$\frac{dx}{dt} = k_3(a-x)^3$$

This is the differential rate law eqn for third order rxn.

Unit of rate constant (k_3)

The rate law eqn for third order rxn is

$$R = k_3[A]^3$$

~~The unit of rate constant (k_3) for third order reaction is $mol^{-2}\ l^2\ s^{-1}$.~~

Example of third order rxn are:

(i) Oxidation of nitric oxide to nitrogen dioxide.

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

(ii) Reaction betn nitric oxide and chlorine

$$2NO + Cl_2 \longrightarrow 2NOCl$$

(Nitrosyl chloride)

	Order of reaction	Rate law equation	Differential rate law equation	Unit of k
1.	Zero order reaction	$R = k_0$	$\frac{dx}{dt} = k_0$	$mol\ l^{-1} s^{-1}$
2.	First order reaction	$R = k_1[A]^1$	$\frac{dx}{dt} = k_1(a-x)$	s^{-1}
3.	Second order rxn	$R = k_2[A]^2$	$\frac{dx}{dt} = k_2(a-x)^2$	$mol^{-1}\ l\ s^{-1}$
4.	Third order reaction	$R = k_3[A]^3$	$\frac{dx}{dt} = k_3(a-x)^3$	$mol^{-2}\ l^2 s^{-1}$

Pseudo order reaction

Consider a general reaction

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

The rate equation of the given reaction is

$$R = k\,[A]\,[B]$$

Actually the given order of above reaction is second order but experimentally reaction is forced to follow first order. Therefore, the higher order of reaction can follow lower order of reaction. This type of reaction is called pseudo order reaction.

In case of elementary reaction, the order and molecularity are same. So pseudo order reaction are also called pseudo molecular reaction.

Give example of zero order reaction

The example of zero order reaction are:-

(i) Thermal decomposition of hydrogen iodide (HI) over gold surface.

$$2HI \xrightarrow[\Delta]{Au} H_2 + I_2$$

(ii) Thermal decomposition of Ammonia (NH_3) vapour over gold surface.

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

The following data were obtained for a hypothetical reaction.

$$x + y \longrightarrow z$$

Expt.	[x] mol L^{-1}	[y] mol L^{-1}	Formation of z mol $L^{-1}s^{-1}$
1.	0.20	0.20	3×10^{-3}
2.	0.40	0.20	1.2×10^{-3}
3.	0.20	0.40	6×10^{-3}
4.	0.60	0.20	9×10^{-3}

i). Calculate the order of reaction with respect to x and y.
ii). Calculate the overall order of reaction.
iii). Calculate the rate constant.

Soln: Let order of rxn w.r.t. x and y be 'a' and 'b' respectively.

(i) From the experiment,
Rate law equation is

$$R = k\,[x]^a\,[y]^b$$

$$3\times10^{-3} = k\,[0.20]^a\,[0.20]^b \quad \text{.....(i)}$$

$$1.2\times10^{-3} = k\,[0.40]^a\,[0.20]^b \quad \text{.....(ii)}$$

$$6\times10^{-3} = k\,[0.20]^a\,[0.40]^b \quad \text{.....(iii)}$$

$$9\times10^{-3} = k\,[0.60]^a\,[0.20]^b \quad \text{.....(iv)}$$

Dividing eqn (iv) by (ii), we get

$$\frac{9\times10^{-3}}{1.2\times10^{-3}} = \frac{\cancel{k}\,[0.60]^a\,\cancel{[0.20]^b}}{\cancel{k}\,[0.40]^a\,\cancel{[0.20]^b}}$$

$$\text{or, } \frac{3}{4} = \left[\frac{3}{2}\right]^a$$

Dividing eqⁿ (iii) by (i), we get

$$\frac{6\times10^{-3}}{3\times10^{-3}} = \frac{k\,[0.20]^a\,[0.40]^b}{k\,[0.20]^a\,[0.20]^b}$$

or, $2 = [2]^b$

$\therefore b = 1$

(ii) Overall order of reaction $= a+b = 1+1 = 2$

(iii) Substituting the value of a and b in eqⁿ (i), we get

$$3\times10^{-3} = k\,[0.20]^1\,[0.20]^b$$

or, $\dfrac{3\times10^{-3}}{0.2\times0.2} = k$

$\therefore k = 0.075$

Hence, rate constant (k) = 0.075

For the gaseous reaction,

$$A_{(g)} + B_{(g)} \longrightarrow C_{(g)} + D_{(g)}$$

It is found that, rate $= k\,[A]^2\,[B]^1$

How many times does the rate of reaction increase or decrease if

(a) the partial pressure of both A and B are double.

(b). the partial pressure of A doubles but that of B remains constant

(c) the volume of reacting vessel is doubled

(d) an inert gas is added which doubles the overall pressure while the partial pressure of A and B remains constant.

(e) the temperature rises by 30°C.

Given Equation is

$$A_{(g)} + B_{(g)} \longrightarrow C_{(g)} + D_{(g)}$$

Rate = $k [A]^2 [B]^1$ where, k = rate constant

If P_A and P_B are the partial pressure of two gases A and B respectively, then the rate constant becomes

$$\text{Rate} = k [P_A]^2 [P_B]^1 \quad \ldots\text{(i)}$$

a. If the partial pressure of both A and B are doubled, then the equation becomes

$$\text{Rate} = k [2P_A]^2 [2P_B]^1$$
$$= 8k [P_A]^2 [P_B]^1$$

The rate of reaction is increased by 8 times, if partial pressure of both A and B are doubled.

b. If the partial pressure of A is doubled and that of B remains constant, the rate constant becomes

$$\text{Rate} = k [2P_A]^2 [P_B]^1$$
$$= 4k [P_A]^2 [P_B]^1$$

The rate of reaction is increased by 4 times, if the partial pressure of reactant A is doubled and B remains constant.

c. We know that the volume of gas at constant temperature is inversely proportional to its pressure. When the volume of reaction vessel is doubled, the partial pressure of A and B is decreased by half and the new pressure becomes $\frac{P_A}{2}$ and $\frac{P_B}{2}$ respectively.

$$\text{Rate} = k\left[\frac{P_A}{2}\right]^2\left[\frac{P_B}{2}\right]^1$$

$$= \frac{1}{8}k\,[P_A]^2\,[P_B]^1$$

The rate of reaction is decreased by 8 times.

d. If the inert gas is added to the gaseous vessel, there is no change in partial pressure of reactant A and B i.e., the partial pressure of A and B remains constant.

e. Experimentally, it is found that the rate of reaction increase or decrease by 2 or 3 times for every 10°C rise or fall in temperature.
Suppose, 'r' be the initial rate of reaction. If the temperature of reaction is increased by 10°C, the rate becomes 2r or 3r.
Again, if temperature of reaction is increased by 10°C, the rate will be 2 or 3 times of 2r or 3r.

$$2\times 2r = 4r \text{ or } 3\times 3r = 9r$$

If temperature of reaction is further increased by 10°C, the rate will be 2 or 3 of 4r or 9r.

$$2\times 4r = 8r \text{ or } 3\times 9r = 27r$$

Therefore, if the temperature of reaction is increased by 30°C, the rate of reaction increases from 8 to 27 times.

2. A first order reaction takes 100 minutes to change 60% reactant to product. How long will it take to complete 75% of the reactant to product?

Soln: For 60% decomposition

Initial concentration of reactant (a) = 100 (Suppose)

After 100 minutes the concentration of reactant becomes, (a-x) = (100-60) = 40

Time taken (t) = 100 min

Rate constant (k) = ?

For first order reaction,

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

$$k = \frac{2.303}{t} \log \frac{100}{100-60}$$

$$k = \frac{2.303}{t} \log \frac{100}{40}$$

$$k = \frac{2.303}{100} \log (2.5)$$

$$k = \frac{2.303}{100} \times 0.397$$

$$k = 9.16 \times 10^{-3} \text{ min}^{-1}$$

For 75% completion

Initial concentration (a) = 100

Final concentration (a-x) = (100-75) = 25

Time taken for completion (t) = ?

For first order reaction

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

$$\text{or, } 9.16 \times 10^{-3} = \frac{2.303}{t} \log \frac{100}{100-75}$$

$$\text{or, } 9.16 \times 10^{-3} = \frac{2.303}{t} \log \frac{100}{25}$$

$$\text{or, } 9.16 \times 10^{-3} = \frac{2.303}{t} \times 0.602$$

$$t = \frac{2.303 \times 0.602}{9.16 \times 10^{-3}}$$

$$= 151.35 \text{ minutes}$$

Hence, the time taken for the completion of 75% is 151.35 minutes.

①. The reaction between X and Y is of first order reaction w.r.t. X and zero order reaction w.r.t. Y. Fill in the blanks in the following table:

Exp. No.	[X] mol l^{-1}	[Y] mol l^{-1}	Initial rate mol $l^{-1}s^{-1}$
1	0.1	0.1	2×10^{2}
2	-	0.2	4×10^{-2}
3	0.4	0.4	-
4	-	0.2	2×10^{-2}

$R = k[X]^1[Y]^0$

$2 \times 10^{-2} = k\,[0.1]$

$\therefore k = 0.2$

$4 \times 10^{-2} = 0.2\,[X]^1[Y]^0$

$4 \times 10^{-2} = 0.2 \times X$

$X = 0.2$

$R = 0.2 \times 0.4$

$= 0.08$

$2 \times 10^{-2} = 0.2\,[X]$

$2 \times 10^{-2} = 0.2 \times X$

$\therefore X = 0.1$

② P+Q ⟶ Product is a third order reaction. Write the possible expression for the rate law equation of this reaction.

Soln. (i) $R = k\,[P]^2\,[Q]^1$ (iii) $R = k\,[P]^0\,[Q]^3$

(ii) $R = k\,[P]^1\,[Q]^2$ (iv) $R = k\,[P]^3\,[Q]^0$

③ Rate of reaction is double when concentration of A is doubled but there is no effect in rate with change in concentration of B.

(i) Write down the rate law.

(ii) What is the unit of rate constant?

Ans. Rate of reaction is doubled when concentration of A is doubled but there is no effect in rate with change in concentration of B,

The rate law becomes

$$\text{Rate} = k\,[A]^1\,[B]^0$$

$$R = k, [A]^1$$

$$k = \frac{R}{[A]^1}$$

$$= \frac{\text{mol}\,L^{-1}\,s^{-1}}{\text{mol}\,L^{-1}}$$

$$= s^{-1}$$

Hence, s^{-1} is the unit of rate constant.

④ The half life periods of two reactions A and B are 3.21×10^2 min and 569 min respectively. Which of these is a faster reaction.

Ans,, $A = 3.21\times10^2 = 321$ minute $\quad t_{1/2} = \frac{0.693}{k}$

$B = 569$ minute

Smaller the value of half life period of reaction, reaction rate will be faster. Because concentration of reactant will decrease faster and formation of product is faster. So, rate of reaction A is faster than B.

2071. What will be the initial rate of reaction if it's rate constant is 1×10^{-3} min^{-1} and the concentration of the reactant is 0.2 mol l^{-1}? How much reactant will be converted into the product in 500 minutes? (0.078 mol l^{-1}).

Soln: Rate constant $(k) = 1\times10^{-3}$ min^{-1}

Let $[A] = 0.2$ mol l^{-1} as unit of k is min^{-1}. This is 1st order reaction.

$R = k[A]^1$

$= 1\times10^{-3}\times0.2$

$= 2\times10^{-4}$ mol l^{-1} min^{-1}

We know,

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$ where, x is reactant converted into product

$$\text{or, } 500 = \frac{2.303}{1\times10^{-3}}\log\frac{0.2}{0.2-x}$$

$$\text{or, } 500 = 2303\log\left(\frac{0.2}{0.2-x}\right)$$

or, $0.2171 = \log(0.2) - \log(0.2-x)$

or, $0.2171 = (-0.69897) - \log(0.2-x)$

or, $0.91607 = -\log(0.2-x)$

or, $0.91607 = \log(0.2-x)^{-1}$

or, $10^{0.91607} = \frac{1}{0.2-x}$

or, $8.2427 = \frac{1}{0.2-x}$

or, $1.64854 - 8.2427x = 1$

or, $8.2427x = 0.64854$

$\therefore x = 0.078$ mol l^{-1}

2. The rate of first order reaction is 1.5×10^2 mol l^{-1} min^{-1} at 0.5 M concentration of the reaction. What is the half life the reaction?

Soln: Given,

Rate of a first order reaction $= 1.5 \times 10^2$ mol l^{-1} min^{-1}

Concentration of reactant $= 0.5$M

We know that

Rate $= k$ [concentration of reactant] where k = rate constant of r

or, $1.5 \times 10^2 = k\,[0.5]$

or, $k = \frac{1.5 \times 10^2}{0.5} = 3 \times 10^2$ minute

We know that,

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^2} = 2.31 \times 10^{-3}$ minute

Hence, the half life of a reaction is 2.31×10^{-3} minute.

3. A first order rxn requires 100 minutes to disintegrate half of the reactant. How will it takes to complete one-third of the reaction?

Soln: Given,

Half life time ($t_{1/2}$) = 100 sec min.

$k = \frac{0.693}{t} = \frac{0.693}{100}$

Time required for one-third completion = ?

Here, let initial concentration = a

Concentration decomposed is 33.33%

$$x = \frac{33.33 \times a}{100}$$

$$= 0.3333a$$

Now, $t = \frac{2.303}{\frac{0.693}{t_{1/2}}} \log \frac{a}{a-x}$

$$= \frac{2.303 \times 100}{0.693} \log \frac{a}{a - 0.3333a}$$

$$= \frac{2.303 \times 100}{0.693} \log \frac{a}{0.6667a}$$

$$= \frac{230.3}{0.693} \log\left(\frac{1}{0.6667}\right)$$

$$= \frac{230.3}{0.693} \times 0.176$$

$$= 58.48 \text{ sec}$$

Theories of rate of reaction

Collision theory

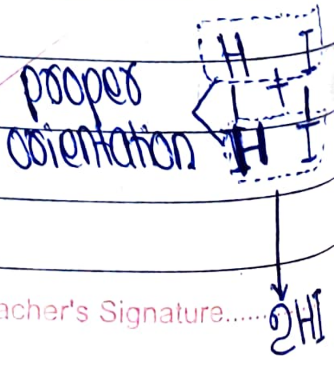
This theory explains the increase in rate of reaction with temperature. For the product formation, the reacting species should collide with each other but all the collisions cannot lead to the product formation. The collisions which leads to the formation are called effective collision. The effective collision depends on the energy of collision and proper orientation of reacting species. The reacting molecules have their own kinetic energy. Every reaction have their own energy barrier known as threshold energy. The average kinetic energy of reacting species is not mostly to overcome the energy barrier. So, an additional energy should be provided to the reacting species to overcome this energy barrier is known as activation energy.

The reaction with higher activation energy is slow whereas with lower activation energy is fast.

Furthermore, for the effective collision, the reacting species should be oriented towards the favourable site of collision known as proper orientation.

$$H_2 + I_2 \longrightarrow 2HI$$

$$H-\boxed{H + I}-I \longrightarrow \text{No product}$$



* Activated complex theory

According to this theory, a transition state is formed between reactants and products ~~with~~ which immediately changes into stable product. It can be summarized as:

a) Fast approaching reactants slow down due to electron cloud repulsion during which kinetic energy changes into potential energy.

b) When the reactants comes closer, the interpenetration of electrons takes place and the valence electrons are rearranged. So, the existing bonds weakend and how bonds are partially formed. This state is called transition state or activated complex.

c) The transition state is high energy state and is momentary which soon converts into stable product.

Consider a reaction

$A{-}B + C \longrightarrow A + B{-}C$

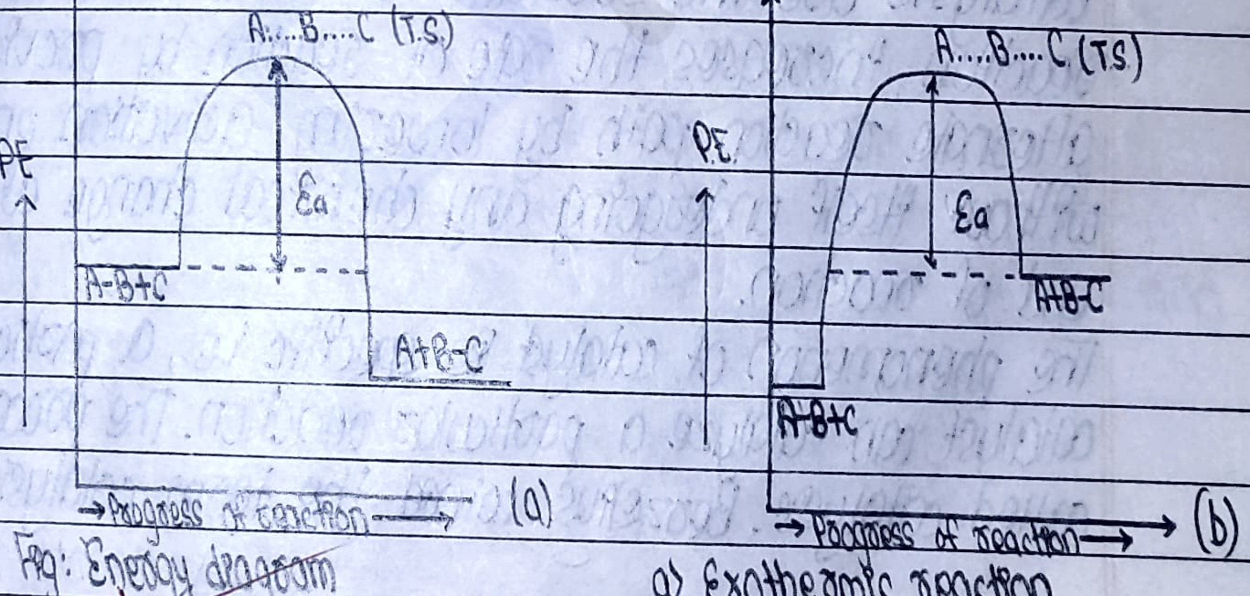


Fig: Energy diagram

a) Exothermic reaction

b) Endothermic reaction

Arrhenius theory:

Relation between rate of reaction (rate constant) and temperature is given by Arrhenius equation which is mathematically given as

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

where, k = Rate constant

A = Frequency factor i.e., Arrhenius consta

Ea = Activation Energy

R = Universal molar gas constant

T = Absolute temperature

At rate constant K_1 and K_2

At temperature 'T_1' and 'T_2', the Arrhenius equation becomes

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

Catalysis and its type

Catalysts are the substances which when added to a reaction, increases the rate of reaction by providing an alternate reaction path by lowering activation energy without itself undergoing any chemical change at the end of reaction.

The phenomenon of catalyst is specific i.e., a particular catalyst can catalyze a particular reaction. The process is called catalysis. Berzelius coined the term catalysis.

Types of catalysis:

i. Homogeneous catalysis: The type of catalysis in which the catalyst is in the same phase as the reactants is known as the homogenous catalysis.

For example:

- Oxidation of SO_2 into SO_3 in presence of NO as a catalyst.

$$2\,SO(g) + O_2(g) \xrightarrow{NO(g)} 2\,SO_3$$

- Hydrolysis of cane sugar in aqueous solution into glucose and fructose in presence of mineral acid as catalyst.

$$C_{12}H_{22}O_{11}(aq) + H_2O \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

ii. Heterogeneous catalysis: The type of catalysis in which the catalyst is in the different physical phase as the reactants (generally reactants are gaseous and catalyst are solid) is known as heterogeneous catalysis. This process is also known as contact catalysis as the reaction takes place on the surface of catalyst.

For example:

- Oxidation of SO_2 into SO_3 in presence of platinum or vanadium pentoxide as a catalyst.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

Similarly, the manufacture of ammonia from nitrogen and hydrogen in presence of iron in Haber's process.

$$3H_2(g) + N_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

- Manufacture of vegetable ghee from vegetable oil and hydrogen gas in the presence of Nickel as catalyst.

$$\text{Vegetable oil}(l) + H_2(g) \xrightarrow{Ni(s)} \text{Vegetable ghee}(s)$$

iii Enzyme catalysis

The proteinous substances which accelerates the biochemical reactions are called enzymes and the mechanism is called as enzyme catalysis.

Some enzymes are associated with some non-protein components called the prosthetic group. If the prosthetic group is a metal ion, it is called a cofactor. When the prosthetic group is a small organic molecule, it is called a coenzyme.

Enzymes work on the basis of lock and key.

The characteristics of enzyme catalysis are as:

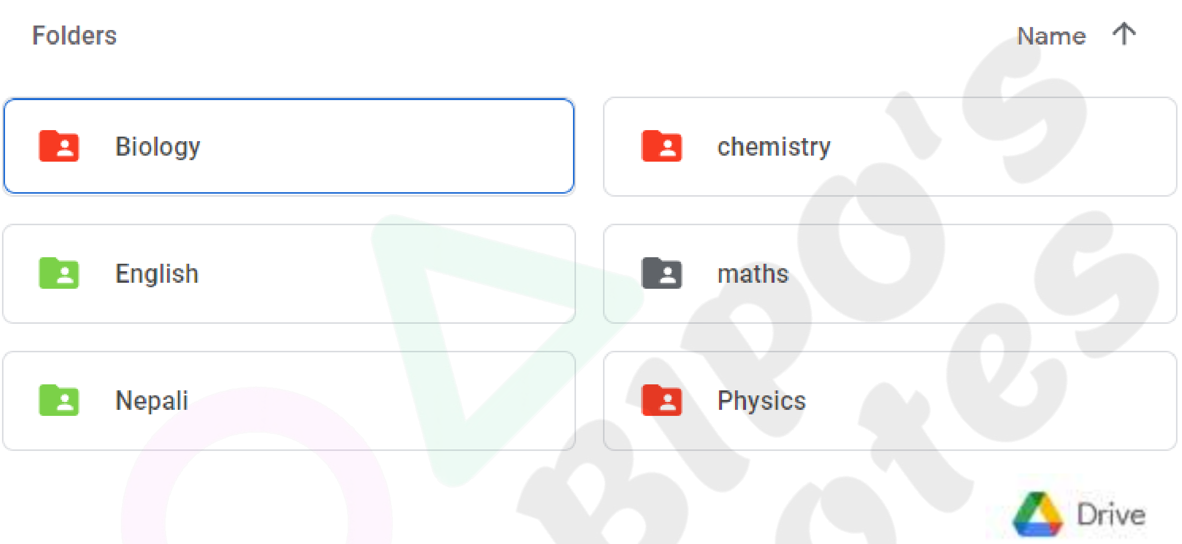
- They are highly specific as the work on the basis of lock and key mechanism.
- The efficiency of enzyme catalysis reaction is maximum at certain temperature and pH called as optimum temperature and optimum pH.
- Present of coenzymes increases efficiency of enzyme catalyze reaction.
- Enzyme catalyzed reaction is more effective than industrial catalyst.

2078/08/24

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



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