CHEMISTRY

11

CH#11

Reaction Kinetics

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Chapter 11
REACTION KINETICS

The branch of Chemistry which deals with rate of reaction, mechanism of reaction and factors that affect the rate of reaction is called Chemical Kinetics or reaction Kinetics.

Some reactions complete in single step and some complete in several steps. The slowest step which controls the rate of a reaction is called rate determining step.

During chemical reaction, the reactants pass through some intermediate steps and then form the final products. It is called mechanism of reaction.

Rate of reaction:— The change in Concentration of reactants or Products per unit time is called rate of reaction. It is equal to the change in concentration of reactants or Products divided by change in time

$$\text{rate of reaction} = \frac{\text{change in Concentration}}{\text{change in time}}$$
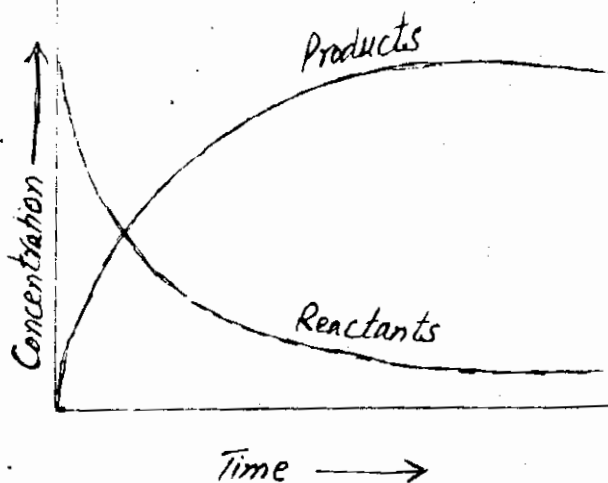
$$\text{rate of reaction} = \Delta c / \Delta t$$

The symbol Δ (delta) means "the change in"

When we plot a graph between concentration and time. then we get two curves. The concentration of reactants decreases with passage of time.

The concentration of products increases with passage of time. At initial stages, the slope of the graph is more steep (زیادہ ڈھلوان).

It indicates high rate of reaction. With passage of time the slope is becoming less steep. Finally the graph becomes horizontal straight line and reaction stops.

Unit of rate of reaction:- The rate of reaction has the unit of concentration divided by time.

$$\text{Unit of rate of reaction} = \frac{\text{moles } dm^{-3}}{\text{sec}}$$
$$= \text{moles } dm^{-3} sec^{-1}$$

For a gaseous reaction the unit is $atm \, sec^{-1}$

Average rate of reaction

The rate of reaction between two specific time intervals is called the average rate of reaction.

We may say that total change in concentration divided by total time is called Average rate of reaction.

$$\text{Average rate} = \frac{\text{Total change in Conc}}{\text{Total time}}$$

Instantaneous Rate of Reaction:-

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

When time interval approaches to zero, then average rate of reaction is called instantaneous rate of reaction. The instantaneous rate of reaction goes on changing every moment

It is very fast at the beginning and very slow at the end of reaction. The average rate and instantaneous rate are equal only for one instant (f) at any time interval.

Consider the reaction

$$A \longrightarrow B$$
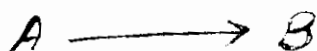
$$\text{Rate of reaction} = - \frac{d[A]}{dt}$$

or Rate of reaction $= + \frac{d[B]}{dt}$

where $d[A]$ and $d[B]$ are changes in concentrations of A and B. The negative sign indicates the decrease in concentration of reactant.

We may also write

$$\text{rate of reaction} = \frac{dx}{dt}$$

where dx is change in concentration and dt is change in time.

Specific rate Constant or Velocity Constant

The rate of a reaction when concentrations of reactants are unity is called specific rate

Constant or velocity constant of a reaction.
Its value changes with temperature.

Consider the reaction

$$a A + b B \longrightarrow c C + d D$$

$$\text{rate of reaction} = K [A]^a [B]^b$$

This equation is called rate equation or rate law.
In the rate law of reaction the constant K
is called specific rate constant.

Let $[A] = 1 \, mol \, dm^{-3}$ and $[B] = 1 \, mole \, dm^{-3}$

So rate of reaction $= K [1]^a [1]^b$

or rate of reaction $= K$ when conc are unity

Order of reaction

The number of reacting molecules whose
concentrations alter (change) as a result of
chemical change is called order of reaction.
OR The sum of all the exponents (توانیں) by
which the Concentration in rate equation are
raised is called order of reaction. The order
of reaction is not predicted from equation of reaction
but it is determined experimentally.

Consider the reaction

$$a A + b B \longrightarrow c C + d D$$

$$\text{rate of reaction} = K [A]^a [B]^b$$

The sum (a+b) is called order of reaction.
The chemical reactions may be of Zero, first
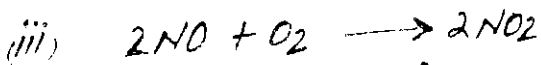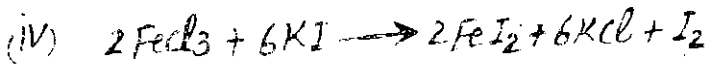
second and third order.

For example

(i) $\quad 2N_2O_5 \longrightarrow 2N_2O_4 + O_2$

$\quad$ Rate $= K[N_2O_5]$ $\quad$ Ist order reaction

(ii) $\quad NO + O_3 \longrightarrow NO_2 + O_2$
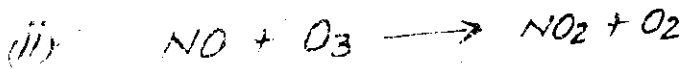
$\quad$ rate $= K[NO][O_3]$ $\quad$ IInd order reaction

(iii) $\quad 2NO + O_2 \longrightarrow 2NO_2$

$\quad$ rate $= K[NO]^2[O_2]$ $\quad$ IIIrd order reaction

(iv) $\quad 2FeCl_3 + 6KI \longrightarrow 2FeI_2 + 6KCl + I_2$

$\quad$ Rate $= K[FeCl_3][KI]^2$ $\quad$ IIIrd order reaction

In this reaction eight molecules of reactants take part but it is third order reaction. This reaction Completes through two steps

$2FeCl_3 + 4KI \xrightarrow{\text{slow}} 2FeI_2 + 4KCl + 2cl$

$2KI + 2cl \xrightarrow{\text{fast}} 2KCl + I_2$
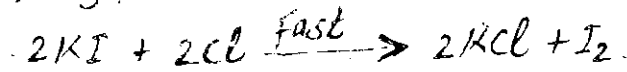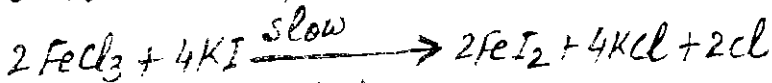
Pseudo First Order reactions

The reactions which involve more than one molecules but they obey (satisfy) first order rate equation are called Pseudo first order reactions. e.g hydrolxsis of tertiary butyl bromide

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + H_2O \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + HBr$$
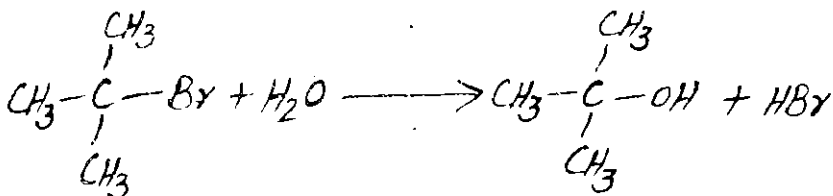
tertiary butyl $\qquad\qquad\qquad$ ter-butyl alcohol
$\quad$ bromide

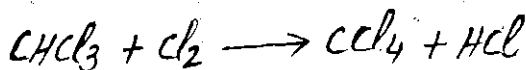In this reaction water is solvent. So it is present in very large excess. Thus its concentration remains constant. Therefore this reaction is an example of Pseudo first order reaction.

$$Rate = K\left[(CH_3)_3CBr\right]$$

Fractional Order Reactions

The order of a reaction is usually Positive integer or zero, but it can be in fraction or with negative value. e.g

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

$$rate = K\,[CHCl_3][Cl_2]^{1/2}$$

$$order\ of\ reaction = 1 + 1/2 = 1.5$$

Zero Order Reaction:- The reaction whose

rate does not depend upon concentration of any reactant is called zero order reaction e.g Photochemical reaction (photosynthesis)

Half Life Period

The time required to convert 50% of the reactants into Products is called half life Period of a reaction. For example, the half life Period for the decomposition of N_2O_5 is 24 minutes at $45°C$. The half life Period for

decompasition of HI is 253 seconds. The half life of $_{92}U^{235}$ is 7.1×10^8 or 710 million years.

Half life Period and Order of a reaction

The half life Period is inversly Proportional to the initial concentration raised to the Power one less than the order of that reaction.

If n is order of a reaction and "a" is initial concentration of reactants, then

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

$$[t_{1/2}]_1 \propto \frac{1}{a^0} \quad OR \quad [t_{1/2}]_1 = \frac{0.693}{K} \quad \text{(First order) reaction}$$
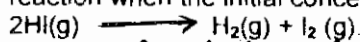
$$[t_{1/2}]_2 \propto \frac{1}{a} \quad OR \quad [t_{1/2}]_2 = \frac{1}{Ka} \quad \text{(second order) reaction}$$

$$[t_{1/2}]_3 \propto \frac{1}{a^2} \quad OR \quad [t_{1/2}]_3 = \frac{1.5}{Ka^2} \quad \left(\text{Third order reaction}\right)$$

The half life Period of First order reaction is independent (does not depend) of initial Concentration of reactant. For a second order reaction the half life Period is inversly Proportional to initial Concentration of reactant. For a third order reaction the half life Period is inversly Proportional to the square of initial Conc of reactant. For example decompasition of N_2O_5 is first order reaction. If 0.10 moles dm^{-3} is initial Concentration of N_2O_5, then after 24 minutes, 0.05 moles dm^{-3} of N_2O_5 will remain.

unreacted. Similarly after 48 minutes 0.025 mol dm^{-3} of N_2O_5 will remain unreacted and after 72 minutes (3 half times) 0.0125 mol dm^{-3} will remain unreacted. Now we take example of $_{92}U^{235}$. Its half life is 710 million years. If initial amount of $_{92}U^{235}$ is 1Kg, then after 710 million years 0.5Kg of it will remain undecayed. After the next 710 million years 0.25Kg $_{92}U^{235}$ will remain undecayed. Thus it is proved that for first order reaction the half life period is independent of initial concentration of reactant.

EXAMPLE:-1 Calculate the half-life period of the following reaction when the initial concentration is 0.05M.
2HI(g) $\longrightarrow$ H₂(g) + I₂ (g).
k=0.079dm³ mol⁻¹ S⁻¹ at 508°C and Rate=k[HI]²

Solution:-

$$2HI \rightleftharpoons H_2 + I_2$$
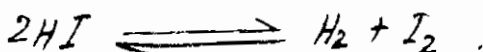
It is second order reaction

$$Rate = K[HI]^2, \quad \text{Initial Conc } a = 0.05M$$

$$n = 2, \quad K = 0.079 \ dm^3 \ mol^{-1} s^{-1}$$

$$[t_{1/2}]_2 = \frac{1}{Ka^{n-1}} = \frac{1}{K[a]^1}$$

$$[t_{1/2}]_2 = \frac{1}{0.079 \times 0.05} = \frac{1}{0.00395}$$

$$[t_{1/2}]_2 = 253 \ seconds$$

Rate determining Step:-

When a reaction takes place in several steps, then one of the steps is the slowest. This slowest step is called the rate determining step or rate limiting step. This step controls the overall rate of reaction. The total number of species (molecules) which take part in rate determining step is called order of reaction.

For example we take following reaction

$$NO_2 + CO \longrightarrow NO + CO_2$$

According to law of mass action, rate $= K[NO_2][CO]$

But experimentally determined rate equation is

$$Rate = K[NO_2]^2$$

This equation shows that rate of reaction does not depend upon Concentration of Carbon monoxide. It means that reaction involves more than one steps. Two molecules of NO_2 take part in rate determining step. Thus mechanism of reaction is as follows

$$NO_2 + NO_2 \xrightarrow{\text{slow}} NO_3 + NO$$

$$NO_3 + CO \xrightarrow{\text{fast}} NO_2 + CO_2$$
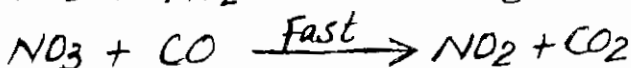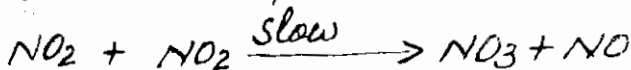
The species such as NO_3 which does not appear in balanced equation is called reaction intermediate. The reaction intermediate is a short lived and unstable species.

It has normal bonds and can be isolated لَطَّ

from reaction mixture under special conditions.

Determination of Rate of Reaction

When a reaction starts, then concentration of
reactants decreases and that of Products increases.

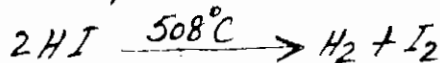$$\text{Rate of reaction} = \Delta C / \Delta t$$

For the determination of rate of reaction, we
plot a graph between time and concentration
In this way a curve is obtained. Then a
tangent is drawn on the curve. Finally we
measure the slope of that tangent. This slope
gives the rate of reaction. For example

$$2HI \xrightarrow{\quad 508°C \quad} H_2 + I_2$$

Let initial concentration of HI is $0.100 \, mol \, dm^{-3}$
The change in conc of HI with time is given in
following table

Time (s)	0	50	100	150	200	250	300	350
Conc of HI (moles dm^{-3})	0.100	0.072	0.056	0.046	0.039	0.034	0.030	0.026

We plot a graph
between time
and conc. It
is shown in
figure. A
curve is obtained.
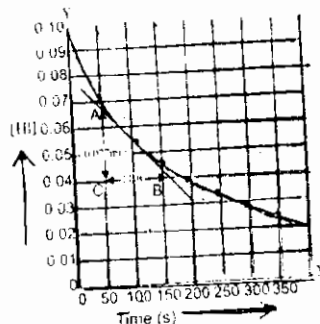
A tangent at 100 seconds is drawn on the curve. The triangle ABC is completed. It is right angle triangle. From this triangle we have $\Delta C = 0.037$ mole dm^{-3} and $\Delta t = 148$ sec

Slope or rate $= \Delta C/\Delta t$

$$= \frac{0.037}{148} \text{ mol } dm^{-3} sec^{-1}$$

$$= 2.5 \times 10^{-4} \text{ mol } dm^{-3} sec^{-1}$$

Physical Methods:-

We can measure rate of reaction by following physical methods.

(i) **Spectrometry** :- This method is applied when a reactant or product absorbs ultraviolet, visible or infrared radiations. The rate of reaction is directly proportional to the absorbed radiations. The apparatus used is called spectrophotometer.

(ii) **Electrical Conductivity Method:-**

This method is applied when reactants or Products involve ionic species. The Conductivity of a solution is directly Proportional to the rate of change of concentration of ions. The apparatus used is called Conductometer.

(iii) **Dilatometric Method:-** This method is applied for those reactions which involve small volume changes. The rate of reaction is directly proportional

to the volume change. The apparatus used is called dilatometer.

(iv) Refractometric Method:- This method is applied for those reactions when reactants or Products change their refractive indices (انعکاس پذیری). The apparatus used is called refractometer.

(v) Optical Rotation Method:- This method is applied for those reactions when anyone reactant or Product is optically active. An optical active substance rotates the Plane Polarized light. The rate of reaction is directly proportional to the optical rotation. The apparatus used is called Polarimeter.

Imp **Chemical Method**

The method in which reaction mixture is analysed chemically is called chemical method.

For example hydrolysis of an ester (Ethyl acetate) in presence of an acid.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$
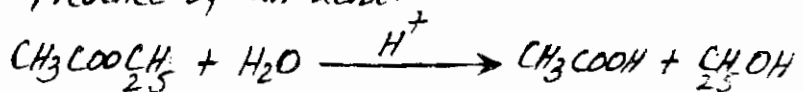
When reaction starts, then concentration of ethyl acetate decreases and that of acetic acid goes on increasing. From time to time withdraw a Sample from reaction mixture by a pipette. It is mixed with ice cold water. The dilution and chilling (ٹھنڈا کرنا) stops the reaction. The concentration of acetic acid (CH_3COOH) is

determined by titration against standard NaOH solution. Then we plot a graph between concentration of acetic acid and time. In this way a curve is obtained. It is shown in fig.
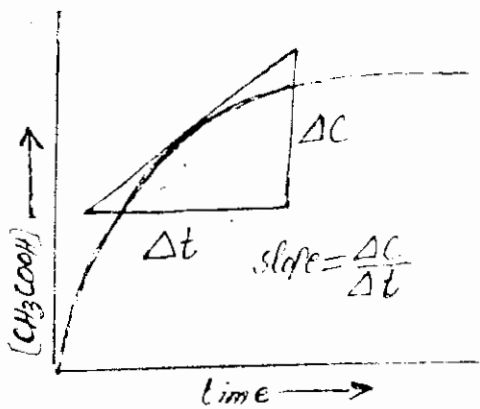
The slope of the curve at any point gives the rate of reaction. At initial stages rate is high. At final stages when curve becomes horizontal, the rate of reaction becomes zero.

Collision theory —

The main points of collision theory are given below.

(i) A chemical reaction is the result of collisions between reactant molecules.

(ii) Not all, only effective collisions can give rise to the products. Two conditions are necessary for an effective collision. The molecules must have sufficient energy and they must have proper orientation.

(iii) The number of collisions per second is called collision frequency. Greater the collision frequency, higher will be the rate of reaction.

(iv) By $10°C$ rise in temperature, the collision frequency becomes double. Hence rate of reaction becomes double. Hence collision frequency and proper orientation of molecules are necessary conditions for the faster rate of reaction.

If all the collisions among reaching molecules are effective, the reaction will be completed in a short time.

Activated Complex

The reactant molecules collide and form an unstable intermediate complex before the formation of final products. It is called activated complex or transition state. It is an unstable combination of atoms with high energy.

The activated complex is a short lived species and decomposes into Products immediately.

For example reaction between molecules A_2 and B_2 for the formation of new molecules AB.

| Reactants | (Activated Complex) | Products |
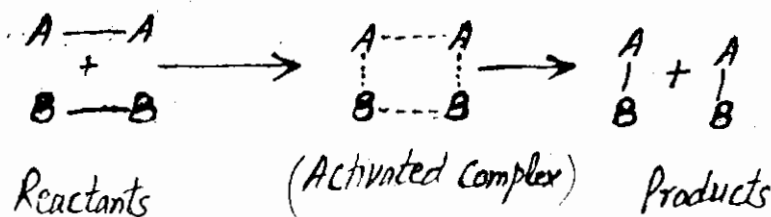
Energy of Activation:-

The minimum amount of energy, in addition to average Kinetic energy, which is must for the molecules to show effective collision is called energy of activation.

OR The minimum amount of energy, in addition to average K.E, which is must for the molecules to form an activated complex is called energy of activation.

It is denoted by E_a. Its unit is $KJ\ mol^{-1}$
For example energy of activation for the
decomposition of N_2O_5 is $103.4\ KJ\ mol^{-1}$
We may say that energy of activation is an
energy hill (energy barrier) between reactants
and products. The reactants have to pass over
(climb up) this hill for the formation of Products.
If energy of molecules is less than E_a, they
will not reach the top of hill and fall back
without forming products

For an exothermic
reaction, the Products
are at lower energy
level than the
reactants. So heat
is evolved.
It is shown in fig.
For an endothermic
reaction, the
Products are at
higher energy level
than the reactants.
So heat is
absorbed. It is
shown in Figure.
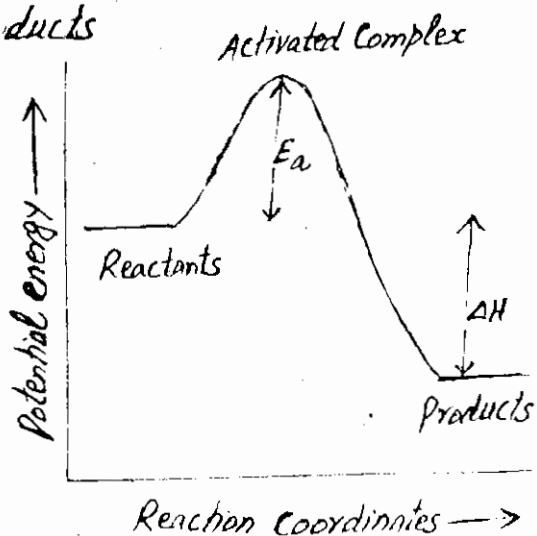
Activated Complex

E_a

Reactants

ΔH

Products

Reaction Coordinates →

Activated Complex

E_a

ΔH

Products

Reactants

Reaction Coordinates →
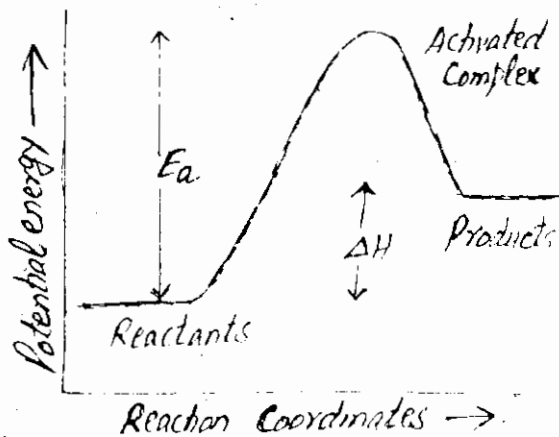
Determination of Order of Reaction

We determine order of a reaction by following methods (i) Half life method

(ii) method of large excess

(iii) Method of hit and trial

(iv) Graphical method

(v) Differential method.

Here we discuss only first two methods.

Half life method:-

We know that half life of a reaction is inversly proportional to the initial concentration of reactant raised to the power one less than the order of reaction

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

We perform a reaction twice by taking two different initial concentrations "a_1" and "a_2". Their half life periods are t_1 and t_2

$$t_1 \propto 1/a_1^{n-1} \quad \text{and} \quad t_2 \propto 1/a_2^{n-1}$$

By dividing the two relations

$$\frac{t_1}{t_2} = \frac{1/a_1^{n-1}}{1/a_2^{n-1}}$$

$$\text{or} \quad t_1/t_2 = \left[\frac{a_2}{a_1}\right]^{n-1}$$

By taking log on both sides

$$\log\left(\frac{t_1}{t_2}\right) = n-1 \log\left(\frac{a_2}{a_1}\right)$$

or $n-1 = \dfrac{\log\left[t_1/t_2\right]}{\log\left[a_2/a_1\right]}$

or $n = 1 + \dfrac{\log\left[t_1/t_2\right]}{\log\left[a_2/a_1\right]}$

By last equation we determine the order of a reaction.

EXAMPLE:-2 In the thermal decomposition of N_2O at $760°C$ the time required to decompose half of the reactant was 255 seconds at the initial pressure of 290mm Hg and 212 seconds at the initial pressure of 360mm Hg. Find the order of this reaction

Solution :- $a_1 = 290\, mm\, Hg$, $t_1 = 255\, sec$

$a_2 = 360\, mm\, Hg$, $t_2 = 212\, sec$

order of reaction, $n = ?$

$$n = 1 + \frac{\log\left[t_1/t_2\right]}{\log\left[a_2/a_1\right]}$$

$$= 1 + \frac{\log\left(255/212\right)}{\log\left(360/290\right)}$$

$$= 1 + \frac{\log\left(1.2028\right)}{\log\left(1.2413\right)}$$

$$= 1 + \frac{0.0802}{0.0940}$$

$$= 1 + 0.85 = 1.85 \approx 2$$

Hence the order of reaction is 2

Method of large excess:-

In this method one of reactant is taken in small amount and other reactants are taken in large excess. The concentration of reactants in large excess remains constant. The conc of reactants in small amount changes with time. Thus we note the order of reaction with respect to this reactant. Similarly we note the order of reaction w.r.t every reactant ~~turn by turn~~ one by one. Finally we calculate the overall order of reaction.

Factors Affecting rate of Reaction

The rate of reaction depends upon following factors.

(i) Nature of Reactants:-

The rate of reaction depends upon nature of reactants. The chemical reactivity of elements depends upon their outermost electronic Configuration. For example elements of I-A group have one electron in outermost S-orbital. So they react with water more swiftly (rapidly). On other hand elements of II-group have two electrons in their outermost s-orbital. So they react with water slowly. The ionic reactions, neutralization and double decomposition reactions are very fast

Because they do not involve transfer of electrons and bond rearrangement. The Covalent and redox reactions are slower because they involve transfer of electrons and bond rearrangement

e.g $HCl + NaOH \longrightarrow NaCl + H_2O$ (fast)

$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$ (fast)

$2CO + O_2 \longrightarrow 2CO_2$ (Slow)
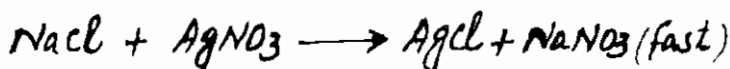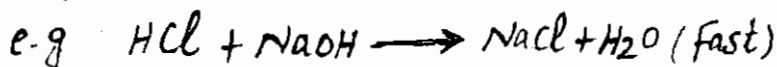
(ii) Surface area.

When Surface area of reactants increases, then rate of reaction increases. The reason is that with increased area of reactants, many atoms and molecules come in contact with each other. Thus rate of reaction increases with Surface area. For example, Al foil (ورق) reacts with NaOH slowly but Al Powder reacts fastly

$2Al + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$
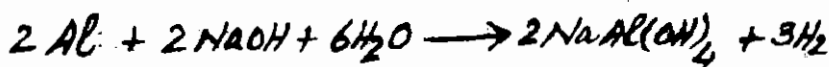
Similarly pieces of $CaCO_3$ (marble سنگ مرمر) react with dilute H_2SO_4 very slowly but Powdered $CaCO_3$ reacts fastly.

(iii) Light:-
Light consists of Photons. When high energy photons collide with reactant molecules, then extra energy is ~~available~~ Provided. So rate of reaction increases. e.g $H_2 + Cl_2 \xrightarrow{Sun\ light} 2HCl$

$CH_4 + Cl_2 \xrightarrow{Sun\ light} CH_3Cl + HCl$

Similarly Light is Vital عامل in Photosynthesis

(iv) Concentration of reactants :-

When we increase Concentration of reactants, then rate of reaction increases. Similarly when we decrease Concentration of reactants, then rate of reaction decreases. For example, in air (21% oxygen) the combustion (جلنا) occurs slowly but in pure oxygen (100%) the Combustion occurs rapidly. The reason is that by increasing Concentration, the molecules are more Crowded. Thus Collision frequency of molecules increases. Hence rate of reaction increases. Now we give another example

$$2 NO + 2 H_2 \xrightarrow{800°C} 2 H_2O + N_2$$
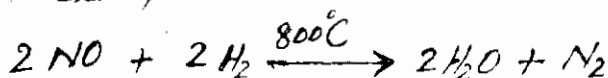
In this reaction six experiments were performed to explain the effect of concentration.

Exp. No	[NO] mol dm⁻³	[H₂] mol dm⁻³	Rate of reaction
1	0.006	0.001	0.025 atm min⁻¹
2	0.006	0.002	0.050 "
3	0.006	0.003	0.075 "
4	0.001	0.009	0.0063 "
5	0.002	0.009	0.025 "
6	0.003	0.009	0.056 "

In first three experiments. Concentration of NO is kept constant and Concentration of H_2

is increased. By doubling the the conc of H_2, the rate of reaction becomes double.

By tripling the conc of H_2, the rate of reaction becomes triple. So rate of reaction is directly Proportional to the fixst Power of conc of H_2.

$$Rate \propto [H_2]^1$$

In next three experiments, the concentration of H_2 is kept constant and conc of NO is increased. By doubling the conc NO, the rate of reaction becomes four times. By tripling the conc of NO, the rate becomes nine times. So rate of reaction is directly Proportional to the Square of concentration of NO

$$Rate \propto [NO]^2$$

By combining two equations, we get

$$Rate \propto [H_2][NO]^2$$
$$Rate = K[H_2][NO]^2$$

Hence reaction is of third order. The final equation is called rate law of reaction

The rate law cannot be Predicted from balanced equation but is determined experimentally.

The Possible mechanism of reaction is given below.

$$2NO + H_2 \xrightarrow{\text{Slow}} N_2 + H_2O_2$$
$$H_2O_2 + H_2 \xrightarrow{\text{fast}} 2H_2O$$
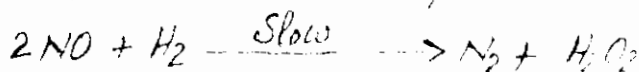
(V) Effect of Temperature on rate of Reaction

The rate of reaction increases by increasing the temperature. When we increase temperature by 10K, the rate of reaction roughly becomes double. The reason is that by increasing temperature the K.E and Collision frequency of molecules increases. So number of effective collisions increases and rate of reaction becomes high

At a given temperature all the molecules do not possess the same energy. Most of the molecules possess (بعض) average energy. A fraction of molecules have energy more than E_a.

The minimum amount of energy in addition to average energy, which is must for the molecules to show an effective collision is called energy of activation. A graph between fraction of molecules and Kinetic energy is shown below.

The shaded area in the graph indicates the fraction of molecules with energy more than E_a.
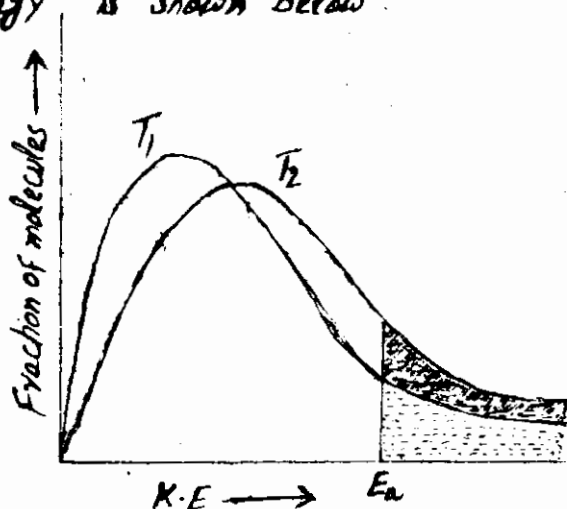
When $T_2 > T_1$, then shaded area increases.
If temperature is raised by 10K, then fraction
of molecules with energy more than E_a becomes
double. So number of effective collisions becomes
double. Hence rate of reaction is doubled.

Arrhenius Equation

An equation which explains the effect of
temperature on the rate constant of a reaction is called
Arrhenius equation. It gives variation of rate constant
with temperature. It is given below.

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

where K is rate constant, R is general gas
constant, A is Arrhenius Constant which
depends upon collision frequency of molecules
T is absolute temperature, E_a is energy of
activation and e is base of natural logarithm.

Arrhenius equation tells that by increasing the
temperature, the rate constant of reaction
increases. By Arrhenius equation we can
determine the energy of activation.

$$K = A e^{-E_a/RT}$$
$$\ln K = \ln A e^{-E_a/RT}$$
$$\ln K = \ln A + \ln e^{-E_a/RT}$$
$$\ln K = \ln A - \frac{E_a}{RT} \ln e$$
$$\ln K = \ln A - E_a/RT \quad (\text{Since } \ln e = 1)$$

we change natural log into common log as

$$2.303 \log K = -\frac{Ea}{RT} + 2.303 \log A$$

Divide whole equation by 2.303

$$\log K = -\frac{Ea}{2.303RT} + \log A$$

It is an equation of straight line. when we plot a graph between $\log K$ and $\frac{1}{T}$, we get straight line

Because temperature is independent variable and rate constant (K) is dependent variable.

So $\frac{1}{T}$ is taken along x—axis and $\log K$ is taken along y—axis

The straight line makes

$$Tan\theta = -slope$$

an angle θ with x—axis. The slope is negative It is equal to $tan\theta$. Its value is $-Ea/2.303R$
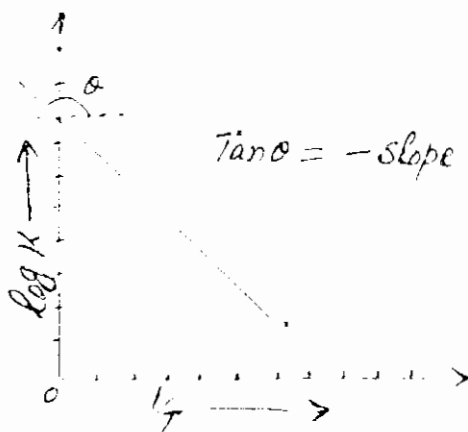
$$slope = -\frac{Ea}{2.303R}$$

$$or \quad Ea = -slope \times 2.303R$$

EXAMPLE:- A plot of Arrhenius equation for the thermal decompositions of N_2O_5 is shown in the following figure. The slope is found to be -5400K Calculate the energy of activation of this reaction
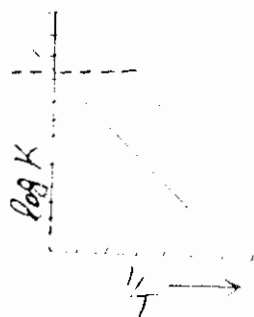
Solution:- $slope = -5400K$

$$R = 8.314\,Jmol^{-1}$$

$$-slope = -Ea/2.303R \quad or \quad -5400 = -\frac{Ea}{2.303 \times 8.31}$$

$$Ea = 5400 \times 2.303 \times 8.31 = 103416\,Jmol^{-1} = 103.4\,KJmol^{-}$$

Catalysis

A Substance which alters the rate of chemical reaction but remains chemically unchanged at the end of reaction is called Catalyst. The Process which takes place in presence of Catalyst is Called Catalysis.

e.g

$$2 KClO_3 \xrightarrow{MnO_2} 2 KCl + 3O_2$$

$$2 H_2 + O_2 \xrightarrow{Platinum (Pt)} 2 H_2O$$

$$4 HCl + O_2 \xrightarrow{CuCl_2} 2 H_2O + Cl_2$$
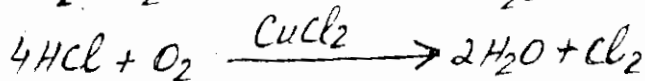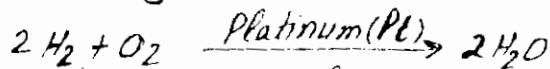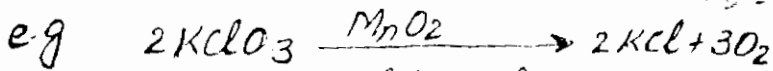
A Catalyst Provides a new reaction Path or mechanism for a reaction. It decreases the energy of activation of a reaction. So a large number of molecules Can Pass over the new energy barrier. Therefore rate of reaction increases.

A graph between energy and reaction Path is shown in figure.

The lower graph is for a Catalyzed reaction and upper graph is for an uncatalyzed (غیر عملی) reaction
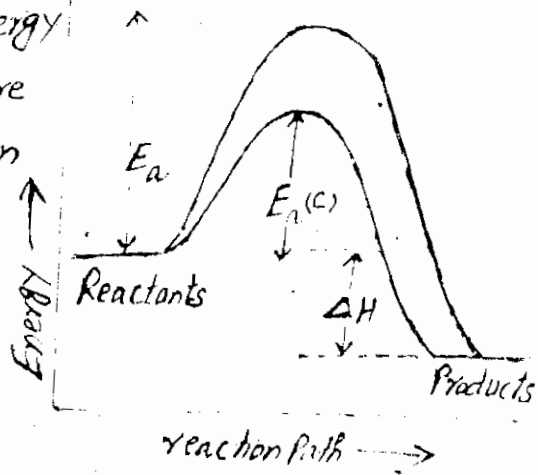
Types of Catalysis

There are two types of Catalysis.

(a) Homogeneous Catalysis.

(b) Heterogeneous Catalysis

(a) Homogeneous Catalysis

The Process (reaction) in which Catalyst and reactants are in Same Phase is called homogeneous catalysis. e.g (i) In the formation of SO_3 by lead Chamber process We use NO (nitric oxide) as Catalyst. Here both the reactants and Catalyst are gases

$$2 SO_2 + O_2 \underset{}{\overset{NO}{\rightleftharpoons}} 2 SO_3$$

(ii) In hydrolysis of ester, the reactants and Catalyst are in solution form.

$$CH_3COOC_2H_5 + H_2O \underset{H_2SO_4}{\overset{H_3O^+}{\rightleftharpoons}} CH_3COOH + C_2H_5OH$$
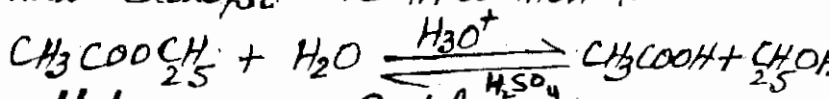
(b) Heterogeneous Catalysis

The Process in which reactants and Catalyst are in different Phases is Called heterogeneous Catalysis. Here mostly the catalyst is solid and reactants are in gaseous or liquid state. e.g

(i) $2 SO_2 + O_2 \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2 SO_3$ (Contact Process)

(ii) $CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$
     ethene   ethane

(iii) $4 NH_3 + 5 O_2 \underset{}{\overset{Pt}{\rightleftharpoons}} 4 NO + 6 H_2O$
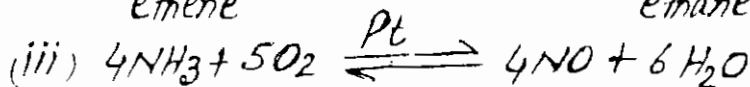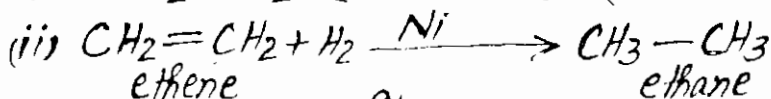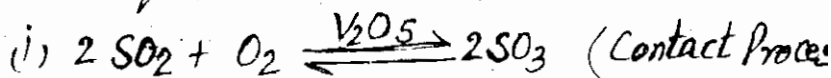
Characteristics of a Catalyst

(i) A Catalyst remains unchanged in mass and chemical composition at the end of reaction. However its physical state may change. e.g $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$

Here we use Catalyst MnO_2 in the form of granules (دانے دار) but at the end it is obtained in Powder form.

(ii) A Catalyst is required in a small quantity. e.g During decomposition of H_2O_2, only 1 g of Platinum is sufficient for thousands dm^3 of H_2O_2.

(iii) A Catalyst is more effective in a finely divided form. e.g In Hydrogenation of vegetable oils. finely divided Ni is used as Catalyst

(iv) A Catalyst does not affect equilibrium Constant or equilibrium Concentrations of a reversible reaction. It only reduces the time to attain equilibrium

(V) A Catalyst can not start a reaction which is not feasible (ممکن) thermodynamically. It means that Catalyst has no effect on total enthalpy (ΔH) of a reaction.

(Vi) A Catalyst has specific action (function)

It means that a Catalyst Catalyses one reaction but not another. A Same reaction gives different Products by use of different Catalysts. e.g

$$HCOOH \xrightarrow{Al_2O_3} H_2O + CO$$

$$HCOOH \xrightarrow{Cu} H_2 + CO_2$$
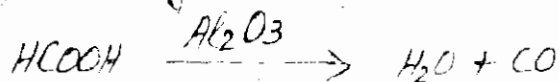
(vii) The role of Catalyst is affected by temperature. e.g Colloidal Platinum Coagulates with rise in temperature. So its Catalytic Power decreases

(viii) If a very small amount of foreign Substance (impurity) is present in a Catalyst then it makes the Catalyst ineffective (ناکارہ) It is called Poisoning of Catalyst. The foreign Substance (impurity) in a Catalyst is called Poison. The Poisoning of Catalyst may be temporary or Permanent. In Permanent poisoning, Catalyst reacts chemically with Poison. For example (i) In decomposition of H_2O_2, the Platinum is used as Catalyst. By Small amount of HCl, Platinum becomes ineffective

(ii) In formation of SO_3 by Contact Process the Platinum is used as Catalyst. The Small amount of Arsenic as an impurity makes the Platinum ineffective.

Activation of Catalyst (Promotor)

A substance which promotes (increases) the activity of a catalyst is called promotor or activator. It is also called "Catalyst for a catalyst". For example

(i) Nickel is used as catalyst in the hydrogenation of vegetable oil. Its catalytic activity is increased by copper and Tellurium.

(ii) In the preparation of NH_3 by Haber Process Fe i used as catalyst. Its catalytic activity is increased by MgO, Al_2O_3, SiO_2

Negative Catalyst :- A substance which retards (decreases) the rate of reaction is called negative catalyst or inhibitor.

e.g Tetraethyl lead, $(C_2H_5)_4Pb$ is added to petrol because it saves the petrol from pre-ignition

Auto Catalysis:- In some reactions. a product formed acts as catalyst. It is called autocatalyst and process is called auto-catalysis. For example,

(i) The reaction between copper and nitric acid is slow in the beginning but speeds up gradually and becomes very fast. It is due to the formation of Nitrous oxide (N_2O) during the reaction

(ii) The reaction of oxalic acid with acidified KMnO4 is slow in the beginning but after sometime the

MnSO₄ Produced in the reaction makes it faster.

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$
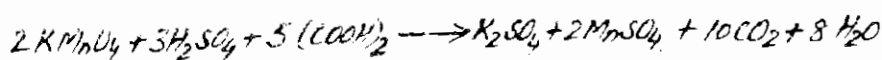
Enzyme Catalysis :- The complex Protein molecules which catalyze the organic reactions in the living cells are called enzymes. e.g Urease, invertase and Zymase. The reaction which takes Place in Presence of enzyme is called enzyme catalysis. Many enzymes have been obtained in Pure crystalline state. The first enzyme was Prepared in laboratory in 1969. Examples are given

(i) Hydrolysis of urea by an enzyme Urease (Present in soyabean)

$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O \xrightarrow{Urease} 2NH_3 + CO_2$$
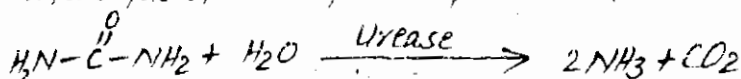
(ii) Hydrolysis of sugar in Presence of invertase

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[Yeast]{Invertase} \underset{(glucase)}{C_6H_{12}O_6} + \underset{(fructose)}{C_6H_{12}O_6}$$
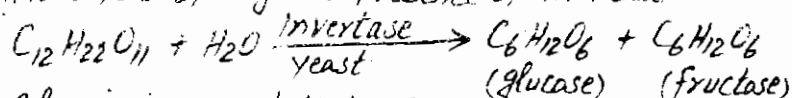
(iii) Glucase is converted into ethanol by enzyme Zymase

$$\underset{(glucase)}{C_6H_{12}O_6} \xrightarrow[Yeast]{Zymase} 2C_2H_5OH + 2CO_2$$
$$\underset{(ethanol)}{}$$
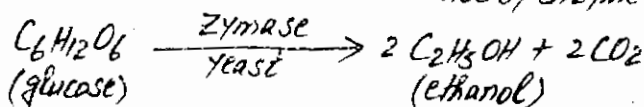
Mode of enzyme action

Enzymes have active sites (centres) on their surfaces. The molecules of a substrate fit into their cavities just as a key fits into a lock. Thus a substrate - enzyme complex is formed. Finally the Products get out of the cavity.

It is shown in following figure

This mechanism for enzyme catalysis was Proposed by Michaulis and Menter in 1913

$$E + S \rightleftharpoons ES \rightleftharpoons P + E$$
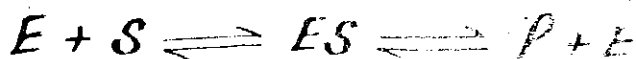
Where E = Enzyme , S = Substrate (reactant)

ES = Activated Complex , P = Products

Characteristics of Enzyme Catalysis

(i)   Enzyme Catalysis is heterogeneous type Catalysis

(ii) Enzymes are the most efficient Catalysts and they lower the energy of activation of a reaction

(iii) Enzymes have specific action. e.g Urease Catalyses the hydrolysis of urea only. It can never Catalyse hydrolysis of any other amide

(iv) Enzyme Catalytic reactions have maximum rates at an optimum temperature

(v) Enzymes Catalytic reactions give maximum rates at an optimum pH

(vi) Enzymes activity Can be retarded by Some Poison. e.g An electrolyte, acid or base

(vii) Co-enzyme or activator increases the Catalytic activity of enzyme

EXERCISE

Q.1 Multiple choice questions.

(i) In zero order reaction, the rate is independent of

(a) temperature of reaction, (b) concentration reactants.

(c) concentration of products (d) non of these

(ii) If the rate equation of a reaction 2A + B → products rate = $k[A]^2[B]$ and A is present in large excess, then order of reaction is

(a) 1 (b) 2 (c) 3 (d) none of these

(iii) The rate of reaction.

(a) increases as the reaction proceeds.

(b) decreases as the reaction proceeds.

(c) remains the same as the reaction proceeds.

(d) may decrease or increase as the reaction proceeds.

(iv) With increases of 10°C temperature the rate of reaction doubles. Th increase in rate of reaction is due to:

(a) decrease in activation energy of reaction.

(b) decrease in the number of collisions between reactant molecules. (c) increase in activation energy of reactants.

(d) increase in number of effective collisions.

(v) The unit of the rate constant is the same as that of the rate of react in

(a) first order reaction (b) second order reaction

(c) zero order reaction, (d) third order reaction.

Answer: (i) b (ii) a (iii) b (iv) d (v) c

Q.2 Fill in the blanks with suitable words.

(i) The rate of an endothermic reaction _____ with the increase temperature.

(ii) All radioactive disintegration nuclear reactions are of _____ ord

(iii) For a fast reaction the rate constant is relatively _____ and half-lif _____.

(iv) The second order reaction becomes____ if one of the reactants is large excess.

(v) Arrhenius equation can be used to find out _____ of a reaction.

Answer: (i) increases (ii) zero (iii) high, short (iv) first order (v) rate constant. energy of activation.

Q.3 Indicate true or false as the case may be.

(i) The half life of a first order reaction increases with temperature.

(ii) The reactions having zero activation energies are instantaneous.

(iii) A catalyst makes a reaction more exothermic.

(iv) There is difference between rate law and the law of mass action.

(v) The order of reaction is strictly determined by the stoichiometry of balanced equation.

Answer: (i) false (ii) true (iii) false (iv) true (v) false

Q4. What is chemical kinetics? How do you compare chemical kinetics with chemical equilibrium and thermodynamics.

Answer:- **Chemical Kinetics:-** The branch of chemistry which deals with rate of reaction, mechanism of reaction and factors that affect the rate of reaction is called chemical kinetics. It is related to both reversible and irreversible reactions.

Chemical Equilibrium:- The state of a reversible reaction at which rate of forward reaction is equal to rate of reverse reaction is called chemical equilibrium. It is only related to reversible reactions.

Chemical thermodynamics:- The branch of chemistry which deals with heat changes of chemical reactions is called chemical thermodynamics. It is related with both reversible and irreversible reactions.

Q5. The rate of a chemical reaction with respect to products is written with positive sign, but with respect to reactants is written with a negative sign. Explain it with reference to the following hypothetical reaction.

$$aA + bB \rightarrow cC + dD$$
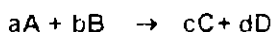
Ans:- The rate of reaction can be written with respect to any reactant or product. The rate of reaction with respect to reactants has negative sign because concentration of reactants decreases with passage of time. The rate of reaction with respect to products has positive sign because concentration of products increases with passage of time.

$$\text{W.r.t reactants, } rate = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

$$\text{W.r.t Products, } rate = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Q6. What are instantaneous and average rates? Is it true that t instantaneous rate of a reaction at the beginning of the reaction greater than average rate, and becomes far less than the average r near the completion of reaction?

Answer. See Page No. 211, 212

Q7. Differentiate between
(i) Rate and rate constant of a reaction
(ii) Homogeneous and heterogeneous catalyses
(iii) Fast step and the rate determining step
(iv) Enthalpy change of reaction and energy of activation of reaction

Answer. See Page No. 210, 212, 218 235

Q8. Justify the following statements
(i) Rate of chemical reaction is an ever changing parameter under t given conditions.
(ii) The reaction rate decreases every moment but rate constant 'k' of t reaction is a constant quantity, under the given conditions.
(iii) 50% of a hypothetical first order reaction completes in one hour. T remaining 50% needs more than one hour to complete.
(iv) The radioactive decay is always a first order reaction.
(v) The unit of rate constant of a second order reaction is dm^3 mol^{-1}s but the unit of rate of reaction is mol dm^{-3} s^{-1}
(vi) The sum of the coefficients of a balanced chemical equation is r necessarily important to give the order of a reaction.
(vii) The order of a reaction is obtained from the rate expression o reaction and the rate expression is obtained from the experiment.

Answer:- (i) According to law of mass action, the rate of a reaction is directly proportional to the Pro of active masses of all reactants. Because ac mass of reactants goes on changing during th reaction. It is the reason that rate of reaction is ever changing Parameter. e.g reaction is v fast in the beginning, slow in the middle and v

Slow at the end of reaction.

(ii) According to law of mass action, the rate of a reaction is directly proportional to the product of active masses of reactants. e.g

$$A + B \longrightarrow Products$$
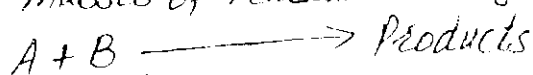
$$\text{rate of reaction} = K[A][B]$$

Because active mass of reactants goes on decreasing every moment during the reaction. It is the reason that rate of reaction decreases every moment. On other hand, rate constant is a constant parameter which remains same (constant) throughout the reaction. Rate constant is equal to rate of reaction when active masses of reactants are unity.

(iii) The time required to convert 50% of reactants into products is called half life of reaction. Let us suppose a first order reaction whose half life is one hour. In first hour 50% reaction will complete. In second hour 50% of remaining reaction (25%) will complete. In third hour 50% of the remaining reaction (12.5%) will complete. Thus after three hours 87.5% reaction will be completed. Hence we may say that first 50% reaction completes in one hour and remaining 50% needs more than one hour for completion.

(iv) In radioactive decay only one specie (reactant) is present. It is called parent nucleus. It decays into daughter nuclei. The rate of decay only depends upon concentration of parent nucleus.

Hence radioactive decay is always of First order.

(V) Rate of reaction $= \dfrac{\text{change in concentration}}{\text{time}}$

or rate of reaction $= \dfrac{mol \; dm^{-3}}{sec} = mol \; dm^{-3} s^{-1}$

So unit of rate of reaction is $mol \; dm^{-3} s^{-1}$

Consider a second order reaction

$$A + B \longrightarrow Products$$
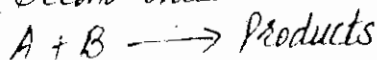
rate of reaction $= K [A][B]$

$mol \; dm^{-3} s^{-1} = K (concentration)^2$

$mol \; dm^{-3} s^{-1} = K (mol \; dm^{-3})^2$

or $K = \dfrac{s^{-1}}{mol \; dm^{-3}}$ or $K = dm^{3} mol^{-1} s^{-1}$

So unit of rate constant for second order
reaction is $dm^{3} mol^{-1} s^{-1}$

(Vi) The number of molecules which take part in
rate determining step (slowest step) of a reaction
is called order of reaction. It is determined
experimentally. Consider the reaction

$$2 H_2 + 2 NO \longrightarrow 2 H_2O + N_2$$

rate of reaction. $\dfrac{dx}{dt} = K[H_2][NO]^2$ (By experiment

The order of reaction is 3 but sum of coefficien
of balanced equation is 4.

(Vii) The number of molecules which take part in
the slowest step of a reaction is called order
of reaction. The slowest step is determined
experimentally. So order of reaction is also

determined experimentally. For example

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$
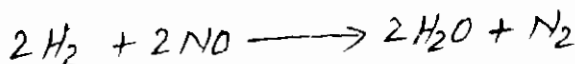
$$\frac{dx}{dt} = K[H_2][NO]^2 \quad (Experimentally\ determined)$$

Q.9 Explain that half life method for measurement of the order of a reaction can help us to measure the order of even those reaction which have a fractional order.

Ans:- By half life method, the order of reaction is determined by following formula.

$$n = 1 + \frac{log(t_1/t_2)}{log(a_2/a_1)}$$

Here n is order of reaction, t_1 and t_2 are half life periods when initial concentrations are a_1 and a_2. By this formula order of reaction even in fractions can be also determined

Q.10 A curve is obtained when a graph is plotted between time on x-axis and concentration on y-axis. The measurement of the slopes of various points give us the instantaneous rates of reaction. Explain with suitable examples

Ans:- see page No. 211

Q.11 The rate determining step of a reaction is found out from the mechanism of that reaction. Explain it with few examples.

Ans:- see page No. 218

Q.12 Discuss the factors which influence the rates of chemical reactions.

Ans:- see page No. 227, 228, 229, 230, 231

Q.13 Explain the following facts about the reaction.

$$2NO\ (g) + 2H_2\ (g) \longrightarrow 2H_2O(g) + N_2(g)$$
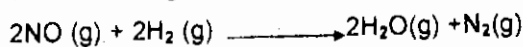
i. The changing concentrations of reactants, change the rates of this reaction.

ii. Individual orders with respect to NO and H_2 can be measured.

iii. The overall order can be evaluated by keeping the concentration of one of the substances constant.

Ans:- see page No. 229, 230

Q.14 The collision frequency and the orientation of molecules are necessary conditions for determining the proper rate of reaction Justify the statement.

Ans:-

A chemical reaction is the result of collisions between reactant molecules. Greater the number of effective collisions, higher will be the rate of reaction. The suitable orientation of molecules is another necessary condition for proper rate of reaction. By 10°C rise in temperature, the number of effective collisions becomes double. Hence rate of reactions becomes double

Q.15 How does Arrhenius equation help us to calculate the energy c activation of a reaction?

Ans:- see page No. 232, 233

Q.16 Define the following terms and give examples

i. Homogeneous catalysis   iv. Auto-catalysis

ii. Heterogeneous catalysis   v. Catalytic poisoning

iii. Activation of a catalyst   vi. Enzyme catalysis

Ans:- see page No. 235, 237, 238

Q.17 Briefly describe the following with examples
i. Change of physical state of a catalyst at the end of reaction
ii. A very small amount of a catalyst may prove sufficient to carr out a reaction.
iii. A finely divided catalyst may prove more effective.
iv. Equilibrium constant of a reversible reaction is not changed i the presence of a catalyst.
v. A catalyst is specific in its action.

Ans:- see page No. 236

Q.18 What are enzymes? Give examples in which they act catalys Mention the characteristics of enzyme catalysis.

Ans:- see page No. 239, 240

Q.19 In the reaction of NO and H_2, it was observed that equimolecul mixture of gases at 340.5 mm Hg pressure was half changed in 102 second: In another experiment with an initial pressure of 288 mm of Hg, th

reaction was half completed in 140 seconds. Calculate the order of reaction

Solution:—

$$a_1 = 340.5 \, mm \, Hg \; , \quad t_1 = 102 \, seconds$$

$$a_2 = 288 \, mm \, Hg \; , \quad t_2 = 140 \, seconds$$

order of reaction, $n = ?$

$$n = 1 + \log(t_1/t_2)/\log(a_2/a_1)$$

$$n = 1 + \frac{\log(102/140)}{\log(288/340.5)}$$

or $\quad n = 1 + \dfrac{\log 0.7286}{\log 0.8458} = 1 + \dfrac{-0.1375}{-0.07273}$

or $\quad n = 1 + 1.89 \quad$ or $\quad n = 2.89$

or $\quad n = 3$. Thus order of reaction is ③

Q.20 A study of chemical kinetics of a reaction
$$A + B \longrightarrow products$$
gave the following data at 25^0C. Calculate the rate law
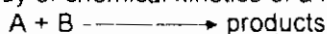
Exp	[A]	[B]	Rate
1	1.00	0.15	4.2×10^{-6}
2	2.00	0.15	8.4×10^{-6}
3	1.00	0.2	5.6×10^{-6}

Solution:— We find order of reaction w.r.t A and B separately. In experiments No 1 and 2, concentration of B remains constant. So we find order w.r.t A.

$$R_1/R_2 = \left(\frac{C_1}{C_2}\right)^n \quad or \quad \frac{4.2 \times 10^{-6}}{8.4 \times 10^{-6}} = \left(\frac{1}{2}\right)^n$$

or $\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^n \quad$ or $n = 1$

In experiments 1 and 3, concentration of A remains constant. So we find order w.r.t B

$$R_1/R_3 = \left(\frac{C_1}{C_3}\right)^n$$

$$\frac{4.2 \times 10^{-6}}{5.6 \times 10^{-6}} = \left(\frac{0.15}{0.20}\right)^n \quad \text{or} \quad \frac{3}{4} = \left(\frac{3}{4}\right)^n$$

$$\text{or} \quad \left(\frac{3}{4}\right)^1 = \left(\frac{3}{4}\right)^n \quad \text{or} \quad n = 1$$

Now overall rate law is given as

$$\text{rate} = K[A][B] \quad \text{or} \quad \text{rate} = K[A]^1[B]^1$$

Q.21   Some reactions taking place around room temperature have activation energies around 50kJ mol^{-1}.

    i.   What is the value of the factor $e^{-Ea/RT}$ at 25^{0}C.

    ii.   Calculate this factor at 35^{0}C and 45^{0}C and note the increase in this factor for every 10 ^{0}C rise in temperature.

    iii.   Prove that for every 10^{0}C rise in of temperature, the factor doubles. And so rate constant also doubles.

Solution: –

(i) $E_a = 50 \, KJ \, mol^{-1} = 50000 \, J \, mol^{-1}$

$$T = 25\overset{\circ}{C} = 25 + 273 = 298 K$$

$$R = 8.314 \, J \, mol^{-1}$$

Factor $e^{-Ea/RT} = ?$

$$e^{-Ea/RT} = e^{-50000/8.314 \times 298}$$

$$= e^{-50000/2477.6}$$

$$= e^{-20.180}$$

$$= 1.71 \times 10^{-9}$$

(ii) $T = 35\overset{\circ}{C} = 35 + 273 = 308 K$

$$R = 8.314 \, J \, mol^{-1}$$

$$E_a = 50000 \, J \, mol^{-1}$$

The factor $e^{-Ea/RT} = e^{-50000/8.314 \times 308}$

$$= e^{-50000/2560.7}$$

$$= e^{-19.52} = 3.31 \times 10^{-9}$$

When $T = 45°C + 273 = 318K$

$R = 8.314 \, J \, mol^{-1}$, $E_a = 50000 \, J \, mol^{-1}$

The factor $e^{-Ea/RT} = e^{-50000/8.314 \times 318}$

$$= e^{-50000/2643.8}$$

$$= e^{-18.91}$$

$$= 6.1 \times 10^{-9}$$

Increase in factor for 10°C rise in temperature

25°C to 35°C, $3.31 \times 10^{-9} - 1.71 \times 10^{-9} = 1.6 \times 10^{-9}$

Temp 35°C to 45°C, then $6.1 \times 10^{-9} - 3.31 \times 10^{-9} = 2.29 \times 10^{-9}$

(iii)

At 25°C the factor $e^{-Ea/RT} = 1.71 \times 10^{-9}$

At 35°C the factor $e^{-Ea/RT} = 3.31 \times 10^{-9}$

At 45°C the factor $e^{-E/RT} = 6.1 \times 10^{-9}$

The factor $e^{-Ea/RT}$ becomes double for 10°C rise in temperature

The ratio of the factor at 25°C and 35°C is

$$\frac{3.31 \times 10^{-9}}{1.71 \times 10^{-9}} = 2$$

The ratio of the factor at 35°C and 45°C is

$$\frac{6.1 \times 10^{-9}}{3.31 \times 10^{-9}} = 2$$

Hence rate constant, K becomes double for every 10°C rise in temperature.

Q.22 H_2 and I_2 react to produce HI. Following data for rate constant at various temperatures (k) have been collected.

Temperature (K)	Rate constant ($cm^3\,mol^{-1}\,s^{-1}$) (k)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

i. Plot a graph between 1/T on x-axis and log k on the y-axis.
ii. Measure the slope of this straight line and calculate the energy for activation of this reactions.

Solution:- First we find 1/T and log k, then we Plot a graph between 1/T and log k.

T(K)	500	550	600	650	700
1/T	0.0020	0.0018	0.0016	0.0015	0.0014
Rate Constant(K)	6.81×10^{-4}	2.64×10^{-2}	0.56×10^{0}	7.31×10^{0}	66.67×10^{0}
log K	-3.16	-1.58	-0.25	+0.86	+1.82

Slope = 7826 K

E_a = Slope × 2.303 R
= 7826 × 2.303 × 8.31
= 149773.4 J
= 149.77 KJ

$Slope = \dfrac{\Delta Y}{\Delta x} = \dfrac{-1.8}{0.00023} = 7826K$

$\Delta Y = -1.8$
$\Delta x = 0.00023$

PAPER CHEMISTRY   CLASS: 11th   (2010)   D.G. KHAN BOARD
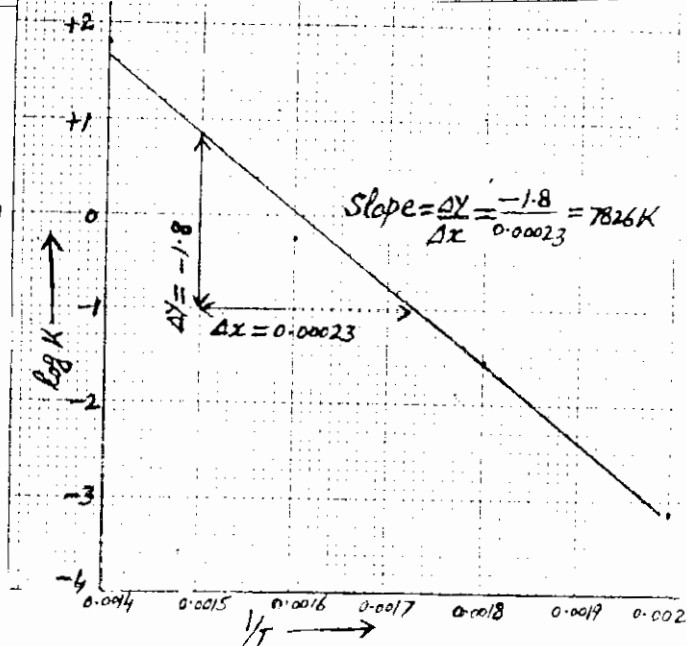
(OBJECTIVE)

Tick the correct answer.

1. One of the substance is used to absorb CO_2 gas in combustion analysis which is that substance.
   (a) 50% KOH   (b) Al_2O_3 (c) $Mg(ClO_4)_2$ (d) SiO_2

2. Number of molecules in one dm^3 of H_2O is close to
   (a) 6.022×10^{23} (b) $18 \times 6.022 \times 10^{23}$ (c) $55.5 \times 6.022 \times 10^{23}$ (d) $\frac{18}{24} \times 10^{23}$

3. In chromatography the stationary phase:
   (a) is a solid   (b) is a liquid   (c) may be liquid or gas   (d) may be solid or liquid

4. Which gas will diffuse more rapidly among the following
   (a) N_2 (b) H_2 (c) CO   (d) NH_3

5. Boiling point of H_2O at Mount Everest would be:
   (a) 98 ^{0}C   (b) 100^{0}C   (c) 101 ^{0}C   (d) 69^{0}C

6. Allotropy is the property of:
   (a) compound   (b) element   (c) atom   (d) mixture

7. Number of neutrons present in $^{39}K_{19}$ is:
   (a) 20   (b) 19   (c) 39   (d) 18

8. Value of the Redberg's constant is:
   (a) 1.7904×10^7 m   (b) 1.9767×10^7 m   (c) 1.09678×10^7 m   (d) 1.6×10^7 m

9. Total number of sigma bonds in ethyne (CH ≡ CH) are:
   (a) five   (b) three   (c) tow   (d) four

10. Which of the following molecules has a co-ordinate covalent bond:
    (a) NH_3 (b) $AlCl_3$ (c) HCl   (d) NH_4Cl

11. Which one of the following process is an exothermic:
    (a) sublimation   (b) respiration   (c) fusion   (d) evaporation

12. PH of rain water is:
    (a) 5.0   (b) 6.0   (c) 6.2   (d) 7.0

13. Equilibrium constant for gaseous equilibrium is represented by:
    (a) Ka   (c) Kc   (c) Kx   (d) Kp

14. Which one of the following is an ideal solution:
    (a) C_2H_5OH and H_2O (b) C_6H_6 and CCl_4 (c) $CHCl_3$ and $(CH_3)_2CO$ (d) H_2O and HCl

15. Oxidation state of carbon in glucose ($C_6H_{12}O_6$) is:
    (a) zero   (b) one   (c) two   (d) four

16. The electrolyte used in fuel cell is
    (a) $NaNO_3$ (b) KOH   (c) Aqueous NaCl   (d) Aqueous H_2SO_4

17. The equation $K = Ae^{-E_a/RT}$ is called:
    (a) Rate Law   (b) Rate equation   (c) Arrheneous equation   (d) general gas equation

(SUBJECTIVE)

2. Write short answers of any twenty two (22) questions of the following.

i) Molecular formula is multiple of empirical formula. Explain with an example.

ii) What is relative abundance of isotopes? How is it determined?

iii) One mole of different gases have different masses but occupies same volume. Explain why?

iv) Differentiate between filtration done by using Gooch and Sintered glass crucible?

v) What is distribution co-efficient? To which technique it is applicable?

vi) How Dalton's Law of partial pressure is useful in determining pressure of a collected over water?

vii) What is critical temperature? It depends on what factors?

viii) Why pressure correction is done by Vander Waals?

ix) Why ethane (C_2H_6) is a gas whereas C_5H_{14} hexane is liquid at STP?

x) Water freezes from surface to the downward direction in Ponds and Lakes. Exp why?

xi) Draw the shape of a unit cell mentioning angles and axes

xii) Cleavage of the crystal is itself anistropic. Give reason.

xiii) Why cathode rays have reducing effect?

xiv) Derive the formula for frequency of photon (only in two steps)

xv) Describe Hund's rule

xvi) What is H ∕ - line in Hydrogen spectrum? Which effect explain these lines

xvii) What is interionic distance? Explain with example.

xviii) Orbital nature also affect the Ionization energy. Explain.

xix) Why π bonds are diffused that sigma (δ) bonds?

xx) Why MOT is superior to VBT?

xxi) Why is it necessary to mention physical states of reactants and products Thermo chemical equation?

xxii) Prove that change in enthalpy is equal to heat of Reaction.

xxiii) How does the equilibrium constant of a chemical reaction tell us the direction chemical reaction?

xxiv) What is K_W? What is the effect of temperature on the value of K_W?

xxv) What are the factors affecting Ionization of acids?

xxvi) Define colligative properties. Name some important colligative properties.

xxvii) What is consulate temperature or critical solution temperature?

xxviii) Explain why $CuSO_4$ give acidic solution when put in water?

xxix) A salt bridge maintains the electrical neutrality in the cell? Explain how?

xxx) The standard oxidation potential of Zn is 0.76V and its reduction potential is -0 justify it.

xxxi) What is the difference in a cell and a battery?

xxxii) What is a pseudo first order reaction?

xxxiii) What is meant by poisoning of a catalyst? Give two examples of catalytic poi

SECTION-II

Attempt any three questions from this section.

3. (a) What are Covalent solids? Discuss the structure of diamond?

(b) The combustion analysis of an organic compound shows it to contain 6 carbon, 5.50% Hydrogen and 29.06% oxygen. What is the empirical formula compound? If the molecular mass of this compound is 110.15 g/mol, ca the molecular formula of the compound

4. (a) Explain VSEPR theory. Discuss structure of SO_3 according to this theory.

(b) Discuss first law of thermodynamics and prove that $\Delta E = q_v$

5. (a) Describe the discovery and properties of nauron in Chadwick experiment.

(b) Define Graham's law. Explain Graham's law of diffusion according to equation.

6. (a) Balance the following equations by oxidation number method

(i) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

(ii) $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

(b) The solubility of PbF_2 at 25°C is 0.63g.dm. Calculate KSP of PbF.

7. (a) Differentiate between hydration and hydrolysis with the help of suitable exa

(b) Define order of reaction. Name any two methods for its determination and half life method in detail.

LAHORE BOARD 1st YEAR 2008
PAPER CHEMISTRY
(OBJECTIVE)

1. Tick mark the correct answer.   17
(i) Height of peak in mass spectrum shows:
Number of isotopes   Mass number   relative abundance   number of protons
(ii) Rate of filtration can be increased using:
Desiccator - Chromatographic tank - Cold finger - Suction flask
(iii) A component having small value of K (distribution coefficient) mostly remains inefficient:
Stationary phase - Mobile phase - chromatographic tank - none of these
(iv) Deviation of a gas from ideal behaviour is maximum at:
-10°C and 5 atm   -10°C and 2 atm   400°C and 2 atm   0°C and 2 atm
(v) If the values of "a" and "b" in van der waal's equation are close to zero for a gas, then the gas is:
Ideal - Non-ideal - Highly polar - Liquefied easily
(vi) Coordination number of Na^+ ion in NaCl is: One - Two - Four - Six
(vii) Vapour pressure of a liquid depends upon:
Amount of the liqu ' surface area - temperature - size of container
(viii) e/m value for posit... rays is maximum for
Hydrogen - Helium - Oxygen - Nitrogen
(ix) According to Bohr's atomic model, radius of second orbit of hydrogen atom is: 0.529 Å - 2.116 Å - 4.0 Å - 5.0 Å
(x) Which of the following species has unpaired electrons in antibonding molecular orbital:
H_2 - He_2 - O_2^{2+} - N_2^{2-}
(xi) A molecular orbital can contain maximum electrons equal to.
One - Two   - Three   - Four
(xii) Enthalpy change for the reaction:
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ is called enthalpy of:
Formation - Combustion - Neutralization - Atomization
(xiii) By adding NH_4Cl to NH_4OH solution, the ionization of NH_4OH:
Increases - decreases - remains same - increases 100 times
(xiv) pH of tomato is: 1.2 - 4.2 - 7.2 - 9.2
(xv) In a mixture of 28 grams of N_2 and 96 grams of O_2, the mole fraction of N_2 is: 1.1 - 0.51 - 0.25 - 0.11
(xvi) Electrolysis is used for: Electroplating - Manufacture of Al
Manufacture of sodium metal - all of these
(xvii) The catalyst used for the reaction:
$HCOOH \rightarrow H_2 + CO_2$, is: Copper - Alumina - Silica - Iron

SECTION-I

2. Write Twenty Two short answers of the following questions
(i) Prove that one mole of each N_2, CO_2 and H_2 contain equal number of molecules.
(ii) The atomic masses may be in fractions. Why?
(iii) Why the experimental yield is mostly less than the theoretical yield?
(iv) What is solvent extraction?
(v) Define sublimation with an example.
(vi) Give two important scales of thermometry. How are these related?
(vii) Gases deviate more from ideal behaviour at 0°C than at 100°C. Why?
(viii) Calculate the value of gas constant R in S.I. units.

(ix) Differentiate between oxidation and reduction.

(x) Calculate the oxidation state of Cr in $K_2Cr_2O_7$ and Cr_2O_3.

(xi) The standard oxidation potential of Zn is +0.76V and its reducti potential is -0.76V. Justify it.

(xi.) Ionic crystals do not conduct electricity in solid state. Give reason.

(x i) Diamond is hard and electrical insulator. Why?

(xi Define Lattice Energy. Give example.

(xv, Crystals showing isomorphism mostly have same atomic ration. Justify

(xvi, Write the electronic configuration of the elements. (i) Cu = 29 (ii) K =

(xvii Define Pauli's exclusion principle.

(xvii What is Stark Effect?

(xix) Give any two points which show the ideality of a solution.

(xx) Define molarity and molality. Give their mathematical expression.

(xxi) Differentiate between hydration and hydrolysis with one example each

(xxii) What are conjugate solutions? Give an example.

(xxiii) Why atomic radius is greater than cationic radius?

(xxiv) Why second ionization energy of an element is always greater than ionization energy?

(xxv) Explain that π-bonds are more diffused than sigma bond.

(xxvi) Differentiate between bonding molecular orbital and anti bon molecular orbital.

(xxvii) Define state and state functions.

(xxviii) Comment that enthalpy of neutralization is merely the heat of forma of one mole of liquid water.

(xxix) Derive Kc expression for the reaction.
$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(xxx) What is an ionic product of water? Give its value at room temperature

(xxxi) What are basic buffer solutions?

(xxxii) What is catalysis? Give an example.

(xxxiii) Differentiate between average and instantaneous rate of reaction.

SECTION-II

Note: Attempt any three questions.

3. (a) What is mass spectrometer? How is it used to determine the re atomic masses of isotopes. 4

(b) Calculate the mass of 1 dm^3 of NH_3 gas at 30°C and 1000 m r pressure considering that NH_3 is behaving ideally. 4

4. (a) What are molecular solids? Give their properties. 5

(b) Write a note on construction and working of bomb calorimeter 3

5. (a) What are cathode rays? How these rays are produced? Write prope

(b) N_2 and H_2 gases combine to give NH_3 gas. The value of this reaction at 500°C is 6×10^{-2}. Calculate the value of K_p for this rea

6. (a) Explain, what do you understand by the term electronegativity? D its variation in the periodic table. How does it affect the bond streng

(b) Give two statement of Raoult's law. Also differentiate between ide non-ideal solutions. 4

7. (a) What is standard electrode potential? Explain the measurem electrode potential? 4

(b) Explain the effect of temperature on the rate of reaction with the Arrhenius Equation. 4

PAPER: CHEMISTRY   11th CLASS   2009 (MULTAN BOARD)
OBJECTIVE

1.   Each question has four possible answers. Choose the correct answer and encircle it.

(i)   Molecular formula is equal to: (a) n x empirical formula
(b) n x compound formula (c) n x atomic formula (d) n x structural formula

(ii)   The number of atoms present in 0.5moles of Na is:
(a) 1.0×10^{23} (b) 6.02×10^{23} (c) 2.04×10^{23} (d) 3.01×10^{23}

(iii)   When an organic compound formed in water is volatile or thermally unstable it is separated by:
(a) crystallization (b) sublimation (c) solvent extraction d) chromatography

(iv)   The absolute zero is: (a) attainable (b) may be attainable
(c) unattainable   (d)may not be attainable

(v)   Heat change for one mole of a solid during converting into liquid is called
(a) molar heat of fusion (b) molar heat of vaporization
(c) molar heat of sublimation (d) enthalpy change

(vi)   Amorphous means (a) arranged (b) Ordered (c) shaped (d) shapless

(vii)   K-series have wave-length (a) longer   (b) smaller
(c) same   (d) different

(viii)   What is the value of (n + l) for the 3 d sub-shell? (a) 2   (b) 1 (c) 5 (d) 3

(ix)   Amount of energy released by absorbing electron in the valance shell is
(a) ionization energy   (b) electron affinity
(c) electro negativity   (d) atomic radius

(x)   Which of the following molecule has zero dipole moment?
(a) NH_3 (b) $CHCl_3$ (c) H_2O (d) BF_3

(xi)   The number of fundamental ways of transferring energy into or out of system is: (a) one   (b) two   (c) three   (d) four

(xii)   When K_C value is small, the equilibrium position lies to:
(a) left   (b) right   (c) Equilibrium   (d) none

(xiii)   Which one of the following salt dissolves in water to form a solution with a pH greater than 7?   (a) NaCl   (b) $CuSO_4$ (c) Na_2CO_3 (d) NH_4Cl

(xiv)   Molarity of pure water is:
(a) 1   (b) 18   (c) 55.5   (d) 6

(xv)   Cathode in NICAD is:
(a) Ag_2O (b) NiO_2 (c) Cd   (d) Zn

(xvi)   Stronger the oxidizing agent, grater is the:
(a) oxidation potential   (b) reduction potential
(c) redox potential (d) E.M.F of cell

(xvii)   Hydrolysis of tertiary butyl bromide has order of reaction:
(a) first order   (b) Pseudo first order   (b) second order   (d) third order

SUBJECTIVE
SECTION-I

2: Write short answers to any twenty two of the following questions.

(i)   NaCl has 58.5 amu as Formula mass and not the Molecular mass. Justify.

(ii)   Prove that one mole of CO_2, N_2 and H_2 contain equal number of Molecules.

(iii)   Why the theoretical yield is mostly greater than actual yield?

(iv)   Give the applications of Limiting Reactant.

(v)   Differentiate between Stationary Phase and Mobile Phase.

(vi)   Differentiate between Sublimation and Condensation.

(vii)   What are various units of Pressure?

SUBJECTIVE
Section I

2. Write short answers to any twenty two of the following question:-   22x2

(i)   Why experimental yield is mostly less than theoretical yield? Give two re

(ii) Define Avogadro's number. How does it relate to the masses of chemical substances?

(iii) Atomic masses may be written in fractions. Why?

(iv) Define Chromatography and explain Adsorption Chromatography

(v)   What are characteristics of an ideal Solvent?

(vi) Explain Lind's method of liquefaction of gases.

(vii) What is General Gas Equation? Derive it in various forms.

(viii) Write four applications of Plasma.

(ix) Explain evaporation as a cooling process.

(x)   Why ice floats on the surface of water?

(xi) Explain why ionic crystals do not conduct electricity in the solid state.

(xii) Why molecular solids are soft and easily compressible?

(xiii) What are defects in Rutherford's atomic model?

(xiv) How mass of electron is calculated by using e/m value?

(xv) Write and explain de-Broglie's equation.

(xvi) Differentiate between frequency and wave number.

(xvii) Explain why dipole moment of CO_2 is zero but that of SO_2 is 1.61 D.

(xviii) Why the atomic radii increases down the group?

(xix) How do electron affinity values vary in the periodic table?

(xx) Give the sequence of molecular orbitals in nitrogen molecule.

(xxi) What is a spontaneous process?

(xxii) Define First Law of Thermodynamics. How is it represented?

(xxiii) What will be the effect of change in pressure on NH_3 synthesis?

(xxiv) How do the Buffers Act?

(xxv) What is meant by Solubility Product Constant?

(xxvi) What are Colligative Properties? Why these are called so?

(xxvii) Define Molality. Explain with one example.

(xxviii) Why a molar solution is more concentrated than a molal solution?

(xxix) Explain the difference between electrolytic cell and voltaic cell.

(xxx) Give two applications of electrolysis processes of industrial importance.

(xxxi) Determine the Oxidation Number of Mn in $KMnO_4$

(xxxii) What is meant by half life Period? Give one example.

(xxxiii) What are Hydrates? Give two examples

SECTION-II

NOTE -   **Attempt any three questions,**

3. a) Define Ionic Solids. Discuss properties of Ionic Solids   4

   b) When Lime Stone is heated. Calcium Oxide is formed $CaCO_3 \longrightarrow CaO+CO_2$
       2.6 Kg of CaO is produced when 4.5 kg of lime stone is roasted. Calculate percentage
       this reaction.   4

4. a) Define Hybridization and discuss the structure of Ethane ($CH_2 = CH_2$).   4

   b) Describe "HESS'S LAW OF CONSTANT HEAT" with an example   4

5. a) Explain Millikan's oil drop experiment to determine the charge of an electron   4

   b) Derive Vander Wall's equation for real gases

6. a) What is Lead Accumulator? Discuss in detail.   4

   b) The solubility of PbF_2 at 25°C is 0.64 g dm^{-3}. Calculate Ksp of PbF_2.   4

7. a) What is Raoult's Law? Explain Raoult's Law when both the components a
       4

   b) What is Order of Reaction? Describe two methods for finding order of rea

LAHORE BOARD 1ST YEAR 2010
PAPER CHEMISTRY
OBJECTIVE

1   Four Possible answers are given. Tick mark (✓) the correct one   17

(i)   The volume occupied by 1.4g N_2 at STP is:
   (a) 22.4dm³   (b) 11.2 dm³   (c) 2.24 cm³   (d) 1.12dm³

(ii)   Silver has isotopes
   (a) 9   (b) 16   (c) 17   (d) 18

(iii)   Solvent extraction is an equilibrium process and is controlled by:
   (a) distribution law   (b) the amount of solvent used
   (c) law of mass action   (d) the amount of solute

(iv)   The molar volume of CO_2 is maximum at
   (a) STP   (b) 127°C and 1atm   (c) 0°C and 2 atm   (d) 273°C and 2 atm

(v)   Ice occupies more space than liquid water
   (a) 9%   (b) 10%   (c) 11%   (d) 12%

(vi)   Structure of crO_4^{2-} is:
   (a) tetrahedral   (b) octahedral   (c) cubic   (d) triclinic

(vii)   Total number of spectral regions in a spectrum is
   (a) 4   (b) 6   (c) 7   (D) 8

(viii)   The value of plank's constant is:
   (a) 6.62×10^{34} J.S   (b) 6.62×10^{27} J.S
   (c) 6.62×10^{41} J.S   (d) 6.62×10^{31} J.S

(ix)   Bond angle between two $H - S - H$ bond is
   (a) 104.5°   (b) 107.5°   (c) 92°   (d) 95°

(x)   S.1 unit of dipole moment is
   (a) Pm   (b) Debye   (c) mC   (d) all

(xi)   The total heat content of a system is called.
   (a) entropy   (b) enthalpy   (c) temperature   (d) internal energy

(xii)   Law of mass action derived by Guldberg and Waage in
   (a) 1909   (b) 1906   (c) 1846   (d) 1864

(xiii)   Ionization of hydrogen sulphide gas is suppressed by.
   (a) KCl   (b) NaCl   (c) HCl   (d) NH_4Cl

(xiv)   10g NaOH dissolved per 250cm³ of solution has morality
   (a) 0.5M   (b) 1.0M   (c) 1.5M   (d) 2.0M

(xv)   Oxidation number of chromium in $K_2Cr_2O_7$ is
   (a) 2   (b) 4   (c) 6   (d) 12

(xvi)   emf of Zn-Cu cell is   (a) 0.0v   (b) 0.5v   (c) 1.0v   (d) 1.1v

(xvii)   A substance which makes the catalyst more effective is called.
   (a) inhibitor   (b) retarder   (c) promoter   (d) autocatalyst

PART-II

2   Write any twenty two (22) short answers of the following questions

(i)   Define actual yield, write formula for the calculation of percentage yield

(ii)   One mg of K_2CrO_4 has thrice the number of ions than the number of formula units when ionized in water

(iii)   Why oxygen cannot be determined directly in combustion analysis?

(iv)   Define distribution law and how it is helpful in solvent extraction

(v)   Define chromatography. Give its two uses

(vi)   State Joule Thomson effect. Write its application

(vii)   Why regular air cannot be used in divers tank?

(viii)   Calculate the density of methane at STP

(ix)   Explain electron gas theory

(x)   Define transition temperature

(xi)   Evaporation causes cooling effect. why?

(xii)   Boiling needs a constant supply of heat. why?

(xiii)   State Auf-bau principle and Pauli's exclusion principle

(xiv)   Explain orbital.

(xv)   Why $\frac{e}{m}$ value of positive rays for different gases are different but those for cathode rays the $\frac{e}{m}$ values are the same? Justify it.

(xvi)   Why atomic spectrum is line spectrum?

(xvii)   Why ionic compounds do not show the phenomenon of isomerism?

(xviii)   Write down two postulates of VSEPR theory?

(xix)   The ionic radius of cation is smaller than atomic radius and that of an anion is greater than atomic radius. Explain with reason.

(xx)   What factors influence the ionization energy?

(xxi)   Define state function and give examples

(xxii)   Justify that heat of formation of compound is sum of all the other enthalpies.

(xxiii)   Explain the term buffer capacity

(xxiv)   Solubility of glucose in water is increased by increasing the temperature Explain with reason

(xxv)   What will be the effect on the position of equilibrium on following system if   (i) Temperature is increased   (b) chlorine is added
$$PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g) \qquad \Delta H = 90 \text{ kj mol}^{-1}$$

(xxvi)   The sum of mole fraction of all the component is always equal to unity for any solution Explain with reason.

(xxvii)   What are azeotropic mixture?

(xxviii)   What is water of crystallization? Give two examples.

(xxix)   Calculate the oxidation number of chromium in $CrCl_3$ and $Cr_2O_7^{2-}$

(xxx)   Salt bridge is not required in lead storage cell. Why?

(xxxi)   What is standard hydrogen electrode?

(xxxii)   What are enzymes? Give two examples in which enzymes act as catalyst?

(xxxiii)   What is half life method for the determination of order of a reaction?

SECTION –I

Note   Attempt any three questions from this part.

3 (a)   Mg metal reacts with HCl to give hydrogen gas. What is the minimum volume of HCl solution (27% by weight) required to produce 12.1g of H_2? The density of HCl solution is 1.14g /cm^3
$$Mg(s) + 2HCl (aq) \rightarrow MgCl_2 (aq) + H_2 (g)$$

(b)   Define hydrogen bonding. How does it explain the indicated properties of following substances.
(i) solubility of hydrogen-bonded molecules. (ii) Structure of ice

4 (a)   Define bond energy Discuss two factors effecting the bond energy

(b)   Explain entahalpy and prove that $\Delta H = q_p$

5 (a)   Define orbital Discuss shape of its two types.

(b)   Describe Dalton's law of partial pressure. Write its three applications.

6 (a)   What is electrochemical series? Give its any three applications.

(b) $Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6}. Calculate the solubility of $Ca(OH)_2$.

7 (a)   Explain elevation of boiling point with the help of figure.

(b)   Distinguish between homogeneous and heterogeneous catal\ suitable explained

MULTAN BOARD PAPER CHEMISTRY 11TH CLASS 2010

OBJECTIVE

1. Choose the correct answer and encircle it.   17

(i) 27 g of Al will react completely with how much mass of O_2 to produce Al_2O_3:-
    (a) 24 g of Oxygen   (b) 8 g of Oxygen
    (c) 16 of Oxygen   (d) 32 g of Oxygen

(ii) A limiting reactant is one which:-
    (a) Is taken in lesser quantity in grams as compared to other reactants
    (b) Is taken in lesser quantity in volume as compared to other reactants
    (c) Gives the minimum amount of the products which is required
    (d) Gives the minimum amount of the products under consideration

(iii) The comparative rates at which the solutes move in paper Chromatography depend on:-
    (a) The size of paper   (b) Temperature of the experiment
    (c) R_f values of solutes   (d) Size of the chromatographic tank used

(iv) Equal masses of CH_4 and O_2 are mixed in an empty container at 25°C. The fraction of total pressure exerted by Oxygen is:-
(a) 1/9   (b) 1/3   (c) 8/9   (d) 16/17

(v) Which of the following is a pseudo solid?
    (a) CaF_2 (b) $NaCl$ (c) Glass   (d) $CaSO_4$

(vi) In order to mention the boiling point of water at 110°C, the external pressure should be -
    (a) Between 760 torr and 1200 torr   (b) Between 200 torr and 760 torr
    (c) 765 torr   (d) 460 torr

(vii) Quantum number values for 2p orbitals are:-
    (a) $n = 2, l = 1$ (b) $n = 1, l = 2$ (c) $n = 1, l = 0$ (d) $n = 2, l = 0$

(viii) Orbitals having same energy are called:-
    (a) Hybrid orbital   (b) Valence orbitals   (c) d-orbital   (d) Degenerate orbitals

(ix) Which of the following hydrogen halide has the highest percentage of ionic character?
    (a) H F   (b) HCl   (c) HBr   (d) HI

(x) Which of the following species has unpaired electrons in anti bonding molecular orbitals:-
    (a) O_2^{+2} (b) N_2^2 (c) B_2 (d) F_2

(xi) The enthalpies of all elements in their standard states ate:-
    (a) Unity   (b) Zero   (c) Always positive   (d) Always negative

(xii) The unit of equilibrium constant K_c for the reaction $H_2 + I_2 \longrightarrow 2HI$, is:-
    (a) $Mole^{-1} dm^3$ (b) $Mole^{-2} dm^3$ (c) $Mole\ dm^{-1}$ (d) None of these

(xiii) Which of the following reactions will be favoured to the forward direction at low pressure:-
    (a) $N_2 + O_2 \longrightarrow 2NO$ (b) $N_2 + 3H_2 \longrightarrow 2NH_3$
    (c) $PCl_5 \longrightarrow PCl_3 + Cl_2$ (d) $H_2 + I_2 \longrightarrow 2HI$

(xiv) Which of the following solutions has the highest billing point?
    (a) 5.85% solution of Sodium Chloride   (b) 18.0% solution of Glucose
    (c) 6.0% Solution of Urea   (d) 4.0% solution of Sucrose

(xv) In which of the following changes there is a transfer of five electrons?
    (a) $MnO_4^2 \longrightarrow MnO_2$ (b) $MnO_4^2 \longrightarrow Mn^{2+}$ (c) $CrO_4^2 \longrightarrow Cr^{3+}$
    (d) $Cr_2O_7^2 \longrightarrow 2Cr^{+3}$

(xvi) Electrolysis is the process in which a chemical reaction takes place at the expense of:-
    (a) Chemical energy   (b) Electrical energy
    (c) Heat energy   (d) Solar energy
    Indicate the enzyme which is used as a catalyst in the following reaction
    $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$

(v)   Define sublimation with an example.

(vi) SO_2 is comparatively non-ideal at 273k but behaves ideally at $328^\circ C$. Why?

(vii)   What are characteristics of Plasma?

(viii)   Calculate the value of gas constant-R in SI units.

(ix)   Write down the reactions in Alkaline battery.

(x)   S H E Acts as anode when connected with Cu electrode but as cathode with Zn electrode. Give reasons.

(xi)   Calculate the oxidation state of Cl in $Ca(ClO_3)_2$ and NaCl.

(xii)   Lower density of ice than water has got significance. Comment.

(xiii)   Define polymorphism with an example.

(xiv)   Why HF is a weaker acid than HCl?

(xv)   What is a unit cell?

(xvi)   Write balance equations for any two nuclear reactions.

(xvii)   Mention two defects of Rutherford's Atomic Model.

(xviii) What is Zeeman effect?

(xix)   Write de-Broglie's equation. What does it show?

(xx)   One Molal solution is dilute as compared to one molar solution of glucose. Why?

(xxi)   What do you mean by percentage (w/w) composition of a solution?

(xxii)   Ethylene glycol may be used in the radiator of an automobile. Give two aspects of its use.

(xxiii) Why the dipole moment of CH_4 is Zero?

(xxiv) Why the covalent bonds are directional?

(xxv)   How M.O.T justifies that He atoms cannot make the He_2 molecules?

(xxvi) The dipole moment of CO_2 is Zero but that of water is 1.85 Debye. Why?

(xxvii) Define ΔH°. Can it be negative, why?

(xxviii) What is Lattice energy? Give example.

(xxix) How does a catalyst effect a reversible reaction?

(xxx)   What is Buffer Capacity?

(xxxi) Define Conjugate Acid and Conjugate Base.

(xxxii) A particular catalyst is suitable for a particular chemical reaction. Justify.

(xxxiii) Define (i) Activation energy   (ii) Activated complex

SECTION-II

Note: Attempt any three questions.

Q.3 (a) Define the following giving one example of each.

    (i) Gram-atom   (ii) Gram Ion   (iii) Percentage yield   (iv) Avogadro's number

(b) $250 cm^3$ of Hydrogen is cooled from $127^\circ C$ to $-27^\circ C$ by maintaining the pressure constant. Calculate the new volume of the gas at low temperature.

4. (a)   Define Metallic bond. How does Electron Sea Theory justifies electrical conductivity and shining.

(b)   Prove that: $\Delta H = q_p$

5 (a)   What are positive rays? Give their properties?

(b)   A buffer solution has been prepared by Mixing 0.2 M CH_3COONa and 0.5 M CH_3COOH in $1 dm^3$ of solution. Calculate the pH of the solution pka. of acid = 4.74.

6. (a)   Give the arrangement of Molecular Orbitals in O_2 molecule. How doe molecular orbitals theory explain the paramagnetic character of Oxy molecule.

(b)   Describe Beckmann's Method for measurement of Freezing Point Depr

7. (a)   Explain THE CONSTRUCTION AND WORKING OF A Volta mention the function of Salt Bridge.

(b)   Write a note on chemical method to determine the rate of

السلام علیکم ورحمتہ اللہ وبرکاتہ

مختصر تعارف

کافی عرصہ سے خواہش تھی کہ ایک ایسی ویب سائٹ بناؤں جس پر طالب العلموں کیلئے کچھ تعلیمی مواد جمع کر سکوں۔ اللہ تعالیٰ نے توفیق دی اور میں نے ایک سال کی محنت کے بعد ایک سائٹ "گلدستہ ڈاٹ پی کے" کے نام سے بنائی جو کہ قرآن و حدیث، اصلاحی، دلچسپ، تاریخی قصے واقعات، اُردو انگلش تحریریں، شاعری و اقوال زریں، F.Sc اور B.Sc کے مضامین کے آن لائن نوٹس، اسلامک، تفریحی، معلوماتی وال پیپرز، حمد و نعت، فرقہ واریت سے پاک اسلامی بیانات، پنجابی نظمیں و ترانے اور کمپیوٹر و انٹرنیٹ کی دنیا کے بارے میں ٹپس، آن لائن کمائی کرنے کے مستند طریقہ کار۔ کے ساتھ ساتھ اور بھی بہت سی چیزوں پر مشتمل ہے۔ اور انشاء اللہ میں مزید وقت کے ساتھ ساتھ اضافہ کرتا جاؤں گا۔ آپ کی قیمتی رائے کی ضرورت ہے۔ عرنان شفیق

اہم نوٹ

ذیل میں جو نوٹس مہیا کیے گئے ہیں وہ کئی گھنٹوں کی لگاتار محنت کے مرتب ہوئے ہیں۔ اور آپ کو بالکل مفت مہیا کر رہے کیے جا رہے ہیں۔ آپ سے ان کی قیمت صرف اتنی سی متوقع ہے کہ ایک بار درودّ ابراھیمی اپنی زبان سے ادا کر دیں۔

درود شریف

بِسْمِ اللهِ الرَّحْمٰنِ الرَّحِيْمِ

اَللّٰهُمَّ صَلِّ عَلٰى مُحَمَّدٍ وَّعَلٰى اٰلِ مُحَمَّدٍ كَمَا

اے اللہ! رحمت بھیج حضرت محمد پر اور حضرت محمد کی آل پر

صَلَّيْتَ عَلٰى اِبْرَاهِيْمَ وَعَلٰى اٰلِ اِبْرَاهِيْمَ

جس طرح تو نے رحمت بھیجی حضرت ابراہیم پر اور حضرت ابراہیم کی آل پر

اِنَّكَ حَمِيْدٌ مَّجِيْدٌ

بے شک تو تعریف کیا ہوا بزرگ ہے۔

اَللّٰهُمَّ بَارِكْ عَلٰى مُحَمَّدٍ وَّعَلٰى اٰلِ مُحَمَّدٍ كَمَا

اے اللہ! برکت دے حضرت محمد کو اور حضرت محمد کی آل کو جس

بَارَكْتَ عَلٰى اِبْرَاهِيْمَ وَعَلٰى اٰلِ اِبْرَاهِيْمَ

طرح برکت دی تو نے حضرت ابراہیم کو اور حضرت ابراہیم کی آل کو

اِنَّكَ حَمِيْدٌ مَّجِيْدٌ

بے شک تو تعریف کیا ہوا بزرگ ہے۔