B.Sc. CHEMISTRY ALLIED

I YEAR – I SEMESTER
COURSE CODE: 7BCHA1

ALLIED COURSE - I – GENERAL CHEMISTRY – I

Unit I States of matter - I

1.1.**Gaseous state:** Postulates of kinetic theory of gases – derivation of expression for pressure of gas on the basis of kinetic theory – deducing the basic gas laws.

1.2.Ideal and real gases. Deviation of real gases from ideal behaviour – reasons for deviation. Derivation of Vander Waals gas equation. Law of corresponding state – reduced equation of state and its significances.

1.3.Average, RMS and most probable velocities (equations only – no derivation). Calculating the above velocities.

Unit II States of matter - II

1.1.**Liquid state:** comparison gaseous and liquid states. Surface tension – viscosity – Trouton's rule and its significances.

1.2.**Solid state:** types of solids. Crystals, crystallographic systems. Conductors, insulators and semiconductors. Intrinsic and extrinsic semiconductors.

1.3.**Colloidal state.** Definition, classifications and examples for hydrophilic and hydrophobic sols. Differences between them. Emulsions, classification and Bancraft's rule. Applications of colloids.

Unit III Thermodynamics

1.1.Energetics: Energy – various forms of energy – internal energy – first law of thermodynamics and its mathematical derivation – enthalpy: Definition – Molar heat capacity at constant volume and constant pressure – relationship between Cp and Cv – Hess's law – applications of Hess's law.

1.2.**Second law of thermodynamics in different forms** – Distinction between reversible and irreversible processes – thermo dynamical criteria for reversible and irreversible processes – entropy – physical significances of entropy - Derivation of Helmholtz free energy change and Gibbs free energy change.

Unit IV Surface processes and kinetics

4.1.**Adsorption:** Definitions of adsorbate, adsorbent and interface. Distinction between physisorption and chemisorptions. Adsorption of gases on solids – Freundlich isotherm. Surfactants definition with examples. Applications of adsorptions.

4.2.**Distribution law:** distribution law and distribution constant. Applications of distribution law. Distribution of a component between two immiscible solvents and Solvent extraction,

4.3.**Chemical Kinetics:** rate and rate constant of a chemical reaction. Order and molecularity of reaction. Factors deciding the rate of a reaction. First order rate equation. Half life of a reaction.

4.4.**Catalysis** : Homogeneous and heterogeneous catalysis – promoters and catalytic poisons – autocatalysis – Acid-base catalysis – Enzyme catalysis.

Unit V **Periodic table:**

5.1. **Modern periodic law** and periodic arrangement of elements. Variation physical and chemical properties. Classification - elements as metals, non-metals and metals. Inert pair effect.

5.2. **Hydrogen**– Position of Hydrogen in the Periodic Table – Resemblance with alkali metals – Resemblance with the Halogens - Isotopes of Hydrogen– Heavy Hydrogen – Ortho and Para Hydrogen – Differences between Ortho and Para Hydrogen

5.3.**Hydrides** – Definition – classification – preparation and properties of lithium aluminium hydride and sodium borohydride.

5.4.**Oxides** – Definition – Classification of oxides based on their oxygen content with suitable examples .

Books for Reference:

1. Advanced Physical Chemistry –Puri, Sharma & Pathania.
2. Text book of Inorganic Chemistry –PL.Soni.
3. Advanced Inorganic Chemistry – SathyaPrakash.

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B.Sc. Chemistry Allied

UNIT –I

A – Hydrogen

Position of Hydrogen in the periodic table

Hydrogen is the simplest element. It is placed in the I group of the periodic table. Its atomic number is one.

Hydrogen is having similarity with I group elements as well as V11 group elements.

Reasons for placing Hydrogen in I group [Alkali metals] of the periodic table

Hydrogen exhibits similarity with I group alkali metals with several respects

1. Electronic Configuration :

Hydrogen is having only one electron in the outer most orbit similarly alkali metals are also having only one electron in its outer most orbit.

H	Li	Na	K
1	2,1	2,8,1.	2,8,8,1

2. Electropositive Character.

Hydrogen as well as alkali metals exhibit an electropositive character in the outer most orbit to form unipositive ion.

H^+ , Li^+ , Na^+ , K^+

3. Valency

Hydrogen as well as alkali metals are monovalent.

4. Formation of Cations

Halides of both hydrogen and the alkali metals, when dissolved in water, give rise to the positive ions H^+, Li^+, Na^+ etc., During electrolysis of these solutions both hydrogen and alkali metals go to the cathode

5. Affinity for Electronegative elements

Hydrogen forms oxides and halides with electronegative elements like oxygen and halogen similar that of alkali metals.

H_2O	Na_2O	K_2O
HCl	NaCl	KCl

6. Reducing agent

Hydrogen is a good reducing agent similar that of alkali metals. Because of the above similarity hydrogen is placed in the I group of the periodic table along with alkali metals.

Reasons for placing Hydrogen in the VII group of periodic table

Hydrogen also exhibit similarity with halogens

1. Atomicity

Hydrogen is a diatomic molecule like halogens.

H_2, F_2, Cl_2, Br_2, I_2

2. Non–metallic character

Hydrogen is a non–metallic element like halogens. Hydrogen is a gas like halogens.

3. Electronic Configuration

Both hydrogen and the halogens contain electrons in their outermost shell one less than the maximum number that can be accommodated there. Thus both of them behave as monovalent electronegative elements in the formation of compounds by gaining one electron.

4. Hydrides and Halides

On electrolysis of fused lithium hydride hydrogen is liberated at the anode just as chlorine is liberated at the anode during the electrolysis of fused sodium chloride.

5. Formation of similar covalent compounds.

Both hydrogen and halogens react with carbon, silicon to form compounds

CH_4	CCl_4
Methane	Carbon tetrachloride
SiH_4	$SiCl_4$

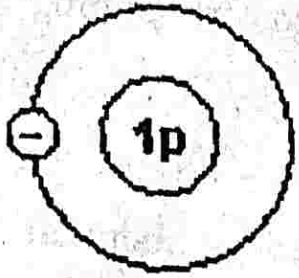
6. Replacement of hydrogen by halogen

Hydrogen can be replaced by halogens which indicates that the similar nature of hydrogen and halogens.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

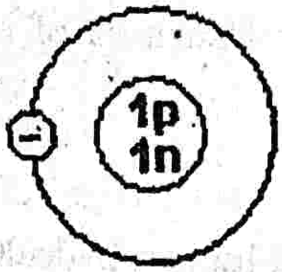
Isotopes of hydrogen

Atoms of the same element with the same atomic number but different mass numbers are called isotopes. The number of elements occurs as isotopic mixtures. Hydrogen has three isotopes. Usually the isotopes of an element bear the name of the element. Since the isotopes of hydrogen are assigned separate names they differ appreciably in their masses.



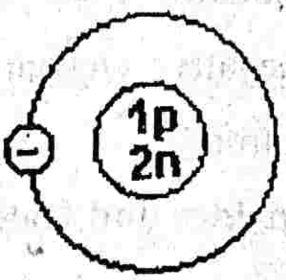
$_1H^1$

Protium (1p)



$_1H^2$

Deuterium (1p, 1n)



$_1H^3$

Tritium (1p, 2n)

These three isotopic forms contain the same number of proton, and electrons. They differ only in the number of neutrons

1. Protium $_1H^1$

This is the most common form of hydrogen. It is ordinary hydrogen and is denoted by the H. Its atomic mass is 1.008123. It consists of one proton in its nucleus and one electron revolving around it. It constitutes 99.98% of total hydrogen available in nature.

2. Deuterium $_1H^2$ or $_1D^2$

This isotope is also called heavy hydrogen and is denoted by D. It consists of one proton and one neutron in the nucleus with one electron revolving around. Its atomic mass is 2.0142 and it is present in hydrogen gas to the extent of one part per 6900 parts. Its chemical properties are similar to those of protium but the rate of reactions are different. The reaction is more slow and less complete than hydrogen.

Heavy hydrogen is prepared from heavy water. It is also separated from the mixture of protium and deuterium.

3. Tritium $_1H^3$ or $_1T^3$

It is an isotope of hydrogen with mass 3. It is denoted by T. Its nucleus contains one proton and two neutron with one electron revolving around the nucleus. It is found in nature very small amount and in ordinary water it exists 7 parts in 10^{17}. It atomic mass is 3.0151. It is very difficult to separate from ordinary hydrogen. It is radioactive with half -life period of 12.4 years. It is very useful tracer element in chemistry. It is used in nuclear fusion reactions to produce hydrogen bombs. It is also used in thermo-nuclear process.

Tritium is normally prepared by the following nuclear reactions.

1). By bombarding deuterium containing compounds such as D_3PO_4, ND_4Cl etc.,

$$_1D^2 + {_1D^2} \rightarrow {_1T^3} + {_1H^1}$$

Deuterium Deuterium Tritium Hydrogen

2). By deuteron bombardment of beryllium

$$_4Be^9 + {_1D^2} \rightarrow {_1T^3} + {_4Be^8}$$

Beryllium Deuterium Tritium

3). By neutron bombardment of boron and nitrogen

$$_5B^{11} + {_0n^1} \rightarrow [{_5B^{12}}] \rightarrow {_4Be^9} + {_1T^3}$$

Boron neutron

$$_7N^{14} + {_0n^1} \rightarrow [{_7N^{15}}] \rightarrow \cancel{_6C1^2} + {_1T^3}$$

$_6C^{12}$

Nitrogen

4). By slow neutron bombardment of lithium

$$_{3}Li^{6} + {}_{0}n^{1} \rightarrow [{}_{2}He^{4}] + {}_{1}T^{3}$$

As the atomic number of three isotopes of hydrogen is the same (equal to 1), they have similar chemical properties. The difference in rate of reaction is due to the difference in the masses of the isotopes.

Isotopes of hydrogen

Property	Protium	Deuterium	Tritium
1. Symbol	H	D	T
2. Atomic number	1	1	1
3. Atomic mass	1.00799	2.0147	3.0170
4. Molecular formula	H_2	D_2	T_2
5. Number of electrons	1	1	1
6. Number of protons	1	1	1
7. Number of neutrons	0	1	2
8. Relative abundance	99.98	0.0156	1part in 10^{27} parts
9. Stability	Stable	Stable	Radio active

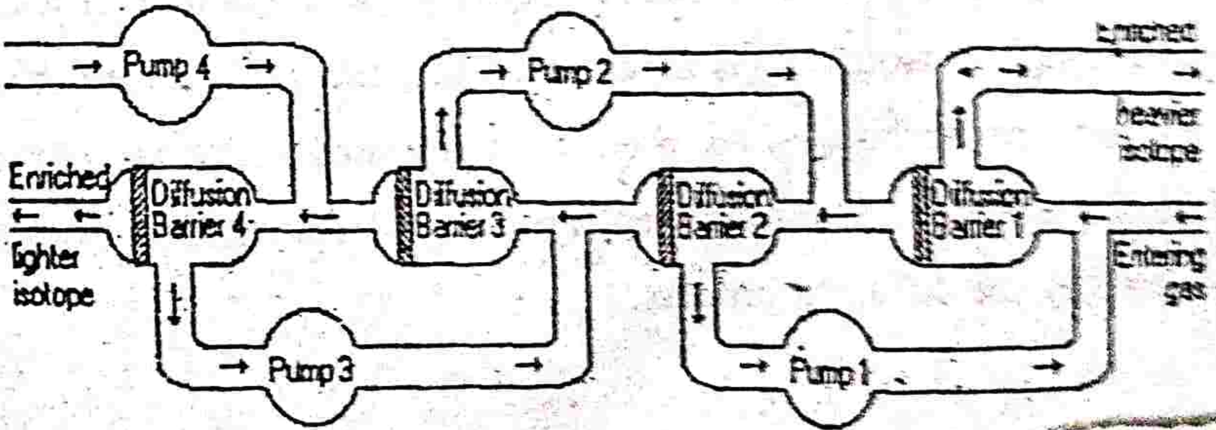
Preparation of Heavy hydrogen

1.Fractional Distillation method

The boiling point of ordinary hydrogen is 20.38K and that of heavy hydrogen is 23.59K. Hydrogen obtained using chemical methods is at first liquefied. The liquid hydrogen is subjected to fractional distillation under reduced pressure when 0.0156% of heavy hydrogen present is obtained.

2.Gaseous diffusion method.

This method is based on the difference in the relative rates of diffusion of the two isotopes, protium and deuterium. Since protium is lighter, it diffuses more readily than deuterium. Hertz separated deuterium using this method .The apparatus used this process consists of a number of porous diffusion units called Hertz diffusion units. The mixture of the two isotopes is allowed to pass into the diffusion units under reduced pressure from left to right. The lighter isotope namely, protium diffuses faster and its proportion increases on the right side. The heavier isotope, deuterium is left behind and is collected into the reservoir placed on the left side. The process is repeated for a number of times to get pure deuterium.



3. From Heavy water

When water containing alkali is electrolyzed, molecules of water containing the lighter isotopes are preferentially decomposed and hence by repeated electrolysis heavy water is obtained in very small quantities. G.N. Lewis electrolyzed 20 litre of water until 1.5 ml of water remained. This contained about 66% heavy water. Gaseous deuterium may be prepared by decomposing heavy water with sodium, red hot iron or tungsten or by electrolysis of solution of anhydrous sodium carbonate in heavy water.

$$\underset{\textbf{Heavy water}}{2D_2O} \xrightarrow{\text{Electrolysis}} \underset{\textbf{Deuterium (at cathode)}}{2D_2} + \underset{\textbf{(at anode)}}{O_2}$$

$$2D_2O + 2Na \rightarrow \underset{\textbf{Sodium deuteroxide.}}{2NaOD} + D_2$$

4. By adsorption on charcoal.

This method is based on the fact that hydrogen(protium) is adsorbed more readily and strongly on finely divided solid surfaces than deuterium. When hydrogen gas containing the two isotopes is passed over coconut charcoal kept at liquid air temperature for a few hours, the lighter isotope gets adsorbed while most of the deuterium passes out unadsorbed. This process is repeated till the fraction enriched in deuterium is obtained. From this fraction, deuterium is recovered by the diffusion process.

5. Chemical method

It is possible to achieve partial separation of deuterium from hydrogen because the lighter hydrogen is more reactive than heavier deuterium. For example, when hydrogen gas is passed over red-hot copper oxide when the lighter hydrogen reacts more readily than the heavy deuterium in the following reaction

$$CuO + H_2 \rightarrow Cu + H_2O$$

The residue will therefore be a fraction enriched in deuterium.

properties

Heavy hydrogen like ordinary hydrogen is a colourless, odourless, tasteless gas. This isotope resembles ordinary hydrogen in all properties which depend upon the electronic configuration but differs in certain properties which depend upon mass. This is due to their atoms having the same electronic configuration but different mass numbers

Dissimilarities in the properties of protium and deuterium

Protium	Deuterium
1. Melting points low 13.95K	Melting point is high 18.65K
2. Boiling point is low 20.38K	Boiling point is high 23.59K
3. Heat of fusion is low	Heat of fusion is high
4. Density is low	Density is high
5. Energy of dissociation is low	Energy of dissociation is high

The deuterium molecule like hydrogen is a mixture of ortho and one part of para form.

Chemical properties

The chemical properties of deuterium are similar to those of hydrogen. The only difference is that deuterium reacts more slowly and less completely than hydrogen.

1. Hydrogen and chlorine combine to give hydrogen chloride. Deuterium and chlorine combine to give deuterium chloride

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$D_2 + Cl_2 \rightarrow 2DCl$$

2. Hydrogen burns in oxygen to give water. Deuterium burns in oxygen to give deuterium oxide or heavy water

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$2D_2 + O_2 \rightarrow 2D_2O$$

3. With nitrogen it combines in the presence of a catalyst to form heavy ammonia

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

$$3D_2 + N_2 \rightarrow 2ND_3$$

Deuteroammonia.

4. When deuterium is passed in to AgCl at 700°C reduction takes place similar that of Hydrogen.

$$D_2 + 2AgCl \rightarrow 2Ag + 2DCl.$$

5. Reaction with unsaturated hydro carbons;

When ethylene is mixed with deuterium and passed over heated nickel, addition reaction takes place

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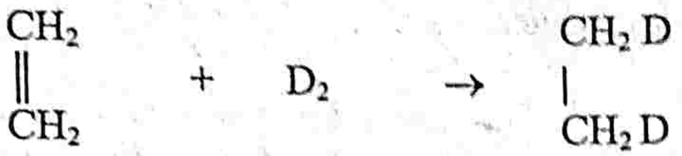


$$CH_2{=}CH_2 + D_2 \rightarrow CH_2D{-}CH_2D$$

Dideuteroethane

6.Exchange Reaction

With deuterium exchange reactions are common in which one or more deuterium atoms exchange with light hydrogen atoms .The following reactions are examples of exchange reactions

$$H_2 + D \rightarrow HD + H$$

$$H_2O + D_2 \rightarrow D_2O + H_2$$

$$C_6H_6 + 3D_2 \xrightarrow{200^\circ C} C_6D_6 + 3H_2$$

Deuterobenzene

$$2NH_3 + 3D_2 \rightarrow 2ND_3 + 3H_2O$$

Trideuteroammonia

$$CH_4 + 2D_2 \rightarrow CD_4 + 2H_2$$

Deuteromethene

Uses of deuterium

1. Deuterium is used as a tracer element in the study of mechanism of chemical reactions and of biological systems.

2. It is used in bombarding atoms in nuclear transformations and artificial radio activity.

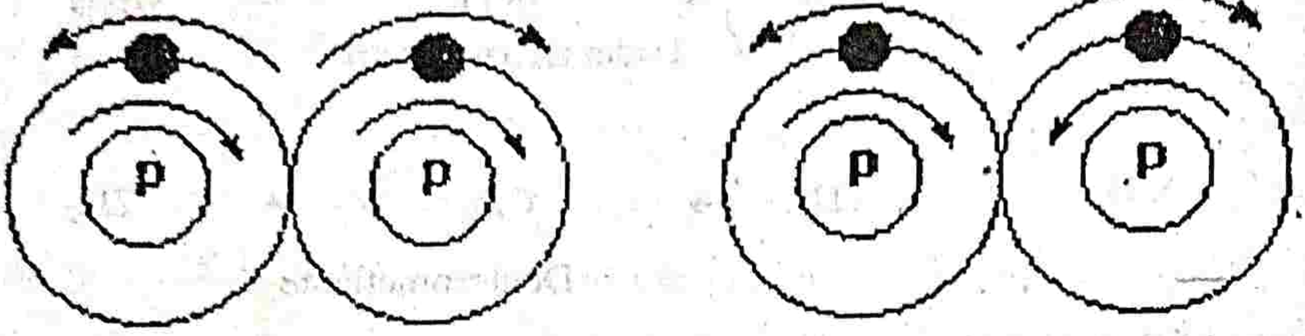
3. It is used in the production of deuterium oxide Hoary water] which is used as a moderator in nuclear reactors.

4. Deuterium is used in the production of deuterium oxide (Heavy water) which is used as a moderator in nuclear reactors.

Ortho and Para hydrogen.

Structure

The hydrogen atom consists of a proton around which one electron revolves. Both the proton and the electron spin around an axis like a top. When two hydrogen atoms combine to form a molecule, the spin of the electrons are always in the opposite directions as otherwise the molecule would not be stable according to Pauli exclusion pinciple. The spin of proton may be either in the same direction or opposite direction giving rise to two allotropes of hydrogen, namely ortho and para hydrogen respectively.



Ortho - Hydrogen   Para - Hydrogen

The two electrons in a hydrogen molecule always spin in the opposite direction. At room temperature ordinary hydrogen consists about 75% ortho and 25% para form. As the temperature is lowered, the equilibrium shifts in favour of para hydrogen. At 25K there is 99% para and 1% ortho hydrogen. The change in the proportion of the two forms of hydrogen requires a catalyst such as platinum or atomic hydrogen or silent discharge.

Separation

The para form was originally prepared by absorbing ordinary hydrogen in activated charcoal in a quart vessel kept at a temperature of 20K. The charcoal absorbs almost pure para hydrogen. By this method pure para hydrogen can be instated.

Conversion of para into ortho hydrogen

Ortho hydrogen is more stable than para hydrogen. The para form changes into ortho form under the conditions given below

(i) By heating with nascent hydrogen

(ii) By heating to 800° C or more

(iii) By mixing with paramagnetic molecules like oxygen.

(iv) By treatment with catalyst like platinum or iron.

(v) By passing an electric discharge

(vi) By mixing with atomic hydrogen

Properties

Ortho and Para hydrogen are similar in chemical properties but differ in some of the physical properties.

(i) Melting point of para hydrogen is 13.83K while that of ordinary hydrogen is 13.95K.

(ii) Boiling point of para hydrogen is 20–26K while that of ordinary hydrogen is 20–39K.

(iii) The vapour pressure of liquid para hydrogen is higher than that of ordinary liquid hydrogen.

(iv) The magnetic moment of para hydrogen is zero since th spins neutralizes each other while in the case of ortho it i twice than that of proton

(v) Para hydrogen possesses a lower internal molecula energy than ortho form. It is not possible to obtain orth hydrogen in pure state.

Hydrides

Binary compounds of hydrogen and other elements are generally called hydrides. This term should be applied to compounds of hydrogen with elements of lower electronegativity.

Classifications :

Hydrides are classified into four classes

- (i) Saline hydrides
- (ii) Metallic hydrides
- (iii) Molecular hydrides
- (iv) Polymeric hydrides

(i). Saline hydrides (or) Ionic hydrides

These are the hydrides of s-block elements viz- alkali and alkaline earth metals (except Be and Mg)

Examples: LiH, NaH, CaH_2, BaH_2

Preparation

Ionic hydrides are generally prepared by heating the metal in a current of hydrogen

$$2Li + H_2 \xrightarrow{400^\circ C} 2LiH$$

$$Ca + H_2 \xrightarrow{300^\circ C} CaH_2$$

Properties

1). The saline hydrides (salt like) colourless crystalline compounds with ionic lattices.

2) Stability :

Hydrides of Li, Ca and Sr are most stable, other decompos above 670K. Thermal stability decreases with increase in atom number of the metal in a given group

3) Presence of hydride ion

Electrolysis of fused LiH produces hydrogen at the anod showing the presence of the hydride ion H^-

$LiH \rightarrow Li^+ + H^-$

$2Li^+ + 2e^- \rightarrow 2Li$ (At cathode)

$2H^- \rightarrow 2e^- + H_2$ (At anode)

4) Action of air

They are oxidized by air, some burn spontaneously at roo temperature

5) Action of water

They are hydrolyzed vigorously by water with the formatio of corresponding hydroxide and hydrogen.

$LiH + H_2O \rightarrow LiOH + H_2$

$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$

6). The ions are held by strong electrostatic force and hence the ion hydrides are solids with high melting and boiling points.

7). Reducing Property

They are powerful reducing agents at high temperatures.

Example:

$4NaH + Fe_3O_4 \rightarrow 3Fe + 4NaOH$

$NaH + CO_2 \rightarrow HCOONa$

Uses

1. Ionic hydrides are used as reducing agents in synthetic organic chemistry
2. LiH and NaH are used for preparing reducing agents like lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$)
3. LiH, NaH, and CaH_2 are employed as a ready source of hydrogen for military purpose
4. Ionic hydrides liberate hydrogen on heating. The liberated hydrogen buns in air spontaneously. Thus these hydrides are used as solid fuels.

(ii). Metallic hydrides or Interstitial Hydrides.

These are formed by some of the transition metals (d- block elements Group.IB to VIIB and VIII)

Structure: In, metallic hydrides, hydrogen is occluded in the interstitial holes of the metal lattice. Hence these hydrides are also known as interstitial hydrides. Since temperature and pressure may proportion of hydrogen, there is no stoichiometric relation between the metal and hydrogen in these compounds. For this reason, the metallic hydrides are often called non-stoichiometric hydrides

Example: $PdH_{0.6}$, $VH_{0.6}$

Some metallic ~~hydrides possess~~ stoichiometric formulae.

Example: CuH, FeH_2, NiH_2, CrH_3

Preparation

(I). By passing hydrogen gas over moderately heated metals

$$Th + H_2 \rightarrow ThH_2$$

(II). By electrodeposition of hydrogen on the metal used as cat excepting palladium (Pd)

Properties

(I). Metallic hydrides are non-volatile solids and have metallic lust

(ii). The metallic lattice expands on account of occlusion of hydrog Thus the densities of the metallic hydrides are usually lower t those of the parent metals.

(iii). They expel hydrogen on heating and hence they are go reducing agents.

(iv). They conduct electricity feebly and hence they are used semiconductors.

Uses

(i) It is used as reducing agent

(ii) It is used as solid fuels

(iii) It is used as semiconductors

(iv) It used in metallurgy and vacuum tubes

(iii). Molecular hydrides (or) covalent hydrides

These are formed by most p- block elements. (Metals and nonmetals of Group III A to VIIIA) and also Be and Mg

Example: CH_4, SiH_4, AsH_3, SbH_2, BeH_2, MgH_2, B_2H_6,

Preparation

(1). Direct combination of the elements (HF, NH_3, H_2O)

(2). Hydrolysis of metal borides, carbides, nitrides, phosphides etc., with water or acid.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

$$Mg_3B_2 + 6HCl \rightarrow 3MgCl_2 + B_2H_6$$

$$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4$$

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

(3). By the reduction of metal halides with nascent hydrogen

$$AsCl_3 + 6H \xrightarrow{Zn/HC} AsH_3 + 3HCl$$

$$GeCl_4 + 8H \xrightarrow{Zn/HCl} GeH_4 + 4HCl$$

(4). By reduction of non- metal halides with lithium aluminum hydride in ether solution

$$SiCl_4 + LiAlH_4 \xrightarrow{Ether} SiH_4 + LiCl + AlCl_3$$

Properties

(1). The molecules of covalent hydrides are held by weak van der Waal's force and hence they are gases or volatile liquids or solids with low melting and boiling point.

(2). The covalent hydrides are non-conductors of electricity in the liquid state and when dissolved in non-polar solvents.

(3)They are readily hydrolyzed by water liberating hydrogen

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

$$SiH_4 + 2H_2O \rightarrow SiO_2 + 4H_2$$

(4). They are strong reducing agents for example, monosilane reduces silver nitrate to metallic silver and copper sulphate to copper silicide

$$4AgNO_3 + SiH_4 \rightarrow Si + 4Ag + 4HNO_3$$

$$2CuSO_4 + SiH_4 \rightarrow Cu_2Si + 2H_2SO_4$$

Uses

(i) It is used as strong reducing agent

(ii) Boron hydrides like diborane are used as rocket fuels (Propellants)

(iii) Silicon hydrides (Silanes) are used to prepare silicon which finds use in transistors and photovoltaic cells

(iv) The hydrides of carbon (hydrocarbons) are used as gaseous fuels for heating and lighting purposes

(iv). Complex hydride

These hydrides are formed by the action of ionic hydrides on the electron deficient compounds of group III elements

Example: $LiAlH_4$ – Lithium aluminum hydride

$LiBH_4$ – Lithium borohydride

$NaAlH_4$ – Sodium aluminum hydride

$NaBH_4$ – Sodium borohydride

Preparation

$$4\,LiH + AlCl_3 \xrightarrow{ether} LiAlH_4 + 3LiCl$$

$$2NaH + B_2H_6 \rightarrow 2NaBH_4$$

Properties

1).The complex hydrides are readily hydrolyzed by water liberating hydrogen

$LiAlH_4 + 4H_2O \rightarrow Li(OH) + Al(OH)_3 + 4H_2$

$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4H_2$

2). They are powerful reducing agents. For example $LiAlH_4$ reduces a number of covalent halides to the hydrides

$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + AlCl_3 + LiCl$

Uses

1). Complex hydrides are used as powerful reducing agents in organic chemistry.

2). $LiAlH_4$ is used for the preparation of hydrides of B, Si, Ge and Sn

3). The alkali metal borohydrides are used as a handy source of diborane.

B. Oxides

Definition:

A binary compound of oxygen with another element is called oxides.

Classification

Based on their chemical behavior or oxygen content, chief classes of oxides are given below.

I. Classification based on their oxygen content.

1.Normal oxides

Oxides, which contain oxygen, as permitted by the normal oxidation number of element are called normal oxide. They have only M-O bonds

Ex: H_2O, MgO, Al_2O_3

2. Poly- Oxides

Oxides containing more oxygen than allowed by normal oxidation number of M are termed polyoxides. They involve O-O bonds as well as M-O bonds. These have been further classified as

(a). Per oxides

These contain O_2^{2-} ion and are derivative of H_2O_2, (H–O–O–H). These produce hydrogen peroxides with dilute acids and liberate oxygen with concentrated acids

Ex: Na_2O_2, BaO_2

$$BaO_2 + H_2SO_4\ (dil.) \rightarrow BaSO_4 + H_2O_2$$

$$2BaO_2 + 2H_2SO_4\ (conc.) \rightarrow 2BaSO_4 + 2H_2O + O_2$$

They associated with peroxide (-O-O-) linkage

H–O–O–H Na–O–O–Na

H_2O_2 Na_2O_2

(b). Super oxides

These conation O_2^- ion. Only super oxides known are KO_2, RbO_2 and CsO_2.

These react with water to give hydrogen peroxide and oxygen

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2$$

(c). Dioxides

Poly- Oxides, which contain higher percentage of oxygen like peroxides but do not give any hydrogen peroxides with dilute acids, are termed dioxides. These oxidize conc. HCl to chlorine

$$MnO_2 + 4HCl\,(conc.) \rightarrow MnCl_2 + 2H_2O + Cl_2$$

When heated with conc. H_2SO_4 it yield oxygen.

$$2MnO_2 + 2H_2SO_4(conc.) \rightarrow 2MnSO_4 + 2H_2O + O_2$$

3. Sub oxides

Oxides, which contain lower percentage of oxygen than the normal oxidation number of M, are called sub oxides, They involve M-m bonds in addition to M-o bonds

Ex : N_2O ---- Nitrous oxide

C_3O_2 ---- O=C=C=C=O

4. Mixed oxides

Some oxides may be considered to be made of two simpler oxides. These oxides are called compound oxides

Fe_3O_4 $[FeO+Fe_2O_3]$ — Ferreso - ferric oxide

Pb_3O_4 $[2PbO+PbO_2]$ — Plumbo-plumbic oxide

Fe_3O_4 given a mixture of ferrous and ferric salts with acids

$$Fe_3O_4 \rightarrow FeO + Fe_2O_3$$

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$$

II. Based on their chemical behavior

(1). Acidic oxides

Oxides which dissolve in water forming acids and neutralize alkalis are called acidic oxides. They are also called acid anhydrides and are generally the oxides of non metals

Examples: N_2O_3, N_2O_5, P_2O_3, SO_2, CO_2, B_2O_3

Properties: (i). These oxides dissolve in water forming acids

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (carbonic acid)}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ (Sulphonic acid)}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \text{ (Sulphuric acid)}$$

(ii) They dissolve in alkali forming salts.

$$CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O$$

$$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$$

(2). Basic oxides These may be

(a). Essentially covalent

Oxides of transition meats MO and M_2O_3 are essentially covalent. These are non volatile insoluble in water and not attacked by it

(b) Essentially Ionic : These are attacked by water to give alkalis. These are oxides of metals. Oxides, which dissolve in acids to form salts, are called basic oxides

Ex: Li_2O, Na_2O, CaO, BaO, Fe_2O_3

Properties: (i). These oxides are dissolved in water to give alkali solutions. Such solutions are termed alkalis

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

(ii). These oxides react with acids to form salts.

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$$

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$

(3). Amphoteric oxides: A few metallic oxides exhibit a dual behavior of both an acidic and basic oxides. They form salts on reactions with both acids and alkalies Ex: ZnO, SnO, SnO_2, Al_2O_3

Properties; (i)With acids

$$ZnO + 2HCl \rightarrow \underset{\text{Zinc chronicle}}{ZnCl_2} + H_2O$$

$$SnO + 2HCl \rightarrow \underset{\text{Stannous chloride}}{SnCl_2} + H_2O$$

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

Aluminum chloride

(ii). With alkalies

$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

Sodium zincate

$SnO + 2NaOH \rightarrow Na_2SnO_2 + H_2O$

Sodium stannite

$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$

Sodium aluminate

(4). Neutral oxides: Those oxides, which are neutral towards litmus, are called neutral oxides these oxides do not form salt either with acids or bases.

Ex: CO — Carbon monoxide
H_2O — water
N_2O — Nitrous oxide
NO — Nitric oxide

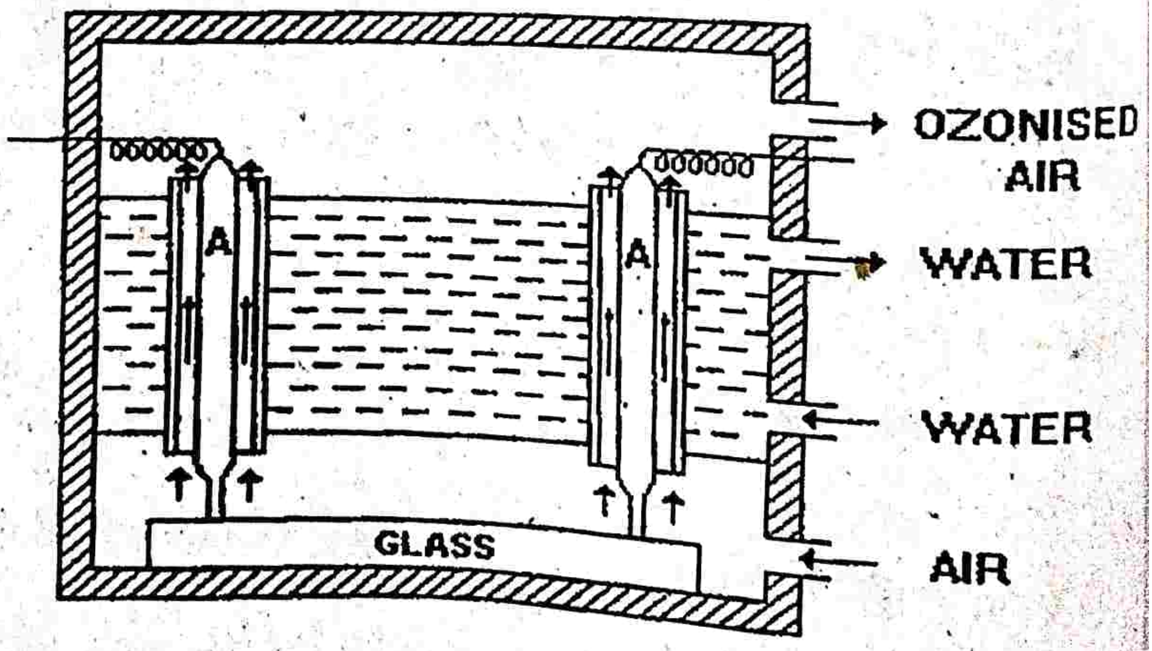
E: Ozone

Molecular formula : O_3

Manufacture of ozone

The manufacture of ozonised air is employed by Siemen Halske's ozoniser. It consists of battery of aluminum cylinders(6- number) resting on an insulating glass plate and enclosed in glass porcelain tubes. These are arranged two abreast in an earthed iron ta divided into three compartments. Through the middle compartm cold water is circulated to keep the apparatus cool. The alumini rods are raised to a high potential of 8,000 – 10,000 volts.

Air is passed in the lower compartment when it is subjected to the action of silent electric discharge. Ozonised air passes out through the exit at the top and is c collected.



Another ozoniser consists of several vertical metall gauges arranged parallel to one another. Each of the gauges protected by glass plates. The air is passed and is subjected silent electric discharges. Oxygen is partially converted into ozone and ozonised air comes out at the upper end of the ozoniser.

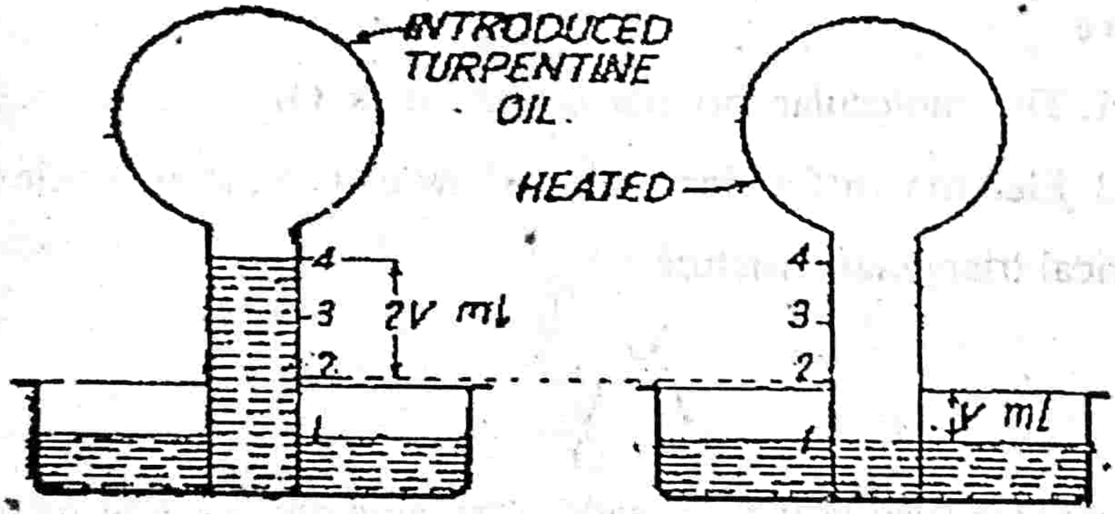
Electrolytic method :

The electrolysis of acidified water with high current density and platinum anode gives a gas on the anode, which consists of 95% ozone rest being oxygen.

Composition of ozone

Soret's Experiment:

Equal volume of ozonised oxygen is enclosed in two flasks of equal capacity having graduated necks. In one of the flasks introduced turpentine oil and heated the other. In the first flask decrease of volume was noticed due to the absorption of ozone. In the second flask an increase of volume took place due to the decomposition of ozone to give oxygen.



The decrease in volume was found to be double increase. i.e., if the increase in volume is one volume the decrease is double (= 2 volumes)

The decrease in volume (= 2 volumes) with turpentine oi directly the volume of ozone present in ozonised oxygen. T increases by one volume on heating when ozone (2 volu decomposes to give oxygen, i.e., the volume of oxygen obtained = volume +1 volume = 3 volume. This shows that two volumes ozone on decomposition by heating yield three volumes of oxyge

Ozone	→	O_2
2 volume		3 volume
2 molecule		3 molecules.

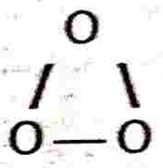
Applying Avogadro's law 2 molecules of ozone yiel molecules of oxygen. Hence the formula of ozone should be O_3.

(ii). Vapour density of ozone has been found to be 24 a molecular weight is 48 which corresponds to the formula O_3. Hen O_3 is the formula of ozone.

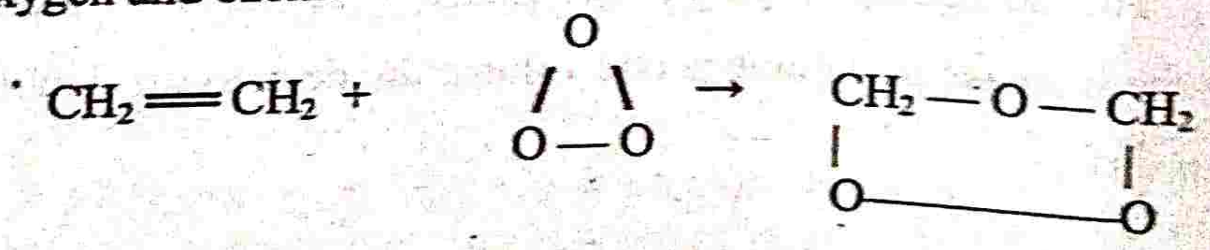
Structure

1. The molecular formula of ozone is O_3

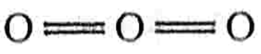
2. Electron diffraction studies show that ozone molecule has symmetrical triangular structure.



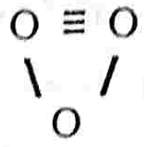
3. The symmetrical structure readily explains the divalent nature o oxygen and ozonide formation



4. In most of the oxidation reactions ozone makes use of nly one oxygen atom. This suggests that one of the oxygen atoms f oxygen atoms of ozone be linked in a different manner. This is xplained by proposing the following unsymmetrical structure.



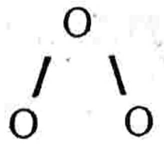
II



III

5. The tetravalency of one of the oxygen atoms as seen in the nsymmetrical structures is established by Bruhl from molar fraction studies

6. (I). The microwave spectra of ozone shows that it is ' V' aped with a bond angle of 111° 49'



(ii). The O – O bond length in ozone is 1.28A°. This is termediate between an O – O single bond (1.48A°) and a O = O uble bond (1.21A°.). This suggests resonance in the molecule and one is regarded as a resonance hybrid of the following structures.

operties

ysical

1. It is a pale – blue gas with strong smell.

2. When inhaled in small quantities it causes head ache and nausea.

3. It is heavier than air.

4. Slightly soluble in water, more soluble in turpentine oil, glacial acetic acid or carbon tetra chloride.

5. It is liquefied to a deep blue liquid when passed through liquid oxygen. (Boiling point : 160.6K)

6. It can be solidified to violet black crystals (Melting point 23.3K).

Chemical Properties.

1. Decomposition

Pure ozone decomposes with an explosive violence while ozonised oxygen decomposes slowly at low temperature. It is almost instantaneous at 573K.

$$2O_3 \rightarrow 3O_2$$

(2). Oxidizing action

It acts as a powerful oxidizing agent due to liberate nascent oxygen.

$$[O_3 \rightarrow O_2 + O]$$

(i). Black lead sulphide is oxidized to white lead sulphate.

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2.$$

(ii). Iodine is liberated from potassium iodide solution.

$$2KI + H_2O + O_3 \rightarrow 2KOH + I_2 + O_2$$

(iii). Halogen acids are oxidized to the corresponding halogens, e.g. hydrochloric acid is oxidized to chlorine.

$$2HCl + O_3 \rightarrow Cl_2 + H_2O + O_2$$

(iv). Potassium manganate is oxidized to potassium permanganate.

$$2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$$

(v). Silver metal is blackened.

$$2Ag + O_3 \rightarrow Ag_2O + O_2$$

(vi). Moist iodine is oxidized to iodic acid

$$I_2 + 5O_3 + H_2O \rightarrow 2HIO_3 + 5O_2$$

Similarly moist sulphur, phosphorus to their corresponding highest oxy acids.

(vii). A Solution of potassium ferro cyanide is oxidized to potassium ferric cyanide.

$$2[K_4 Fe(CN)_6] + O_3 \rightarrow 2[K_3 Fe(CN)_6] + 2KOH + O_2$$

(viii). When passed through mercury it loses its meniscus and sticks to glass due to the formation of Hg_2O. This phenomenon of mercury sticking to glass is called tailing of mercury.

$$2Hg + O_3 \rightarrow Hg_2O + O_2$$

(ix). It is a good bleaching agent due to its oxidizing action on organic matter.

3) Reaction with peroxides.

Reaction of ozone with barium peroxide and hydrogen peroxide results in their mutual reduction with the liberation of oxygen.

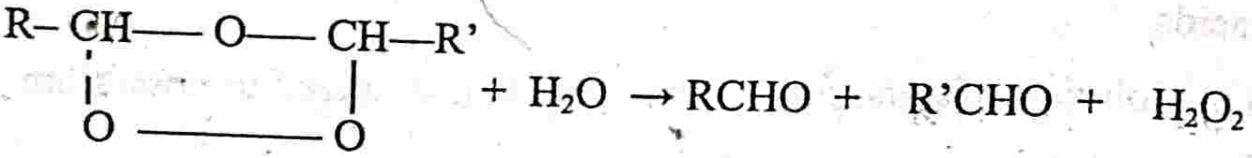
$$BaO_2 + O_3 \rightarrow BaO + 2O_2$$

$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2$$

(4). Addition Reaction.

With unsaturated organic compounds containing double bonds, it forms addition products called ozonide.

These ozonide are decomposed by water or dilute acids giving aldehyde and hydrogen peroxide



The identification of the aldehyde thus obtained helps in locating the position of the double bond in the molecule of the original unsaturated compound.

User of ozone:

1. As germicide and disinfectant.
2. For bleaching oils silk, wool , ivory , starch etc.,
3. For the manufacture of potassium permanganate by oxidation of potassium manganate.
4. In the manufacture of artificial silk and synthetic camphor.
5. It is used to purify air in crowded places like cinema theatres, auditorium, mines, etc.,
6. It is used to locate the position of ethylenic double bonds in organic compound.

Unit II

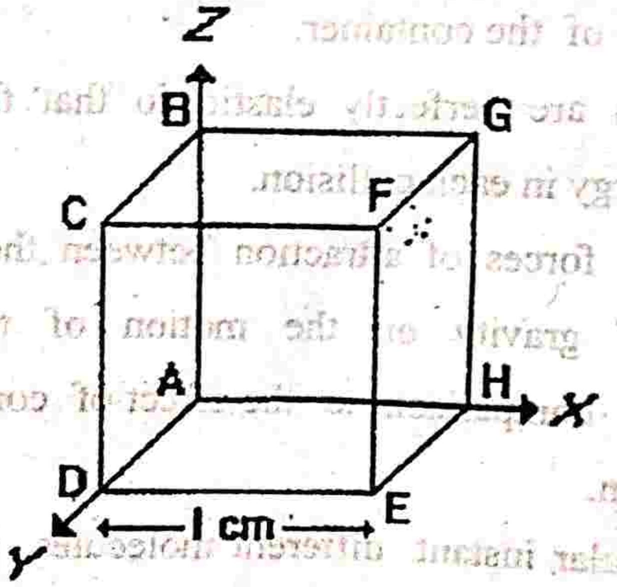
A. Gaseous State

Postulates of kinetic theory of gas

- Gases consist of tiny particles called molecules, which are in continuous motion.
- Molecules are so small and so far apart that on the average, the actual volume of the molecules is negligible compared to the empty space between them.
- The molecules are moving very fast in a straight lines at random colliding with each other and with walls of the container.
- Pressure exerted by gases in each collision of the molecules with the walls of the container.
- The molecules are perfectly elastic so that there is no net loss of kinetic energy in each collision.
- There are no forces of attraction between the molecules.
- The effect of gravity on the motion of the molecules is negligible in comparison to the effect of continued collisions between them.
- At a particular instant different molecules in a sample have different speeds and hence different kinetic energies. However the average kinetic energy of the molecules is directly proportional to the absolute temperature.

Derivation.and expression for pressure of an ideal gas on the b of kinetic theory

Consider a gas enclosed in a cube. The sides of which is cm long. Let the number of molecule in the cube be 'n' and average velocity of the mole cube be 'u' cm / second. Actually6 molecules will be moving in different direction in a zigzag mann But their average velocity 'u' can be resolved into three componen u_x, u_y, and u_z. Along the three co-ordinate axes x, y, z mutual perpendicular to each other and perpendicular to the bases of the cub The magnitude of average velocity is related to its components by th expression.



$$u^2 = u_x^2 + u_y^2 + u_z^2 \quad \text{------------- (1)}$$

Since no direction of motion is preferred it can be assumed that

$$u_x^2 = u_y^2 = u_z^2 \quad \text{-------------(2)}$$

$$u^2 = u_x^2 + u_x^2 + u_x^2 \quad \text{-------------(3)}$$

$$u^2 = 3u_x^2 \quad \text{-------------(4)}$$

$$\overline{u_x^2} = \frac{u^2}{3} \quad \text{———(5)}$$

Before collision momentum = mu_x ———(6)

Consider the moment of a single molecule between the opposite faces ABCD and EFGH, parallel to the x axis, its momentum is mu_x. After striking the face EFGH, it will rebound with the same velocity in the opposite direction.

After collision the momentum = mu_x ———(7)

The change of momentum of one molecule= $mu_x - (-mu_x)$

$$= 2mu_x \quad \text{———(8)}$$

The molecule travels a distance 2l cm for one collision, so the number of collision per second on the face EFGH will be

Number of collision /sec. = $\frac{u_x}{2l}$ ———(9)

The total change in momentum due to u / 2l collision of molecule

$$= 2mu_x \times \frac{ux}{2l}$$

$$= \frac{2\,mu_x^2}{2l} = \frac{mu_x^2}{l} \quad \text{———(10)}$$

Substitute equation (5) in equation (10)

$$= \frac{mu^2}{3l} \quad \text{———(11)}$$

Multiplying and dividing this equation by N

$$= \frac{mNu^2}{3lN} \quad \text{———(12)}$$

$$\frac{u^2}{N} = c^2 \quad \text{———(13)}$$

c^2 is square mean velocity. Substitute equation (13) in equation (12)

$$= \frac{mNc^2}{31} \qquad \text{--------------(14)}$$

This represents the total force on the cube , But pressure 'P' is equal to Force / Area.

$$P = \text{Force} \ / \ \text{Area} \qquad \text{-------------- (15)}$$

$$P = \tfrac{1}{3} \frac{mNc^2}{1 X 1^2} \qquad \text{-----------(16)}$$

$$P = \tfrac{1}{3} \ mNc^2 / 1^3 \qquad \text{----------(17)}$$

$$1^3 = V \qquad \text{----------(18)}$$

Substitute equation (18) in (17)

$$P = \tfrac{1}{3} \ mNc^2 / V \qquad \text{----------(19)}$$

$$PV = \tfrac{1}{3} \ mNc^2 \qquad \text{------------(20)}$$

Equation (20) is the fundamental equation of the kinetic theory of gases. Giving the relationship between pressure and volume is known as kinetic energy of gas.

Deducing the basic laws

Various gas laws can be deduced from the kinetic equation as follows.

1). Boyle's law

At constant temperature the volume of a given mass of the gas is inversely proportional to its pressure

$$V \ \alpha \ \frac{1}{P} \qquad \text{--------------(1)}$$

$$PV = \text{constant} \qquad \text{--------------(2)}$$

According to kinetic equation.

$$PV = \tfrac{1}{3} \ mNc^2 \qquad \text{-----------(3)}$$

Right hand side of the equation (3) is multiplied and divided by 2

$$PV = \frac{2}{3} \times \frac{1}{2} mNc^2 \quad \text{--------------(4)}$$

$$PV = \frac{2}{3} N \times \frac{1}{2} mc^2 \quad \text{--------------(5)}$$

Where $\frac{1}{2} mc^2$ represents the average kinetic energy of the molecule. According to the kinetic energy, the average kinetic energy of the molecule E_n is directly proportional to the absolute temperature

$$E_n \quad \alpha \quad \frac{1}{2} mc^2 \quad \alpha \quad T \quad \text{--------------(6)}$$

$$\frac{1}{2} mc^2 = kT \quad \text{--------------(7)}$$

where k is proportionality constant

Substitute (7) in (5)

$$PV = \frac{2}{3} NkT \quad \text{--------------(8)}$$

At constant temperature and for a given mass of a gas, T and N are constant. Hence the equation (8) becomes.

$$PV = \text{constant}$$

Charles' law

According to Charles' law pressure remaining constant, the volume of given mass of gas is directly proportional to the absolute temperature.

$$PV = \frac{2}{3} NkT \quad \text{-------------- (1)}$$

N is number of molecules.

$$V = \frac{[2\,Nk\,]}{3\,P} \cdot T \qquad \text{-----------------(2)}$$

At constant pressure P and for a given mass of gas [

constants]

$$\frac{2\,kN}{3P} = \text{constant}$$

$$V \;\alpha\; T$$

(3). Graham's law of gaseous diffusion.

According to Graham's law rate of diffusion of gas is inversely proportional to the square root of its density at constant pressure.

According to kinetic equation for gas

$$PV = \tfrac{1}{3}\, mNc^2 \qquad \text{-----------------(1)}$$

For 1 mole of a gas having N_A (Avogadro number) molecules.

$$m \times N_A = M \;\; (\text{M is molar mass}) \qquad \text{-----------------(2)}$$

Substitute equation (2) in (1)

$$PV = \tfrac{1}{3}\; Mc^2 \qquad \text{-----------------(3)}$$

$$c^2 = \frac{3\,PV}{M} \qquad \text{-----------------(4)}$$

Both numerator and denominator is divided by V

$$c^2 = \frac{3PV/V}{M/V}$$

$$c^2 = \frac{3P}{M/V} \qquad \text{-----------------(5)}$$

$$M/V = \rho \qquad \text{-----------------(6)}$$

[mass / volume = density]

Substitute the equation (5) in (6)

$$c^2 = \frac{3P}{\rho} \quad \text{-----------------(7)}$$

If P is kept constant

$$c^2 \; \alpha \; \frac{1}{\rho} \quad \text{-----------------(8)}$$

$$c \; \alpha \; \sqrt{\frac{1}{\rho}} \quad \text{-----------------(9)}$$

Now ‘ r’ the rate of diffusion of gas is directly proportional to the rms’ velocity of the molecule.

$$r \; \alpha \; c \quad \text{----------------- (10)}$$

$$r \; \alpha \; \sqrt{\frac{1}{\rho}} \quad \text{-----------------(11)}$$

Avogadro’s law

Equal volume of all the gases under similar conditions of emperature and pressure contain equal number of molecules.

Consider equal volumes V of two different gases X and Y under the same pressure P and temperature T.

Let the gas X contains N_1, molecules each of mass m_1, having oot mean square velocity c_1, while the gas Y contains N_2, molecules each of mass m_2, having root mean square of velocity c_2. . Then

$$PV = \tfrac{1}{3} \; m_1 \; N_1 \, c_1^2 \quad \text{-------------------(1)}$$

$$PV = \tfrac{1}{3} \; m_2 \, N_2 c_2^{\;2} \quad \text{-------------------(2)}$$

under similar condition equation (1) = equation (2)

$$\tfrac{1}{3}\ m_1 N_1 c_1^2 = \tfrac{1}{3}\ m_2 N_2 c_2^2 \qquad \text{------------(3)}$$

As the temperature is same the average kinetic energy pe molecule for both gases should be the same.

$$\tfrac{1}{2}\ m_1 c_1^2 = \tfrac{1}{2}\ m_2 c_2^2 \qquad \text{------------(4)}$$

Dividing equation (3) by (4).

$$\frac{\tfrac{1}{3}\ m_1 N_1 c_1^2}{\tfrac{1}{2}\ m_1 c_1^2} = \frac{\tfrac{1}{3}\ m_2 N_2 c_2^2}{\tfrac{1}{2}\ m_2 c_2^2}$$

$$N_1 = N_2$$

Kinetic energy of an ideal gas

The molecule of a gas in a state of constant rapid motions an possesses kinetic energy due to motion. The total kinetic energy o translation of the molecule present in one mole of any gas can b calculated with the help of kinetic equation as follows

From the kinetic gas equation

$$.PV = \tfrac{1}{3}\ mNc^2 \qquad \text{-----------------} \ (1)$$

An ideal gas equation

$$PV, = nRT \qquad \text{-----------------} \ (2)$$

Substitute the value of PV in equation (2)

$$\tfrac{1}{3}\ mNc^2 = nRT \qquad \text{-----------------} \ (3)$$

The left hand side of equation (3) is multiplied and divided b 2

$$\tfrac{2}{3}\ [\tfrac{1}{2}\ m\, c^2\ ]N = nRT \qquad \text{-----------------} \ (4)$$

$$\text{Average kinetic energy } \overline{E}_k = \tfrac{1}{2}\ mc^2 \qquad \text{---------------} \ (5)$$

his is for individual molecule. Hence total kinetic energy of N_A olecule present in the sample.

$$E_k = N_A \bar{E}_k = \tfrac{1}{2}\ mNc^2 \quad \text{-----------------} \ (6)$$

Substitute equation (6) in (4)

$$\tfrac{2}{3}\ E_k = nRT \quad \text{---------------} \ (7)$$

$$E_k = 3/2\ nRT \quad \text{-------------} \ (8)$$

$$n = 1$$

Total kinetic energy per mole

$$E_k = 3/2\ RT \quad \text{---------------} \ (9)$$

Total kinetic energy per molecule

$$\frac{E_k}{N_A} = \frac{3\,RT}{2\,N_A} \quad \text{---------------} \ (10)$$

$$\frac{R}{N_A} = K$$

Where K is Boltzman constant

$$\frac{E_k}{N_A} = \frac{3}{2}\ KT \quad \text{-----------------} \ (11)$$

$$\frac{E_k}{N_A} = \epsilon_k \quad \text{------------------} \ (12)$$

Substitute equation (12) in equation (11)

$$\epsilon_k = \frac{3\ KT}{2} \quad \text{------------------} \ (13)$$

$$\epsilon_k \ \alpha \ T \quad \text{------------------} \ (14)$$

Deviation of real gases from ideal behavior

A gas is termed an ideal gas or a perfect gas if it obeys gas law or the gas equation.

$$PV = nRT$$

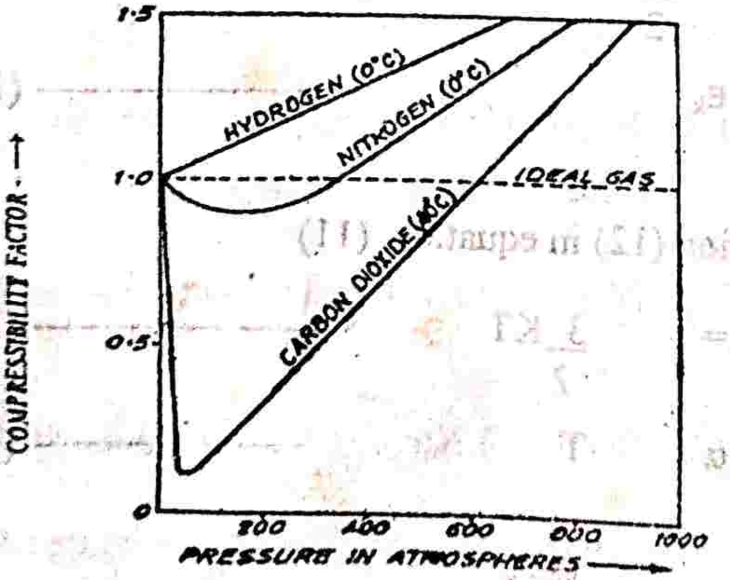
rigidly for all values of temperature and pressure.

Actually no gas is ideal. Most gases show deviation from gas laws under the conditions of high pressure and low temperature. Thus those gases which do not obey the gas laws and gas equation under all condition are called Real gases.

The deviation of real gases from the ideal behavior varies with the nature of gas. In general the most easily liquefied and highly soluble gases such as NH_3, SO_2 and CO_2 show large deviation than the gases such as H_2, O_2 and N_2.

(a). Deviations from Boyle's law:

The magnitude and nature of deviation from Boyle's law may be seen from the plots of PV/ RT (compressibility factor, Z) verses pressure of different gases at constant temperature.



The compressibility factor Z is the ratio observed molar volume (V), to the ideal molar volume (V_{ideal}) = RT/ P

$$Z = \frac{V_{obs}}{V_{ideal}} = \frac{V}{RT/P}$$

$$Z = \frac{PV}{RT}$$

At constant temperature

$$Z \alpha PV$$

For an ideal gas obeying Boyle's law the curve is horizontal dotted straight line.

For an ideal gas obeying Boyle's law

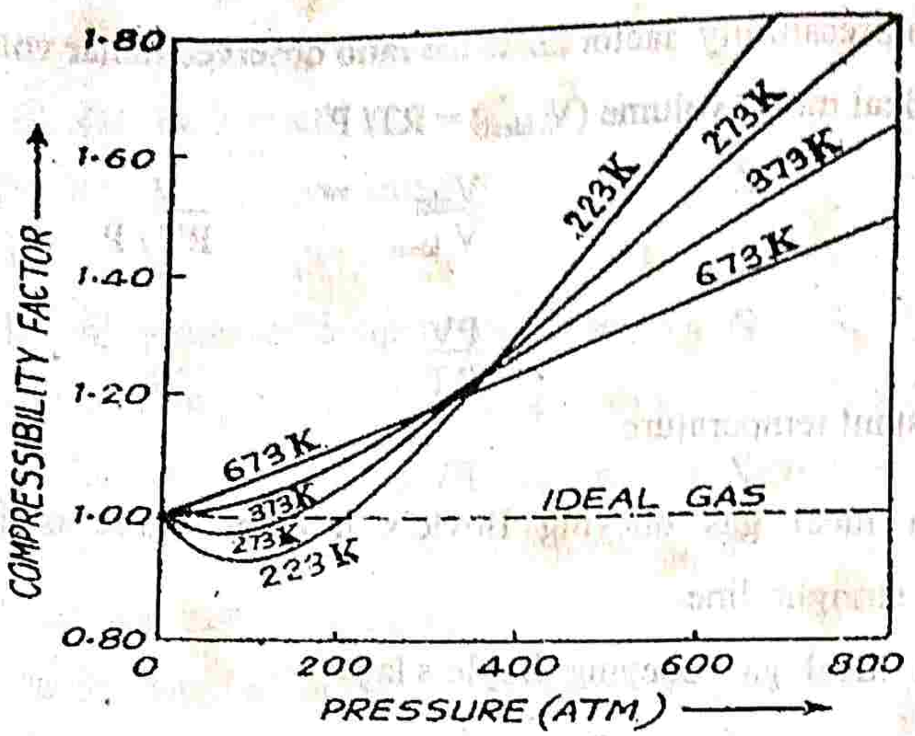
$$Z = 1$$

and is independent of temperature and pressure.

Effect of Pressure.

In the above figure the value of Z for hydrogen increases with increase of pressure. He and Ne resemble hydrogen in this respect. In the case of nitrogen (N_2), Carbon dioxide (CO_2) the value of Z at first decreases, passes through minimum and then increases continuously. The deviation in the case of CO_2 are more pronounced than in the case of N_2.

In this figure relative value of compressibility factor PV/ RT for Nitrogen have been plotted against pressure for a number of temperature. It is seen that at low temperature the slope of the curve is negative.



The shapes of the curves reveal that at higher temperatures nitrogen resembles hydrogen while at lower temperatures it resembles carbon dioxide.

It appears that the nature of deviation from Boyle's law depends on the temperature not on the nature of gas. It has been observed that the gases obey Boyle's law generally at very low pressure and moderately high temperature.

In figure it seen that at very low temperature the slope of Z vs P is negative. At sufficiently high temperature the slope is positive. At some intermediate temperature the slope is zero. This temperature is called Boyle's temperature.

Deviations from Charles' law.

According to Charles law volume of a given mass of gas is directly proportional to its temperature on absolute scale.

$$V \quad \alpha \quad T$$

Pressure of a given mass of a gas is directly proportional to its temperature.

$$P \; \alpha \; T$$

Combining the above two equations

$$PV \; \alpha \; T \quad \text{(or)}$$

$$PV = RT$$

R is a gas constant.

Plot of PV verses T for different gases should produce identical straight line but in practice such identical straight lines are not obtained excerted low pressure.

Deviations from Avogadro's law.

The volume occupied by 1 mole of an ideal gas at STP has been found to be 22.4 lit. If Avogadro's law were strictly true, one mole of every gas should occupy this volume at STP. However, one mole of none of the real gases occupies exactly this volume at STP.

In general the deviations are the greatest in the case of gases which are very easily liquefied e.g., ammonia and ethyl chloride. Further difference is greater at low temperature and high pressure.

Reasons for deviation

The kinetic theory of gases was propounded to explain the behavior of gases. Two possible source of error could arise: either (i) there is something wrong with the postulates describing the model or, (ii). the mathematical treatment is not exact. The gas laws were derived from the kinetic theory of gases on the basis of the following two important assumptions.

(a). Gases consist of tiny molecules which are so small and so far apart that on the average the actual volume of the molecule is negligible compared to the empty space between them.

(b). There are no attractive forces between the molecules. They are therefore completely independent of each other.

(i). Actual volume of the molecules is not negligible. The volume of a gas can be reduced by cooling and compression until it changes into liquid and then solid. This suggests that the molecules of the gas must have an appreciable volume of the same order as volume occupied by the molecules in the solid state.

It has been shown that under normal conditions of temperature and pressure, the actual volume of the molecules is only 0.014 per cent of the total volume. This is negligible fraction. At very high pressure or at very low temperatures the total volume of the gas decreases while the actual volume of the molecules does not change. Hence under these conditions the volume of the molecule is no longer a negligible fraction of the total volume. Therefore this assumption is not valid at high pressure and low temperatures.

(ii). There are attractive forces between the molecules. Gases can be liquefied by cooling and compression. One of the fundamental properties of the liquid is cohesion due to attraction between its molecules.

These forces are inversely proportional to the 6th or 7th power of distance(d) between the molecules.

$$F_{attr} \propto \frac{1}{d^6} \text{ or } \frac{1}{d^7}$$

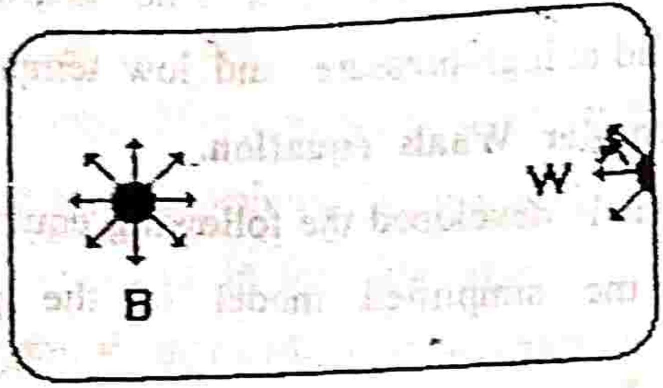
When the pressure is low and temperature is high, the volume of the gas is large, the distance between the molecules of the gas is large. The force of attraction would be negligible small. At higher pressure and low temperature, the intermolecular distance becomes less and therefore, force of attraction is not negligible. Thus this postulate is not valid at high-pressure and low temperature.

Derivation of van der Waals equation.

van der Waals developed the following equation for the real gas by modifying the simplified model of the perfect gas as follows.

(i). **Volume correction.** At high pressure the volume occupied by gas is small. In comparison to this small volume, the volume occupied by the gas molecules is not negligible. Each molecule of a real gas occupies a finite volume which can not be neglected. In the derivation of the ideal gas equation it assumed that the molecules are points having no finite volume. But , they have some finite size actually. So the effective volume available for the molecules to move about will be less than the measured volume of the gas. If V is the measured volume of a gas b is the volume correction, then the corrected volume is (V – b). Where 'b' is van der Waals constant known as co-volume.

(ii). Pressure correction. According to kinetic theory, the pressure of the gas is due to the impacts of the molecules on the walls of the container. The correction for the pressure term is based on the concept of intermolecular attraction. The intermolecular attraction is more pronounced at high pressure and low temperature. A molecule in the interior of the container is subjected to attractive forces on all directions. The force of attraction get cancelled and there is no resultant attractive force on the molecule.



But a molecule near the walls of the container is subjected to attractive forces unequally. The result is the molecule is subjected to inward pull as a result of unbalanced molecular attraction. Hence the observed pressure of the gas is less than the ideal pressure.

corrected pressure = observed pressure + Pressure correction.

The attractive force experienced by a molecule near the walls of the container is proportional to the density of the gas and also to the total number of molecules present per unit volume of a gas. Thus the attractive force experienced by a single molecule near the wall is directly proportional to the square of the density of the gas. But the density of the gas is inversely proportional to its volume.

$$\text{Total inward forces} \quad \alpha \quad \rho^2$$

$$p \quad \alpha \quad \frac{1}{V}$$

$$\text{Pressure correction} \quad \alpha \quad \frac{1}{V^2}$$

Introducing a constant of proportionality 'a', the pressure correction is '$\frac{a}{V^2}$'

$$\text{corrected pressure} \quad = \quad P + \frac{a}{V^2}$$

upon introducing both volume and pressure corrections, the equation of state for a real gas can be written as

$$(P + \frac{a}{V^2})(V - b) = RT$$

Explanation for the behavior of real gases on the basis of van der Waals gas equation

The van der Waals gas equation for one mole of a gas

$$(P + \frac{a}{V^2})(V - b) = RT \qquad \text{----------} \; (1)$$

can also be written as

$$PV + \frac{aV}{V^2} - Pb - \frac{ab}{V^2} = RT \qquad \text{----------} \; (2)$$

Since the values of 'a' and 'b' are very small, the product 'ab' will be negligible small. Hence neglecting '$\frac{ab}{V^2}$' in the above equation, we get

$$PV + \frac{aV}{V^2} - Pb = RT \qquad \text{----------} \; (3)$$

$$PV + \frac{a}{V} - Pb = RT \qquad \text{----------} \; (4)$$

$$= P_i V_i \qquad \text{----------} \; (5)$$

RT

where P_i and V_i are the pressure and the volume of the gas if the gas were ideal.

(i). At low pressure

When the pressure is low, the volume is large. In such a case small addition of pressure due to mutual attraction plays an important part while the volume of the gas molecules themselves, 'b' is negligible as compared to the large total volume V.

$$PV + \frac{a}{V} - Pb = P_i V_i$$

$$PV = P_i V_i - \frac{a}{V}$$

which shows that the observed 'PV' less than RT or $P_i V_i$, the value expected for an ideal gas. As pressure increases, V decreases so that a/V increases.

(ii). At high pressure.

When the pressure is high the volume is small. In this case, therefore, small volume occupied by molecules themselves can not be neglected. Whereas in comparison with the high pressure, small addition of pressure due to mutual attraction is negligible. As such neglecting a/V in equation

$$PV - Pb = RT = P_i V_i$$

$$PV = P_i V_i + Pb$$

i.e., the observed PV is greater than $P_i V_i$, the value expected for an ideal gas by an amount equal to Pb. As the pressure increases, Pb increases and $PV = P_i V_i + Pb$ also increases. This explains the rise in PV value after reaching a minimum when the pressure becomes higher and higher.

(iii). At low temperature.

At ordinary temperature, the term a / V predominates over Pb at low pressure while at high pressure Pb predominates over a / V At some intermediate range of pressure the two terms (Pb and a / V) are nearly equal.

$$\text{Hence} \qquad \frac{a}{V} - Pb = 0$$

$$\text{or } PV = P_i V_i$$

i.e., the gas behave like an ideal gas.

(iv). At high temperature.

At a given pressure, when temperature is very high both P and V are large. Hence the terms b and a / V^2 in the van der Waals equation.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

are both comparatively very small and negligible.

Neglecting the terms in the above equation

$$PV = RT = P_i V_i$$

In other words, the gas behaves like an ideal gas.

B. *Average velocity, Most probable velocity and Root mean square velocity of gaseous molecule.*

The molecules in a gas are moving very fast in a straight lines at random frequently colliding with each other. Their velocities are, therefore, constantly changing. For a quantitative description of the behavior of gas we make use of three different kinds of molecular velocities.

(1). Average velocity ($\bar{u}$)

(2). Most probable velocity (u_p)

(3). Root mean square velocity (RMS velocity c or $\sqrt{\overline{u^2}}$)

(1). Average velocity ($\bar{u}$)

It is defined as the average of various velocity possessed by the molecule at any given temperature, It is obtained by dividing the speed of all the molecule by the total number of molecule. It is denoted by

$$\bar{u} = \frac{u_1 + u_2 + u_3 + \text{-------} + u_n}{N}$$

Thus average velocity $\bar{u} = \sqrt{\frac{8RT}{\pi M}}$

(2). Most probable velocity (u_p)

It is defined as the velocity possessed by the maximum number of molecules of the gas.

s denoted by u_p .

$$u_p = \sqrt{\frac{2RT}{M}}$$

). Root mean square velocity (RMS velocity) c or $\sqrt{\overline{u^2}}$

It is defined as the square root of the mean of the squares of l the velocities of the molecule at any given temperature.

Let u_1 , u_2 , u_3 --- --- u_n be the velocities of various dividual of a gas.

$$c = \sqrt{\frac{u_1 + u_2 + u_3 + \text{--} \;\; \text{--} + u_n}{N}}$$

Then

$$c = \sqrt{\frac{3RT}{M}}$$

Relationship between $\bar{u}$, u_p , c

Mathematical expressions have been derived for the above three types of velocities relating them with molar mass and temperature of gas molecules.

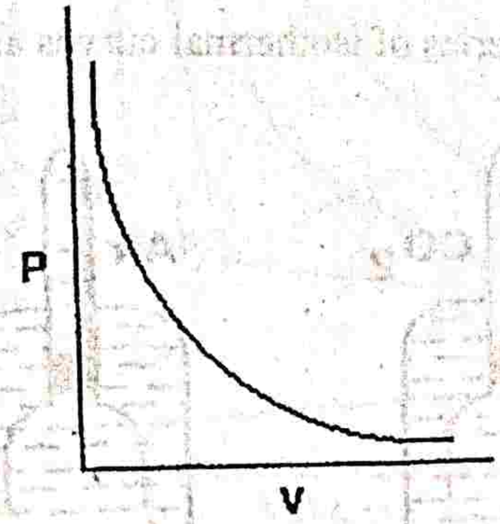
Thus average velocity $\bar{u} = \sqrt{\frac{8RT}{\pi M}}$ --------(1)

Most probable velocity $u_p = \sqrt{\frac{2RT}{M}}$ ---------(2)

Root mean square velocity $c = \sqrt{\frac{3RT}{M}}$ -----------(3)

Dividing equation (1) by (3)

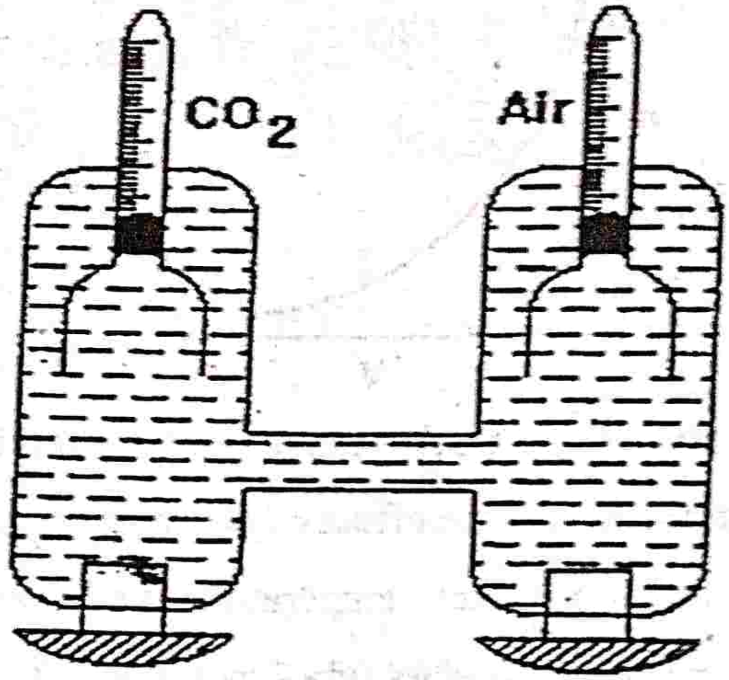
For an ideal gas obeying Boyle's law, it will be a rectangular perbola as shown in fig



ndrew's work on the isotherms of carbon dioxide

Andrew studied the effect of pressure on the volume of carbon oxide at various constant temperature. Andrew's apparatus consists two similar graduated glass tubes mounted side by side. One end of e glass tubes was sealed, while the other end was kept open. In one be, dry CO_2 was enclosed and in the other tube air was enclosed to rve as the reference. These tubes were mounted in copper cylinders hich were connected together and filled with water. The cylinders ere provided with screw plungers. By means of these screw lungers pressure could be varied. The whole apparatus was kept in a onstant temperature bath.

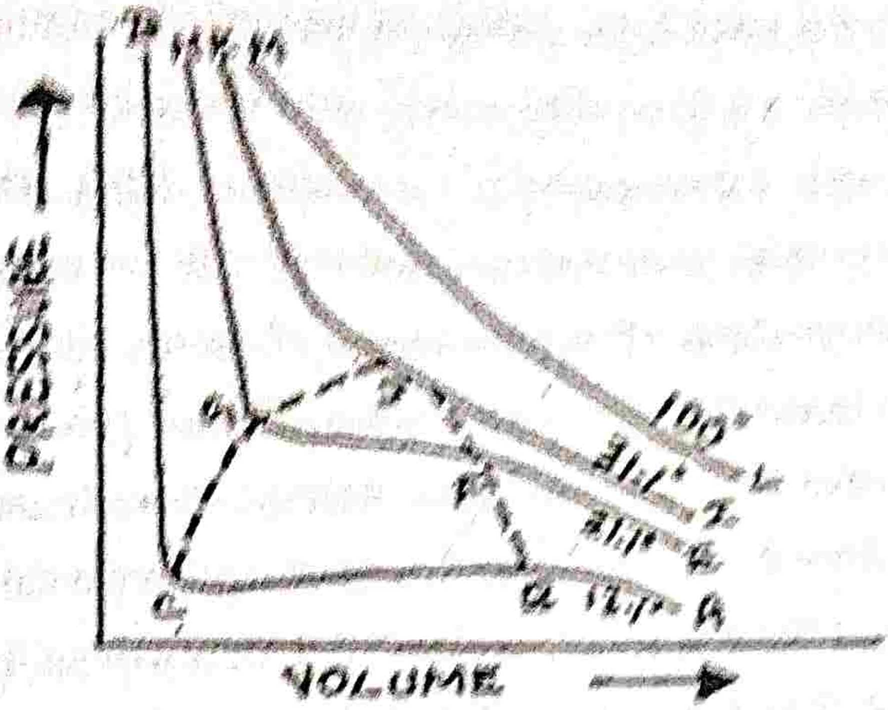
Andrew applied various pressures by means of the screw lungers at constant temperature. In each case he noted down the orresponding volume of carbon dioxide at that temperature. The ressure applied was found out from the volume of air present in the ther tube. This procedure was repeated for various temperatures by changing the temperature of the bath. The volumes of carbon dioxide at different pressure and various constant temperatures were plotted by Andrew. He obtained a series of isothermal curves as shown in fig.



Discussion of the results

At high temperature 100°C, the curve LM is rectangular hyperbolic as required by Boyle's law for an ideal gas.

At 13.1°C the isotherm ABCD is obtained. The point A represents carbon dioxide in the gaseous state occupying a certain volume under a certain pressure. On increasing the pressure there is a gradual decrease in volume as indicated by the curve AB shows the effect of pressure on the volume of carbon dioxide gas. At the point B, the gas begins to liquefy. As liquefaction continues, there is a rapid decrease in the volume as indicated by the line BC.



The very nearly horizontal nature of the line BC is due to the enormous decrease in volume even for a very slight increase in pressure. At the point C, the liquefaction is complete.

As liquids are only slightly compressible, any further increase in pressure at the point C results in a very small decrease in volume. This is clearly seen from the steep line CD which is almost identical.

Thus, along the curve AB, CO_2 exists as a gas and along the curve CD, it exists as a liquid whereas along the horizontal line BC both gas and liquid coexist.

At 21.1°C the isotherm obtained namely EFGH is similar to ABCD. However, the liquefaction begins at a higher pressure and the horizontal portion FG is smaller than BC.

Thus at still higher temperature, the horizontal portion of the curve becomes smaller and smaller. At 31.1°C, in the isotherm obtained namely IJK, the horizontal portion has been reduced just to a point J. At this point J, the distinction between gas and liquid is lost and CO_2 exists in a state called *critical state* where the gas passes into the liquid state indistinguishably (*continuity of state*). This point is known as *critical point* and the isotherm IJK is termed *critical temperature isotherm* . This phenomenon of the smooth merging of a gas into its liquid state is called the critical phenomenon.

Above 31.1°C the isotherms obtained resemble the ideal gas isotherm. They do not have even a trace of the horizontal portion. It shows that if the temperature is above 31.1°C, it will not be possible to liquefy carbon dioxide however high the applied pressure may be.

Similarly, it has been shown that for other gases also there is a limit of temperature above which they can not be liquefied by mere application of pressure however great the pressure may be. This limiting temperature is called the critical temperature.

Thus the critical temperature of carbon dioxide is 31.1°C at or below which only it can be liquefied by applying enough pressure.

On joining the ends of the horizontal portions of the isotherms and the critical point J, a boundary curve CGJFB represented by the dotted line is got. Within the area of the ***boundary*** curve both liquid and gas can co-exist whereas outside this area either liquid or gas alone can exist.

Thus, Andrew's experiments have shown that the critical temperature is the lower limit to the gaseous state and the upper limit to the liquid state. The change from the liquid to gaseous state or vice takes place continuously. So, the liquid and gaseous states are tinuous and not abrupt.

uefaction of gases.

When the gas is cooled the kinetic energy of its molecules reases with the result that some of the sluggish molecules are able to resist the force of intermolecular attraction. They come ser and closer till they change into liquid state. Since increase of essure can also bring the molecules of a gas closer, this may also be lpful in converting a gas into the liquid state. Hence a gas may liquefied by cooling and compressing.

The two essential conditions required for the liquefaction of ases are

). Low temperature, (ii). High pressure

Liquefaction of gases started in 1823, when Faraday succeeded in liquefying chlorine, sulphur dioxide, hydrogen chloride and ammonia etc., by applying pressure and cooling. He failed to liquefy nitrogen, hydrogen, oxygen etc., and hence called them permanent gases.

The recent methods used for liquefying gases make use as the following principles.

(i). Joule Thomson effect

(ii). Adiabatic expansion

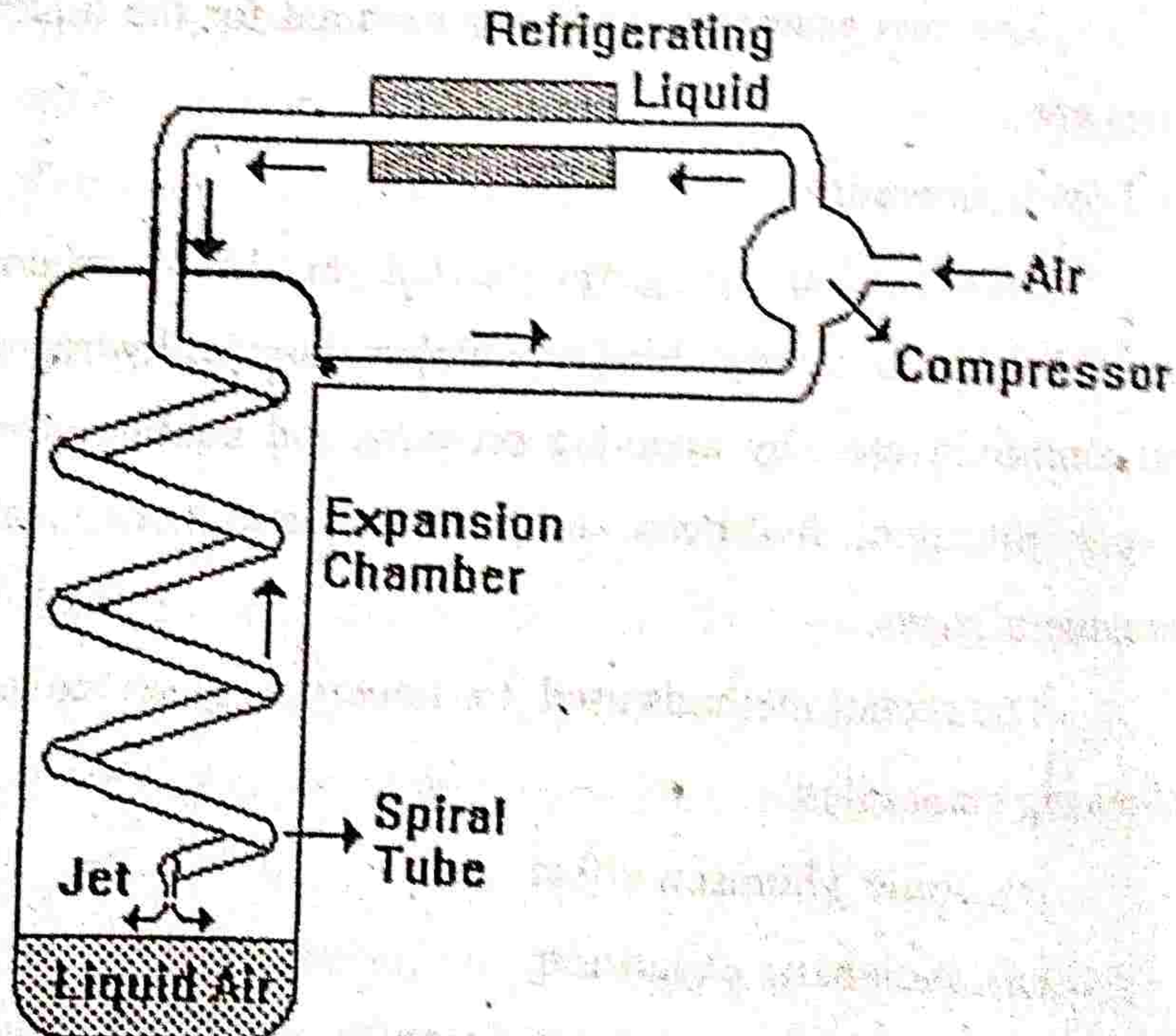
(iii). Adiabatic demagnetization.

Joule Thomson effect.

When a highly compressed gas at a certain temperature is allowed to expand through a porous plug or a small orifice the temperature falls. This cooling effect on expansion is known as Joule – Thomson effect.

Linde's method.

This method makes use of Joule – Thomson effect and is used to liquefy air or any other gas. Pure air or any gas is first compressed to about 200 atmosphere and is allowed to enter the inner tube of the concentric pipes to expand suddenly into the wider chamber.

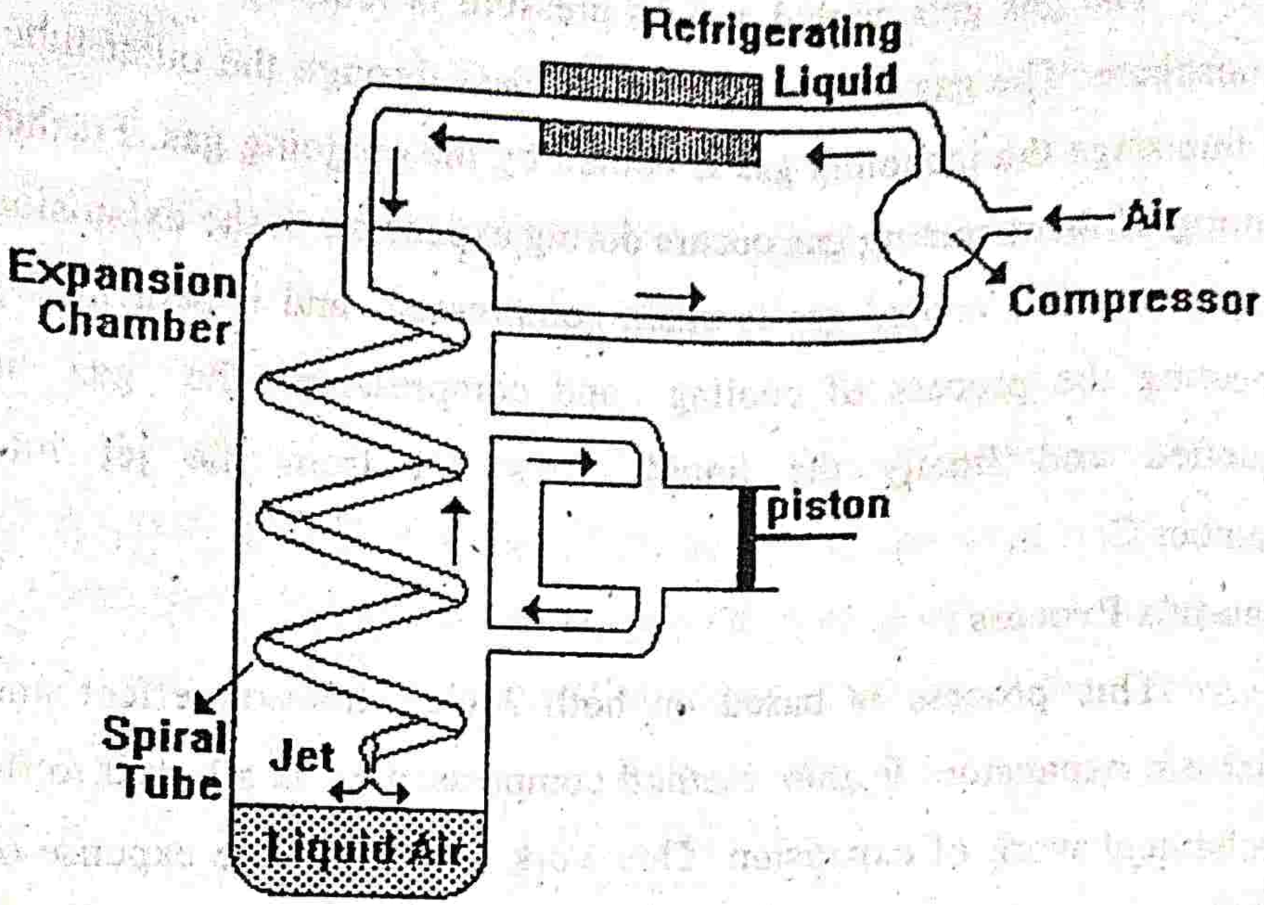


The gas gets cooled and its pressure is reduced to about 50 atmosphere. The gas is now allowed to pass through the outer tube.

The gas gets cooled and its pressure is reduced to about 50 atmosphere. The gas is now allowed to pass through the outer tube. At this stage the incoming gas is cooled by the outgoing gas. Further cooling of the incoming gas occurs during expansion in the expansion chamber . The cooled gas is again compressed and is sent in. By repeating the process of cooling and compression the gas is liquefied and finally the liquid drops out from the jet into chamber C.

Claude's Process

This process is based on both Joule–Thomson effect and adiabatic expansion. In this method compressed air is allowed to do mechanical work of expansion. This work is done at the expense of the kinetic energy of the gas and hence a fall of temperature is noted. This principle is utilized in Claude's process of liquefaction of air. Air compressed to about 200 atmosphere passes through the pipe. A part of air goes down the spiral towards the jet and a part of the air is led into the cylinder provided with an air fight piston. Here the air moves the piston outwards and does external work as a result of which considerable cooling is produced. The cooled air passes up the liquefying chamber during which process it cools the portion of the incoming compressed air. The well cooled incoming compressed air then experience Joule –Thomson expansion when passed through jet and gets cooled further. The above processes take place again and again till the air is liquefied.



Adiabatic demagnetization method.

P. Debye and W. F. Giauque suggested this method based on experimental results. In this method demagnetization of a magnetic substance is brought about under adiabatic conditions. When it is demagnetized external work is done by it and the temperature falls. This method works well at low temperature. In actual practice the substance is first cooled and then adiabatic demagnetized is effected. The lowest temperature which could be obtained by this method is of the order of 10K. This method is used in the liquefaction of gases.

Inversion temperature.

Experiments show that the cooling occurs only if gas is allowed to expand below a certain temperature. This temperature is

Critical Temperature.

The maximum temperature at which a gas can be liquefied is called the critical temperature. At any temperature above the critical temperature the gas can not be liquefied no matter how much pressure is applied.

Critical Pressure

The pressure required to liquefy a gas at critical temperature is called critical pressure.

Critical volume

The volume occupied by 1 mole of a gas at a critical temperature and under critical pressure is called critical volume.

UNIT – III

Comparison Gaseous and Liquid states

States of Matter – III

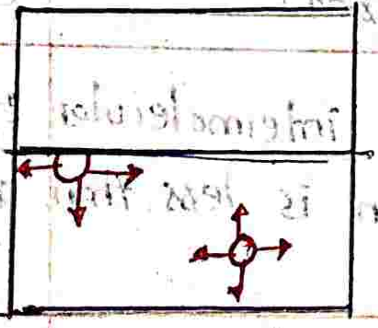
Properties	Liquids	Gases
1) Rigidity	Liquids are not rigid	Gases are not rigid.
2) shape & volume	Liquids have definite volume but not definite shape	Gases have neither definite shape nor definite volume.
3, Fluidity	Liquids can flow from higher to a lower Level.	Gases can flow in all Directions.
4, compressibility	Liquids can be easily compressed.	Gases can be easily compressed.
5) Intermolecular attraction	Liquids intermolecular attraction is less than solids.	Gases intermolecular attraction in the least.
) Storage	Liquids cannot be stored without a vessel.	Gases can be stored in closed vessels only.

Surface tension

Surface tension is the force experienced by the Molecules present in the surface of a liquid. is attracted equally in all directions by the neighbouring moleaules and hence the net pull on the Molecules and it is zero.

A Molecules in the surface of the liquid is partially surrounded by other Molecules and experences a net downward pull.

This downward force acting on the surface of a Liquid is called surface tension. It is defined as the force in dynes at right angles an the surface of a liquid one centemeter length.



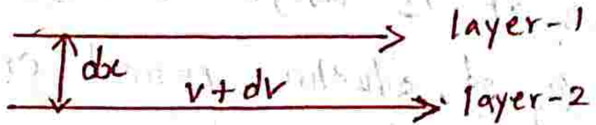
The unit of surface tension is dynes/cm (CGS system) (or) Newton/metre (SI system)

Liquid	ST in dynes/cm
water	73.5
Benzene	29.3
Alcohol	21.7

Viscosity

The molecules in a liquid are arranged in a series of the parallel layers moving one over the other. They move with different velocities. The movement of one layer is opposed by its adjacent layer. This internal resistance to flow is called viscosity.

Consites a layer of liquid with area A cm^2 which is at a distance dx from its adjacent layer and has the velocity difference dv.



The force of friction required to maintain a constant velocity different is given by.

$$F = \eta A \frac{dv}{dx}$$

where η is called the coefficient of viscosity. When $A = 1 cm^2$, $dv = 1\ cm\ sec^{-1}$ and $dx = 1 cm$

$$F = \eta$$

Hence the coefficient of viscosity may be defined as the force per unit area required to maintain a unit velocity difference between two layers of unit distance apart. The unit of viscosity coefficient is poise

1 poise = 1 dyne cm^{-2} sec^{-1} (CGS system)

1 poise = 1 newton m^{-2} sec^{-2} (SI system)

Ionic solids :

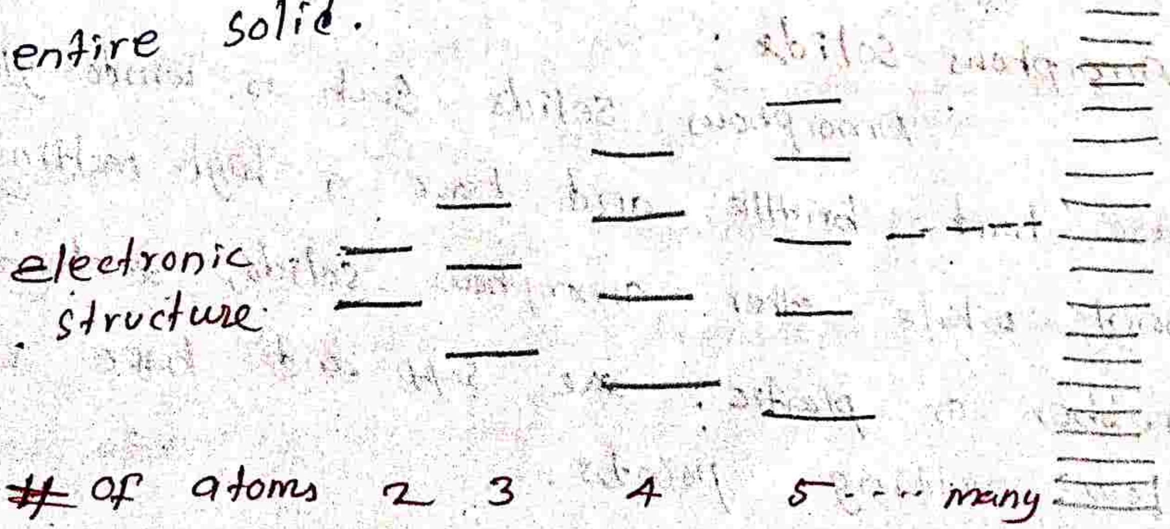
Ionic solids consists of cations and anions held together by the strength of their opposite charges. The force the holds oppositely charged particles together is called an "electrostatic force. .

In ionic compounds we treated all ionic solids as if they consisted of crystals in which all the ions has identical sizes. As you can probably guess, ions come in wide variety of sizes.

eg: sodium chloride.

Metallic solids :

It was explained that metals are good conductors of electricity and heat, have high malleability, high ductility and are shiny, As it turns out the properties of metals stem from the nature of metallic bonds. The cations in a metallic solid remain in stationary crystalline positions while the valence electrons from each metal are free to wander throughout the entire solid.



The dotted line in this structure corresponed to the intermolecular force holding the water molecules together in the crystal.

Molecular solids frequently have low melting points and are easily broken apart.

Molecular solids are also extremely poor conductors of electricity. Aside from ice, other examples of molecular solids are sugar and dry ice.

Atomic solids :

Atomic solids are formed when the noble gases become cold enough to freeze. As with molecular solids, there are very weak intermolecular forces known as "London dispersion forces" that hold these atoms together. Because their interactions are extremely weak, frozen noble gases tend to be soft and have very low melting points.

Amorphous solids :

Amorphous solids such as windo glass, are hard, brittle, and have a high melting point, while other amorphous solids, such as rubber or plastic, are soft and have very low melting points.

crystal :

A crystal (or) crystalline solid is a solid material whose constituents are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all direction.

Crystallographic systems :

The terms crystal system, crystal family and lattice system each refer to one of several classes of space groups, lattices, point groups, or crystals. Crystal systems, crystal families are lattice systems are similar.

In particular the trigonal crystal system is often confused with the rhombohedral lattice system and the term "crystal system is sometimes used to mean lattice system or crystal family.

Conductors :

In electronics, a conductor is a substance in which electrical charge carriers move easily from atom to atom with the application of voltage. conductivity in general is the capacity to transmit something, such as electricity or heat.

eg: mercury, saturated salt-water

insulator:

A material or an object that does not easily allow heat, electricity, light, or sound to pass through. it air, cloth and rubber are good electrical insulators. feathers and wool make good thermal insulators compare conductor.

Semiconductor:

A Semiconductor material has an electrical conductivity value falling between that of a conductor, such as metallic copper, and an insulator such as glass..

Some eg of semiconductors are silicon, germanium, gallium arsenide, and elements near the so called metalloid staircase on the periodic table.

Intrinsic and extrinsic semiconductors.

In Intrinsic semiconductor also called an undoped semiconductor or i type semiconductor is a pure semiconductor without any significant dopant species present. The number of charge carrier is therefore determined by the properties of the material itself instead of the amount of impurities.

The electrical conductivity of intrinsic semiconductors can be due to crystallographic defects or electron excitation. In an intrinsic semiconductor the number of electrons in the conduction band is equal to the number of holes in the valence band. An example is $Hg_{0.8}$ $Cd_{0.2}$ Te at room temperature.

Extrinsic Semiconductors :

In an extrinsic semiconductor it is these foregn dopant atoms in the crystal lattice that mainly provide the charge carriers which carry electric current through the crystal.

The doping agents used are of two types, resulting in two types of extrinsic semiconductor. An electron donor dopant is an atom which, when incorporated in the crystal, release a mobile conduction electron into the crystal lattice.

An extrinsic semiconductor which has been doped with electron donor atom is called an n- type semiconductor.

An electron acceptor dopant is an atom from the lattice creating a vacancy where an electron should be called a hole the crystal like a positively charged particles.

Doped with electron acceptor atoms is called a p- type semiconductor.

Colloidal state

The colloidal state is a particulate phase in which the particles range in size from 1.0 nm to 10^1 nm dispersed in a continuous phase, the dispersion medium. The extremely large interface between the two phase dictates that on surface energy considerations alone, the colloidal state is thermodynamically unstable.

Classification of colloids :

Colloids consist of a dispersed phase and dispersion medium. They are classifield on the basis of different properties of the dispersed phase and the medium.

Hydrophilic colloids :

These are water-loving colloids. The colloid particles are attracted to the water. They are also known as rerersible sols.

Examples include Agar, gelatin, pectin etc.

Hydrophobic colloids :

These are the opposite in nature to hydrophilic colloids. The colloid particles are repelled by water. They are also called irreversible sols.

eg : gold sols, clay particles etc

Emulsions

An emulsion can be defined as a colloid consisting of two or more non- homogeneous type of liquids wherein one of the liquid contains the dispersion of different form of liquids.

Dispersed phase	Dispersed medium	Type of colloid	Example
Solid	Solid	Solid	Some coloured glasses and gemstones
solid	Liquid	solid	paints, cell fluids
Solid	Gas	Aerosal	smoke, Dust
Liquid	Solid	Gel	cheese, Butter, Jellies
Liquid	Liquid	Emulsion	milk, Hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid	pumice stone, Foam – Rubber
Gas	Liquid	Foam	Froth, whipped cream, soap Lather

Applications and uses of Emulsion :

Emulsions are very much famous in various fields of science. It is utillized in the tanning and dyeing industries, used in the manufacturing process of lastics and synthetic rubber.

* usually used in
phamaceuticals, personal hygiene.

* microemulsions are used to deliver vaccines to kill various microbes.

* It is used in fire fighting.

* Nanoemulsions such as soybean oil are used to kill microbes.

* mayonnaise is an oil an water emulsion with egg yolk or sodium stearoyl lactylate.

Classification and Bancraft's rule

Bancroft's Rule states that "The phase in which on emulsifier is more soluble constitutes the continuous phase. It's not a rule, because it is frequently wrong. But it has a grain of truth and a wild variety of explanations.

If you use HLD-NAC you don't need Bancraft.

Classifications of Emulsions

Oil in wates (o/w)

wates in oil (w/o)

Oil in wates emulsions :

* Oil is the dispersed phase and water is a dispersion medium.

* If water is added it is miscible with the emulsion.

- If oil is added it is not miscible with the emulsion.
- Addition of small amount of electrolyte makes emulsion conducting.
- water is a continuous phase.
- Basic metal sulphates water-soluble alkali metal soaps are used as emulsifiers.

water in oil type (w/o)

In the type of emulsions water is the dispersed phase and oil is the dispersion medium. eg: cod liver oil in which particles of water are dispersed in oil, cold creams.

Application of colloids :

Colloids play a very important role in everyday life as well as in industry, agriculture, Medicine and biology.

Foods:

Many of our foods are colloidal in nature for example :

⇒ Milk is an emulsion of fat dispersed in water.

⇒ Gelatin is added to ice cream as a protective agent so as to pressure it's smoothness

⇒ whipped cream, fruit jellies, salad dressings eggs and a host of other materials used as food, ~~are~~ are colloidal in nature.

Medicine:

A number of medicinal and pharmaceutical preparation are emulsion, colloidal in nature. In this form they can be more effective and are easily assimilated. Colloidal calcium and gold, for instance, are administered by injections to raise the vitality of the human system.

Industrial :

⇒ Soap the index of modern civilization, is a colloidal electrolyte. The same is true of a series of never detergents and welling agents, that have been produced in recent years.

⇒ paints, varnishe's, enamels, celluloses, resine gums, glus, and other adhesives. rayon, nylon, terylene, leather, paper etc. are all colloidal.

Cottrell precipitator:

Smoker and dusts are a noisance and create health problems in industrial areas. Actually these are dispersions of electrically charged colloidal particles in air. the removal of these particles from air involves the principle of electrophoresis.

Sewage disposal:

Sewage water consists of particles of dirt, rubbish, mud etc. which are of colloidal dimensions and carry electric charge and therefore, do not settle down easily. On creating an electric field in the sewage tank, these particles migrate to the oppositely charged electrodes, get neutralised and settldown at the bottom. It will be seen that here, too, the electrophoretic property of colloids has been made use of.

Clasification of water:

Sometimes slight turbidity is noticed in water. This is due to the presence of

(-ve)ly charged particles of very [illegible] clay The addition of potash alum (or) aluminium Sulphate furnishes the trivalent aluminium ions (Al^{3+}) which cause the coagulation of the clay particles. which. therefore, settles down leaving water in clear state.

Detergent action of Soap:

Most of the dirt or dust sticks on to grease or Some Oily material which Some how gathers on cloth. As grease is not readily wetted by water. It is difficult to clean the garment by water alone. The addition of Soap lowers the interfacial tension between and and grease and thus causes the emulsification of grease in water. The mechanical action such as rubbing etc. releases the dirt.

Artifical rain:

clouds consist of charged particles of water dispersed in air. Rain is caused by the aggregation of these minute particles. Some scien have succeeded in causing such aggregation by artifical means such as by throwing electrified sand from aeroplane.

Formation of deltas:

The deltas of the mouths of great rivers are formed by the precipitation of the charged clay particles, carried as suspension in the river water, by the action of salts present in sea water.

Smoke screens:

Smoke screens are used in warfare for the purpose of concealment and camouflage. Smoke screens generally consist of very fine particles of titanium oxide dispersed in air and are rejected from the aireplanes. As titanium oxide is very heavy, the smoke screen drops down rapidly as a certain of dazzling whiteness.

Bancroft's Rule

The Bancroft rule states: "The phase in which on emulsifier is more soluble constitutes the continuous phase".

In all of the typical emulsions, there are tiny particles (discrete phase) suspended in a liquid (continuous phase). In an oil-in-water emulsion, oil is the discrete phase, while water is the continuous phase.

what makes an emulsions oil-in-wat (or) water-in-oil is not the relative percentag. of oil or water, but which phase the emulsifi is more soluble in. So eventhough there may be a formula that's 60% oil and 40% water. If the emulsifier chosen is more soluble in wate it will create an oil-in-water system.

There are some exuptions to Bancro rule, but it's a very careful rule of thumb for most systems.

The hydrophilic - lipophilic balance (HLB) of a surfactant can be used in order to determen whether it's a good choice for the desired emulsion or not.

* In oil in water emulsions - use emulcifying agents that are more soluble in water than in oil (High HLB surfactants)

* In water in oil emulsions - use emulsifying agents that are more soluble in oil than in water [Low HLB surfactants]

Bancroft's rule suggests that the type of emulsion is dictated by the emulsifier and that the emulsifier should be soluble in the continuous phase. This empirical observation can be nationallised by considering the interfacial. tension at the oil- surfactant and water surfactant interfaces.

CHAPTER 1✓

THERMODYNAMICS

1.1 Thermodynamic Variables (or) Properties

Intensive and Extensive properties

Properties whose values do not depend on the amount of the material present in the system are called intensive properties. Examples: Density, surface tension, specific gravity, pressure, temperature, boiling point, melting point, refractive index, viscosity, molar volume *etc.*

Properties whose values depend on the amount of material present in the system are called extensive properties. Ex.: volume, number of moles, mass, free energy, entropy, heat capacity *etc.*

State functions and Path functions

The variables which are determined by the initial and final states of the system are called the state functions. The examples are internal energy, entropy, free energy and enthalpy.

The variables which depend upon the path followed in transferring from the initial state to the final state are called the path functions. Examples are heat and work.

System and Surrounding

A system is defined as any particular part of the universe about which we are interested. The rest of the universe is called Surrounding. There are different types of system, viz., isolated, closed, and open systems.

i) Isolated system: A system which can exchange neither energy nor matter with its surrounding is called an isolated system. Example: Water contained in an insulated closed vessel.

ii) Closed system: A system which can exchange energy but not matter with its surrounding is called a closed system. Example: Water contained in a closed but not insulated vessel.

iii) Open system: A system which can exchange both matter and energy with its surrounding is called an open system. Example: Water taken in an open beaker.

1.2 Thermodynamic Processes

Cyclic process

When a system after completing a series of changes returns to its original state, it is said to have completed a cycle. Such a process is known as a cyclic process.

Reversible process

A thermodynamically reversible process is a process which is carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force. In other words, a reversible process is a process in which the direction of the process can be reversed at any step by an infinitesimally small change in temperature or pressure.

The following are the conditions for reversibility:

i) There should be equilibrium at every intermediate stage of the process.

ii) The process should be capable of proceeding in both directions.

iii) The process should take place very slowly.

iv) The initial state of process should be attainable back without any permanent effect on the surrounding.

Irreversible process

An irreversible process is a spontaneous process and it proceeds in only one direction. All natural processes are irreversible. An irreversible process does not consist of an infinite series of infinitesimally small steps which can be reversed from one equilibrium state to another.

Isothermal process

A process in which the temperature remains constant throughout the course is said to be isothermal. For an isothermal process, the change in the internal energy of the system, ΔE is zero. The amount of heat absorbed by the system is completely converted in to work. It is possible only when there is transfer of heat from system to surrounding and vice versa. Example: An exothermic reaction gives out its energy to the surroundings so that the temperature of the system remains constant.

Adiabatic process

A process which is carried out in an insulated system is known as an adiabatic process. In this process no heat can leave or enter the system from the surrounding. The temperature of the system decreases during the process. The work done for the process is equal to the decrease in the internal energy of the system. i.e., $W = -\Delta E$.

Isobaric process

If the pressure of the system remains unchanged during a process, it is said to be an isobaric process.

Isochoric process

If the volume of the system remains unchanged during a process, it is said to be an isochoric process.

Spontaneous process

If a process occurs on its own accord, it is said to be a spontaneous process. Many of the spontaneous processes are natural processes and also irreversible. Example: heat flow from a hot end to a cold end.

Non-spontaneous process

If a process does not occur on its own accord, it is said to be a non-spontaneous process.

1.3 Laws of Thermodynamics

1) Zeroth law of thermodynamics

Zeroth law of thermodynamics states that when two bodies have equality of temperature with a third body, they in turn have an equality of temperature with each other.

This law has introduced the concept of temperature. The relation between centigrade scale (°C) and absolute scale (K) is $T = t + 273.15$

Zeroth law does not need any further experiments on its support since it logically precedes the first and the second law of thermodynamics.

2) First law of thermodynamics

The various statements of the first law are:

i) The energy can neither be created nor destroyed.

ii) Energy may change from one form into another form and the total energy of an isolated system always remains unchanged. Therefore, the First law is also known as *law of conservation of energy.*

iii) It is impossible to construct a perpetual motion engine.

iv) Whenever a quantity of one kind of energy is produced, an exactly equivalent amount of another kind must be used.

Mathematical statement of this law is given as:

$$\Delta E = q \pm W$$

where, ΔE is the change in energy of a system, q is the quantity of heat and W is the work done.

If the work is done by the surrounding on the system (compression) W is positive, so that

$$\Delta E = q + W = q + P\Delta V$$

If the work is done by the system on the surrounding (expansion), W is negative, so that

$$\Delta E = q - W = q - P\Delta V$$

ΔV is the change in volume.

Internal Energy

Every substance is associated with a certain amount of energy known as internal energy (E). The internal energy is the sum of internal potential energy and internal kinetic energy. It varies with temperature, volume, pressure, and chemical composition. The change in the internal energy is given by $\Delta E = E_2 - E_1$ where E_1 and E_2 are the internal energies of a system in the initial and final state respectively. Therefore it is a state function.

According to first law of thermodynamics, $\Delta E = Q - W$ where Q is the heat change and W is the work done and equal to $P\Delta V$.

Therefore, $\Delta E = Q - P\Delta V$

At constant volume, $P\Delta V = 0$ and hence $\Delta E_V = Q_V$

That is, at constant volume, change in internal energy is equal to change in heat content of the system in going from reactant state to product state.

Enthalpy

Thermal changes at constant pressure are expressed in terms of enthalpy or heat content of the system. The enthalpy is defined as sum of internal energy and PV. i.e.,

$$H = E + PV$$

It is a state function. It varies with P, V, T and concentration.

$$\Delta H = H_P - H_R$$

H_R and H_P are the enthalpies of the reactants and products (initial and final state) of the system, respectively.

Relation between ΔH and ΔE

Enthalpy change at constant pressure is ΔH and enthalpy change at constant volume is ΔE. considering the enthalpy at initial state (H_1) and final state (H_2),

$$\Delta H = H_2 - H_1$$

We know

$$H_1 = E_1 + P_1V_1$$

$$H_2 = E_2 + P_2V_2$$

Therefore,

$$\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

$$= (E_2 - E_1) + P_2V_2 - P_1V_1$$

$$= \Delta E + P_2V_2 - P_1V_1$$

At constant pressure, $P_2 = P_1 = P$ and $(V_2 - V_1) = \Delta V$

$$\Delta H = \Delta E + P\Delta V$$

Putting the initial and final states as reactants and products, respectively,

$$P\Delta V = n_PRT - n_RRT = (n_P - n_R)RT$$

$$P\Delta V = \Delta n_g RT$$

Therefore, $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta n_g = \begin{pmatrix}\text{number of moles of}\\ \text{gaseous products}\end{pmatrix} - \begin{pmatrix}\text{number of moles of}\\ \text{gaseous reactants}\end{pmatrix}$$

Endothermic and exothermic reactions

In an exothermic reaction, $H_P < H_R$

That is, $\Delta H = H_P - H_R < 0$ (negative)

In an endothermic reaction, $H_P > H_R$

That is, $\Delta H = H_P - H_R > 0$ (positive)

For example,

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad (\Delta H = +131.4 \text{ kJ/mol})$$

As ΔH is positive, this reaction is endothermic in nature.

Sign conventions of ΔE, ΔH and W

Heat is absorbed by the system, ΔH is positive

Heat is given out by the system, ΔH is negative

Energy is absorbed by the system, ΔE is positive

Energy is given out by the system, ΔE is negative

Work is done on the system, W is positive

Work is done by the system, W is negative

Physical significance of enthalpy

Every substance or system has some definite energy. This energy stored within the substance available for conversion into heat is called the heat content or enthalpy. Absolute value of enthalpy cannot be measured, but in thermodynamics, change in enthalpy can be measured experimentally.

A positive enthalpy change indicates that the change (reaction) is endothermic and a negative enthalpy change indicates that the change is exothermic.

Molar heat capacity (C)

C_P is the molar heat capacity of a gas at constant pressure and it can be defined as the amount of heat required to raise the temperature of one mole of the gas at constant pressure through one degree.

$$C_P = \frac{dH}{dT} = \frac{q_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

C_V is the molar heat capacity of a gas at constant volume and it can be defined as the amount of heat required to raise the temperature of one mole of the gas at constant volume through one degree.

$$C_V = \frac{dE}{dT} = \frac{q_v}{dT} = \left(\frac{\partial E}{\partial T}\right)_V$$

Or, it can be written as

$$dH = C_P\, dT = C_P\,(T_2 - T_1)$$

$$dE = C_V\, dT = C_V\,(T_2 - T_1)$$

Relation between C_P and C_V

We know that

$$C_P = \frac{dH}{dT} \quad \text{and} \quad C_V = \frac{dE}{dT}$$

For one mole of an ideal gas,

$$H = E + PV \quad \text{and} \quad PV = RT$$

Therefore, $H = E + RT$

Differentiating with time,

$$\frac{dH}{dT} = \frac{dE}{dT} + R\frac{dT}{dT}$$

Thus

$$C_P = C_V + R \text{ (or)}, \quad C_P - C_V = R$$

Limitations of First law of thermodynamics

- The first law indicates that there is a transformation between different forms of energy, but it does not give out any information about the feasibility of such transformations.
- The first law does not provide any information whether the process is spontaneous or not.

- The first law states that the work obtained is equivalent to heat absorbed, but it gives no information regarding the conditions under which a conversion is possible, that is, the first law does not specify the conditions or the controlling factors.

3) Second Law of Thermodynamics

Statements:

1) All spontaneous processes like the flow of heat from hot end to cold end, diffusion of gas from high pressure to low pressure, the flow of water down a hill, *etc*. are irreversible

2) It is impossible to convert all heat completely into work and some heat must be lost somewhere.

3) All reversible heat engines working between the given two temperatures will have the same efficiency.

4) Planck's statement: It is impossible to construct a machine working in cycles which can convert heat completely into equivalent amount of work without producing changes elsewhere.

5) Classius statement: Without the use of external agency, heat cannot itself pass from a cold body to a hot body.

6) In a reversible process the entropy changes of the system and the surrounding taken together remains constant ($\Delta S = 0$). A reversible process that involves no change in entropy ($\Delta S = 0$) does not proceed on its own accord and is termed as a non-spontaneous process. In an irreversible process it increases ($\Delta S > 0$). That is, a process accompanied by an increase in entropy ($\Delta S > 0$) tends to be a spontaneous process. A process which proceeds on its own accord, without any outside assistance is termed as a spontaneous or natural process.

7) In a reversible (non-spontaneous) process the free energy change (ΔG) of the system and surrounding taken together remains constant. In an irreversible (spontaneous) process, it decreases, *i.e.* $\Delta G \leq 0$.

Combined form of First and Second laws

$$dq = dE + PdV \qquad \text{(I law)}$$

$$TdS = dq_{rev} \qquad \text{(II law)}$$

Therefore,

$$TdS = dE + PdV \qquad \text{(I and II laws combined)}$$

Criteria of spontaneity

i) A spontaneous change is one way and for a reverse change to occur, work has to be done.

ii) A spontaneous process may take place very rapidly or very slowly.

iii) A spontaneous change is accompanied by a decrease of internal energy and enthalpy. It implies that only such processes which are exothermic will occur.

iv) For any spontaneous process it is possible to devise a machine by which we can obtain useful work.

v) The force which is responsible for the spontaneity of a process is called the driving force.

vi) A minimum energy is required for spontaneity.

For an infinitesimal small change, the condition for spontaneity can be written as

$$dS_{system} + dS_{surrounding} \geq 0 \qquad (1)$$

Where the sign '>' stands for irreversible (or) spontaneous (or) feasible process and the sign '=' for reversible (or) non-spontaneous (or) equilibrium process.

The various criteria may be deduced as under:

We know,

$$dS_{surrounding} = -\frac{dq_{rev}}{T} \qquad \text{(surrounding loses heat)}$$

$$= -\frac{(dE + PdV)}{T} \qquad (\because \text{I law}) \qquad (2)$$

From eq. (1)

$$dS_{system} \geq 0 - dS_{surrounding}$$

Substituting eq. (2)

$$TdS \geq dE + PdV \qquad (3)$$

Eq. (3) is also the basic one for predicting the feasibility of a process. In this equation, '>' stands for spontaneous (irreversible) and '=' for non-spontaneous (reversible) process.

Case (i) - In terms of entropy change:

If the internal energy and volume of the system are kept constant (that is, dE = 0 and dV = 0), eq. (3) becomes

$$(TdS)_{E,V} \geq 0$$

That is $$(dS)_{E,V} \geq 0 \qquad (4)$$

where '>' stands for irreversible and '=' for reversible process. That is, if the entropy change is positive (entropy increases during the process), the change is spontaneous. And, if the entropy change is zero (entropy remains constant during the process), the change is reversible.

Case (ii) – In terms of internal energy change (dS = 0)

$$(dE)_{S,V} \leq 0 \qquad (5)$$

This implies that under constant entropy, if the volume change is accompanied by a decrease of internal energy, the process is irreversible. If the internal energy does not change, the process is reversible.

Case (iii) – In terms of enthalpy

$$H = E + PV$$
$$dH = dE + PdV + VdP$$
$$dH - VdP = dE + PdV \qquad (6)$$

Comparing eqs. (3) and (6),

$$TdS \geq dH - VdP$$

If dS =0 and dP = 0, then

$$(dH)_{S,P} \leq 0 \qquad (7)$$

where '<' stands for irreversible and '=' for reversible process. That is, if the enthalpy change is negative (enthalpy decreases during the process), the change is spontaneous. And, if the enthalpy change is zero (enthalpy remains constant during the process), the change is reversible.

Case (iv) – In terms of free energy

$$G = H - TS$$
$$G = E + PV - TS$$
$$dG = dE + PdV + VdP - TdS - SdT$$

$$dE + PdV = dG - VdP + TdS + SdT \qquad (8)$$

Comparing eqs. (3) and (8),

$$TdS \geq dG - VdP + TdS + SdT$$
$$0 \geq dG - VdP + SdT$$

At constant pressure and temperature,

$$(dG)_{P,T} \leq 0 \qquad (9)$$

where '<' stands for irreversible and '=' for reversible process. That is, if the free energy change is negative (free energy decreases during the process), the change is spontaneous. And, if the free energy change is zero (free energy remains constant during the process), the change is reversible and said to be in equilibrium. If the free energy change is positive (free energy increases during the process), the change is not feasible.

Heat engine

A machine which can do work by heat that flows out spontaneously from a high temperature source to a low temperature sink is called a heat engine.

The efficiency of the heat engine depends upon the temperature of the source and sink. It does not depend upon the working substance and design of the engine.

Efficiency = $\frac{W}{Q} = \frac{(T_2 - T_1)}{T_2}$ where W is the total work done by engine and Q is amount heat absorbed in the first step. T_2 and T_1 are the temperatures of source and sink respectively.

Entropy

Entropy (S) refers to disorderliness of a system. The change of entropy (ΔS) of the system is defined as the integral of all terms involving heat change (q) divided by the absolute temperature during the process. i.e., $\Delta S = \int \frac{q_{rev}}{T}$

For an engine working irreversibly, the efficiency is less than one. There in a reversible cycle, the sum of (q_{rev}/ T) terms is less than zero.

i.e., $\oint \frac{q_{rev}}{T} < 0$

Unit of entropy: cal /deg (or) eu (entropy unit) or Joules per Kelvin.

Entropy change for an ideal gas under different conditions

We know

$$TdS = dE + PdV$$

For 1 mole of an ideal gas, the equation becomes

$$TdS = C_V dT + \frac{RT}{V} dV \qquad (\because C_V = \frac{dE}{dT} \text{ and } PV = RT)$$

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V}$$

If volume changed from V1 to V2 when the temperature changes from T1 to T2, then the entropy change accompanying the process is given as

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = C_V \ln\frac{T_2}{T_1} + R \ln\frac{V_2}{V_1} \qquad (10)$$

Eq. (10) can be written as

$$\Delta S = (C_P - R)\ln\frac{T_2}{T_1} + R\ln\frac{T_2 P_1}{T_1 P_2} \qquad (\because C_P\text{-}C_V = R \text{ and } PV = RT)$$

That is

$$\Delta S = C_P \ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2} \qquad (11)$$

Eqs. (10) and (11) are used to obtain the entropy changes for an ideal gas under different conditions.

Case (i) – Isothermal ($T_1 = T_2$)

Eq. (11) becomes

$$(\Delta S)_T = R\ln\frac{P_1}{P_2} = R\ln\frac{V_2}{V_1}$$

CHAPTER 2

REACTION KINETICS

Chemical Kinetics deals with the study of rates of chemical reactions and with the description of the mechanism by which the reactions proceed.

2.1 Concept of reaction rate

In a reaction as of given below

$$A + 3B \rightleftharpoons 2C$$

One molecule of A and three molecules of B react in the forward reaction to give two molecules of C. The molecules A and B are called the reactants and the molecule C is called the product. Similarly, in the backward reaction, two molecules of C decompose to give one molecule of A and three molecules of B. In the forward reaction, as the reaction proceeds, the concentration of the reactants (A and B) decreases and that of the product (C) increases.

The rate or velocity of a reaction is defined as a very small change in concentration of either the reactant or the product in a very small interval of time. For the reaction given above,

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}[C]$$

Rate has the unit, mol lit^{-1} sec^{-1} (or) mol dm^{-3} sec^{-1}

Rate of a reaction is not uniform throughout the reaction and decreases exponentially with time.

Rate law and rate equation

Rate law states that the rate of a reaction is directl proportional to the active mass (concentration) of the reactants. Fo the simple reaction A + B → C + D, the rate law can be depicted as

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

Or, $$-\frac{d[A]}{dt} = k[A][B]$$

This is the rate equation, where *k* is called the rate constant.

For example, $N_2 + 3H_2 \rightleftharpoons 2NH_3$

The rate law is written as: $Rate = -\frac{d[N_2]}{dt} \propto [N_2][H_2]^3$

The rate equation is written as: $-\frac{d[N_2]}{dt} = k[N_2][H_2]^3$

It must be noted that the form of rate law cannot be deduced from the stoichiometric equation, but be decided by experiment. For example,

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O$$

$$Rate = -\frac{d[NO]}{dt} \propto [NO]^2[H_2]$$

$$-\frac{d[NO]}{dt} = k[NO]^2[H_2]$$

Types of chemical reactions

1. Ionic reactions: Reactions between ions

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$

2. Molecular reactions: Reactions between molecules

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

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

2.2 Factors influencing reaction rates

Factors that influence the reaction rates of chemical reactions include the concentration of reactants, temperature, the physical state of reactants, and their dispersion, the solvent and the presence of a catalyst.

i) Concentration effects

Increase of concentration of a reactant provides more reactant particles and as a result, the number of particles that collide per unit time increases. The reaction rate usually increases as the concentration of the reactants increases.

ii) Temperature effects

Increasing the temperature of a system increases the average kinetic energy of its constituent particles. As a result, the particle move faster, possess greater energy and collide more frequently per unit time. Hence, the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate decreases with decreasing temperature. For example, refrigeration decreases the rate of biochemical reactions in bacteria and hence retards their rate of growth in foods.

Increase of temperature in some reactions produces different products. For example,

$$2CH_3CH_2OH \xrightarrow{H_2SO_4,\ 100^{o}C} CH_3CH_2OCH_2CH_3 + H_2O$$

$$CH_3CH_2OH \xrightarrow{H_2SO_4,\ 180^{o}C} C_2H_4 + H_2O$$

iii) Phase and Surface Area effects

If the reactants are uniformly dispersed in a single homogeneous solution, the reaction rate depends on concentration and temperature. If the reaction is heterogeneous, however, the reactants are in two different phases, the collisions between the reactants can occur only at interfaces between phases. Hence, the reaction is substantially reduced. Thus, the reaction rate of heterogeneous reaction depends on the surface area of the more condensed phase.

For example, in automobile engines, the gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigourous reaction.

iv) Solvent effects

The nature of solvent can also affect the reaction rates of solute particles.

For example, the reaction between sodium acetate and methyl iodide

$$CH_3CO_2Na_{(soln)} + CH_3I_{(l)} \rightarrow CH_3CO_2CH_3\ _{(soln)} + NaI_{(soln)}$$

This reaction is 10000 times faster in dimethylformamide (DMF; dielectric constant = 36.7) than in methanol (dielectric constant =

32.6). The hydrogen bonding ability of methanol reduces the reactivity of the oxygen atoms in sodium acetate.

Solvent viscosity is also important in determining reaction rates. The reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

v) Catalyst effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. Therefore, the catalyzed reactions proceed much faster than the corresponding uncatalyzed reactions. Also, catalysts favour the formation of a particular product in some reactions.

There are also some substances which, when added to the reaction mixture, decreases the reaction rates. These substances are known as negative catalysts or inhibitors.

2.3 Molecularity and Order of reactions

Molecularity: The minimum number of molecules of the same or different reactants involved in a chemical reaction is called the molecularity of the reaction. It can be known from the stoichiometry of the reaction.

$A \rightarrow$ product(s) – Molecularity is one; unimolecular.

$A + B \rightarrow$ product(s) – Molecularity is two; bimolecular.

$RCl + H_2O \rightarrow ROH + HCl$ – Molecularity is two; bimolecular.

$A + B + C \rightarrow$ product(s) – Molecularity is three; termolecular

$A + 2B \rightarrow C + D$ – Molecularity is three; termolecular

$RCOOR' + H_2O + H_3O^+ \rightarrow RCOOH + R'OH + H_3O^+$ – Molecularity is one; Pseudo unimolecular

Order: The number of atoms or molecules of the reactants whose concentrations determine the rate (or) the sum of powers of the concentration terms that appear in the rate equation is called the order of the reaction.

For a rate law $\frac{d[x]}{dt} = k$, order is zero (zero-order reaction)

For a rate law $\frac{d[x]}{dt} = k[A]$, order is one (First-order reaction)

For a rate law $\frac{d[x]}{dt} = \mathrm{k[A]}^2$, order is 2 (second-order reaction)

For a rate law $\frac{d[x]}{dt} = \mathrm{k[A][B]}$, order is 2.

For the reaction $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, order seems to be four, but actually it is three as is evident from the rate law is $\frac{dx}{dt} = k[NO]^2[H_2]$. Therefore, order is an experimental quantity.

Problem 2.1: Determine the order with respect to each species and overall order of the following reactions.

i) $2HCrO_4^- + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 8H_2O$

The rate law is $Rate = k[HCrO_4^-][I^-]^2[H^+]^2$

First order with respect to $HCrO_4^-$

Second order with respect to I^-

Second order with respect to H^+

The overall order is $1 + 2 + 2 = 5$

ii) $H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$

The rate law is $Rate = k[H_2O_2][I^-]$

First order with respect to H_2O_2

First order with respect to I^-

Zero order with respect to H^+

The overall order is 1 + 2 = 3

Differences between order and molecularity

Order	Molecularity
corresponds to number of molecules taking part in the rate-determining step of the reaction.	corresponds to the number of molecules taking part in the stoichiometry of the reaction.
is equal to the sum of powers of the concentration terms in the rate equation	is equal to the number of molecules which take part in a single step chemical reaction
is an experimental quantity; can't be known without arriving at the rate law.	can be known from the stoichiometry of the reaction.
can be a whole or fractional number, even zero	can be a whole number only and can never be zero
mechanism cannot be known from order of a reaction	mechanism can be known from molecularity of a reaction

Pseudo unimolecular reaction

The acid hydrolysis of ester involves reaction between one ester molecule and one water molecule and it seems to be a bimolecular reaction.

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH + H_3O^+$$

As water is present in large excess in the reaction mixture, change its concentration during the course of reaction is negligible. The rat of this reaction depends only on the concentration of ester and doe not depend on the concentration of water. Therefore, this reaction called a pseudo unimolecular reaction.

In general, reactions in which one of two reactants (A and B is present in large excess ([A] >> [B]) follows first-order kinetics with respect to B, and is considered as pseudo unimolecular reactions.

2.4 Derivation of rate constant

A) First-order reactions

In a reaction of first-order, only one molecule reacts to give the product(s).

$$A \longrightarrow \text{Product(s)}$$

Let *a* be the number of moles of A at time zero, *x* be the number of moles of product formed after a time, *t sec*. Therefore the number of moles of A remaining unreacted at time *t sec* is $(a - x)$.

According to Law of mass action,

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

Rearranging,

$$\frac{dx}{(a-x)} = k.dt \qquad (1)$$

On integration,

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

$$-\ln(a-x) = kt + C \tag{2}$$

where *C* is the integration constant. The value of C is found as:

At $t = 0$, $x = 0$ and therefore $(a-x) = a$; Equation (2) becomes

$$-\ln a = C$$

Substituting this value in equation (2), we get

$$-\ln(a-x) = kt - \ln a$$

$$\ln a - \ln(a-x) = kt$$

$$k = \frac{1}{t}\ln\frac{a}{a-x}$$

Converting to logarithm

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \tag{3}$$

Equation (3) is the rate expression for a first-order reaction.

The unit for first-order rate constant can be shown as

$$k = \frac{2.303}{\sec}\log\frac{mol/lit}{mol/lit} = \sec^{-1}$$

Half-life period

The time required to reduce the concentration of a reactant to half of its initial value is known as the half-change time or half-life period ($t_{1/2}$).

That is, at $t_{1/2}$, $(a-x) = a/2$

Equation (3) is written as

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

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

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k}$$

Thus, the half-life period of a first-order reaction is independent of initial concentration of the reactant.

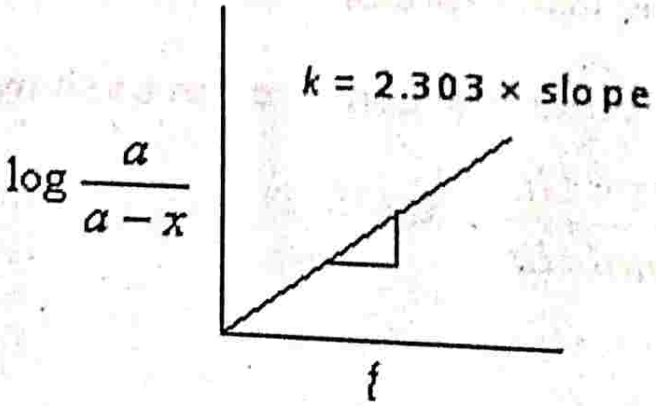
Determination by graphical method

The first-order rate constant expression is

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

On rearranging,

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



A graph is plotted between $\log \frac{a}{a-x}$ and t and a straight line passing through origin is obtained. The slope is equal to k/2.303. Therefore,

k = 2.303 × slope

Examples for first-order reactions

i) Dehydration of oxalic acid

$$(COOH)_2 \xrightarrow{\Delta} CO + CO_2 + H_2O$$

This reaction can be followed by finding out the concentration of oxalic acid at definite interval of time by titrating a small of volume of the reaction mixture against standardized $KMnO_4$. The volume of $KMnO_4$ used for each titration is directly proportional to $(a - x)$.

ii) Decomposition of H_2O_2

$$2H_2O_2 \rightarrow 2H_2O + O_2 \; (H_2O_2 \rightarrow H_2O + O \text{ (slow)}; \; O + O \rightarrow O_2 \text{ (fast)})$$

This reaction is followed by titrating equal volume of H_2O_2 against $KMnO_4$ at definite interval of time. The titre value is proportional to $(a - x)$.

iii) Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 \text{ (glucose)} + C_6H_{12}O_6 \text{ (fructose)}$$

This reaction is a pseudo unimolecular reaction and obeys first-order kinetics. It is followed by measuring the change in optical rotation of the reaction mixture by polarimetry.

B) Second-order reactions

i) When both the reactants are of same concentration

	A	+	B	→	Products
at time 0	a		a		
at time t	$a - x$		$a - x$		

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

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

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k}$$

Thus, the half-life period of a first-order reaction is independent of initial concentration of the reactant.

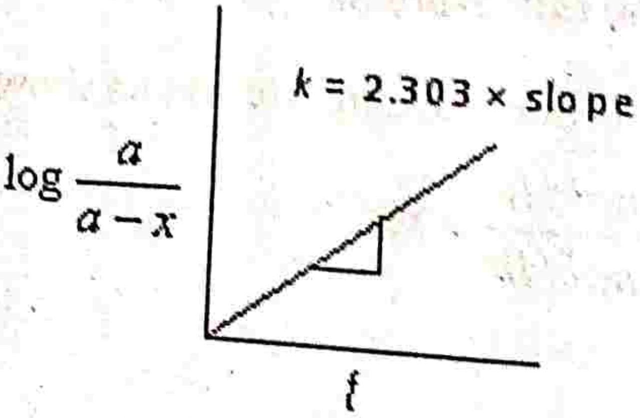
Determination by graphical method

The first-order rate constant expression is

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

On rearranging,

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



A graph is plotted between $\log \frac{a}{a-x}$ and t and a straight line passing through origin is obtained. The slope is equal to $k/2.303$. Therefore,

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

UNIT – V

Surface process and kinetics

4.3 Adsorption

When a finely divided solid is stirred into a dilute solution of a dye, the depth of colour in the solution is much decreased. If a finely divided solid is exposed to a gas at low pressure, the pressure decreases noticeably. The dye or gas is adsorbed on the surface.

Adsorption is the process in which the molecules, atoms (or) ionic species of a substance get attached to the surface of another. Example: Ammonia is adsorbed on charcoal. Here, ammonia is known as the *adsorbate* and charcoal as *absorbent*. The phenomenon of adsorption is known as *surface phenomena*.

Adsorption and Free Energy Relation

As a result of adsorption there is a decrease in the residual force acting along the surface of the adsorbate. Consequently, there is a decrease of surface energy which appears as heat. The adsorption is accompanied by the evolution of heat. The amount of heat evolved when one mole of a gas (or) a vapour is adsorbed on a solid is known as *molar heat of adsorption*.

The ΔH for this process is negative since the state of adsorbate gets changed from more random gaseous state to less random adsorbed state on the surface of the solid. The adsorption is also accompanied by decrease of entropy of the system. We know that

$$\Delta G = \Delta H - T\Delta S$$

Since ΔH and ΔS are both negative, ΔG should also be negative. T heat of adsorption per molecule of the adsorbate goes on decreasi and ΔH becomes equal to $T\Delta S$.

$$\Delta H = T\Delta S \qquad \text{i.e. } \Delta G = 0$$

This is the state at which the equilibrium is established.

4.1.1 Types of adsorption

There are two types of adsorption, *viz.*, i) Physical adsorptio (or) physisorption and (ii) Chemical adsorption (or) chemisorption.

The two types of adsorption differ upon the interactio between adsorbate and the adsorbent. If the adsorbate and th adsorbent are held together by means of van der Walls' forces, the this type of adsorption is known as *Physisorption*.

If the adsorption is by a chemical process (chemical interaction between the surface of the atom of the adsorbent and the atom o the adsorbate, then this type of adsorption is known as *Chemisorption*.

Differences between physisorption and chemisorption

Characteristics	Physisorption	Chemisorption
Nature of the operating force	Weak van der Walls forces	Strong van der Walls forces
Occurrence	At ordinary temperature	At high temperature
Heat of adsorption	Low	High
Specificity	Non-specific	Highly specific
Reversibility	Almost completely reversible	Irreversible

Structure of the adsorbed layer	Multi-layers	Monolayer
When temperature increases	Adsorption decreases	Adsorption increases and then decreases

At the temperature of liquid nitrogen (~190 °C), nitrogen is physically adsorbed on iron as nitrogen molecules. The amount of N_2 adsorbed decreases with rise in temperature. At room temperature iron does not adsorb nitrogen at all. At high temperatures, ~500 °C, nitrogen is chemisorbed on the iron surface as nitrogen atoms.

4.1.2 Factors affecting adsorption

The following are the factors which affect the adsorption,

(1) Nature of the adsorbate (gas) and adsorbent (solid)

(i) In general, easily liquefiable gases e.g., CO_2, NH_3, Cl_2 and SO_2 *etc.* are adsorbed to a greater extent than the elemental gases e.g. H_2, O_2, N_2, He *etc.* (while chemisorption is specific in nature.)

(ii) Porous and finely powdered solid *e.g.* charcoal, fullers earth, adsorb more as compared to the hard non-porous materials. Due to this property powdered charcoal is used in gas masks.

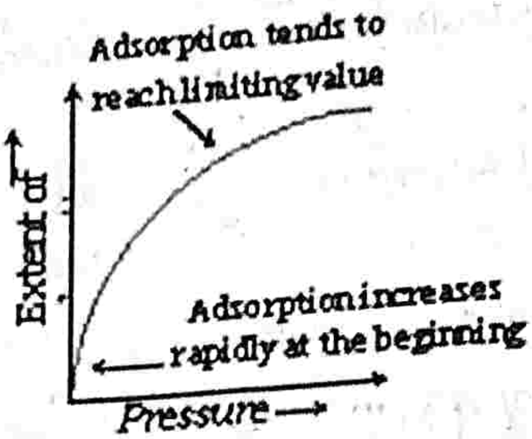
(2) Surface area of the solid adsorbent

(i) The extent of adsorption depends directly upon the surface area of the adsorbent, *i.e.* larger the surface area of the adsorbent, greater is the extent of adsorption.

(ii) Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

(3) Effect of pressure on the adsorbate gas

(i) An increase in the pressure of the adsorbate gas increases the extent of adsorption.

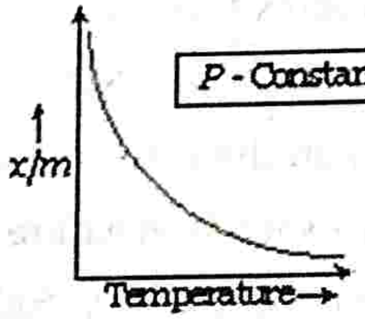


(ii) At low pressure, adsorption increases rapidly with pressure.

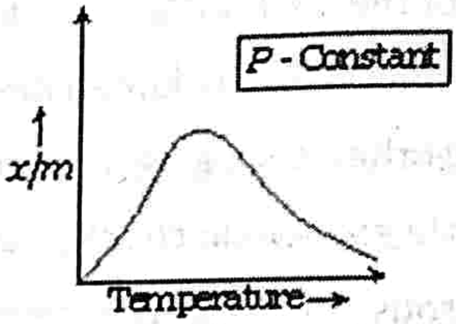
(iii) Small range of pressure, the extent of adsorption is found to be directly proportional to the pressure.

(iv) At high pressure (closer to the saturation vapour pressure of the gas), the adsorption tends to achieve a limiting value.

(4) Effect of temperature



Physical adsorption



Chemical adsorption

(i) As adsorption is accompanied by evolution of heat, so according to the Le-Chatelier's principle, the magnitude of adsorption should decrease with rise in temperature.

(ii) The relationship between the extent of adsorption and temperature at any constant pressure is called adsorption isobar.

(iii) A physical adsorption isobar shows a decrease in x/m (where 'm' is the mass of the adsorbent and 'x' that of adsorbate) as the temperature rises.

(iv) The isobar of chemisorption shows an increase in the beginning and then decrease as the temperature rises.

4.1.3 Adsorption Isotherms

An adsorption isotherm is the relationship between the pressure of a gas and the amount adsorbed on the adsorbent at constant temperature.

1) Freundlich adsorption isotherm

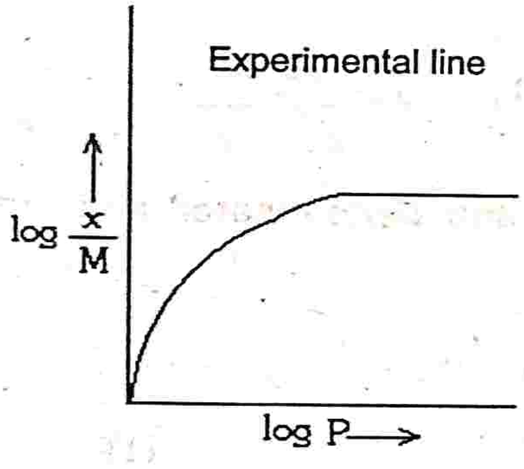
The variation in the amount of gas adsorbed per unit mass of the adsorbent with pressure at constant temperature is given by the expression

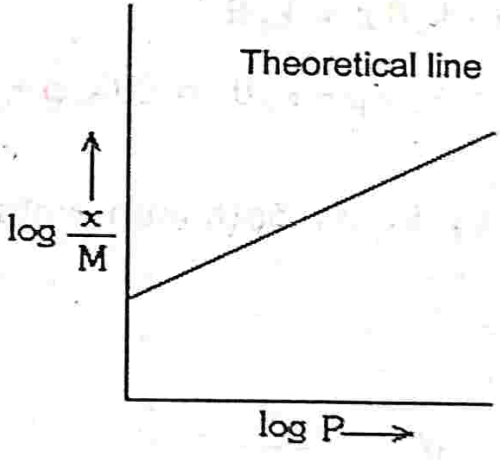
$$\frac{x}{M} = KP^{1/n}$$

where x is the mass of the gas adsorbed, M is the mass of the adsorbent, P is the equilibrium pressure and K and n are the constants which depend upon the nature of the adsorbate and adsorbent and the temperature. Therefore,

$$\log\frac{x}{M} = \log K + \frac{1}{n}\log P$$

A plot of $\log\frac{x}{M}$ against *log P* should be a straight line with slope $\frac{1}{n}$ and intercept *log K*.





It is found that the Freundlich adsorption isotherm is obeyed at low pressures of the adsorbate and it fails if the concentration (or pressure) of the adsorbate is too high.

Distribution law :

When a solute distributes itself between two immiscible solvents in contact with each other, there exists for similar molecular species at a given temperature. a constant ratio of distribution between the two solvents irrespective of the total amount of the solute and irrespective of any molecular species.

Distribution of a component between two immiscible solvents and solvent extraction

The most important application of the distribution law is in the process of extraction in the laboratory as well as in industry. In the laboratory for instance, it is frequently used for the removal of a dissolved organic substance from aqueous solution with solvents. such as benzene. ether chloroform, carbon tetrachloride etc. The advantage is taken of the fact that the partition coefficient of most of the organic compounds is very largely in favour of organic solvents.

The Same principle applies in the desilverization of lead by parke's process. The argentiferous is heated to 800°c molten zinc is then added behave as two immiscible liquid, and silver behaves as a Solute which is more soluble in zinc than in lead, the portition coefficient being of the order of 300 at 800°c silver therefore passes readily from the heavier lead light into lighter zinc layer which is separated by repeating the process three or four times, almost the entire amount of silver passes in to the zinc layer.

we can derived from general formula

$$K_D = \frac{W_1/v}{(W - W_1)/v}$$

$$W_1 = W \cdot \frac{K_D v}{K_D v + v}$$

$$W_2 = W_1 \frac{K_D v}{K_D v + v} = W\left(\frac{K_D v}{K_D v + v}\right)^2$$

$$W_n = W\left(\frac{K_D v}{K_D v + v}\right)^n$$

KD n should be as large as possible but n×v is equal to the total volume of the extracting liquid available it is a constant. n is large and v is small. The efficiency of extraction increase by increasing the number of extractions using only a small amount of the extracting solvents.

Distribution constant:

The distribution constant KD is the equilibrium constant for the distribution of an analyte in two immiscible solvents.

$$[A]_i = \left(\frac{V_{aq}}{V_{org} K_D + V_{aq}} \right)^i [A]_0$$

Where $[A]_i$ is the concentration of a remaining after extracting V_{aq} milliliters of solution with original concentration of $[A]_0$ with i portions of the organic solvent each with a volume of V_{org}.

Application of distribution law :

* solvent extraction
* partition chromatography
* release of drug from dosage forms.
* passage of drug through membrances
* preservation of emulsion and creams
* formation of solubilized system.

2.1 Concept of reaction rate

In a reaction as of given below

$$A + 3B \rightleftharpoons 2C$$

One molecule of A and three molecules of B react in the forward reaction to give two molecules of C. The molecules A and B are called the reactants and the molecule C is called the product. Similarly, in the backward reaction, two molecules of C decompose to give one molecule of A and three molecules of B. In the forward reaction, as the reaction proceeds, the concentration of the reactants (A and B) decreases and that of the product (C) increases.

The rate or velocity of a reaction is defined as a very small change in concentration of either the reactant or the product in a very small interval of time. For the reaction given above,

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}[C]$$

Rate has the unit, mol lit^{-1} sec^{-1} (or) mol dm^{-3} sec^{-1}

Rate of a reaction is not uniform throughout the reaction and decreases exponentially with time.

Rate law and rate equation

Rate law states that the rate of a reaction is directly proportional to the active mass (concentration) of the reactants. For the simple reaction A + B → C + D, the rate law can be depicted as

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

Or, $$-\frac{d[A]}{dt} = k[A][B]$$

This is the rate equation, where *k* is called the rate constant.

For example, $N_2 + 3H_2 \rightleftharpoons 2NH_3$

The rate law is written as: $$Rate = -\frac{d[N_2]}{dt} \propto [N_2][H_2]^3$$

The rate equation is written as: $$-\frac{d[N_2]}{dt} = k[N_2][H_2]^3$$

It must be noted that the form of rate law cannot be deduced from the stoichiometric equation, but be decided by experiment. For example,

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O$$

$$Rate = -\frac{d[NO]}{dt} \propto [NO]^2[H_2]$$

$$-\frac{d[NO]}{dt} = k[NO]^2[H_2]$$

Types of chemical reactions

1. Ionic reactions: Reactions between ions

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$

2. Molecular reactions: Reactions between molecules

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

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

2.2 Factors influencing reaction rates

Factors that influence the reaction rates of chemical reactions include the concentration of reactants, temperature, the physical state of reactants, and their dispersion, the solvent and the presence of a catalyst.

i) Concentration effects

Increase of concentration of a reactant provides more reactant particles and as a result, the number of particles that collide per unit time increases. The reaction rate usually increases as the concentration of the reactants increases.

ii) Temperature effects

Increasing the temperature of a system increases the average kinetic energy of its constituent particles. As a result, the particle move faster, possess greater energy and collide more frequently per unit time. Hence, the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate decreases with decreasing temperature. For example, refrigeration decreases the rate of biochemical reactions in bacteria and hence retards their rate of growth in foods.

Increase of temperature in some reactions produces different products. For example,

$$2CH_3CH_2OH \xrightarrow{H_2SO_4,\ 100\,^oC} CH_3CH_2OCH_2CH_3 + H_2O$$

$$CH_3CH_2OH \xrightarrow{H_2SO_4,\ 180\,^oC} C_2H_4 + H_2O$$

iii) Phase and Surface Area effects

If the reactants are uniformly dispersed in a single homogeneous solution, the reaction rate depends on concentration and temperature. If the reaction is heterogeneous, however, the reactants are in two different phases, the collisions between the reactants can occur only at interfaces between phases. Hence, the reaction is substantially reduced. Thus, the reaction rate of heterogeneous reaction depends on the surface area of the more condensed phase.

For example, in automobile engines, the gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigourous reaction.

iv) Solvent effects

The nature of solvent can also affect the reaction rates of solute particles.

For example, the reaction between sodium acetate and methyl iodide

$$CH_3CO_2Na_{(soln)} + CH_3I_{(l)} \rightarrow CH_3CO_2CH_3\,_{(soln)} + NaI_{(soln)}$$

This reaction is 10000 times faster in dimethylformamide (DMF; dielectric constant = 36.7) than in methanol (dielectric constant =

32.6). The hydrogen bonding ability of methanol reduces the reactivity of the oxygen atoms in sodium acetate.

Solvent viscosity is also important in determining reaction rates. The reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

v) Catalyst effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. Therefore, the catalyzed reactions proceed much faster than the corresponding uncatalyzed reactions. Also, catalysts favour the formation of a particular product in some reactions.

There are also some substances which, when added to the reaction mixture, decreases the reaction rates. These substances are known as negative catalysts or inhibitors.

2.3 Molecularity and Order of reactions

Molecularity: The minimum number of molecules of the same or different reactants involved in a chemical reaction is called the molecularity of the reaction. It can be known from the stoichiometry of the reaction.

$A \rightarrow$ product(s) – Molecularity is one; unimolecular.

$A + B \rightarrow$ product(s) – Molecularity is two; bimolecular.

$RCl + H_2O \rightarrow ROH + HCl$ – Molecularity is two; bimolecular.

$A + B + C \rightarrow$ product(s) – Molecularity is three; termolecular

$A + 2B \rightarrow C + D$ – Molecularity is three; termolecular

$RCOOR' + H_2O + H_3O^+ \rightarrow RCOOH + R'OH + H_3O^+$ – Molecularity is one; Pseudo unimolecular

Order: The number of atoms or molecules of the reactants whose concentrations determine the rate (or) the sum of powers of the concentration terms that appear in the rate equation is called the order of the reaction.

For a rate law $\frac{d[x]}{dt} = k$, order is zero (zero-order reaction)

For a rate law $\frac{d[x]}{dt} = k[A]$, order is one (First-order reaction)

For a rate law $\frac{d[x]}{dt} = k[A]^2$, order is 2 (second-order reaction)

For a rate law $\frac{d[x]}{dt} = k[A][B]$, order is 2.

For the reaction $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, order seems to be four, but actually it is three as is evident from the rate law is $\frac{dx}{dt} = k[NO]^2[H_2]$. Therefore, order is an experimental quantity.

Problem 2.1: Determine the order with respect to each species and overall order of the following reactions.

i) $2HCrO_4^- + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 8H_2O$

The rate law is $Rate = k[HCrO_4^-][I^-]^2[H^+]^2$

First order with respect to $HCrO_4^-$

Second order with respect to I^-

Second order with respect to H^+

The overall order is $1 + 2 + 2 = 5$

ii) $H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$

The rate law is $Rate = k[H_2O_2][I^-]$

First order with respect to H_2O_2

First order with respect to I^-

Zero order with respect to H^+

The overall order is 1 + 2 = 3

Differences between order and molecularity

Order	Molecularity
corresponds to number of molecules taking part in the rate-determining step of the reaction.	corresponds to the number of molecules taking part in the stoichiometry of the reaction.
is equal to the sum of powers of the concentration terms in the rate equation	is equal to the number of molecules which take part in a single step chemical reaction
is an experimental quantity; can't be known without arriving at the rate law.	can be known from the stoichiometry of the reaction.
can be a whole or fractional number, even zero	can be a whole number only and can never be zero
mechanism cannot be known from order of a reaction	mechanism can be known from molecularity of a reaction

Pseudo unimolecular reaction

The acid hydrolysis of ester involves reaction between one ester molecule and one water molecule and it seems to be a bimolecular reaction.

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH + H_3O^+$$

As water is present in large excess in the reaction mixture, change in its concentration during the course of reaction is negligible. The rate of this reaction depends only on the concentration of ester and does not depend on the concentration of water. Therefore, this reaction is called a pseudo unimolecular reaction.

In general, reactions in which one of two reactants (A and B) is present in large excess ([A] >> [B]) follows first-order kinetics with respect to B, and is considered as pseudo unimolecular reactions.

2.4 Derivation of rate constant

A) First-order reactions

In a reaction of first-order, only one molecule reacts to give the product(s).

$$A \longrightarrow \text{Product(s)}$$

Let *a* be the number of moles of A at time zero, *x* be the number of moles of product formed after a time, *t sec*. Therefore the number of moles of A remaining unreacted at time *t sec* is (*a* – *x*).

According to Law of mass action,

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

Rearranging,

$$\frac{dx}{(a-x)} = k.dt \qquad (1)$$

On integration,

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

$$-\ln(a-x) = kt + C \qquad (2)$$

where *C* is the integration constant. The value of C is found as:

At $t = 0$, $x = 0$ and therefore $(a - x) = a$; Equation (2) becomes

$$-\ln a = C$$

Substituting this value in equation (2), we get

$$-\ln(a-x) = kt - \ln a$$

$$\ln a - \ln(a-x) = kt$$

$$k = \frac{1}{t}\ln\frac{a}{a-x}$$

Converting to logarithm

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \qquad (3)$$

Equation (3) is the rate expression for a first-order reaction.

The unit for first-order rate constant can be shown as

$$k = \frac{2.303}{\sec}\log\frac{mol/lit}{mol/lit} = \sec^{-1}$$

Half-life period

The time required to reduce the concentration of a reactant to half of its initial value is known as the half-change time or half-life period ($t_{1/2}$).

That is, at $t_{1/2}$, $(a - x) = a/2$

Equation (3) is written as

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

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

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k}$$

Thus, the half-life period of a first-order reaction is independent of initial concentration of the reactant.

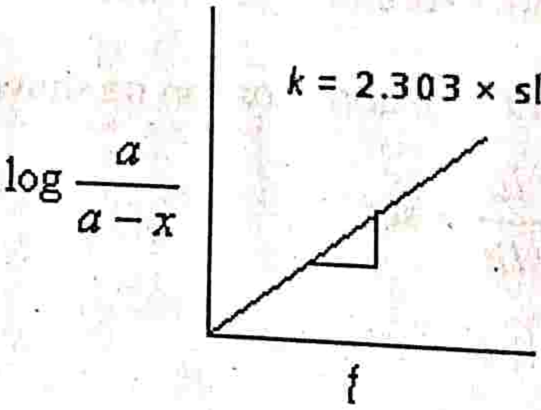
Determination by graphical method

The first-order rate constant expression is

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

On rearranging,

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



A graph is plotted between $\log \frac{a}{a-x}$ and t and a straight line passing through origin is obtained. The slope is equal to $k/2.303$. Therefore,

$k = 2.303 \times$ slope

Catalyst:

Catalyst is a substance which alters the rate of a chemical reaction with out it self under going any chemical change.

Characteristics of a catalyst :

i. A catalyst remains chemically unchanged at the end of the reaction. However a change in physical from may take place. e.g., coarse MnO_2 used in the decomposition $KClO_3$ becomes finely powdered at the end.

ii. Minute amounts of catalysts are sufficient to alter the rate of reaction. e.g., 1 mg of fine Pt powder is enough to catalyse the combination H_2 and O_2.

iii. The catalyst are usually specific (i.e, efficient only for a particular recation).

iv. The catalyst can only alter the speed of a reaction, but does not affect the state of equilibrium (it alters the rates of forward and backward reactions to the same extent).

v. A catalyst can not start a reaction, but only increase or decrease its rate.

Positive Catalyst :

If a catalyst increases the rate of the reaction it is called a positive catalyst. E.g., MnO_2 increase the rate of decomposition of $KClO_3$.

Negative catalyst (Inhibitor) :

If a catalyst decreases the catalytic activity of a catalyst of the reaction it is called a negative catalyst. E.g., Alcohol retards the oxidation of chloroform.

Catalysis:

Catalysis is a phenomenon in which a substance is used to alter the rate of a chemical reaction.

Types of Catalysis:

There are two main types of catalysis, namely,

i. Homogeneous catalysis

ii. Heterogeneous catalysis.

1. Homogenous Catalysis :

In this type of catalytic reaction, catalyst, reactants and products remain in the same phase and the reacting system as a whole remains homogeneous throughout.

i. Gas phase homogeneous catalysis :

There are few known cases of this type of catalysis. Nitric oxide gas catalyses the combination of sulphur dioxide and oxygen in the lead chamber process of the manufacture of sulphuric acid.

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

The nitric oxide gas also acts as a catalyst in the oxidation of carbon monoxide with oxygen.

$$2CO + O_2 \xrightarrow{NO} 2CO_2$$

ii. Liquid phase homogeneous catalysis :

Hydrolysis of cane sugar in aqueous solution in the presence of a mineral acid as catalyst is an example for liquid phase homogeneous catalysis.

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Hydrolysis of methyl acetate in the presence of an acid is another example.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

2. Heterogeneous catalysis :

In this type of catalysis, the catalyst and the reactants are in different phases. This type of catalysis is of industrial importance and has been studied in detail than homogeneous catalysis. The catalysts which are generally used in this type are : Pt, Ni, Cu and Fe usually in a state fine power. Oxides of Zn, Cr, Bi and Mo are also used as catalysts.

a. Heterogeneous catalysts having gaseous-reactants and solid catalysis:

There are large number of gaseous reactions which are examples for, heterogeneous catalysis. A few of them are as follows :

i. Oxidation of sulphur dioxide to sulphur trioxide in the contact process of the manufacture of sulphuric acid with V_2O_5 as catalyst.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

ii. Combination of hydrogen and oxygen to give water in the presence of Pt as catalyst.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

iii. Formation of ammonia from hydrogen and nitrogen in the presence of Fe_2O_3 as catalyst.

$$N_2 + 3H_2 \xrightarrow{Fe_2O_3} 3NH_3$$

b. Heterogeneous catalysts having liquid reactants and solid catalysts:

Decomposition of hydrogen peroxide in presence of colloidal platinum.

$$2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$$

iv. Decomposition of aqueous solution of a hypochlor in presence of oxides of nickel.

$$Ca(ClO)_2 \xrightarrow{NiO} CaCl_2 + O_2$$

ifferences between homogeneous and heterogeneous atalysis

	Homogeneous catalysis	Heterogeneous catalysis
Nature of catalyst and reactants	They remain in the same phase.	They are in different phases.
Example	Liquid phase acid hydrolysis of methyl acetate. The catalyst and reactant remain in solution	Oxidation of SO_3 to SO_2 in presence of V_2O_5 reactants gases catalyst solid.
Catalytic poison	Not known	Possible E.g., Co to Fe in Haber process.
Promotor Action	Not known	Possible E.g. Fe Promoter to Ni in the hydrogenation of oils
Mechanism	Supposed to proceed via the formation of intermediate compound	Supposed to proceed through adsorption of reactants on the surface of the catalyst.

Auto catalysis :

In some reactions one the products of the reaction acts as a catalyst the recation. This phenomenon is called auto catalysis.

E.g. The rate of the hydrolysis of ethylacetate by water increases ith passage of time.

$$CH_3COOC_2H_5 + HOH \rightleftharpoons CH_3COOH + C_2H_5OH$$

The product CH_3COOH slightly dissociates producing H^+ ions. This ts as a positive catalysts for the hydrolysis of the ester. With passage ime, the amount of the product CH_3COOH and hence that H^+ increases. the rate of reaction also increases with the passage of time.

4. Enzyme catalysis :

Enzymes are complex organic compounds produced by living plants and animals. Many reactions are catalysed by enzymes. E.g,

i Invertase converts sucrose into glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

ii. Zymase converts glucose into alcohol

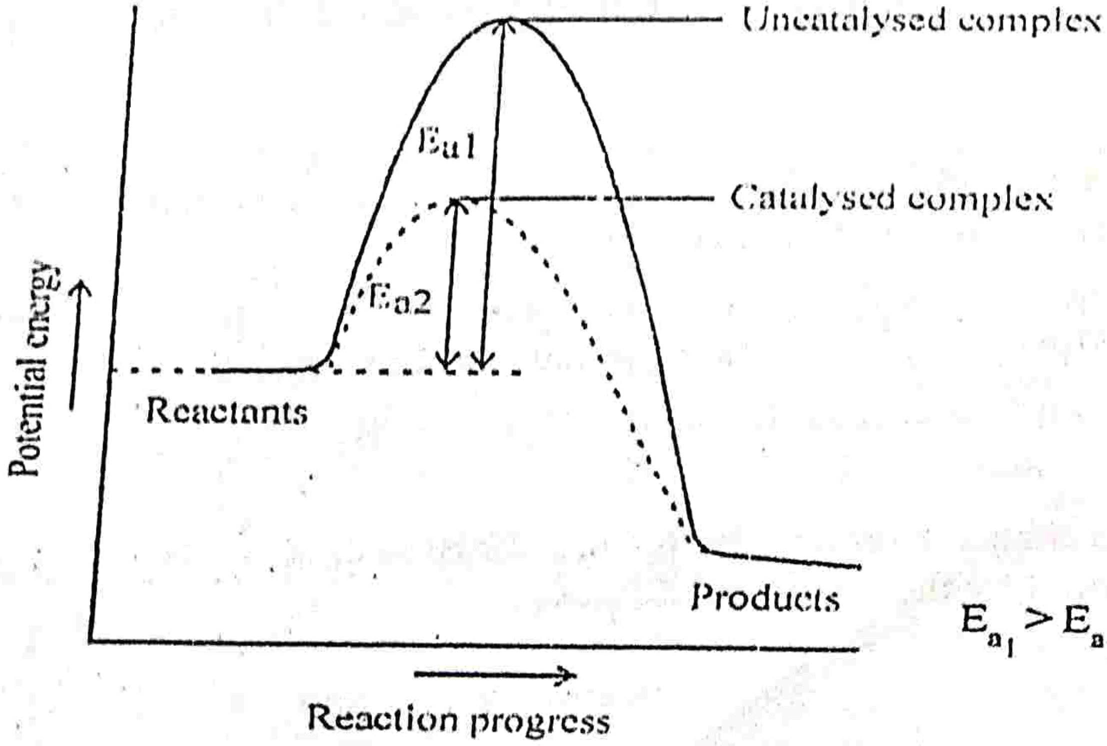
$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{alcohol}}{2C_2H_5OH} + 2CO_2$$

Theories of homogeneous and heterogeneous catalysis

Function of a catalyst in terms of energy of activation :

1. **Intermediate compound formation theory :** (for homogeneous catalysis)

For a chemical reaction to occur the reacting substances must posses the necessary activation energy (E_a). In cases where the reacting substances don't posses this activation energy, a catalyst provides an alternate route to the reaction, requiring lower energy of activation.



$E_{a_1} > E_{a_1}$

ostulates :

First the catalyst (C) forms an intermediate compound (SC) with the irst substrate S_1.

$$S_1 + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S_1C \qquad - \qquad (1)$$

k_1 and k_2 are the rate constants of the forward and backward reactions espectively.

The intermediate compound then reacts with the other substrate (S_2) form the product (P). The catalyst is regenerated.

$$S_1C + S_2 \xrightarrow[\text{slow}]{k_3} P + C \qquad - \qquad (2)$$

This reaction is slow. It is the rate-determining step.

Thus rate of reaction is Rate $\propto [S_1C]\,[S_2]$

The regenerated catalyst again undergoes reactions (1) and (2) to rm more and more number of products.

Thus the rate of homogeneous catalysis reaction depends on the ncentration of the catalyst. This means that the rate of the reaction uld increase if the concentration of the catalyst is increased. This is und to be so.

camples :

The formation of ether when alcohol is treated with concentrated lphuric acid may be explained by this theory as follows :

$$\underset{\text{Substrate-1}}{C_2H_5OH} + \underset{\text{Catalyst}}{H_2SO_4} \longrightarrow \underset{\text{Intermediate compound}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + \underset{\text{Substrate-2}}{C_2H_5OH} \longrightarrow C_2H_5OC_2H_5 + H_2SO_4$$

The reaction in lead chamber process for the manufacture of sulphuric d may also be explained by this theory as follows:

$$\underset{\text{Substrate-1}}{O_2} + \underset{\text{catalyst}}{2NO} \longrightarrow \underset{\text{intermediate compound}}{2NO_2}$$

$$2NO_2 + \underset{\text{Substrate-2}}{2SO_2} \longrightarrow 2SO_3 + 2NO$$

Merits of the theory :

1. This theory explains the mechanism of homogeneous catalysis.
2. This explains the fact that the rate of the homogeneous, catalytic reaction depends upon the concentration of the catalysis.
3. This theory explains the specific nature of the catalyst.

Demerits / Failure :

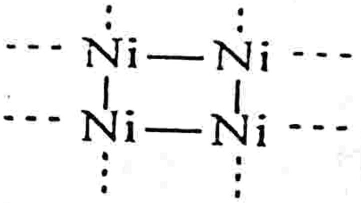
i. This theory does not explain the mechanism of heterogeneous catalysis.

ii. It fails to explain the action of catalytic poisons and promoters.

II. Adsorption and free valency theory :

(for heterogeneous catalysis)

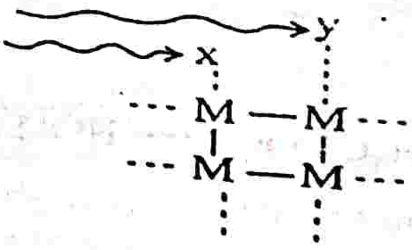
The theory of heterogeneous catalysis is based on the phenomenon of adsorption. The action of a heterogeneous catalyst is due to the presence of free valencies on its surface. This free valencies help the reactant molecules to react chemically on the surface of the catalyst.



An atom within the body of a catalyst is bonded to the neighbouring atoms. So all its valencies are satisfied. The atoms present on the surface of the catalyst possess a free valency pointing outward. According to this theory, the mechanism of heterogeneous catalysis proceeds through the following steps.

1. Diffusion :

When the reactants (X and Y) enter a reaction vessel containing the catalyst (M), their molecules from the gaseous or liquid phase diffuses (moves) on the surface of the catalyst (Fig. a).



(a)

Hence, the rate of reaction is independent of pressure and a zero order kinetics is followed.

Industrial catalysts

Commercial catalysts usually consist of a primary catalytic agent and various additives such as promoters, inhibitors and poisons.

Catalytic promoters : Substances which temselves are not catalysts but promote the activity of a catalyst in a chemical reaction are called *promoters* or *activators*. These are usually added during the preparation of the catalyst.

Examples

i) Molybdenum promotes the catalytic activity of iron in the manufacture of ammonia by Haber process

ii) Copper acts as promoter in the hydrogenation of oils in which nickel is used as the catalyst

Catalytic inhibitors : A substance which reduces the catalytic activity to a considerable extent is called an *inhibitor* or *deactivator*. It is added to the catalyst during its preparation.

Examples

i) Iron oxide suppresses the oxidation of naphthalene to phthalic anhydride by inhibiting the catalytic action of V_2O_5

ii) $BaSO_4$ deactivates palladium catalyst in the conversion of acid chlorides to aldehydes (Rosenmund's reduction)

Catalytic poisons : Certain substances present in the reactants as impurities destroy the activity of the catalyst. Such substances are called *catalytic poisons*. Note that the inhibitors are not termed poisons as they are *added* for a specific purpose. Catalytic poisoning is due to the preferential adsorption of the poison on the catalyst surface.

Examples

i) Presence of arsenic poisons platinum or V_2O_5 (catalyst) in the Contact process for manufacturing sulphuric acid

ii) The decomposition of H_2O_2 catalysed by colloidal platinum is retarded by HCN (poison).

iii) CO acts as poison to Fe in the manufacture of NH_3 by Haber process

iv) Traces of bromine vapour act as poison to finely divided nickel in hydrogenation of oils.

Theories of catalysis

1. Intermediate compound formation theory

(Theory of Homogeneous cataysis)

This theory assumes that catalysis is a two step process :

i) The catalyst forms an intermediate compound with one of the reactants

ii) The intermediate compound then decomposes or reacts with other reactants to give the product and the catalyst is regenerated.

Uncatalysed reaction

$$A + B \longrightarrow AB$$

Catalysed reaction

$$\underset{\text{(Catalyst)}}{A + X} \longrightarrow \underset{\text{(Intermediate compound)}}{AX}$$