LECTURE NOTES

Subject: Surface Chemistry and Nuclear Chemistry

Faculty: Dr. Monalisa Mohapatra

Subject Code: CH-425

2nd Semester 2yr M.Sc. and 8th Semester 5yr Int. M.Sc.

Module-I: (10 Hours)

Phase Rule and Catalysis: Derivation of Phase Rule, Brief Concept on One and Two Component System, Application of Phase Rule to Three Component Systems of Both Solids and Liquids.

Kinetics of Catalytic Reactions: Acid-Base Catalysis, Enzyme Catalysis, Heterogeneous Catalysis.

Module-II: (10 Hours)

Adsorption: Surface Tension, Capillary Action, Adsorption, Types of Adsorption, Gibbs Adsorption Isotherm, Freundlich's Adsorption Isotherm, Langmuir's Adsorption Isotherm and Its Limitations, BET Adsorption Isotherm and Its Applications, Heat of Adsorption, Estimation of Surface Areas of Solids from Solution Adsorption Studies.

Module-III: (10 Hours)

Micelles: Concepts on Micelle, Surface Active Agents, Classification of Surface Active Agents, Micellization, Hydrophobic Interaction, Critical Micellar Concentration (CMC), Kraft Temperature, Factors Affecting the CMC of Surfactants, Counter Ion Binding to Micelles, Thermodynamics of Micellazation, Phase Separation and Mass Action Models, Solubilization, Microemulsion, Reverse Micelles.

Module-IV: (10 Hours)

Nuclear Chemistry: Classification of Nuclides, Nuclear Stability, Binding Energy and Nuclear Models. Characteristics of Radioactive Decay, Decay Kinetics, Parent-Daughter Decay Growth Relationships, Detection and Measurement of Radioactivity, Advances in the Solid and Liquid Scintillation Counting Techniques, Methods for the Determination of Half Life

Period of Single and Mixed Radionuclides. Nuclear Fission, Nuclear Fuels and Nuclear Reactors, Nuclear Fuel Reprocessing, Fast Breeder Reactors, Radiological Safety Aspects and Radioactive Waste Managements. Interaction of Radiation with Matter, Effect of Ionizing/Non-ionizing Radiations on Water, Aqueous Solutions and Organic Compounds, Radiation Dosimetry. Preparation and Separation of Radioactive Isotopes, Application of Radioisotopes and Radiations in Various Fields, Isotopic Dilution Techniques, Neutron Activation Analysis and Its Applications.

Prescribed Books:

1. K.L. Kapoor, *A Textbook of Physical Chemistry, Volume I–IV*, 3rd Edition, Macmillan, 2012.

2. D.N. Bajpai, *Advanced Physical Chemistry*, 2nd Edition, S. Chand & Sons, 2001.

3. A. Bahl, B.S. Bahl, and G.D. Tuli, *Essential of Physical Chemistry*, 19th Edition, S. Chand & Sons, 2012.

4. S.K. Dogra and S. Dogra, *Physical Chemistry through Problems*, 2nd Edition, New Age International, 2015.

5. D.V.S. Jain and S.P. Jauhar, *Physical Chemistry: Principles and Problems*, 1st Edition, Tata McGraw-Hill, 1988.

6. G. Friedlander, J.W. Kennedy, E.S. Macias, and J.M. Miller, *Nuclear and Radiochemistry*, 3rd Edition, John Wiley & Sons, 1981.

7. B.G. Harvey, *Introduction to Nuclear Physics & Chemistry*, Prentice Hall, 1969.

8. R.T. Overman, *Basic concept of Nuclear Chemistry*, Chapman & Hall, 1965.

9. N. Nesmeyanov, *Radiochemistry*, Mir Publication, 1974.

10. J.W.T. Spinks and R.J. Woods, *An Introduction to Radiation Chemistry*, 3rd Edition, John Wiley & Sons, 1990.

11. H.J. Arnikar, *Essentials of Nuclear Chemistry*, 4th Edition, New Age International, 1995.

12. G. Choppin, J.-O. Liljenzin, J. Rydberg, and C. Ekberg, *Radiochemistry and Nuclear Chemistry*, 4th Edition, Elsevier, 2013.

13. W.D. Loveland, D.J. Morrissey, and G.T. Seaborg, *Modern Nuclear Chemistry*, 1st Edition, John Wiley & Sons, 2006., 1983.

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MODULE – I

INTRODUTCTION:

A phase is defined as any homogeneous and physically distinct part of a system bounded by a surface and is mechanically separable from other parts of the system. A phase may be gaseous, liquid or solid. It is perfectly homogeneous and distinct from every other phase that is present in the system. There must be a definite boundary between any two phases. This boundary is known as the interface.

Air constitutes a single phase only as it contains a mixture of nitrogen, oxygen, carbon dioxide, water vapour etc., A system consisting of only one phase is said to be homogeneous. A mixture of two immiscible liquids such as water and benzene, will exist in two distinct liquid phases and in addition there will be a vapour phase. Thus there will be three phases each separated from the other by a well-defined bounding surface.

A system consisting of more than one phase is said to be heterogeneous. When various phases are in equilibrium with one another in a heterogeneous system, there can be no transfer of energy or mass from one phase to another. This means that at equilibrium, the various phases must have the same temperature and pressure and their respective compositions must remain constant all along. The homogeneous reversible reactions can be studied using the law of mass action. For heterogeneous reversible reactions, the phase rule given by J. W. Gibbs is used.

GIBB'S PHASE RULE:

Phase rule may be defined as:

When a heterogeneous system in equilibrium at a definite temperature and pressure, the number of degrees of freedom is equal to by 2 the difference in the number of components and the number of phases provided the equilibrium is not influenced by external factors such as gravity, electrical or magnetic forces, surface tension etc.

It is applicable for all the universally present heterogeneous systems.

Mathematically, the rule is written as; $F = C - P + 2$

Where; F= Number of degrees of freedom, C= Number of components and P= Number of phases of the system. For understanding the various applications of phase rule a clear understanding of the various terms, phases (P), components (C) and degrees of freedom (F) present in the phase rule, is essential which have their specific meanings.

EXPLANATION OF TERMS:

Phase (P): A phase is defined as a homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces.

Example: 1. Liquid phase:

The number of liquid phase depends on the number of liquids present and their miscibility.

i) If two liquids are immiscible, they will form two separate liquid phases. Example: benzene and water

ii) If two liquids are miscible they will form one liquid phase only. Example: alcohol and water

2. Solid phase

Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it. Example: Many forms of sulphur can exist together, but these are all separate phases.

3. Gaseous phase

Since a gaseous mixture are thoroughly miscible in all proportions, it will form one phase only.
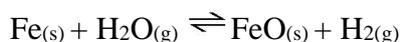
Example: a mixture of N_2 and H_2 forms one phase only.

4. A solution of a substance in a solvent consists of one phase only, e.g. glucose solution.

5. A heterogeneous mixture like:

$CaCO_{3 (s)} \rightleftharpoons CaO_{(s)} + CO_{2 (g)}$

consists of three phases (i.e., two solids and one gaseous).

In the equilibrium reaction,

$Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2(g)}$

There are two solid phases, Fe and FeO and one gaseous phase consisting of $H_2O_{(g)}$ and $H_{2(g)}$.

Thus three phases exist in equilibrium.

6. At freezing point, water consists of three phases:

Ice $_{(s)} \rightleftharpoons$ Water $_{(l)} \rightleftharpoons$ Water vapour $_{(g)}$
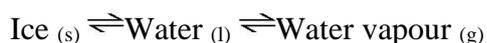
7. A homogeneous solid solution of a salt forms a single phase.

Example: Mohr's salt [$FeSO_4. (NH_4)_2SO_4.6H_2O$] solution has a single phase.

Component (C): Component is defined as the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation.

Example: i) In the water system, Ice $_{(s)} \rightleftharpoons$ Water $_{(l)} \rightleftharpoons$ Water vapour $_{(g)}$

The chemical component of all the three phases is H_2O and therefore it is one component system.

ii) Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is S. Thus it is an one component system.

iii) A system of saturated solution of NaCl consists of solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H_2O. Therefore, it is a two component system.

iv) The system, $CuSO_4.5H_2O_{(s)} \rightleftharpoons CuSO_4.3H_2O_{(s)} + 2H_2O_{(g)}$ is a three phase and two component system. It requires two constituents $CuSO_4$ and H_2O to express the composition of each phase of the system.

v) In the thermal decomposition of $CaCO_3$,

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

The composition of each of the three phases can be expressed in terms of at least any two of the independent variable constituents, $CaCO_3$, CaO and CO_2. Suppose $CaCO_3$ and CaO are chosen as the two components, then the composition of different phases is represented as follows:

Phase : $CaCO_3 = CaCO_3 + 0CaO$

Phase : $CaO = 0CaCO_3 + CaO$

Phase : $CO_2 = CaCO_3 - CaO$
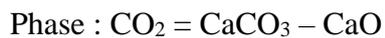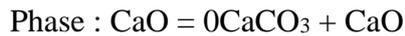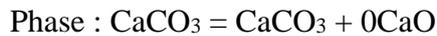
Thus, it is a two component system.

vi) In the equilibrium, $Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2\,(g)}$, the minimum components required to express the composition of each phase is three. Thus it is a three component system.

vii) In the dissociation of NH_4Cl, the following equilibrium occurs:

$NH_4Cl_{(s)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)}$

The system consists of two phase namely solid NH_4Cl and the gaseous mixture containing $NH_3 + HCl$.

When NH_3 and HCl are present in equivalent quantities the composition of both the phases can be represented by the same chemical compound NH_4Cl and hence the system will be a one component system.

Degree of freedom (F): Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely. A system having 1,2,3 or 0 degrees of freedom is called univariant, bivariant, trivariant and nonvariant respectively.

Example: i) Consider the water system,

Ice $_{(s)} \rightleftharpoons$ Water $_{(l)} \rightleftharpoons$ Water vapour $_{(g)}$
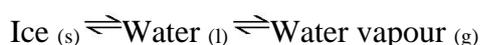
The three phases can be in equilibrium only at particular temperature and pressure. Therefore, when all the three phases are present in equilibrium, then no condition need to be specified.

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The system is therefore zero variant or invariant or has no degree of freedom. In this system if pressure or temperature is altered, three phases will not remain in equilibrium and one of the phases disappears.

ii) Consider a system consisting of water in contact with its vapour,

Water $_{(l)}$ $\rightleftharpoons$ Water vapour $_{(g)}$

To define this system completely, we must state either the temperature or pressure Thus degree of freedom is one and the system is univariant.

iii) For a system consisting of water vapour phase only, we must state the values of both the temperature and pressure in order to define the system completely. Hence the system is bivariant or has two degrees of freedom.

iv) For a gaseous mixture of N_2 and H_2, we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degrees of freedom or bivariant system.

v) Consider a system consisting of

NaCl $_{(s)}$ $\rightleftharpoons$ NaCl-water $_{(aq)}$ $\rightleftharpoons$ Water vapour $_{(g)}$
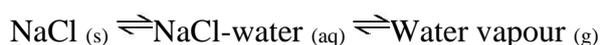
we must state either the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence the system is univariant.

MERITS OF THE PHASE RULE:

1. It is applicable to both physical and chemical equilibria.

2. It requires no information regarding molecular/micro-structure, since it is applicable to macroscopic systems.

3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.

4. It helps us to predict the behaviour of a system, under different sets of variables.

5. It indicates that different systems with same degree of freedom behave similarly.

6. It helps in deciding whether under a given set of conditions:

   a) various substances would exist together in equilibrium or (b) some of the substances present would be interconverted or (c) some of the substances present would be eliminated.

LIMITATIONS OF PHASE RULE:

1. It can be applied only for system in equilibrium. Consequently, it is of little value in case of very slow equilibrium state attaining system.

2. It applies only to a single equilibrium system; and provide no information regarding any other possible equilibria in the system.

3. It requires at most care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus even if a trace of phase is present, it accounts towards the total number of phases.

4. It conditions that all phases of the system must be present simultaneously under the identical conditions of temperature and pressure.

5. It conditions that solid and liquid phases must not be in finely-divided state; otherwise deviations occur.

DERIVATION OF PHASE RULE EQUATION:

The Gibb's phase rule can be derived on the basis of thermodynamic principle as follows.

Let us consider a heterogeneous system consisting of P (P, P, P3 ...P) number of phases and C (C1, C2, C3... C) number of components in equilibrium. Let us assume that the system is non-reacting i.e. the passage of a component from one phase to another does not involve any chemical reaction. When the system is in equilibrium state it can be explained completely by specifying the following variables: (i) Pressure (ii)Temperature (iii) Composition of each phase.

(a) Total number of variables required specifying the state of system:

(i)Temperature: same for all phases

(ii) Pressure: same for all phases

(iii) Concentration

Independent concentration variables for one phase with respect to the C components = C - 1 [

Conc. of last component is independent]

Independent concentration variables for P phases with respect to the C components = P (C - 1)

Total number of variables = P (C - 1) + 2 ……......(1)

(b) The total number of equilibria:

The various phases present in the system can remain in equilibrium only when the chemical

potential (μ) of each component is the same in each phases, i.e.

μ_1, P_1= μ_1, P_2= μ_1, P_3= …...= μ_1, P   Component 1

μ_2, P_1= μ_2, P_2= μ_2, P_3= …...= μ_2, P   Component 2

:   :   :   :

:   :   :   :

:   :   :   :

μ_c, P_1= μ_c, P_2= μ_c, P_3= …...= μ_c, P   Component C

(a) For each component the no of equilibria for P phases = (P - 1)

(b) For C component the no of equilibria for P phases = C (P - 1)

Total no. of equilibria involved (E) = C (P - 1) ………...(2)

From eq. 1 and 2 we get

$\quad$ F= [P(C - 1) + 2] - [C(P - 1)]

$\quad$ F= [CP - P + 2 - CP + C]

$\quad$ F= C - P + 2

This above equation is Gibb's phase rule equation.

Some conclusions from the phase rule equation:

(a) For a system having a specified number of components, the greater the number of phases, the lesser is the number of degrees of freedom. For example,

(i) When the system consists of only one phase, we have C = 1 and P = 1

So, according to the phase rule, F= C - P + 2 = 1 - 1 + 2 = 2. The system has two degrees of freedom.

(ii) When the system consists of two phases in equilibrium, we have C = 1 and P = 2

F= C - P + 2 = 1 - 2 + 2 = 1. The system is monovariant.

(b) A system having a given number of components and the maximum possible number of phases in equilibrium is non-variant.

For a one component system, the maximum possible number of phases is three. When a one-component system has three phases in equilibrium, it has no degree of freedom or non-variant system.

(c) For a system having a given number of phases, the larger the number of components, the greater will be the number of the degrees of freedom of the system. For example, For one-component system: C= 1, P = 2

F= C - P + 2 = 1 - 2 + 2 = 1

For two-component system: C= 2, P = 2

F= C - P + 2 = 2 - 2 + 2 = 2

The two-component system has a higher number of degrees of freedom.

PHASE DIAGRAMS:

Phase diagram is a graph obtained by plotting one degree of freedom against another. If the phase diagram is plotted between temperature against pressure, the diagram is called P-T diagram. P-T diagram is used for one component system.

If the phase diagram is drawn between temperature against composition, the diagram is called T-C diagram. T-C diagram is used for two component system. A phase diagram consists of areas, curves or lines and points.

Uses of Phase diagram:

1. From the phase diagram, it is possible to predict whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.

2. The phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.

3. The study of low melting eutectic alloys, used in soldering, can be carried out using phase diagrams.

APPLICATIONS OF PHASE RULE TO ONE COMPONENT SYSTEM:

Water is a one component system which is chemically a single compound involved in the system. The three possible phases in this system are: ice (solid phase), water (liquid phase) and vapour (gaseous phase).

Hence, water constitutes a three-phase, one-component system. Since water is a three-phase system, it can have the following equilibria

$$ice \rightleftharpoons vapour,$$

$$ice \rightleftharpoons water;$$

$$water \rightleftharpoons vapour$$
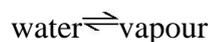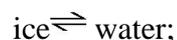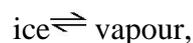
The existence of these equilibria at a particular stage depends upon the conditions of temperature and pressure, which are the variables of the system. If the values of vapour pressures at different temperatures are plotted against the corresponding temperatures, the phase diagram of the system is obtained.

The phase diagram of the water system is shown in Fig. 1.1. The explanation of the phase diagram of water system is as follows:
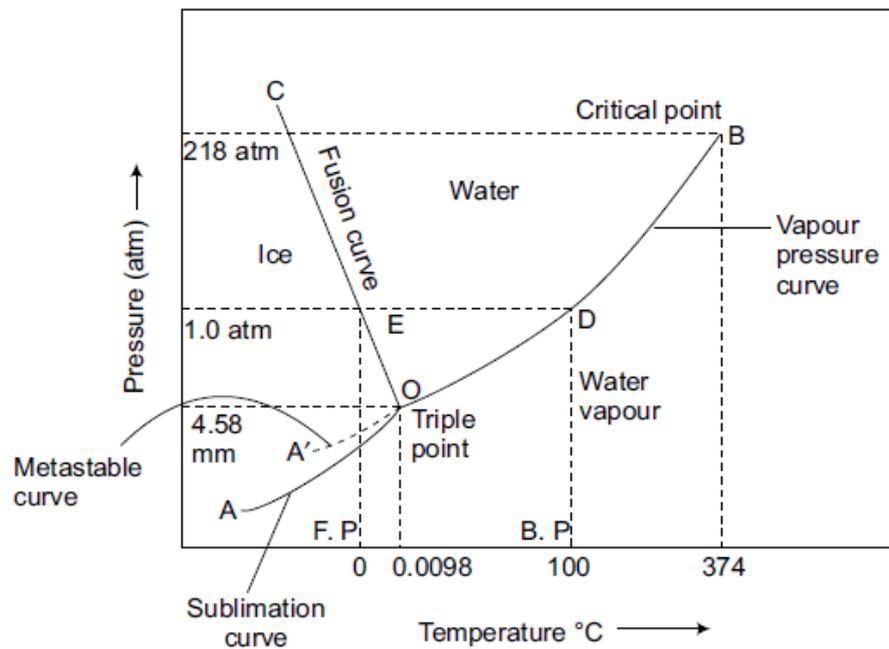

Figure 1.1: Phase diagram of water system

(a) **Curves**

The phase diagram of the water system consists of three stable curves and one metastable curve, which are explained as follows:

(i) Curve OB: The curve OB is known as vapour pressure curve of water and tells about the vapour pressure of water at different temperatures. Along this curve, the two phases-water and vapour exist together in equilibrium.

At point D, the vapour pressure of water become equal to the atmospheric pressure (100°C), which represents the boiling point of water. The curve OB finishes at point B (temp. 374°C and pressure 218 atm) where the liquid water and vapour are indistinguishable and the system has only one phase. This point is called the critical point.

Applying the phase rule on this curve, C= 1 and P= 2; F = C - P + 2 = 1 - 2 + 2 = 1

Hence, the curve represents a univariant system. This explains that only one factor (either temperature or pressure) is sufficient to be fixed in order to define the system.

(ii) Curve OA: It is known as sublimation curve of ice and gives the vapour pressure of solid ice at different temperatures. Along sublimation curve, the two phases ice and vapour exist together in equilibrium. The lower end of the curve OA extends to absolute zero (-273°C) where no vapour exists.

(b) **Areas**

	Area	Phase exits	Component
(i)	Area AOC	ice	H_2O
(ii)	Area COB	Water	H_2O
(iii)	Area below BOA	Vapour	H_2O

Thus, for every area contains C=1 and P=1; therefore, applying phase rule on areas

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Hence, each area is a bivariant system. So, it becomes necessary to specify both the temperature and the pressure to define a one phase-system.

(c) **Triple point (Point O)**

At triple point all the three phases namely ice, water and vapour coexist. Thus the value of P is 3. Applying phase rule equation, the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are 0.0098 °C and 4.58 mm respectively.

At this triple point, neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases. The triple point is not the same as the ordinary melting point of ice (i.e., 0 °C). It's value has been increased due to the fact that 0 °C is the melting point of ice at 760mm of mercury and a decrease of 4.58 mm will rise the melting point to 0.0098 °C.

(d) **Curve OA' (Metastable equilibrium)**

The curve OA' is called vapour pressure curve of the super-cool water or metastable equilibrium. Where the following equilibrium will exist.

Super-cool water $\rightleftharpoons$ Vapour

Sometimes water can be cooled below 0 ºC without the formation of ice, this water is called super-cooled water. Supercooled water is unstable and it can be converted into solid by 'seeding' or by slight disturbance.

Table 1.1: Some salient features of the water system

Curve/area/ point	Name of the system	Phases in equilibrium	No. of phase (P)	Degree of the freedom (F)
Curve OB	Vapourisation curve	Liquid & vapour	02	01(Univariant)
Curve OA	Sublimation curve	Solid & vapour	02	01(Univariant)
Curve OC	Fusion curve	Solid & liquid	02	01(Univariant)
Curve OA'	Metastable vaporization curve	Liquid & vapour	02	01(Univariant)
Area AOC		Ice	01	02(Bivariant)
Area BOC		Water	01	02(Bivariant)
Area AOB		Vapour	01	02(Bivariant)
Point O		Ice & water & vapour	03	0(Invariant)

TWO COMPONENT SYSTEMS:

When the two independent components are present in a heterogeneous system, the system is referred to as a two-component system. Hence, according to the phase rule, for a two-component system having one phase,

$F = C - P + 2 = 2 - 1 + 2 = 3$

Therefore, the two component system having one phase will have three degrees of freedom or three variables would be required to define the system. The three variables are pressure (P), temperature (T) and concentration (C). This will require a three-dimensional phase diagram for the study of a two-component system. However, in order to simplify the study, a two-component system is usually studied in the form of a condensed system. A condensed system

can be studied by reducing a comparatively less important variable. This reduces the degree of freedom of the system by 1 and the system can easily be studied with the help of a two-dimensional phase diagram.

It can have a maximum of following four phases:

Solid lead, Solid silver, Solution of molten silver and lead and Vapours

The boiling points of silver and lead are considerably high and the vapour pressure of the system is very low. So, the vapour phase can be ignored and the system can be studied as a condensed system. This system thus can be easily studied with the help of a two dimensional T- C diagram and the reduced phase rule equation, $F = C - P + 1$, can be used. This system is generally studied at constant pressure (atmospheric). The phase diagram of Lead-Silver system is shown in Fig. 1.2.
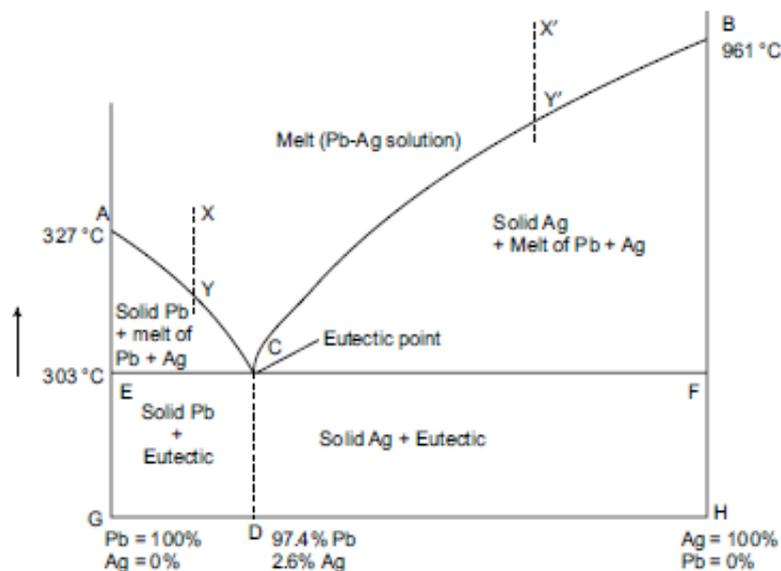

Figure 1.2: Phase diagram of Pb-Ag system

(a) **Curves**

The phase diagram of the lead-silver system consists of following curves, which are explained as follows:

(i) Curve AC (Freezing point curve of lead): The AC curve shows the variation of the melting point of lead on addition of silver. The pure lead melts at 327°C (point A). Addition of silver lowers its melting point along curve AC. The added silver dissolves in molten lead to form Ag-Pb solution with the separation of some part of solid lead. Therefore, the two phases, solid lead and Ag-Pb solution remain together in equilibrium along the curve AC.

Hence, P = 2, (solid Pb and melt of Ag-Pb)

C = 2 (Pb and Ag)

So, C= 2 and P = 2, On applying the reduced phase rule F = C - P + 1 = 2 - 2 + 1 = 1 The system is univariant.

(iii) Area BCF: The area consists of two phases-solid Ag and a solution of Pb and Ag. Hence it is also univariant.

(iv) Area DCFH: This area also has the two phases which are solid Ag crystals and solid eutectic crystals. Hence C = 2 and P = 2, the system is univariant.

(iv) Area CEGD: The area also has the solid Pb crystals and solid eutectic crystals phases. The system is univariant.

Table 1.2: Some salient features of the Pb-Ag system

Curve/ area/ point	Name of the system	Phases in equilibrium	No. of phase (P)	Degree of freedom (F)
Curve AC	Freezing curve of Pb	Pb & Melt (Pb+ Ag Solution Pb & Ag)	02	01(Univariant)
Curve BC	Freezing curve of Ag	Ag & Melt Pb & Ag)	02	01(Univariant)
Area ACE	.....	Pb & melt	02	01(Univariant)
Area BCF	.....	Ag & melt	02	01(Univariant)
Area above ACB	.....	Liquid (melt)	01	02(Bivariant)
Area ECF	.....	Pb & Ag both in solid	02	01(Univariant)
Point O	Eutectic point	Pb, Ag & melt	03	0(invariant)

Desilverisation of Argentiferrous Lead (Pattinson's Process)

The process, which is used for the recovery of silver from argentiferrous lead is called Pattinsonss process and involves the desilverisation o lead in accordance to the phase diagram of lead-silver system.

The argentiferrous lead contains a small percentage of silver (less than 0.1%). For its recovery, the argentiferrous lead is heated above its melting point when a liquid melt consisting of silver-lead solution is obtained. Now if the silver lead solution is cooled, then Pb continues to separate out and is regularly removed. In the end, a eutectic solution containing 2.6% Ag (corresponding to point C) is obtained. Thus, the above process increases the percentage of silver in the argentiferrous lead. Therefore, the eutectic mixture containing 2.6% silver can be treated for the recovery of silver profitably.

THREE COMPONENT SYSTEMS:

A ternary system is one with three components. We can independently vary the temperature, the pressure, and two independent composition variables for the system as a whole. A two-dimensional phase diagram for a ternary system is usually drawn for conditions of constant TT and pp.
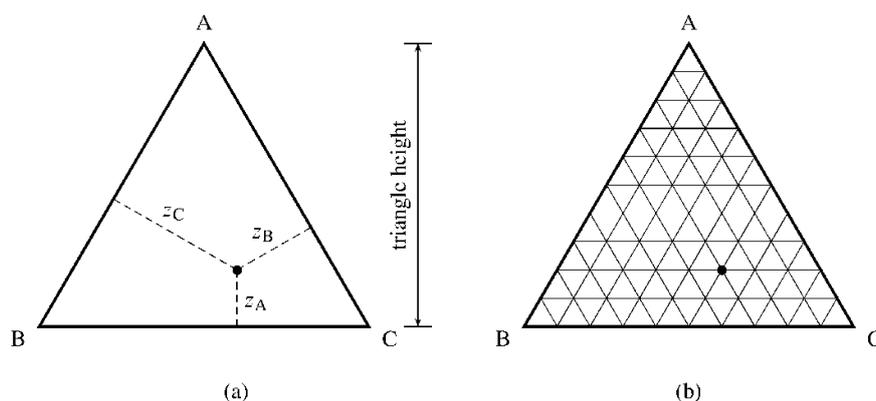

Figure 1.3: Representing the composition of a ternary system by a point in an equilateral triangle.

Although we could draw a two-dimensional phase diagram with Cartesian coordinates to express the mole fractions of two of the components, there are advantages in using instead the triangular coordinates shown in Fig. 1.3. Each vertex of the equilateral triangle represents one of the pure components A, B, or C. A point on the side of the triangle opposite a vertex represents a binary system of the other two components, and a point within the triangle represents a ternary system with all three components.

To determine the mole fraction z_A of component A in the system as a whole represented by a point within the triangle, we measure the distance to the point from the side of the triangle that is opposite the vertex for pure A, then express this distance as a fraction of the height of the triangle. We follow the same procedure to determine z_B and z_C. The concept is shown in Fig. 1.3 (a).

As an aid for the conversion between the position of a point and the overall composition, we can draw equally-spaced lines within the triangle parallel to the sides as shown in Fig. 1.3(b). One of these lines, being at a constant distance from one side of the triangle, represents a constant mole fraction of one component. In the figure, the lines divide the distance from each side to the opposite vertex into ten equal parts; thus, adjacent parallel lines represent a difference of 0.1 in the mole fraction of a component, starting with 0 at the side of the triangle and ending with 1 at the vertex. Using the lines, we see that the filled circle in the figure represents the overall composition $z_A = 0.20$, $z_B = 0.30$, and $z_C = 0.50$.
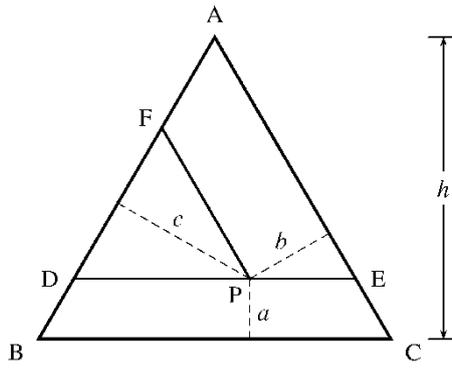
Figure 1.4: Proof that the sum of the lengths aa, bb, and cc is equal to the height hh of the large equilateral triangle ABC. ADE and FDP are two smaller equilateral triangles. The height of triangle ADE is equal to h−ah−a. The height of triangle FDP is equal to the height of triangle ADE minus length bb, and is also equal to length cc: h−a−b=ch−a−b=c. Therefore, a+b+c=ha+b+c=h.

The sum of $z_A z_A$, $z_B z_B$, and $z_C z_C$ must be 11. The method of representing composition with a point in an equilateral triangle works because the sum of the lines drawn from the point to the three sides, perpendicular to the sides, equals the height of the triangle. The proof is shown in Fig. 1.4.

Two useful properties of this way of representing a ternary composition are as follows:

1. Points on a line parallel to a side of the triangle represent systems in which one of the mole fractions remains constant.
2. Points on a line passing through a vertex represent systems in which the ratio of two of the mole fractions remains constant.
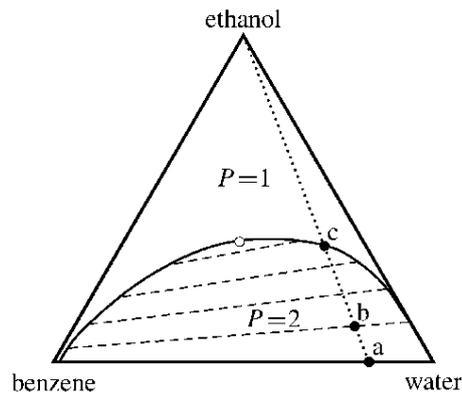
THREE LIQUIDS:

Figure 1.5: Ternary phase diagram for ethanol, benzene, and water at 30 °C and 1bar. The dashed lines are tie lines; the open circle indicates the plait point.

Figure 1.5 is the ternary phase diagram of a system of ethanol, benzene, and water at a temperature and pressure at which the phases are liquids. When the system point is in the area labeled P=1P=1, there is a single liquid phase whose composition is described by the position of the point. The one-phase area extends to the side of the triangle representing binary mixtures of ethanol and benzene, and to the side representing binary mixtures of ethanol and water. In other words, ethanol and benzene mix in all proportions, and so also do ethanol and water.

When the overall composition is such that the system point falls in the area labelled P=2P=2, two liquid phases are present. The compositions of these phases are given by the positions of the ends of a tie line through the system point. Four representative tie lines are included in the diagram, and these must be determined experimentally. The relative amounts of the two phases can be determined from the lever rule. In the limit of zero mole fraction of ethanol, the tie line falls along the horizontal base of the triangle and displays a miscibility gap for the binary system of benzene and water. (The conjugate phases are very nearly pure benzene and pure water).

The *plait point* shown as an open circle in the figure is also called a *critical solution point*. As the system point approaches the plait point from within the two-phase area, the length of the tie line through the system point approaches zero, the miscibility gap disappears, and the compositions of the two conjugate liquid phases become identical.

Suppose we have the binary system of benzene and water represented by point a. Two liquid phases are present: one is wet benzene and the other is water containing a very small mole fraction of benzene. If we gradually stir ethanol into this system, the system point moves along the dotted line from point a toward the vertex for pure ethanol, but can never quite reach the vertex. At point b, there are still two phases, and we can consider the ethanol to have distributed itself between two partially-miscible solvents, benzene and water. From the position of point b relative to the ends of the tie line passing through point b, we see that the mole fraction of ethanol is greater in the water-rich phase. As we continue to add ethanol, the amount of the water-rich phase increases and the amount of the benzene-rich phase decreases, until at point c the benzene-rich phase completely disappears. The added ethanol has increased the mutual solubilities of benzene and water and resulted in a single liquid phase.

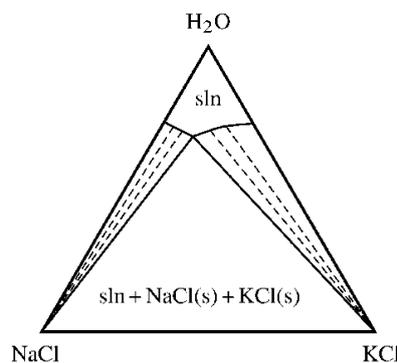**TWO SOLIDS AND A SOLVENT:**

Figure 1.6. Ternary phase diagram for NaCl, KCl, and water at 25 °C and 1bar. The dashed lines are tie lines in the two-phase areas.

The phase diagram in Fig. 1.6 is for a ternary system of water and two salts with an ion in common. There is a one-phase area for solution, labeled sln; a pair of two-phase areas in which the phases are a single solid salt and the saturated solution; and a triangular three-phase area. The upper vertex of the three-phase area, the *eutonic point*, represents the composition of solution saturated with respect to both salts. Some representative tie lines are drawn in the two-phase areas.

A system of three components and three phases has two degrees of freedom; at fixed values of T and p, each phase must have a fixed composition. The fixed compositions of the phases that are present when the system point falls in the three-phase area are the compositions at the three vertices of the inner triangle: solid NaCl, solid KCl, and solution of the eutonic composition $x_{NaCl}=0.20$ and $x_{KCl}=0.11$.

From the position of the curved boundary that separates the one-phase solution area from the two-phase area for solution and solid KCl, we can see that adding NaCl to the saturated solution of KCl decreases the mole fraction of KCl in the saturated solution. Although it is not obvious in the phase diagram, adding KCl to a saturated solution of NaCl decreases the mole fraction of NaCl. These decreases in solubility when a common ion is added are examples of the *common ion effect*.

KINETICS OF CATALYTIC REACTIONS:

ACID BASE CATALYSIS:

In acid catalysis and base catalysis a chemical reaction is catalyzed by an acid or a base. The acid is the proton donor and the base is the proton acceptor, known as Brønsted-Lowry acid and base respectively. Typical reactions catalyzed by proton transfer are esterfications and aldol reactions. In these reactions the conjugate acid of

the carbonyl group is a better electrophile than the neutral carbonyl group itself. Catalysis by either acid or base can occur in two different ways: specific catalysis and general catalysis. Many enzymes operate by acid-catalysis.

Two kinds of acid catalysis are recognized, specific acid catalysis and general acid catalysis

Specific catalysis

In specific acid catalysis, protonated solvent is the catalyst. The reaction rate is proportional to the concentration of the protonated solvent molecules SH^+. The acid catalyst itself (AH) only contributes to the rate acceleration by shifting the chemical equilibrium between solvent S and AH in favor of the SH^+ species. This kind of catalysis is common for strong acids in polar solvents, such as water.

$$S + AH \rightarrow SH^+ + A^-$$
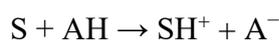
For example, in an aqueous buffer solution the reaction rate for reactants R depends on the pH of the system but not on the concentrations of different acids.

$$\text{rate} = -\frac{d[R^1]}{dt} = k[SH^+][R^1][R^2]$$

This type of chemical kinetics is observed when reactant R^1 is in a fast equilibrium with its conjugate acid R^1H^+ which proceeds to react slowly with R^2 to the reaction product; for example, in the acid catalysed aldol reaction.

General Catalysis

In general acid catalysis all species capable of donating protons contribute to reaction rate acceleration. The strongest acids are most effective. Reactions in which proton transfer is rate-determining exhibit general acid catalysis, for example diazonium coupling reactions.

$$\text{rate} = -\frac{d[R^1]}{dt} = k_1[SH^+][R^1][R^2] + k_2[A^1H][R^1][R^2] + k_3[A^2H][R^1][R^2] + \ldots$$

When keeping the pH at a constant level but changing the buffer concentration a change in rate signals a general acid catalysis. A constant rate is evidence for a specific acid catalyst. When reactions are conducted in nonpolar media, this kind of catalysis is important because the acid is often not ionized. Enzymes catalyze reactions using general-acid and general-base catalysis.

ENZYME CATALYSIS:

In the previous lecture, we discussed the importance and basics of enzymatic reactions in biological systems. Let us now understand how one can interpret the kinetics of an enzyme catalysed reaction. To understand the mechanism of any catalytic reaction, one should study the kinetic behaviour of the reaction systems, where the rate of the reaction can be obtained at various concentrations of the enzyme and the substrate.

Formation of enzyme substrate complex is a critical event in an enzyme-catalyzed reaction. Michaelis and Menten proposed that the binding of the substrate and the enzyme is reversible and derived a kinetic model for a simple single substrate enzymatic reaction. This laid the basis for understanding the various factors that influence rate of the reaction, such as concentration, temperature and pH of the system.

Single Substrate Reactions

Consider a simple single substrate reaction, where the free enzyme E binds to the substrate S to form a complex ES, the forms product P and then dissociates.
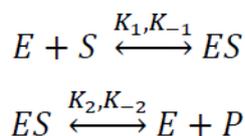
$$E + S \xrightleftharpoons{K_1, K_{-1}} ES$$
$$ES \xrightleftharpoons{K_2, K_{-2}} E + P$$

The dissociation of ES complex into free enzyme and product is the slowest and hence it is the rate-limiting step in the reaction. Throughout the reaction, the total concentration of the enzyme

will be the sum of concentration of total free enzyme [E] and concentration of total enzyme bound with substrate [ES].

The dissociation of ES complex into free enzyme and product is the slowest and hence it is the rate-limiting step in the reaction. Throughout the reaction, the total concentration of the enzyme will be the sum of concentration of total free enzyme [E] and concentration of total enzyme bound with substrate [ES].

At pre-steady state, substrate concentration is more than that of the enzyme concentration. As reaction proceeds, the concentration of the enzyme substrate complex increases with time and reaches a steady state. After this stage, the concentration does not change further with time.

Assumptions in Michaelis and Menten Kinetics

a) Once the system attains a steady state, the concentration of ES remains the same throughout the process.

$$\frac{d[ES]}{dt} = 0$$

b) Initially, there is no product formation and hence the reverse conversion of the product to the substrate cannot happen. Hence, K_2 can be neglected.

$$E + S \xrightleftharpoons{K_1, K_{-1}} ES \xrightarrow{K_2} E + P$$
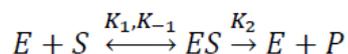
The free enzyme [E] at any point of time in the reaction will be equal to the concentration of the enzyme substrate complex [ES] subtracted from the total enzyme concentration [ET].

[E] = [ET] − [ES]

Rate of formation of ES = K1 ([ET] − [ES]) [S]

Rate of breakdown of ES = K-1 ([ES] + K2 [ES]

From the steady state assumption,

rate of formation = rate of breakdown

K1 ([ET] – [ES]) [S] = K-1 ([ES] + K2 [ES]

K1 ([ET] [S] – K1 [ES]) [S] = (K-1 + K2) [ES]

K1 ([ET] [S] = [ES] (K-1 + K2 + K1[S])

[ES] = (K-1 + K2 + K1[S])

$$ES = \frac{K_1\,([E_T][S])}{(K_{-1} + K_2 + K_1\,[S])}$$

$$ES = \frac{[E_T][S]}{\dfrac{K_{-1} + K_2}{K_1} + [S]}$$

Here, Michaelis-Menten rate constant is defined as,

$$\frac{K_{-1} + K_2}{K_1} = K_m$$

The equation can be simplified as:

$$ES = \frac{[E_T][S]}{K_m + [S]}$$

Rewriting the rate for breakdown of ES, we can represent ES as V0 in the above equation to get,

V0 = K2 [ES]

[ES]= V0 / K2

Substituting [ES] as V0 gives

$$V_0 = \frac{K_2[E_T][S]}{K_m + [S]}$$

Maximum velocity can be obtained only when the enzyme is completely saturated. At this point, the total enzyme concentration will be equal to the concentration of enzyme substrate complex alone.

Changing [ES]= [ET] and V0 = Vmax , Vmax = K_2 [ET]

Therefore, the expression for V0 can be rewritten as,

$$V_0 = \frac{V_{max}[S]}{K_m + [S]}$$

This is the MM equation for a single substrate enzyme catalysis reaction. Michaelis Menten kinetics also gives the numerical interpretation that V0 is half the Vmax.

When

$$V_0 = \frac{V_{max}}{2}$$

$$\frac{V_{max}}{2} = \frac{V_{max}[S]}{K_m + [S]}$$

$$\frac{1}{2} = \frac{[S]}{K_m + [S]}$$

$$K_m = [S]$$

The MM kinetic expression forms a rectangular hyperbola and the graph is given in Fig 1.7 below
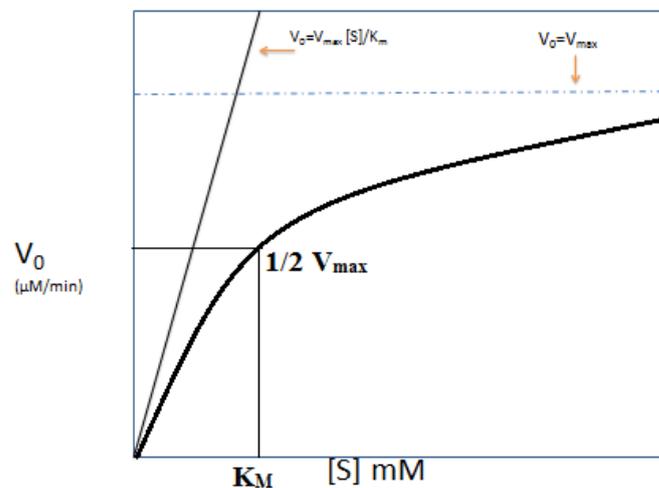

Figure 1.7: A typical plot of the Michelis Menten kinetics

Lineweaver-Burk (double reciprocal plot)

By taking reciprocal of the MM equation, we arrive at a relation that resembles the equation of the straight line $y = mx + b$

$$\frac{1}{V_0} = \frac{K_m}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}}$$

Here,

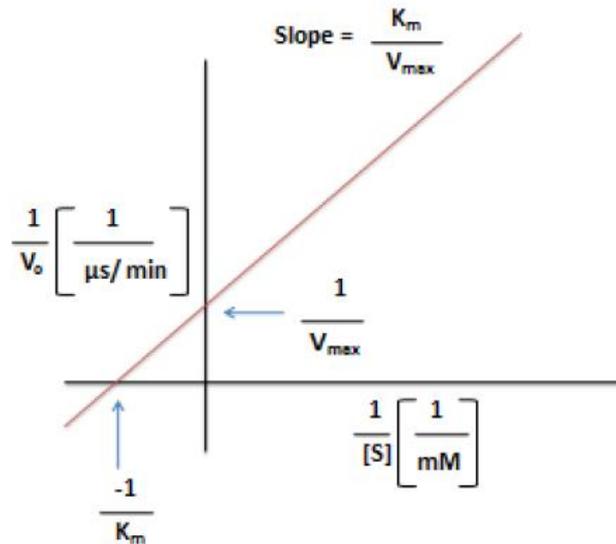y = 1/Vo ; m (slope) = Km/Vmax ; x = 1/[S] ; y- intercept, b = 1/Vmax

Figure 1.8: Lineweaver-Burk double reciprocal plot

This plot helps in accurate determination of Vmax and Km, classification of different mechanisms of action of enzymes and the effect of the inhibitors. Other plots like Hanes –Wolf plot are also used to calculate the Michaelis-Menten kinetics of an enzymatic reaction. So far, we have understood how the kinetics of single substrate enzymatic reaction is interpreted. In the next lecture, we shall discuss how the enzyme inhibition happens with the structural analogs of the substrate molecules.

HETEROGENEOUS CATALYSIS:
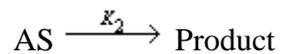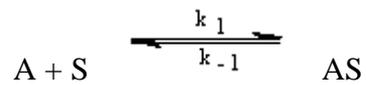
Reaction on surfaces

In the case of a solid immersed in a solution, the reactants in the solution must diffuse to the interface, get adsorbed there and participate in a given reaction mechanism on the solid surface. The product on the surface must then desorb and diffuse into the solution.

Unimolecular surface reactions

Consider the surface catalysis of isomerisation or dissociation of a substance A on surface S as follows.

The substance S gets adsorbed on the surface forming AS and then dissociates into products.

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AS$$

$$AS \xrightarrow{k_2} Product$$

Reaction velocity, $\quad v = k_2 C_{AS}$

Where, $\quad C_{AS} = \text{concentration} \left(\dfrac{\text{moles}}{\text{cm}^2}\right) \text{of A on the surface}$

If, and $\quad C_S = \text{total of surface sites/cm}^2 \quad$ represents the surface sites covered by A, then

$C_{AS} = C_S \theta$

or, reaction velocity,

$v = k_2 C_S \theta$

Let $C_a = \quad$ concentration $\quad$ of $\quad$ A $\quad$ either $\quad$ in $\quad$ gas $\quad$ or $\quad$ solution

Since C_S is constant, it can be incorporated into the rate constant
$v = k_2 \theta$

Applying the steady state approximation to AS,

$$\frac{dC_{AS}}{dt} = 0 = k_1 C_a (1 - \theta) - k_{-1}\theta - k_2\theta$$

$$\theta = \frac{k_1 C_a}{k_1 C_a + k_{-1} + k_2}$$

$$\therefore v = \frac{k_1 k_2 C_a}{k_1 C_a + k_{-1} + k_2},$$

$$\frac{1}{v} = \frac{1}{k_2} + \frac{k_{-1} + k_2}{k_1 k_2 C_a}$$

A plot $\frac{1}{v}$ vs $\frac{1}{C_a}$ of yields $\frac{1}{k_2}$ as the intercept and $\frac{k_{-1} + k_2}{k_1 k_2}$ as the slope.

Usually it is more convenient to use limiting cases as follows:

Case I

k_2, the rate of decomposition is very large compared with the rate of adsorption and desorption. In this case,

$k_2 \gg (k_1 C_a + k_{-1})$ and hence,

$\therefore$ $v = k_1 C_a$

Physically, the assumption that k_2 is large implies that an adsorbed molecule decomposes immediately after coming in contact with the surface. This situation is found for the decomposition of Hl on Pt and N_2O on gold.

Case II

k_2 is very small (negligible) in comparison to $(k_1 C_a + k_{-1})$ and hence

$$\therefore v = \frac{k_1 k_2 C_a}{k_1 C_a + k_{-1}}$$

$$= \frac{k_2 K C_a}{K C_a + 1} \quad , \quad K = \frac{k_1}{k_{-1}}$$

at low concentration of the species A, $KC_a \ll 1$
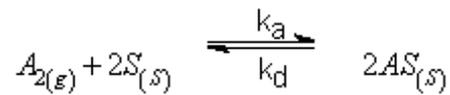
$$\therefore v = k_2 K C_a$$

Whereas at high concentration $KC_a \gg 1$ or $\theta \simeq 1$

$$\therefore v = k_2$$

Sub-Case of I

A diatomic molecule A_2 dissociates upon adsorption to the surface. This reaction can be written as

$$A_{2(g)} + 2S_{(s)} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2AS_{(s)}$$

$$K_C = \frac{k_a}{k_d} = \frac{[AS]^2}{[A_2][S]^2}$$

Because two surface sites are involved in the adsorption and desorption process, the rates of adsorption, ν_a, and desorption ν_d, are

$$\nu_a = k_a p_{A_2} (1-\theta)^2 C_s^2$$

$$\nu_d = k_a \theta^2 C_s^2$$

Where, C_s = total surface sites/cm^2, = fraction of the surface covered and p represents the pressure of the molecules A_2.

At equilibrium, these rates are equal, and so

$$k_a p_{A_2} (1-\theta)^2 = k_d \theta^2$$

$$K p_A (1-\theta)^2 = \theta^2$$

$$\theta = \frac{K^{1/2} p_{A_2}^{1/2}}{1 + K^{1/2} p_{A_2}^{1/2}}$$

$$\frac{1}{\theta} = 1 + \frac{1}{K^{1/2} p_{A_2}^{1/2}}$$

A plot of $\frac{1}{\theta}$ vs $\frac{1}{p_{A_2}^{1/2}}$ will yield a straight line with slope $\frac{1}{K^{1/2}}$ and intercept 1.

Bimolecular Surface reactions

A bimolecular reaction between two molecules A and B on a surface may occur through different alternative steps out of which following two are important

i) Langmuir Hinshelwood mechanism

The two reacting molecules A and B react after being adsorbed on neighbouring sites on the surface of the catalyst. This mechanism is called as Langmuir - Hinshelwood mechanism. Reaction rate ν, for such reaction may be written as follows:

$$\nu = k\theta_A \theta_B$$

Putting the values of θ_A and θ_B, we get

$$\nu = \frac{kK_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$

Above equation could be subjected to two special cases as follows:

1. If the pressures of A and B species, p_A and p_B are both sufficiently low so that $K_A p_A$ and $K_B p_B$ may be neglected in comparison with unity, the rate equation becomes,

$$\nu = kK_A K_B [A][B]$$

This would mean reaction to be second order. This is a frequently observed behaviour in Langmuir –Hinshelwood mechanism.

2. If a reactant A is very weakly adsorbed, $k_A\, p_A$ in the denominator of equation may be neglected, and the rate equation become,

$$v = \frac{kK_AK_Bp_Ap_B}{(l+K_Bp_B)^2}$$

Reaction of hydrogen with ethylene on copper follows a nearly similar rate law as follows:

$$v = \frac{K[H_2][C_2H_4]}{(1+K[C_2H_4])^2}$$

If reactant B is adsorbed very strongly such that $K_B\, p_B \gg 1$, equation becomes

$$v = \frac{kK_Ap_A}{K_Bp_B}$$

The rate is now inversely proportional to P_B. Such behaviour is observed in reaction between carbon monoxide and oxygen on quartz and on platinum. In these cases, rate in inversely proportional to the pressure of carbon monoxide, which must be strongly adsorbed.

ii) *Langmuir - Rideal mechanism*

If reaction is due to collision of gaseous molecules A with adsorbed B molecules, the mechanism is known as Langmuir – Rideal mechanism and the rate law in this case will be,

$$v = k\theta_B p_A$$

or, $$v = \frac{kK_Ap_Ap_B}{1+K_Ap_A+K_Bp_B}$$

The reaction of ethylene and H_2 on copper surface presents a case of Langmuir – Rideal mechanism. C_2H_4 gets adsorbed much strongly on the surface. Rate equation for the reaction of C_2H_4 and H_2 on copper surface follows as below:

$$v = \frac{k[H_2][C_2H_4]}{(1+c[C_2H_4])^2}$$

MODULE -II

SURFACE TENSION:

It is a phenomenon between liquids and gases. It causes objects that usually sink due to their higher density to swim or that paints achive good wetting on some and collect into drops on other surfaces.

The phenomenon of surface tension arises due to the two kinds of intermolecular forces

(i) Cohesion : The force of attraction between the molecules of a liquid by virtue of which they are bound to each other to remain as one assemblage of particles is known as the force of cohesion. This property enables the liquid to resist tensile stress.

(ii) Adhesion: The force of attraction between unlike molecules, i.e. between the molecules of different liquids or between the molecules of a liquid and those of a solid body when they are in contact with each other, is known as the force of adhesion. This force enables two different liquids to adhere to each other or a liquid to adhere to a solid body or surface.
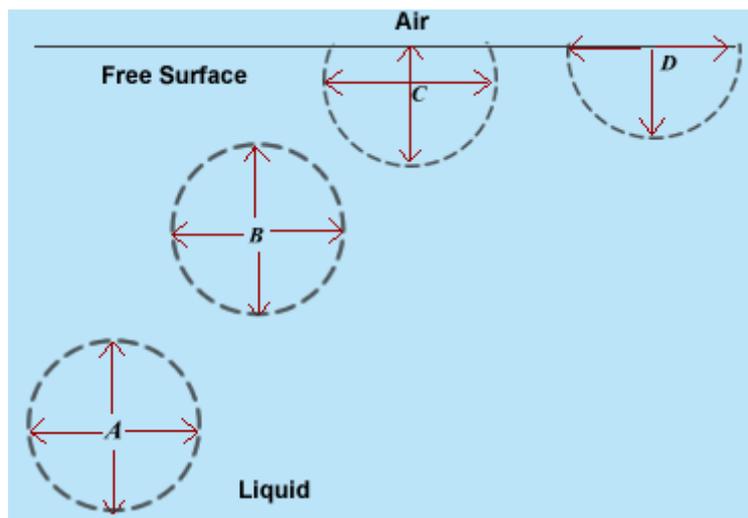

Figure 2.1: The intermolecular cohesive force field in a bulk of liquid with a free surface

A and B experience equal force of cohesion in all directions, C experiences a net force interior of the liquid The net force is maximum for D since it is at surface

Work is done on each molecule arriving at surface against the action of an inward force. Thus mechanical work is performed in creating a free surface or in increasing the area of the surface. Therefore, a surface requires mechanical energy for its formation and the existence of a free surface implies the presence of stored mechanical energy known as free surface energy. Any system tries to attain the condition of stable equilibrium with its potential energy as minimum. Thus a quantity of liquid will adjust its shape until its surface area and consequently its free surface energy is a minimum.

The surface tension is defined as 'the amount of force (Nm) necessary to expand the surface (m^2) of a liquid by one unit'.

Therefore, the surface tension is measured in N/m ($Nm/m^2 = N/m$). Occasionally, the surface tension is given in dyn/cm.

1 dyn/cm = 1 mN/m

The surface tension of water at 20 °C is 72,75 mN/m.

CAPILLARY ACTION:

The interplay of the forces of cohesion and adhesion explains the phenomenon of capillarity. When a liquid is in contact with a   solid, if the forces of adhesion between the molecules of the liquid and the solid are greater than the forces of cohesion among the liquid molecules themselves, the liquid molecules crowd towards the solid surface. The area of contact between the liquid and solid increases and the liquid thus wets the solid surface.

The reverse phenomenon takes place when the force of cohesion is greater than the force of adhesion. These adhesion and cohesion properties result in the phenomenon of capillarity by

which a liquid either rises or falls in a tube dipped into the liquid depending upon whether the force of adhesion is more than that of cohesion or not (Fig.2.2).

The angle θ as shown in Fig. 2.2, is the area wetting contact angle made by the interface with the solid surface.
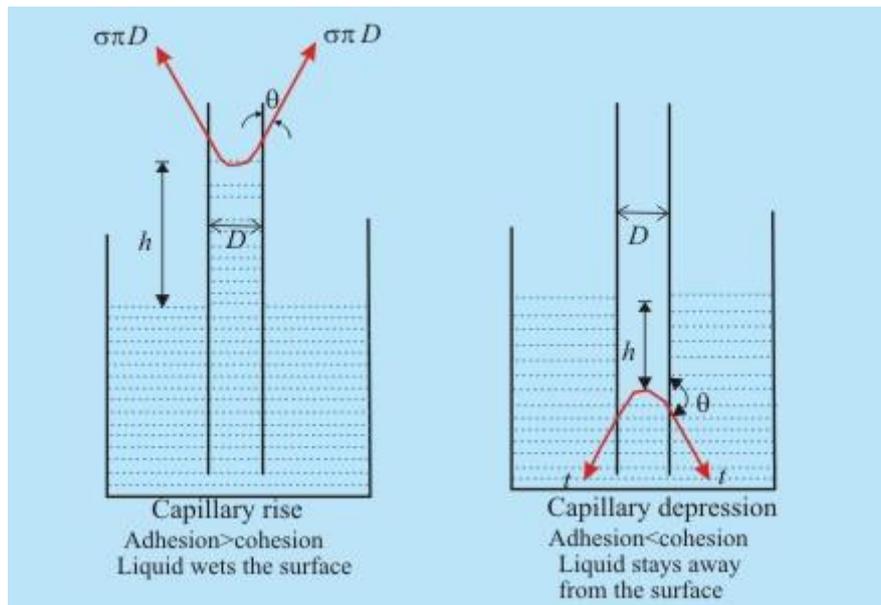

Figure 2.2: Phenomenon of Capillarity

For pure water in contact with air in a clean glass tube, the capillary rise takes place with θ = 0. Mercury causes capillary depression with an angle of contact of about 1300 in a clean glass in contact with air. Since h varies inversely with D as found from Eq. ($h = \dfrac{4\sigma \cos \theta}{\rho g D}$), an appreciable capillary rise or depression is observed in tubes of small diameter only.

ADSORPTION:

Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk.

The process of adsorption arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. These unbalanced residual forces have tendency to attract and retain

the molecular species with which it comes in contact with the surface. Adsorption is essentially a surface phenomenon.

Adsorption is a term which is completely different from Absorption. While absorption means uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. When both Adsorption and Absorption processes take place simultaneously, the process is called sorption.

Adsorption process involves two components Adsorbent and Adsorbate. Adsorbent is the substance on the surface of which adsorption takes place.Adsorbate is the substance which is being adsorbed on the surface of adsorbent. Adsorbate gets adsorbed.

Adsorbate + Adsorbent gives rise to Adsorption
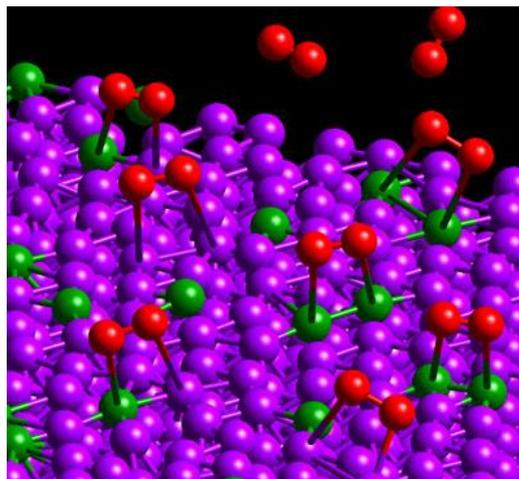
Oxygen molecules (red) adsorb on a bimetallic surface of platinum (purple) and cobalt (green).

Some modern techniques have been used to study surface.

1. Low energy electron diffraction (LEED).

2. Photo electron spectroscopy (PES).

3. Scanning Tunneling microscopy (STM).

ADSORPTION IN LIQUIDS

Adsorption can be understood by considering a simple example. In case of liquid state, water molecule present on the surface is attracted inwards by the molecules of water present in the bulk. This gives rise to surface tension. While the molecule of water present within the bulk is equally attracted from all the sides and the net force experienced by the water molecule in bulk is zero. This clearly shows that particles at surface and particles at the bulk are in different environment.

molecules of water present at the surface molecule of water present in bulk.
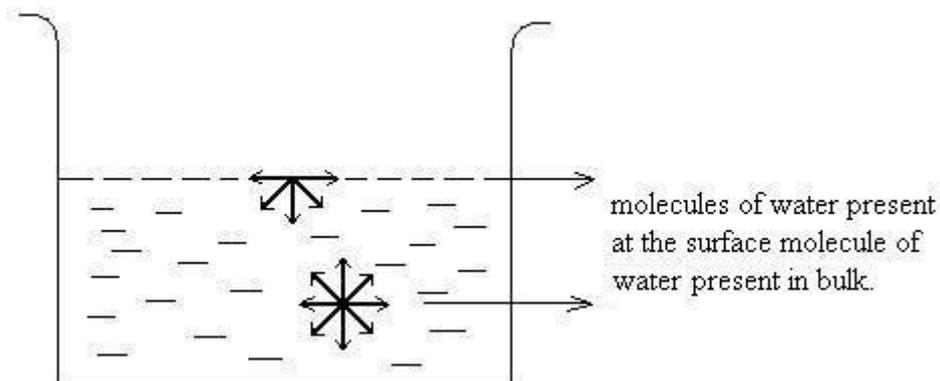
Water molecule on surface experiencing unbalanced forces as compared to molecule inside which experiences forces from all direction.

ADSORPTION IN SOLIDS

In case of solid state these residual forces arise because of an unbalanced valence forces of atoms at the surface. The generation of these forces on solid surface can be explained diagrammatically as follows:
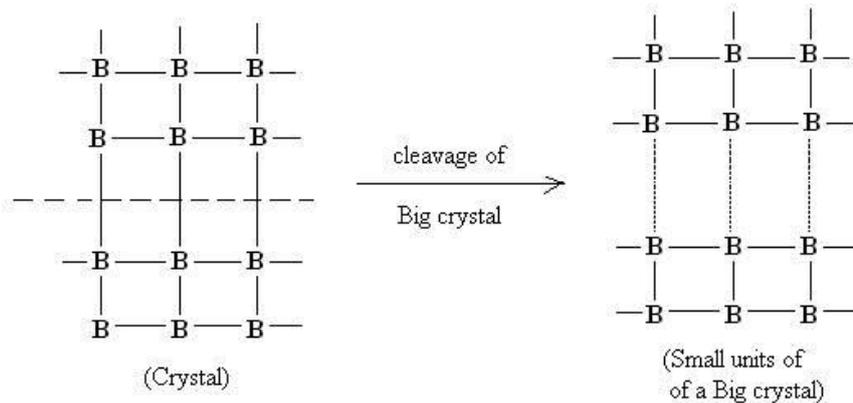
Cleavage of a big crystal into smaller unit

Due to cleavage of a big crystal into smaller unit, residual forces or vacancies gets generated on the surface of the solid. Occupancy of these vacancies by some other molecular species results into Adsorption.

FACTS ABOUT ADSORPTION PROCESS

Adsorption is a spontaneous process

For reaction or process to be spontaneous, there must be decreases in free energy of the system i.e. ΔG of the system must have negative value.

Also we know, $\Delta G = \Delta H - T\Delta S$

And during this process of adsorption, randomness of the molecule decreases which ΔS is negative. We can rewrite above equation as

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

Therefore, for a reaction to be spontaneous ΔH has to be negative and

$$|\Delta H| > |T\Delta S|$$

Adsorption is an exothermic process

Adsorption process takes place by adsorbate getting adsorbed on adsorbent. Forces of attraction exist between adsorbate and adsorbent and due to these forces of attraction, heat energy is released. So adsorption is an exothermic process.

TYPES OF ADSORPTION

Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vanderwaal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption.

Physical Adsorption or Physisorption

When the force of attraction existing between adsorbate and adsorbent are weak Vanderwaal forces of attraction, the process is called Physical Adsorption or Physisorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. $\Delta H_{adsorption}$ is 20-40KJ/mol.

It takes place at low temperature below boiling point of adsorbate.As the temperature increases in, process of Physisorption decreases.
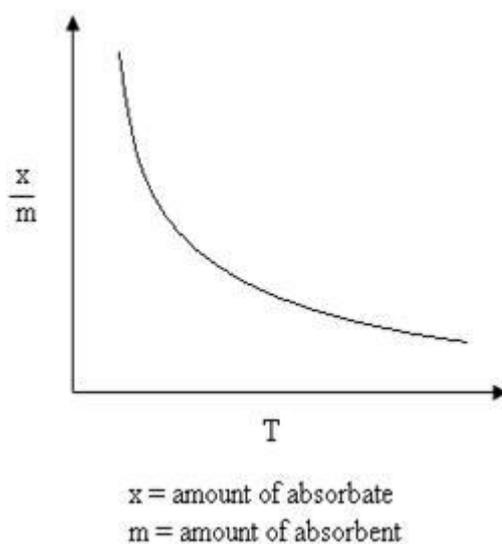

x = amount of absorbate
m = amount of absorbent

Figure 2.3: Physical Adsorption vs. Temperature graph

Chemical Adsorption or Chemisorption

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption i.e. $\Delta H_{adsorption}$ is 200-400KJ/mol.

It can take place at all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

$$\frac{x}{m}$$

x = amount of absorbate
m = amount of absorbent

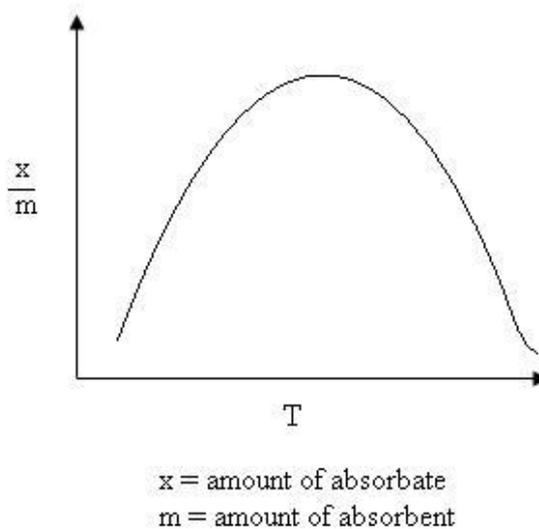**Figure 2.4:** Chemical Adsorption vs. Temperature Graph

ADSORPTION ISOTHERM

The process of Adsorption is usually studied through graphs called as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature.

FACTORS ON WHICH ADSORPTION DEPENDS

TEMPERATURE

Adsorption increases at low temperature conditions.

$$A + B \Longleftrightarrow AB + Heat$$
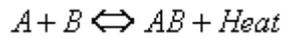
Adsorption process is exothermic in nature. According to LeChatleir principle, low temperature conditions would favour the forward direction

PRESSURE

As depicted by Adsorption Isotherm, with the increases in pressure, adsorption increases up to a certain extent till saturation level is achieved. After saturation level is achieved no more adsorption takes place no matter how high the pressure is applied.

SURFACE AREA

Adsorption is a surface phenomenon therefore it increases with increase in surface area.

ACTIVATION OF ADSORBENT

Activation of adsorbent surface is done so as to provide more number of vacant sites on surface of adsorbent. This can be done by breaking solid crystal in small pieces, heating charcoal at high temperature, breaking lump of solid into powder or other methods suitable for particular adsorbent.

GIBB'S ADSORPTION ISOTHERM:

This isotherm normally considers the case when adsorbents are liquids and adsorbates are soluble or partially soluble in it e.g., surfactants / water or organic liquid / water system.

Considering a system having a plane interface between them, the Gibb's free energy of a system containing two components could be written as follows:

$$G = n_1 \mu_1 + n_2 \mu_2$$

Where n_1 and n_2 are the number of moles and μ_1 and μ_2 are the chemical potentials of the two components respectively. While dealing with the adsorption of one of the components on

the surface of another, an additional term of surface energy has to be introduced, and hence, equation modifies to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma$$

where γ is the surface energy per unit area and σ is the surface area. It is now clear that first equation is for bulk while second equation will be applicable for the surface of the absorbent liquid. The complete differential of second equation may be written as

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma$$

We find that the total free energy G of the whole system depends on independent variables , namely , T,P,n_1,n_2 and σ, thus,

$$G = f(T, P, n_1, n_2, \sigma)$$

and complete differential of G will be,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\sigma} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\sigma} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\sigma} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,\sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma}\right)_{T,P,n_1,n_2} d\sigma$$

or $dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$

At constant temperature and pressure, above equation reduces to,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$$

Comparing the equations, we get

$$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0$$

A corresponding equation for the bulk of the system may be,

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$$

Where n_1^0 and n_2^0 are the number of moles of adsorbent liquid and solute in the bulk.

Hence, we get

$$-\frac{d\gamma}{d\mu_2} = \frac{(n_2 - n_1 n_2^0 / n_1^0)}{\sigma}$$

Here, the term $\dfrac{(n_2 - n_1 n / n_1^0)}{\sigma}$ represents the corresponding excess moles of solute per

unit area on the surface of the adsorbent and now be represented by Γ_2

$$\therefore \quad -\frac{d\gamma}{d\mu_2} = \Gamma_2$$

The chemical potential of solute $\mu_2 = \mu_2^0 + RT \ln a_2$

or $d\mu_2 = RTd \ln a_2$

When solution is very dilute, the activity a_2 of solute could be replaced by its concentration.

$$\therefore \quad \Gamma_2 = -\frac{c_2}{RT}\left(\frac{d\gamma}{\partial c_2}\right)_T$$

or, in general for any solute and liquid adsorbent,

$$\Gamma = -\frac{c}{RT}\left(\frac{\partial \gamma}{\partial c}\right)_T$$

In the above equation γ is essentially surface energy per unit area, which may easily be replaced by surface tension (force/length).

The application of the above equation is as follows. If the detergent (solute or adsorbate) tends to accumulate at the interface its surface excess is positive, and so $\dfrac{d\gamma}{dc}$ is negative. This means surface tension decreases when a solute accumulates at the surface.

Example: The surface tensions of the dilute solutions of phenol in water at $27^{\circ}C$ are the following:

Mass % phenol	0.024	0.05	0.125	0.25	0.40
γ x 10 3/(Nm $^{-1}$)	72.7	72.2	71.3	70.3	69.3

Calculate surface excess concentration (Γ) at a concentration of 0.15 mass of phenol. Comment on the significance of the observed value of Γ.

Solution : A plot of γ us mole of phenol gives a curvature with negative slope for 0.15 mol of phenol slope is $-\dfrac{1.7}{0.1875}$, putting values in equation,
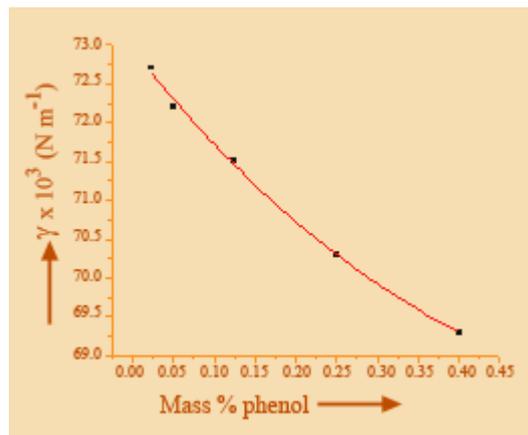

Figure 2.5: Surface tension of phenol vs mass %

$$\Gamma = -\frac{c}{RT}\left(\frac{\partial \gamma}{\partial c}\right)_{\!\tau}$$

$$\Gamma = -\frac{0.15}{8.31 x 300^{0} k}\left(-\frac{1.7}{0.1875}\right)$$ = 5.45 x 10-4 mol m^{-2}

The positive value of Γ signifies that phenol is surface active and accumulates at the interface.

FREUNDLICH ADSORPTION ISOTHERM:

In 1909, Freundlich gave an empirical expression representing the isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation.

$$\frac{x}{m} = k P^{\frac{1}{n}}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature.

Explanation of Freundlich Adsorption equation

At low pressure, extent of adsorption is directly proportional to pressure (raised to power one).

$$\frac{x}{m} \propto P^1$$

At high pressure, extent of adsorption is independent of pressure (raised to power zero).

$$\frac{x}{m} \propto P^0$$

Therefore, at intermediate value of pressure, adsorption is directly proportional to pressure raised to power 1/n. Here n is a variable whose value is greater than one.

$$\therefore \frac{x}{m} \propto P^{\frac{1}{n}}$$

Using constant of proportionality, k, also known as adsorption constant we get

$$\frac{x}{m} = k P^{\frac{1}{n}}$$

The above equation is known as Freundlich adsorption equation.

Plotting of Freundlich Adsorption Isotherm

As per Freundlich adsorption equation

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Taking log both sides of equation, we get,

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p$$

The equation above equation is comparable with comparable with equation of straight line, y = m x + c where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between log(x/m) and log p, we will get a straight line with value of slope equal to 1/n and log k as y-axis intercept.
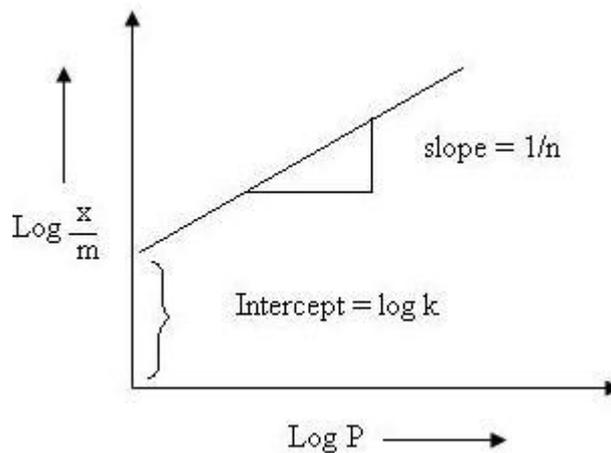

Figure 2.6: log(x/m) vs. log p graph

Limitation of Freundlich Adsorption Isotherm

Experimentally it was determined that extent of adsorption varies directly with pressure till saturation pressure Ps is reached. Beyond that point rate of adsorption saturates even after applying higher pressure. Thus Freundlich Adsorption Isotherm failed at higher pressure.
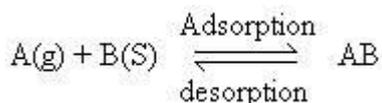
LANGMUIR ADSORPTION ISOTHERM:

In 1916, Irving Langmuir proposed another Adsorption Isotherm which explained the variation of Adsorption with pressure. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.

2. All the vacant sites are of equal size and shape on the surface of adsorbent.

3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.

4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{desorption}{\overset{Adsorption}{\rightleftharpoons}} AB$$

Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.
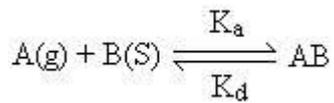
5. Adsorption is monolayer or unilayer.

Derivations of the Langmuir Adsorption Equation

Calculation of Equilibrium Constant

Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be

calculated.

$$A(g) + B(S) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} AB$$

Where K_a represents equilibrium constant for forward reaction and K_d represents equilibrium constant for backward direction.

According to Kinetic theory,

Rate of forward reaction = K_a [A] [B]

Rate of backward reaction = K_d [AB]

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a [A] [B] = K_d [AB]$$

$$\text{Or, } \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

$$K = \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

The above equation represents the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

Derivation

Langmuir Equation which depicts a relationship between the number of active sites of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.

To derive Langmuir Equation and new parameter 'θ' is introduced. Let θ the number of sites of the surface which are covered with gaseous molecules. Therefore, the fraction of surface which are unoccupied by gaseous molecules will be $(1 - \theta)$.

Now, Rate of forward direction depends upon two factors: Number of sited available on the surface of adsorbent, $(1 - \theta)$ and Pressure, P. Therefore, rate of forward reaction is directly proportional to both mentioned factors.

Rate of forward reaction $\propto$ P $(1 - \theta)$
Rate of adsorption $\propto$ P $(1 - \theta)$
Or, Rate of adsorption $= K_a P (1 - \theta)$

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

Rate of desorption $\propto \theta$
Or, Rate of desorption $= K_d \theta$

At equilibrium, rate of adsorption is equal to rate of desorption.

$K_a P (1 - \theta) = K_d \theta$

We can solve the above equation to write it in terms of θ.

$K_a P - K_a P \theta = K_d \theta$

$K_a P = K_a P \theta + K_d \theta$

$K_a P = (K_d + K_a P) \theta$

$$\theta = \frac{K_a P}{K_d + K_a P}$$

Divide numerator and denominator on RHS by K_d, we get

$$\theta = \dfrac{\dfrac{K_a}{K_d}P}{\dfrac{K_d}{K_d} + \dfrac{K_a}{K_d}P}$$

Now put

$$K = \dfrac{K_a}{K_d}$$

in above equation we get

$$\theta = \dfrac{KP}{1 + KP}$$

This is known as Langmuir Adsorption Equation.

Alternate form of Langmuir Adsorption Equation

Langmuir adsorption equation can be written in an alternate form in terms of volume of gas adsorbed. Let V be volume of gas adsorbed under given sets of conditions of temperature and pressure and V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules.

$$\theta = \dfrac{V}{V_{mono}}$$

Substituting the value of θ in Langmuir equation

$$\dfrac{V}{V_{mono}} = \dfrac{KP}{1 + KP}$$

$$\text{Or } V_{mono} = 1 + \dfrac{1}{KP}$$

Or in terms of pressure P we get,

$$\dfrac{P}{V} = \dfrac{P}{V_{mono}} + \dfrac{1}{KV_{mono}}$$

Langmuir Adsorption Equation in alternate form

Thus, if we plot a graph between P/V Vs P, we will obtain a straight line with

$$slope = \frac{1}{V_{mono}} \quad and \quad Intercept = \frac{1}{KV_{mono}}$$

Limitations of Langmuir Adsorption Equation

1. The adsorbed gas has to behave ideally in the vapor phase. This condition can be fulfilled at low pressure conditions only. Thus Langmuir Equation is valid under low pressure only.

2. Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other. *BET theory* proposed by Brunauer, Emmett and Teller explained more realistic multilayer adsorption process.

3. Another assumption was that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid if homogeneous. But we all know that in real solid surfaces are heterogeneous.

4. Langmuir Equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.

5. The adsorbed molecules have to be localized i.e. decrease in randomness is zero ($\Delta S = 0$). This is not possible because on adsorption liquefaction of gases taking place, which results into decrease in randomness but the value is not zero.

From above facts we can conclude that, *Langmuir equation is valid under low pressure conditions.*

FREUNDLICH ADSORPTION EQUATION: A SPECIAL CASE OF LANGMUIR EQUATION:

We consider Langmuir Equation

$$\theta = \frac{KP}{1+KP}$$

At low pressure value of KP<<1. Therefore,

$$\theta = KP \quad \text{Or} \quad \theta \propto P \quad ...(1)$$

The above equation shows linear variation between extent of adsorption of gas and pressure.

At high pressure value of KP>>1

$$\therefore \theta = \frac{KP}{KP} = 1 \quad ...(2)$$

The extent of adsorption, θ is independent of pressure at high pressure conditions. The reaction at this stage becomes zero order

Combining the results of equations, we can conclude that

$$\theta = Kp^{0-1}$$
$$or \; \theta = Kp^{1/n} \quad ...(3)$$

Equation (3) is in agreement with Freundlich adsorption equation.

We can say that Freundlich adsorption equation is a special case of Langmuir equation.

MULTILAYER ADSORPTION:

An important assumption of Langmuir theory is the formation of a monolayer. Because of monolayer formation a saturation in adsorption would reach at higher equilibrium concentration of the adsorbate. This type of adsorption occurs due to short range chemical

forces which do not allow penetration through the primary adsorbed molecules. Multilayer formation has been observed when molecules are adsorbed through weak forces (long range forces, normally under physical adsorption) due to cohesive forces exerted by the molecules of the adsorbate.

At high pressure multilayer adsorption takes place. The theory of multimolecular (multilayer) adsorption was developed by Stephen Brunauer, Paul Emmet and Edward Teller and is called BET isotherm. This isotherm derived by them successfully accounts for all types of adsorption.

BET ADSORPTION ISOTHERM:

It assumes that the surface possess uniform, localised sites and that adsorption on one site does not affect the adsorption on neighbouring sites just as in the Langmuir theory. Also, molecules can be adsorbed in second, third… and nth layers with the surface available for layer equal to the coverage of the next lower layer.

The rate constants for adsorption and desorption of the primary layer are ka and kd and those of the subsequent layers are all ka' and kd'. The number of sites corresponding to zero, monolayer, bilayer, … coverage at any stage are N_0, N_1, N_2, etc. and N_i in general. The condition for equilibrium of the initial layer is the equality of the rates of its formation and desorption,

$$k_a p N_0 = k_d N_1$$

The condition for equilibrium of the next layer is

$$k_a' p N_1 = k_d' N_2 \quad \text{and in general} \quad k_a' p N_{i-1} = k_d' N_i, \quad i = 2, 3, \ldots$$

This condition may be expressed in terms of N_0 as follows:

$$N_i = \left(\frac{k_a'}{k_d'}\right)pN_{i-1}$$

$$= \left(\frac{k_a'}{k_d'}\right)^2 p^2 N_{i-2} \quad = \quad \left(\frac{k_a'}{k_d'}\right)^{2-1} p^{i-1}.N_1 \quad = \quad \left(\frac{k_a'}{k_d'}\right)^{i-1}\left(\frac{k_a}{k_d}\right)p^i N_0$$

$$N_i = \left(\frac{k_a'}{k_d'}\right)^{i-1}\left(\frac{k_a}{k_d}\right)p^i N_0$$

writing $\dfrac{k_a'}{k_d'} = x$ and $\dfrac{k_a}{k_d} = cx$, then

$$N_i = x^{i-1}cxp^i N_0$$

$$N_i = c(xp)^i N_0$$

Now, we calculate the total volume, V, of adsorbed material. V is proportional to the total number of particles adsorbed, and so

$$V = N_1 + 2N_2 + 3N_3 + ... = \sum_{i=1}^{\infty} iN_i$$

Because each layer contributes number of particles according to its thickness, i.e., a monolayer one particle, a bilayer site two particles etc.

If there were complete monolayer coverage the volume adsorbed would be Vmono, with

$$V_{mono} = N_0 + N_1 + N_2 + ... = \sum_{i=1}^{\infty} N_i$$

Because each site contributes only one particle to the total, it follows that

$$V = \sum_{i=0}^{\infty} iN_i = \sum_{i=1}^{\infty} ic(xp)^i N_0$$

$$= cN_0 \sum_{i=1}^{\infty} i(xp)^i$$

$$= cN_0 xp \sum_{i=1}^{\infty} i(xp)^{i-1}$$

$$= cN_0 xp \frac{1}{(1-xp)^2}$$

$$V = cN_0 xp(1-xp)^{-2}$$

Hence,

$$V_{mono} = \sum_{i=0}^{\infty} N_i = N_0 + N_1 + N_2 + \ldots$$

$$= N_0 + \sum_{i=1}^{\infty} N_i$$

$$= N_0 + \sum_{i=1}^{\infty} c(xp)^i N_0$$

$$= N_0 + \frac{cN_0 xp}{1-xp}$$

$$= N_0 + cN_o xp\left(1 + xp + (xp)^2 + \ldots\right)$$

$$\because (1-xp)^{-1} = 1 + xp + (xp)^2 + \ldots$$

We have,

$$\frac{V}{V_{mono}} = \frac{cN_0 xp(1-xp)^{-2}}{N_0 + cN_0 xp(1-xp)^{-1}}$$

$$= \frac{cxp}{1 + (c-2)xp + (1-c)(xp)^2}$$

$$= \frac{c(p/p*)}{1 + (c-2)p/p* + (1-c)p^2/p*^2}$$

$$= \frac{cz}{1 + (c-2)z + (1-c)z^2}$$

$$x = \left(\frac{K'_a}{k'_d}\right) = \frac{1}{p^*},$$

$p^* =$ equilibrium pressure, (ads) $\Leftrightarrow$ vapour putting $z = p / p^*$

$$\frac{V}{V_{mono}} = \frac{cz}{1+cz-2z+z^2-cz^2} = \frac{cz}{(1-z)\{1-(1-c)z\}}$$

$$= \frac{c.p/p^*}{(1-p/p^*)\{(1-1+c)p/p^*\}}$$

$$= \frac{c.p/p^*}{(1-p/p^*)\left[1+(c-1)p/p^o\right]}$$

$$\frac{V}{(z/(1-z))} = \frac{V_{mono}c}{1(1-c)z}$$

$$\frac{V}{(z/(1-z))} = \frac{V_{mono}c}{1(1-c)z}$$

$$\frac{z}{(1-z)}\cdot\frac{1}{V} = \frac{1}{cV_{mono}} + \frac{(c-1)z}{cV_{mono}}$$

$\dfrac{(c-1)}{cV_{mono}}$ can therefore be obtained from the slope of a plot of $\dfrac{z}{(1-z)V}$ against z, and cVmono can be found from the intercept at z = 0, the result combined to give c and Vmono from the corresponding value of Vmono at 273 K and 1 atm, number of molecules present in Vmono could be calculated. By knowing the contact area of a molecule, surface area of the adsorbent per unit mass could be determined.
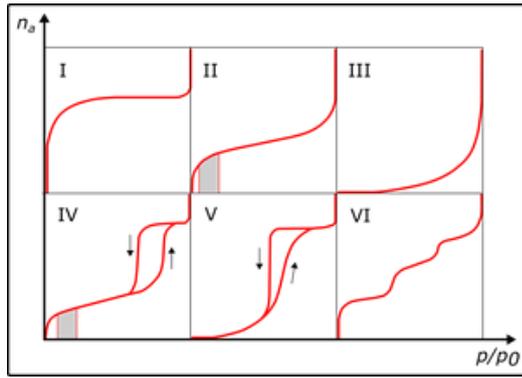
$$\frac{p}{n_a(p_0 - p)} s_{total} = \frac{1}{n_m C} + \frac{(C-1)}{n_m C} \cdot \frac{p}{p_0}$$

Figure 2.7: BET adsorption isotherms.

DETERMINATION OF HEAT OF ADSORPTION:

The temperature dependence of K can be used to determine the isoseric enthalpy of adsorption

(ΔH^θ , the enthalpy of adsorption at a fixed surface coverage).

From Langmuir adsorption isotherm, fraction of covered surface, $\theta = \dfrac{Kp}{1 + Kp}$

or $Kp = \dfrac{\theta}{1-\theta}$, where θ is constant

$\ln K + \ln p = \text{constant}$ so, from the So from free.equation $\left(\dfrac{d \ln K}{dT}\right)_\theta = \dfrac{\Delta H^\theta}{RT^2}$,

$\therefore \left(\dfrac{\partial \ln P}{\partial T}\right)_\theta = -\left(\dfrac{d \ln K}{dT}\right)_\theta = -\dfrac{\Delta H^\theta}{RT^2}$

using $\dfrac{d\left(\dfrac{1}{T}\right)}{dT} = -\dfrac{1}{T^2}$, this rearranges to,

$\left(\dfrac{\partial \ln P}{\partial T}\right)_\theta = +\dfrac{\Delta H^\theta}{R} \times \left(\dfrac{d\left(\dfrac{1}{T}\right)}{dT}\right)$

$$\left(\frac{\partial \ln P}{\partial T}\right)_\theta \left(\frac{dT}{d\frac{1}{T}}\right)_\theta = \frac{\Delta H^\theta}{R}$$

$$\left(\frac{d \ln P}{d\frac{1}{T}}\right)_\theta = \frac{\Delta H^\theta}{R}$$

Thus, a plot of lnP against 1/T should be a straight line with slope $\frac{\Delta H^\theta}{R}$.

Therefore ΔH^θ could be determined from the slope.

SURFACE AREA OF ADSORBENT:

As adsorption is a surface phenomenon, surface area offered by Adsorbent becomes important factor for consideration.

Volume of an ideal gas at STP = 22.4 L= 22.4 dm³

Also the number of gaseous molecules present at STP = $6.023*10^{23}$ molecules

Vmono be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules. Let the total number of molecules of gas adsorbed corresponding to volume Vmono be N whose value is given as

$$N = \left(\frac{V_{mono}}{22.4 dm^3 mol^{-1}}\right) \times 3.023 \times 10^{23} mol^{-1}$$

Now area of a molecule having density ρ and occupying volume V is calculated as follows

$$\rho = \frac{M}{V_m}$$

Where Vm is the total volume of the surface

Now Total volume Vm is equal to volume of each molecule (V) multiplied by total number of molecule (N_A) adsorbed on the surface at volume, V.

$$V_m = N_A V$$

$$\rho = \frac{M}{V N_A}$$

$$V = \frac{M}{\rho N_A}$$

Molecule being spherical in nature, Volume of the molecule V is also given as

$$V = \frac{4}{3}\pi r^3 = \frac{M}{\rho N_A}$$

The radius, r occupied by each gas molecule is

$$r = \left(\frac{3}{4\pi} \frac{M}{\rho N_A} \right)^{\frac{1}{3}}$$

Area occupied by each gas molecule is

$$\text{Area} = \pi r^2 = \pi \left(\frac{3}{4\pi} \frac{M}{\rho N_A} \right)^{\frac{2}{3}}$$

This is the area occupied by one molecule. If the value multiplied by the total number of molecules adsorbed on the surface of adsorbent, we will get the total surface area of the adsorbent.

$$\text{Total Surface Area} = N.\pi \left(\frac{3}{4\pi} \frac{M}{\rho N_A} \right)^{\frac{2}{3}}$$

Or,

$$\text{Total Surface Area} = \left(\frac{V_{mono}}{22.4 dm^3 mol^{-1}} \right) \times 6.023 \times 10^{23} mol^{-1} \times \pi \left(\frac{3}{4\pi} \frac{M}{\rho N_A} \right)^{\frac{2}{3}}$$

APPLICATION OF ADSORPTION:

The process of adsorption is very important as it has many applications in domestic as well as in industrial processes. Some of them are as follows:

1. In heterogeneous catalysis: Surface active materials are widely used as catalysts mostly due to adsorption processes. If the surface active materials (adsorbents) have a different phase from that of substrates, then the catalysis is called heterogeneous catalysis. A system where both the catalyst and the substrate are in same phase is called homogeneous (catalysis).

2. In removal of colouring material: Many coloured materials or impurities are removed through adsorption by suitable surface active materials like charcoal. Activated charcoal has been extensively used for this purpose.

3. In ion exchange resins: Several polymeric materials are used for the separation of ionic substances in chromatography through ion-exchange.

4. In adsorption indicators: Several dyes like eosin and fluoresein are used as indicators in the titrations of Cl -, Br - etc., against Ag +(Fajan's method).

5. In gas masks : Activated charcoal is used to remove toxic gases in gas masks.

6. In dyeing of cloth: Many substances work as mordants for dyeing of cloths. Several metal cyanogen complexes and alums work as efficient mordants in dyeing cloths.

7. In de humidizers: Many substances, when they adsorb water, change their colour. Silica and alumina gels are used as adsorbents for removing moisture. Silica is colourless but after adsorbing water becomes blue.

MODULE –III

SURFACE ACTIVE AGENTS/ SURFACTANTS:

Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. The term *surfactant* is a blend of *surface active agent.* Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their *tails*) and hydrophilic groups (their *heads*). Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in the water phase.
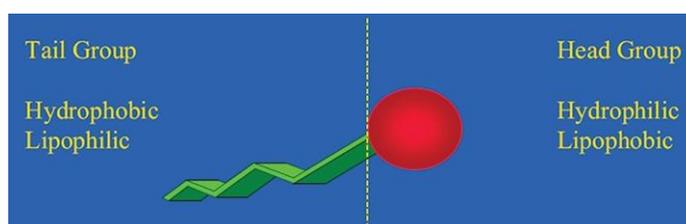

Figure 3.1: Structure of surfactant

CLASSIFICATION OF SURFACE ACTIVE AGENTS:

One of the methods to classify the surfactants is by the type of head-groups they possess. As per this method, the surfactants are classified into four types: anionic, cationic, zwitterionic and nonionic.

The surfactants can also be classified based upon their origin, structural features, or behavior in solution, e.g., gemini surfactants and biosurfactants. These surfactants can be any of the anionic, cationic, zwitterionic or nonionic types.

Anionic surfactants

The head-group of an anionic surfactant is negatively charged, which is electrically neutralized by an alkali metal cation. The soaps ($RCOO^-$ Na^+), alkyl sulfates (RSO_4^- Na^+) and alkyl benzene sulfonates ($RC_6H_4SO_3^-$ Na^+) are the well-known examples of the anionic surfactants. These surfactants readily adsorb on the positively charged surfaces.

The anionic surfactants are the most widely used surfactants in industrial practices. The linear alkyl benzene sulfonates have the highest consumption. Some of the anionic surfactants (e.g., salts of fatty acids) are precipitated from the aqueous solution in presence of salts containing Ca^{+2} and Al^{+3} ions. Therefore, their use may be restricted in certain media (e.g., hard water). The calcium and magnesium salts of alkyl benzene sulfonates are soluble in water. Therefore, they are much less sensitive to hard water.

Cationic surfactants

The head-group of a cationic surfactant has a positive charge. The cationic surfactants are useful for adsorption on negatively charged surfaces. Some of the common uses of the cationic surfactants are in ore flotation, textile industries, pesticide applications, adhesion, corrosion inhibition and preparation of cosmetics.

Most of the cationic surfactants have good stability in a wide range of pH. The relatively less use of cationic surfactants in industry is due to their rather poor detergency, lack of suspending power for carbon, and higher cost. Some well-known cationic surfactants are, long chain amines (RNH_3^+ X^-), quaternary ammonium salts [$RN(CH_3)_3^+$ X^-] and quaternary salts of polyethylene oxide-amine derivatives [$RN(CH_3)$ $\{(C_2H_4O)_xH\}_2^+$ Cl^-].

Zwitterionic surfactants

These surfactants have both positive and negative charges on the surface-active part of the molecule. The long chain amino acids ($RN^+H_2CH_2COO^-$) are the well-known examples of the zwitterionic surfactants.

The main advantage of these surfactants is that they are compatible with both anionic and cationic surfactants due to the presence of both positive and negative charges. They are less irritating to eye or skin. Therefore, they find wide use in cosmetics. They are also used as fabric softeners and bactericides.

Most of these surfactants are sensitive to pH. They show the properties of anionic surfactants at high pH whereas they behave as cationic surfactants at low pH. The sulfobetaine-type of surfactants [$RN^+(CH3)2(CH2)$ $xSO3^-$] remain zwitterionic in a wide range of pH.

Nonionic surfactants

The nonionic surfactants are second most widely used surfactants in the industry. They do not have any significant electric charge on their surface-active part. Therefore, there is very little or no electrical interaction between the head-groups. These surfactants are stable in presence of electrolytes.

They are compatible with most other types of surfactants. These surfactants disperse carbon well. Therefore, they have a large number of industrial uses. Most of the nonionic surfactants are available in the form of viscous liquids. They usually generate less foam than the ionic surfactants.

Some nonionic surfactants are virtually insoluble in water, but soluble in organic solvents. However, some nonionics are soluble both in water and organic liquids, although the extent of solubility differs. The solubility depends on the structure of the surfactant molecules.

The alkyl phenol ethoxylate [$RC_6H_4(OC_2H_4)_xOH$] category of surfactants is widely used in emulsions, paints and cosmetics. The alcohol ethoxylates [$R(OC_2H_4)_xOH$] are biodegradable.

They are quite resistant to hard water. Therefore, in the applications involving saline media where the anionic surfactants are salted out of the solution, these surfactants find extensive use. The polyoxypropylene glycols are used in a wide range of molecular weights (e.g., 1000 - 30000). They are mainly used as dispersing agents for pigments in paints, foam-control agents and for removing scales of boilers. The polyoxyethylene mercaptans [$RS(C_2H_4O)_xH$] are stable in hot and alkaline solutions. They are used in textile detergents, metal cleaning and shampoos. They are also used with quaternary ammonium-type of cationic surfactants to enhance the effectiveness of the latter.

The long chain esters of carboxylic acids have very good emulsifying properties. However, they are unstable to acid and alkali, especially under hot conditions. The edible sorbitol esters are used in food products such as ice creams, beverages, desserts and various confectionary products. These surfactants are also used in pharmaceutical products. The alkanolamines have good stability in the alkaline media. They are mainly used as laundry detergents, thickeners for liquid detergents, shampoos, rust inhibitors and fuel oil additives. The polyoxyethylene silicones are used as wetting agents.

Gemini surfactants

These surfactants belong to a relatively new class of surfactants as compared to the conventional surfactants discussed before. They have two or three hydrophobic, and usually two hydrophilic groups, as illustrated in Fig. 3.2.
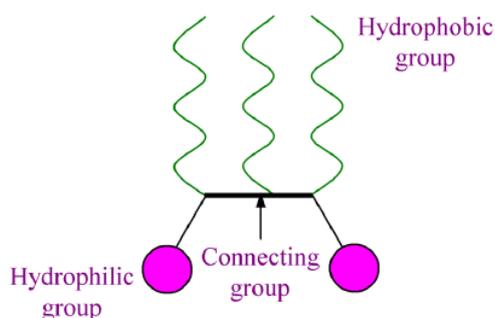

Figure. 3.2: Gemini surfactant.

The hydrophobic groups are connected by a linkage that is close to the hydrophilic groups. The properties of these surfactants vary greatly depending upon the structure of these three parts of the molecule. The interfacial effects of these surfactants may be much stronger than the surfactants having a single hydrophilic and hydrophobic group. The gemini surfactants can have negative, positive or both types of charges. They can be nonionic as well. Since these surfactants have a large number of carbon atoms in their hydrophobic part, they show a penchant for adsorbing at the interface. However, at the same time, their solubility in water may be less. The hydrophilic groups prevent this difficulty. These surfactants require only a small amount to saturate the interface.

Biosurfactants

Biosurfactants are amphiphilic compounds produced on living surfaces, mostly microbial cell surfaces, or excreted extracellularly and contain hydrophobic and hydrophilic moieties that reduce surface tension and interfacial tensions between individual molecules at the surface and interface, respectively.

Interest in microbial surfactants is due to their diversity, environmentally friendly nature, possibility of large-scale production, selectivity, performance under extreme conditions, and potential applications in environmental protection. A few of the popular examples of microbial biosurfactants includes Emulsan produced by *Acinetobacter calcoaceticus*, Sophorolipids produced by several yeasts belonging to *candida* and the *starmerella* clade, and Rhamnolipid produced by *Pseudomonas aeruginosa* etc. Biosurfactants enhance the emulsification of hydrocarbons, have the potential to solubilize hydrocarbon contaminants and increase their availability for microbial degradation. The use of chemicals for the treatment of a hydrocarbon polluted site may contaminate the environment with their by-products, whereas biological treatment may efficiently destroy pollutants, while being biodegradable themselves. Hence, biosurfactant-producing microorganisms may play an

important role in the accelerated bioremediation of hydrocarbon-contaminated sites. These compounds can also be used in enhanced oil recovery and may be considered for other potential applications in environmental protection. Other applications include herbicides and pesticides formulations, detergents, healthcare and cosmetics, pulp and paper, coal, textiles, ceramic processing and food industries, uranium ore-processing, and mechanical dewatering of peat.

Several microorganisms are known to synthesize surface-active agents; most of them are bacteria and yeasts. When grown on hydrocarbon substrate as the carbon source, these microorganisms synthesize a wide range of chemicals with surface activity, such as glycolipid, phospholipid, and others. These chemicals are synthesized to emulsify the hydrocarbon substrate and facilitate its transport into the cells. In some bacterial species such as *Pseudomonas aeruginosa*, biosurfactants are also involved in a group motility behavior called swarming motility.

MICELLIZATION AND CMC:

One fundamental property of the surfactants is to adsorb at the interfaces. Surfactants have another very important property; the property of *self-assembly*. When sufficient amount of a surfactant is dissolved in water, the surfactant molecules form colloidal clusters. For many ionic surfactants, typically 40–100 surfactant molecules assemble to form such clusters. These are called *micelles*, and the process of formation of micelles is known as *micellization*. The number of surfactant molecules in a micelle is known as *aggregation number*. These clusters can have a wide variety of shape, such as spherical, cylindrical and lamellar, as shown in Fig. 3.3.
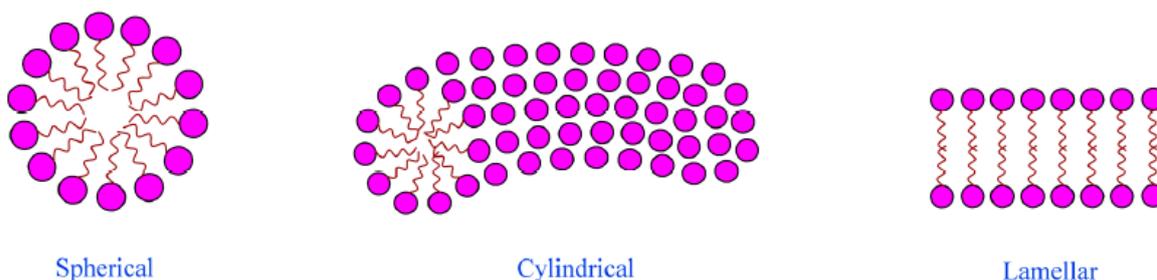
Spherical   Cylindrical   Lamellar

Figure 3.3: Micelles of various types.

The threshold concentration at which the formation of micelle begins is known as *critical micelle concentration* (CMC). The CMC of some surfactants in water are given in Table 3.1.

Table 3.1: CMCs of surfactants

Surfactant	Formula	CMC (mol/m^3)
Cetyltrimethylammonium bromide	$C_{16}H_{33}N(CH_3)_3{}^+ Br^-$	0.90
Sodium dodecyl sulfate	$C_{12}H_{25}SO_4{}^- Na^+$	8.10
Tween 20	$C_{58}H_{114}O_{26}$	0.05
Triton X-100	$C_{14}H_{22}O(C_2H_4O)_{9.5}$	0.20

Several properties of surfactant solution show sharp change in the vicinity of CMC, such as surface tension, equivalent conductivity, osmotic pressure and turbidity, as shown in Fig. 3.4.
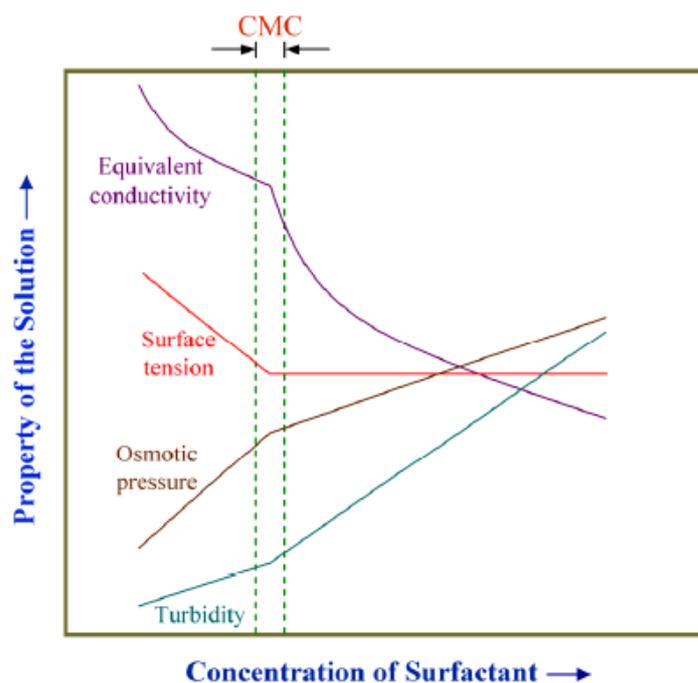

Figure 3.4: Variation of properties of surfactant solution near the CMC.

These variations can be explained as follows. Near the CMC, the surface is almost saturated by the adsorption of the surfactant molecules. Therefore, the surface tension ceases to decrease when the surfactant concentration is increased beyond the CMC. The equivalent conductivity of the solution decreases at the CMC owing to the lower mobility of the micelles as compared to the surfactant molecules. When the critical micelle concentration is approached, the slope of the osmotic pressure curve decreases and the slope of the turbidity curve increases due to the increase in the average molecular weight of the solute. The size and shape of the micelles depend on the properties of the solution such as the concentration of electrolyte and the pH of the solution. To illustrate, the aggregation number of sodium dodecyl sulfate micelle is ~80, which increases to ~130 in 0.4 mol/m^3 NaCl solution. With the addition of electrolyte (such as NaCl), the critical micelle concentration of ionic surfactants decreases. The electrolytes mask the electrostatic repulsion between the ionic head-groups of the surfactant molecules. This favors more adsorption of the surfactant molecules at the interface, which causes the reduction in CMC. Sometimes, increase in pH favors ionization. If the charge density increases by changing the pH, the CMC may increase.

The aggregation number increases with increasing length of the hydrocarbon chains of the surfactant molecules. For example, the aggregation number of decyltrimethylammonium bromide is ~36 whereas, the same for tetradecyltrimethylammonium bromide is ~75. The critical micelle concentration decreases with the increasing chain length. The CMC also depends on the size of the hydrophilic group. As the size of the hydrophilic group gets larger, the repulsion between them increases.

The shape of some micelles changes with surfactant concentration. Some micelles change their structure from spherical to cylindrical to lamellar with increasing surfactant concentration. This transformation can be facilitated by electrolytes also. The mechanism of aggregation of

surfactant molecules is believed to be reversible. The surfactant molecules join and leave the micelle very rapidly ($\sim 10^{-6}$ s). The counterions at the surface of the micelles exchange at even faster rates. The water molecules which are bound to the micelles are highly mobile as well. The typical lifetime of water molecules in the micelle is about 10^{-8} s.

STRUCTURE OF MICELLES:

The structures of the micelles of anionic and cationic surfactants are essentially the same. The micelles of nonionic surfactants are sometimes very large, and the number of surfactant molecules in these clusters can be much greater than 100.

The diameter of the cylindrical micelles is of the order of a few nanometers.

However, their length can be large. For example, the micelles of an ethoxylated C16 alcohol and ethylene oxide were found have diameter in the range of 3–8 nm, but their length was ~ 1000 nm. The micelles of nonionic surfactants may have several hundreds of molecules.

McBain (1913) proposed that the micelles can have lamellar and spherical shapes. Hartley proposed the 'core model' in 1936, in which a liquid-like hydrocarbon core is surrounded by a hydrophilic surface layer, which is constituted by the head-groups of the surfactant molecules. The central core is mainly hydrocarbon.

The hydrophilic head-groups of the surfactant molecules repel each other electrically whereas the hydrophobic groups attract each other by hydrophobic attraction. Therefore, two opposing forces act in the interfacial region: one tends to increase and the other tends to decrease the head-group area. This is shown in Fig. 3.5.
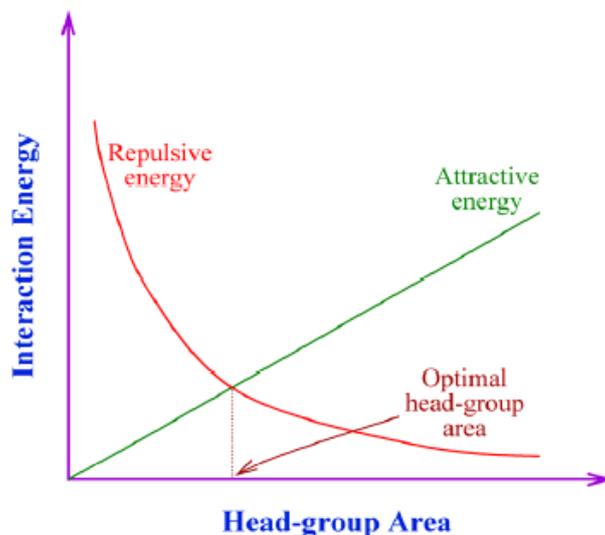
Figure 3.5: Energy diagram for optimal head-group area.

The optimal area is the area corresponding to the intersection of the two energy curves. When the surfactant molecules pack together to assume a geometrical structure, the relative size of the head-group and hydrophobic chain determines the size and shape of the micelle. The effects of hydration, repulsion between the ions and the effects of the counterion are also important in the packing of the molecules.

APPLICATIONS OF MICELLES:

The micelles present in water can dissolve organic molecules. Conversely, the reverse micelles can solubilize water molecules. The liquid dissolves in the micelle. This depends on the chemical nature of the liquid as well as the surfactant. The extent to which a liquid can be solubilized by the micelles depends on the concentration of the surfactant in the solution. The amount of surfactant necessary to solubilize an organic liquid is large.

Micelles have been used as reaction-vessels for the manufacture of nanoparticles. The nanoparticles formed inside the micelles are organized inside them. Metal nanoparticles (e.g., gold, silver and platinum) have been synthesized by this technique. The micelles created from block copolymers such as poly styrene– ethylene oxide have been used to generate well-ordered compartments.

Block copolymer micelles can act like water-soluble biocompatible nanocontainers with great potential for delivering hydrophobic drugs.

Reactions of organic compounds are sometimes significantly enhanced in the aqueous micellar solutions of ionic surfactants. This is known as *micellar catalysis*.

Micelles have also been used to remove pollutants from wastewater. The pollutant molecules are trapped inside the micelles. These micelles are then separated by ultrafiltration. This method is known as *micelle-enhanced ultrafiltration* (MEUF).

HYDROPHILIC-LIPOPHILIC BALANCE (HLB):

A major commercial use of the surfactants is to formulate emulsion-stabilizing agents, or *emulsifiers*. Emulsions can be divided into two types: oil-in-water (O/W) emulsions, and water-in-oil (W/O) emulsions. In the oil-in-water type of emulsions, oil droplets are dispersed in the continuous aqueous phase whereas, in water-in-oil type of emulsions, the aqueous phase is dispersed in the continuous oil phase.

Some surfactants stabilize the O/W emulsions whereas the other surfactants are more efficient in stabilizing the W/O emulsions. A rule of thumb is that the most stable emulsion is formed when the surfactant has higher solubility in the continuous phase.

Therefore, according to this rule, a water-soluble surfactant should stabilize oil-in-water emulsions more than water-in-oil emulsions, and the reverse is expected for a surfactant that is soluble in oil. This rule is known as *Bancroft's rule*.

Griffin (1949) developed a method to correlate the structural properties of the surfactants with their ability to act as emulsifiers. This method is known as *hydrophilic-lipophilic balance (HLB) method*.

The solubility of surfactants in water varies depending on their HLB value, as shown in Table3.3.

Table 3.3 HLB values and types of emulsion formed

Range of HLB value	Solubility in water	Emulsion type
1–4	Insoluble	Water-in-oil
4–7	Poor unstable dispersion	Water-in-oil
7–9	Stable opaque dispersion	–
10–13	Hazy solution	Oil-in-water
13 and higher	Clear solution	Oil-in-water

As the name suggests, the balance between the hydrophilic and lipophilic parts of the surfactant molecule is important in this method. Values have been assigned to these parts for various surfactants. A group-number method is used for calculating the HLB value of a surfactant from its chemical formula.

$$\text{HLB} = \Sigma(\text{hydrophilic group-numbers}) - \Sigma (\text{group-number per -CH}_2\text{-group}) + 7$$

KRAFT TEMPERATURE:

The solubility of the surfactant molecules in water decreases with increasing length of the hydrophobic part, and the solubility increases if the hydrophilic part is more soluble. The solubility of surfactant is also dependent on temperature. The solubility of ionic surfactants increases very rapidly after a temperature, termed *Krafft point*.

At this temperature, the micelles are formed, and the solubility is significantly increased. This temperature is important in industrial preparations, especially where concentrated surfactant solutions are required. The Krafft temperature increases with the increasing number of carbon atoms in the hydrophobic part.

The Krafft point decreases linearly with the logarithm of CMC for many anionic surfactants. It is strongly dependent on the addition of electrolyte, the head-group and the counterion. Electrolytes usually raise the Krafft point. There is no general trend for the dependence on counterions. However, the Krafft point is typically much higher in presence of divalent counterions than monovalent counterions. For alkali alkanoates, Krafft point increases as the

atomic number of the counterion decreases. The opposite trend is observed for alkali sulfates or sulfonates. For cationic surfactants, the Krafft point is usually higher for bromides than chlorides, and still higher for the iodides. The variation of Krafft point with the number of carbon atoms in the alkyl chain is shown in Fig. 3.6 (a).

The solubility of some nonionic surfactants (such as the ethoxylates) decreases dramatically above a certain temperature. This temperature is termed *cloud point*. These surfactants are quite soluble at the low temperatures (273–278 K). However, they come out of solution upon heating. These surfactants dissolve in water by hydrogen bonding. With increasing temperature, the hydrogen bonds disrupt. This causes reduction in solubility. Cloud point decreases with the increasing chain length of the hydrophobic part. The variation of cloud point with the number of oxyethylene units is depicted in Fig. 3.6 (b).

$\Diamond$ $C_nH_{2n+1}CH(SO_3^-Na^+)CH_2OH$
$\bigcirc$ $C_nH_{2n+1}CH(CH_3)C_6H_4SO_3^-Na^+$
$\triangle$ $C_nH_{2n+1}SO_4^-Na^+$
$\square$ $Na^+SO_4^-(CH_2)_nSO_4^-Na^+$

(a)

$\square$ $C_6H_{13}(OC_2H_4)_mOH$
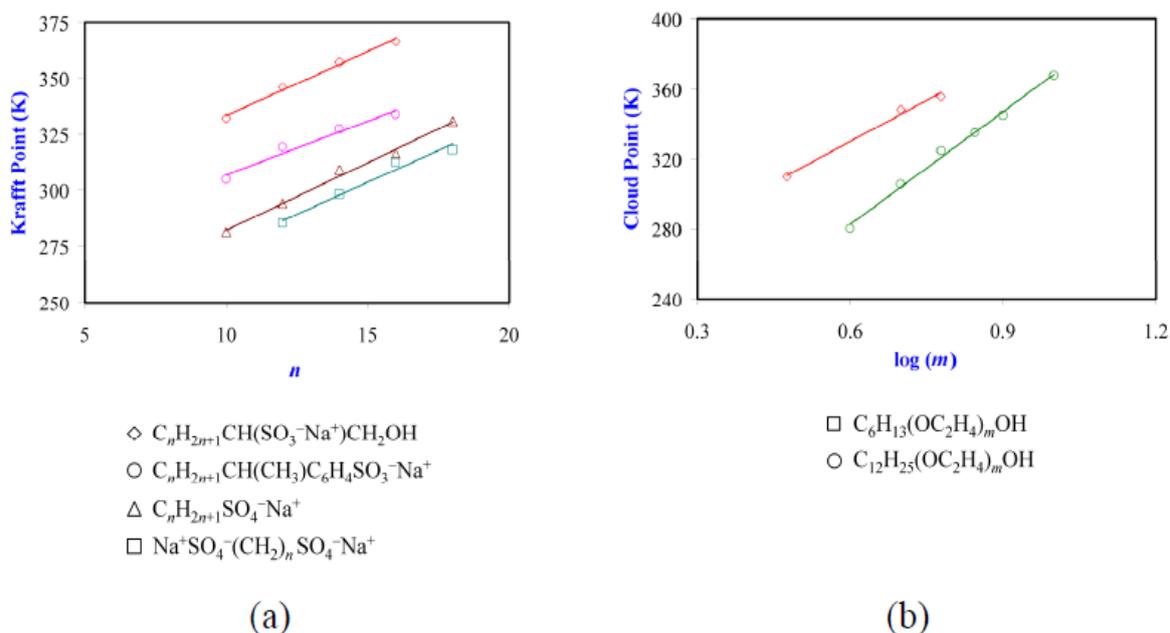$\bigcirc$ $C_{12}H_{25}(OC_2H_4)_mOH$

(b)

Figure 3.6: (a) Variation of Krafft point with the number of carbon atoms in the alkyl chain, and (b) variation of cloud point with the number of oxyethylene units.

FACTORS AFFECTING THE CMC AND MICELLAR SIZE:

Structure of the hydrophobic group

Increase in length of the hydrocarbon chain results in: a decrease in CMC, which for compounds with identical polar head groups is expressed by the linear equation: log [CMC] = A − Bm where m is the number of carbon atoms in the chain and A and B are constants for a homologous series. a corresponding increase in micellar size.

Nature of the hydrophilic group

Non-ionic surfactants generally have very much lower CMC values and higher aggregation numbers than their ionic counterparts with similar hydrocarbon chains. An increase in the ethylene oxide chain length of a non-ionic surfactant makes the molecule more hydrophilic and the CMC increases.

Type of counterion

Micellar size increases for a particular cationic surfactant as the counterion is changed according to the series $Cl^- < Br^- < I^-$, and for a particular anionic surfactant according to $Na^+ < K^+ < Cs^+$. Ionic surfactants with organic counterions (e.g. maleates) have lower CMCs and higher aggregation numbers than those with inorganic counterions.

Addition of electrolytes

Electrolyte addition to solutions of ionic surfactants decreases the CMC and increases the micellar size. This is because the electrolyte reduces the forces of repulsion between the charged head groups at the micelle surface, so allowing the micelle to grow at high electrolyte concentration the micelles of ionic surfactants may become non-spherical.

Effect of temperature

Aqueous solutions of many non-ionic surfactants become turbid at a characteristic temperature called the cloud point. At temperatures up to the cloud point there is an increase in micellar

size and a corresponding decrease in CMC. Temperature has a comparatively small effect on the micellar properties of ionic surfactants.

**THERMODYNAMICS OF MICELLIZATION:**

As mentioned above, the process of micellization is one of the most important characteristics of surfactant solution and hence it is essential to understand its mechanism (the driving force for micelle formation). This requires analysis of the dynamics of the process (i.e. the kinetic aspects) as well as the equilibrium aspects whereby the laws of thermodynamics may be applied to obtain the free energy, enthalpy and entropy of micellization. Below a brief description of both aspects will be given and this will be followed by a picture of the driving force for micelle formation.

Two general approaches have been employed to tackle micelle formation. The first and simplest approach treats micelles as a single phase, and is referred to as the phase separation model. Here, micelle formation is considered as a phase separation phenomenon and the c.m.c. is then the saturation concentration of the amphiphile in the monomeric state whereas the micelles constitute the separated pseudophase. Above the c.m.c., a phase equilibrium exists with a constant activity of the surfactant in the micellar phase. The Krafft point is viewed as the temperature at which solid hydrated surfactant, micelles and a solution saturated with undissociated surfactant molecules are in equilibrium at a given pressure.

In the second approach, micelles and single surfactant molecules or ions are considered to be in association–dissociation equilibrium. The c.m.c. is merely a concentration range above which any added surfactant appears in solution in a micellar form. Since the solubility of the associated surfactant is much greater than that of the monomeric surfactant, the solubility of the surfactant as a whole will not increase markedly with temperature until it reaches the c.m.c. region. Thus, in the mass action approach, the Krafft point represents the temperature at which the surfactant solubility equals the c.m.c.

Phase Separation Model

Consider an anionic surfactant, in which n surfactant anions, S^-, and n counter ions M^+ associate to form a micelle, i.e.,

$$nS^- + nM^+ \rightleftharpoons S_n \quad \text{--------(1)}$$
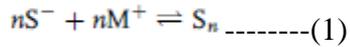
The micelle is simply a charged aggregate of surfactant ions plus an equivalent number of counter ions in the surrounding atmosphere and is treated as a separate phase.

The chemical potential of the surfactant in the micellar state is assumed to be constant, at any given temperature, and this may be adopted as the standard chemical potential, $\mu^o{}_m$, by analogy to a pure liquid or a pure solid. Considering the equilibrium between micelles and monomer, then,

$$\mu^\circ_m = \mu^\circ_1 + RT \ln a \quad \text{---------(2)}$$

where μ_1 is the standard chemical potential of the surfactant monomer and a_1 is its activity, which is equal to $f_1 x_1$, where f_1 is the activity coefficient and x_1 the mole fraction. Therefore, the standard free energy of micellization per mol of monomer, $\Delta G^o{}_m$, is given by,

$$\Delta G^\circ_m = \mu^\circ_m - \mu^\circ_1 = RT \ln a_1 \simeq RT \ln x_1 \quad \text{---------(3)}$$

where f_1 is taken as unity (a reasonable value in very dilute solution). The c.m.c. may be identified with x_1 so that

$$\Delta G^\circ_m = RT \ln[\text{c.m.c.}] \quad \text{----------(4)}$$

In Eq. (3), the c.m.c. is expressed as a mole fraction, which is equal to $C/(55.5 + C)$, where C is the concentration of surfactant in mole dm^{-3}, i.e.,

$$\Delta G^\circ_m = RT \ln C - RT \ln(55.5 + C) \quad \text{----------(5)}$$

ΔG^o should be calculated using the c.m.c. expressed as a mole fraction as indicated by Eq. (5). However, most quoted c.m.c.s are given in mole dm^{-3} and, in many cases, $\Delta G^o{}_s$ have been quoted when the c.m.c. was simply expressed in mol dm^{-3}. Strictly speaking, this is incorrect,

since ΔG° should be based on x_1 rather than on C. ΔG° obtained when the c.m.c. is expressed in mol dm^{-3} is substantially different from that found with c.m.c. expressed in mole fraction. For example, for dodecyl hexaoxyethylene glycol the quoted c.m.c. is 8.7 x 10^{-5} mol dm^{-3} at 25 °C. Therefore,

$$\Delta G^\circ = RT \ln \left[\frac{8.7 \times 10^{-5}}{55.5 + 8.7 \times 10^{-5}} \right] = -33.1 \text{ kJ mol}^{-1} \tag{6}$$

when the mole fraction scale is used. However,

$$\Delta G^\circ = RT \ln 8.7 \times 10^{-5} = -23.2 \text{ kJ mol}^{-1} \tag{7}$$

when the molarity scale is used.

The phase separation model has been questioned for two main reasons. Firstly, according to this model a clear discontinuity in the physical property of a surfactant solution, such as surface tension, turbidity, etc. should be observed at the c.m.c. This is not always found experimentally and the c.m.c. is not a sharp break point. Secondly, if two phases actually exist at the c.m.c., then equating the chemical potential of the surfactant molecule in the two phases would imply that the activity of the surfactant in the aqueous phase would be constant above the c.m.c. If this was the case, the surface tension of a surfactant solution should remain constant above the c.m.c. However, careful measurements have shown that the surface tension of a surfactant solution decreases slowly above the c.m.c., particularly when using purified surfactants.

Mass Action Model

This model assumes a dissociation–association equilibrium between surfactant monomers and micelles – thus an equilibrium constant can be calculated. For a nonionic surfactant, where charge effects are absent, the equilibrium constant K_m is given by Eq. (2.15).

$$K_m = \frac{[S_n]}{[S]^n} \tag{8}$$

The standard free energy per monomer is then given by

$$-\Delta G_m^\circ = -\frac{\Delta G}{n} = \frac{RT}{n}\ln K_m = \frac{RT}{n}\ln[S_n] - RT\ln[S] \quad \text{----------(9)}$$

For many micellar systems, n > 50 and, therefore, the first term on the right-hand side of Eq. (9) may be neglected, resulting in Eq. (10) for ΔG°_m

$$\Delta G_m^\circ = RT\ln[S] = RT\ln[\text{c.m.c.}] \quad \text{------------(10)}$$

which is identical to the equation derived using the phase-separation model.

The mass action model allows a simple extension to be made to the case of ionic surfactants, in which micelles attract a substantial proportion of counter ions, into an attached layer. For a micelle made of n-surfactant ions, (where n - p) charges are associated with counter ions, i.e. having a net charge of p units and degree of dissociation p/n, the following equilibrium may be established (for an anionic surfactant with Na$^+$ counter ions),

$$nS^- + (n-p)Na^+ \rightleftharpoons S_n^{p^-} \quad \text{---------(11)}$$
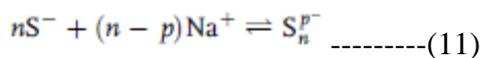
$$K_m = \frac{[S_n^{p^-}]}{[S^-]^n[Na^+]^{(n-p)}} \quad \text{------------(12)}$$

Phillips has given a convenient solution for relating ΔG_m to [c.m.c.], arriving at Eq. (13),

$$\Delta G_m^\circ = [2 - (p/n)]RT\ln[\text{c.m.c.}] \quad \text{--------------(13)}$$

For many ionic surfactants, the degree of dissociation (p/n) is ~0.2 so that,

$$\Delta G_m^\circ = 1.8RT\ln[\text{c.m.c.}] \quad \text{------------(14)}$$

Comparison with Eq. (10) clearly shows that, for similar ΔG_m, the [c.m.c.] is about two orders of magnitude higher for ionic surfactants than with nonionic surfactant of the same alkyl chain length (Table 2.1).

In the presence of excess added electrolyte, with mole fraction x, the free energy of micellization is given by the expression,

$$\Delta G_m^\circ = RT\ln[\text{c.m.c.}] + [1 - (p/n)]\ln x \quad \text{----------(15)}$$

Eq. (15) shows that as x increases the [c.m.c.] decreases.

It is clear from Eq. (13) that as p → 0, i.e. when most charges are associated with counter ions,

$$\Delta G_m^\circ = 2RT \ln[\text{c.m.c.}]$$ -----------(16)

whereas when p~n, i.e. the counter ions are bound to micelles,

$$\Delta G_m^\circ = RT \ln[\text{c.m.c.}]$$ ------------(17)

which is the same equation as for nonionic surfactants.

Although the mass action approach could account for a number of experimental results, such as the small change in properties around the c.m.c., it has not escaped criticism. For example, the assumption that surfactants exist in solution in only two forms, namely single ions and micelles of uniform size, is debatable. Analysis of various experimental results has shown that micelles have a size distribution that is narrow and concentration dependent. Thus, the assumption of a single aggregation number is an oversimplification and, in reality, there is a micellar size distribution. This can be analyzed using the multiple equilibrium model, which can be best formulated as a stepwise aggregation,

$$S_1 + S_1 \rightleftharpoons S_2$$
$$S_2 + S_1 \rightleftharpoons S_3$$
$$S_{n-1} + S_1 \rightleftharpoons S_n$$
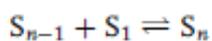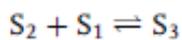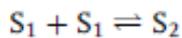
For surfactants with not too high a c.m.c., the size distribution curve has a very deep minimum, the least stable aggregates being present in concentrations many orders of magnitude below those of the most abundant micelles. For surfactants with predominantly spherical micelles, the polydispersity is low and there is then a particularly preferred micellar size.

SOLUBILISATION:

The *maximum amount of solubilisate* that can be incorporated into a given system at a fi xed concentration is termed the *maximum additive concentration* (MAC). Solubility data are expressed as a solubility versus concentration curve or as three-component phase diagrams,

which describe the effect of varying all three components of the system (solubilisate, solubiliser and solvent).

The *site of solubilisation* within the micelle is closely related to the chemical nature of the solubilisate (Figure 3.7): Non-polar solubilisates (aliphatic hydrocarbons, for example) are dissolved in the hydrocarbon core of ionic and non-ionic micelles (position 1).

Water-insoluble compounds containing polar groups are orientated with the polar group at the core–surface interface of the micelle, and the hydrophobic group buried inside the hydrocarbon core of the micelle (position 2 and 3).

In addition to these sites, solubilisation in non-ionic polyoxyethylated surfactants can also occur in the poly– oxyethylene shell (palisade layer) which surrounds the core (position 4).
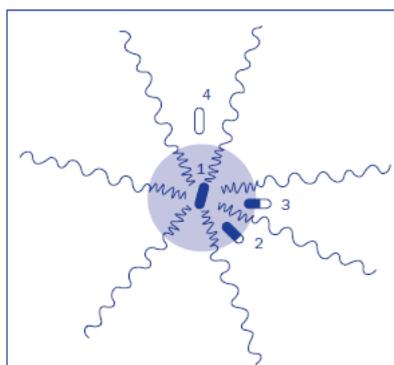

Figure 3.7: Schematic representation of sites of solubilisation depending on the hydrophobicity of the solubilisate.

Pharmaceutical applications of solubilisation:

The solubilisation of phenolic compounds such as cresol, chlorocresol, chloroxylenol and thymol with soap to form clear solutions for use in disinfection.

Solubilised solutions of iodine in non-ionic surfactant micelles (iodophors) for use in instrument sterilisation.

Solubilisation of drugs (for example, steroids and waterinsoluble vitamins), and essential oils by non-ionic surfactants (usually polysorbates or polyoxyethylene sorbitan esters of fatty acids).

MICROEMULSION:

One of the best definitions of microemulsions is from Danielsson and Lindman "a microemulsion is a system of water, oil and an amphiphile which is a single optically isotropic and thermodynamically stable liquid solution". In some respects, microemulsions can be considered as small-scale versions of emulsions, i.e., droplet type dispersions either of oil-in-water (o/w) or of water-in-oil (w/o), with a size range in the order of $5-50$ nm in drop radius. Such a description, however, lacks precision since there are significant differences between microemulsions and ordinary emulsions (or macroemulsions). In particular, in emulsions the average drop size grows continuously with time so that phase separation ultimately occurs under gravitational force, i.e., they are thermodynamically unstable and their formation requires input of work. The drops of the dispersed phase are generally large (> 0.1 μm) so that they often take on a milky, rather than a translucent appearance. For microemulsions, once the conditions are right, spontaneous formation occurs. As for simple aqueous systems, microemulsion formation is dependent on surfactant type and structure. If the surfactant is ionic and contains a single hydrocarbon chain (e.g., sodium dodecylsulphate, SDS) microemulsions are only formed if a co-surfactant (e.g., a medium size aliphatic alcohol) and/or electrolyte (e.g., 0.2 M NaCl) are also present. With double chain ionics (e.g., Aerosol-OT) and some non-ionic surfactants a co-surfactant is not necessary. This results from one of the most fundamental properties of microemulsions, that is, an ultra-low interfacial tension between the oil and water phases, $\gamma_{o/w}$. The main role of the surfactant is to reduce $\gamma_{o/w}$ sufficiently $-$ i.e., lowering the energy required to increase the surface area $-$ so that spontaneous dispersion of water or oil

droplets occurs and the system is thermodynamically stable. Ultra-low tensions are crucial for the formation of microemulsions and depend on system composition.

A well-known classification of microemulsions is that of Winsor who identified four general types of phase equilibria:

- Type I: the surfactant is preferentially soluble in water and oil-in-water (o/w) microemulsions form (Winsor I). The surfactant-rich water phase coexists with the oil phase where surfactant is only present as monomers at small concentration.

- Type II: the surfactant is mainly in the oil phase and water-in-oil (w/o) microemulsions form. The surfactant-rich oil phase coexists with the surfactant-poor aqueous phase (Winsor II).

- Type III: a three-phase system where a surfactant-rich middle-phase coexists with both excess water and oil surfactant-poor phases (Winsor III or middle-phase microemulsion).

- Type IV: a single-phase (isotropic) micellar solution, that forms upon addition of a sufficient quantity of amphiphile (surfactant plus alcohol).

Depending on surfactant type and sample environment, types I, II, III or IV form preferentially, the dominant type being related to the molecular arrangement at the interface (fig 3.8). As illustrated in Figure 3.8, phase transitions are brought about by increasing either electrolyte concentration (in the case of ionic surfactants) or temperature (for non-ionics).
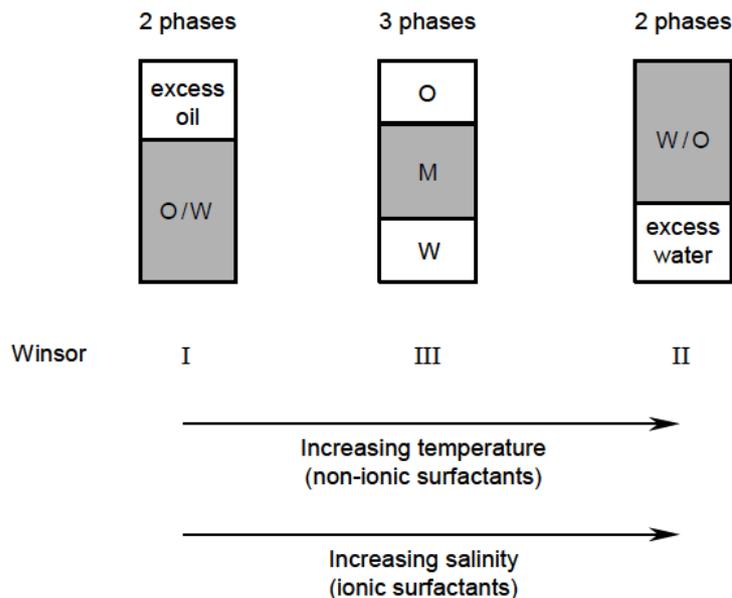
Figure 3.8: Winsor classification and phase sequence of microemulsions encountered as temperature or salinity is scanned for non-ionic and ionic surfactant respectively. Most of the surfactant resides in the shaded area. In the three-phase system the middle-phase microemulsion (M) is in equilibrium with both excess oil (O) and water (W).

REVERSE MICELLES:

When the value of the packing parameter exceeds unity, some surfactants form *reverse micelles* in non-polar media. The surfactant molecules assemble in structures in which the head-groups are oriented inwards and the hydrophobic groups are oriented towards the solvent (Fig. 3.9).
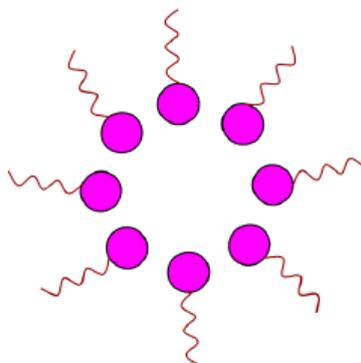

Figure 3.9: Reverse micelle.

The aggregation number in reverse micelles is usually much smaller than the aggregation number in the aqueous micelles. The negative enthalpy change during micellization is believed to be an important stabilizing factor for the reverse micelles.

Surfactants soluble in organic liquids can form reverse micelles. There are some surfactants, such as Aerosol OT, which can form normal as well as reverse micelles.

MODULE-IV

NUCLIDE:

A nuclide (called nuclear species) is a species of atom that characterized by the following specific constitution of its nucleus:

1- *Proton* (atomic) number (Z)

2- *Neutrons* number (N)

3- The *energy* of the nuclear state

Both proton and neutrons are called *nucleons*, and thus, nuclides are composite particles of nucleons. The basic components of nucleons are elementary particles called *quarks*. Therefore, nuclides can be considered composite particles of quarks

Let A to be the number of nucleons in a nuclide, A is called also *mass number,* i.e $N = A - Z$.

- The notation for a nuclide with mass number A and atomic number Z is represented by a symbol of its element X, as $_{Z}^{A}X$

- According to A, Z, and the nuclear energy state of a nuclide, we can characterize the following categories of nuclides:

1- *Isotopes*: nuclides of the same element (same Z) but different in A

Example: $_{6}^{12}C$, $_{6}^{13}C$ and $_{6}^{14}C$ are isotopes of Carbon element.

2- *Isobars:* nuclides with the same A (equal in weight) but different in Z (different elements)

Example: $_{6}^{14}C$ and $_{7}^{14}N$ are isobars.

3- *Isotones:* Nuclides with the same N,

Example: $_{6}^{13}C$ and $_{7}^{14}N$ are isotones.

4- *Isomers*: nuclides with the same Z and A, (i.e same isotopes) but different in their nuclear energy state (excitation state).

Example: Technetium nuclides: $_{43}^{99}Tc$ and $_{43}^{99m}Tc$

5- *Mirror Nuclides*: neutron number (Z) and proton number (Z) is exchanged.

Example: ^3_1He and ^3_2He

NUCLEAR STABILITY:

What is the nuclear stability? Nuclear stability means that nucleus is stable meaning that it does not spontaneously emit any kind of radioactivity (radiation). On the other hand, if the nucleus is unstable (not stable), it has the tendency of emitting some kind of radiation, i.e., it is radioactive. Therefore, the radioactivity is associated with unstable nucleus: Stable nucleus – non-radioactive and Unstable nucleus – radioactive.

Keep in mind that less stable means more radioactive and more stable means less radioactive. We want to know why there is a radioactivity. What makes the nucleus a stable one? There are no concrete theories to explain this, but there are only general observations based on the available stable isotopes. It appears that neutron to proton (n/p) ratio is the dominant factor in nuclear stability. This ratio is close to 1 for atoms of elements with low atomic number and increases as the atomic number increases. Then how do we predict the nuclear stability? One of the simplest ways of predicting the nuclear stability is based on whether nucleus contains odd/even number of protons and neutrons:

Protons	Neutrons	Number of Stable Nuclides	Stability
Odd	Odd	4	least stable
Odd	Even	50	
Even	Odd	57	↓
Even	Even	168	most stable

Nuclides containing odd numbers of both protons and neutrons are the least stable means more radioactive. Nuclides containing even numbers of both protons and neutrons are most stable means less radioactive. Nuclides contain odd numbers of protons and even numbers of neutrons are less stable than nuclides containing even numbers of protons and odd numbers of neutrons. In general, nuclear stability is greater for nuclides containing even numbers of protons and neutrons or both.

Example

Based on the even-odd rule presented above, predict which one would you expect to be radioactive in each pair?

(a) $^{16}_{8}O$ and $^{17}_{8}O$

(b) $^{35}_{17}Cl$ and $^{36}_{17}Cl$

(c) $^{20}_{10}Ne$ and $^{17}_{10}Ne$

(d) $^{40}_{20}Ca$ and $^{45}_{20}Ca$

(e) $^{195}_{80}Hg$ and $^{196}_{80}Hg$

Answer

(a) The $^{16}_{8}O$ contains 8 protons and 8 neutrons (even-even) and the $^{17}_{8}O$ contains 8 protons and 9 neutrons (even-odd). Therefore, $^{17}_{8}O$ is radioactive.

(b) The $^{35}_{17}Cl$ has 17 protons and 18 neutrons (odd-even) and the $^{36}_{17}Cl$ has 17 protons and 19 neutrons (odd-odd). Hence, $^{36}_{17}Cl$ is radioactive.

(c) The $^{20}_{10}Ne$ contains 10 protons and 10 neutrons (even-even) and the $^{17}_{10}Ne$ contains 10 protons and 7 neutrons (even-odd). Therefore, $^{17}_{10}Ne$ is radioactive.

(d) The $^{40}_{20}Ca$ has even-even situation and $^{45}_{20}Ca$ has even-odd situation. Thus, $^{40}_{20}Ca$ is radioactive.

(d) The $^{195}_{80}Hg$ has even number of protons and odd number of neutrons and the $^{196}_{80}Hg$ has even number of protons and even number of neutrons. Therefore, $^{195}_{80}Hg$ is radioactive.

NUCLEAR BINDING ENERGY:

The nuclear binding energy is an energy required to break up a nucleus into its components protons and neutrons. In essence, it is a quantitative measure of the nuclear stability. The concept of nuclear binding energy is based on Einstein's famous equation, $E = mc^2$, where E is the energy, m is the mass and c is the velocity of light, and according to which the energy and mass are inter-convertible.

Nucleus contains mainly two particles – protons and neutrons- in addition to many other elementary particles. Thus, the mass of the nucleus is primarily coming from the masses of protons and neutrons. But the experiments have shown that the sum of the masses of protons and neutrons is always greater than experimentally determined nuclear mass. Why is it so? The answer to this question lies in the way the nature creates nucleus. When nature creates nucleus, it takes protons and neutrons and binds them together and puts them in a tiny space called nucleus. In order to bind protons and neutrons together, some energy is needed, which is taken out of the masses of protons and neutrons. It means that nature is very smart, it does not spend any of its own energy rather it converts some of the masses of protons and neutrons into an energy and utilizes that energy to bind the protons and neutrons within the nucleus. If we know how much mass (known as mass defect) is utilized, we can convert it into binding energy using the Einstein's equation. Let us see how this is done.

Consider $^{56}_{26}\text{Fe}$ that has an atomic mass of 55.934942 amu (experimental) that is created using 26 protons and 30 neutrons:
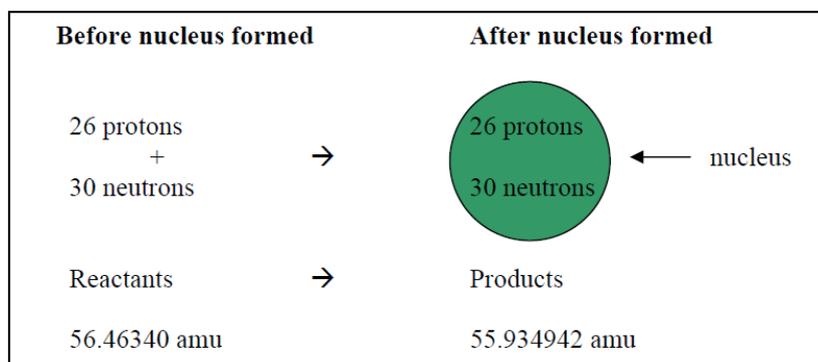
This nucleus has 26 protons and 30 neutrons. Knowing the mass of proton and neutron, we can calculate the total mass of the nucleus, i.e., total mass of 26 protons and 30 neutrons. The mass of proton ($^{1}_{1}\text{H}$) is 1.007825 amu and that of neutron ($^{1}_{0}\text{n}$) is 1.008665 amu. Thus

Mass of 26 protons = 26 x 1.007825 = 26.20345 amu

Mass of 30 neutrons = 30 x 1.008665 = 30.25995 amu

Total mass of 26 protons and 30 neutrons is

26.20345 amu + 30.25995 amu = 56.46340 amu

This mass is larger than 55.934942 amu (the experimentally determined mass) by 0.52846 amu.

The difference between experimental mass of the atom and the sum of the masses of its protons, neutrons, and electrons is known as mass defect (Δm), which is calculated as

Δm = mass of products – mass of reactants

= experimental mass of an atom – calculated mass of an atom

= 55.934942 amu – 56.46340 = - 0.52846 amu

Note that Δm is a negative quantity. As a consequence, the calculated energy will also be negative because the formation of ^{56}Fe from 26 protons and 30 neutrons is an exothermic reaction meaning that the energy is released to the surrounding. Also note that Δm does not include the mass of electron, as electron mass is much smaller than mass of either proton or neutron and hence it can safely be omitted.

This mass defect can be further transformed into energy using Einstein's equation in the following form:

$\Delta E = \Delta m \times c^2$

In this equation, ΔE is the change in energy in joule, Δm is the mass defect in amu, and c is the velocity of light that is equal to 3.0×10^8 m/s. Substituting these values into above equation and converting all the units to joules gives the energy in proper units (J), which is of course little bit tedious. To make things simpler, one can directly convert the mass defect into energy using the following conversation factor (if you are interested, see the following box for derivation of this relationship). 1amu = 1.4945×10-10 J

Let Δm = 1 amu. Then

$\Delta E = \Delta m \times c^2$ = 1 amu $\times$ (3.0 $\times$ 10^8 m/s)^2
= 9 $\times$ 10^{16} amu m^2/s^2

We further utilize the following relations to convert amu m^2/s^2 into joules.

1 kg = 6.022 $\times$ 10^{26} amu
and 1 J = 1 kg m^2/s^2

Then ΔE = 9 $\times$ 10^{16} amu m^2/s^2 $\times$ (1kg / 6.022 $\times$ 10^{26} amu) $\times$ (1 J / 1kg m^2/s^2)

= 1.4945 $\times$ 10^{-10} J

That is, 1 amu = 1.4945 $\times$ 10^{-10} J

Therefore,

$\Delta E = \Delta m \times 1.4945 \times 10^{-10}$ J/amu $= -0.528458$ amu $\times$ 1.4945 $\times$ 10^{-10} J/amu

$= - 7.8978 \times 10^{-11}$ J/ nucleus

This is the amount of energy released when one iron-56 nucleus is created from 26 protons and 30 neutrons. Therefore, the nuclear binding energy for this nucleus is 7.8978 $\times$ 10^{-11} J, which is also the amount of energy required to decompose this nucleus into 26 protons and 30 neutrons. The above calculated energy is per nucleus. The energy released for the formation of 1 mole of iron nuclei is calculated by multiplying the above energy with Avogadro's number.

$\Delta E = -7.8978 \times 10^{-11}$ J $\times$ 6.022 $\times$ 10^{23} /mol $= - 4.7560 \times 10^{13}$ J /mol

$= - 4.7560 \times 10^{10}$ kJ /mol

Therefore, the nuclear binding energy for 1 mole of iron-56 is 4.7560 $\times$ 10^{10} kJ (this is about 48 billion), which is a tremendous amount of energy, considering the energy of ordinary chemical reactions that are usually in the order of 200 kJ. How tremendous this energy is? Well, it will heat up about 40 million gallons of water from room temperature to boiling point. Can you imagine just about 56 g of iron-56 has the ability to heat up about 40 million gallons of water? Pretty impressive, is it not?

Binding energies are usually reported per nucleon to facilitate the comparison between various binding energies, which is calculated using the following formula.

$$nuclear\ binding\ energy\ per\ nucleon = \frac{nuclear\ binding\ energy}{number\ of\ nucleons}$$

For the iron-56 nucleus, we have

$$nuclear\ binding\ energy\ per\ nucleon = \frac{7.8978x10^{-11}\ j}{56} = 1.4070x10^{-12}\ j\,/\,nucleon$$

NUCLEAR MODELS:

Atomic nucleus is a complex quantum system of neutrons and protons, governed principally by the strong nuclear interaction and the comparatively weak electromagnetic interaction. Such a complex system cannot be described from first principles. Moreover, our knowledge of nuclear interaction is still not complete. It is thus necessary to invoke models to understand the behavior of nucleus under various conditions. Over the decades, various models were developed. All these models, however, can be traced back to one of the two basic models, the shell model and the collective model. In this chapter, the models used in this work will be briefly outlined.

Liquid drop model

Historically, the liquid drop model was the first model developed to explain various properties of nuclei. It was put forward to explain the saturation properties of nuclear interaction in analogy with the attractive forces between the constituents of a classical liquid. The saturation properties of nuclear interaction were inferred from the binding energy per nucleon of a nucleus as function of mass number *A,* which is found to be fairly constant and have a value equal to

$$\left.\frac{B(N,Z)}{A}\right|_{A>12} \simeq -8.5\ [\ \text{MeV/nucleon}\ ]$$

The saturation of nuclear interaction indicates their short range. Had it been a long range interaction, the binding energy of the system of *A* nucleon, in this case, would have been proportional to the number of pairs, i.e. *A (A* -1), which is not found to be the case. However, the liquid drop model cannot be pushed too far, since there exist essential differences between a nucleus and a classical liquid. The average distance between the two nucleons in a nucleus is

found experimentally to be around 2.4 *fm.* This is much larger than 0. 7 *fm* which is the mean internucleon distance predicted by the liquid drop model. This is due to the fact in a nucleus the Pauli and the Heisenberg uncertainty principle and the hard core play important roles. For example, the Pauli principle increases the mean free path of a nucleon inside the nucleus by avoiding its frequent collisions with other nucleons.

Shell model

The appearance of magic numbers at 2, 8, 20, 28, 50, 82 and 126 has been the strongest motivation for the formulation of the shell model. At these numbers the nuclei are strongly bound in comparison with their neighbors. This effect is quite analogous to the extra stability of noble atoms. The experimental signatures of magic numbers include the deviation in the single particle separation energies from a value of 8 MeV at these numbers towards a higher value and the higher excitation energy of the first excited states.

The existence of magic numbers indicates towards the existence of shells (or quantized energy states) which are grouped together quite close in energy and a large gap between the groups. Similar to the atomic case, this requires a central field. Thus the core concept of the shell model involves the existence of a mean field in which the motion of nucleons are described. Unlike the atomic case where the central mean field is provided by the Coulomb field of the heavy nucleus at the center of mass, in the nuclear case the mean field is produced by the nucleons themselves. Throughout the shell model theories, the central problem has been of finding a mean field which reproduces the interaction felt by a nucleon due to all other nucleon as accurately as possible. Unfortunately, in addition to an average mean field there still exists a residual interaction between the nucleons. Since the strength of the residual interaction is often weak as compared with the strength of the mean field, it can therefore be treated as perturbation. The Hamiltonian of a system of *A* nucleon in this model can be written as

$H = H_\circ + V_{res}$ with

$$H_o = \sum_i T_i + \sum_i V_i \ ,$$

where v; is the mean field for the *ith* nucleon and is equal to $\Sigma_{i,j} V_{i,j}$- V_{res} and V_{res} is the residual interaction not taken into account by the mean field. In microscopic theories, like Hatree-Fock theory, the mean field can be derived from microscopic two body interactions. However, in the literature an analytic phenomenological *Woods-Saxon potential*

$$V^{w.s}(r) = -V_o \left[1 + exp \left(\frac{r - R_o}{a} \right) \right]^{-1}$$

have been used extensively as a mean field. In the above expression *V(r)* has been shown to depend on *r* only. Such a potential is spherically symmetric and hence the model is called *the spherical shell model,* in contrast to the deformed shell model where this spherical symmetry of the potential is broken. The quantum numbers *n* the principal quantum number, *l* the orbital angular momentum and *j* are good quantum numbers and can be used to label the single particle wavefunctions, which are solutions of the single particle form re-written here as

$$h\psi(t) = (T_i + V_i)\psi(t)$$

If a spherically symmetric harmonic oscillator potential $V_{osc} = \frac{1}{2} m\hbar\omega_o^2(r^2 - R_o^2)$ is used as a mean field, where *Ro* is the mean radius of nucleus, the shell energies are given by

$$\epsilon = \hbar\omega_o \left(N + \frac{3}{2} \right)$$

with $N = 2(n-1) + l$. The above shell energies still do not reproduce the experimentally observed magic numbers above 20.

For getting the magic numbers, a *spin-orbit interaction* of the form f(r)l.s has been added to the mean field by Mayers and Jensen in 1950's. This interaction splits up the degeneracy in j = $l \pm 1/2$ levels. The total angular momentum *j* is now a good quantum number. The expectation value of the spin-orbit interaction can be written as

$$\langle snljm|f(r)\mathbf{l.s}|snljm \rangle \propto j(j+1) - l(l+1) - \frac{3}{4}$$

which for $j = l \pm 1/2$ gives the splitting of energy

$$\Delta E \sim 2l + 1$$

It can be seen that for an attractive spin-orbit potential, the levels with $j = l - 1/2$ are lowered in energy in agreement with the experimental results.

In the extreme case of shell model, called as extreme single particle shell model, the properties of the nucleus are determined by the outermost valance nucleon only. Ground state properties of many nuclei very close to magic numbers are explained successfully by this model. But for most of the nuclei it necessary to take into account more than one nucleon.

Collective model

In above section, the success of shell model in explaining the properties of nuclei close to the magic numbers was mentioned. It was noted that for a nucleus with mass number A near the magic number, many of the properties can be explained by the degrees of freedom of the valance particles only. As one moves away from the magic numbers, the complexity of nuclear spectra expected within shell model increases dramatically. Also the feasibility to carrying out shell model calculations with increase in particle number decreases very rapidly. However, while moving further away from the closed shells, some simple and systematic features start to show up. For example, odd-A nuclei in the midshell regions are characterized by exceptionally large positive quadrupole moments Q and

even-even nuclei in the same region have a rather low-lying first excited state with $I = 2+$. Furthermore, several low lying states were found to have remarkable regularities, *viz.* their excitation energy follows very closely a simple formula

$$E(I) = AI(I+1) + BI^2(I+1)^2$$

These observations suggest that in these nuclei, there is a coherent participation of nucleons

towards the various nuclear properties. In other words, the *3A* degrees of freedom of a nucleus is now reduced to a few degrees of freedom and the variables having these freedoms are called as collective variables. This lead to the development of a model of nucleus based on these collective variables, widely known as the *geometric collective model,* by A. Bohr and B. Motelsson.

$\lambda = 0$ $\lambda = 1$ $\lambda = 2$ $\lambda = 3$
(monopole)   (dipole)   (quadrupole)   (octupole)
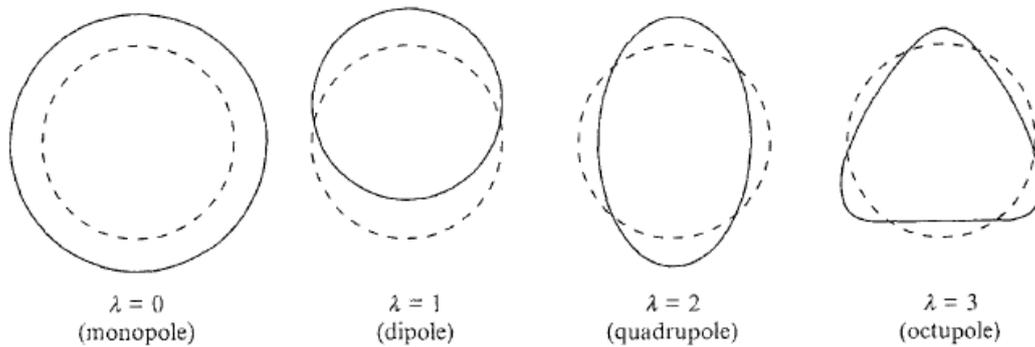
Nuclear shapes with $\lambda = $ 0, 1, 2, 3

The basic assumption of the model is of considering a nucleus as a liquid drop of constant density and a sharp nuclear surface. The collective variables are the surface parameters $\alpha^*_{\lambda\mu}(t)$ describing the dynamics of nuclear surface. With these assumptions, the nuclear surface can be described as an expansion in spherical harmonics

$$R(\theta, \phi, t) = R_o[1 + \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \alpha^*_{\lambda\mu}(t) Y_{\lambda\mu}(\theta, \phi)]$$

where $R(\theta, \phi, t)$ denotes the nuclear radius in the direction (θ, ϕ) at time t and *Ra* is the radius of spherical nucleus. The multipole terms in the above expansion have different physical meaning and the shape they describe

a) $\lambda = 0$ is called as monopole mode and describes the compression of nuclear matter. For low energy spectra this mode in unimportant since it requires a large amount of energy to compress nuclear matter.

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b) $\lambda = 1$ is called as the dipole mode and describes the shift in the center of mass of the nucleus and does not refer to any physical change.

c) $\lambda = 2$ is called as the quadrupole deformation mode. It describes the deviation of a nuclear surface from the spherical surface and is the most important term in nuclear spectroscopy of bound states. The surface looks like an ellipsoid.

d) $\lambda = 3$ is called as the octupole deformation mode. Like quadrupole mode it also describes the deviation of nuclear surface from the spherical surface. In this case the surface is like a pear.

Restricting to $\lambda = 2$ terms in the expansion and making transformation to intrinsic frame with axis 1,2 and 3, the five deformation parameters $\alpha_{\lambda\mu}$ reduces to two real independent parameters a_{20} and $a_{22} = a_{2-2}$ describing the shape of nucleus while the remaining three describes the orientation of the intrinsic frame in space. The nuclear surface in the intrinsic frame can be written as

$$
\begin{aligned}
R(\theta, \phi) &= R_\circ[1 + a_{20}Y_{20}(\theta, \phi) + a_{22}Y_{22}(\theta, \phi) + a_{2-2}Y_{2-2}(\theta, \phi)] \\
&= R_\circ[1 + \beta\sqrt{\frac{5}{16\pi}}(\cos\gamma(3\cos^2\theta - 1) + \sqrt{3}\cos\gamma \sin^2\theta \sin2\phi)]
\end{aligned}
$$

where the Hill-Wheeler coordinates β, γ ($\beta>0$) introduced through the relations

$a_{20}=\beta\cos\gamma$

and $a_{22}=(1/\sqrt{2})\beta\sin\gamma$

are used.

An expression describing the change of the length of principal axis from the spherical radius *Ro* in the intrinsic frame can be obtained

$$\delta R_1 = R\left(\frac{\pi}{2}, 0\right) - R_\circ = R_\circ \sqrt{\frac{5}{4\pi}} \, \beta \cos\left(\gamma - \frac{2\pi}{3}\right) \, ,$$

$$\delta R_2 = R\left(\frac{\pi}{2}, \frac{\pi}{2}\right) - R_\circ = R_\circ \sqrt{\frac{5}{4\pi}} \, \beta \cos\left(\gamma + \frac{2\pi}{3}\right) \, ,$$

$$\delta R_3 = R(0,0) - R_\circ = R_\circ \sqrt{\frac{5}{4\pi}} \, \beta \cos\gamma \, ,$$

$$\delta R_\kappa = R_\circ \sqrt{\frac{5}{4\pi}} \, \beta \cos\left(\gamma - \frac{2\pi}{3}\kappa\right) \, , \quad \kappa = 1, 2, 3 \, .$$

From these expressions, the shape of the nucleus for different values of deformation parameter can be easily visualized. The parameter β describes the degree of deformation while the parameter γ describes the shape of the nucleus, *i.e.* whether it is an oblate, a prolate or a triaxial. It also called the triaxiality parameter. From the expression above it can be seen that for $\gamma = 0$o, 120°, 240° the shape of the nucleus corresponds to a prolate spheroid whereas for $\gamma = 180°$, 300°,60° it corresponds to an oblate spheroid with the 3, 1 and 2 axes as the axes of symmetry. For γ not equal to the multiple of 60° the nuclear shape is triaxial. Due to discrete symmetries, the interval $0 < \gamma < 60°$ is sufficient to describe all the quadrupole shapes. All this information can be conveniently described in β and γ plane.
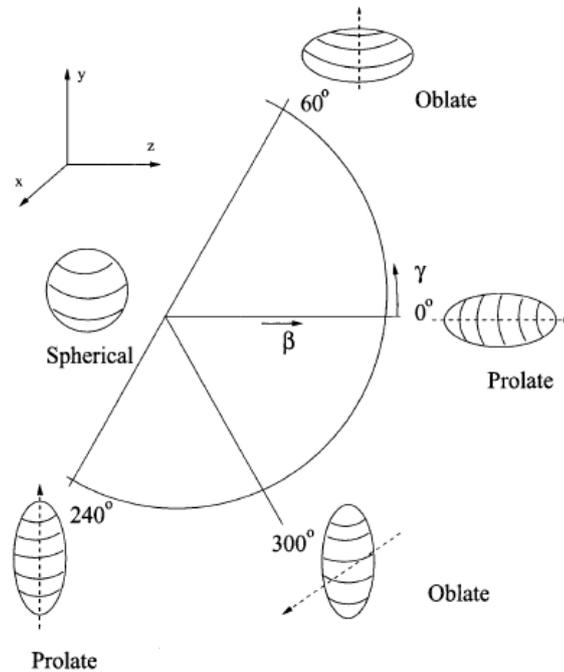
Nuclear shapes in β,γ plane. On the top left is shown the principal axes of intrinsic frame.

The dynamic of the system is described by the Hamiltonian, also called as *Bohr Hamiltonian*, in the intrinsic frame

$$H_{coll} = \frac{1}{2}\sum_{\kappa=1}^{3} J_{\kappa}\omega_{\kappa}^2 + \frac{1}{2}B_2(\dot{\beta}^2 + \beta^2\dot{\gamma}^2) + V(\beta,\gamma)$$

$$V(\beta,\gamma) = \frac{1}{2}C_{20}\left(a_{20}(\beta,\gamma) - a_{20}^0\right)^2 + C_{22}\left(a_{22}(\beta,\gamma) - a_{22}^0\right)^2$$

$$J_{\kappa} = 4B_2\beta^2\sin^2\left(\gamma - \frac{2\pi}{3}\kappa\right), \quad \kappa = 1,2,3.$$

The form of potential corresponds to rotation and vibration around a mean deformation given by $\beta 0$, $y0$. The rotation and vibration degrees of freedom are coupled by the dependence of moment of inertia Jk, on deformation parameters. For deformation $\beta 0 = 0$, the collective Hamiltonian becomes the Hamiltonian describing the pure vibration of nuclear surface.

RADIOACTIVE DECAY

Naturally occurring radioactive nuclei undergo a combination of α, β and γ emission. Artificially produced nuclei may also decay by spontaneous fission, neutron emission and even proton and heavy-ion emission. Any decay process is subject to the same basic law.

Radioactive decay law:

The rate of decay (number of disintegrations per unit time) is proportional to N, the number of radioactive nuclei in the sample $dN/dt \; \alpha \; -\lambda N$

The negative sign signifies that N is decreasing with time. is called the decay constant - probability per unit time that a given radioactive nucleus will decay.

Large λ →rapid decay; small λ → slow decay.

$N(t) = N_0 \exp(-\lambda t)$ where N_0 = number of radioactive nuclei at $t = 0$.

Activity and Half-life

Activity: Number of disintegrations per unit time:

$A(t) = \lambda N(t) = \lambda N_0 \exp(-\lambda t) = A0 \exp(-\lambda t)$

This has the same exponential fall off with time as $N(t)$.

Half-life: Time for half the radioactive nuclei in the sample to decay.

Substituting $N_0 = N_0/2$ and $t = t_{1/2}$ gives $t_{1/2} = \ln2/\lambda$

The figure above shows the activity of a sample decaying at a rate of $\exp(-t)$. The half-life of this sample = $\ln2$ (≈ 0.7 s).

DECAY CHAINS

When nuclei A decay into stable nuclei B, the number of each present at time t is

$N_A(t) = N_A(0)e^{-\lambda t}$ and $N_B(t) = N_A(0)(1 - e^{-\lambda t})$

where only nuclei A are present initially.

The number of nuclei A (parent nuclei) decreases with time.

The number of nuclei B (daughter nuclei) increases from zero, initially, and approaches $N_A(0)$ as $t \to \infty$, i.e. all the parent nuclei eventually become daughter nuclei.

The total number of nuclei is constant: $N_A(t) + N_B(t) = N_A(0)$.

If nuclei B are also radioactive, the above equations do not apply, since, as nuclei B are produced, they also decay. The daughter nuclei of B may also be radioactive and a decay chain is set up: A $\to$B$\to$ C… etc.

TYPES OF RADIOACTIVE DECAY

The figure below shows how a variety of decay mechanisms transform an initial (parent) nucleus $^A_Z X_N$ into different final (daughter) nuclei.
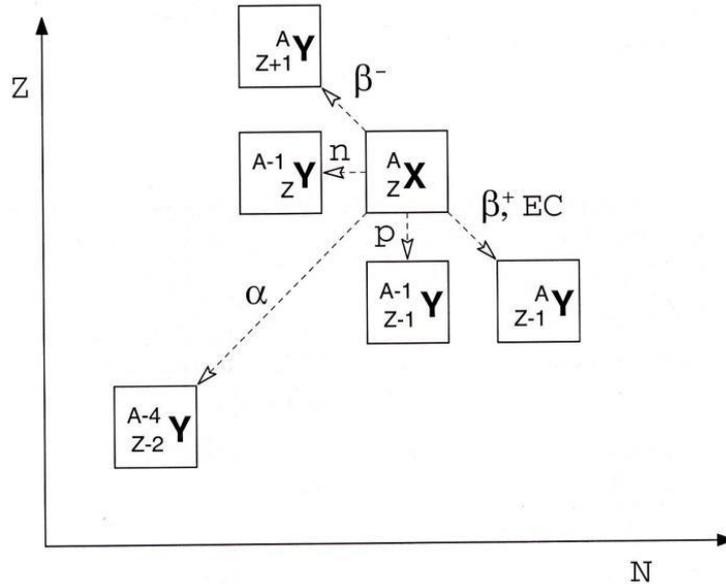
Here we shall consider a number of basic decay mechanisms. They are: alpha decay; beta decay; gamma decay and internal conversion; spontaneous fission.

DETECTION & MEASUREMENT OF RADIOACTIVITY:

All substance are made of atoms. These have electrons (e) around the outside, and a nucleus in the middle. The nucleus consists of protons (p) and neutrons (n), and is extremely small. (Atoms are almost entirely made of empty space!). In some types of atom, the nucleus is unstable, and will decay into a more stable atom. This radioactive decay is completely spontaneous. You can heat the substance up, or subject it to high pressure or strong magnetic fields - in fact, do whatever you like to it - and you won't affect the rate of decay in the slightest. When aunstable nucleus decays, there are three ways that it can do so. It may give out:-

   • an alpha particle (symbol α)

   • a beta particle (symbol β)

   • a gamma ray (symbol γ)

Many radioactive substances emit α particles and β particles as well as γ rays. Although some forms of electromagnetic energy, such as light and heat, can be detected by the human senses. One of the greatest draw backs to high energy radiation is the inability to detect it. We cannot

see, feel, taste, smell, or hear the various forms of ionizing radiation. Fortunately, ionizing radiation interacts with matter which makes detection and measurement possible by utilizing specialized equipment. In this section we want to introduce you to the various ways and means of detecting and measuring ionizing radiation.

Becquerel discovered radioactivity because it left marks on photographic film. However, there are more definitive means commonly used by scientists and technicians who study and work with radiation. The equipment utilized for the detection and measurement of radiation commonly employs some type of substance or material that responds to radiation. Many common methods use either an ionization process or molecular excitation process as a basis. Remember that radiation interacts with matter. For detection and measurement purposes the process of ionization is the most commonly employed technique, based on the principle of charged particles producing ion pairs by direct interaction. These charged particles may collide with electrons, which remove them from their parent atoms, or transfer energy to an electron by interaction of electric fields.

How do you choose a detection device?

Important considerations for choosing a particular type of detection device include the application, the type of radiation, the energy of the radiation, and the level of sensitivity needed. Remember from previous discussion that radiation exists as waveforms with varying energies and may be either particulate or electromagnetic in nature.

There are three types of radiation detection devices:

- o The Electroscope
- o The Cloud Chamber
- o Other Detection Devices

For *measuring radioactivity*, three types of devices are available:

1. Gas-filled tube counters e.g. the Geiger Muller Counter

2. Scintillation Counters

3. Semi-conductor Detectors

1. **The Geiger Counter:** A potential difference just below that required to produce a discharge is applied to the tube (1000 V). Any atoms of the gas struck by the γ-rays entering the tube are ionized, causing a discharge. Discharges are monitored and counted by electronic circuitry and the output is reported as counts/sec or Rontgens/hr or mR/hr.

2. **Scintillation Counters:** Crystals of certain substances e.g. cesium fluoride, cadmium tungstate, anthracine and sodium iodide emit small flashes of light when bombarded by γ-rays. The most commonly used phosphor in scintillation counters is NaI with a minute quantity of thallium added. In the instrument, the crystal is positioned against a photocell which in turn is linked to a recording unit. The number of flashes produced per unit time is proportional to the intensity of radiation. Small portable scintillation counters are available.

3. **Semi-Conductor Detectors:** A semi-conductor is a substance whose electrical conductivity is between that of a metal and an insulator. It is noted that Ge(Li) semi-conductors ate excellent detectors of γ-rays with a resolution ten times higher than NaI (Th) scintillometers. The main disadvantage of these is a lower efficiency for higher energy x-rays. Besides, Ge(Li) semi-conductors need to be cooled by liquid nitrogenand are hence cumbersome and not suitable as field instruments.

Besides the above there are instruments known as γ-ray spectrometers, which can distinguish different energy peaks and hence make it possible to identify the source of radiation.

A Geiger counter will record "counts per minute", but this doesn't tell us what the radioactive substance is actually doing, merely what is reaching the detector. It also tells us nothing about the amount of damage being done to you. Thus we need several different units in order to measure radioactivity.

• The activity of a source is measured in Becquerels (Bq), One Becquerel is one decay per second.

• The amount of radiation that your cells absorb is measured in grays (Gy), One gray is one Joule of energy absorbed by 1kg of your body. This is the dose you receive.

• To measure the harm done to you, we need to remember that α particles ionise very strongly, and cause 20 times more cell damage than the same dose of β particles, γ rays or X-rays. We measure the "dose equivalent" in sieverts (Sv).

• A dose of 1 gray of β-particles, γ-rays or X-rays will give you a dose equivalent of 1 sievert. A dose of 1 gray of α-particles will give you a dose equivalent of 20 sieverts The sievert is quite a large unit, so we usually work in millisieverts (mSv) or microsieverts (μSv).

UNIT OF MEASURING RADIOACTIVITY:

The number of decays per second, or *activity*, from a sample of radioactive nuclei is measured in *becquerel* (Bq), after Henri Becquerel. One decay per second equals one becquerel. An older unit is the *curie*, named after Pierre and Marie Curie. One curie is approximately the activity of 1 gram of radium and equals (exactly) 3.7×10^{10} becquerel. The activity depends only on the number of decays per second, not on the type of decay, the energy of the decay products, or the biological effects of the radiation.

SAFETY PRECAUTIONS:

Some of the principle safety precautions commonly used in working with radioactivity/radiation are time, distance, and shielding. Recall our earlier discussion of the dentist wanting to photograph your teeth. Have you ever wondered why the dentist lays a heavy apron across your chest? The dentist is practicing a means of protection from exposure. In that, they are using distance and shielding from the source of radiation. The concepts of these three principles are fairly simple. The first principle is time. The less time you spend around a

radioactive material the less exposure you will receive. The second principle states that the greater the distance away from a radioactive source the lesser your exposure to the radiation. Lastly, if you can protect yourself with some type of material to act as a shielding device you will also reduce your overall exposure.

LIQUID SCINTILLATION COUNTING

Liquid scintillation counting is an analytical technique which is defined by the incorporation of the radiolabeled analyte into uniform distribution with a liquid chemical medium capable of converting the kinetic energy of nuclear emissions into light energy. Although the liquid scintillation counter is a sophisticated laboratory counting system used the quantify the activity of particulate emitting (ß and a) radioactive samples, it can also detect the auger electrons emitted from ^{51}Cr and ^{125}I samples.

LIQUID SCINTILLATION PRINCIPLES

Figure provides a graphic illustration of the way the emitted radiation interacts with the cocktail (a mixture of a solvent and a solute) leading to a count being recorded by the system.
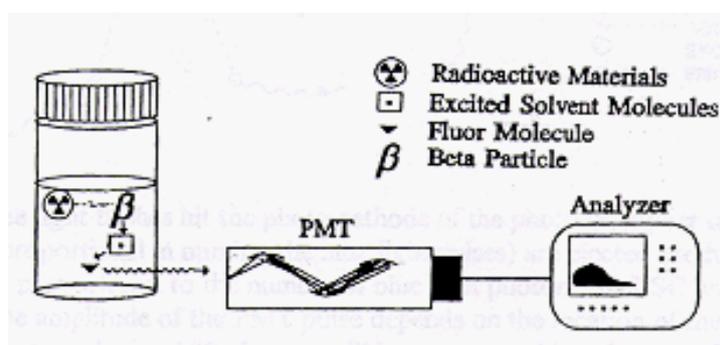
Step 1. Beta particle is emitted in a radioactive decay. To assure efficient transfer of energy between the beta particle and the solution, the solution is a solvent for the sample material.

Step 2. In the relatively dense liquid, the beta particle travels only short distances before

all of its kinetic energy is dissipated. Typically, a beta particle will take only a few nanoseconds to dissipate all its kinetic energy. The energy is absorbed by the medium in 3 forms: heat, ionization and excitation. Some of the beta energy is absorbed by solvent molecules making them excited (not ionized).

Step 3. Energy of the excited solvent is emitted as UV light and the solvent molecule returns to ground state. The excited solvent molecules can transfer energy to each other and to the solute (Figure 2). The solute is a fluor. An excited solvent molecule which passes its energy to a solute molecule disturbs the orbital electron cloud of the solute raising it to a state of excitation. As the excited orbital electrons of the solute molecule return to the ground state, a radiation results, in this case a photon of UV light. The UV light is absorbed by fluor molecules which emit blue light flashes upon return to ground state. Nuclear decay events produce approximately 10 photons per keV of energy. The energy is dissipated in a period of time on the order of 5 nanoseconds. The total number of photons from the excited fluor molecules constitutes the scintillation. The intensity of the light is proportional to the beta particle's initial energy.

Step 4. Blue light flashes hit the photo cathode of the photo multiplier tube (PMT). Electrons (proportional in number the blue light pulses) are ejected producing an electrical pulse that is proportional to the number of blue light photons. A LSC normally has two PMT's. The amplitude of the PMT pulse depends on the location of the event within the vial. An event producing 100 photons will be represented by a larger pulse if the event is closer to the PMT than if the event is more remote. The signal from each PMT is fed into a circuit which produces an output only if the 2 signals occur together, that is within the resolving time of the circuit, approximately 20 nanoseconds (coincidence circuit). By summing the amplitude of the pulses from each PMT, an output is obtained which is proportional to the total intensity of the scintillation. This analog pulse rises to its maximum amplitude and falls to zero.

Step 5. The amplitude of the electrical pulse is converted into a digital value and the digital value, which represents the beta particle energy, passes into the analyzer where it is compared to digital values for each of the LSC's channels. Each channel is the address of a memory slot in a multi-channel analyzer which consists of many storage slots or channels concerting the energy range from 0-2000 keV.

Step 6. The number of pulses in each channel is printed out or displayed on a CRT. In this manner, the sample is analyzed and the spectrum can be plotted to provide information about the energy of the radiation or the amount of radioactive material dissolved in the cocktail.

NUCLEAR FISSION AND FUSION:
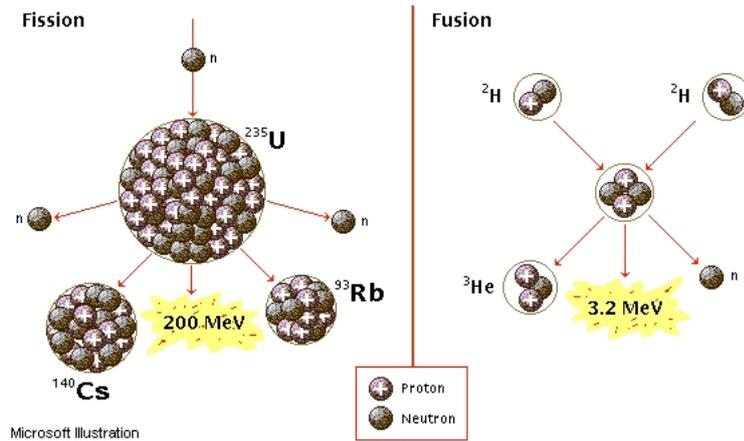
Mass Defect & Einstein's Equation

The mass of the nucleus is actually about 1% smaller than the mass of its individual protons and neutrons. This difference is called the mass defect.
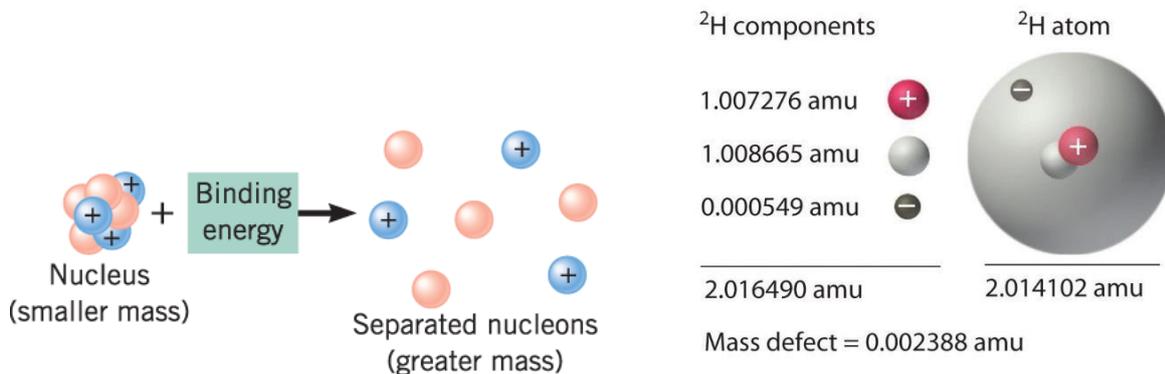
The mass defect results from the energy released when the protons and neutrons bind together to form the nucleus. This energy is called the nuclear binding energy. The binding energy determines which nuclei are stable and how much energy is released in a nuclear reaction. The higher the binding energy, the more stable the nucleus.

Very heavy nuclei and very light nuclei have low binding energies. This implies:

1. a heavy nucleus will release energy when it splits apart (what we call fission)

Fission

Fusion

^{235}U

^{93}Rb

200 MeV

^{140}Cs

Microsoft Illustration

^{2}H ^{2}H

^{3}He 3.2 MeV

Proton
Neutron

2. two light nuclei will release energy when they join (what we call fusion).

The mass defect and binding energy are related by Albert Einstein's formula, $E = mc^2$ which shows that matter and energy are interchangeable. This equation states, mass (m) can be converted into an amount of energy (E), where c is the speed of light. Because the speed of light is a large number and thus c squared is huge, a small amount of matter can be converted into a tremendous amount of energy. This equation is key to the power of nuclear weapons and nuclear reactors.

Nuclear Fission

Very large nuclei (mass number greater than 230) tend to be unstable and can split into two or more parts. This is called fission.

$^{1}_{0}n$

$^{235}_{92}U$

$^{236}_{92}U$

Unstable nucleus

$^{92}_{36}Kr$

ENERGY

$3\ ^{1}_{0}n$

$^{141}_{56}Ba$
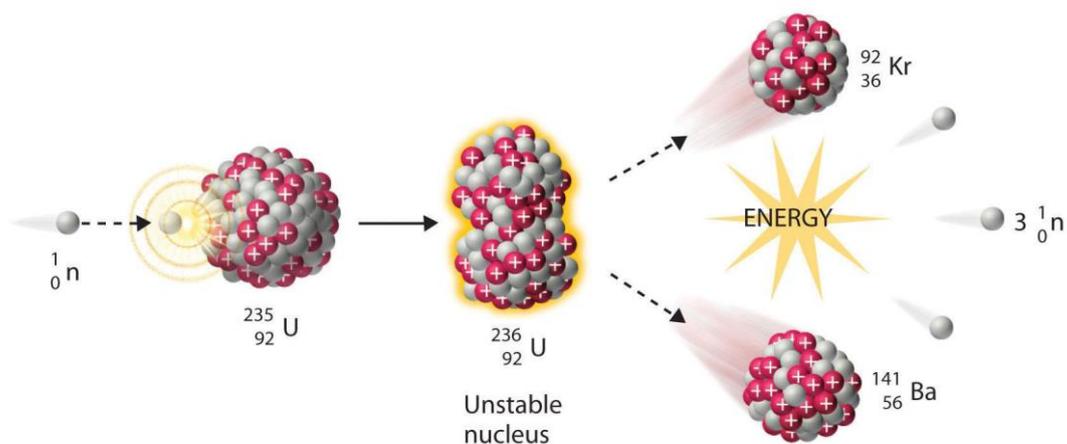
☐ Fission is not a spontaneous process. It can only occur when a slow moving neutron strikes an unstable nucleus.

☐ In this decay process, the nucleus will split into two nearly equal nuclei and release several free neutrons and huge amounts of energy.

☐ These nuclei are isotopes of more stable elements. If left alone, they decay radioactively by emitting alpha or beta particles.

☐ On average, three neutrons are released. These can go on to be absorbed by other nuclei if they are slowed down by a moderator (a medium, such as graphite, heavy water, and beryllium that causes the neutrons to travel more slowly).

☐ If these neutrons are absorbed by other nuclei, this causes a chain reaction.
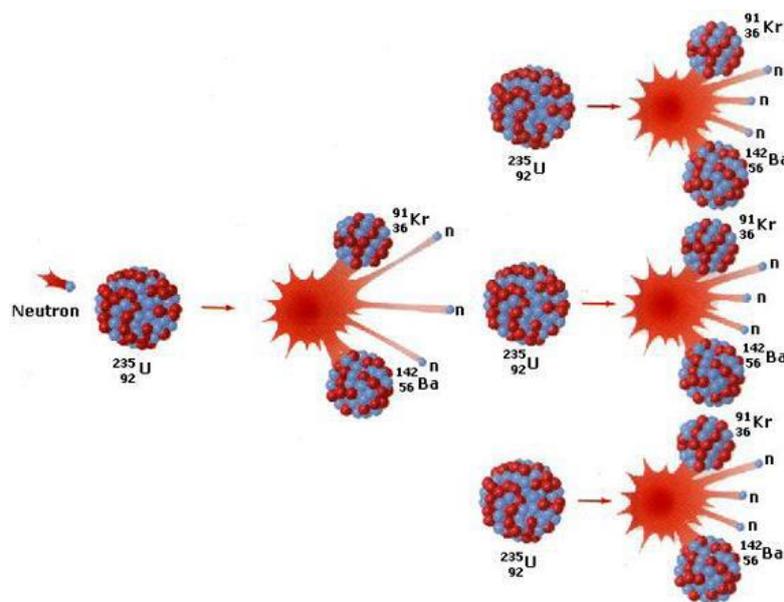
☐ For the chain reaction to occur, there has to be a critical mass.

☐ For uranium, this is about the size of a tennis ball. The critical mass has a mass of about 15 kg (uranium has a very high density, 19 g/cm^3). Anything less, the neutrons escape without setting off a chain reaction.

☐ If the chain reaction is not controlled, a nuclear explosion will occur.

Nuclear Fusion

Very light nuclei can combine to form heavier atoms in a process known as fusion.
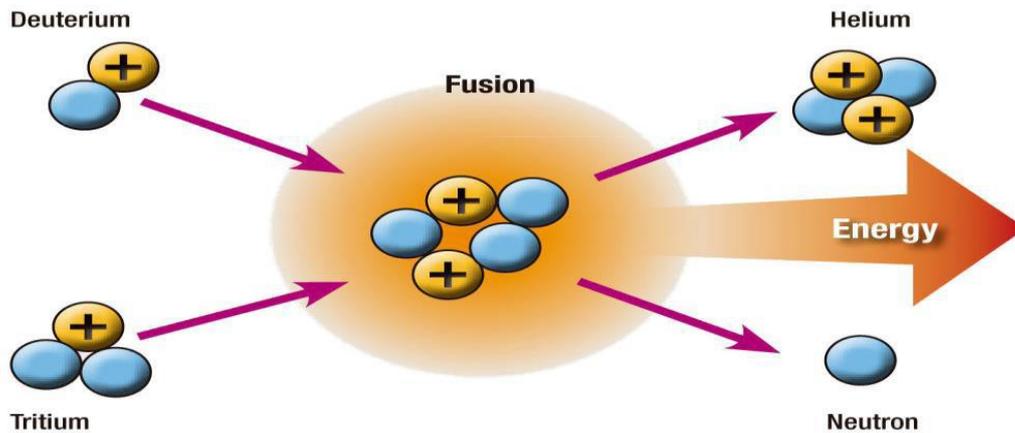
☐ When fusion happens, the products have a larger binding energy than the reactants. The mass defect results in the release of huge amounts of energy.

☐ Actually produces more energy per gram of products than fission and produces no by-products

☐ Why isn't it used yet then for energy production?

o It currently requires more energy to initiate the reaction than it produces.

o Heat produced is so intense that containment vessels melt.

Why does fusion require energy?

o To combine, two nuclei must be close enough for the strong nuclear force to join them. But when the positive nuclei approach, the electrostatic force of repulsion is greater than the nuclear force. This means that the nuclei must be HIGHLY energetic to overcome the repulsion force.

o This means HIGH temperatures (millions of degrees Celsius), which is difficult to achieve while containing the atoms.

☐ Nuclear fusion is the energy-producing process taking place in the core of the Sun and stars.

o The core temperature of the Sun is about 15 million °C. At these temperatures, four hydrogen atoms fuse in a series of reactions to form a single helium atom and give off huge amounts of energy.

FAST BREEDER REACTOR:

Fast reactors generate energy from nuclear fuel through their irradiation with fast neutrons. In a thermal reactor, neutrons produced as a result of neutron absorption in fuel possess high kinetic energy of the order of MeV. These are slowed by elastic collision with moderator resulting in thermal neutrons with energies as low as 0.025 eV. Since the fast reactor utilizes fast neutrons, moderation is not required. To be precise, moderation is undesirable in a fast reactor. Hence fast reactors do not contain moderating materials like water, heavy water and graphite in the core.

The fission cross section of U-235 in fast spectrum is low, compared to that of Pu- 239. Hence Pu-239 is used as the main fissile isotope, though enriched U-235 is used at the start to initiate the chain reaction.

Fast reactors are normally configured for breeding. This requires absorption of neutrons by a blanket of fertile material. Also neutron losses in structural components are to be minimized. Hence layers of blankets containing fertile material are used, to ensure that more fuel is breed than that burnt, qualifying the definition of a breeder.

The most common coolants like water and heavy water cannot be used as coolants in a fast reactor. Non-moderating materials like Helium and liquid metals like sodium, lead, lead-bismuth eutectic qualify to be coolants owing to their non-moderating nature.

Based on the coolant, fast (breeder) reactors are further classified as follows:

(i) sodium cooled fast reactor

(ii) lead cooled fast reactor

(iii) helium cooled fast reactor

Both sodium cooled fast reactor and lead cooled fast reactor are called Liquid Metal Cooled Fast Breeder Reactor (LMFBR). Due to better transport and neutronic properties, sodium is the most preferred choice for coolant. One of the advantages of using sodium as coolant is the possibility of achieving a high coolant (sodium) outlet temperature, while maintaining a pressure much lower than those maintained for light water and heavy water reactors. This is due to the high boiling point of sodium even at atmospheric pressure. Hence problems associated with high pressures are circumvented to a large extent.

Sodium cooled fast breeder reactors use two cycles of coolant flows. The primary circuit involves the circulation of sodium through the core. Relatively low temperature sodium enters the core at the bottom and leaves at the top at higher temperature. This sodium, called primary sodium is radioactive due to exposure to neutrons while passing through the core. Another circuit involves heat transfer between the radioactive primary sodium and secondary sodium in separate heat exchangers. The secondary sodium in turn transfers heat to water in steam generator, thus producing steam. The use of secondary coolant between primary coolant and steam is aimed at preventing contact of radioactive sodium with water in case of leakage. While it is to be noted that sodiumwater reaction itself is exothermic and needs to be prevented, contact of radioactive sodium with water would also involve concerns with radioactivity. Hence preventing contact between radioactive sodium and water eliminates the radioactivity concerns.

2 Types of sodium cooled fast breeder reactor

There are two types of sodium cooled fast breeder reactor: loop-type reactor, pooltype reactor. This classification is based on the location of (primary) heat exchanger used for transferring heat from primary sodium to secondary sodium.

Loop-type fast reactor

The schematic diagram of a loop-type fast reactor is shown in Figure. In loop-type reactor (see figure 1), the heat exchanger used for heat transfer from primary to secondary sodium and the primary sodium pumps is located outside the reactor vessel, but still within the biological shield.
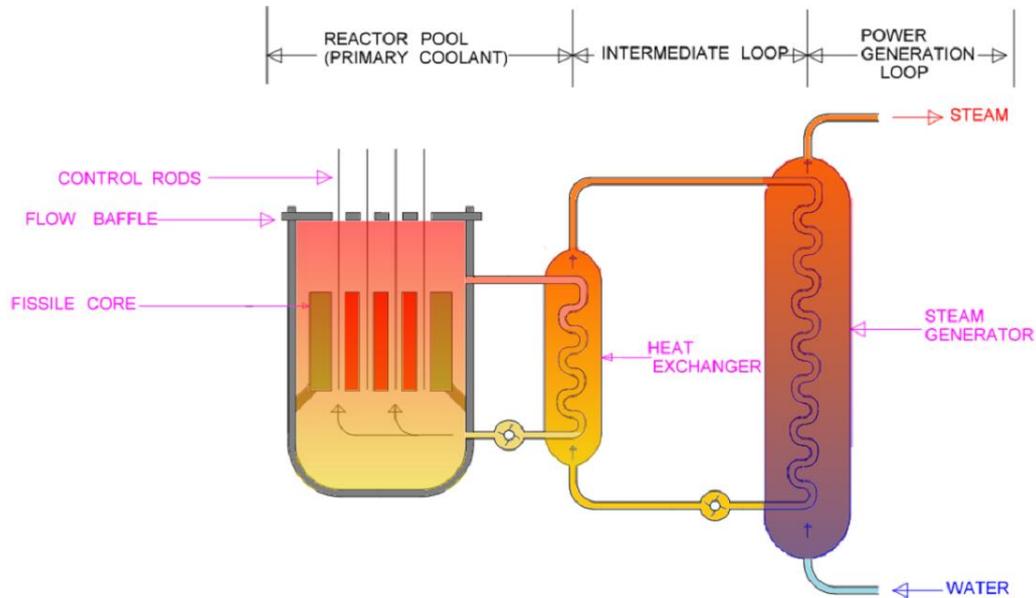
Pool-type fast reactor

In pool-type reactor, the primary heat exchanger and pumps for primary sodium are placed inside the reactor tank. As a result, the diameter of reactor tank is higher for the pool design compared to that of loop design.
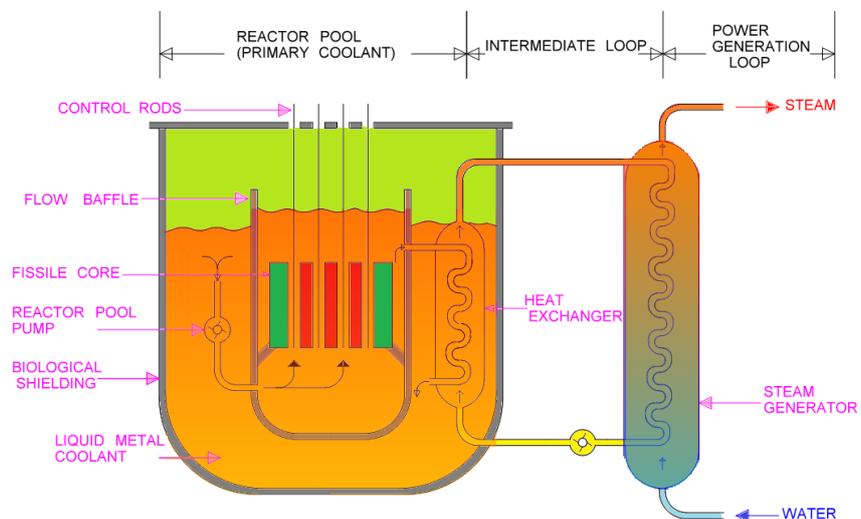
Also, the thermal inertia of sodium is higher in pool type reactors compared to that in loop-type reactors. For example, when there is a drop in the rate of circulation of primary sodium in the core, the temperature of the coolant due to this transient will slowly increase from the steady-state temperature due to higher heat capacity (product of specific heat and mass). Hence the higher mass of sodium in the pool contributes to the higher thermal inertia.

Other advantages of pool type reactors over loop type reactors are:

(i) Radioactive materials are confined within a single vessel

(ii) Availability of independent and dedicated sodium loop for removing decay heat reliably

(iii) Reduction in the amount of external piping

(iv) No penetrations leading to higher structural integrity of the vessel

(v) Lower neutron dose

(vi) Sodium leakage will not result in Loss of Coolant Accident (LOCA) leading to higher reliability

APPLICATIONS OF RADIOACTIVE ISOTOPES:

• Nuclear power plants

• Medical diagnosis and treatment e.g. PET scan monitors glucose metabolism in brain using C-11 isotope; I-131 measures activity of thyroid

• Carbon dating (measure amount of C-14 remaining in a sample)

• Synthesis of new elements

• Irradiation of food - preserves food & destroys parasites

• Nuclear Weapons (Atomic bombs and H bombs)

NEUTRON ACTIVATION ANALYSIS:

Neutron Activation Analysis (NAA) is a quantitative and qualitative method of high efficiency for the precise determination of a number of main-components and trace elements in different types of samples. NAA, based on the nuclear reaction between neutrons and target nuclei, is a useful method for the simultaneous determination of about 25-30 major, minor and trace elements of geological, environmental, biological samples in ppb-ppm range without or with chemical separation. In NAA, samples are activated by neutrons. During irradiation the naturally occurring stable isotopes of most elements that constitute the rock or mineral samples, biological materials are transformed into radioactive isotopes by neutron capture.

Then the activated nucleus decays according to a characteristic half-life; some nuclides emit β particles only, but most nuclides emit gamma-quanta (gamma-photon), too, with specific energies. The quantity of radioactive nuclides is determined by measuring the intensity of the characteristic gamma-ray lines in the spectra. For these measurements a gamma-ray detector and special electronic equipment are necessary. As the irradiated samples contain radionuclides of different half-lives different isotopes can be determined at various time intervals. Although the development of analytical techniques has led to the expansion of new methods (ICP-AAS, ICP-MS, etc.), which can also be widely applied in analytical chemistry, NAA is still competitive in many areas. The indisputable advantage of the method is its sensitivity and accuracy especially in respect of some trace elements. The method is of a multielement character, i.e. it enables the simultaneous determination of many elements without chemical separation. In the case of instrumental determination, the preparation of samples involves only the preparation of representative samples, i.e. pulverization or homogenization in most cases, and this reduces the danger of contamination to a minimum and accelerates the whole analytical process. If the determination of some special elements or groups of elements can be carried out only through chemical separation, it is possible to carry out after irradiation. Thus the pollution

caused by the different chemicals will not get activated, the chemical yield can be measured by feeding inactive carriers and the chemical processes can be better controlled. During NAA the neutrons get into interaction with the nucleus, therefore, the chemical composition and crystal structure of the substance under analysis will have an effect on the result only in exceptional cases. The development of the method has contributed to the elaboration of some very simple and accurate methods of standardization, which lead to a surpassingly accurate analysis. The widespread application of NAA is hindered, however, by some conditions. Among the different fields of application, the Instrumental Neutron Activation Analysis (INAA) following a reactor irradiation is the most competitive. In view of the increasing protest against nuclear energy, a number of research reactors have been shut down; therefore, the possibilities of irradiation are limited in many countries. The equipment needed for the analysis is rather expensive and requires special laboratories and a highly qualified staff.

Principles of the NAA method

In the process of NAA the neutrons interact with the stable isotopes of the target element converting them to radioactive ones. The so-called compound nucleus emits gamma rays promptly with extremely short half-lives in the order of ps and these can be measured during irradiation through a technique called prompt gamma activation analysis (PGAA). In most cases, the radioactive isotopes decay and emit beta particles accompanied by gamma quanta of characteristic energies, and the radiation can be used both to identify and accurately quantify the elements of the sample. Subsequent to irradiation, the samples can be measured instrumentally by a high resolution semiconductor detector, or for better sensitivity, chemical separations can also be applied to reduce interferences. The qualitative characteristics are: the energy of the emitted gamma quanta ($E\gamma$) and the half-life of the nuclide ($T\frac{1}{2}$). The quantitative characteristic is: the $I\gamma$ intensity, which is the number of gamma quanta of energy $E\gamma$ measured per unit time.

1. Step of the analysis: sample preparation means in most cases only pulverising, homogenising, mass determination, packing, as well as the selection of the best analytical process and the preparation of the standards, if any.

2. Step of the analysis: for irradiation one can choose from the various types of neutron sources according to need and availability.

3. Step of the analysis: after the irradiation the analysts face the dilemma whether or not a chemical separation should be carried out for better sensitivity. If it is needed, the measurement shall be made after the separation. If there is no chemical treatment, the measurement is performed after a suitable cooling time (tc).

4. Step of the analysis: measurement, evaluation and calculation involve taking the gamma spectra and the calculating trace element concentrations of the sample. The most widely used gamma spectrometers consist of germanium based semiconductor detectors connected to a computer used as a multichannel analyser for spectra evaluation and calculation.