B.Sc. SEM-III CORE PAPER VII PHYSICAL CHEMISTRY-III

Unit-I

Phase Equilibria-I

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SYLLABUS

Unit-II: Phase Equilibria I

Concept of phases, components and degrees of freedom, derivation of Gibbs Phase Rule for nonreactive and reactive systems, Clausius- Clapeyron equation and its applications to solid-liquid, liquidvapour and solid-vapour equilibria, phase diagram for one component systems, with applications (H2O and sulphur system). Phase diagrams for systems of solid-liquid equilibria involving eutectic (Pb-Ag system, desilverisation of lead), congruent (ferric chloride-water) and incongruent (sodium sulphatewater) melting points, completely miscible solid solutions (intermediate, medium, maximum

freezing points).

Terminology used…..

Phase: It is a form of matter which is uniform throughout in chemical composition and physical state.

e.g.

- A system containing only liquid water is one-phase system
- Asystem containing water and water vapour (gas) is a two phase system
- A system containing liquid water, water vapour and solid ice is a three phase system.
- Pure substances (solid, liquid, or gas) made of one chemical species only, is considered as one phase,

Component

• **It is defined as minimum number of chemically independent species which are required to express the composition of all the phases present in the system.**

- \bullet e.g.
- Water system has three phases and the composition of all these phases is expressed in one chemical formula. Hence one component only.
- Sulphur system has four phases: rhombic sulphur, monoclinic sulphur, liquid sulphur and sulphur vapour and the composition of all these phases is expressed by one chemical individual.
- •Therefore Sulphur system is one component system.

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Degrees of freedom or Variance

• It is defined as smallest number of intensive variables (such as temperature, pressure and conc.) that can be changed independently without disturbing the number of phases in equilibrium

e.g.

• State of a pure gas may be described by any two of the three variables P, T and density. If any two known third can be calculated. Hence it has two degrees of freedom called **bivariant system**.

•**Univariant** in which water and water vapor are in one system

- •If all phases of water exist in equilibrium, no condition needs to be specified as the phases can coexist only at particular temp and pressure.
- •This system has no degrees of freedom hence called **invariant system**.

Phase rule

- It was first presented by Gibbs in 1875.
- It is very useful to understand the effect of intensive variables, such as temperature, pressure, or concentration, on the equilibrium between phases as well as between chemical constituents.
- It is used to deduce the number of degrees of freedom (F) for a system. Sometimes called: "the variance of the system".

Phase rule

It states that :

For every heterogeneous system in equilibrium, the sum of number of phases and degrees of freedom is greater than the number of components by two i.e.:

> $F+P=C+2$ **F= C-P+2**

Advantages of Phase rule

- 1. Provides convenient method of classification of equilibrium states of system.
- 2. Predict the behavior of system with changes in the intensive variables.
- 3. Indicate that different systems having the same number of degrees of freedom behave in the same manner.
- 4. Applicable to macroscopic system
- 5. It takes no account of nature of reactant and products in phase
- 6. Applicable to physical and chemical equilibria.

- 1. Applicable only for the system in equilibrium
- 2. Applicable to a single equilibrium state
- 3. Considers only intensive variables
- 4. Considers only number of phases not quantity of phases
- 5. It requires that all the phases to be present under the same conditions of temperature and pressure.

Clausius-Clapeyron Equation

- The Clausius-Clapeyron equation relates the latent heat (heat of transformation) of vaporization or condensation to the rate of change of vapor pressure with temperature.
- In the case of a solid-liquid transformation, it relates the latent heat of fusion or solidification to the rate of change of melting point with pressure.
- We consider an infinitely small reversible Carnot cycle whose isotherms are at temperature T-dT.
- These two isotherms represent two states of a two-phase system.
- Let the system absorb the amount of heat (Q_1) in transition from phase 2.
- During this transition, the volume of the system changes from (V_2) to (V_1) at a pressure P.
- In the reverse process, the volume changes from (V_1) to (V_2) at a pressure (P-dP), and the system liberates the amount of heat (Q_2) .
- Since the heat (Q_1) is utilized in the phase transition, ($Q_1 = L$), where L is the latent heat of transition.

Derivation of the Clausius-Clapeyron equation

The work done in this cycle will be

$$
W=P(V_1-V_2)+(P-dP)(V_2-V_1)=(V_1-V_2)dP \quad \rightarrow (1)
$$

Then the efficiency of the cycle is ۰

$$
\eta=W/Q_1=(V_1-V_2)dP/L\quad\rightarrow (2)
$$

On the other hand, the efficiency of the Carnot cycle is given by ٠

$$
\eta = 1 - (T_2/T_1) = 1 - ((T - dT)/T) = dT/T \quad \rightarrow (3)
$$

Comparing (2) and (3), we obtain ٠

$$
\frac{dP}{dT}=\frac{L}{T(V_1-V_2)}\quad\rightarrow (4)
$$

This equation is known as the Clausius-Clapeyron equation. ٠

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Melting, Vaporization, and Sublimation

- In case of the liquid-vapour phase transition, the volume change ΔV $= V_g - V_1$ is always positive and hence dP/dT > 0
- i.e. the boiling point increases with increase of pressure.
- If the vapour pressure is low, $V_g \gg V_l$. $dP/dT = L/TV$
- where L is the latent heat of vaporization. Regarding the vapour as an ideal gas, $V_g = RT/P$ and then $dP/P = (L_v/R) (dT/T²)$.

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On integrating, we get
ln [P(T) / P_c(T_c)] = (Lv/R)((1/T_c) - (1/T))or
P(T) = P_c(T_c) \exp [(Lv/R)((1/T_c) - (1/T))]
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Where Pc and Tc are the critical pressure and critical temperature, respectively, corresponding to the critical point C.

For the solid-liquid phase transition, (4) can be represented as $dP/dT = Lm/T (V_1 - V_2)$

Where Lm is the latent heat of melting, Vg and Vs are the specific volumes of the liquid and solid phase, respectively, on the melting line. In this case, V_1 and V_2 are usually close to each other and two cases are possible:

The volume change ΔV is negative, then $dP/dT < 0$ and the melting point decreases with increase of pressure.

In case of the solid-vapour phase transition, (4) takes the form $dP/dT = L/T(V - V_2) \rightarrow (9)$

Where L is the latent heat of sublimation, V and V_2 are the specific volume of vapour and solid phase, respectively, on the sublimation line. In this case $V \gg V_2$ and $V = RT/P$.

Review of thermodynamics

 $dP/dT = (L/R)(dT/T^2) \rightarrow (10)$

on integration, we get

 $InP = -(L/RT) + A \rightarrow (11)$

- Vapour pressure of solids are usually measure over only a small range of temperature. Within this range, (11) can be expressed in the form $InP = -(B/T) + A \rightarrow (12)$
- Where A and B are constant of a given system.
- The triple point satisfies the condition $g_s = g_1 = g_g \rightarrow (13)$
- The temperature and pressure corresponding to the triple point are denoted by T_r and P_r . For water, they are $T_r = 0.01$ °C and $P_r = 6P_a$.
- Consequently under normal condition and atmospheric pressure equilibrium of all phase water cannot be observed at the triple point.

Phase Diagram

- 1. It is a convenient graphical representation formed by plotting the values of intensive variables for equilibrium conditions between two phases.
- 2. It shows the properties such as mp, bp, phase transition point and triple point.
- 3. The complex city of phase diagram increase with increase in number of component in the system.
- 1. For a simple substance (one component system) phase diagram is two dimensional plot where $P \& T$ are independent variables.
- 2. The phase diagram of a two component system is a three dimensional plot, where third axis is for composition.

Phase Diagram

- 6. Three dimensional plot can also converted into two dimensional plot by keeping one variable constant.
- Isobaric
- Isothermal
- 7. When one of the variable kept constant then phase rule equation is reduced to :

 $F = C - P + 1$

8. This is known as reduced phase rule.

Phase Diagram

Water System

- 1. Water exist in three possible phases: ice, water, vapors
- 2. It is a one component system so maximum degrees of freedom is two, when one phase is stable at equilibrium. $F = C-P+2 = 1-1+2=2$
- 3. Phase diagram of water is two dimensional plot where P & T are taken as axes.

Areas of Phase Diagram of Water System

Phase diagram is divided into three areas:

- 1. Area BOC where ice has stable existence
- 2. Area COA– where water has stable existence
- 3. Area BOA– where water vapors has stable existence

Phase Rule for this system:

 $F = C-P+2=2$

Degrees of freedom is two hence bivariant system.

Various Curves of Phase Diagram of Water System

- 1. Melting point Curve (Curve OC)
- 2. Vaporization curve or vapor pressure curve (Curve OA)
- 3. Metastable equilibrium (Curve OA')
- 4. Sublimation Curve (Curve OB)
- 5. Triple point O

- 1. Also known as melting point curve or freezing point curve or fusion curve.
- 2. Represents equilibrium between ice & water
- 3. It is enough to know either T or P because other variable gets automatically fixed.
- e.g.At atmospheric pressure, ice & water can be in equilibrium only at one temperature i.e. at freezing point of water.
- 4. Thus ice- water equilibrium line (Curve OC) has only one degree of freedom (Univariant system).

Phase Rule:
$$
F = C - P + 2 = 1 - 2 + 2 = 1
$$

Vaporization Curve or vapor pressure curve (Curve OA)

- Represents the equilibrium between two phases water $\&$ vapor..
- 2. It enough to know either T or P because other variable gets automatically fixed.
- 3. Because at any temperature, Pressure of vapor in equilibrium is fixed in value.
- 4. Thus water & vapor equilibrium line OA has only one degree of freedom so univariant system.

Phase Rule:
$$
F = C - P + 2 = 1 - 2 + 2 = 1
$$

Vaporization Curve or vapor pressure curve (Curve OA)

- 6. At higher end, curve OAterminates at pointAwhich is critical temperature (374⁰C) and Pressure (218atm.) of water.
- 7. At this point liquid & vapor phases become indistinguishable & merge into single fluid phase.
- 8. Under normal conditions terminus point is O where water freezes to form ice.

Vaporization Curve or vapor pressure curve (Curve OA')

- 1. Curve OA'represents the meta-stable equilibrium.
- 2. Under some special conditions pure water may be cooled down much below the freezing point without forming ice.
- 3. Thus it is possible to extend vapor pressure curve even below freezing point of water.
- 4. This equilibrium can be approached by cooling liquid water and not by heating ice.
- 5. Metastable vapor pressure of super cooled liquid is higher than the vapor pressure of ice.

Sublimation Curve (Curve OB)

- 1. Represents the condition for equilibrium between ice and vapors.
- 2. Shows vapor pressure of ice at different temperature
- 3. In order to describe the system along line OB either value of T or P need to be specified.
- 4. Because at any temperature, value of vapor pressure of ice is fixed.

IMP terms

- **1. Critical Point:** a point on a phase diagram at which both the liquid and gas phases of a substance have the same density, and are therefore indistinguishable.
- **2. Triple point:** The temperature and pressure at which a substance can exist in equilibrium in the liquid, solid, and gaseous states.
- 3. The **triple point** of pure **water** is at 0.01°C (273.16K, 32.01°F) and 4.58 mm (611.2Pa) of mercury

Phase Diagram of Sulphur

Sulphur Exist in four forms:

- 1. Rhombic Sulphur (S_R) $(m.p. 114^{\circ}C)$
- 2. Monoclinic Sulphur (S_M) $(m.p. 120^{\circ}C)$
- 3. Liquid sulphur (S_L)
- 4. Vapour Sulphur (S_V)

Monoclinic Sulphur Rhombic Sulphur

Phase Diagram of Sulphur

Curves In Phase Diagram

- Curve AB: Sublimation Curve of Rhombic Sulphur
- Curve BC: Sublimation Curve of Monoclinic Sulphur
- Curve CD: Vapor Pressure Curve of Liquid Sulphur
- Curve CE: Fusion Curve of Monoclinic Sulphur
- Curve BE: Transition Curve Solid Sulphur
- Curve EG: Fusion Curve of Rhombic Sulphur

At any curve, phase rule becomes:

$$
F=3-P=3-2=1 \text{ (univariate)}
$$

Triple Points

- Triple Point **B**
- Triple Point **C**
- Triple Point **E**
- At any Triple Point, phase rule becomes: $\overline{F} = 3-P = 3-3 = 0$ (nonvarient)

Areas

- Area ABEG (Rhombic Sulphur)
- Area BCEB (Monoclinic Sulphur)
- Area DCEG (Sulphur Liquid)
- Area ABCD (Sulphur Vapors)
- In an area, Phase Rule becomes: $F = 3-P = 3-1 = 2$ (bivariant)

Dashed curve

- \triangleright curve BF (sublimation curve of metastable SR) **≻curve CF** (vapour press. Curve of supercooled liquid sulphur) Sourve FE (fusion curve of metastable SR)
SR) SR)
- One triple point F
- 3 areas: AreaABFE (Metastable SR) AreaABFCD (Sulphur vapours) Area DCFE (supercooled liquid sulphur)

Phase Diagram for Two component system

- 1. In two component system with $P=1$, the number of degrees of freedom are highest order is three.
- 2. In two component system phase diagram may be represented by three dimensional diagram of P, composition and T.
- 3. In this diagram two axes represents two variables while third variable is held constant.
- 4. Phase Diagram may be constructed as :
	- 1. P-T diagram keeping conc. Constant
	- 2. P- Conc. Diagram T constant
	- 3. T-C diagram keeping P constant.

Solid – Liquid Equilibria or condensed phase rule

• When PB kept tonstant, vapour phase of system is not considered. In this case system is said to be condensed and phase rule reduced to:

$F = C - P + 1$

- This is called condensed phase rule or reduced phase rule.
- T vs. Composition diagrams are shown to represents the solid-Liquid equilibria.
- Two component system is to be classified depending upon miscibility of two components in molten state and also on basis of solid phases that separates out on cooling.

Solid – Liquid Equilibria or condensed phase rule or reduced phase

- When two components that are completely miscible in liquid state are allowed to cool at low Temperature and components begin to separate out as solid in any of following three forms:
- 1. Components are not miscible in solid state and form eutectic mixture. Pb-Ag alloy, Cd-Bi alloy
- 2. Components form a stable solid compound which melts at constant temperature to give a liquid with same composition. Such compounds are said to have congruent melting points.: Zn-Mg system
- 3. Components form a solid compound which is unstable and decomposes below its mp to give a new solid phase and liquid that is different in composition from original compound. Such compounds have incongruent mp e.g. : Na-K system

Eutectic System

- Two component system in which both the components are completely miscible in liquid phase but do not react chemically is called a eutectic system e.g.Ag-Pb System
- **Eutectic Temperature and composition:** for a pure substanceA, the freezing point is higher and upon increasing the conc. of B freezing point decreases to lowest value. This is called eutectic temperature and composition at this state is called eutectic composition.
- **Eutectic Point:** (easily melted) is defined as the lowest melting point attained by the mixture

Thissystemhas two components and four phases.

The phases are :

(*i) solid silver; (ii) solid lead;* **(***iii)solution of molten silver and lead; and (iv) vapour.*

- It is a simple eutectic system in which silver and lead are completely soluble in liquid state.
- They do not react to form a any compound but on solidification they form an easy melting mixture.(eutectic system)
- Four phases that take part in equilibrium are:
	- 1. solid silver
	- 2. solid lead
	- 3. solution of Lead & silver
	- 4. Vapor
- Boiling point of Ag $\&$ Pb being high, so Gas phase is absent, so pressure has negligible effect.
- So S-L equilibrium without gas phase is known as condensed system.

Areas (Bivariant System)

- 1. Area aboveAOB: only molten mixture of Ag and Pb exist in this system
- 2. Areas enclosed by BOF: only molten mixture of Ag and Pb and solid Pb exist.
- 3. Areas enclosed byAOE: only molten mixture of Ag and Pb and solidAg exist.

Curves of Ag-Pb System (Univariant System)

- **1. CurveAO**
- Since mp of silver is 961 ^oC, continuous addition of Pb lowers mp alongAO.
- Two phases exists in equilibrium alongAO solidAg and solution of Ag & Pb
- If more Pb is added, it separate out as solid

Curves of Ag-Pb System (Univariant System)

2. Curve BO

- Since mp of Pb is 327C, continuous addition of Ag lowers mp along BO.
- Two phases exists in equilibrium along BO solid Pb and solution of Ag $\&$ Pb 961
- System is univariant.

Diagram is divided into two regions below the line EF:

- On the left of the line OD, crystallineAg and eutectic mixture are stable
- On the right of the line OD crystalline Pb and eutectic mixture are stable.

- AO and BO meets at point at O, O is common to both the curves, solid Pb, solidAg and their liquid solution coexist.
- At this point degrees of freedom is zero and it is non- variant.
- Point O is lowest T of 303C at which liquid exist.
- If liquid cooled below this temperature both Ag $\&$ Pb separates in solid form as 2.6% Ag and 97.6 % Pb.
- In an alloy of Ag and Pb, Ag melts at 303C which is lower than melting point of Ag and Pb called eutectic mixture.

KI-Water System

It has **four phases :**

(i) Solid KI ; (ii) Solution of KI in water ; (iii) Ice; and (iv) Vapour.

Only two chemical constituents KI and H_2O being necessary to depict the composition of all the four phases, it is a two-component

system

(a)The Curves AO and OB (b)The Eutectic Point O (c)The area above AOB and the areas below the curves OA and BO

KI-Water System

The Curve AO: the Freezing point curve of Water $F' = 2 - 2 + 1 = 1$

Thus the system is monovariant.

The Eutectic point: The lowest point attainable by the addition of KI along the curve OA is O.

Here the solution becomes saturated with KI and the solid KI appears as the third phase. This point is termed the Eutectic point.

 $F' = 2 - 3 + 1 = 0$

Hence the system is nonvariant. That is, both the temperature (-22°C) and composition $(52\% \text{ KI} + 48\% \text{ ice})$ are fixed.

The Curve BO: the Solubility curve of KI.

 $F' = 2 - 2 + 1 = 1$

That is, the condensed system solid KI/solution is monovariant.

KI-Water System

The Area above *AOB: It representsthe single phase system 'solution'. Applying the phase rule* equation, *F = C – P + 1 = 2 – 1 + 1 = 2* Therefore the system is *bivariant.*

As labelled in the diagram, the area below *AO showsthe existence of ice and solution, while the* area below *BO depicts the presence of solid KI and solution. Below the eutectic temperature line,* there can exist ice and solid KI only.

Phase diagram of $\text{FeCl}_3-\text{H}_2\text{O}$

System **In this system, four congruently melting compounds are formed which**

are,

- \cdot dodecahydrate $(Fe_2Cl_6.12H_2O)$
- •heptahydrate $(Fe_2Cl_6.7H_2O)$
- •pentahydrate $(Fe₂Cl₆$.5H₂O)
- •tetrahydrate($Fe₂Cl₆$.4H₂O).
- The phase diagram consists of four maxima corresponding to the formation of these hydrates.
- Points N, P, R, T represent the congruent melting points of dodeca, hepta, penta, and tetra hydrates respectively.
- The congruent melting point of a salt hydrate is also known as the dystectic point.

Phase diagram of $\text{FeCl}_3-\text{H}_2\text{O}$ System

Phase diagram of $\text{FeCl}_3-\text{H}_2\text{O}$ System

There are five cryohydric points at M, O, Q, S, and U.

•L is the melting point of ice.

•Addition of Fe2Cl6 lowers the melting point along LM.

•At the cryohydric point M, the solution becomes saturated w.r.t dodecahydrate and represents the lowest temperature that can be attained with this system.

Curves MNO, OPQ, QRS, and STU represent the solubilities of dodeca, hepta, penta, and tetra respectively, while UV represents the solubility characteristic of the anhydrous salt. In the diagram, the solubility of each hydrate increases with the rise of temperature.

Now consider the phase changes that result when an unsaturated solution represented by point k is concentrated isothermally by adding anhydrous ferric chloride along ku.

•Firstly a saturated solution of dodecahydrate results at l.

•At m the whole mass solidifies to form dodecahydrate which melts when more of ferric chloride is added.

- Dodecahydrate disappears beyond n and between n and o an unsaturated solution exists.
- The solution becomes saturated with respect to heptahydrate at o.
- Further addition of ferric chloride increases the amount of solid heptahydrate in the solution and at p the whole solution solidifies yielding heptahydrate.
- The heptahydrate persists up to q.
- Between q and r the solution remains unsaturated, at r the pentahydrate begins to crystallize out.
- At s solidification of the whole mass into pentahydrate occurs.
- Between s and t a mixture of penta and tetrahydrate exists which is completely converted into tetrahydrate at t, beyond which tetrahydrate decomposes into anhydrous ferric chloride and at u only the anhydrous salt remains.

INCONGRUENT M.P. SYSTEM

Na2SO⁴ ‐ H2O

SODIUM SULPHATE- WATER SYSTEM

Sodium sulphate forms following phases:

- 1. decahydrate
- 2. heptahydrate
- 3. anhydrous sodium sulphate rhombic
- 4. monoclinic form

5. ice

- 6. Liquid phase
- 7. Vapour phase
	- The vapour phase can be ignored.

The Sodium-Sulphate Water system is a six phase condensed system.

The system consists of four curves and three points.

1.The curveAB (*The melting point curve of ice*)

Ais the melting point of ice, curve RS shows the lowering of melting point of ice on the addition of anhydrous sodium- sulphate.

Applying the reduced phase rule $F = C - P + 1$ $= 2 - 2 + 1$ $=$ 1

Thus the system is univariant.

2.The curve BC(*The solubility curve of sodium sulphate decahydrate*): Along this curve, saturated solution of sodium sulphate and sodium sulphate decahydrate are in equilibrium. Curve BC shows the solubility of sodium sulphate decahydrate increases with temp. until the point C is reached.

. Applying the reduced Phase Rule,

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

Thus the system is univariant along the curve

3.The curve CE (*The solubility curve of rhombic sodium sulphate*):

If heating is continued at point T, all the sodium sulphate decahydrate will disappear and only two phases i.e., anhydrous sodium sulphate and solution will be left.

Applying the reduced phase rule:

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

1.The point B *(Eutectic point***) :**

At this point B, three phases (ice, sodium sulphate deca hydrate and solution) coexist in equilibrium.Applying reduced phase rule :

> $F = C - P + 1$ $= 2$ 3+ 1 $= 0$

Thus the system is nonvariant at this point.

2. The point C (*The Transition point***):**

At point C, the sodium sulphate decahydrate decomposes into the anhydrous rhombic sodium sulphate. So the temp. corresponding to this point "C" represents the transition temperature (32.4). This temp. may also be regarded as the incongruent melting point of sodium sulphate decahydrate.

Applying the reduced phase rule,

 $F = C - P + 1$ $= 2 - 3 + 1$ $= 0$

Thus the system is invariant.

3. The point E (*The transition point***):**

At this point , the anhydrous sodium sulphate exist in rhombic, monoclinic and solution form. So applying the reduced phase rule.

```
F = C - P + 1= 2 - 3 + 1= 0
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Thus point "E" is also invariant point.

ANY QUESTIONS? THANK YOU