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(AUTONOMOUS)

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III B.Sc. Chemistry- semester- V

E-Notes

COURSENAME:PHYSICALCHEMISTRY-I	**CODE:FCH53**
UNIT-II PHASE RULE Definition of the terms - Phase, Components and Degrees of freedom - Derivation of Gibbs phase rule - Applications of phase rule - One component system - Water and 77 Sulphur system - Thermal Analysis and Cooling Curves- Reduced phase rule - Two components system - Simple eutectic system - Lead-silver system. Compound formation with congruent and incongruent melting points.Zn-Mg,Na-k,FeCl3-H2O,KIH2O systems. Freezing Mixtures.	
Learning Objective: To impart knowledge about the Phase diagram, Phase Rule and its Applications	
Learning Outcome: To understand the phase diagrams of one Component and two Component systems having congruent and incongruent melting points.	

PHASE RULE:

The phase rule, also known as Gibbs' phase rule, is a thermodynamic principle that describes the relationship between the number of phases, components, and degrees of freedom in a system

The phase rule is used to characterize the chemical state of geologic systems and predict the equilibrium relations of the phases present. It also allows the construction of phase diagrams to represent and interpret phase equilibria.

UNIT- I I PHASE RULE

- The phase rule is used for quantitative treatment of systems in equilibrium,
- **J.W.Gibbs** propose the **phase rule in 1876**, he investigate, the behaviour of heterogeneous system in equilibrium,
- According to phase rule, for a system in complete internal equilibrium,

$$F = C - P + 2$$

Where F- degree of freedom,

C- Number of components,

P- Number of phases,

Definition of the terms

Phase:

I t is defined as any **homogeneous part** bounded on surface which is physically distinct and mechanically separable fr om other part (Heter ogeneous) of the system in equilibrium.

Ex:

1) Gas has single phase since it is completely miscible,
2) Completely miscible liquid make one- phase systems,
3) Immiscible liquid for m different phasesEx:

H_2O- CCl_4

4) Decomposition of calcium car bonate has three phases

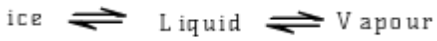
$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

Components:

I t is defined as smallest number of independently variable constituents by means of which "**the composition of each phase** can be expressed in terms of chemical equations**".**

Ex:

1) **Water** exist three phase expressed as H_2O. hence, it is a **one- componentsystem.**



2) **Sulphur** exist four phase expressed as sulphur (S). so, it is a **one- componentsystem.**

3) An aqueous sucr ose solution is **two- component system**. The composition of the solution expressed by the amount of sugar and water.

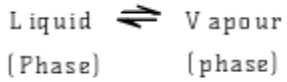
Degree of freedom (F)

I t is defined as the number of **independent variables** such as **temperature, pressure** and **concentr ation** (or composition) which must be denoted in or der defines the system completely.

Ex:

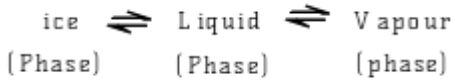
1) Pure gas has **two degree of freedom(F)**, the state of the gas denoted by two var iables T or P and V [volume is related to mass (or concentr ation) calculated for m chemical equation of state]

2) Consider one- component system (Ex: water) having two phases in equilibrium, it has **one degree of freedom(F)**,



Because the equilibrium will have only one fixed value (either T or P variable),

3) Consider one- component system (Ex: water) having three phases in equilibrium,



It has **zero degree of freedom(F)** due to these three phases coexist only

at one particular temperature under one particular pressure.

If F = 0, the system is called invariant

F = 1 univariant (monvariant), F = 2 bivariant, F = 3 traivariant, etc.

- The number of **component is greater** in system, the number of degree of freedom (F) is **greater** for a given number of phases.
- The number of **phases are greater** , the number of degree of freedom (F) **issmaller**
- A one- component have maximum **three phases** and a two- component system have**four phases.**

Gibbs phase rule

J. Willard Gibbs, states that if the equilibrium in a heter ogeneous system is notaffected by gravity or by electrical and magnetic forces,

According to phase rule F = C- P + 2

Where F- degree of freedom,

C- Number of components,

P- Number of phases,

Derivation:

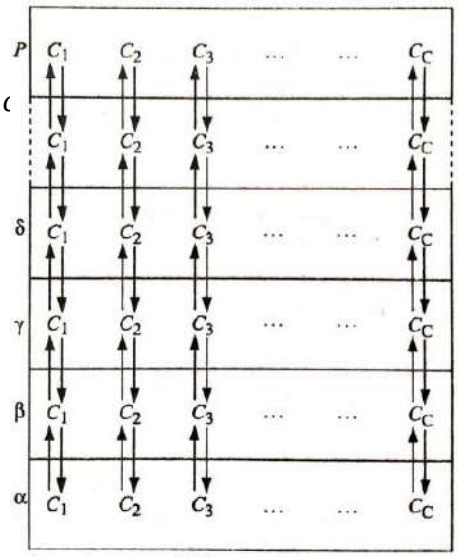
1) Consider a system $(C_1,C_2,C_3,\ldots\ldots\ldots C_C)$distributed between phases $P(\alpha,\beta,\gamma,\delta,\ldots\ldots\ldots P)$ as shown in figure,

2) The system and its each phases is denoted by

$$T,P,(x_{1\alpha},x_{2\alpha},\ldots\ldots x_{c\alpha},)$$

$$(x_{1\beta},x_{2\beta},\ldots\ldots x_{c\beta},)\ldots\ldots\ldots(x_{1P},x_{2P},\ldots\ldots x_{cP},)$$

Where x_{cP} is composition of component



A system of *C* components distributed through *P* phases.

3) The total number of variable **[degree of freedom(F)]** in system is CP + 2

4) All the variables are not independent since in each phase, sum of mole fraction(x_{cP}) must equal unity,

$$(x_{1,\alpha} + x_{2,\alpha}) + (x_{1,\beta} + x_{2,\beta}) = 1$$

The Equ: ② become

$$\sum_i x_i P = 1 \quad (i = C_1, C_2, C_3, \ldots\ldots\ldots C_c) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots ②$$

5) The chemical potential of each component must be the same in each phase forcomplete equilibrium exist between the phase,

$$\left.\begin{array}{l} \mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \ldots \mu_{1,P} \\ \mu_{2,\alpha} = \mu_{2,\beta} = \mu_{3,\gamma} = \ldots\ldots\ldots \mu_{3,P} \\ \mu_{c,\alpha} = \mu_{c,\beta} = \mu_{c,\gamma} = \ldots \mu_{c,P} \end{array}\right\} \ldots\ldots\ldots\ldots\ldots\ldots ③$$

6) For each component has P - 1 separate equations, for C components, the numberequations is C(P - 1)

7) Equilibrium of chemical reaction require chemical affinity ($A_{f,i}$), it must be zero foreach reaction at equilibrium,

$$(A_{f,}) = 0 \qquad (i = C_1, C_2, C_3, \ldots\ldots\ldots r') \ldots\ldots\ldots\ldots\ldots ④$$

Where r' is chemical reaction equation

8) So total number of restricting conditions is

$$P + C(P-1) + r' \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots ⑤$$

9) The degree of freedom (F) is given by

F = (the number of variables in system)- (the number of restrictions)

$$= (CP+2) - [P + C(P-1) + r']$$

$$= (CP+2) - (P + CP - C + r')$$

$$= (CP+2) - P - CP + C - r')$$

$$\boxed{F = 2 + (C - r') - P}$$

…….....⑥

10) The Equ: ⑥ is known as Gibbs Phase rule

11) if there is no reaction take place in system then r ' = 0, so the Phase rule becomeF = (C- P)

+ 2

Applications of Phase rule

One component system

Water system

i. water exist three possible phases, solid, liquid and vapour phases, it has following equilibrium

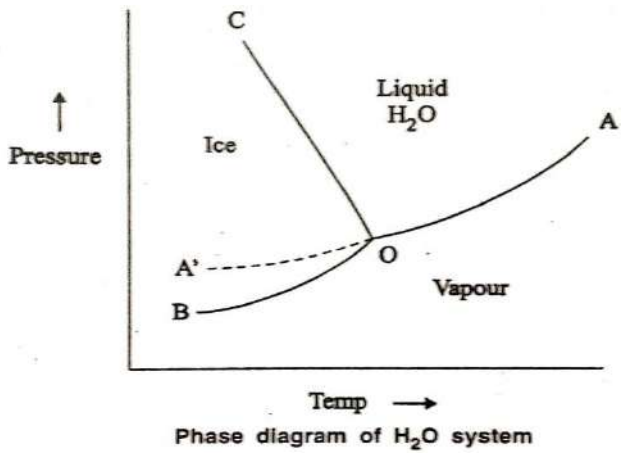
$$\text{solid} \rightleftharpoons \text{Liquid}$$

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

$$\text{solid} \rightleftharpoons \text{Vapour}$$

ii. Each equilibrium has two phases, if one- component system has two phases, thedegree of freedom is one, either temperature or pressure,

iii. it is explained by phase diagram is shown in figure, contains cur ve, areas andtriple point,



Phase diagram of H_2O system

Curves

- the each curve OA, OB, OC have only one degree of freedom (F)F = (C- P) + 2

  F = (1- 2) + 2⇒1
- Hence each curve of the system is univariant (monovariant)

Curve OA:

1) it shows the equilibrium between liquid and vapour called as **vapourisation curve,**

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

2) This equilibrium stay until **critical temperature** (374^0C), Beyond thattemperature equilibrium disappear and only vapour phase will exist.

Curve OB:

1) It represents the equilibrium between solid and vapour, called as **sublimation curve,**

$$\text{solid} \rightleftharpoons \text{Vapour}$$

2) The equilibrium stay upto absolute zero temperature (-273^0C), where novapour phase present and only solid will exist.

Curve OC:

1) It denotes the equilibrium between solid and liquid, called as melting point curve.

$$\text{solid} \rightleftharpoons \text{Liquid}$$

2) This curve slightly inclined towards the pressure axis that shows the melting point of solid decrease with increase of pressure, it is related to **Lechatelier principle,**

Curve OA' (Metastable equilibrium)

1) This curve is called vapour pressure curve of super-cool liquid (or) metastable equilibrium,

$$\text{Super cool liquid} \rightleftharpoons \text{Vapour}$$

2) Sometime water is cooled below 0^0C without formation solid (ice), is **calledsuper cool water**, it is unstable and can be converted into solid

Areas:

1) The areas AOC, BOC and AOB represent liquid, solid and vapour respectively,

2) In order to define the system at any point in area, two variants temperature and pressure is need

3) The degree of freedom of the system is two, so the system is **Bivariant**

$$F = (C-P) + 2F$$

$$= (1-1) + 2 \Rightarrow 2$$

Triple point

The three curves OA, OB, and OC meet at a point C where three phases (solid,liquid and vapour) coexist in equilibrium, is called **triple point**,

$$\text{solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Vapour}$$

1) The degree of freedom (F) at this point is **zero**, so the system is **non-variant,**

2) At this point the variants temperature is 0.0075^0C and pressure is 4.58mm.

Sulphur system

i. Sulphur is **one component system** shows polymorphism and solid-solid transformation,

ii. It exist **four phases**

a) Rhombic sulphur (S_R)

b) Monoclinic sulphur (S_M)

c) Liquid sulphur (S_L)

d) Vapour sulphur (S_V)

iii. All four phases cannot coexist, maximum **three phases** can be coexist inequilibrium

$$F = (C - P) + 2$$

$$P = (C - F) + 2$$

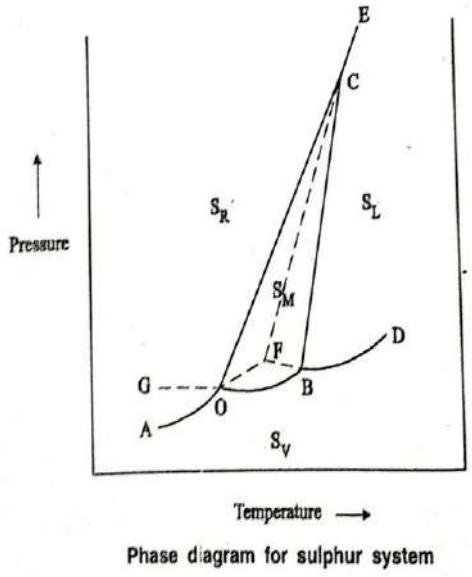
$$= (1 - 0) + 2$$

$$F = 3$$

∴ if F = 0

C = 1

iv. Phase diagram of sulphur is given below, it consist of



Phase diagram for sulphur system

Six stable curves OA, OB, OC,BC, BD and CE Four metastable curves OF, BF, CF and OGFour areas AOCE, OCB, DBCE and AOBD

Triple points O, B, C and F

Curves

1) When two phase are in equilibrium in one component system, the degree of freedom is one.

$$F = (C - P) + 2$$

$$= (1 - 2) + 2$$

$$F = 1$$

∴ C = 1

P = 2

2) Each curve has two phases in equilibrium and it is univariant system

Curve	Name of the curve	Phase in equilibrium
OA	Sublimation curve of S_R	$S_R \rightleftharpoons S_V$
OB	Sublimation curve of S_M	$S_M \rightleftharpoons S_V$
OC	Transition point curve of S_R	$S_R \rightleftharpoons S_M$
BC	Melting point curve of S_M	$S_M \rightleftharpoons S_L$
BD	Vapourisation curve of S_L	$S_L \rightleftharpoons S_V$
CE	Melting point curve of S_R	$S_R \rightleftharpoons S_L$

3) The curve OC is sloping towards right shows that the transition point of S_R increases with increase of pressure,

4) Similarly the curve BC is also sloping towards right shows that the meltingpoint of S_M increase with increase of pressure,

5) When S_L is cooled under ordinary conditions, S_M crystals are formed, but S_L is directly converted into S_R at 428K temperature and 1288 atm pressure.

Metastable curves:

1) **OF** is called the metastable **sublimation curve of** S_R, when S_R is heated rapidly above its transition point, it cannot converted into S_M. In this curve S_R and S_V are in equilibrium,

2) **OG** is metastable **sublimation curve of** S_M, this is a continuation of curve BO, along this curve S_M and S_V are in equilibrium,

3) **BF** is metastable **vapour isation cur ve of** S_L**,** this is a continuation of cur ve BD, along this cur ve S_L and S_V are in equilibrium,

4) **FC** is metastable **melting point of** S_R**,** this cur ve shows the effect of pressure on the melting point of S_R.

Areas:

1) When only one phase exist in a one- component system, the degree of freedom is two,

$F = (C-P) + 2$

$= (1-1) + 2$

$F = 2$

$\therefore C = 1$

$P = 1$

2) Thus the area represent Bivariant system, to determine the system completely, two variants temperature and pressure must be specified.

Area	Phase
AOCE	S_R
OCB	S_M
DBCE	S_L
AOB D	S_V

Tr iple points

1) In sulphur system points O, B, C and F are called tr iple points, at this points three phases are coexist in equilibrium, so that the degree of freedom (F) is zero

$F = (C-P) + 2$

$= (1-3) + 2$

$F = 0$

$\therefore C = 1$

$P = 3$

2) In this points, either temperature or pressure can be altered without alter ing the number of phases of the system.

Point	Phase in equilibrium
O	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$
B	$S_M \rightleftharpoons S_L \rightleftharpoons S_V$
C	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$
F	$S_R \rightleftharpoons S_V \rightleftharpoons S_L$

3) The temperature and pressure at this point is

Point	Temperature	Pressure
O	368.5	0.006
B	393	0.04
C	428	1288
F	388	0.03

Point F is called **metastable triple point**, is reached when S_R is heatedrapidly.

Reduced Phase rule

1) For solid- liquid equilibrium, the effect of pressure is negligible since the vapourpressure of solids is small,

2) Such system in which solid and liquids alone are considered, are known as**condensed system.**

3) **The restriction of constant pressure** introduced in the phase rule equation, itbecome following form

$$F = (C-P) + 1$$

This equation is known as **Reduced Phase rule.**

Two Component systems

1) In this if system consists of only one phase, the degree of freedom (F) is 3F

$$= (C- P) + 2$$

$$= (2- 1) + 2$$

$$F = 3$$

$$\therefore C = 2$$

$$P = 1$$

2) Therefor e, the three variables (Temperature, pressure and concentr ation) must be denoted to define the system completely,

3) These relations represented by three axes are mutually perpendicular to each other,

4) Such a three- dimensional representation of the variables on a paper is not convenient.

Simple Eutectic system

Lead – Silver system

1) It is **two component system**

2) Molten Ag and molten Pb are miscible to give homogeneous solution, but not reactchemically to form compounds,

3) The phase diagram of Ag - Pb system is given below.

Curves

1) Point A and B represents the melting point of pure Ag and Pb respectively,

2) The cur ve AC is **called as the melting point (or) freezing point cur ve of Ag** and it shows the effect of addition of Pb on the melting point of Ag.

3) Similarly the cur ve BC is **called as the melting point (or) freezing point curve ofPb** and it shows the effect of addition of Ag on the melting point of Pb.

4) In curve AC two phases are in equilibrium

$$\text{Solid Ag} \rightleftharpoons \text{Liquid}$$

Applying reduced phase rule equation

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

$$= 2 - 2 + 1$$

$$F' = 1$$

$\therefore C = 2$

$P = 2$

So the system is univariant.

5) Melting point of Ag decrease up to the lower point C by addition of Pb and it form saturated solution, further addition of Pb solid phase is separate out.

6) Similarly in curve BC two phase are in equilibrium and the system is **univariant.**

Solid Pb $\rightleftharpoons$ Liquid

Areas

1) Both areas ACD and BCE has two phases in equilibrium, so the area representsystem is **univariant,**

2) In above these area, Ag and Pb are in homogeneous liquid solution, so there isonly one phase in this area,

Applying reduced phase rule equation,

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

$$= 2 - 1 + 1$$

$$F' = 2$$

$\therefore C = 2$

$P = 1$

The system is **bivariant** in this area.

3) Below the line DCE, there are two regions

a) solid Ag + Eutectic region in which crystalline Ag and solid eutectic are stable.

b) solid Pb + Eutectic region in which crystalline Pb and solid eutectic are stable.

Eutectic Point

1) Both curves AC and BC meet at point C is **known as Eutectic point,**

2) It is lower temperature at which the liquid is in equilibrium with solids of Agand Pb,

3) At this point three phases coexist,

Applying reduced phase rule equation,

$F' = C - P + 1$

$= 2 - 3 + 1$

$\therefore C = 2$

$P = 3$

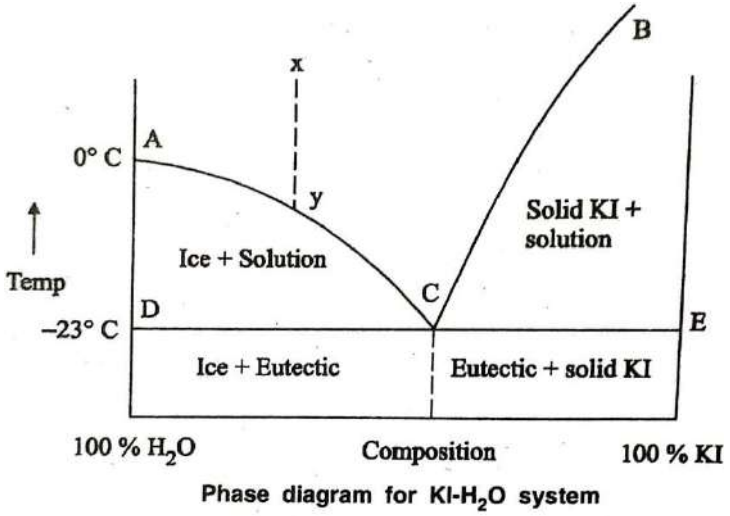
$F' = 0$

4) Eutectic temperature is 303^0C and Eutectic composition Ag(2.6%) and Pb(97.4%)

5) The eutectic point represents system is **invariant.**

6) The phase diagram of Ag - Pb system is utilized in the separation of Ag fromargentiferous Pb by **Pottinson's process.**

KI - H_2O System



Phase diagram for KI-H_2O system

1. It is **two component system**, its phase diagram closely resemble toAg - Pb system,

2 The phase diagram contains following

Curves

AC- Freezing point curve of H_2O

BC- Solubility curve of KIAreas

- ACD, BCE

Cryohydric point, C

a) **Curves**

Curve AC**:**

1) Point A is the pure melting point of ice, its freezing point decreases byaddition of KI,

2) This curve AC is called as the freezing point curve of H_2O, has two phase in equilibrium

$$\text{Solid (ice)} \rightleftharpoons \text{Liquid}$$

The degree of freedom (F') is one, so the curve shows the system is **monovariant**

Applying reduced phase rule equation,

$F' = C - P + 1$

$= 2 - 2 + 1$

$F' = 1$

$\therefore C = 2$

$P = 2$

Curve BC**:**

1) Point B is the pure melting point of KI, its solubility is increase slowly withrising temperature,

2) This curve is called solubility curve of KI, has two phase in equilibrium

$$\text{Solid KI} \rightleftharpoons \text{Liquid}$$

The degree of freedom(F') is **one,** so the curve shows the system is**monovariant**

Areas

1) The areas ACD and BCE shows that the system is **univariant** because of bothareas have two phases in equilibrium,

In A C D area: Solid (ice) $\rightleftharpoons$ Liquid

In B C E area: Solid K I $\rightleftharpoons$ Liquid

Applying reduced phase rule equation, $F' =$

$C - P + 1$

$= 2 - 2 + 1$

$\therefore C = 2$

$P = 2$

$F' = 1$

2) But the area ACB represents the system **is bivariant** since one phase exists,

3) Below the line DCE, solid (ice)+eutectic are present to the left of C and solidKI and eutectic are present to the right of C.

b) Cryohydric point

1) The two curves AC and BC meet at the point C **is known as the eutectic point,** it is also called as the **cryohydric point,**

2) At this point three phases [solid (ice), solid KI and liquid) are in equilibrium

3) At this point temperature is -23^0C

Composition is KI (52%), Ice (48%)

4) The degree of freedom(F') at this point is zero, so the system is non- variant, Applying reduced phase rule equation,

$F' = C - P + 1$

$= 2 - 3 + 1$

$\therefore C = 2$

$P = 3$

$F' = 0$

Freezing mixtures

1) Mixture of salt and ice are used to get low temperature, such mixtures are **knownas freezing mixtures,**

2) Addition of salts to ice results in the melting of some ice and lowering of

temperature,

3) The greater the amount of salt, greater will be the lowering of temperature,

4) This lowest temperature is called **cryohydric point.**

Criteria for a good mixture

1) The cryohydric point should be low,

2) The materials should be cheap,

3) The solubility of salts must be increases with increase of temperature,

4) Easy to mix the solid components,

Ex:

Components		**% of A**	**Cryohydric temperature**
A	**B**		
NH4Cl	Ice	20	-15.4^0C
NH4NO3	Ice	43	-17.5^0C
NaNO3	Ice	33.3	-17.8^0C
KI	Ice	52	-23^0C
NaCl	Ice	23.3	-21^0C
NaBr	Ice	40.3	-28^0C

Thermal analysis and cooling curves

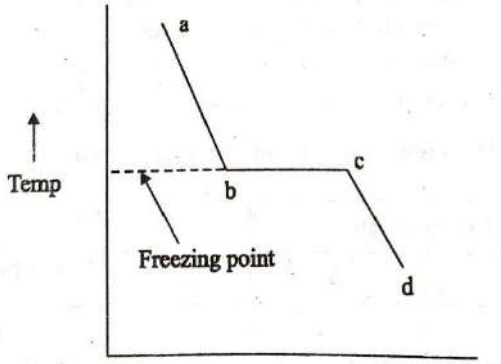
1) It helps to determining the equilibrium between solid and liquid phase in twocomponent system,

2) It is based on cooling curves,

3) By studying cooling curves during solidification, various composition of any systemcan be determined by thermal analysis.

Cooling curve for pure substance

1) Fused state of a pure substance (A) is allowedto cool and temperature is noted atdifferent time interval.



Cooling curve for pure substance (A)

The graph is plotted temperature against time,

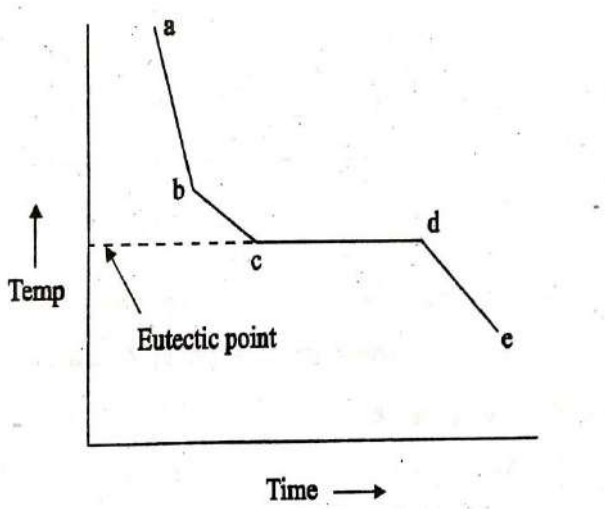
2) At initial, cooling is continuous, when it reaches the point b solid begins to appear, the temperature remains constant until the liquid completely solidified atthe point c.

3) The **hor izontal line bc** represents the equilibrium between the solid and the liquid,

4) After the point C, the temperature of the solid decr eases fr om c to d

5) The temperature cor responding to the line bc is the **melting point of the solid** or **freezing point** of the liquid.

Cooling curve for mixture of two substances



Cooling curve for mixture of two substances (A&B)

If a **mixture of two substances** (A and B) in the fused state is allowed to cool slowly, the cooling cur ve is obtained,

Initially the rate of cooling is continuous, when it reaches the point b one of the substance (either A or B) begins to solidify,

On fur ther cooling at point c, the second compound also begins to solidify.

The temperature remains constant from point c to d until the liquid melt is completelysolidified that point that horizontal line is known as **Eutectic point,**

The experiment is repeated for different compositions of mixtures and the variouscooling curves are recorded,

From the cooling curves the composition and phase diagram of system can be drawn byplotting temperature against composition.

Uses of cooling curves

1) Melting point and Eutectic temperature can be noted
2) Purity of compound is noted
3) Behaviour of compounds can be fined out
4) It is used to derive the phase diagram of any two component system.

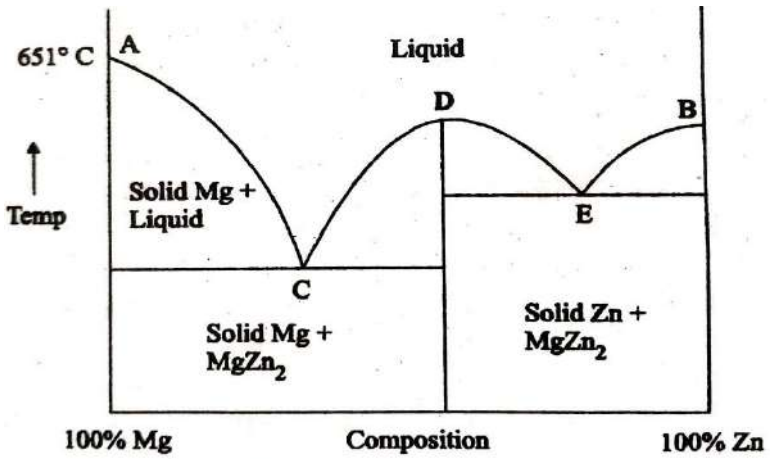
Compound forming with Congruent melting point

When two components are melted together , **at constant temperature** it has same composition that temperature **is known as congruent melting point.** On cooling, they form one or more compounds of crystals,

Ex: Zn - Mg system

1) The phase diagram of Zn - Mg is shown in figure,
2) It binary alloy system consist of two phase diagrams placed side-by-side.
    i. Left side consists of Mg - $MgZn_2$ system,
    ii. Right side consists of Zn - $MgZn_2$ system,

3) The phase diagram contains curves, Areas, Eutectic points and melting point,



Phase diagram for Zn-Mg system

Curves

1) I 'n respectively,

2) The curve AC is called as the freezing point curve of Mg caused by addition of Znto Mg, it reduces freezing point along AC,

3) At any point on AC, two phases are in equilibrium

$$\text{Solid Mg} \rightleftharpoons \text{Liquid alloy}$$

Applying reduced phase rule equation, $F' =$

$$C - P + 1$$

$$= 2 - 2 + 1$$

$\therefore C = 2$

$P = 2$

$F' = 1$ so the curve shows the system is **univariant.**

4) Similarly the curve BE shows the effect of addition of Mg on the freezing point of Zn

5) At any point on the curve BE, two phases (solid Zn + liquid alloy are inequilibrium, so the system is **univariant.**

Areas:

1) Below the line AC contains solid Mg and the liquid

2) Below the line BE contains solid Zn and the liquid

3) Below the line CDE contains solid $MgZn_2$ and the liquid

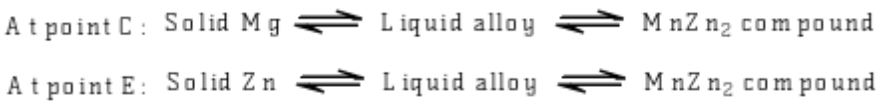
4) Below the point C and E contains solid Mg + solid $MgZn_2$ and solid Zn + solid $MgZn_2$ respectively,

5) Above the line ACDEB consists of only liquid phase.

Eutectic points

1) Zn - Mg system has two eutectic points C and E

2) At these points (C and E) three phases are in equilibrium



$F' = C - P + 1$

$= 2 - 3 + 1$

$\therefore C = 2$

$P = 3$

$F' = 0$ So these points shows the system is **invariant (or) non-varian t**

3) The eutectic temperature at point C is 345^0C and E is 400^0C.

4) Along the cur ves CD and DE, the pure compound $MgZn_2$ is present.

Melting point

1) The point D is the maximum at the cur ve CDE, called as the melting point (575^0C) of the pure compound MgZn .

2

2) At point D both the solid and liquid phases have the same composition, is called as congr uent melting point; it means, two component system becomes one component at this point,

Applying reduced phase rule equation, $F' =$

$C - P + 1$

$= 1 - 2 + 1$

$\therefore C = 1$

$P = 2$

$F' = 0$ so the point D is **non- variant.**

3) The humps in the temperature and composition phase diagram shows the presence of a compounds, the number of humps shows number of compounds for med.

Ferric chloride – water system

1) Ice and anhydrous Fe_2Cl_6 make following hydrates as solid phases in Fe_2Cl_6 - H_2Osystem.

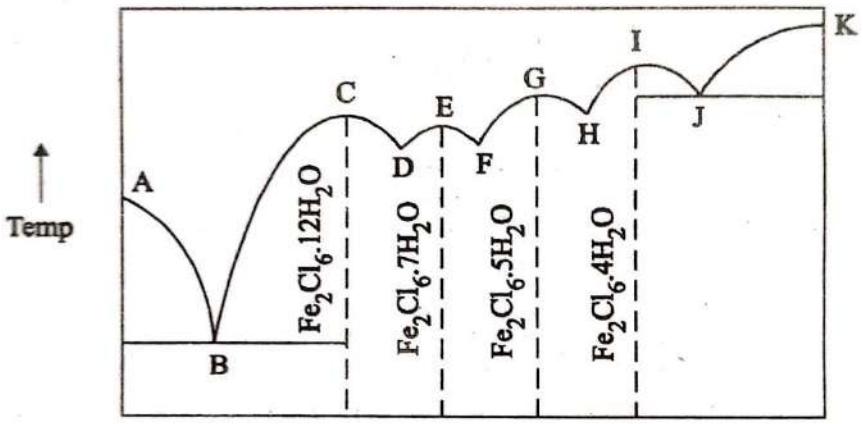
$Fe_2Cl_6.12H_2O$

$Fe_2Cl_6.7H_2O$

$Fe_2Cl_6.5H_2O$

$Fe_2Cl_6.4H_2O$

2) All the hydrates have congruent melting points, its phase diagram is given infigure.



Phase diagram for Ferric chloride - water system

3) The phase diagram contains curves, areas, eutectic points and congruent meltingpoints

Curves

1) Point A is the melting point of pure H_2O, the curve AB is called as freezing pointof H_2O obtained by addition of Fe_2Cl_6 degreases its freezing point,

2) At point B, solid $Fe_2Cl_6.12H_2O$ formed as new phase and three phases are in equilibrium called as **Cryohydric point or Eutectic point,**

$$\text{Ice} \rightleftharpoons \text{Solid } Fe_2Cl_6.12H_2O \rightleftharpoons \text{solution}$$

Applying reduced phase rule equation,

$F' = C - P + 1$

$= 2 - 3 + 1$

$\therefore C = 2$

$P = 3$

$F' = 0$ So the point B is **invariant or non- variant.**

3) Further addition of Fe_2Cl_6 to the solution and warm, the curve BC is obtainedknown as solubility curve of $Fe_2Cl_6.12H_2O$. At point C ice phase is disappears, only solid phase and solution (same composition) are exist is known as **congruent melting point** of $Fe_2Cl_6.12H_2O$ (dodecahydrate)

4) Further addition of Fe_2Cl_6, the melting point of dodecahydrate decreases until point D and another compound $Fe_2Cl_6.7H_2O$ is formed, the curve CD is called as the melting point of $Fe_2Cl_6.12H_2O$, **the point D is eutectic point** have three phases, so this point is invariant.

$$\text{Solid } Fe_2Cl_6.12H_2O \rightleftharpoons \text{Solid } Fe_2Cl_6.7H_2O \rightleftharpoons \text{solution}$$

5) On further addition of Fe_2Cl_6, $Fe_2Cl_6.12H_2O$ is disappeared and the curve DE is formed called as solubility curve of $Fe_2Cl_6.7H_2O$, **Point E is congruent melting point** of $Fe_2Cl_6.7H_2O$,

6) Further addition of Fe_2Cl_6, the melting point of $Fe_2Cl_6.7H_2O$ decreases along EF until point D is reached and another compound $Fe_2Cl_6.5H_2O$ is formed, the curve EF is called as the melting point of $Fe_2Cl_6.7H_2O$, **the point F is eutectic point** have three phases, so this point is invariant.

7) The curve FG is the solubility curve of $Fe_2Cl_6.5H_2O$ and point **G is congruent** melting point of $Fe_2Cl_6.5H_2O$

8) The curve GH is the melting point of $Fe_2Cl_6.5H_2O$ and point **H is eutectic point** and also invariant, in this point $Fe_2Cl_6.4H_2O$ hydrate is appeared,

9) The curve HI is the solubility curve of $Fe_2Cl_6.4H_2O$ and point **I is congruent** melting point of $Fe_2Cl_6.4H_2O$

10) Point **J is eutectic point** at which anhydrous Fe_2Cl_6 is formed and it is invariant

point.

11) The curve JK is the solubility curve of anhydrous Fe_2Cl_6. No other solid phase formed along this curve.

12) The number of humps indicate the number of hydrates exist as the solid state,

13) In the phase diagram, the **maximum points C,** F,G and I **are congruent points** of various Fe_2Cl_6 hydrates and **minimum points B,** D, F, H and J **are Eutectic points.**

Point	Temp-erature	Phases in equilibrium
Eutectic point B	– 55°C	Ice, $Fe_2Cl_6 \cdot 12H_2O$, solution.
Congruent melting point C	37°C	$Fe_2Cl_6 \cdot 12H_2O$, solution.
Eutectic point D	26°C	$Fe_2Cl_6 \cdot 12H_2O$, $Fe_2Cl_6 \cdot 7H_2O$, solution.
Congruent melting point E	32.5°C	$Fe_2Cl_6 \cdot 7H_2O$, solution.
Eutectic point F	30°C	$Fe_2Cl_6 \cdot 7H_2O$, $Fe_2Cl_6 \cdot 5H_2O$, solution.
Congruent melting point G	56°C	$Fe_2Cl_6 \cdot 5H_2O$, solution.
Eutectic point H	55°C	$Fe_2Cl_6 \cdot 5H_2O$, $Fe_2Cl_6 \cdot 4H_2O$, solution.
Congruent melting point I	73.5°C	$Fe_2Cl_6 \cdot 4H_2O$, solution.
Eutectic point J	66°C	$Fe_2Cl_6 \cdot 4H_2O$, anhydrous Fe_2Cl_6, solution.

Formation of compound with incongruent melting point

1) In certain system, combination of two components form compounds on decompose it by heating instead of melting congruently,

2) The temperature at which the compound decomposes to give new solid phase and a solution with different composition from the solid phase is known as **incongruent melting point.** it is also called as **peritectic (or) meritectic temperature.**

Ex:

1) Benzene – Picric acid system

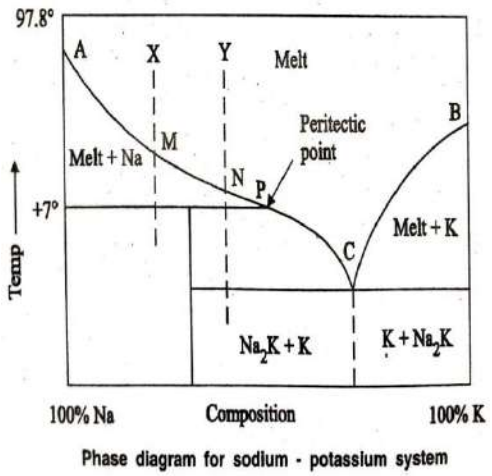
2) Sodium – Bismuth system

3) Sodium chloride – water system

4) Sodium – Potassium system

Sodium – Potassium system

1) The phase diagram of Na - K system is given below



Phase diagram for sodium - potassium system

2) Point A and B are the melting point of Na and K respectively,

3) On cur ve AP, solid Na is in equilibrium with melt (mixture of Na and K) which is a solution of K in Na

4) Similarly, along BC solid K is in equilibrium with melt which is a solution of Na in K

By continuous addition of Na toK, the compoundNa_2K is formed at point C (-12^0C) is the **eutectic point,** at this point three phases are in equilibrium.

$$\text{Solid K} \rightleftharpoons \text{Solid } Na_2K \rightleftharpoons \text{Melt}$$

Further addition of Na at point C mor e and mor e Na_2K compound is for med with disappearance of solid K, so that only two phases are remains (solid Na_2K and melt) at point C and the system become unvariant.

On adding mor e Na and heating, the cur ve CP is obtained, in this cur ve compound Na K is equilibrium with melt. Point P (7^0C) is the incongr uent melting point of Na_2K, at this temperature, the compound decomposed as the equation.

The compound NaK_2 is stable only between -12^0C and 7^0C.

PRACTICE QUESTIONS:

1. Define phase rule
2. Explain one component system
3. Discuss about Simple eutectic system
4. Evaluate the application of Phase rule
5. Draw and explain Lead -silver system

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