

Q₁(b), Q₂(b) - CFTB(II) Chemical Equilibria & Phase Equilibria.

In a closed system, equilibria between 2 or more phases is called as phase equilibria.

System :- A system is a mass of material, solid, liquid or gaseous or a combination of these 3 states, a system may be homogeneous or heterogeneous.

Homogeneous system :-

If a system contains such part which do not have different physical properties and different chemical properties, and also they are not separated from one another by bounding surfaces then such system is called homogeneous system.

If a system is uniform throughout its whole extent and have identical physical properties and chemical properties then such system is called homogeneous system.

Homogeneous system

Example :- Saturated solution of NaCl in water.

(2) Heterogeneous System

If a system contain such parts, which have different physical properties and different chemical properties & also they are separated from one another by bounding surfaces then such system is called heterogeneous system.

Example:- System having ice, water & vapour.

Important Definitions:

Phase :- 'P' Denoted by 'P'
A homogeneous part of a system which is separated from other parts by distinct boundaries.

Example:- i) Mixture of gases have phase = 1

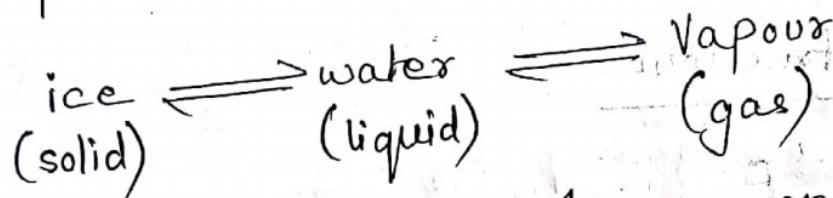
ii) freezing water contain 3 phases.

ice \rightleftharpoons water \rightleftharpoons vapour.

Component :- Denoted by 'C'

The number of component of a system at equilibrium is the smallest number of independent variable constituent by means of which the composition of each phase can be expressed either directly or in the form of a chemical equilibrium.

Example:— water system contain the equilibrium.



(solid)
The water system contains 1 component, because
composition of each of the 3 phases can be
directly expressed as H_2O .

calculation of number of components of a system

A) In chemically reactive systems, where various chemical reactions take place between species, the number of components 'C' is calculated by formula.

$$C = S - F \quad \text{--- (1)}$$

$S = \text{Number of chemical species present in the system.}$

(4)

R = Number of independent chemical reactions which various species undergo.

b) When ions are also present in system then the condition of electroneutrality modifies equation.

(1) as.

$$C = S - (R + 1) \quad \text{--- (2)}$$

3) Degree of freedom

Denoted by 'F'

The minimum number of independent variables such as pressure, temp. & composition of phase which must be specified in order to define system completely is called as degree of freedom.

$F = 0 \rightarrow$ system is invariant/non variant

$F = 1 \rightarrow$ System is monovariant

$F = 2 \rightarrow$ system is bivariant

$F = 3 \rightarrow$ system is trivariant.

Example:-

(5)

for a gaseous mixture of N_2 & H_2 we must state 'P' & 'T' because if 'P' & 'T' are fixed the volume automatically become definite, so for a gaseous system 2 factor must be stated in order to define it completely, so it has '2' degree of freedom (Bivariant system).

PHASE RULE

Phase rule was 1st introduced by J. Willard Gibbs (1876). Phase rule is useful to study heterogeneous system at equilibrium.

When the equilibrium between any number of phases is influenced only by temp., pressure & concentration but not influenced by gravity or electrical or magnetic forces or by surface action then the number of degree of freedom (F) of the system is related to the number of components (c) and number of phases (P) by following phase rule equation

$$F + P = c + 2$$

P = Number of phases.

F = degree of freedom

⑥

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$C = \text{number of components}$
 $2 \rightarrow \text{accounts for effect of temp. (T)}$
 $\& \text{ pressure (P)}$

By application of this rule a diagram called as phase diagram can be drawn with the help of which effect of pressure, temp. & concentration on the equilibrium system can be predicted.

Advantage:-

- ① Phase rule is applicable to both chemical & physical equilibria.
- ② Phase rule is applicable to macroscopic system.
- ③ Behaviour of system can be predicted under different conditions.
- ④ According to phase rule different system behave similarly if they have same degree of freedom.

⑤ Limitations / Drawback:-

- ① It consider only number of phases, rather than their amount.
- ② Phase rule is applicable only for systems which are in equilibrium. It is not of much use for those systems which attain equilibrium state very slowly.
- ③ Only 3 degree of freedom viz temp., pressure & composition are allowed to influence equilibrium system.

One Component System

⑦

Water System

In one component system with $C=1$, the maximum number of degree of freedom can be 2 because we have

$$F = C - P + 2$$

$$F = 1 - P + 2$$

$$= 3 - P$$

Since a system must have minimum one phase, therefore in such system

$$F = 3 - 1 = 2$$

hence one component system must have maximum 2 degrees of freedom. i.e. such a system above its critical temperature is fully determined by 2 variables only. The 2 variables are temperature & pressure, concentration is not a variable in it.

If 2 phases are in equilibrium. (as in the case of water in contact with its vapor)

$$\text{Then } F = 3 - 2 = 1$$

hence number of degree of freedom is 1, it means out of 2 variables, one variable either temp. or pressure is sufficient to express the system, such system is called as monovariant

(8)

3) If 3 phases are in equilibrium. (such as ice, water & vapor)

Then

$$F = 3 - 3 = 0$$

hence degree of freedom (F) is zero, it means no variable is required to express the system, such a system is called invariant or non variant

In phase diagram non variant system is represented by a point called as triple point

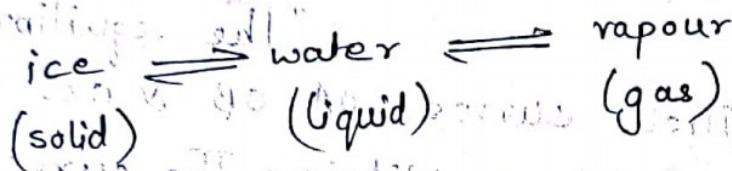
Mono variant system is represented or shown by a curve and bivariant system is represented by area.

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(g) one-component system.

It can exist in 3 states. ice, water and water

We can have 1, 2 or 3 phases present according to the conditions.



Thus the 3 form can lead to following equilibrium:

Thus the 3 form ~~can~~ ^{can't} be in equilibrium. (It is represented by area)

Solid (ice)

liquid (water)

Gas (water vapour)

Two phase equilibrium: (It is represented by curves).

② Two phase equilibrium

Solid \rightleftharpoons liquid

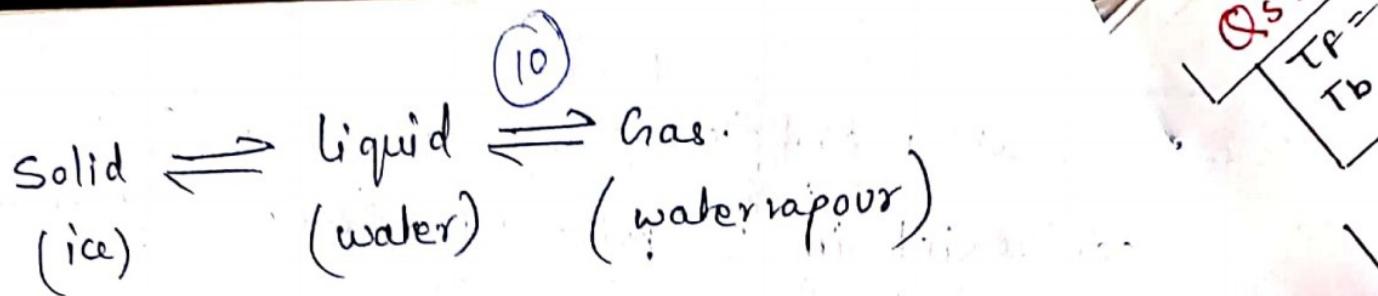
i) Solid ~~water~~
(ice)

$$\Rightarrow \text{liquid} \rightleftharpoons \text{Gas}$$

(water) (water vapour)

$$3) \text{ Solid } \xrightleftharpoons[\text{(ice)}]{} \text{ Gas.} \quad (\text{water vapour})$$

③ Three phase equilibrium. (It is represented by triple point)



The various equilibria in water system is shown in figure below (fig no. 1) which is a phase diagram obtained by plotting temp. against pressure.

The equilibria diagram contains 3 distinct curves OA, OB & OC representing the 3 univariant equilibria. The curves divide the diagram into 3 areas - AOB, BOC & AOC, in each area only one phase is present i.e. vapour, solid & liquid respectively. In any area system is bivariant.

'O' represent or shows the point where 3 curves OA, OB & OC are meeting, here all the 3 phases water, ice & water vapour are in equilibrium with one another & the system is in variant

This point is called TRIPLE POINT)

Qs 1(b)

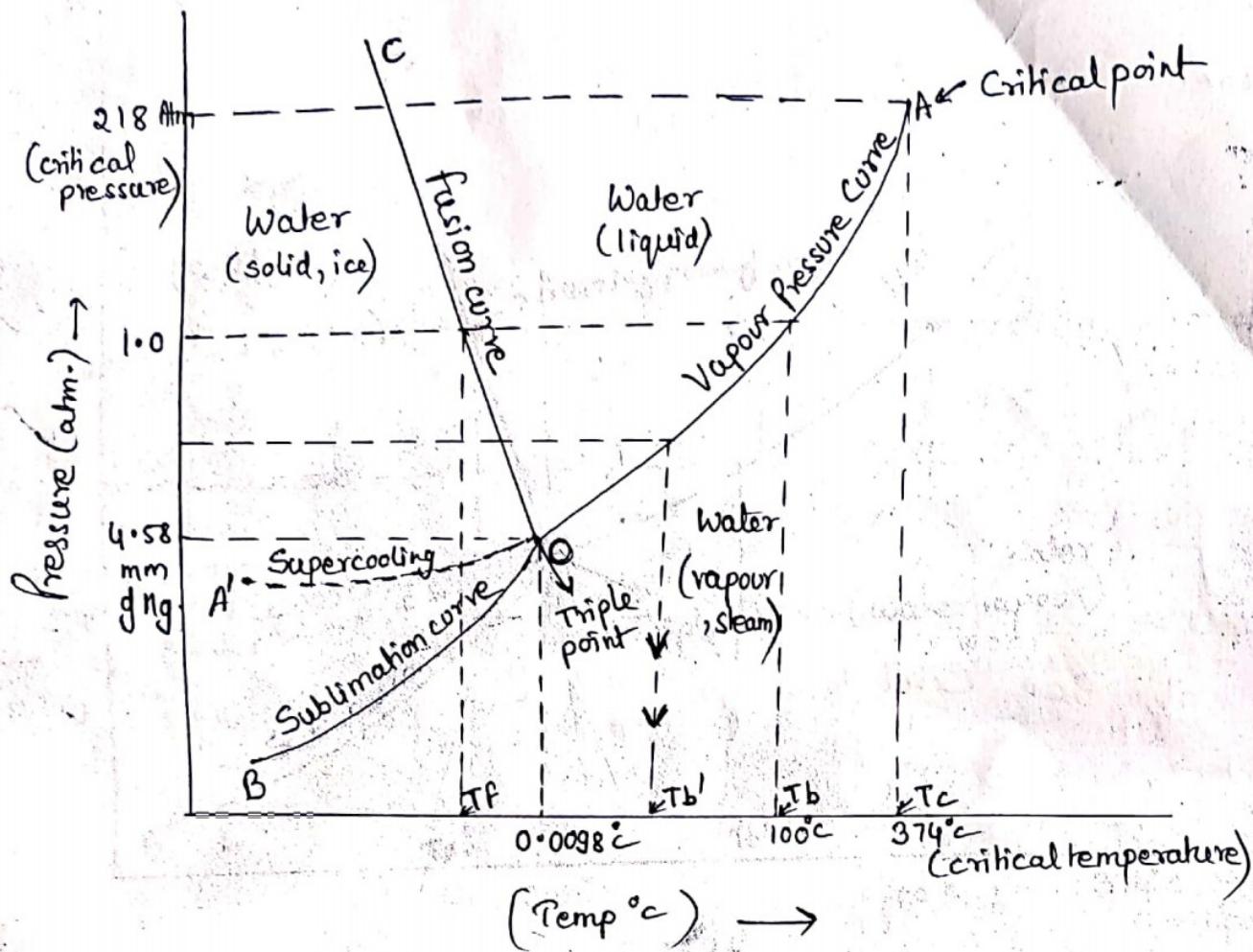
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T_f = Freezing point
 T_b = Boiling point

T_c = Critical temp.

T_b' = Boiling point of water decreases because external pressure is less at Mountain



Study of Area

There are 3 areas AOB , AOC & BOC , each area contains only one phase (one phase equilibria).

$AOB \rightarrow$ Area below AOB curve shows vapour phase.

$BOC \rightarrow$ Area on left of the curve BOC shows solid phase (ice)

$AOC \rightarrow$ Area on right of the curve AOC shows liquid phase (water)

② In these single phase areas, system is
Bivariant & Temp., & Pressure must be specified to define state of system

Here $P = 1$

$$F = C - P + 2$$

$$= 1 - 1 + 2 = 2$$

Study of Curves

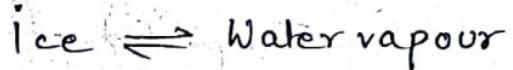
$$\begin{aligned} F + P &= C + 2 \\ F + 2 &= 1 + 2 \\ F + 2 &= 3 \end{aligned}$$

$$\rightarrow P = 3 - 2 = 1$$

for curve degree of freedom = 1 (monovariant)

Curve OB \Rightarrow (Sublimation curve / Sublimation line)

The curve OB, shows the sublimation curve of ice, Above OB only ice exists and below OB only water vapour exists. Along curve OB both ice & water vapour exist in equilibrium.



Curve OA :— (Vapour pressure curve) / steam line curve

The curve OA represents or shows the vapour pressure curve of water. Above this OA only liquid water exists and below this curve OA only water vapour exists.

Along curve OA liquid water and water vapour are in equilibrium. Curve OA is also known as steam line or Vaporization curve.

The point 'A' is also known as critical temperature (374°C) , If we increase.

ed to temperature beyond this value i.e 374°C then existing water phase convert to vapour phase. After this temperature we get only one phase i.e vapour phase, the pressure value at this temperature is called critical pressure (218 Atm.)

We can use the curve.

The curve OC shows how the boiling temperature varies with changing external pressure.

Curve OC

The curve OC is called as freezing point curve or fusion curve or melting point curve of ice. The curve OC separates solid ice from liquid water. The curve OC shows the effect of pressure on the melting point of ice. As the curve OC slopes to left, it is clear that melting point of ice decreases as the pressure increases.

Along curve OC

ice (solid) & liquid water are in equilibrium. The reason:

or this uncommon behavior is a decrease in volume. Ice has open crystal structure, in which the water molecules are held apart by hydrogen bonds between them. This open cage structure collapse on melting &

④ liquid is denser than solid. (14)

When pressure is increased it is favourable for ice (solid) to transform into the denser liquid.

Curve OA' (supercooling curve)

Dotted line OA' is extension of OA and it represents liquid water and water vapour phase in metastable equilibrium. Dotted line are used in phase diagrams to indicate less stable equilibria. These are known as metastable equilibria.

Explanation: It is sometimes possible to cool liquid water below the point 'O' without solidification as shown by dotted curve OA'. The liquid below the freezing point is in the supercooled state, which is not quite stable & is called as metastable state.

Along OA'

curve liquid water & vapour are in equilibrium; it is called metastable equilibrium, because as soon as a small particle of ice is brought in contact with supercooled liquid, the entire liquid solidifies.

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of points:-

At point 'O' solid, liquid & water vapour are in equilibrium with each other. A point at which 3 phases are in equilibrium is called as triple point.

Calculation of degree of freedom at triple point in one component system when 3 phases (solid, liquid, gas) are in equilibrium Here $P = 3$

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 3 + 2 \\ &= 0 \end{aligned}$$

It means that at a triple point the system is invariant/non variant (no degrees of freedom), both pressure & temp. are automatically fixed.

for water system, the triple point corresponds to a pressure of 4.58 mm Hg & temp. of 0.0098°C or 273.16 K

Liquid-Solid phase diagram

Phase rule for two component system
(condensed phase Rule)

for 2 component system

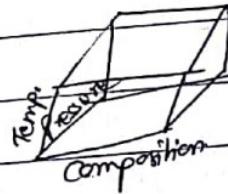
$c = 2$, so phase rule equation becomes-

$$F + P = C + 2$$

$$F + P = 2 + 2$$

$$F + P = 4$$

$$F = 4 - P$$



A sys. atleast has one phase always.

$$\text{Thus } P = 1$$

$$P = 4 - 1 = 3$$

It means 3 variables, T, P & composition must be specified in order to define system completely, so phase dig. of binary system can be or may be represented by 3 dimensional dig. of P, T & composition

Let consider an alloy in which Solid \rightleftharpoons Liquid. In above sys. no gas phase is there, such system in which vapour phase is not considered and pressure is kept constant is known as condensed system. As pressure is constant, it will reduce the degree of freedom of system by one. Thus Reduced phase rule equation is applicable for such system.

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$$F + P = C + 1$$

$F = C - P + 1 \rightarrow$ Condensed phase Rule.

Reduced phase rule for 2 component system

$$C = 2$$

$$F + P = C + 1$$

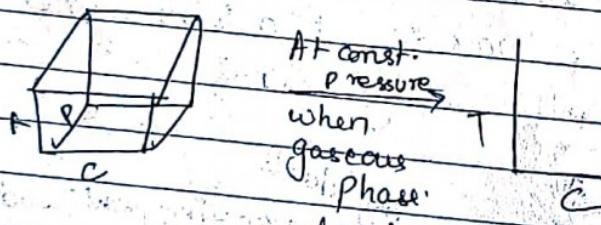
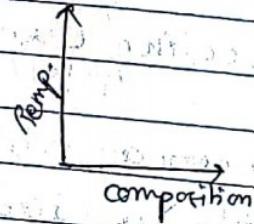
$$F + P = 2 + 1$$

$$P = 3 - P$$

$$F = 3 - 1 = 2$$

{when $P = 1$ }

Thus 2 variables temp. & composition of constituents are there.



At const. pressure

when gaseous

Phase absent

{ $T = \text{temp.}$, $P = \text{pressure}$, $C = \text{composition}$ }

For solid-liquid equilibria are represented on temp. — composition diagrams.

For Solid \rightleftharpoons liquid equilibria.

for making phase diagrams, it is necessary to find out the composition of the mixture at different temperatures.

This is done by thermal analysis.

Thermal analysis is basically study of cooling curves of various (compounds) compositions of a system during solidification.

for any mixture of definite composition

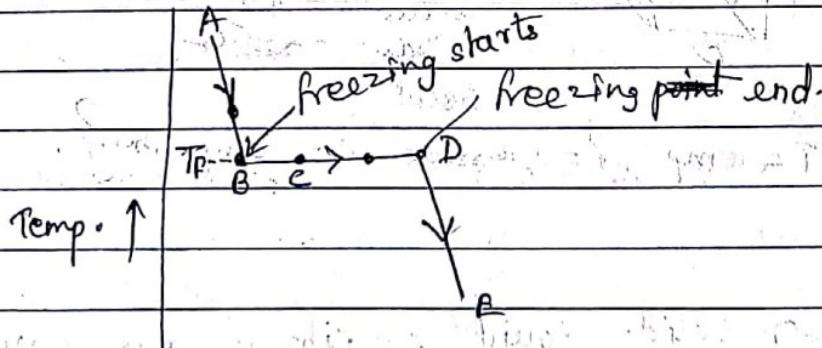
it is possible to find following from the cooling curves.

- a) freezing point b) Eutectic point

Cooling Curves :-

(I)

When a pure substance in the molten state is allowed to cool at a slow rate & temp. is noted at definite times, then we get cooling curve



Cooling curve of pure substance.

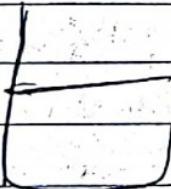
At point A pure substance is in molten state, falling in temp. is continuous

(Part AB of curve).

At freezing point (T_f)

The temp. become constant (β). The temp. remain constant at freezing point. The constancy of temp. continue till 'D' (further liquid)

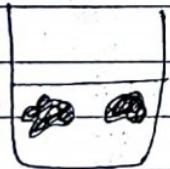
until the liquid is completely solidified. further temp. falls. (DB curve) and it become continuous which indicate a hot solid cools down till its temp. is equal to room temp.



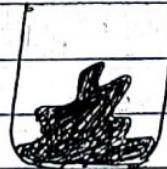
A. Pure substance
in molten state



B. Nucleation of crystals.
in the melt.

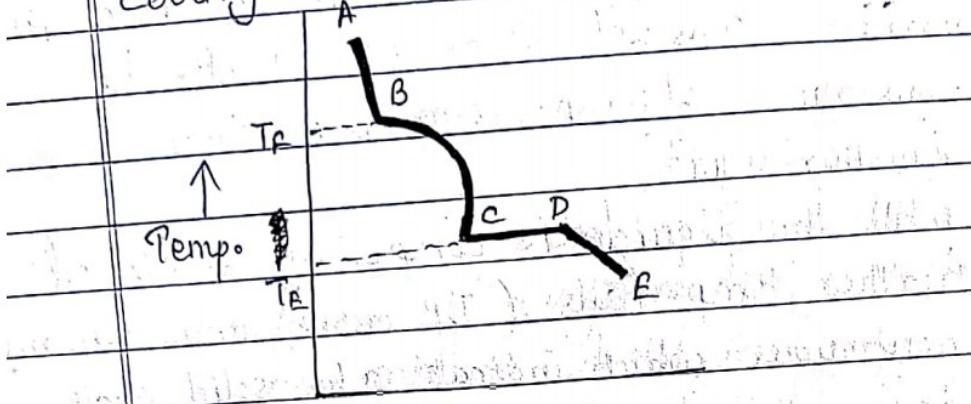


C. Growth of
crystals in the melt



D. crystallization and
solidification is complete

II) When a mixture of two solids in the molten state is allowed to cool slowly, a continuous cooling curve is obtained:



Cooling curve of molten mixture of two solids.

- Initially (part AB) $\alpha = \infty$, when solid phase starts to form, the rate of cooling changes and cooling curve (AB) exhibit a break at point 'B'.

In part BC temp. changes continuously at a different rate, fall in temp. continue till point 'C' which is eutectic point (T_E) (Minimum freezing point attained by eutectic mixture)

further temp. remain constant, i.e. until solidification is complete and point 'D' is reached.

In part CD crystallization of eutectic mixture occurs, & further fall in temp. become uniform (part DE)

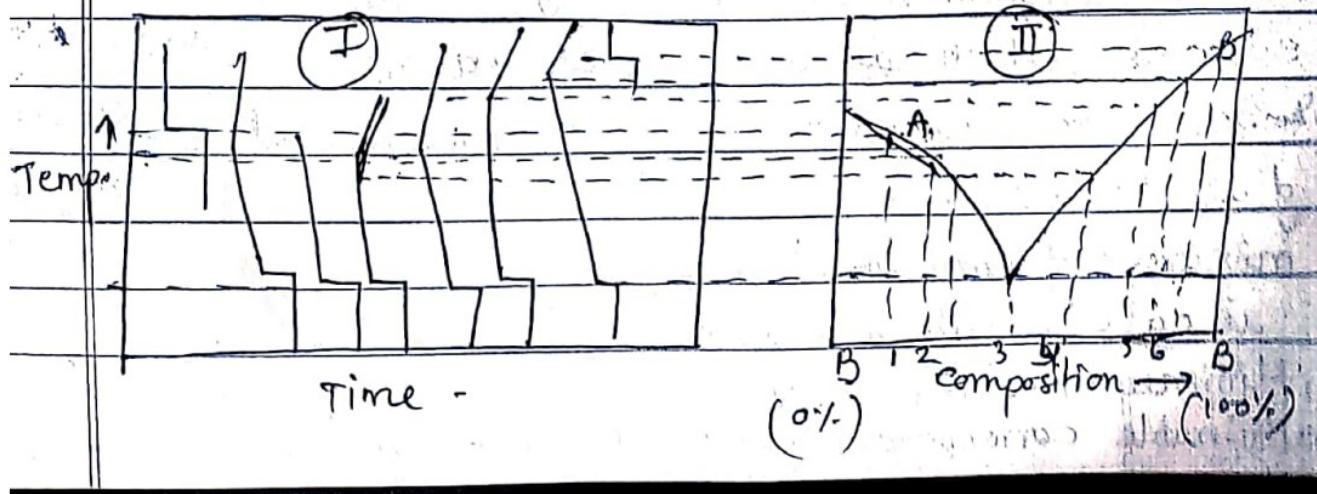
* Freezing point are different for different compositions of system but, eutectic points are same for a given system.

* When portion BC is shorter and halt CD is larger, it means composition of system is near to eutectic

* When curve show no break corresponding to BC & halt appears only at eutectic point it means that the mixture coincides with the eutectic composition.

For 2 component system, thermal analysis procedure is used to obtain phase diagram. The cooling curve of a series of alloys of known composition are drawn and these freezing points are noted.

Now freezing points are plotted against composition to obtain phase diagram (to complete dig, freezing point of pure component is also required)



- (I) Cooling curve for different compositions
 (II) phase diagram in a 2 component system forming a eutectic

Classification of 2 component Solid-Liquid Equilibria

Two component system

component chemically react with each other

No

Eutectic Mixture

Solid solution of such two component systems, which has the lowest freezing point of all the possible mixtures of component is called eutectic mixture

Yes.

Stable

compound formation

congruent

melting compound

Unstable

compound formation

Incongruent

Melting compound

Minimum freezing point attainable corresponding to eutectic mixture \rightarrow eutectic point

Date: / / 20

Congruent Melting compound: → A compound which melts at a constant temp. to give a liquid having same composition as that of solid compound; then that compound is said to have congruent melting point.

In 2 component system, if (Binary alloy) it is seen that components undergo chemical combination in stoichiometric ratio & form one or more compounds which melt at particular temp. without changing composition. Such compounds are called compound having congruent melting point.

Example: —

Mg-Zn system

Mg-Al

Incongruent Melting compound →

Compound which decompose below its M.P. to give a new solid phase and a melt with a composition different from that of compound is called incongruent then that compound is said to have incongruent M.P.

In 2 component system.

The 2 components undergo chemical.

combination to form a new compound which is unstable such compound decompose below its M.P & give new solid phase & a melt with composition different from that of compound.

The temp. at which decomposition occurs is called: Peritectic / Meritectic or Transition temp.

Eg :—

Na-Bi system

Na-K

Eutectic System

A binary system in which 2 components are miscible in all proportion in the liquid (molten) state, they do not react chemically and each component has the property of lowering each other's freezing point, such binary system is called eutectic system (easy to melt sys.)

Eutectic mixture.

has definite composition and sharp melting point, it melts giving a liquid of same composition. Eutectic mixture is not a compound because components are not present in stoichiometric proportions.

Physical.

properties such as density & heat of solution of eutectic solid were almost equal to the mean values of the constituent, hence eutectic mixture is not a chemical compound.

Application of eutectic system:-

- 1) Eutectic system because of there Low M.P are also used for joining 2 metal pieces together.
- 2) Eutectic alloys of Na & K are liquid at

room temp. & are used as coolant
in experimental fast neutron nuclear
reactors.

Copper Silver system

• Copper & silver are both metals.

• Both are good conductors of heat.

• Both are good conductors of electricity.

• Both are good materials for making wires.

• Both are good materials for making coins.

• Both are good materials for making jewelry.

• Both are good materials for making ornaments.

• Both are good materials for making utensils.

• Both are good materials for making pipes.

• Both are good materials for making containers.

• Both are good materials for making buildings.

• Both are good materials for making roads.

• Both are good materials for making bridges.

• Both are good materials for making ships.

• Both are good materials for making aircrafts.

• Both are good materials for making vehicles.

• Both are good materials for making electronic components.

• Both are good materials for making batteries.

• Both are good materials for making cables.

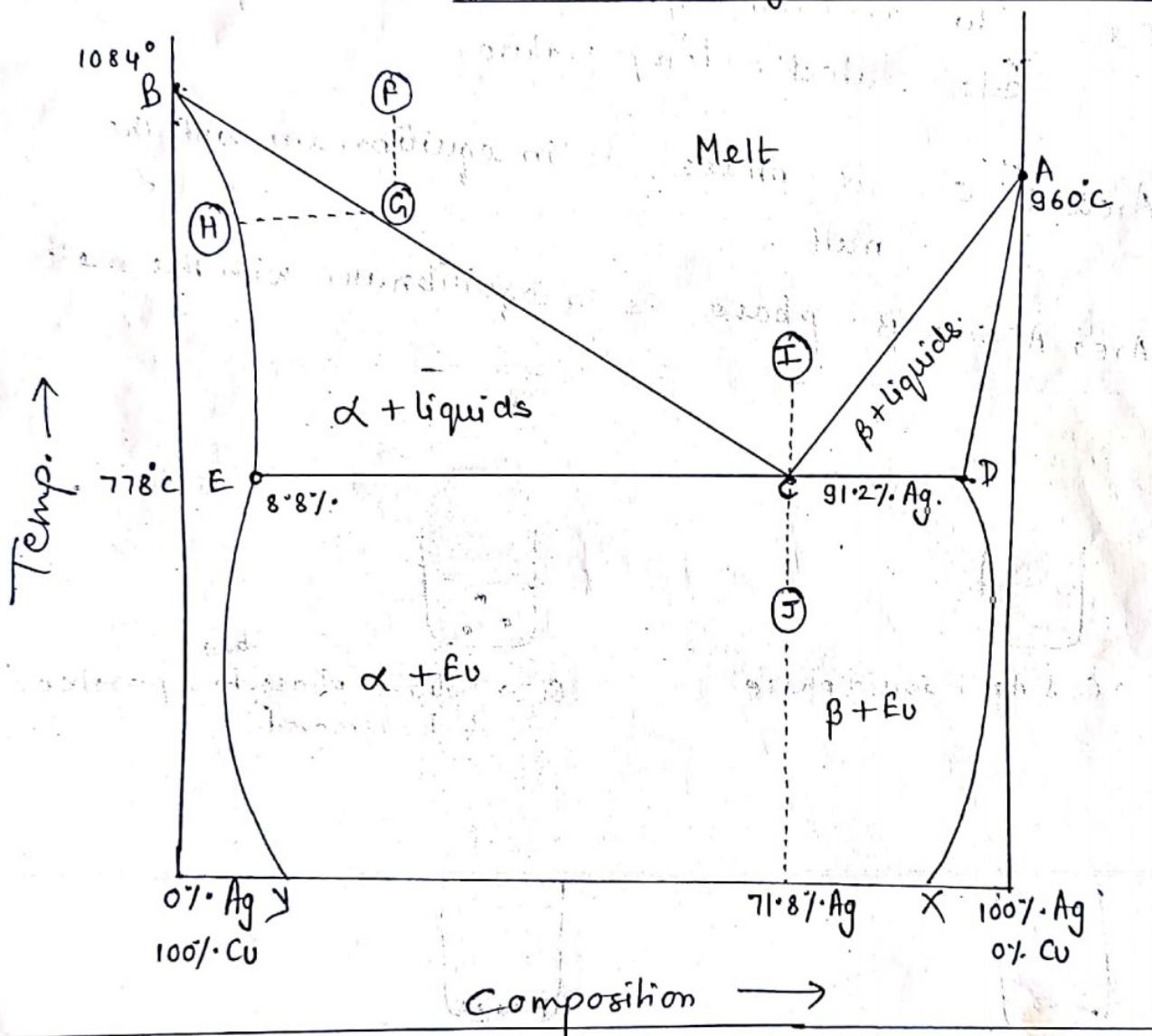
• Both are good materials for making wires.

COPPER - SILVER SYSTEM

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Copper Silver (Cu-Ag) System. are completely miscible in the molten state. In solid solution they are partly miscible.

phase diagram of Copper (Cu)-Silver(Ag) system



- Point A → Melting point of silver (Ag) (960°C)
 Point B → Melting point of copper (Cu, 1084°C)
 Point C → Eutectic point of Cu-Ag system (778°C & 8.8% Ag)
 AC = Depression in freezing point of silver on addition of copper along AC
 BC = Depression in freezing point of copper on addition of silver along BC
 AD = Composition of β -phase of a solid solution of copper in silver

(28) BE = The composition of the α -phase of a copper rich solid phase of silver.

DX = The variation of β -phase with temperature below eutectic temperature

EY = The variation of α -phase with temperature below eutectic temperature.

Area BEC = α -phase is in equilibrium with the melt

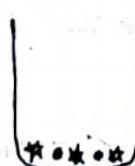
Area ADC = β -phase is in equilibrium with the melt



F \rightarrow Cu & Ag in liquid phase



G \rightarrow Solid α -phase begin to separate out & is removed.



I \rightarrow Melt continues to be richer and richer in silver till Eutectic point (c) is reached. J \rightarrow separate crystals of eutectic mixture are seen when molten eutectic mixture of composition 'C' is cooled.

(29)

Explanation of Phase diagram :-

(29)

When silver (Ag) is added to copper, then freezing point of copper reduces (\downarrow) along BC, and copper-rich solid phase of silver called α phase, separate out from the melt (Mixed Cu & Ag). $\xrightarrow{\text{liquid}}$

- ② When melt of overall composition 'F' is slowly cooled, then at point 'G' (α -phase solid) & phase (solid) separate out having composition given by 'H', the melt will be rich in silver (Ag); on cooling further composition of liquid proceed along GC till point 'C' is reached.
- ③ When Copper (Cu) is added to silver (Ag), then freezing point of silver reduce (decrease) along AC.
- ④ At point 'C' the liquidus AC & BC meet & 3 phases (α , β & liquid phases) exist in equilibrium.
Thus $P = 3$ (P=Phases)
- By applying Reduced phase rule equation for 2 component ($C=2$) copper-silver system.

Reduced phase rule $\rightarrow F + P = C + 1$

$$F + 3 = 2 + 1$$

$$F = 0$$

Point 'C' is the eutectic point of Cu-Ag system.
(eutectic point \rightarrow Minimum freezing point attainable corresponding to eutectic mixture.)

The composition of eutectic mixture is 71.8% Ag

28.2% Cu, & the eutectic temp. (at 'c') is $778^\circ C$.

Below point 'c' only solid phase exist. At $778^\circ C$ i.e. at eutectic point 'c', eutectic mixture of Cu & Ag melt or solidify sharply like a pure metal.

- ⑥ A melt (Cu & Ag mix) of composition less than 71.8% Silver on cooling below $778^\circ C$ (temp. at eutectic point 'c') give a heterogeneous mixture of α -phase and eutectic. EY represent or show the variation of composition of α -phase with temperature below eutectic temperature.
- ⑦ A melt of composition higher than 71.8% Silver (Ag) on cooling below $778^\circ C$ give a heterogeneous mixture of β phase with eutectic, DX show variation in composition of β -phase with temp. below $778^\circ C$

30°