

* Introduction

A substance can exist in various states. e.g.: water can exist in three states i.e. solid, liquid or vapour. Each state is referred to as phase.

A change in state of a substance is called phase transition.

* PHASE

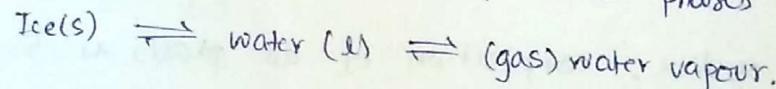
A phase is a homogeneous physically distinct and mechanically separable part of a system which is separated by other parts of system by definite boundaries.

OR

i) phase is a state of matter, uniform throughout, not only in chemical composition but also in physical state.

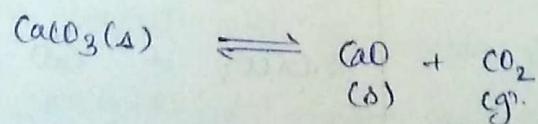
* A system consisting of one phase is called homogeneous system, otherwise heterogeneous system.

* examples : At freezing pt., water consists of three phases

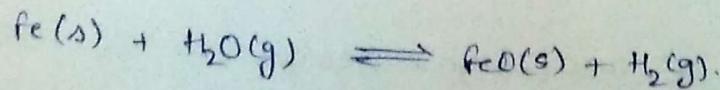


ii) A gaseous mixture, uniform throughout consisting of miscible gases forms one phase only.

iii) If two liquids are miscible (alcohol & water), it forms one phase.
 iv) If two liquids are immiscible (benzene & water), it forms two separate phases.
 v) A solution of substance in solvent, consists of one phase only.
 vi) When CaCO_3 is heated in closed vessel, it decomposes to CO_2 & CaO .



vii) It consists of two solid phases & one gaseous phase. It's a three phase sys



It consists of two solid phases and a gaseous phase (H_2O & H_2).
 3-phase system.

- viii) A homogeneous solution of salt is a single phase system.
e.g. Mohr's salt solution.
- ix) Saturated solution of water and sugar is a two phase system
(Sugar + water) solution & sugar settled at bottom)
- x) A mixture of two allotropes is a two-phase system.

* Components.

The no. of components (C) of a system is the smallest no. of independently variable constituents at equilibrium, by means of which composition of each phase can be expressed either directly or in form of chemical equation.

NOTE : The no. of components of a system is not the same as no. of constituents or chemical entities present in system.

* examples :

i) In water system, $\text{Ice(s)} \rightleftharpoons \text{water(l)} \rightleftharpoons \text{gas(water vapour)}$.

The composition of each phase is H_2O . One-component system.

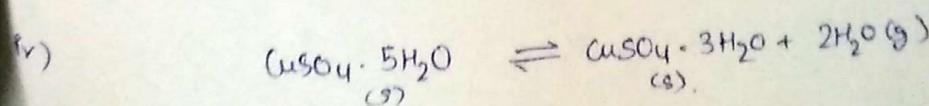
ii) In sulphur system, composition of all phases is S. One-component sys.

iii) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. (3 phase-system).

composition of each of three phase can be expressed in terms of any two constituents. So, a two component system.

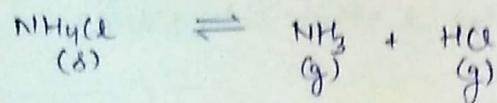
If CaCO_3 and CaO are constituents,

| Phase | Composition. |
|-----------------|---------------------------------|
| CaCO_3 | $\text{CaCO}_3 + 0.6\text{CaO}$ |
| CaO | $0.4\text{CaCO}_3 + \text{CaO}$ |
| CO_2 | $\text{CaCO}_3 - \text{CaO}$ |



Knowing components, CuSO_4 & H_2O , composition of each phase can be determined.
i.e. 2-component system.

vi) In dissociation of Ammonium chloride in vacuum, eqm occurs as:

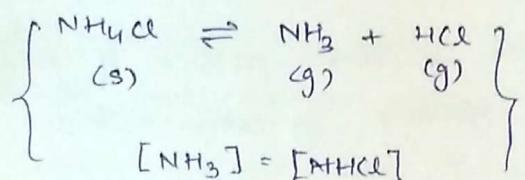


It is a two phase system consisting of a solid phase NH_4Cl and a gaseous mixture of NH_3 , HCl and NH_4Cl . \therefore NH_3 and HCl are formed in fixed stoichiometric proportions and also, composition of each phase is NH_4Cl .
c. It is a one-component system. If either of HCl or NH_3 would be in excess, system becomes two component system.

* No. of components of a system may alternatively be defined as no. of chemical constituents of system minus the no. of equations relating these constituents in eqm. state.

$$\text{i.e. } C = S - R.$$

For above eg: $R=2$ and $S=3$: relations are :



$$\therefore C = 3 - 2 = 1.$$

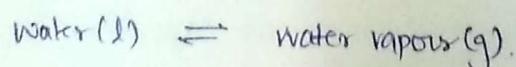
* degree of freedom or variance :

The degree of freedom is the minimum no. of independently variable factors, like Temp, pressure, conc., which must be specified to represent condition of a system.

i) For water system, $\text{Ice}(s) \rightleftharpoons \text{water}(l) \rightleftharpoons \text{water vapour}(g)$.

It occurs at a particular temp. and pressure and is invariant, zero variant or non-variant or zero no. degree of freedom.

ii) When water is in contact with its vapour,



So, either pressure or Temp. is to be specified \therefore univariant.

iii) $\text{NaCl}(s) \rightleftharpoons \text{NaCl}(aq) \rightleftharpoons \text{water vapour}(g)$. (saturated)

either pressure or Temp. is to be specified (so that saturation solubility is fixed) \therefore univariant.

- iv) For system consisting of water vapours only, both T and P are needed to be specified \therefore Bivariant system.
- v) For pure gas, $f=2$ because when we specify P & T - V is fixed automatically \therefore Bivariant system.

* Derivation of phase rule

Consider a heterogeneous system of 'P' phases and 'C' components. Degree of freedom is equal to total no. of independent variables minus the no. of relationships existing between them since, each relation diminishes the no. of independent variables by one.

So, total no. of independent variables :

i) Temperature : At eqm, there is same temp. of all phases \therefore there is only one temp. variable for entire system.

ii) Pressure : At eqm, there is same pressure of every phase \therefore there is only one pressure variable for entire system.

iii) Concentration : Generally, concentration of each component is expressed in terms of mole fraction. Suppose, if there are two components A & B in one phase, if composition or conc. of A is known (say 0.4) then, B has conc = $1 - 0.4 = 0.6$. So, there are $(C-1)$ composition variables for each phase.

for 'P' phases, there are $P(C-1)$ composition variables.

$$\therefore \text{Total no. of independent variables} = 1 + 1 + P(C-1) \\ = P(C-1) + 2.$$

Now, total no. of relationships is to be calculated.

The chemical potential (μ) of a particular component should be same in all phases in which it appears. For one component in two phases, $\mu(A) = \mu(B)$

for one component in three phases, $\mu(A) = \mu(B) \quad \left. \right\} \\ \mu(B) = \mu(C)$

\therefore for each component in 'P' phases, no. of relations = $P-1$
for C components in 'P' phases, no. of relations = $C(P-1)$

\therefore degree of freedom (F) = total no. of independent variables
- no. of relations

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

$$\boxed{F = C-P+2} \longrightarrow \text{phase rule.}$$

* Advantages (Merits) of Phase rule:

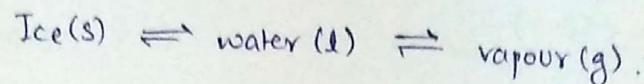
- i) it is applicable to both physical & chemical equilibria.
- ii) it requires no info. regarding molecular structure as it can also be applied to macroscopic systems.
- iii) convenient method to classify equilibrium states into no. of phases, components and degree of freedom.
- iv) it indicates that different systems having same degree of freedom behave in a like manner.
- v) it helps to predict behaviour of system when allowed to changes in variables such as temp, pressure, conc. etc.
- vi) it predicts that under a given sets of condition,
 - * whether various substances would exist together in eqm.
 - * whether some of them would be interconverted.
 - * whether some of them would disappear.

* Limitations of phase rule:

- i) it is applied to systems in eqm. So, systems slow in reaching state of eqm are not convenient for its application.
- ii) it is applied to a single equilibrium \therefore provides no information regarding any other eqm in system.
- iii) it requires utmost care in deciding the no. of phases, \because it considers only no. of phases, not their concentration. So, that, a trace of a phase also accounts for the no. of phases.
- iv) it conditions all phases must be present simultaneously under identical conditions of temp. and pressure.
- v) it conditions that both solid and liquid phases must not be in finely divided state \rightarrow otherwise deviation will occur.

* WATER SYSTEM.

The water system consists of three phases viz. ice, water and vapour.

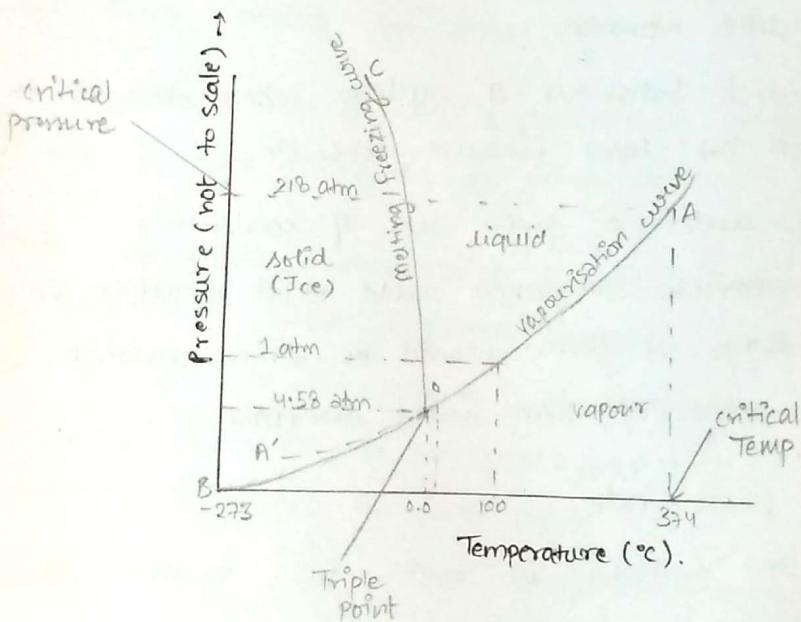


Since, H_2O is only compound involved, it is single or one-component system. From phase rule, $C=1$

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

- (i) for $P=1 \therefore F=2$ (Bivariant)
- (ii) for $P=2 \therefore F=1$ (univariant)
- (iii) for $P=3 \therefore F=0$ (invariant)

The water system is shown in following fig:

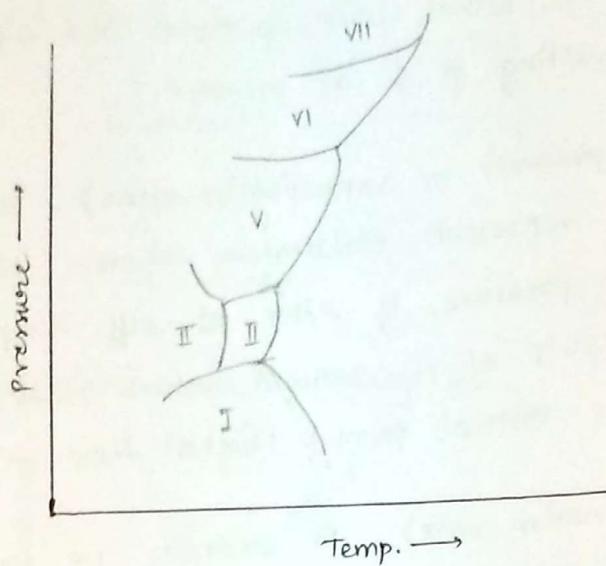


- i) Areas: Area BDC , AOC and AOB represents the field of existence of ice, liquid and vapour phase respectively. These are single-phase areas, system is bivariant because to locate any point in the area, both temp. and pressure coordinate are needed to be fixed. e.g. suppose Temp. be -100K , then it will correspond to more than one point in that area & hence does not define the system completely & \therefore Temp. should also be fixed. It also follows from phase rule eqn: $F = 3 - P = 3 - 1 = 2$.

- ii) Boundary lines : Separating these areas are curves OA, OB and OC. To locate any point on the curve, either temp. or pressure is needed to be fixed because other one gets automatically fixed. $\therefore f=1$. It also follows from phase rule eqn : $f = 3 - P = 3 - 2 = 1$.
- a) curve OC (melting / freezing curve) : It represents the equilibrium between ice and water and separates ice from water region. It represents how melting point of ice varies with pressure. The slope of OC from pressure axis shows that melting pt. \downarrow as pressure \uparrow .
- b) curve OA (vapour pressure or vaporisation curve) : It separates water from vapour region and represents equilibrium between water and vapour phase. It represents vapour pressure of water at diff. temp. The curve has an upper limit of 374°C at A, beyond which water and vapour merges & are indistinguishable (critical point) (highest temp. at which water exists).
- c) curve OB (sublimation curve) : It separates ice from vapour region & represents equilibrium between the two. The point B has lower limit of -273 K beyond which two phases gets merged. The curve shows vapour pressure of solid ice at diff. temp.
- iii) Triple point : The point O, at which curves OA, OB and OC meets and all three phases co-exists simultaneously is called triple point. It occurs at 273.16 K or 0.00980c and 4.58 mm of Hg pressure. System is invariant ($f=0$) and neither of pressure or temp. can be altered.
- iv) Metastable state OA' : It is continuation of curve OA and represents vapour pressure of super cooled water. As water does not freeze at 0°C , so if vessel containing water & vapour is free from dust and perfectly clean, then it is possible to supercool water. This curve represents metastable system.

NOTE : SUPERCOOLING : process of lowering temp. of liquid below its freezing pt, without causing it to become a solid.

* Polymorphism: The phenomenon in which a substance could exist in two or more crystalline forms, possessing diff. phys. or chemical properties. It was observed that at high pressure (5×10^3 atm), besides ice, water can exist in six other forms. These have different density and other physical properties. Each of these forms a separate phase. The phase diagram is: (Ice I - VII).



- * Regions I, II, III, IV, VI, VII shows stability of respective ice in these regions.
- * Except ice II, all other ice can coexist with water.
- * Melting point of ordinary ice is lowered with ↑ in pressure, to about -22°C at pressure of 2040 atm. further, pressure ↑ results in transformation of Ice I to VII, whose melting pt. is increased by ↑ in pressure.
- * It is possible to other triple points also. At these points, other three phases can coexist (a) three forms of ice (b) two forms of ice & water.
- * Not more than three phases can exist in eqm because if $P=4$ (sat), $f = 3-4 = -1$ (not meaningful).
- * At high pressure, melting pt. of ice is considerably raised & Ice VII melts at 190°C at pressure of 40,000 atm.

THE SULPHUR SYSTEM

* THE SURFACE one-component, four phase system. The four phases are:

- i) rhombic sulphur, S_R
 ii) Monoclinic sulphur, S_m
 iii) Liquid sulphur, S_L
 iv) vapour sulphur, S_v .

Since, four phases can be represented by single chemical entity 'S' ::
it is a one-component system.

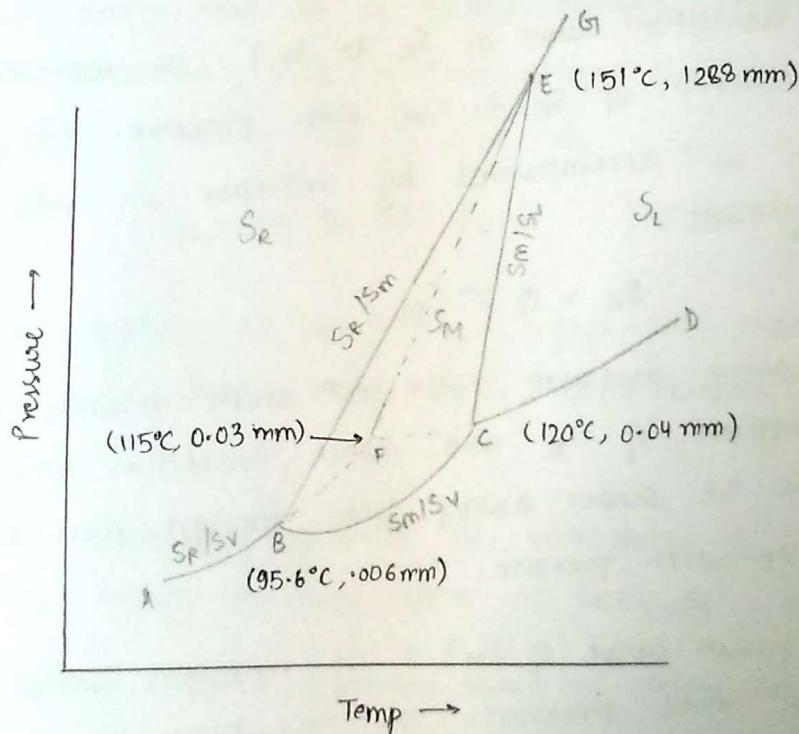
$$\text{By phase rule, } F = C - P + 2 = 3 - P$$

$$p=1 \quad F = 2 \quad (\text{Bivariant})$$

$$P = 2 \quad F = 1 \quad (\text{cunivariant})$$

$$P=3 \quad f=0 \quad (\text{nonvariant})$$

\therefore if cannot be -ve \therefore not more than three phases can coexist in eqm.

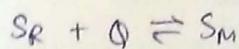


The diagram consists of :

- i) Areas: The diagram is divided into four areas i.e. ABEG, ABCD, DCFG & BCE which represents phases S_p , S_v , S_l and S_m respectively. In these single phase areas, system is bivariant, because to locate any point in these areas, both Temp. and pressure are needed to be specified. It also follows phase rule: $P=1 \Rightarrow F = 3-1=2$.

2) Curves : There are six stable curves AB, BE, BC, CD, CE and EG. representing equilibrium between two phases. These curves are univariant because one of the variable is needed to be fixed and other gets fixed automatically. It also follows from phase rule : $f = 3 - p = 3 - 2 = 1$

- Curve AB (vapour pressure curve of S_R) : It represents vapour pressure of S_R at diff. temperatures. S_R is stable upto point B ($95.6^\circ C$), above which it gets converted into monoclinic sulphur. The curve ends at A ($50^\circ C$) because below it, vapour pressure of S_R is unmeasurable. ($S_R \rightleftharpoons S_v$)
- Curve BC (vapour pressure curve of S_M) : It shows variation of vapour pressure of S_M with temp. and monoclinic sulphur is stable upto C ($120^\circ C, 0.04 \text{ mm}$). ($S_M \rightleftharpoons S_v$)
- Curve CD (vapour pressure curve of liquid sulphur) : It shows variation of vapour pressure of S_L with temp. ($S_L \rightleftharpoons S_v$)
- Curve BE (transition curve of S_R to S_M) : It represents variation of transition temp. of S_R to S_M with pressure. ($S_R \rightleftharpoons S_M$). The transformation is accompanied by increase in volume and absorption of heat.



So, on increasing pressure, the eqⁿ shifts towards left side, causing ease of formation of S_R and hence transition temp. also \uparrow . That is why line BE slopes away from pressure axis showing \uparrow in transition temp. with pressure.

- Curve CE (fusion curve of S_M) : It represents variation of melting point of S_M with pressure. S_M has higher density than S_v and increase in pressure results in \uparrow in melting pt. (acc. to Le Chatelier principle). The curve at E gets terminated because monoclinic sulphur ceases to exist beyond it. ($S_M \rightleftharpoons S_L$)
- Curve EG (fusion curve of S_R) : ($S_R \rightleftharpoons S_L$) It represents melting curve of S_R .

* Triple points

There are three stable triple points i.e. B, C and D. At those triple points, system is non-variant because even slight variation in any of variables will cause atleast one phase to disappear. It also follows from phase rule.

$$P = 3 \Rightarrow f = 3 - P = 0.$$

- i) Triple point B: S_R , S_m and S_v coexists at this point. The curve AB, BC & PC meets at this point. At B, S_R changes to S_m and process is reversible (95.6°C , 0.006 mm).
- ii) Triple point C: S_m , S_l and S_v coexist at this point. The curve BC, EC & CB meets at this point. At C, S_m gets melted (120°C).
- iii) Triple point D: S_R , S_m and S_l coexist at this point.

+ Metastable equilibrium.

The transformation of S_R to S_m is a slow process. If enough time is not given for this change and S_R is heated rapidly, then it is possible to pass well above transition point without getting S_m . So, in this case, there exists only three phases: S_R , S_l and S_v .

$$S_R \rightleftharpoons S_l \rightleftharpoons S_v. \quad \} \text{metastable equilibrium}$$

In such case, phase diagram of sulphur is just like that of water consisting of three areas (AFE, DFE & AFD), three curves (BF, CE, EF) & a one triple point.

- * Dashed curve BF: It represents variation of metastable S_R 's vapour pressure. It is continuation of vapour pressure curve of stable S_R . ($S_R \rightleftharpoons S_v$)
- * Dashed curve CF: It is vapour pressure curve of supercooled liquid Sulphur. It is back prolongation of DC. It depicts metastable eqm b/w S_R & S_l .
- + Dashed curve FE: It is melting / fusion curve of metastable S_R . It depicts metastable eqm b/w S_R and S_l . FE shows that melting point of metastable S_R is increased with pressure. Beyond E, the curve shows the condition of stable equilibrium S_R/S_l as metastable S_R disappears.
- * Metastable Triple point f: The three metastable phases i.e. S_e , S_l & S_v are in eqm. The temp. corresponding to f is 115°C .

* EUTECTIC SYSTEM :

A binary system consisting of two components, which are miscible in all proportions in liquid phase but do not react chemically, is known as "eutectic system".

* EUTECTIC MIXTURE: It is a solid solution of two or more components which have lowest freezing point of all the possible mixtures of components and the lowest freezing point is called eutectic point.

* Application of Eutectics: Low-melting alloys (eutectics) are used in safety devices.

* Phase rule for two component alloy system.

In a two-component system, with $P=1$, $f = C-P+2 = 2-1+2 = 3$.

So, max. no. of degrees of freedom is three which signifies that to completely define the system, a 3D diagram is required, which cannot be completely and conveniently shown on paper.

In a solid-liquid equilibrium of an alloy, there is no gas phase involved and so, pressure has negligible effect on this equilibrium. Keeping pressure of a system constant, then it is called condensed system. So, pressure variable will have no effect & \therefore

$$f = C-P+1$$

It is known as condensed/reduced phase rule

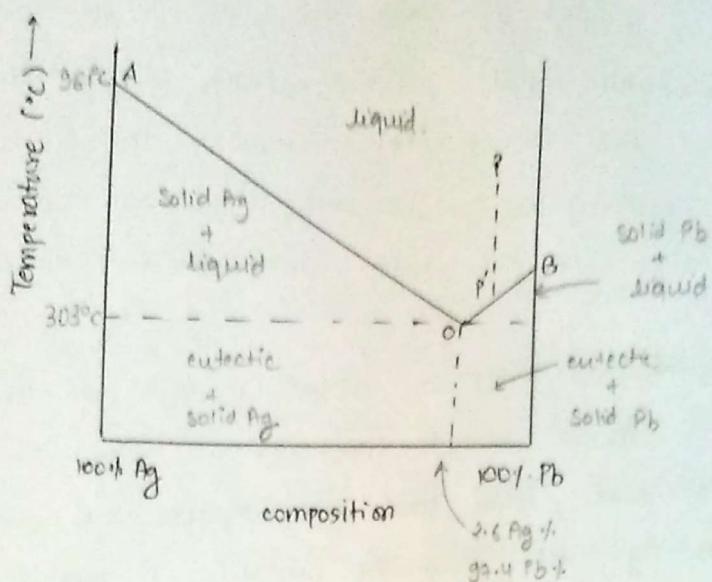
* LEAD-SILVER SYSTEM : Simple Eutectic formation.

It is a two component four phase system, with four possible phases i) solid Ag ii) solid Pb iii) solution of Ag+Pb iv) vapour.

Since, pressure has negligible effect on this type of equilibrium \therefore system can be completely defined using Temp. and concentration plot.

So, reduced phase rule: $C-P+1 = 2-4+1 = 3-P$ will be applicable.

i) curve AO : (freezing point curve of Ag) : It shows the effect on freezing point of Ag on addition of lead in small amounts. The curve starts at A (961°C), melting point of Ag, where pure Ag coexists as liquid & solid. It indicates that freezing point (or melting point) gradually falls, till Point O is reached, where solution gets saturated w.r.t Pb.



Now, no more lead go into the solution and melting point does not falls. If any lead is added, then it separates out as solid Pb. Along AO, solid Ag and solution coexists and hence system becomes univariant ($F = 3 - P = 3 - 2 = 1$). On cooling, whole mass crystallises out as such.

2) curve BO : (freezing point curve of Pb): It shows effect on freezing point on Pb on addition of small amounts of Ag. Point B is melting point of pure lead. Along BO, melting point of Pb gradually falls till it reaches O, where solution gets saturated w.r.t Ag and hence mp. does not fall anywhere more. On cooling, whole mass crystallises out. Along AO, both solid Pb and solution phase exists and hence system becomes univariant.

3) point O (eutectic point) : The curves AO and BO meets at O, where three phases (solid Ag, solid Pb and solution) coexists and hence system is non-varient according to Reduced phase rule ($F = 3 - P = 3 - 3 = 0$). Point O represents a fixed composition (2.6% Ag and 97.4% Pb) called eutectic composition and at this point, temp. remains constant, untilt whole of melt gets solidified to become solid eutectic mixture. However, further cooling results in crystallisation of mixture.

Below temp. line of eutectic temp., there are two regions:

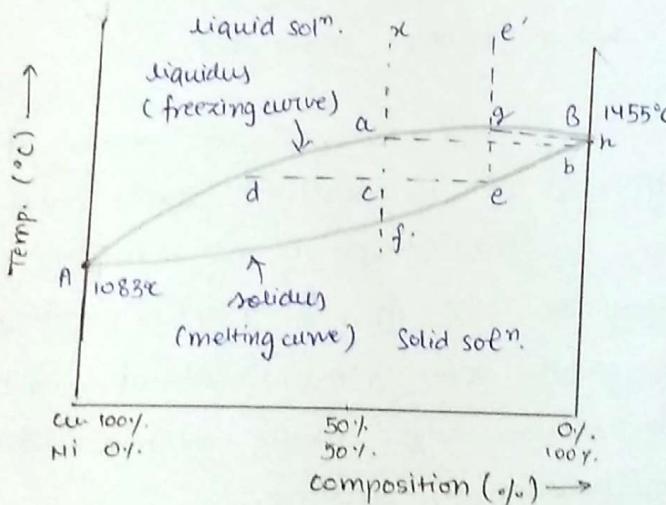
- i) region marked : eutectic + solid Ag
- ii) region marked : eutectic + solid Pb.

* Area AOB : represents solution of Pb + Ag. If a sample of lead containing less than 2.6% of Ag is taken, say P, on allowing mass to cool, the temperature gradually falls without change in concentration, till it reaches P' on curve BO. On further decreasing the temperature (cooling), lead precipitates (separates) out and composition varies along BO till it reaches O. On further cooling, whole mass solidifies to eutectic comp.

* Application of Fettinson's process : above principle is used in desilverisation of lead. If a sample (argentiferous lead) containing < 2.6% Ag is allowed to cool, then lead will separate out and it will become richer in Ag. till 2.6% Ag condition is reached. However, if Ag > 2.6%, then silver will separate out along curve AO and lead content will be more, till O is reached.

* COPPER-NICKEL ALLOY SYSTEM.

Copper and nickel are soluble in each other in all proportions. The phase diagram of copper-alloy system is shown below as Temp-concn. plot. The addition of nickel to copper raises its freezing pt. whereas addition of copper to nickel depresses its freezing pt. So, the freezing pt. of a mixture of Cu and Ni of any composition will be in between the individual freezing pts of Ni and Cu.



The upper curve represents the liquidus or freezing curve as the system is completely liquid above it. The lower curve is representing solidus or melting curve as system is completely solid below it. In between liquidus and solidus, both phase (l) & (d) co-exist.

The composition of liquid solution in eqm with solid solution is given by tie line, so, a liquid solution of composition a is in eqm with a solid soln. of composition b.

Effect of cooling: Any mixture of Cu and Ni in molten state represented by 'x' has 2 degrees of freedom. As it is a two component one phase system. [$F = C - P + 1 = 2 - 1 + 1 = 2$]. Such a liquid can be cooled directly without change in composition till point a is reached. At a, solid phase appears. Now, the system consists of two phases (both solid & liq.) and $\therefore F = C - P + 1 = 2 - 2 + 1 = 1$ \therefore system is univariant and hence now it can't be cooled without change in composition. The ratio of Ni to Cu is higher in solid state than in liquid state. Since presence of Cu diminishes freezing pt., so, the liquid, if cooled, will freeze at still lower temperature.

Due to exothermic nature of this change, rate of cooling is slowed down. The system at c consists of liquid soln of composition d and solid soln. of composition e. ace is tie line. By lever rule at c,

$$\frac{\text{amount of solid}}{\text{amount of liquid}} = \frac{ce}{cd}$$

The residual liquid (left after separation of solid) will be richer in Cu and poorer in Ni. The composition of liquid soln varies along af & that of Ni along Bf.

* **Fractional crystallisation:** A mixture of Cu and Ni represented by 'x' can be cooled directly without change in conc. upto point A. After that, due to introduction of solid phase, it cannot be cooled without change in concn. The composition of liquid soln varies from aA and that of solid solution varies along curve Bf. The mean composition of solid phase will be at e. This solid is separated out and heated to form molten mass of same composition e and then again cooled to form solid solution of composition h, in which Ni% is higher than at e. \therefore Progressing in same manner, the Ni% st in new solid will be greater than that at previous stage & \therefore pure component Ni can be obtained.

for Cu, the liquid solution is needed to be cooled, and then liquid will be richer in Cu and finally after repeating this many times, it can be extracted.