# Government College of Engineering and Research, Avasari(Khurd)

## **Department**: Mechanical Engineering

# Learning Resource Material (LRM)

**Name of the course:** Engineering Metallurgy **Course Code:** 202048

**Name of the faculty: J. M. Arackal** **Class:** SE(Mech)

SYLLABUS(Unit 1& 2)

**Unit I: Overview of Metallurgy** (6 **Hrs)** Methods of metal extraction (Principle only of pyro , hydro & electro metallurgy), cast v/s wrought products, Related terms and their definitions : System, Phase, Variable, Component, Alloy, Solid solution, Hume Ruther's rule of solid solubility, Allotropy and polymorphism, Concept of solidification of pure metals & alloys, Nucleation : homogeneous and heterogeneous,
Dendritic growth, super cooling, equiaxed and columnar grains, grain & grain boundary effect.
Cooling curves, Plotting of Equilibrium diagrams, Lever rule, Coring, Eutectic system, Partial eutectic and isomorphous system.
.
**Unit II: Micro & macroscopic study of Metals (6 Hrs)** Classification of metal observations: their definition, difference & importance.
Microscopy: Various sampling techniques, specimen preparation, specimen mounting (hot & cold mounting) electrolytic polishing, etching procedure and reagents, electrolytic etching.
Microscopic techniques : optical microscopy, electron microscopy, transmission electron microscopy (TEM),scanning electron microscopy ( SEM), scanning probe microscopy (SPM ), AFM etc. ( principal & application only )
Study of Metallurgical microscope .Measurement of grain size by different methods & effect of grain size on various mechanical properties.
Macroscopy: Sulphur printing, flow line observations, spark test.

**Lecture Plan format:**

**Name of the course**: Engineering Metallurgy **Course Code** 202048

Name of the faculty: J. M. Arackal Class: SE(Mech)

| Unit No | Lecture No. | Topics to be covered | Text/Reference Book/ Web Reference |
|---|---|---|---|
| | | **Unit 1: Overview of Metallurgy** | |
| 1 | 1 | Methods of metal extraction | 1 |
| 1 | 2 | Cast v/s wrought products, Related terms and their definitions | 1 |
| 1 | 3 | System, Phase, Variable, Component, Alloy, Solid solution, Hume Ruther's rule of solid solubility, Allotropy and polymorphism | 1 |
| 1 | 4 | Concept of solidification of pure metals & alloys, Nucleation : homogeneous and heterogeneous | 1 |
| 1 | 5 | Dendritic growth, super cooling, equiaxed and columnar grains, grain & grain boundary effect.<br>Cooling curves | 1 |
| 1 | 6 | Plotting of Equilibrium diagrams, Lever rule, Coring, Eutectic system, Partial eutectic and isomorphous system | 1 |
| | | Unit 2: **Micro & macroscopic study of Metals** | |
| 2 | 1 | Classification of metal observations: their definition, difference & importance | |
| 2 | 2 | Microscopy: Various sampling techniques, specimen preparation, specimen mounting | |
| 2 | 3 | Microscopic techniques : optical microscopy, electron microscopy, transmission electron microscopy (TEM) | |
| 2 | 4 | Study of Metallurgical microscope .Measurement of grain size by different methods | |
| 2 | 5 | Effect of grain size on various mechanical properties. | |
| 2 | 6 | Macroscopy: Sulphur printing, flow line observations, spark test | |

**List of Text Books /Reference Books/ Web Reference**


***1-*** *Material Science & Metallurgy For Engineers", Dr. V.D. Kodgire & S. V. Kodgire , Everest Publication.*

***2-*** *Introduction to Physical Metallurgy, Avner, S.H., Tata McGraw-Hill*

## Hume - Rotherys Rules of Solid Solubility

Limit of solute in the solvent is governed by certain factors.

i) Atomic size factor: If atomic size of solute & solvent differ by less than 15%, its said to have a fovourable size factor for solid solution formation.

ii) Chemical Affinity factor: The greater the chemical affinity of two metals, the more restricted is their solubility & greater is the tendency to form a compound.

iii) Relative valence factor: A metal of higher valency can dissolve only a small amount of a lower valency metal, while the lower valency metal may have a good solubility for higher valency metal.

iv) Crystal structure factor: Metals having same crystal structure will have greater solubility.

Q: The atomic radii of Al & Si are 0.143 nm & 0.117 nm respectively. Do they satisfy Hume rotherys first rule for solid solubility?

Ans).

$r_{Al} = 0.143$

$r_{Si} = 0.117$

$$\%\text{ Atomic diff} = \frac{0.143 - 0.117}{0.143} \times 100$$

$$= 18.2\%$$

They do not satisfy Hume Rotherys Rule.

## Gibbs phase Rule.

Under equilibrium condition.

$R = P + F = C + 2$.

P = No of phases existing in a system under consideration

F = DoF [no of variables like temp, pressure or concentration (composition) that can be changed independently without changing the no of phases existing in the system.

C = no of components in the system.

2 → any two variables out of above 3

Most of the studies are done at ~~const~~ atmospheric pressure

∴ $P + F = C + 1$

## Polymorphism.

- More than one stable crystalline form.
- changes of crystal structure due to change of pressure / temp or both.
- The composition remains same.
- Also known as alotropy.
- Transformation is reversible
- such materials are called polymorphs.
- polymorphs have different densities & mechanical properties.
- di – trimorphic.

They are classified to two types:

1) Enantitropy: Mutually transformable reversible at some temperature (transition/transformation temp or Inversion point), two crystalline form co-exist in equilibrium, at given pressure. Any deviation from this temp results in transformation of one form in other.

eg: Fe, Zr, Ti etc

i) Monotropy: Irreversible in solid state. occurs at temp above melting point.
obtained from liquid or vapour state of the material by rapid cooling.
so they cant be transformed from one to another in solid state.

## Solidification of a Pure Metal:

Solidification occurs by the nucleation & growth of crystals in the melt

Nuclei — first step in solidification process
Nucleus – small cluster of atoms having right crystalline arrangement.

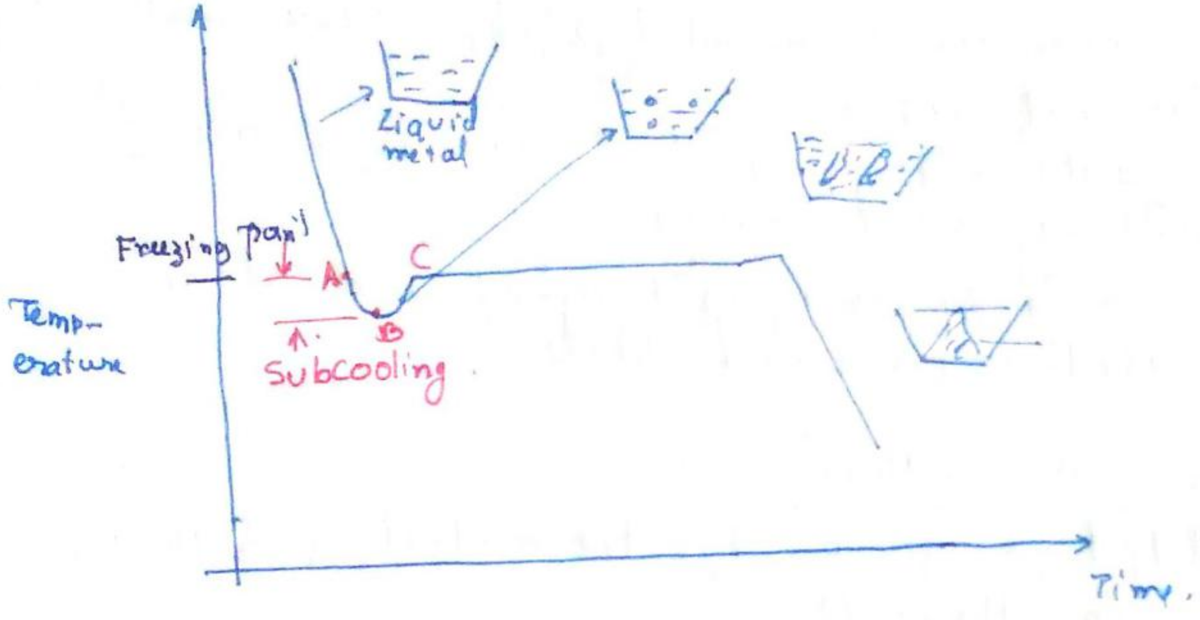
When ~~metal~~ melt is cooled below the melting point nuclei begin to form at many parts of the melt at the same time.

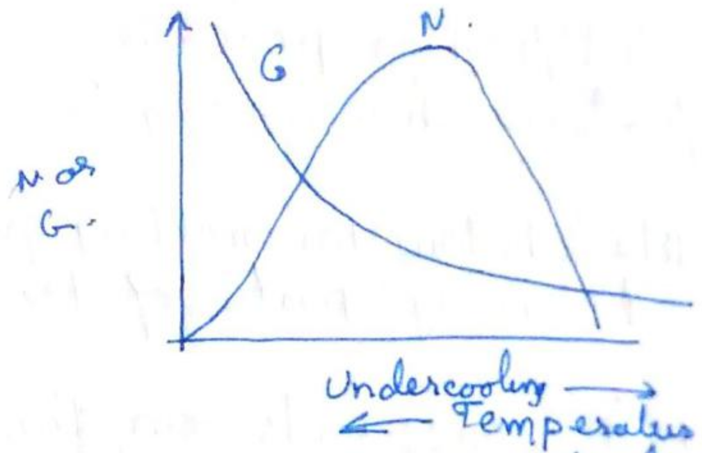
The rate of nucleation depends on the degree of undercooling / supercooling, & also on presence of impurities. which facilitates nucleation,

At any temperature below melting point nucleus has to be of a certain minimum size, called. critical size, so that it grows, this size is greatest near the melting point, but the probability of formation is less.

Particles smaller than the critical size will be dissolved by the vigorous bombardment of neighbouring atoms & cannot grow, they are called embryos.

Critical size of nucleus decreases with the decrease in temperature, or increasing degree of undercooling. Hence at lower temperature nuclei becomes progressively smaller in size but number greatly increases.




N ⟶ rate of nucleation
G - ~~growth~~ rate of growth.

growth rate of nuclei occur by diffusion

## Critical size of nucleus.

Consider a volume of liquid phase under consideration such that transformation to solid is thermodynamically possible.

$\Delta F_v$ ⟶ ~~volume~~ free energy per unit volume.

If a spherical particle of solid of radius r is to form, an interface has to be created between the solid & the liquid, overall change in free energy is given by ($\Delta f$).

$\gamma$ = Energy needed to create one unit area.

$$\Delta f = \underbrace{4\pi r^2 \gamma}_{} + \underbrace{\frac{4}{3}\pi r^3 \Delta F_v}_{}.$$

Energy needed to create interface. → always positive.

Energy released by volume of solidifying phase. → negative

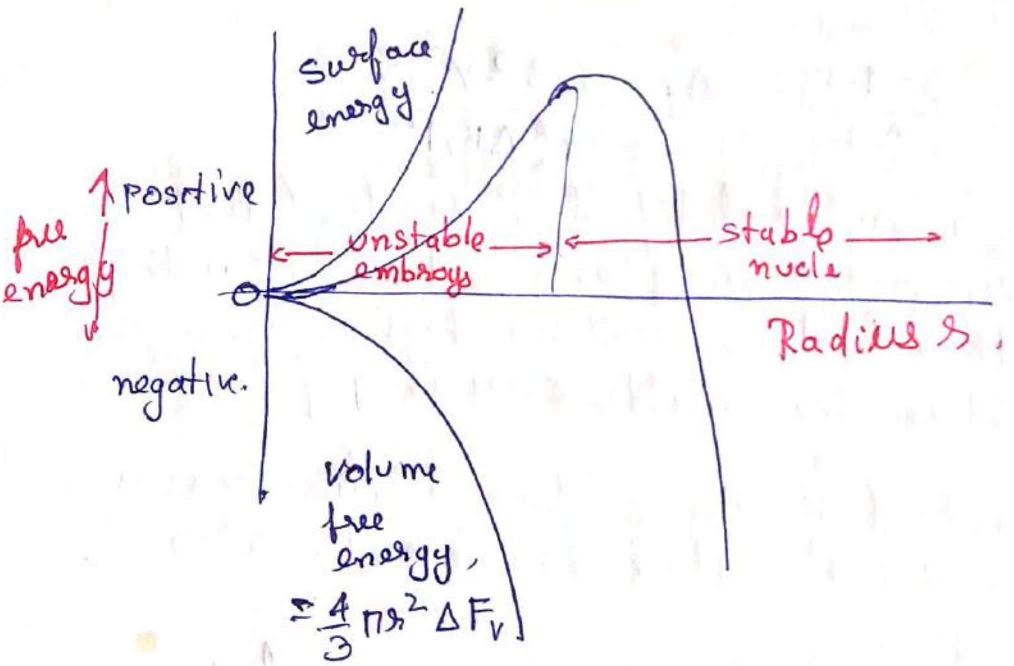
differentiating w.r.t. to $r$.

$$\frac{d}{dr}(\Delta f) = 8\pi r \gamma + \frac{4}{3}\pi(3r^2)\Delta F_v.$$

$$0 = 8\pi r \gamma + \frac{4}{3}\pi(3r^2)\Delta F_v.$$

$$\frac{4}{3}\pi(3r^2)\Delta F_v = -8\pi r \gamma$$

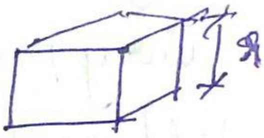
$$\boxed{r^* = -\frac{2\gamma}{\Delta F_v}}$$




Corresponding value of

$$\Delta f^* = \frac{16\pi \gamma^3}{3(\Delta F_v)^2}.$$

Q) Derive an expression for the critical size of cube shaped nuclei, homogeneously nucleating during the solidification of a melt, in terms of $\Delta F_v$, the free energy change per unit volume & $\gamma$, the surface energy per unit area of the interface.




Ans). for a cube

surface area = $6r^2$.

volume = $r^3$.

$\therefore \Delta f = (6r^2)\gamma + r^3 \Delta F_v$.

diff w.r.t. r.

$0 = (12r)\gamma + (3r^2)\Delta F_v$.

$(12r)\gamma = -3r^2 \Delta F_v$,

$r^* = \frac{-4\gamma}{\Delta F_v}$ $\quad \Delta f = \frac{32\gamma^3}{(\Delta F_v)^2}$.

As soon as solidification starts, latent heat is given out. The temperature near the vicinity of the crystals will be higher than at other points in the melt, causing formation of nuclei.

As a result of this temperature rises from B to C. This phenomenon is also called <u>recalescence</u>.

In some cases it is accompanied by glowing effect.

## Shape of crystals.

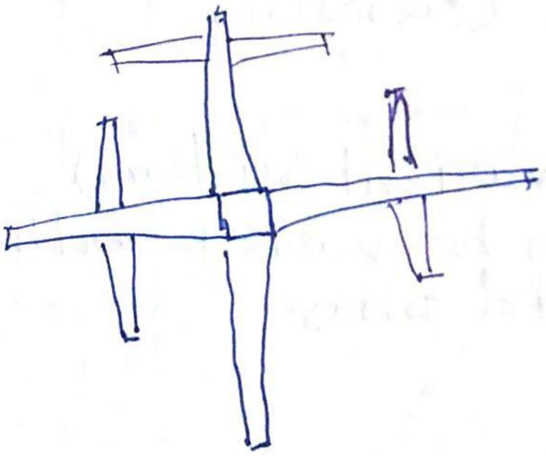
Slow cooling favours growth of crystals uniformly in all directions & gives equiaxed crystals.

Rapid cooling favous tree like crystals called dendrites.

## Dendritic growth.

A considerable amount of latent heat is evolved in the direction of crystal growth, causing the temperature of the adjacent liquid to rise. This temperature may exceed the freezing temperature of a metal, so that further growth of the crystal in this direction will be stopped.

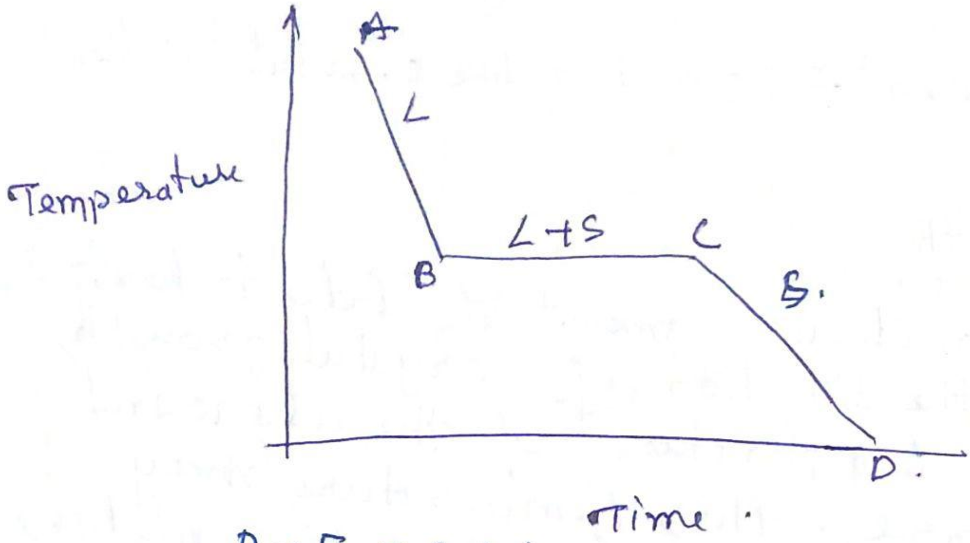
In perpendicular direction, liquid will have lower temperature, since there was no crystallization. this process continues.



Cast components show dendritic structure & hence dendritic structures are typical of cast components.

Types of cooling curves.

A) For pure Metals.




$P+F=C+1$

P = no of phase.

F = DoF

C = no of components.

In region AB.

$P+F=C+1$

$P=1 \quad C=1$. (pure metal)

$1+F=1+1$

$F=1$ (Univarient System)

Temperature can be varied without changing the liquid phase

In region BC.

$P+F=C+1$

$P=2 \quad C=1$.

$2+F=1+1$

$F=0$ (non varient or Invarient system)

Temperature can't be changed without changing the liquid & solid phases existing in the system

In region CD.

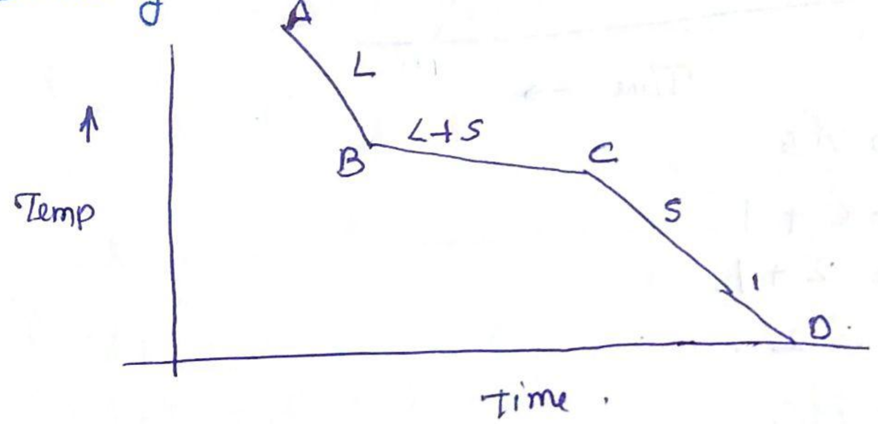
$P + F = C + 1$.

$P = 1 \quad C = 1$.

$1 + F = 1 + 1$

$F = 1$ (Univariant).

B) For Binary Solid solution. (Alloy).




In region AB.

$P + F = C + 1$

$P = 1 \quad C = 2. \Rightarrow 1 + F = 2 + 1$

$F = 2$

⇒ Both temperature & concentration can be varied without changing the liquid phase.

In region BC.

$P + F = C + 1$

$P = 2 \quad C = 2.$

$F = 1$. (Any one variable can be changed)

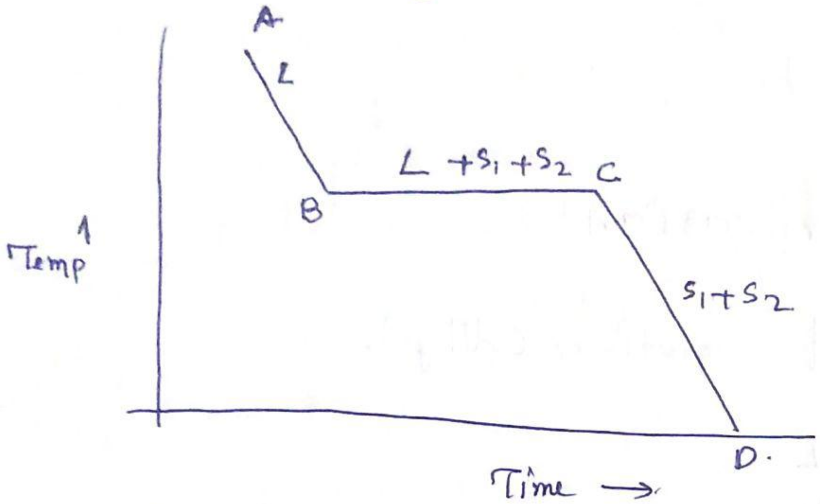
In region CD.

$P + F = C + 1$

$P = 1 \quad C = 2$

$F = 2$.

c) Binary Eutectic Alloys




In region AB

$P + F = C + 1$.

$1 + F = 2 + 1$.

$F = 2$.

In region BC.

$P + F = C + 1$

$3 + F = 2 + 1$

$F = 0$.

In region CD.

$P + F = C + 1$

$2 + F = 2 + 1$

$F = 1$.

Binary eutectic is a homogeneous mixture of two solids which forms at constant temperature during cooling & melts at constant temperature during heating.

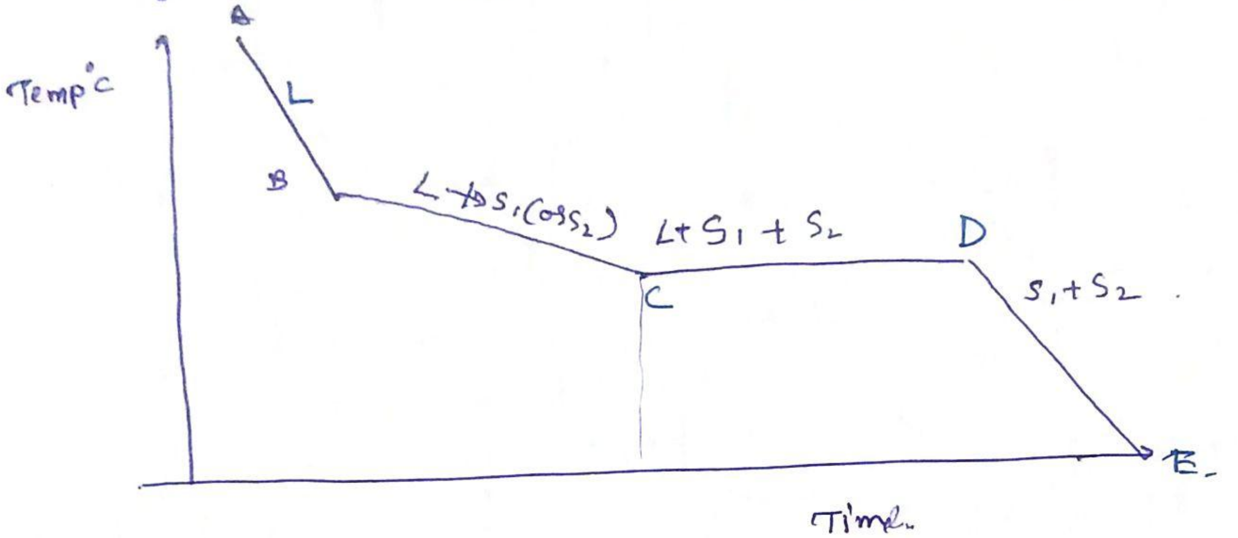
$$L \xrightarrow{\text{const. temp}} S_1 + S_2$$

The mixture appears in definite morphological form & is usually lamellar; in certain cases, it may be granular or some other type of morphology.

The temperature at which this transformation occurs is called eutectic temperature & is the lowest temperature of transformation in the system. It occurs at definite composition called Eutectic composition.

For off Eutectic binary alloy.

Eutectic transformation occurs at definite composition 6. Called eutectic composition. If the composition of the alloy differs, its called off-eutectic. They can be Hypoeutectic (less) or Hypereutectic (more)




i) In region AB

$P + F = C + 1$

$1 + F = 2 + 1$

$F = 2$ (Bivarient)

ii) In region BC.

$P + F = C + 1$

$2 + F = 2 + 1$

$F = 1$. (Any one variable can be changed)

iii) In region CD.

$P + F = C + 1$.

$3 + F = 2 + 1$

$F = 0$ (nonvarient / Invarient).

iv). In region DE

$P + F = C + 1$

$2 + F = 2 + 1$

$F = 1$

Start of solidification temperature is called liquidus temperature because above this metal/alloy is in liquid state. The ends of solidification is called solidus temperature, because below thes → solid

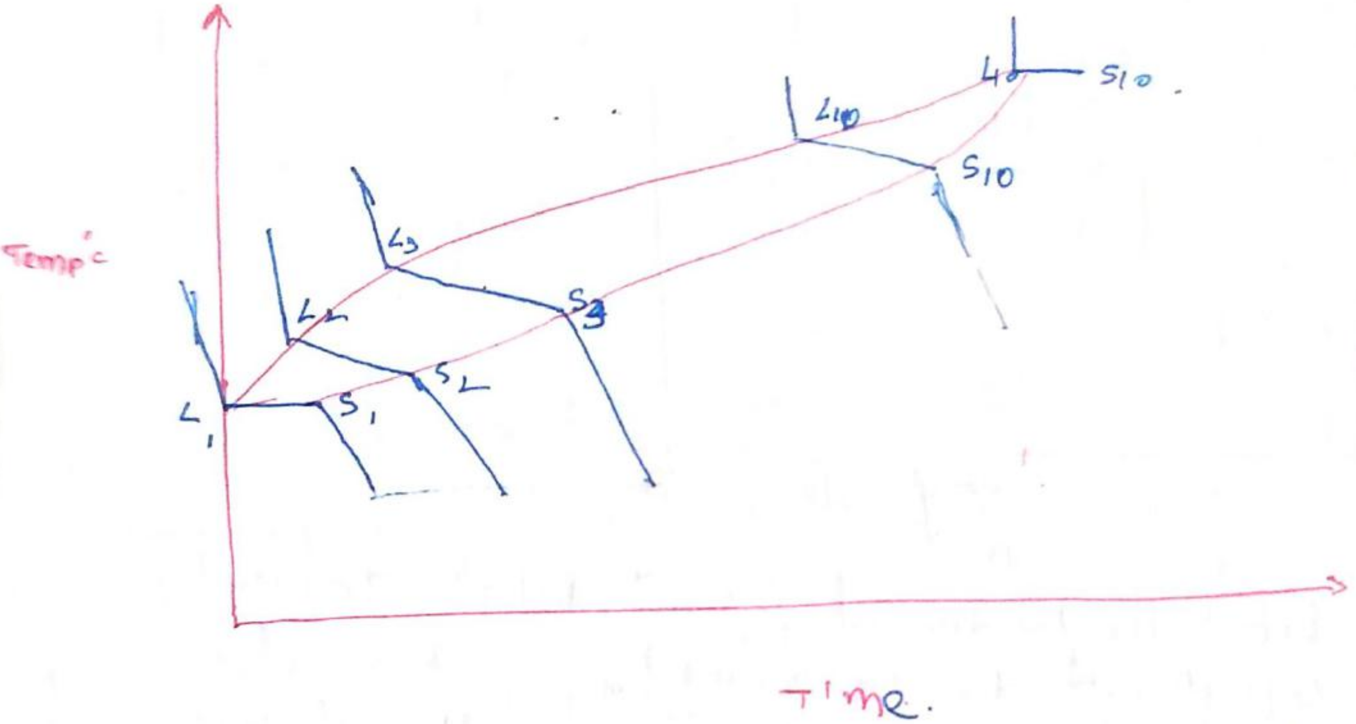
* underscooling not shown for simplicity.

## Plotting of Equilibrium Diagrams.

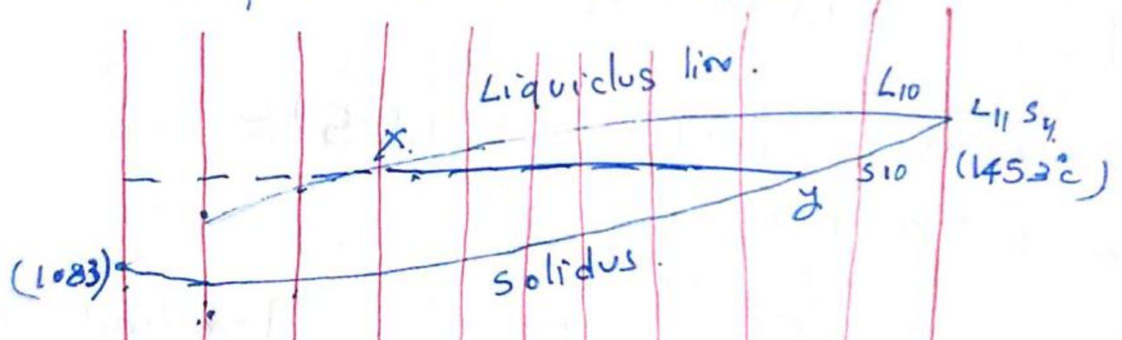
Mostly plotted by thermal Analysis.

Consider a binary Cu-Ni system, having 100% solubility in liquid & solid state & they form a series of solid solution.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| %Cu (1083) | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| % Ni (1453) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100. |



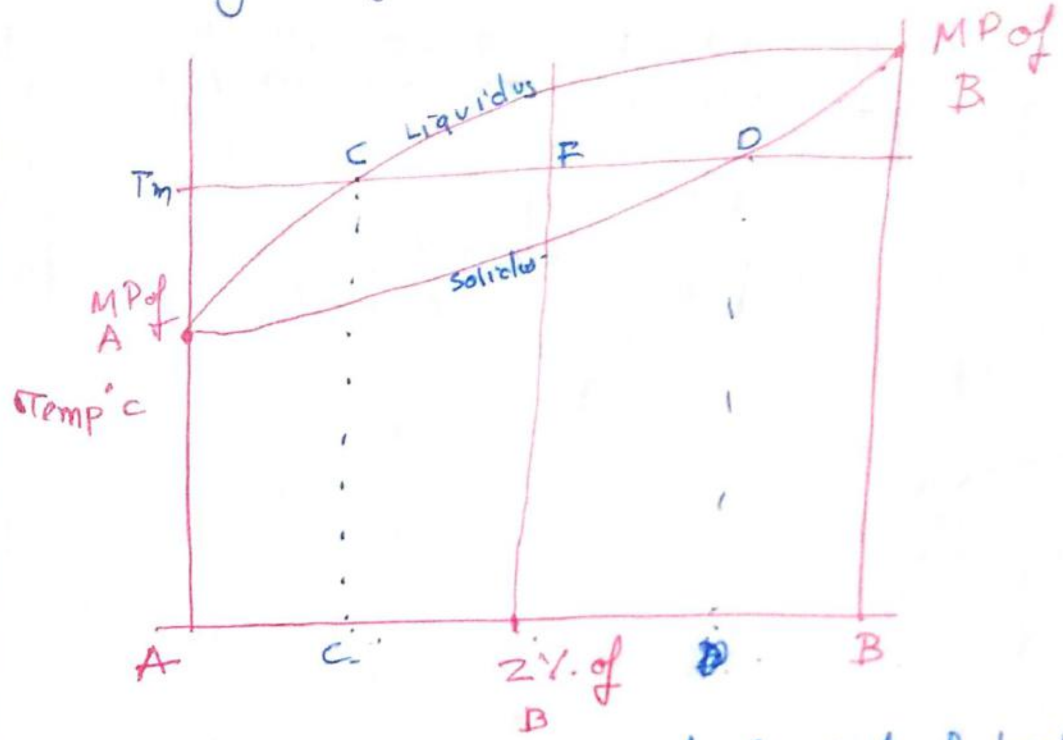

Transfer this to temp_composition graph




At any temperature such as T, the average composition of the existing liquid is given by X & the average composition of the existing solid is given by the point Y. The amount of solid & liquid is calculated by using lever arm principle or lever rule.

Lever Rule.

Used for finding out the amounts of phases existing in a binary system for a given alloy at any temperature under consideration




Let s be the amount of solid & 1-s amount of Liquid at the Temperature Tm

Amount of B in the alloy = Amount of B in solid state + Amount of B in Liquid state

$$Z = s.D + (1-s)C.$$

$$Z = sD + C - sC.$$

$$s = \frac{Z-C}{D-C} = \frac{F-C}{D-C} = \frac{\text{Arm length } CF}{\text{Arm length } CD}.$$

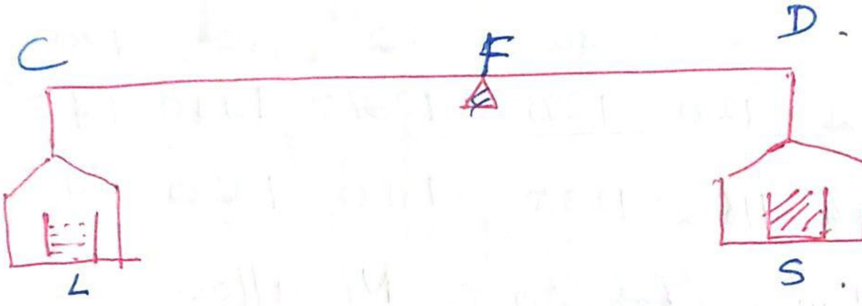
$$s = \frac{\text{opposite length of Arm}}{\text{Total length of Arm}}.$$

Similarly.

~~Arm len~~ $L = \frac{\text{Arm length FD}}{\text{Arm length CD}}$.

$L = \frac{\text{opposite length of Arm}}{\text{Total length of Arm}}$.

$\frac{\text{Amount of solid}}{\text{Amount of Liquid}} = \frac{\text{Arm CF}}{\text{Arm FD}}$.




Amount of Solid × its lever arm = Amount of Liquid × its lever arm.

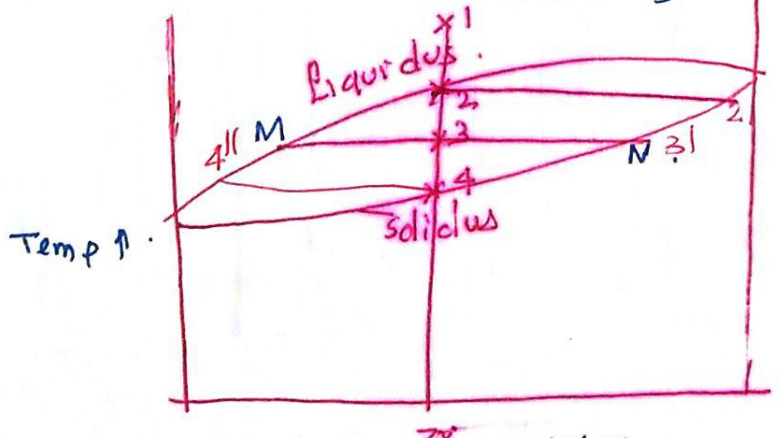
## Common types of phase diagrams:

- Isomorphous systems.
- Eutectic systems.
- Partial Eutectic systems.
- Layer type systems.

## Isomorphous Systems:

obtained for two metals having complete solubility in the liquid as well as solid state.

- Cu-Ni, Au-Ag, Bi-Sb (Antimony), Mo-W.



The average composition of existing solid is indicated by solidus line while that of liquid by liquidus line.

At point 3.

$$\text{Amount of liquid (M\% of B)} = \frac{\text{length } 3N}{\text{length } MN}.$$

Q) From the data given below for Cu-Ni system, plot the equilibrium diagram to scale & label the diagram

| wt %. Ni. | 0 | 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|---|
| Liquidus temp°c. | 1084 | 1200 | 1275 | 1345 | 1440 | 1455 |
| solidus temp°c. | 1084 | 1166 | 1235 | 1310 | 1380 | 1455. |

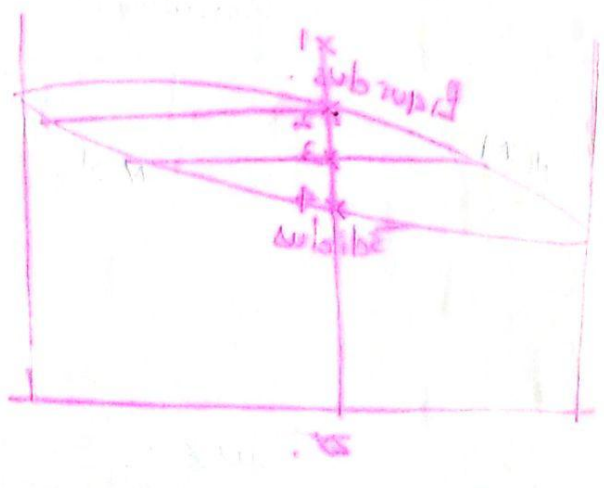
Answer the following for 70 %. Ni alloy.

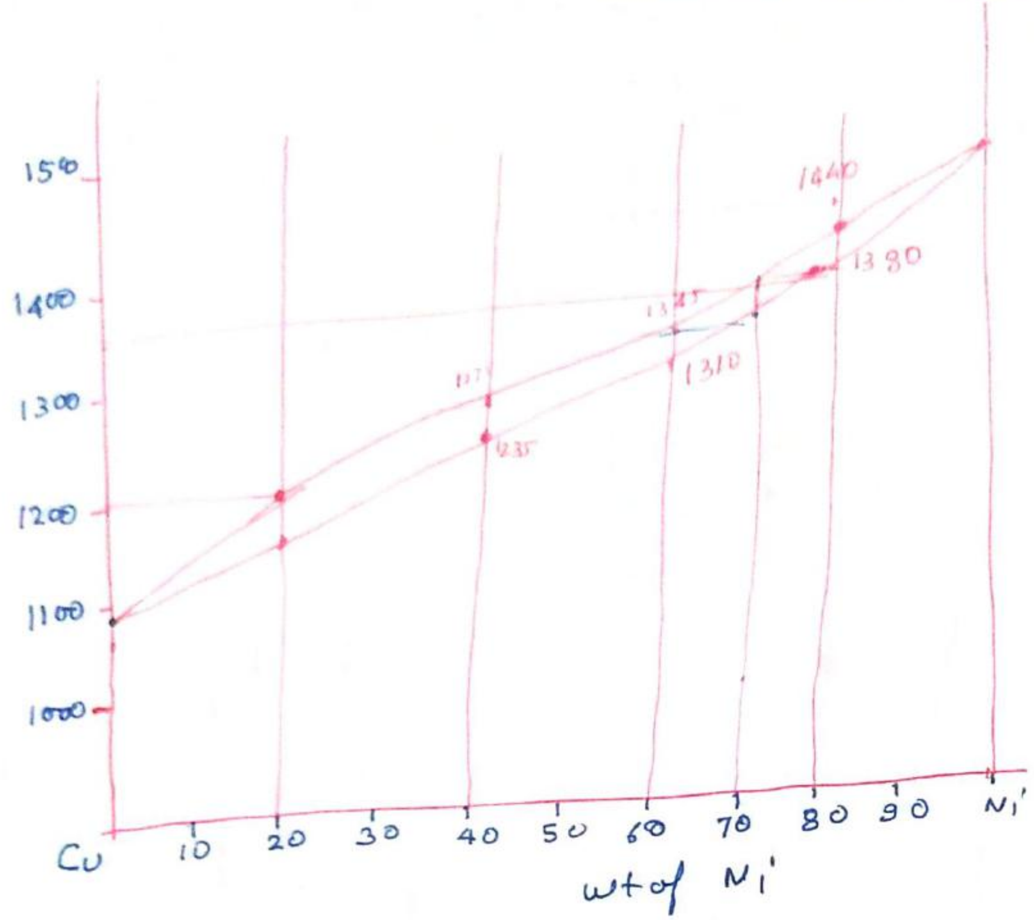
a) what is the composition of first solid crystallizing out from the liquid ?

b) what is the composition of last solid & last liquid formed at the end of solidification ?

c) what are the amounts of solid & liquid at 1360 °c ?

→ $$\text{Amount of Solid (of M\%. B)} = \frac{3M}{MN}$$






a). first solid - 78 %.
b) Last solid. - 70
Last Liquid - 59 %.

c). % Solid = $\frac{70-66}{78-63}$ = ~~26~~. 65.. (In. 78%. Ni)

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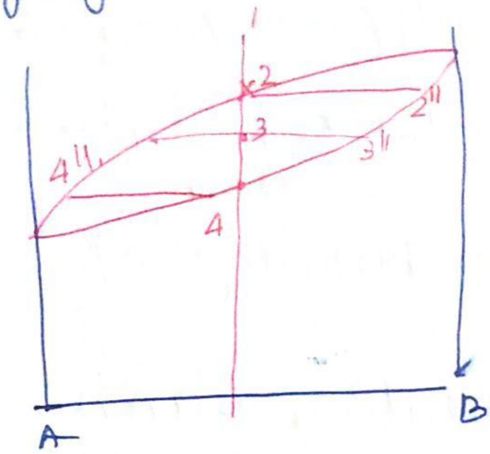
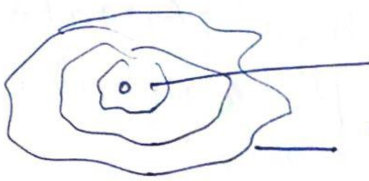
Coring

Variation in composition is observed from point to point or centre to surface of a grain or dendrite in a solidified alloy at room temperature. This micro segregation is called coring




on cooling from 1 to 2 the first solid is 2'' (Rich in B & surface solid will be rich in A.




Such difference in concentration are called cored structure

coring seen under optical microscope by colour differences developed through etching effect.

Coring is common in cast components like brasses, bronzes & stainless steel. Its undesirable because

- gives brittleness
- non uniform mechanical & physical properties
- Increases susceptibility to corrosion

Coring can be eliminated by

- using slow cooling rates during solidification of the alloy, giving more opportunity of diffusion.

Slow cooling rates, causes grain size to be largest resulting in inferior mechanical propert so this method is not used commercially.

ii) By homogenization heat treatment.

Heated to a temperature just below solidus temperature & held for a long time thereby causing diffusion.

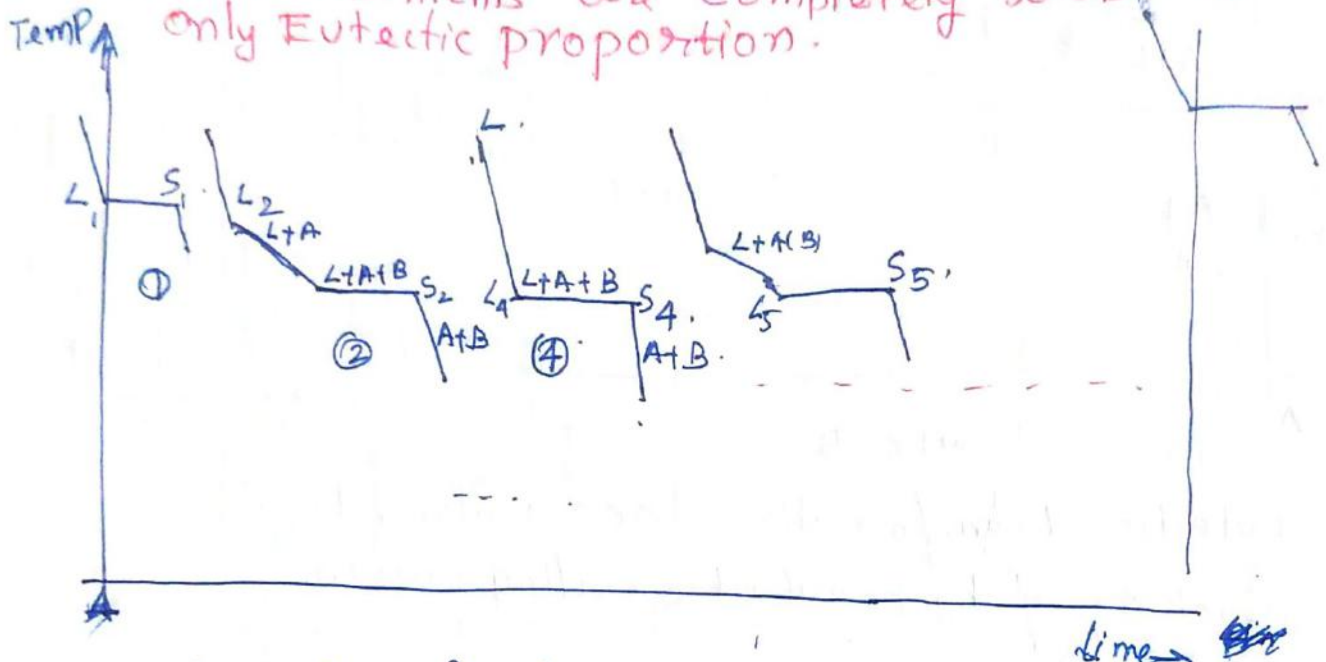
If heated above Solidus temperature, it can cause oxidation near grain boundaries, resulting in burning of alloys.

The result of overheating can be removed by a suitable heat treatment. so overheating are not permanent.

# Eutectic systems.

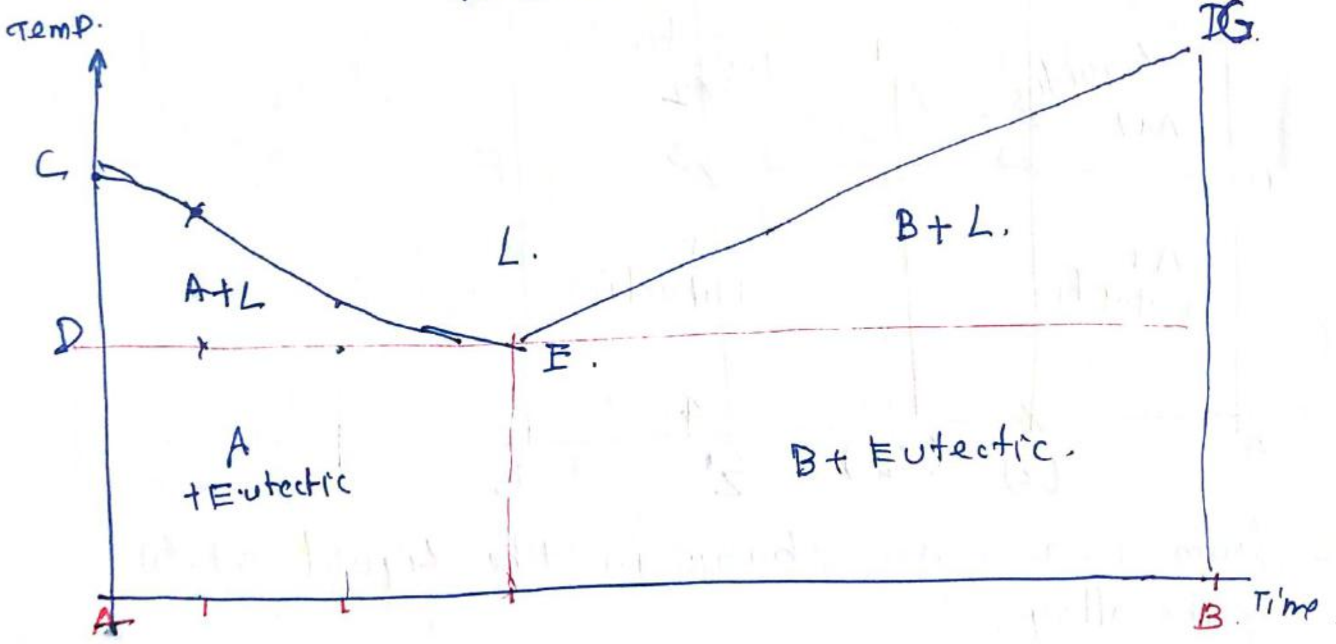


- If two elements/metals are eutectic then their melting temperatures are lowered.
- The two elements are completely soluble at only Eutectic proportion.



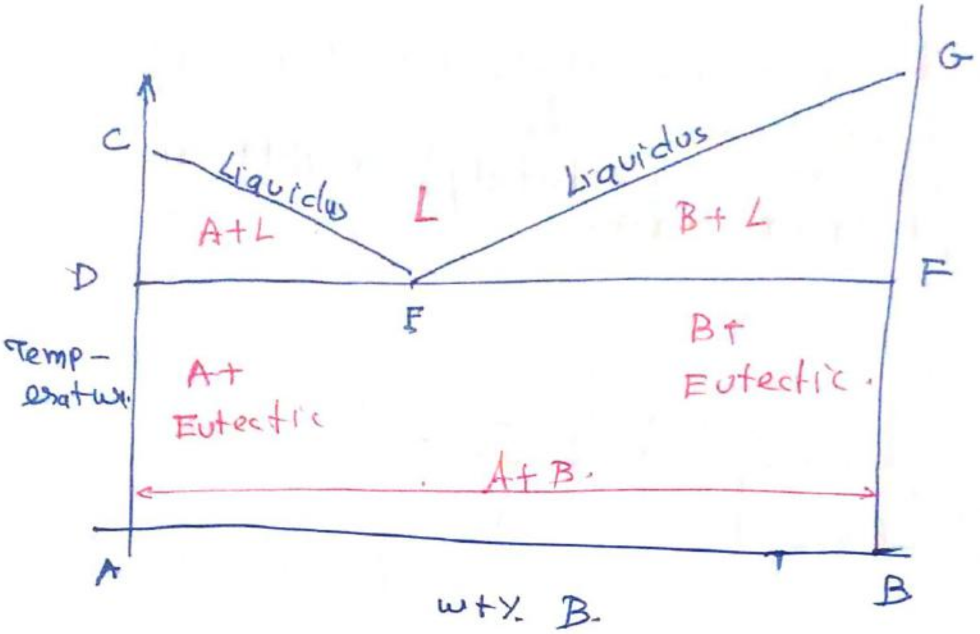

| | 1 | 2 | 3 | 4 | | | | |
|---|---|---|---|---|---|---|---|---|
| Let B | 0 | 10 | 20 | 30 | 40 | 50 | 60 | -- -- 0 |
| A. | 100 | 90 | 80 | 70 | 60 | 50 | 40 | |

↑ Eutectic.



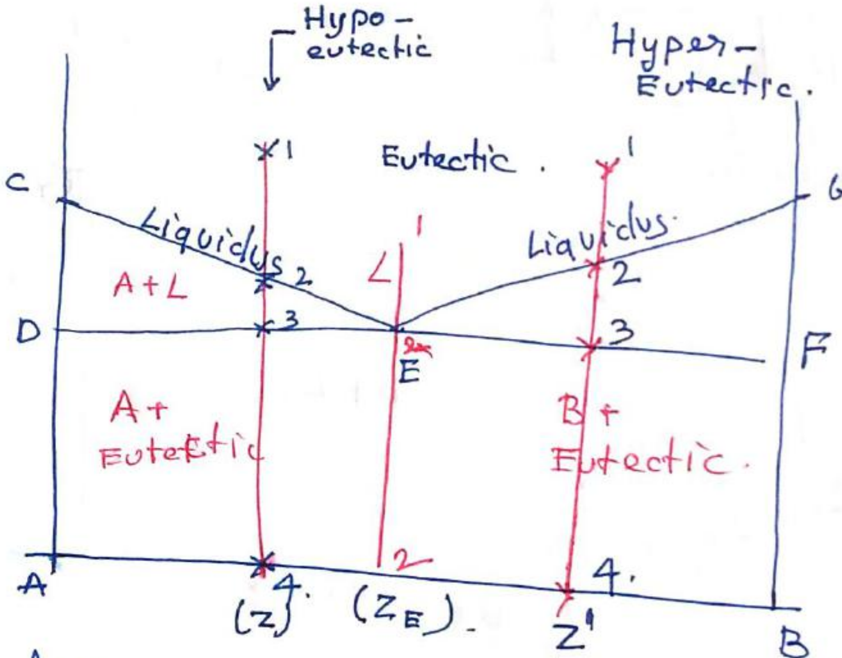

weight % B

eg: Pb-As, Br-Cd, Th-Ti, Au-Si 




Eutectic transformation occurs along DF.

1) <u>Cooling of hypoeutectic alloy with.</u>
<u>Z% B.</u>




- from 1-2 - no change in the Liquid state of the alloy.

- Below 2, A starts its solidification because its <u>melting point has decreased.</u>

- The composition of liquid varies along CE, but the composition of A does not change. as its has no solubility with A.

At just above 3. Amount of Liquid can be found by Lever Rule.

12

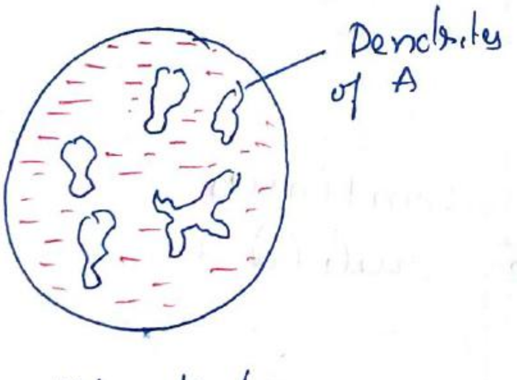
Amount of A (solid). $= \frac{3E}{DE}$.

Amount of liquid (at composition of E) $= \frac{D3}{DE}$

This phase A which has seperated before the eutectic transformation is called. free or primary A, its also called as proeutectic.

@ 3 – the (eutectic composition). liquid $\frac{D3}{DE}$ solidifies at constant temperature. & transforms to an eutectic mixture of. A & B, usually in a lamellar form.

$$\text{Liquid (of eutectic composition)} \xrightarrow[\text{temperature}]{\text{Constant}} A + B$$




Microstructure Just above 3.

Microstructure.

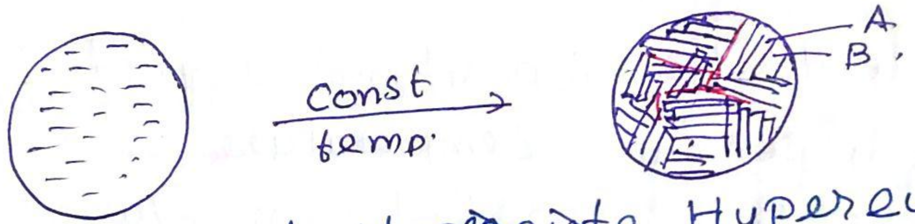
Amount of eutectic will be same as. amount of liquid $\frac{D3}{DE}$

## ii) Cooling of an eutectic alloy with composition $Z_E$ % B.

1 – E – Liquid.
At just below E.

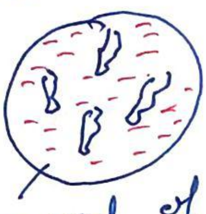
Liquid (of eutectic composition) $\xrightarrow[\text{temperature}]{\text{Constant}}$ A + B.

~~The amount~~
The amount of A & B in the eutectic will be same as in the original alloy.




## III) Cooling of ~~Hypoeute~~ Hypereutectic alloy with Z' % B (Refer graph).

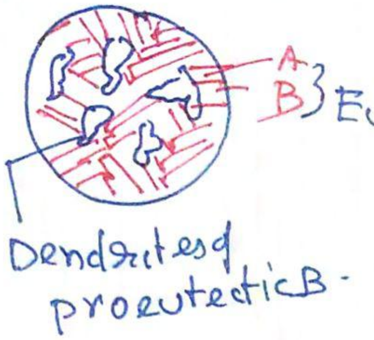
- 1-2 → no change in the liquid state.
- Below 2 – B seperates out.




The above process continues till 3. applying Lever rule @ 3.

Amount of Liquid (@ Eutectic composition) = $\frac{3F}{EF}$.

The above amount of Liquid, which is at eutectic composition, ~~fo~~ solidifies & forms at eutectic mixture of A & B in lamellar morphology.




Q) From the data given below for Bi-Cd system, plot the equilibrium diagram to scale & find.

1) Amount of eutectic in 20% Cd alloy. &
11) Free Cd in 70% Cd alloy.

Given

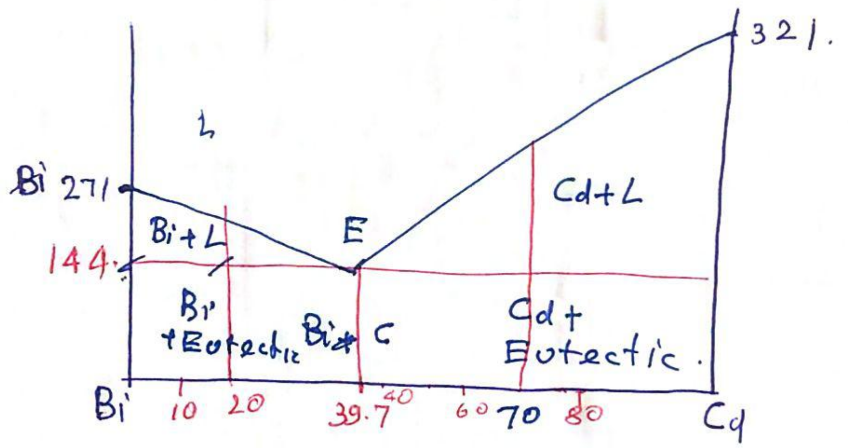
Melting temp of Bi = 271°c.

Melting temp of Cd = 321°c.

Eutectic temp of = 144°c.

Eutectic composition = 39.7% Cd.

Ans).




i) Amount of eutectic at = amount of Liquid at 144°c $= \frac{20-0}{39.7-0} = 50.4\%$.

ii). Upto eutectic - Cd is formed (dendrite) which is nothing but amount of free Cd.

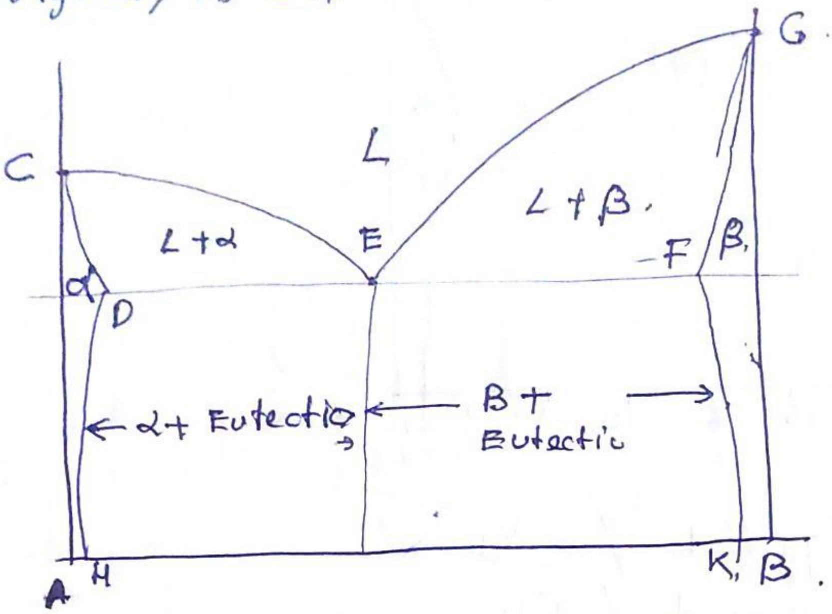
∴ Amount of free Cd $= \frac{70-39.7}{100-39.7}$

$= 50.2\%$.

## Partial Eutectic Systems

These diagrams are obtained for two metals which have complete solubility in liquid state & Partial solubility in the solid state.

eg: Ag-Cu, Pb-Sn, Sn-Bi, Pb-Sb, Al-Si.




Liquidus Line CEG

Solidus Line . CDEFG

α - solid solution of B in A

β - Solid solution of A in B.

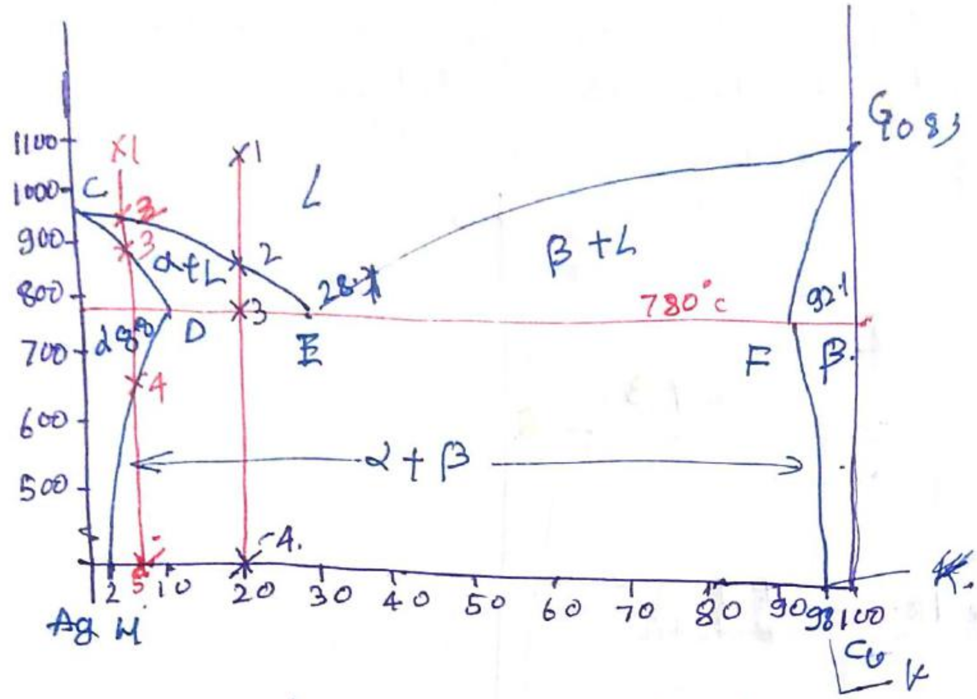
The line/curve HD indicates solubility of B in A from room temperature to Eutectic temp.

The line/curve KF indicates solubility of A in B. from room temperature to Eutectic temp

Both the curves are called solvus lines. as they indicate solubilities of one into the other at different temperatures.

Eutectic arm DEF

Phase diagram. Ag - Cu is shown below

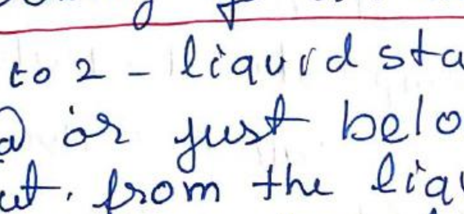



C - Melting point of Ag.
G - Melting point of Cu.
Eutectic temperature = 780°c.
Eutectic composition = 28.1 % Cu.
D = Max solubility of Cu in Ag.
F - Max solubility of Ag in Cu.

1) Cooling of an alloy with 6% Cu.

- 1 to 2 - liquid stage.
@ or just below 2, α starts seperating out, from the liquid.
Last liquid that solidifies at 3 gives 100% α solid solution

3-4 - no change.




Below point 4, the solubility of Cu decreases & it seperates out as β.

~~Amount of $\alpha$ =~~ @ room temperature

Amount of $\alpha$ (at 2% Cu) $= \frac{SK}{HK}$

$= \frac{98-6}{98-2} = 95.83$

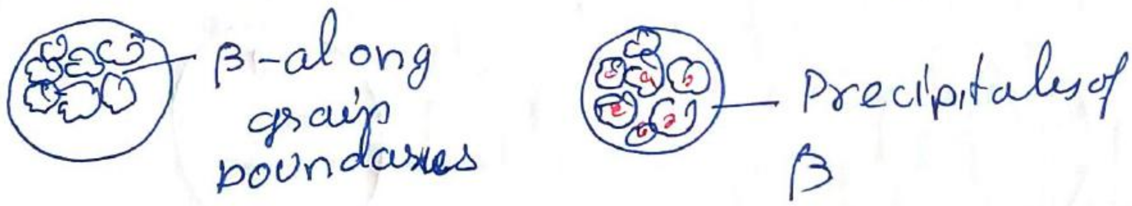
Amount of $\beta$ (@ 98% Cu) $= \frac{S-H}{HK}$

$= \frac{6-2}{~~98~~} = 4.2\%$

$\beta$ may appear as grain boundaries of $\alpha$ or may get entrapped in the grains depending on cooling rate.

If slower cooling, $\beta$ formed at grain boundaries.

Higher cooling - precipitate of particle




ii) Cooling of Hypoeutectic alloy with 20% Cu

(Refer Diagram Ag-Cu).

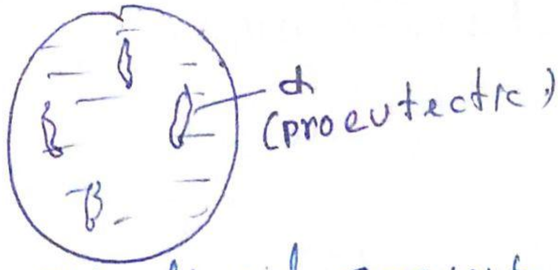
1-2 - Liquid state.

2-3 - Just below 2 $\alpha$ starts seperating out from the liquid, $\alpha$ increases up to 3.

@ 3 applying Lever rule.

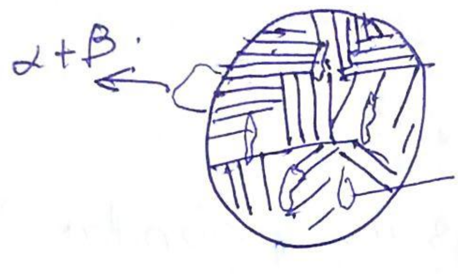
Amount of $\alpha$ $= \frac{3E}{DE} = \frac{28.1-20}{28.1-8.8} = 42\%$

Amount of Liquid $= \frac{3D}{DE} = \frac{20-8.8}{28.1-8.8} = 58\%$.

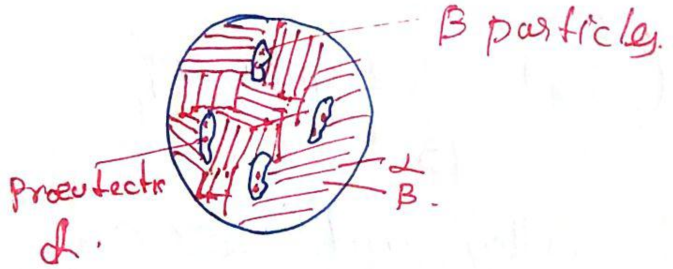



→ This liquid converts to (α & β).

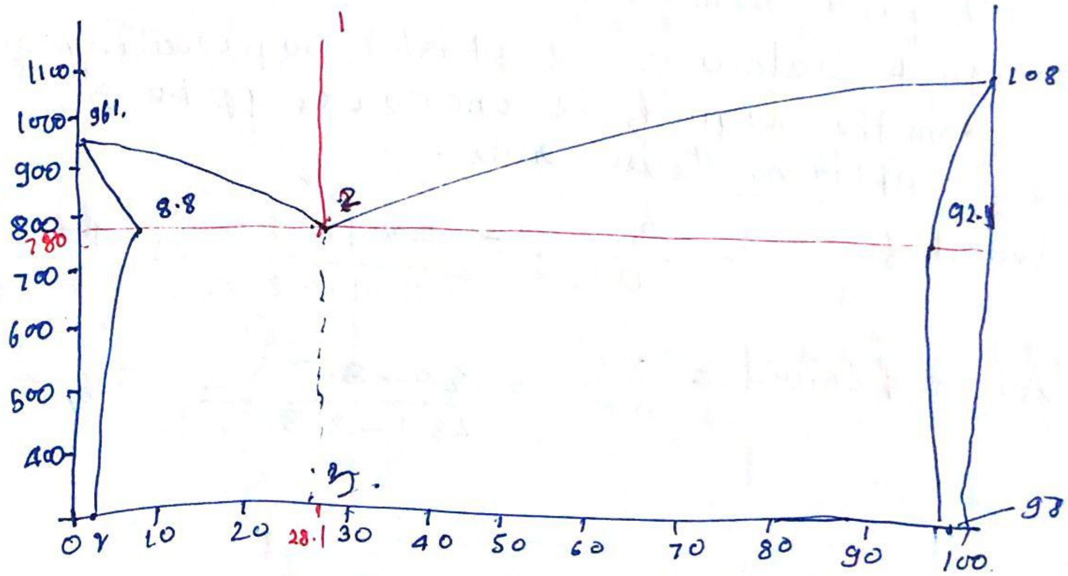
Liquid (28.1% Cu) ⟶ α (8.8% Cu) + β (92.1% Cu).

→ 


→ Below 3 the solubility of α is decreasing along D H & that of β along F K, this countinue till 4.
so α, seperates from β & β seperates from α.




III) Cooling of eutectic alloy with. 28.1 % of Cu.



Liquid (28·1% Cu) ⟶ $\alpha$ (8·8 % Cu) + $\beta$ (92·1 % Cu).

Amount of $\alpha$ = $\dfrac{92·1 - 28·1}{92·1 - 8·8}$

= 76·8 %

Amount of $\beta$ = 23·2.


At room temperature.

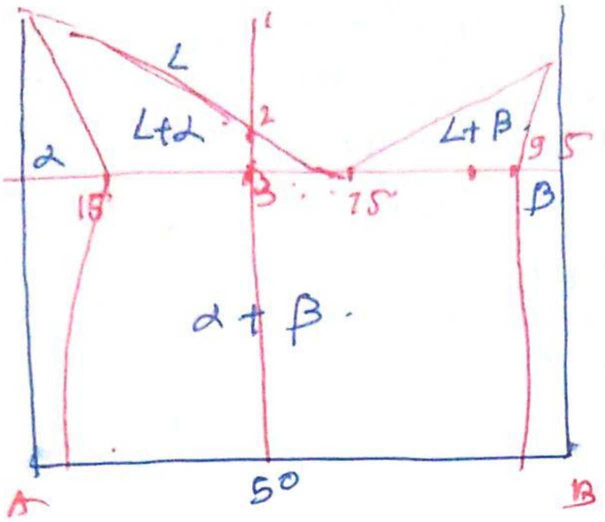
Amount of $\alpha$ = $\dfrac{98 - 28·1}{98 - 2}$

= 72·8

Amount of $\beta$ = 27·2.

iv) cooling of Hypereutectic alloy:
Similar to hypoeutectic, except replacing $\beta$ instead of $\alpha$.

a) In an eutectic alloy system A-B, the composition of the three conjugate phases of the eutectic are:
$\alpha$ = 15% B, L = 75% B & $\beta$ = 95% B.
Assuming equilibrium freezing of an alloy composed of equal parts of A & B to a temperature just below the eutectic temperature, calculate
a) Percentage of primary $\alpha$.
b) The percentage of Eutectic $\alpha$.




i) Primary α (@ 15% B) = ~~95-75~~

@ 50% of A & B @ point 3

Amount of α = $\frac{75-50}{75-15}$ = 41.67 %.

ii) Amount of eutectic @ just below 3, for that we need to find amount of liquid.

Amount of Liquid (amount of eutectic) = $\frac{50-15}{75-15}$ = 58.33 %.

∴ Percentage of α = 41.67 %.

% of α in 100 % eutectic = $\frac{95-75}{95-15}$

= 25 %.

∴ α in 58.33 % eutectic

= 58.33 × 0.25

= 14.58 %.