

Constitution of Alloys

pure metals are not employed to any great extent in engg. applications as they do not possess the required properties for some definite purpose. To meet the requirements mostly alloys are used in engg. applications. In pure metals only the atoms of the one metal are required in the ~~lattice~~ space lattice.

Alloy — ~~mixture~~ ^{combination} of two or more elements having metallic properties. Largest proportion is metal and the others are metals or non-metals.

Base metal — largest proportional element. (Parent metal).
Also called solvent.

Other elements — solute.

Binary system — combination of two elements.

Ternary system — combination of three elements.

system: part of the universe under study.
Combination of phases of one or more components.

phase: A phase is a homogeneous portion of a system having a single composition and at some physical and chemical properties through out its volume.

variables — A particular phase exists under various conditions of temp, pr. and concentration. These parameters are called as variables.

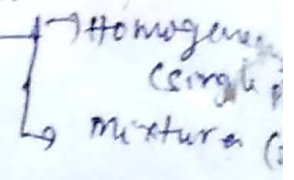
Components — elements present in the system.

Necessity of Alloying:

- ① To change the chemical composition
- ② To get increase strength, hardness etc
- ③ To change magnetic & electrical properties
- ④ To make suitable for engg. applications.

Classification of Alloys

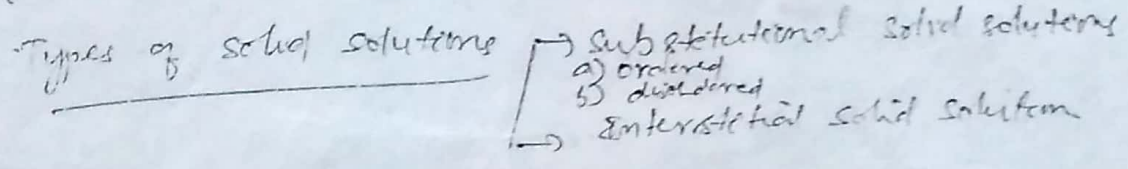
In solid phase there are three possible phases.



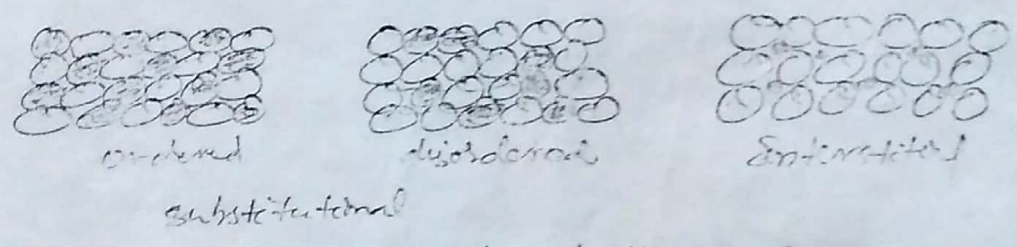
- ① pure metal
- ② Intermediate alloy phase or compound.
- ③ Solid solution.

Solid Solution : It is an alloy in which the atoms of solute are distributed in the solvent and has the same structure as that of the solvent. Thus, a solid solution ~~there are two types.~~

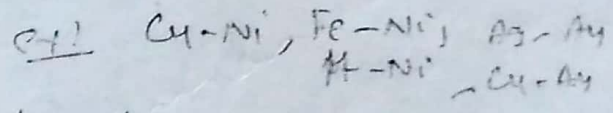
Consists of several components in a single type of crystal lattice and constitutes a single phase.



Substitutional solid solution - substitution of ^{solute} solvent atoms for certain solvent atoms in the crystal structure.



Complete regularity throughout the structure is possible only when the two metals are mixed in some fixed proportion.



Substitutional solid solution is favoured if the atomic sizes of the two metals are nearly equal, equal no. of valence electrons and the lattice pattern of two metals is same. Orderly substitutional solid solution alloys in general are hard and require more energy for plastic deformation than disordered substitutional solid solution.

Interstitial solid solution - Atoms of solute metal occupy the vacant position or interstices between the solvent atoms.

They may be favoured if the dia. of solute atoms is less than the dia. of solvent atoms. The elements which can form interstitial solid solutions are with iron are carbon, boron, oxygen, hydrogen and nitrogen.

In general solid solutions are soft, ductile and malleable. and therefore they can be easily cold rolled, pressed or worked.

Hume-Rothery's Rules of Solid Solubility

In formation of solid solutions, the solubility limit of solute in the solvent is governed by certain factors. These factors are known as Hume-Rothery's rules of solid solubility. These are -

- ① Atomic size factor - favourable if difference in radii of two ~~metal~~ atoms of two metals is less than 15%. If it is more, solid solubility is limited.
- ② Chemical affinity factor - Greater the chemical affinity of two metals, the more restricted is their solid solubility.
- ③ Relative valency factor: A metal of higher valency can dissolve only a small amount of a lower valency metal while the lower valency metal may have good solubility for the higher valency metal.
- ④ Crystal structure factor - Same crystal structure will have greater solubility. Difference in crystal structure limits the solid solubility.

Intermediate phases, when solute element is added to the solvent in such a way that the limit of solid solubility is exceeded, a second phase appears with the solid solution.

⑤ This 2nd phase may be another solid solution or an intermediate phase. This intermediate phase differs in composition.

~~These intermediate phases~~
(X) (X) These phases may have either narrow or wide ranges of homogeneity and may or may not have simple chemical formula.

Some intermediate phases have a fixed composition and they are called intermetallic compounds. Generally these intermetallic compounds are hard and brittle and have high melting points.

The intermediate phases in which the ratio of no. of free electrons to the no. of atoms is constant, are called electron compounds and they exhibit similar characteristics.

Mechanical Mixtures: Two components (which do not react chemically and miscible in solid state) will form a mechanical mixture.

- No solubility and no tendency to combine with each other. Each metal of alloy solidifies independently of the other and does not allow the other in its crystal lattice.

The final solid consists of discrete regions of the pure components, as a mechanical mixture rather than as a solid solution or compound.

~~7, 24, 32, 5A01, 4, 6~~

7, 24, 32, 5A01, 4, 6

(X) (X) as well as crystal structure from the parent metal and hence their properties are also different.

⑦ ⑧
a definite proportion, which is expressed by a chemical formula. Ex: H_2O - $NaCl$.

When a compound is formed, the elements lose their individual identity and characteristic properties to a large extent. Ex. $NaCl$.

Many types of compounds have been found in alloys, depending upon the properties of the combining elements. These compounds could be:

Chemical compounds,

Intermetallic compounds,

Interstitial compounds and

electron compounds.

Chemical compounds: - These are formed between two chemically dissimilar elements having greater chemical affinity for each other. Their compounds satisfy valency laws, and they generally show ionic or covalent bonding. They are non-metallic in properties and have poor electrical conductivity. They are brittle and have high melting points. These are also known as valency compounds.
Ex: Mg_2Si , $AlSb$, ZnS , Mg_2Sn .

Intermetallic compounds: - Some compounds which are very similar in nature to chemical compounds are called intermetallic compounds. These are characterized by high hardness, brittleness and melting point. The major difference between intermetallic and chemical compounds is that intermetallic compounds

rarely obey the laws of chemical valence, whereas chemical compounds invariably do.

Another difference is that the intermetallic compounds ~~not~~ will have metallic bonding and the valence electrons will be free to move about in the lattice.

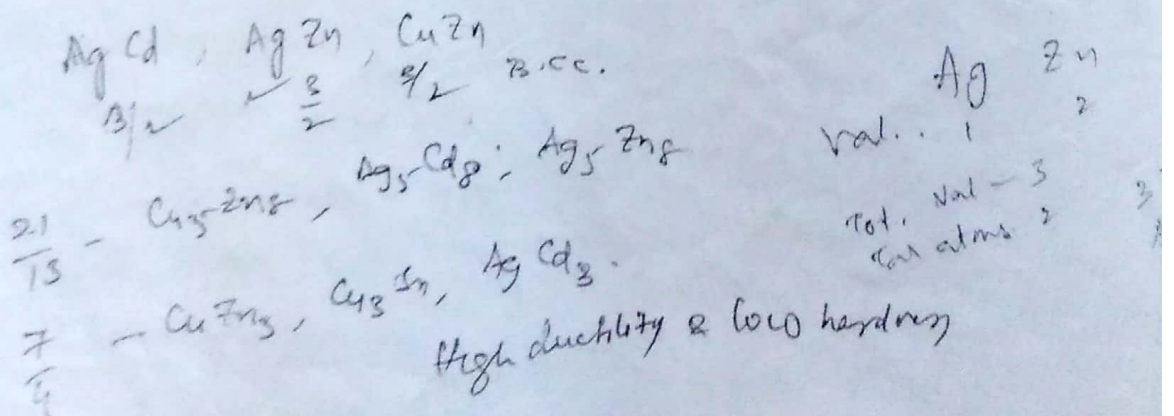
eg:
Cu₃Zn
Ag₅Zn
Ag₅Cd
Cu₃Zn

Ex: Cu₃Zn; Cu₃Al; Sn₃Sb etc.
low ductility; low electrical conductivity

Interstitial Compounds: - When the solubility of interstitial element in a solid solution is exceeded interstitial compounds are formed.

Atoms having small radii (like H, O, C, B₂) occupy interstitial positions in the lattice structures of ~~most~~ transition metals such as scandium, titanium, Ta & Fe. These are extremely hard, metallic nature and have high melting points.

Electron Compounds: In many alloys, intermediate phases of similar crystal structures are formed having a definite ratio of valence electrons to atoms. These phases are called electron compounds. The valence electrons to atom ratios at which they are formed, are 3:2, 21:13 & 7:4.



EQUILIBRIUM DIAGRAMS.

Gibb's phase Rule: It states that under equilibrium conditions, the following condition must be satisfied:

$$P + F = C + 2$$

Where P = no. of phases existing in a system
 F = degree of freedom, i.e. the no. of variables such as temp. or concentrations that can be changed independently without changing the no. of existing phases

C = no. of components (elements) in the system.

2 = represents any two variables out of the three i.e., temp, P & concentrations.

Most of the studies are done at const. P . and hence P is no more a variable. In such conditions, Gibb's phase rule becomes

$$P + F = C + 1$$

Polymorphism: Many substances exist in more than one crystalline form. The various forms have the same composition but different crystal structures.

Change in crystal structure is observed due to either change in P , or temp. or both. Such a change of structure is called polymorphism.

- This is observed in pure elements as well as in chemical compounds.

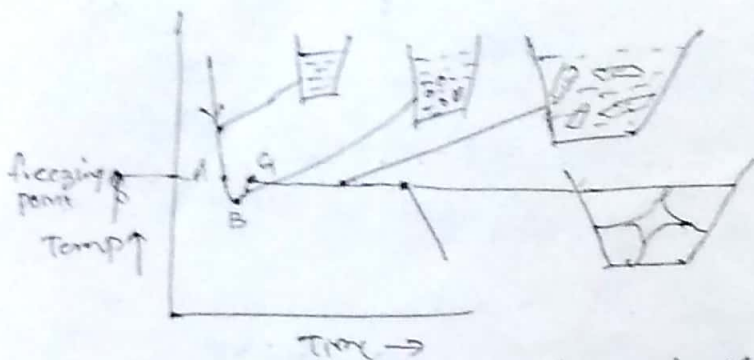
Allotropy: If the polymorphism ^{of metals} is reversible, i.e. transformation of structure is reversible then with change in temp. or P then it is called allotropy of metals.

The polymorphs have different densities and mechanical ^{prop.} ~~prop.~~

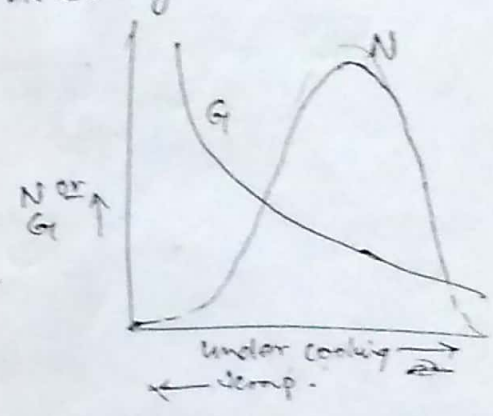
Properties: ex: Iron upto 910°C - BCC, α -iron
 911°C to 1400°C - FCC, γ -iron
 1400 - 1539 (M.P.) - BCC, δ -phase

Solidification — a) Nucleation and b) Growth

Two steps
 ① Nucleation (N)
 ② Grain growth (G)



Some degree of undercooling is necessary to start solidification (i.e., nucleation). The extent of undercooling (temp. A - temp. B) varies from metal to metal and also depends on the impurities present in the metal.



Types of cooling curves:

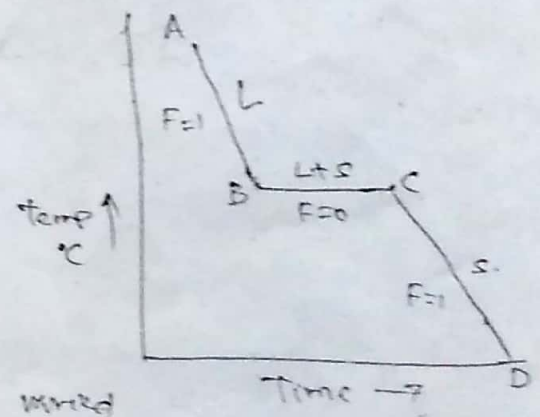
① Cooling curve for pure metals: A typical cooling curve of pure metals is shown in fig.

freezing starts at B and completes at C.

Application of phase rule in various regions:

i) In region AB
 $P + F = C + 1$
 $1 + F = 1 + 1 \Rightarrow F = 1$

That means, the temp. can be varied without changing the liquid phase existing in the system.



ii) BC
 $P + F = C + 1$
 $2 + F = 1 + 1 \Rightarrow F = 0$

i.e., temp cannot be varied without changing the liquid and solid phases existing in the system. If temp is increased, the metal goes into the liquid state and if decreased it goes into the solid state. Hence pure metals solidify at const. temp.

iii) CD

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

i.e. temp. can be varied without changing the solid phase existing in the system.

② Cooling curve for binary solid solution alloys

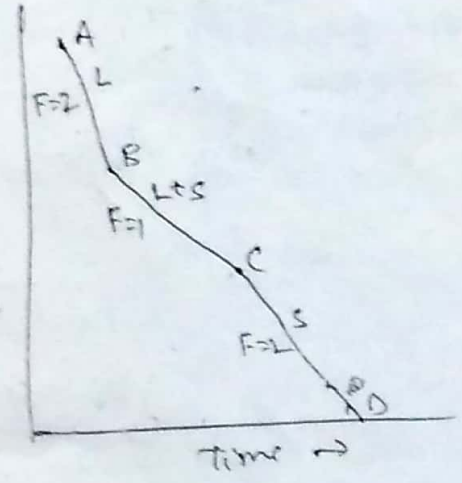
Application of phase rule:

i) AB

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

i.e., both temp. & concentration can be varied independently without changing the liquid phase existing in the system.

temp. ↑
°C



ii) BC

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

i.e., any one variable out of temp. & composition can be changed independently without changing the liquid and solid phases existing in the system.

Therefore solid solution alloys solidify over a range of temp. i.e., melting starts at one temp. and finishes at another temp.

iii) CD

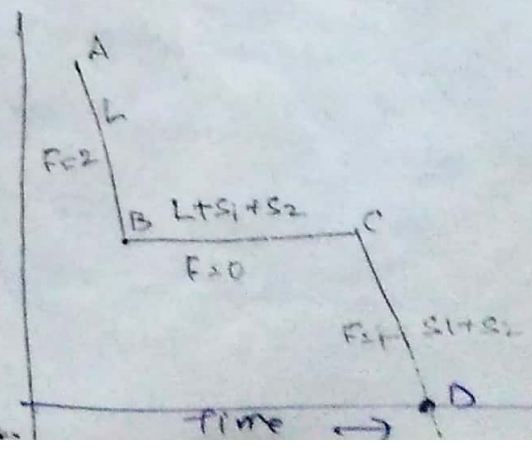
$P + F = C + 1$
 $1 + F = 2 + 1 \Rightarrow F = 2$

therefore $F=2$ is already explained in (i).

③ Cooling curve for binary eutectic alloys

Freezing starts at B and simultaneously two solids S_1 & S_2 start separating out from the liquid. This continues upto E and gives a mixture of S_1 & S_2 .

Temp ↑
°C



3 Arts. $P + F = C + 1$
 $1 + F = 2 + 1 \Rightarrow F = 2$ - bivariant system

ii) BC

$$P + F = C + 1$$

$$3 + F = 2 + 1 \Rightarrow F = 0$$
 - Nonvariant or univariant system

hence, eutectic alloys solidify at const. temp. similar to that of pure metals.

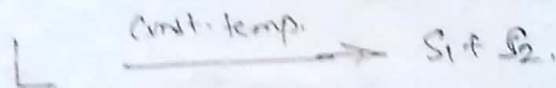
iii) CD

$$P + F = C + 1$$

$$2 + F = 2 + 1 \Rightarrow F = 1$$
 - univariant system

Binary eutectic is a homogeneous mixture of two solids which forms at const. temp. during cooling and melts at const. temp. during heating.

Binary eutectic transformation can be shown as below:



The temp. at which this transformation occurs is called eutectic temp. and is the lowest temp. of transformation in the system.

④ Cooling Curve for Off-eutectic binary alloys:

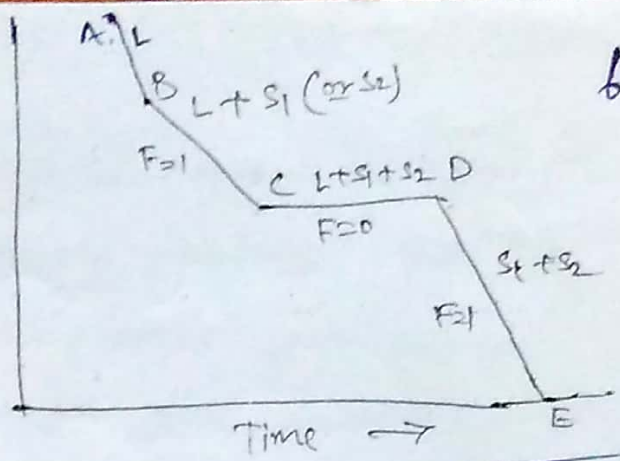
eutectic transformation occurs for a definite composition called eutectic composition. If the composition of the alloy differs from it, it is called off-eutectic alloy.

Off-eutectic alloys are of either hypoeutectic or hypereutectic type.

Hypo eutectic alloys have compositions less than the eutectic composition while hypereutectic alloys have compositions more than the eutectic composition.

A typical cooling curve of such alloys is shown in Fig.

from the liquid depending on whether alloy is eutectic or hypoeutectic. this continues upto C. the remaining liquid at C solidifies at const. temp. and forms a mixture of S_1 & S_2 .



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Phase rule:

- i) AB $P+F=C+1$
 $1+F=2+1 \Rightarrow F=2$ — bivariant.
- ii) BC $P+F=C+1$
 $2+F=2+1 \Rightarrow F=1$ — univariant.
- iii) CD $P+F=C+1$
 $3+F=2+1 \Rightarrow F=0$ — invariant.
- iv) DE $P+F=C+1$
 $2+F=2+1 \Rightarrow F=1$ — univariant.

Freezing starts at B and either S_1 or S_2 separates out.

liquidus temp. — start of solidification temp. Above this, alloy is in liquid state.

solidus temp. — end of solidification temp. Below this, the alloy is in the solid state.

Plotting of equilibrium diagrams:

- can be plotted by using several techniques like thermal analysis, dilatometry, optical & electron microscopy, x-ray and electron diffraction etc.

- Most of the times, equilibrium or phase diagrams are plotted by the method of thermal analysis using the data obtained from cooling curves.

The basic method of plotting the diagrams by the use of cooling curves is explained below.

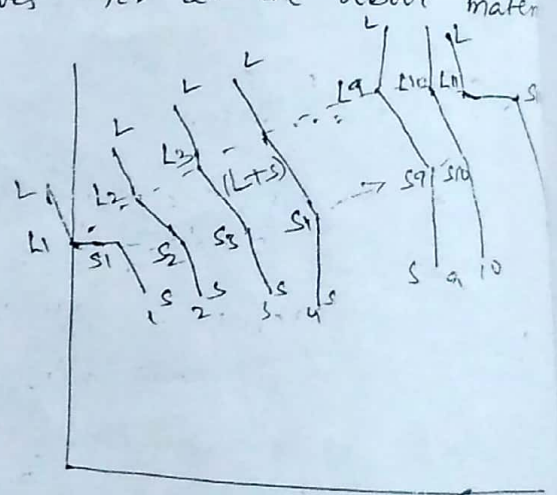
Let us consider a binary Cu-Ni system. Cu & Ni 100% solubility in the liquid and solid states they form series of solid solutions. Following steps are used to obtain 100 equilibrium.

Step 1) prepare large no. of alloys of varying compositions with a variation of 10% Ni and name them as below

% Cu	100	90	80	70	60	50	40	30	20	10	0
% Ni	0	10	20	30	40	50	60	70	80	90	100
Mat. no.	1	2	3	4	5	6	7	8	9	10	11

Nos 1 & 11 are pure metals and 2-10 are alloys.

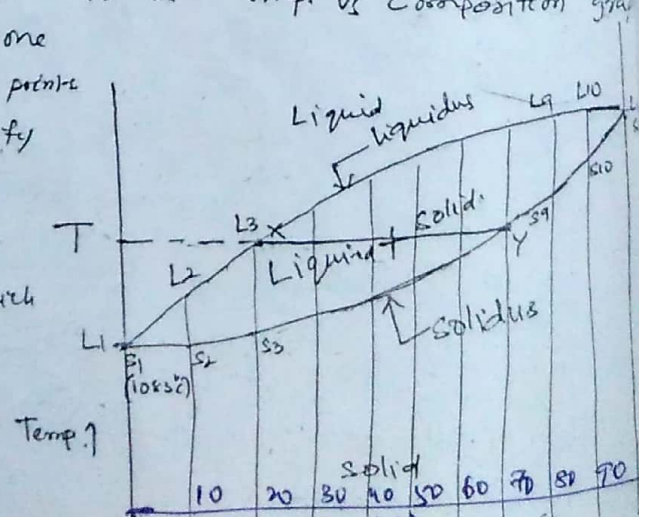
Step 2: plot cooling curves for all the above materials



Step 3) Note down the liquidus and solidus temps. of these materials. Liquidus temps are $L_1, L_2, L_3, \dots, L_9, L_{10}, L_{11}$ and solidus temps are $S_1, S_2, S_3, \dots, S_9, S_{10}, S_{11}$.

Since 1 & 11 are pure metals $L_1 = S_1$ & $L_{11} = S_{11}$.

Step 4) Transfer these temps. to a temp. vs composition graph. For pure Cu & Ni, we get only one point and for others we get two points because solid solution alloys solidify over a range of temp.



Step 5) Draw smooth curves thru the points L_1 to L_{11} and S_1 to S_{11} which represent liquidus & solidus.

The resulting loop type of curve is called phase or equilibrium diagram.

At any point T, the average composition of the existing liquid is X and that of solid is Y. The amount of solid and liquid can be calculated by the lever rule.

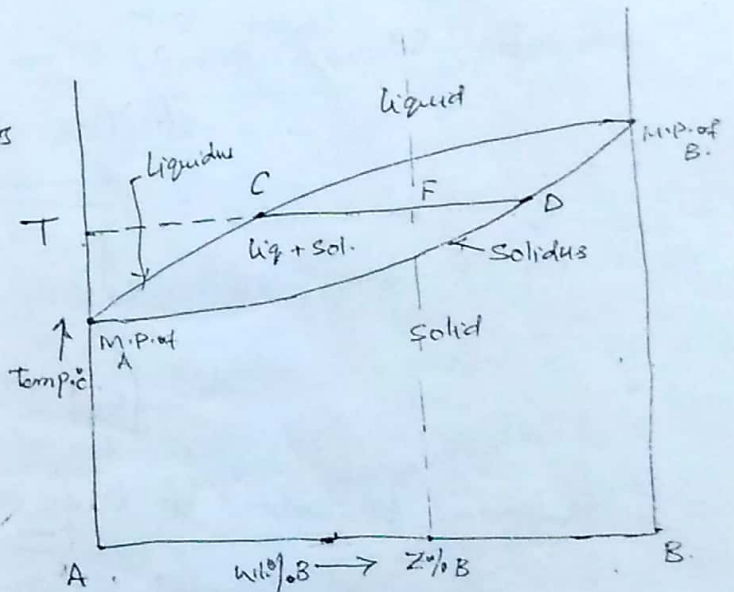
Lever Rule: - Used for finding out the amounts of phases existing in a binary system for a given alloy at any temp. under consideration.

Let us consider an isomorphous system of two metals A & B. Let Z be the composition of the alloy and T be the temp. at which the amounts of phases are to be found out.

At temp. T, the existing phases are solid and liquid.

Let S = amount of solid

L = amount of liquid
 = (1-S) if the total amount = 1



The amount of B in the alloy = Amount of B in the solid + Amount of B in the liquid

the amount of B in the phase (i.e. liq. or sol.) = the amount of phase × composition in terms of B.

At temp. T, the composition of solid is D and the composition of liquid is C.

$$\therefore Z = S \cdot D + (1-S) \cdot C$$

$$= SD + C - SC \Rightarrow S(D-C) + C$$

$$\therefore Z - C = S(D - C)$$

$$\therefore S = \frac{Z - C}{D - C} = \frac{F - C}{D - C} = \frac{\text{arm length CF}}{\text{arm length CD}}$$

$$\therefore S = \frac{\text{Opposite length of arm}}{\text{Total length of arm}}$$

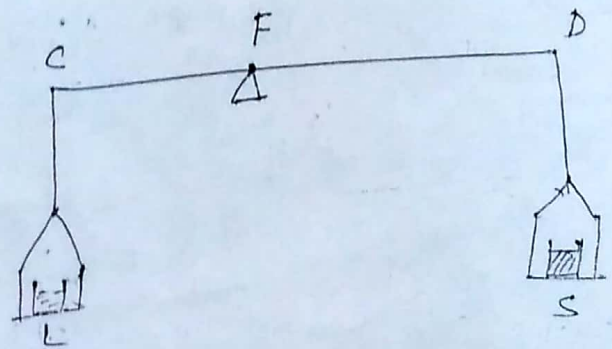
and $L = 1 - S = 1 - \frac{\text{arm length CF}}{\text{arm length CD}} = \frac{\text{arm length FD}}{\text{arm length CD}}$

= ~~Opposite~~ length of arm / total length of arm

$$\therefore \frac{\text{Amount of solid}}{\text{Amount of liquid}} = \frac{C}{L} = \frac{\text{arm CF} / \text{arm CD}}{\text{arm FD} / \text{arm CD}}$$

$$= \frac{\text{arm CF}}{\text{arm FD}}$$

\therefore Amount of solid \times arm FD = amount of liq. \times arm CF
 i.e., the line CD acts as a lever arm and the point F acts as a fulcrum point. Hence it is called lever arm principle or lever rule.



$$\therefore \text{Amount of solid} \times \text{its lever arm} = \text{Amount of liquid} \times \text{its lever arm.}$$

At any other temp., the amounts of solid and liquid phases can be determined in a similar manner. The rule also holds good for other phases such as $\alpha + \beta$ or $\beta + \gamma$ and is not restricted only to solid and liquid phases.

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Common types of phase diagrams (see backside of page 9)

- Depending on the solubility of one metal into the another in liquid and solid states, phase diagrams are classified as:

- 1) Isomorphous systems
- 2) Eutectic systems
- 3) partial eutectic systems.
- 4) Layer type systems.

Isomorphous systems (Two metals completely soluble in the liquid and solid states):-

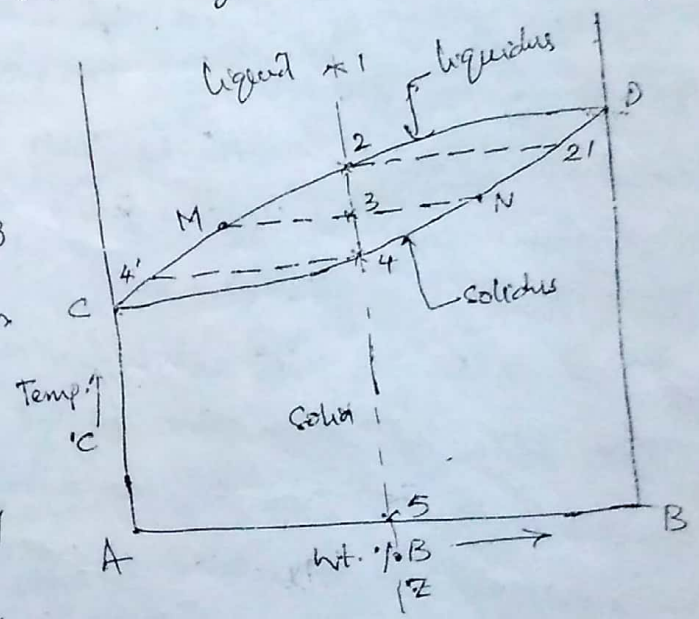
Examples: Copper-Nickel (Cu-Ni), Bismuth-Antimony (Bi-Sb), Au-Ag, Au-Cu, Mo-W, Mo-V, Mo-Ti, W-V, Au-Ni etc.

A typical diagram for such a system is shown in fig.

C - melting point of A
D - melting pt. of B.

Cooling of an alloy with Z% B

- i) 1-2 - liquid state: NO changes
- ii) At just below 2, solidification starts and solid phase starts separating out from the liquid.
- iii) At 4 - end of solidification.
- 2-4 - solid + liquid.



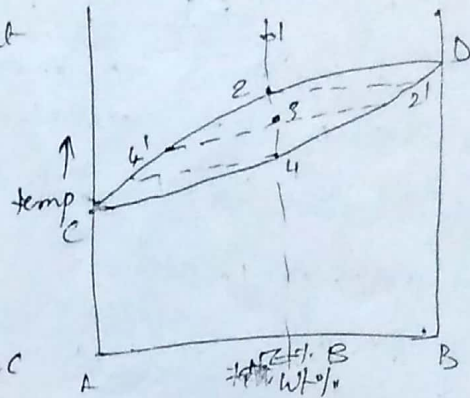
At any temp. under consideration, amounts of solid and liquid phases can be obtained by applying lever rule.

At 3, average composition of the existing liquid is - M
and average composition of the existing solid is - N.

Amount of liquid of composition M (% B) = $\frac{\text{length } 3N}{\text{length } MN}$
 NO change occurs between 4 to 5.

CORING → Variation in composition is observed from point to point or centre to surface of a grain in a solidifying alloy at room temp. This microsegregation is called coring.

The first solid which separates out from the liquid at pt 2 has a composition given by the pt 2'. As the temp. decreases, the average composition of the existing solid changes along the solidus line D4C



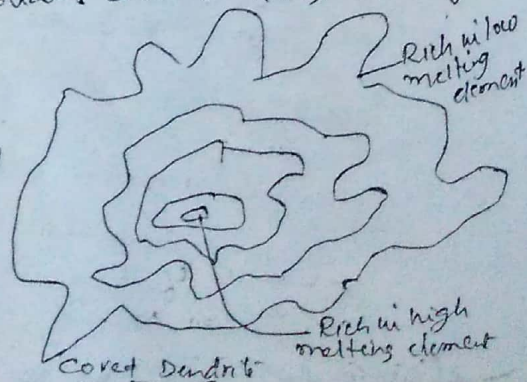
and that of liquid along the liquidus line D2C. At pt 4 last liquid solidifies. Therefore, the composition of last liquid which solidifies at 4 is given by the pt 4'. Hence the last solid formed has a composition corresponding to pt 4'.

This shows that, the first solid i.e., centre of grain or dendrite will be rich in B and the last solid i.e., surface will be rich in A. However, the average composition of the grain or dendrite will be the same as the original.

Due to the inability of the alloy for continuous adjustments in compositions of the phases required for equilibrium solidification, concentration differences are observed in the structure at room temp. such structures are called Cored structures.

The extent of coring increases with increasing separation of liquidus and solidus curves i.e., in alloys with a wide freezing range.

Coring is seen under optical microscope by colour differences developed through an etching effect.



Coring is common in cast components of some alloys like brasses, bronzes and stainless steels and is not desirable due to the following reasons:

- i) It increases brittleness.
- ii) It is non-uniform mech. & physical properties.
- iii) It increases susceptibility to corrosion.

Therefore coring is eliminated by either of the following methods:

① By using slow cooling rates during solidification of alloy.
 On this method, the composition will be adjusted by diffusion. Drawbacks - ① Because of slow cooling, grain size is become large resulting in inferior mech. properties.
 ② Rate of production is low.

② By homogenization heat treatment to the cored castings
 Alloy castings are heated to a temp. just below the solidus temp. and held there for a long time for diffusion. The time of heat treatment depends on the temp. at which the process is carried out. Higher the temp., faster will be the diffusion and lesser will be the time required. ~~temp~~ However in no case, the temp. should exceed the solidus temp. of the alloy.

$2/4 \cdot 18/8/2$	$9/4 \cdot 27/3$
1, 24, 37, 40, 52,	13, 14, 24, 37, 38, 41, 43,
	6.

Classification of phase Diagrams

1. Components completely soluble in the liquid state and
 - a. completely soluble in the solid state (Type I)
 - b. Insoluble in the solid state; The eutectic reaction (Type II)
 - c. partially soluble in the solid state; The eutectic reaction (Type III)
 - d. Formation of a congruent melting intermediate (Type IV)
 - e. The peritectic reaction (Type V)
2. Components partially soluble in the liquid state (The monotectic reaction - Type VI)
3. Components insoluble in the liquid state and insoluble in the solid state (Type VII)
4. Transformations in the solid state.
 - a) Allotropic change
 - b) Order-Disorder
 - c) The eutectoid reaction
 - d) The peritectoid reaction.

Eutectic Systems:-

- Two metals having complete solubility in the liquid state and complete insolubility in the solid state.

Ex: Pb-As, Bi-Cd, Th-Ti & Al-Si, ~~Pb-Zn~~ ~~Sn-Zn~~ ~~Al-Si~~

C - M.P. of A

G - M.P. of B

On adding A to B or B to A, the melting temp. is lowered along the line CE & GE respectively.

E - eutectic point i.e. lowest temp. at which mixture of A & B melts.

CEG - liquidus line
CDEFG - solidus line

- eutectic transformation takes place along DF except at D & F.

- The temp at E → eutectic temp.
- the composition at E - eutectic composition.

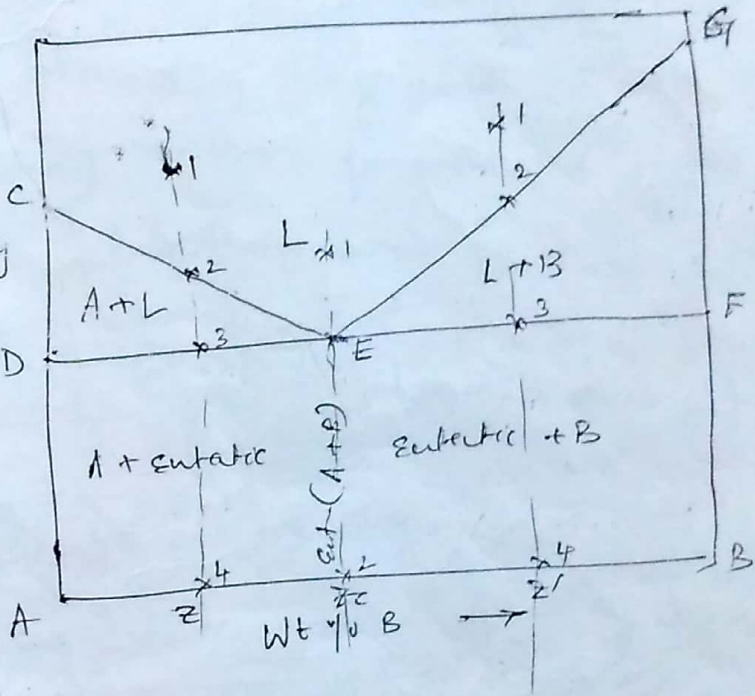
(*) the cooling of hypoeutectic alloy with Z% B. A lot

i) 1 to 2 - no change.

Just below 2, - A separates out from the liquid and solidified.

Further cooling increases the amount of A. This continues upto 3.

The composition of liquid varies along the liquidus line CE and the composition of it does not change (*)



(*) because of no solubility of B in A.

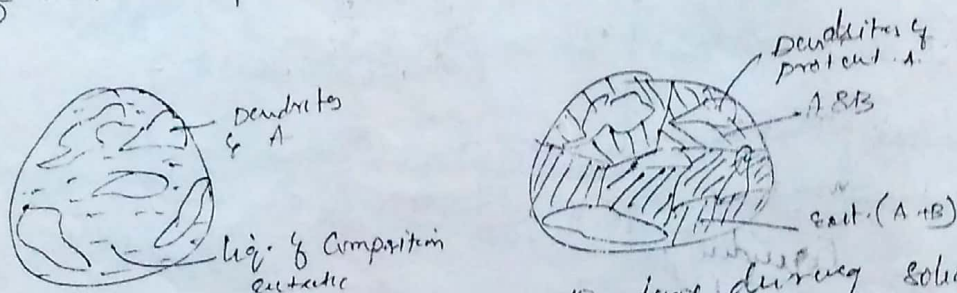
At just above 3
 the amount of A = $\frac{BE}{DE}$

and the amount of liquid = $\frac{DB}{DE}$ or $(1-A)$
 (of composition E)

The phase A which has separated before the eutectic transformation is called proeutectic or free or primary A.

ii) At 3, the liquid of eutectic composition of amount $\frac{DB}{DE}$ solidifies at const. temp. and transforms to an eutectic mixture of A & B.

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



change in structure during solidification of a hypoeutectic alloy

The alloy completely solidifies at 3. The amount of eutectic will be same as the amount of liquid $\frac{DB}{DE}$.

iii) 3 to 4 = no change occurs in the structure.

The total A in the alloy which is 1-2 will be equal to the proeutectic A plus A in the existing eutectic.

Amount of A in the existing eutectic

$$= A \text{ in the eutectic} \times \text{amount of eutectic}$$

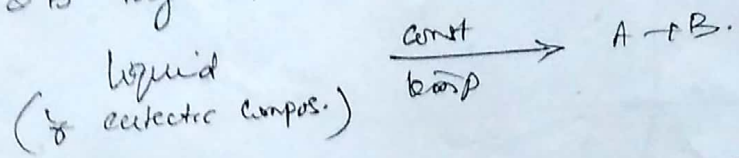
$$= \frac{EF}{DF} \times \frac{DB}{DE}$$

$$\therefore 1-2 = \frac{BE}{DE} + \frac{EF \times DB}{DF \times DE}$$

ii) Cooling of an eutectic Alloy with $z < E\%$ B :-

From 1 - E \rightarrow No change

At just below E \rightarrow the liquid of eutectic composition freezes at const. temp. and gives an uniform lamellar mixture of A & B by an eutectic transformation.



the microstructure change is shown in fig



From E to 2 — NO change

iii) Cooling of a hypoeutectic alloy

From 1 - 2 \rightarrow NO change

Just below 2 \rightarrow B separates out. As temp \downarrow - amount of B \uparrow .

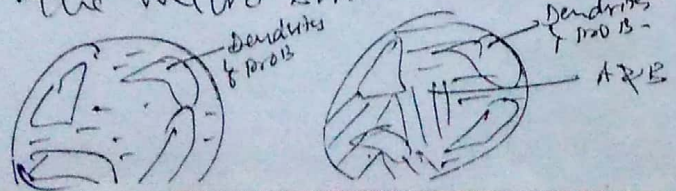
The liquid composition is varied along EG and solid will vary along the line GF. Since GF is a vertical line due to complete insolubility of A in B, B composition does not change.

this continues upto 3.

At 3, the amount of liquid (of eutec. compos) = $\frac{3F}{EF}$

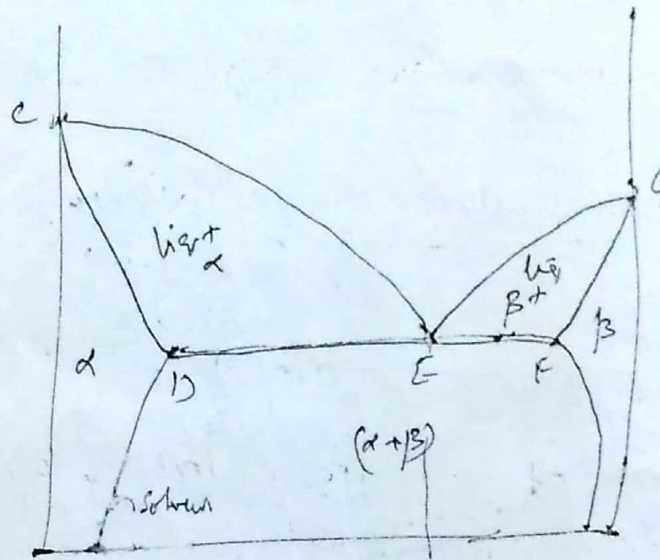
and the amount of B = $\frac{ES}{EF} = 1 - \frac{3F}{EF}$

the micro structure is shown below.



At 3, the liquid $\frac{3F}{EF}$ solidifies at const. temp. and forms A + B.

From 3-4 - NO change.



7/4-1913
 1, 3, 5, 6, 7, 11, 13, 14, 15, 20,
 23, 24, 27, 29, 30, 31, 32, 34,
 35, 36, 37, 38, 41, 43, 45, 47,
 51, 52, 54, 56, 58.
5, 6

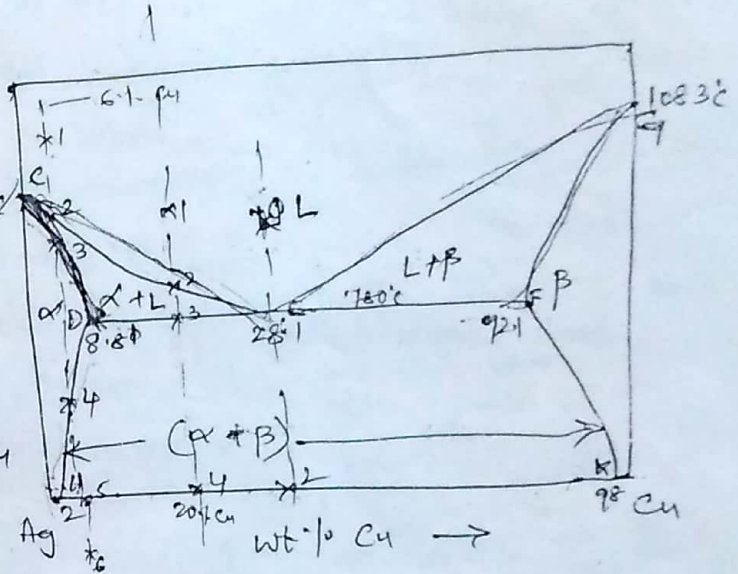
partial Eutectic systems :-

- Two metals which have complete solubility in the liquid state and partial solubility in the solid state.

Ex: Ag-Cu, Pb-Sn, Sn-Bi, Pb-Sb, Cd-Zn and Al-Si.

A typical phase diagram for such a system is shown in fig. for Ag-Cu system.

C - m.p. of Ag
 G - m.p. of Cu
 CEG - liquidus line
 CDEFG - solidus line
 E = eutectic point. Temp
 eutectic temp = 780°C
 eutectic composition = 28.1% Cu



~~phase~~
 α - solid solution of Cu in Ag
 β - solid solution of Ag in Cu
 H - solubility of Cu in Ag at room temp. - 2% Cu
 K - solubility of Ag in Cu at room temp. - 2% Ag
 D - max. solubility of Cu in Ag at eutectic temp. - 8.8% Cu
 F - max. solubility of Ag in Cu " " " " - 7.9% Ag

As the temp. decreases from the eutectic temp. to room temp, the solubility of Cu in Ag and that of Ag in Cu, decreases from D to H & F to K along the lines DH & FK respectively.

DH & FK - solvus lines.

1) Cooling of an Alloy with 6% Cu:

- a) 1-2 - no change occurs.
- b) just below 2, - α starts separating out from the liquid.
 - As the temp. decreases, the amount of α increases.
 The composition of α varies along the solidus line CD

And the composition of liquid varies ~~along~~ ^{the} along the liquidus line CE.

c) At 3, last liquid solidifies and gives 100% α solid solution. the microstructure is shown below.

d) 3-4 - no change occurs in the structure.



e) Below 4, the solubility of Cu in Ag which is indicated by α -solvus line i.e., line DH is less than 6%. As the alloy contains 6% Cu and therefore during cooling below 4, Cu separates out from α in the form of β solid solution.

Cu cannot separate out as pure Cu because of some solubility of Ag in Cu in the solid state. As temp. decreases, amount of β increases and this continues upto room temp. upto 5.

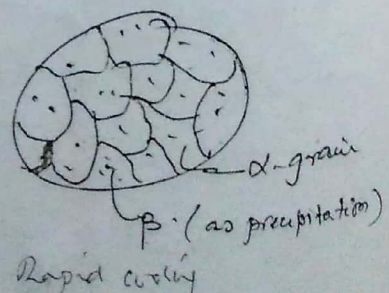
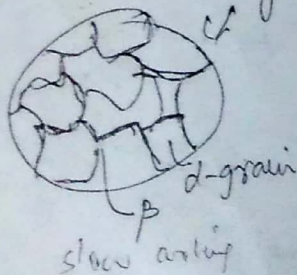
At room temp:

$$\text{Amount of } \alpha \text{ (of 20\% Cu)} = \frac{5K}{4K} = \frac{98-6}{98-2} = \frac{92}{96} = 95.8\%$$

$$\text{and Amount of } \beta \text{ (of 98\% Cu)} = \frac{H5}{HK} = \frac{6-2}{98-2} = \frac{4}{96} = 4.2\%$$

This β may appear at the grain boundaries of α or may get entrapped in the grains, depending on the cooling rate. ~~Chances~~ ^{Slower the cooling,} Chances of β to appear at the grain boundaries are higher.

The microstructure under slow cooled condition is shown in fig.



Rapid cooling suppresses the separation of β and the structure becomes similar to earlier but becomes supersaturated. This super saturated structure gives β precipitate in α -grain at elevated temps, as shown in fig.

11) Cooling of hypo eutectic alloy with 20% Cu =

a) 1-2 — NO change.

b) At just below 2 — α starts separating out from the liquid.

As the temp. decreases, the amount of α increases and this continues up to 3.

The composition of α changes along the line CD and the composition of liquid changes along the line CE.

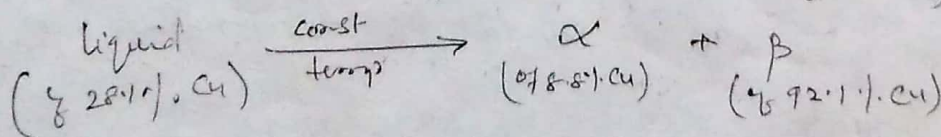
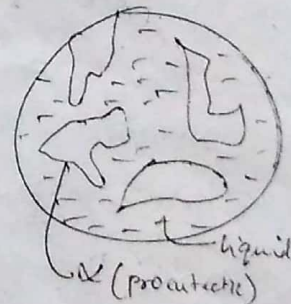
Applying lever rule at 3,

$$\text{Amount of } \alpha \text{ (of 88\% Cu)} = \frac{3E}{DE} = \frac{28.1 - 20}{28.1 - 8.8} = \frac{8.1}{19.3} = 42\%$$

$$\text{Amount of liquid (of 28.1\% Cu)} = \frac{D3}{DE} = \frac{20 - 8.8}{28.1 - 8.8} = \frac{11.2}{19.3} = 58\%$$

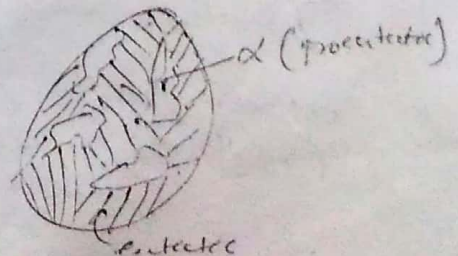
The microstructure is shown below.

c) At 3, this liquid of eutectic composition solidifies at const. temp. and transforms to an eutectic mixture of α & β .



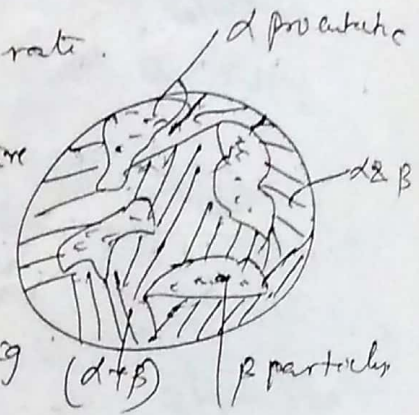
The microstructure is shown below.

d) Below 3, the solubility of α is decreasing along the line DH and that of β along the line FK.



Due to this, β separates out from α and α separates out from β . This continues upto 4.

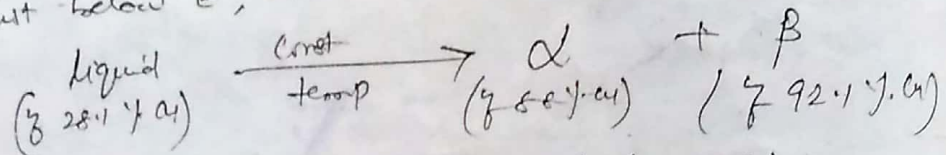
i.e., from proeutectic α , β separates out and thus β may appear at grain boundaries or inside the grains depending upon the cooling rate. Therefore, at room temp, microstructure may show particles of β in the proeutectic α along with the eutectic mixture of α & β as shown in fig.



iii) Cooling of eutectic alloy with 28.1% Cu:

a) 1-E — NO change.

b) At just below E, —



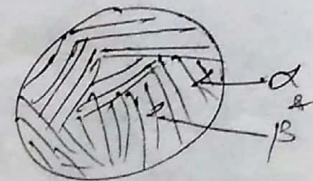
The amount of α & β in the eutectic are:

$$\text{Amount of } \alpha \text{ (78.8\% Cu)} = \frac{EF}{DF} = \frac{92.1 - 28.1}{92.1 - 8.8} = \frac{64}{83.3} = 76.8\%$$

$$\text{Amount of } \beta \text{ (92.1\% Cu)} = \frac{DE}{DF} = \frac{28.1 - 8.8}{92.1 - 8.8} = \frac{19.3}{83.3} = 23.2\%$$

The microstructure is shown below —

c) E-2 — NO change in the structure except slight changes



in the amounts of α & β in the eutectic mixture due to changes in solubilities of α & β with decreasing temp.

Amount of α & β in the eutectic at room temp are:

$$\text{Amount of } \alpha \text{ (72\% Cu)} = \frac{2K}{HK} = \frac{98 - 28.1}{98 - 2} = \frac{69.9}{96} = 72.8\%$$

$$\text{Amount of } \beta \text{ (98\% Cu)} = \frac{HJ}{HK} = \frac{28.1 - 2}{98 - 2} = \frac{26.1}{96} = 27.2\%$$

iv) Cooling of hypereutectic alloys:

14

The microstructural changes during cooling of hypereutectic alloys are very much similar to that of hypoeutectic alloys except that the proeutectic phase will be β instead of α .

Layer Type Systems:- these are obtained for two metals which have complete miscibility in the liquid as well as solid state

Ex: Cu-Mo ; Cu-W ; Ag-W ; Ag-Fe etc

C = M.P. of A
D = M.P. of B

Cooling of an alloy with z% B

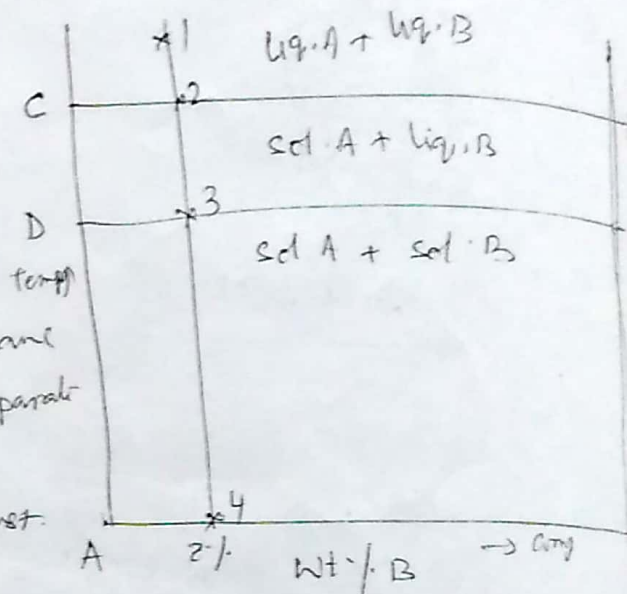
1-2 - no change. Both are in liq. state as separate liquids.

2 - liq. A solidify at const. temp.

2-3 → solid A + liq. B remains

At 3 - liq. B solidifies separately at const. temp.

3-4 - no change. solid A + solid B.

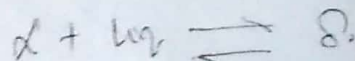


Peritectic System

① Alloy 1: (75% Pt, 25% Ag) alloy

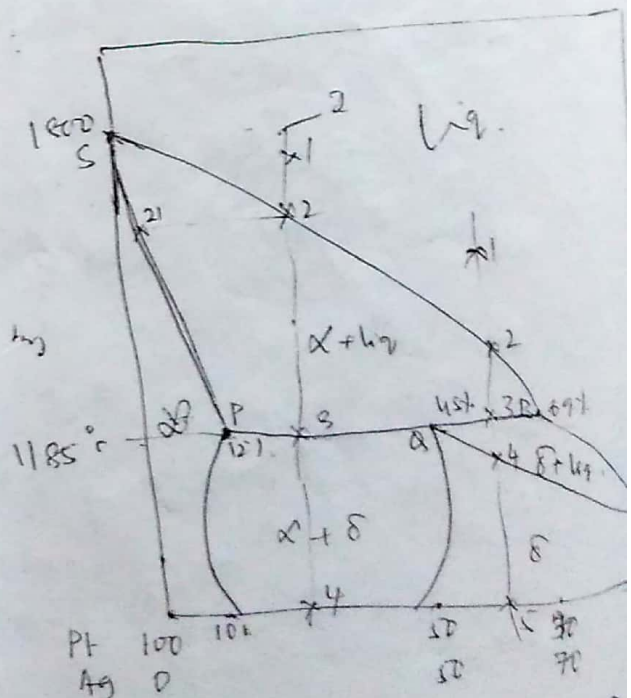
1-2 - no change
At 2 - α - cooling out. The composition of α is given by 2'. This continues until 1185°C.

At pt. 3 (1185°C), peritectic reaction takes place



At 2, α has 12% Ag, δ has 45% Ag.

below 3 α + δ



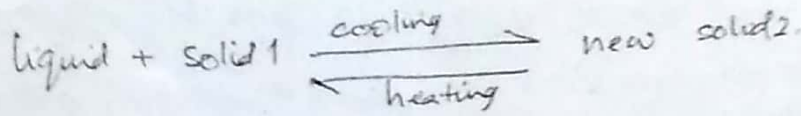
② Alloy 2: (55% Ag + 45% Pt)

1-2 - no change
below 2 - α + liq. upto 3
At 3. Peritectic reaction takes place

③ Alloy 3: (100% Pt) alloy

The peritectic Reaction :

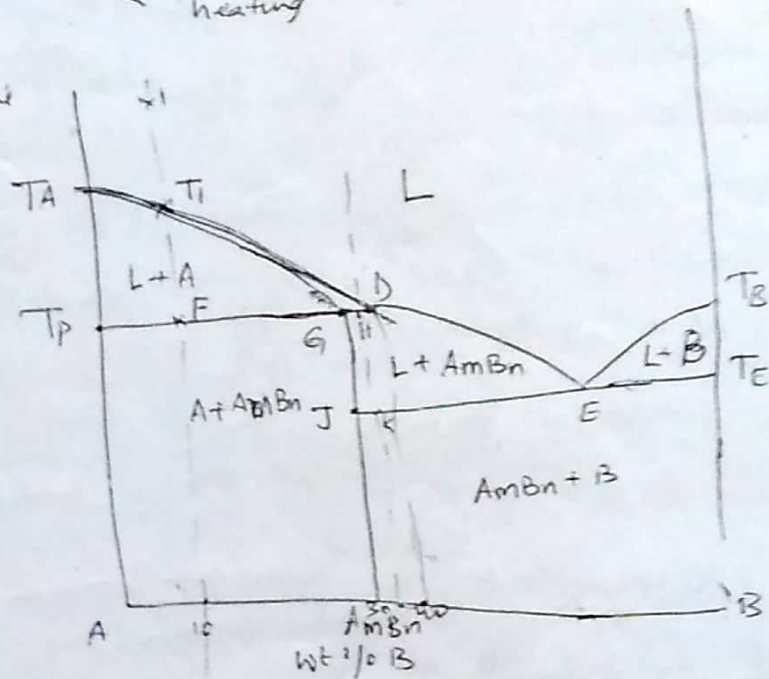
In this, a liquid and a solid react isothermally to form a new solid on cooling.



$T_A D E T_B$ - liquidus line

$T_A T_p G J T_C T_B$ - solidus line

$T_p D$ - peritectic reaction line



The new solid formed is usually an intermediate phase, but in some cases it may be a terminal solid solution.

Eg. shows that the compound $AmBn$ when heated to the peritectic temp. point G , decomposes into two phases, liquid and solid A . Therefore this is an example of an incongruent-melting intermediate alloy.

The peritectic reaction is just the reverse of the eutectic reaction, where a single phase forms two new phases on cooling.

Alloy -1

1 - T_i - No change.

Just below T_i - solidification starts and A separates out from the liquid

As the temp. falls, the liquid is decreasing in amount, and its composition is moving down along the liquidus line TAD

At just above the peritectic temp, T_p
 the phases are liquid and solid A

the amount of liquid = $\frac{T_p F}{T_p D} = \frac{10}{40} = 0.25 = 25\%$

the composition of liquid = 60A - 40B

the amount of solid = $\frac{F D}{T_p D} = \frac{3}{4} = 75\%$

the composition of solid = 100A

The conditions that exist just below the peritectic temp. T_p are

phases — AmBn and A

the amount of AmBn — $\frac{T_p F}{T_p G} = \frac{10}{30} = 33\%$

the composition of AmBn — 70A - 30B

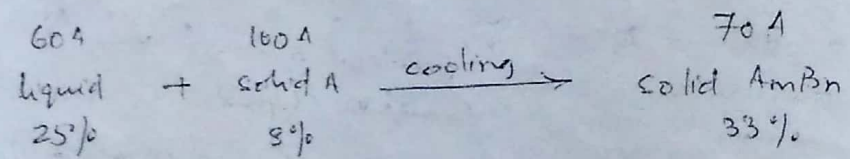
the amount of A — $\frac{T_p G}{T_p G} = 67\%$

the composition of A — 100A

i.e. The liquid at the horizontal line has disappeared and the compound AmBn is formed.

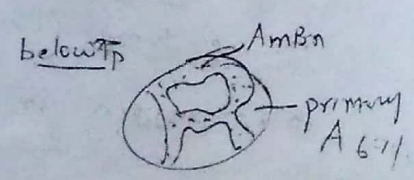
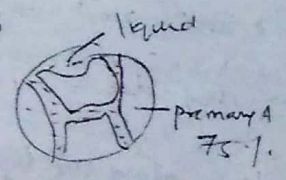
However if we consider the chemical compositions as above, this is not possible. The liquid contains 60A, while AmBn contains 70A. The liquid is not rich enough in A to form the compound by itself. The liquid must therefore react with just the right amount of solid A, hence it is so to bring its composition to that of the compound AmBn.

The following reaction must have taken place at the peritectic temp



The microstructure is

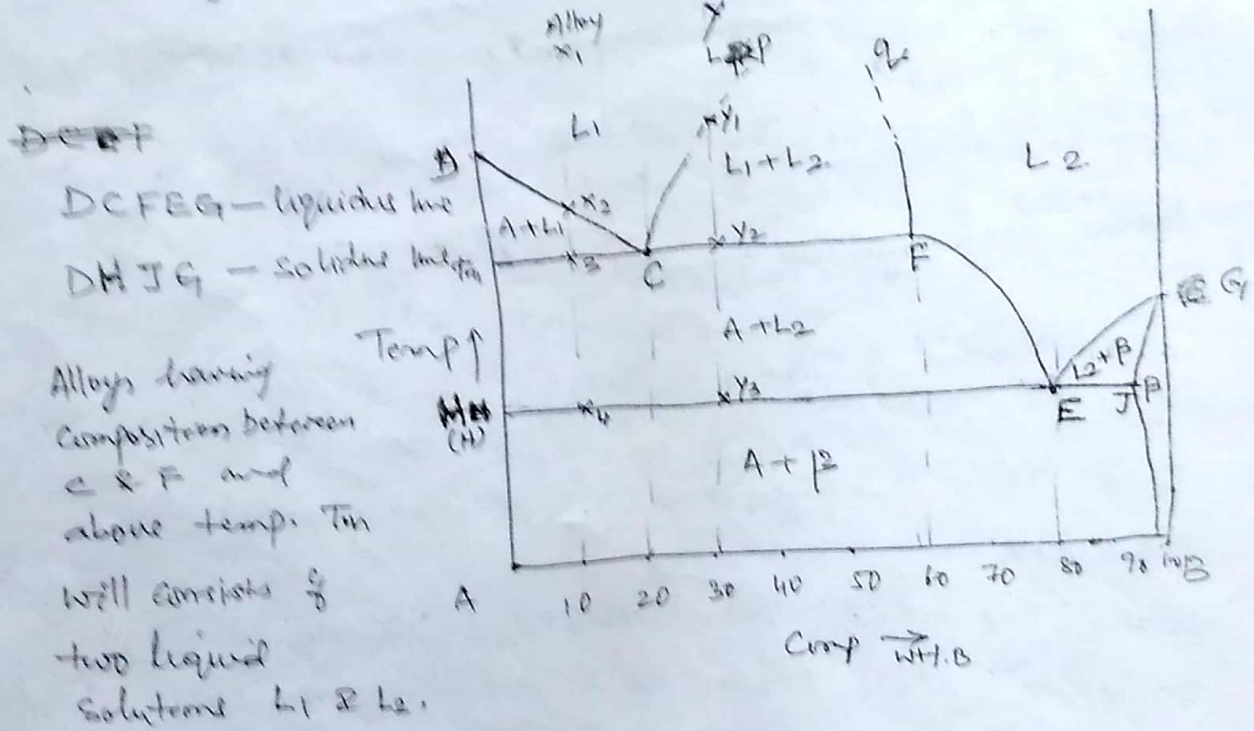
① Above T_p



Two liquids partly soluble in the liquid state -
 The monotectic Reaction: -

It is possible that over a certain composition range two liquid solutions are formed that are not soluble in each other. Substances that are not soluble in each other, such as oil and water are said to be immiscible. Substances that are partly soluble in each other are said to show a miscibility gap.

The equilibrium diagram for this type is shown in fig. Ex: Cu-Pb



The lines CP & FQ shows the composition of two liquid phases in equilibrium with each other at higher temps. Since these lines tend to approach each other, it is possible that at higher temps, the area will be closed and a single homogeneous liquid solution exists.

L_1 - liquid solution of B dissolved in A.

L_2 - liquid sol of A dissolved in B.

slow cooling of alloy 'x': (10% B)

$x_1 - x_2$ - single phase liquid sol. L_1 .

At x_2 - solidification starts and pure 'A' comes out.
 L_1 becomes richer in B.

At T_m , when x_3 reached, the liquid comp. ~~becomes~~ is given by point 'c', which is 80A & 20B.

Monotectic reaction takes place at (c)

Composition	80A	40A	100A
Equation	L_1	$\xrightarrow{\text{cooling}}$	$L_2 + \text{solid A}$
Relative amount	50%		17% 33%

Above T_m , Amount of A = $\frac{x_2 \cdot C}{T_m \cdot C} \times 100 = \frac{(20-10)}{(20-0)} \times 100 = 50\%$

Amount of $L_1 = 1 - A = 50\%$.

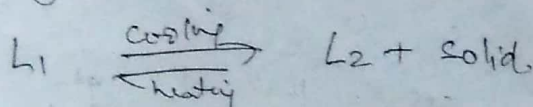
Below T_m . Amount of A = $\frac{x_2 F}{T_m F} = \frac{(60-10)}{(60-0)} = \frac{50}{60} \times 100 = 83\%$

Amount of $L_2 = \frac{T_m x_2}{T_m F} = \frac{(10-0)}{(60-0)} = \frac{10}{60} \times 100 = 17\%$

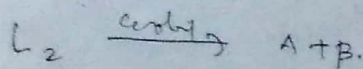
\therefore At 'c', 50% of L_1 must have formed 17% L_2 & 33% A.

When one liquid forms another liquid plus a solid on cooling - it is known as a monotectic reaction.

The general equation for monotectic reaction is



below point 'H', eutectic reaction takes place



Consider the slow cooling of a hypermonotectic alloy 'y'.

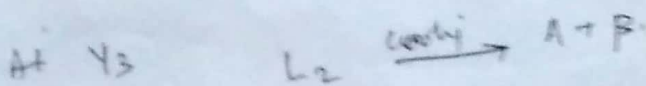
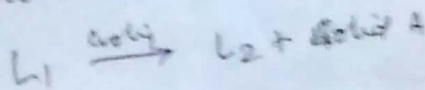
Upon cooling, the limit of liquid immiscibility is crossed at y_1 , and the second liquid L_2 will make its appearance.

The composition of L_2 may be obtained by using lever rule.

As the temp \downarrow , L_2 amount \uparrow .

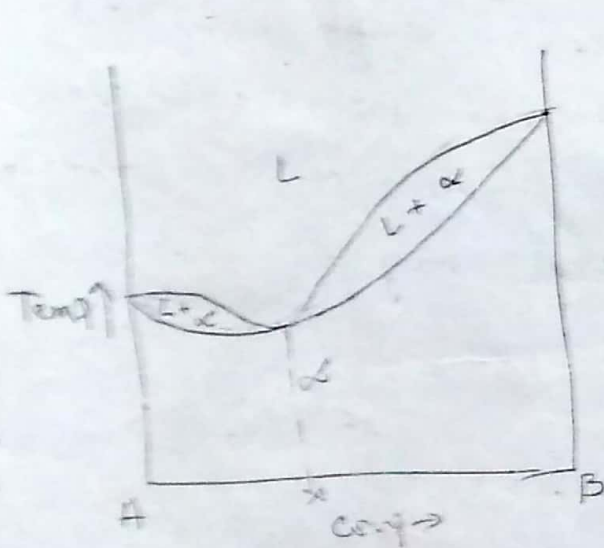
At T_m , amount of $L_2 = \frac{C_{Y_2}}{C_F} = \frac{30-20}{60-20} = \frac{10}{40} = 25\%$

At T_m - monotectic reaction takes place

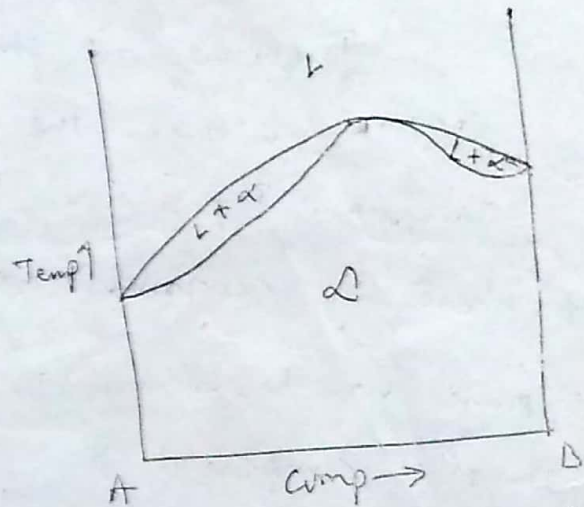


Variation of Solid Solution - Congruent Melting Alloys.

Every alloy in the isomorphous (solid-solution) system has a melting point between the melting points of A & B. It is possible to have a system in which the liquidus and solidus lines go thru' a minimum or a maximum, as shown in fig.



Solid Sol. System showing a minimum



Sol. Soln. system showing a max.

(2) The eutectic solidification however is incongruent since there is a diff. in composition between the liq. and the individual solid phases.

The alloy composition 'x' in fig. behaves just like a pure metal. There is no difference in the liquid and solid composition. It begins and ends solidification at a const. temp. with no change in composition and its cooling curve will show a horizontal line. Such alloys are known as congruent melting alloys.

Examples of alloys systems that show a minimum are Cu-Au and ~~Ni-Pd~~ Ni-Pd. Those showing a maximum are rare and there are no known metallic systems of the type. (X)

isothermally (at const. temp.) and without any change in chemical composition, it is said to be congruent phase change or congruent transformation.

All pure metals solidify congruently.

Intermediate phases are single phases that occur between the terminal phases on a phase diagram. Fig. shows the formation of an intermediate phase by congruent melting. Any intermediate

phase may be treated as

another component on a phase diagram.

Since the intermediate phase is a compound

it is indicated as A_mB_n

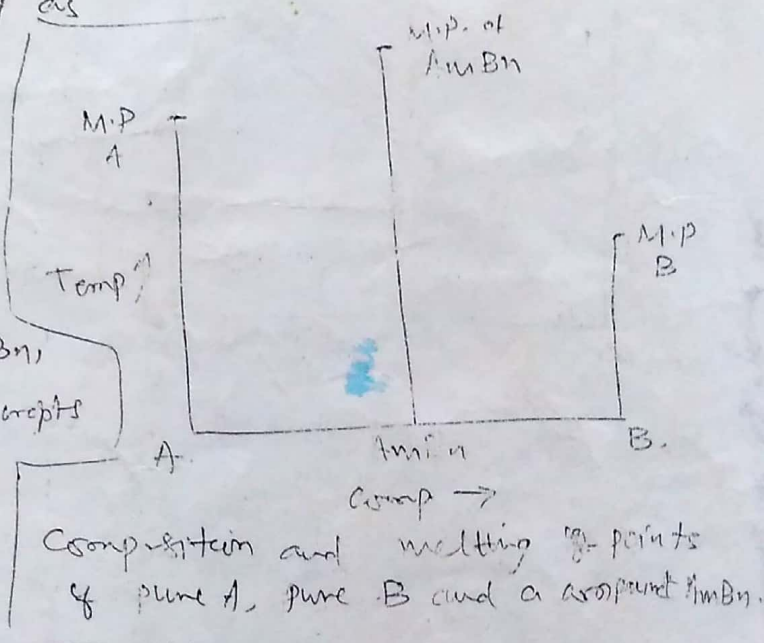
where m & n are subscripts which indicate the no.

of atoms combined in the compound:

Ex: Mg_2Sn

1 - Mg : $m = 2$

1 - Sn : $n = 1$



⊗⊗ The congruent melting Intermediate phase

When one phase changes ~~isothermally~~ into another phase