



**MATERIAL SCIENCE &  
METALLURGY  
2131904**

**Chapter 6  
Phase and Phase equilibrium**

Prepared by  
Prof. Naman M. Dave  
Assistant Professor,  
Mechanical Engg. Dept.  
Gandhinagar Institute of Technology.

Please do not blindly follow the presentation files only, refer it just as reference material.

More concentration should on class room work and text book-reference books.

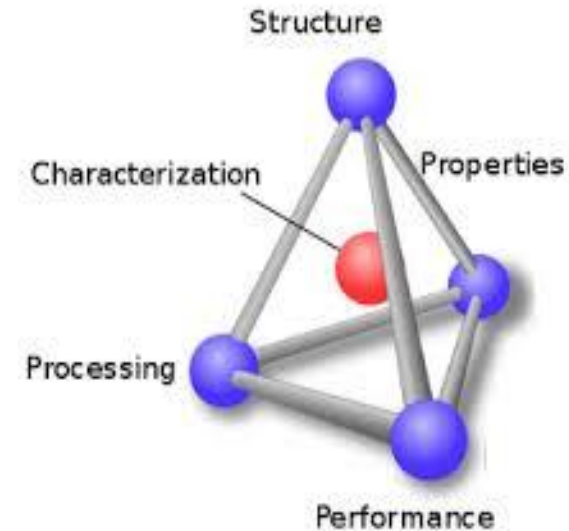
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# Basic terms

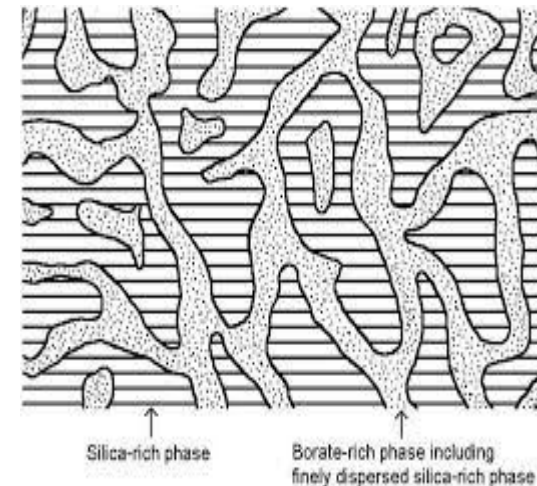
## 1. System

- Thermodynamically, a system is an isolated body of matter which is under study.
- A substance or a group of substances so **isolated from its surroundings** that it is totally **unaffected by the surroundings** but changes in its overall composition, temperature, pressure or total volume can be **allowed as per the desire of the person who investigates it**.
- A system may **contain** solids, liquids, gases or their combination.
- It may have metals ,non-metals separately or in combined form.



## 2. Phase

- A phase is a substance or a portion of matter which is homogenous, physically distinct and mechanically separable..
- **Physically distinct and mechanically separable** means that the phase will have a definite boundary surface.
- Different phases are given different names or symbols like  $\alpha$  (alpha),  $\beta$  (Beta),  $\gamma$  (Gamma), etc.



# Introduction - Components - Phase

- Components are pure metals and/or compounds of which an alloy is composed. For example, in a copper–zinc brass, the components are Cu and Zn.
- It refers to a **independent chemical species**. The components of a system may be elements, ions or compounds.
- A component can exist in many phases.
  - Water exists as ice, liquid water, and water vapor.
  - Carbon exists as graphite and diamond.

# Components and Phases

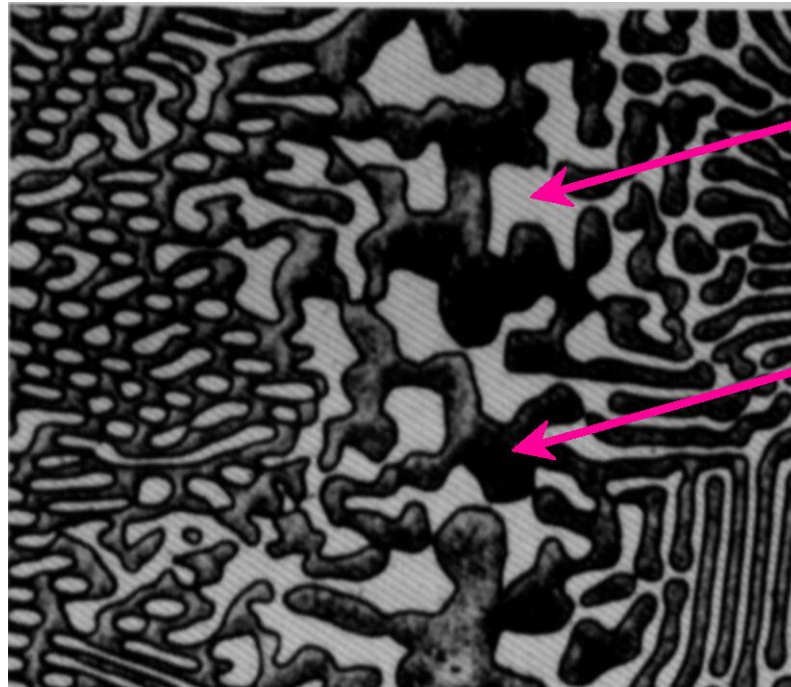
- **Components:**

The elements or compounds that are mixed initially (Al and Cu).

- **Phases:**

A phase is a homogenous, physically distinct and mechanically separable portion of the material with a given chemical composition and structure (a and b).

Aluminum-  
Copper  
Alloy



$\beta$  (lighter  
phase)

$\alpha$  (darker  
phase)

# Basic terms

## 3. Equilibrium :

- Equilibrium in a **system** is the **state of minimum free energy** under any specified combination of overall *composition, temperature, pressure and overall volume*.
- Once equilibrium is achieved, even a minor change in these parameters of composition, temperature, pressure, volume within the system means an increase in free energy.

## 4. Degrees of Freedom:

- It is also known as **variance of system**.
- It is defined as number of external or internal factors of the system (temperature, pressure and concentration) that **can be independently changed without altering equilibrium** i.e. **without causing disappearance of a phase or formation of a new phase in the system**.

## 5. Structural Constituent

- **Phase distribution** in a system is **not necessarily uniform throughout the structure**.
- These phases are **associated in different ways to form the structure**. This **association of phases in a recognizably distinct fashion** is referred to as “structural constituent” of the alloy.

# Basic terms

## 6. Single and Multiphase Solids

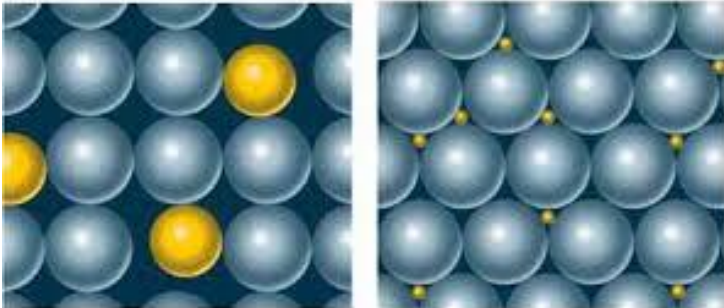
- A single crystal of a material may consist of one phase only while polycrystalline material may be single or multi-phase depending upon the nature of individual crystals or grains present.
- Examples : All **pure metals** are single phase solids
- Alloys like **Iron and Steel, Rocks, ceramics, wood, fibre-glass, polymers**, etc. are examples of multi-phase solids.
- Properties of multi-phase solids is dependent upon...
  1. Physical and chemical natures of phases present
  2. Amount of each phase (%)
  3. Distribution of each phase in relation to other phases
  4. Size of domain occupied by each phase



# Basic terms

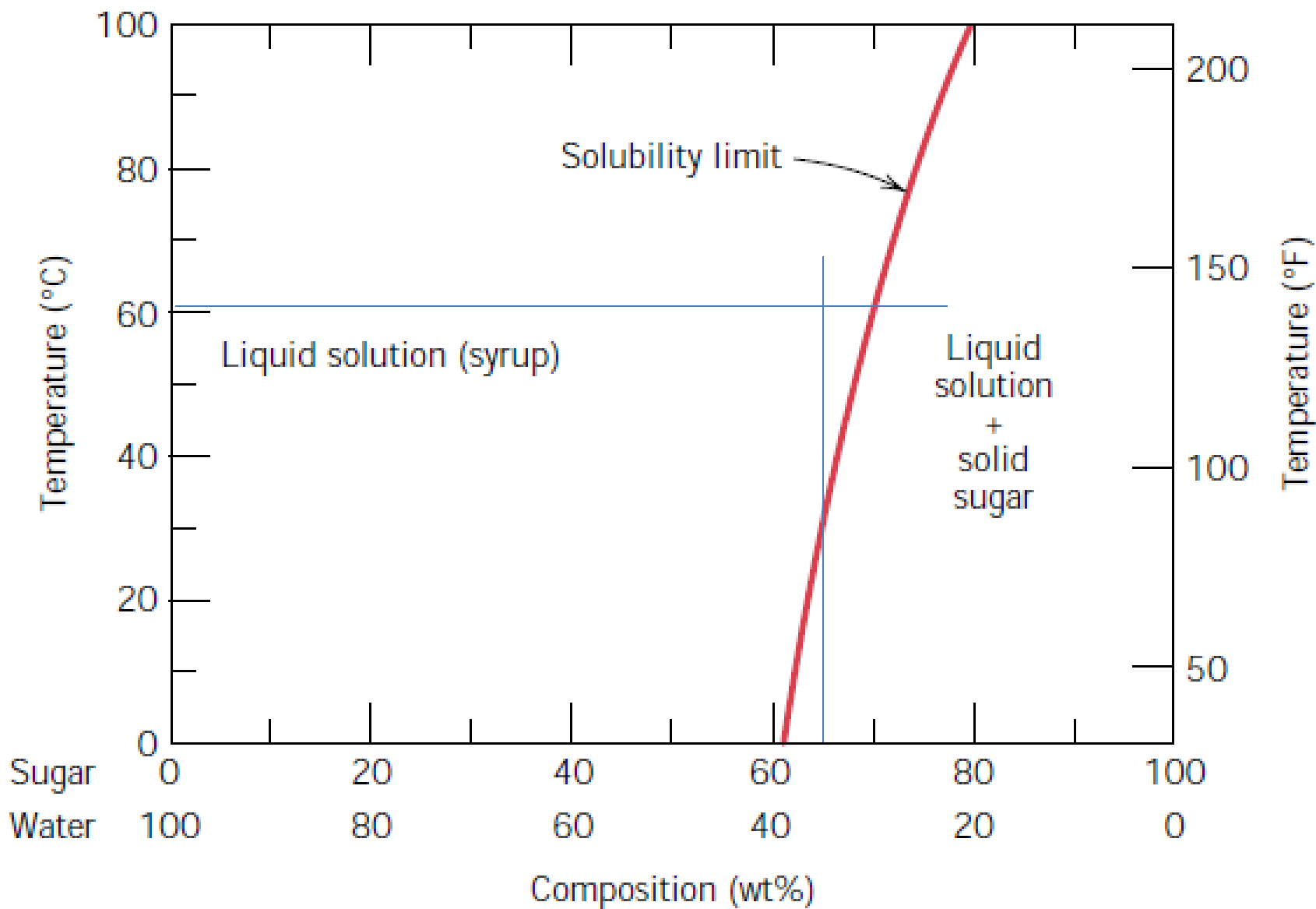
## 7. Alloys

- Pure metals because of their poor physical and mechanical properties are seldom used in engineering applications. Most of useful metallic materials are combinations of metals which are called alloys.
- An alloy can be defined as a substance possessing metallic properties, having metallic bond and composed of two or more than two elements out of which at least one of them is metal.
- Metal present in larger proportion is called base metal while other metallic or non-metallic element is known as alloying element.
- Elements may combine in different ways to form alloys.
- These elements of alloys usually show complete solubility in liquid state. However, on cooling them to solid state, they may form mechanical mixtures or homogenous phases.

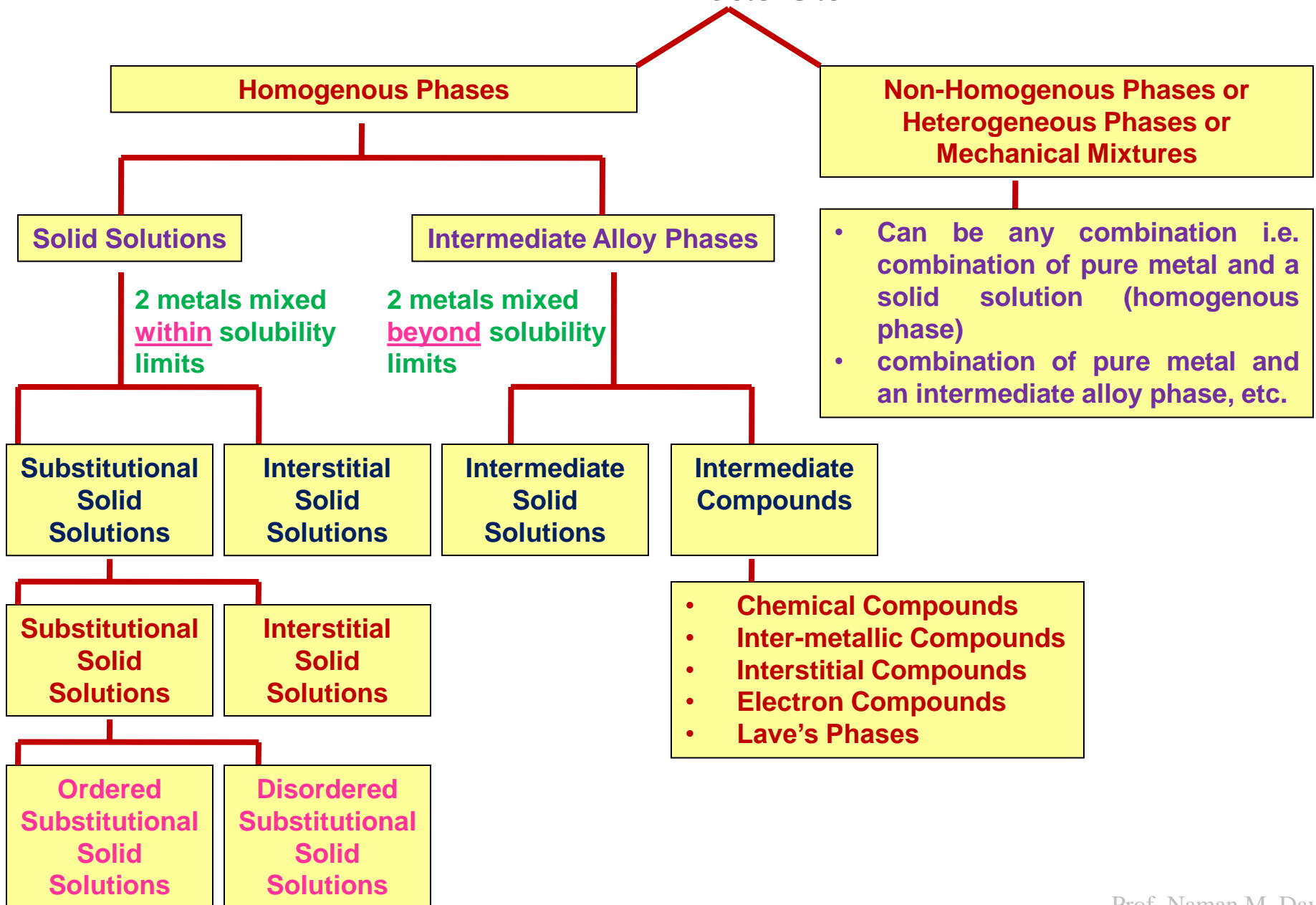


# Phases - Solution

- A solution (liquid or solid) is phase with more than one component; a mixture is a material with more than one phase.
- Solute (minor component of two in a solution) does not change the structural pattern of the solvent, and the composition of any solution can be varied.
- In mixtures, there are different phases, each with its own atomic arrangement. It is possible to have a mixture of two different solutions!
- For many alloy systems and at some specific temperature, there is a **maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution**; this is called a **solubility limit**.
- The addition of solute in excess of this solubility limit results in the formation of another solid solution or compound that has a distinctly different composition.



# Phases



# Homogenous phases

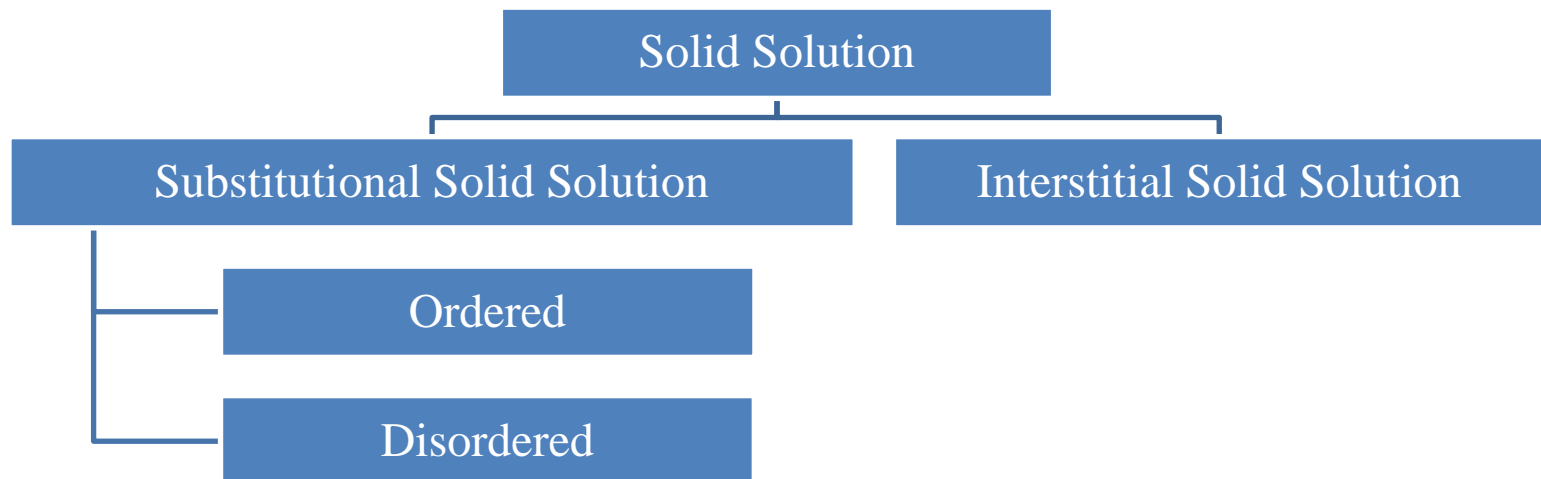
- When two elements are completely soluble when coming into solid state from liquid state and form compounds by chemical reaction, they form phases known as **homogenous phases**.
- Each component of such phases loses its own identity, properties and crystal structure.

## 1. Solid Solutions

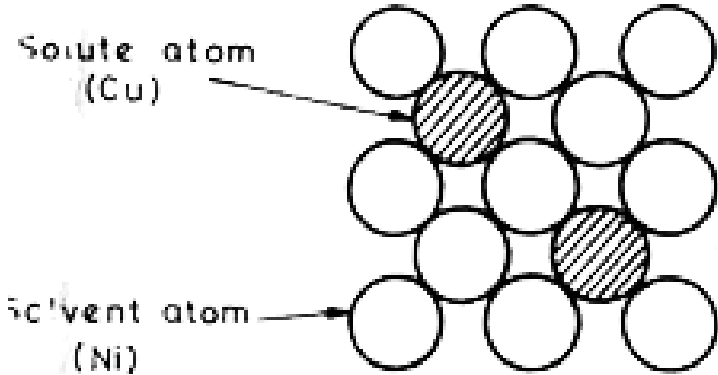
- When two elements completely mix or dissolve in each other in liquid as well as solid state (during process of solidification), then the resulting structure or phase is known as a **solid solution**.
- In a solid solution, there can be more than two components. But in general, the metal which is in higher proportion is known as **base metal or solvent** and the other component (metal or non-metal) is called **alloying element or solute**.
- There are **two types** of Solid Solutions – **Substitutional Solid Solution** and **Interstitial Solid Solution**.

# Solid solutions

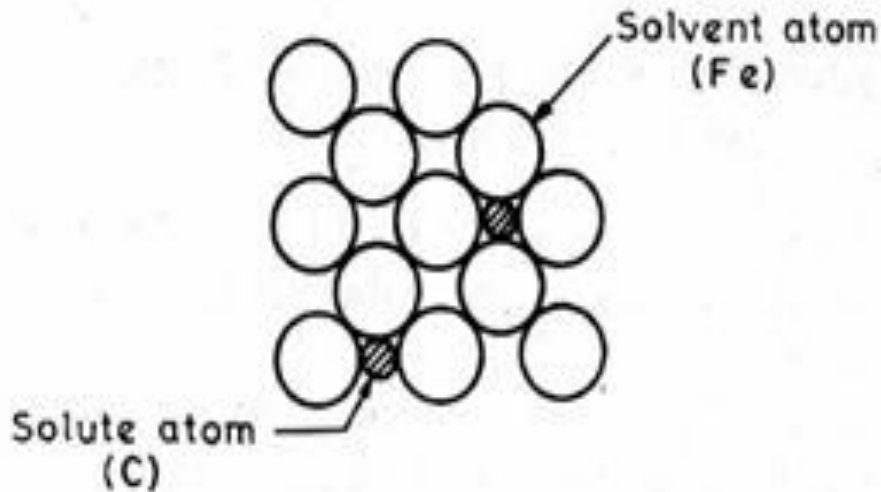
- A solid solution is simply a solution in the solid state that consists of **two kinds of atoms combined in one type of space lattice**.
- There is a homogeneous distribution of two or more constituents in the solid state.
- A solid solution is the **result of, metals dissolving in each other's crystal lattice**.



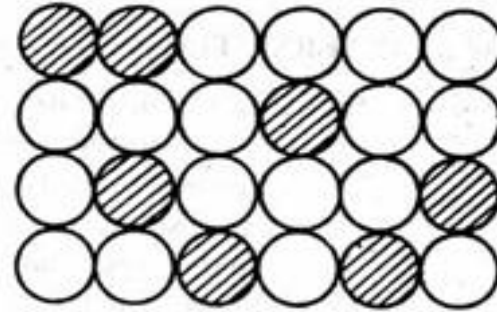
# Solid solutions



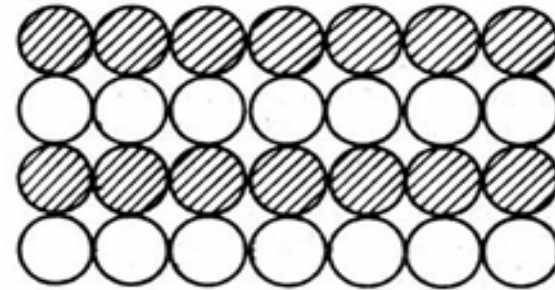
Substitutional Solid Solution



Interstitial Solid Solution



Disordered Substitutional Solid Solution



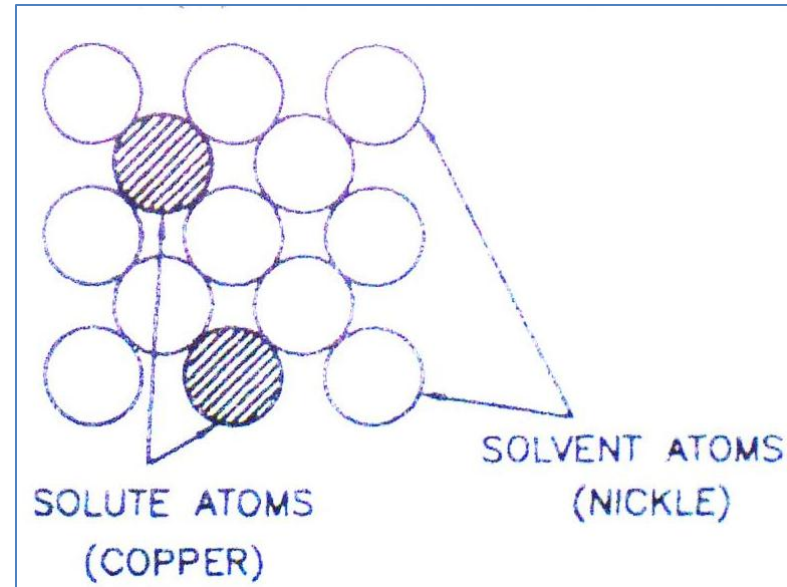
Ordered Substitutional Solid Solution

# Types of Solid Solutions

- When a solid solution form, the atoms of alloying element (solute) occupy certain places in the lattice structure of the base metal (solvent).
- Depending upon the types of places occupied by the solute atoms, solid solutions formed are of two types

## 1) Substitutional Solid Solution

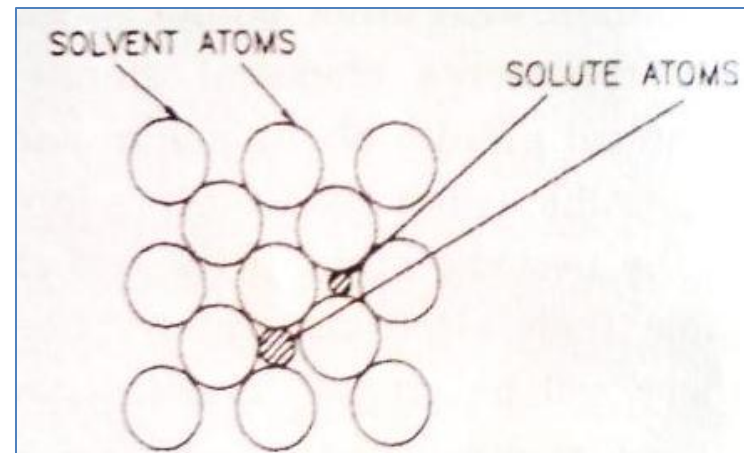
- If atoms of alloying element (solute) replace the atoms of the base metal (solvent) and occupy their normal lattice sites, the resulting solid solution is known as Substitutional solid solution.
- For example, Copper atoms may substitute Nickel atoms without disturbing their FCC structure of Nickel.
- Thus they have unlimited solid solubility whereas in case of Brass, FCC Copper atoms (base/solvent) are replaced by HCP i.e. Zinc atoms (alloying element/solute) which has limited solubility.





## 2) Interstitial Solid Solution

- In Interstitial Solid Solution, the alloying element (solute) atoms do not replace the base metal (solvent) atoms but enter into the empty spaces or interstices of the lattice structure of the solvent atoms.
- As the empty spaces of lattice structure are limited in size, the interstitial solid solution can only form when the solute atom is small enough to fit into these spaces.
- The radii of atoms of commercial alloys is in the range of  $1.2-1.6\text{\AA}$ . It means that the atoms with atomic radius less than  $1\text{\AA}$  are likely to form interstitial solid solution.
- It may be noted that if the alloying element is a transition element, there are maximum chances of formation of Interstitial Solid Solution. This is not only because of their small atomic radii but also due to their unusual electronic structure.
- Examples of Interstitial Solid Solutions are – C in Steel causing hardening, N in Steel causing hardening, H in Steel during welding causing embrittlement of weld area.



## Types of Substitutional Solid Solutions

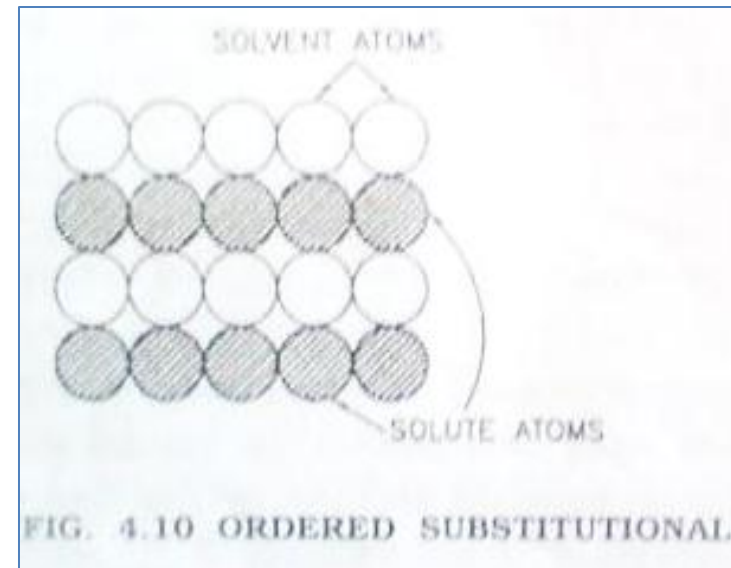
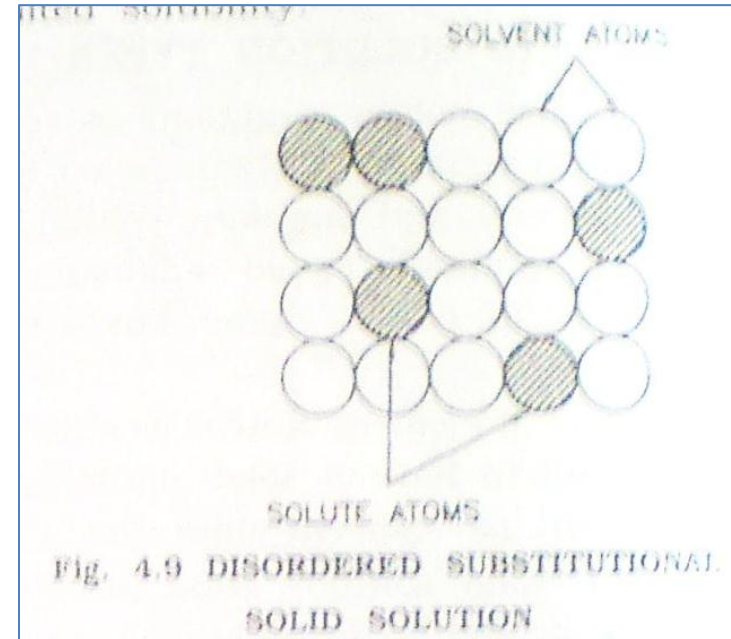
- Depending on the order of replacement of base metal (solvent) atoms by alloying element (solute) atoms, there are two types of solid solutions

### 1. Disordered or Random Substitutional solid solution

- This is formed when the alloying element (solute) atoms do not occupy any specific orderly positions but replace the atoms in lattice structure of base metal (solvent) atoms at random then the phase is known as disordered or random substitutional solid solution. It is normally observed at high temperatures.

### 2. Ordered Substitutional solid solution

- This is formed when the alloying element (solute) atoms occupy specific orderly positions in the lattice structure of base metal (solvent) atoms then the phase is known as ordered substitutional solid solution. It is normally observed at room temperatures.



# Intermediate Alloy Phases

- Addition of an alloying element to a given metal to an excessive amount than solid solubility results in a second phase appearance with the solid solutions. This second phase is known as Intermediate Alloy Phase.
- It differs in both crystal structure and properties from solid solutions.
- Intermediate phases may range between ideal solid solutions on one hand and ideal chemical compounds on the other hand.
- Intermediate alloy phases could be either intermediate solid solutions or intermediate compounds.

# Types of Intermediate Alloy Phases

## 1. Intermediate Solid Solutions

- In many alloy systems, crystal structures or phases are found which are different from those of elementary components (pure metals).
- If these structures occur over a range of compositions, they are, in all respects, solid solutions and therefore known as intermediate solid solutions.
- They have lattice structure which is different from that of solvent (base metal) lattice.

## 2. Intermediate Compounds

- When different type of atoms combine in a definite proportion they form compounds.
- Compounds can be denoted by chemical formula.
- Most common examples of compounds are water ( $\text{H}_2\text{O}$ ) and common salt ( $\text{NaCl}$ ).
- Unlike mechanical mixtures, the combining elements in compounds lose their individual identity and characteristic properties. For example – Sodium is very active metal and oxidizes rapidly. Therefore, it is usually stored under kerosene. Chlorine, if inhaled, is a poisonous gas. Now, when Sodium and Chlorine combine they form Sodium Chloride or table salt which is a harmless compound.

## Types of Intermediate Compounds

- Depending upon the characteristics of combining elements, the compounds can be of different types. They are as under.

### 1. Chemical Compounds :

- They are known as valency compounds.
- When two chemically dissimilar elements have greater chemical affinity for each other , they form chemical compounds.
- For example, mixing of electropositive elements like Na, K, Al, Mg, etc. with electronegative elements like Sn, Pd, As, Sb, Se, S, etc. result into chemical compounds like AlSb,  $Mg_3As_2$ ,  $Mg_2Sn$ , MgSe,  $Cu_2Se$ , CaSe, etc.
- Properties
- Composition of these compounds satisfy the valency laws
- They have generally ionic or covalent bonds
- They are non-metallic in properties
- They are generally hard, brittle and poor conductors with high melting points.

## Types of Intermediate Compounds

### 2. Intermetallic Compounds :

- Unlike chemical compounds, intermetallic compounds rarely obey the laws of chemical valence.
- They have complex lattice structures and are characterized by high hardness, brittleness and melting point.
- Examples are  $\text{Cu}_2\text{Zn}_3$ ,  $\text{Cu}_3\text{Sn}_4$ ,  $\text{CuAl}_2$ ,  $\text{SnSb}$ , etc.
- These type of compounds have metallic bonding and valence electrons are free to move in lattice giving good electrical conductivity property to these substances.

### 3. Interstitial Compounds :

- These can be considered as a special case of intermetallic compounds.
- They are formed when the solubility limit of interstitial elements in a solid solution is exceeded.
- The open spaces between the atoms are known as interstices.
- Atoms of elements like H, O, C, B and N have small radii and therefore they can occupy the interstitial space between atoms of other metals.
- The base metal (solvent) is generally a transition, metal like Sc, Ti, Ta, W, Fe, etc

## Types of Intermediate Compounds

### 4. Interstitial Compounds :

- Like most intermetallic compounds, interstitial compounds do not obey normal valency rules.
- Interstitial compounds are extremely hard, metallic in nature and have high melting and boiling points.
- Their hardness is utilized in dispersion hardened alloys and high speed cutting tool tips.
- $\text{Fe}_3\text{C}$  is an important interstitial compound of steel which governs many properties.
- Other examples of this group include  $\text{TiC}$ ,  $\text{Fe}_4\text{N}$ ,  $\text{W}_2\text{C}$ ,  $\text{TiH}$ , etc.

### 5. Electron Compounds

- These are intermediate phases which again do not obey the normal valency rules.
- They are formed in metals having similar electrochemical properties and a favourable size factor but different no. of valence electrons.
- They can be characterized by a definite ratio of valence electrons to the no. of atoms ( $3/2$ ,  $21/13$  or  $7/4$ ) with a particular crystal lattice corresponding to each ratio.

## Types of Intermediate Compounds

### 6. Electron Compounds

- Electronic compounds can be formed by 2 metals from following groups :
- Group-1 : Cu, Ag, Au, Fe, Co, Ni, Pd and Pt
- Group-2: Be, Zn, Cu, Al, Sn and Si
- Electron compounds are found in many alloys of commercial importance like copper-zinc, copper-tin, copper-aluminium, copper-silicon, etc.

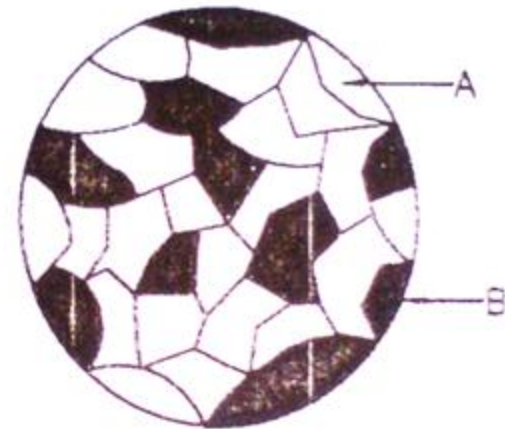
### 7. Lave's Phases

- When the difference between the atomic radii of two elements is about 20-30% then Lave's phases are formed.
- The stoichiometric formula of this compound is  $AB_2$ .
- The atomic radii of the elements forming these phases are in a ratio of approximately 1:1.2.
- Examples are –  $MgCu_2$ ,  $MgZn_2$ ,  $MgNi_2$ , etc.



# Non-homogenous Phases / Mechanical Mixtures

- When two elements are completely insoluble when coming into solid state from liquid state and cannot form compounds by chemical reaction, they form phases known as **mechanical mixtures**.
- Each component of such phases retains its own identity, properties and crystal structure.
- Suppose two such metals A and B are mixed and melted together and the microstructure after solidification is as under.
- Properties of mixture will be between A and B i.e. depending upon proportion of each
- Now if you separate A and B from the mixture by converting it to liquid state (using heat) and then cool them down individually, you will find that properties of both A and B are same as they were in pure form.



Microstructure of A  
Mechanical Mixture (Schematic)

# Hume Rothery Rule's for Solid Solution

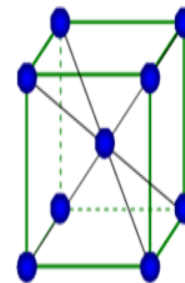
- Hume Rothery's rules govern the formation of substitutional solid solution and aid in the proper selection of such alloying elements :

1. Crystal Structure Factor
2. Relative Size Factor
3. Chemical Affinity Factor
4. Relative Valance Factor

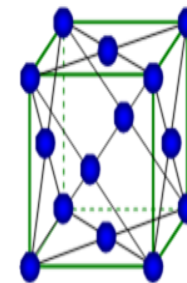


**1. Crystal Structure Factor of two metals (elements) should be same.**

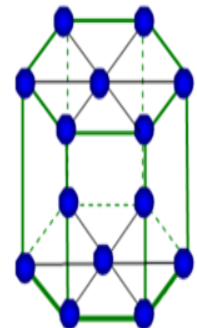
Crystal lattice examples



Cubic body centered (bcc)



Cubic face centered (fcc)



Hexagonal

# 2. Relative Size Factor

- Atomic diameter shall be fairly similar, since atoms differing directly greatly in size cannot be accommodated readily in the same structure (as a substitutional solid solution).
- When the term size factor is employed and extensive solid solubility is encountered only when the two different atoms differ size by less than 15%, called a favorable size factor.
- If the relative size factor is between 8%-15%, the alloy system usually shows a minimum and If this factor is greater than 15% substitutional solid solution formation is very limited.

$$\% \text{ difference} = \left( \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \right) \times 100 \leq 15\%.$$

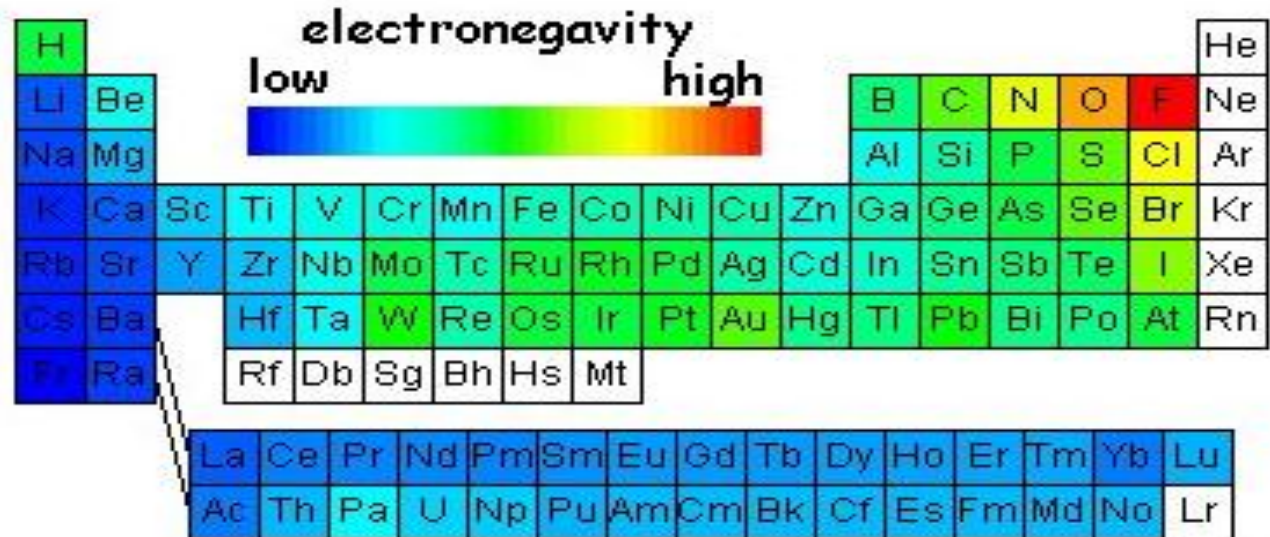
Periodic Table of Atomic Radii (in Angstrom Units)

0.30 H 1																	0.93 He 2
1.23 Li 3	0.89 Be 4											0.80 B 5	0.77 C 6	0.70 N 7	0.66 O 8	0.64 F 9	1.12 Ne 10
1.57 Na 11	1.36 Mg 12											1.25 Al 13	1.17 Si 14	1.10 P 15	1.04 S 16	0.99 Cl 17	1.54 Ar 18
2.02 K 19	1.74 Ca 20	1.44 Sc 21	1.32 Ti 22	1.22 V 23	1.19 Cr 24	1.18 Mn 25	1.17 Fe 26	1.16 Co 27	1.15 Ni 28	1.18 Cu 29	1.21 Zn 30	1.25 Ga 31	1.22 Ge 32	1.21 As 33	1.17 Se 34	1.14 Br 35	1.69 Kr 36
2.16 Rb 37	1.91 Sr 38	1.62 Y 39	1.45 Zr 40	1.34 Nb 41	1.30 Mo 42	1.27 Tc 43	1.25 Ru 44	1.25 Rh 45	1.28 Pd 46	1.34 Ag 47	1.38 Cd 48	1.42 In 49	1.42 Sn 50	1.39 Sb 51	1.37 Te 52	1.33 I 53	1.90 Xe 54
2.35 Cs 55	1.98 Ba 56	1.56 La 57	1.44 Hf 72	1.34 Ta 73	1.30 W 74	1.28 Re 75	1.26 Os 76	1.26 Ir 77	1.30 Pt 78	1.34 Au 79	1.39 Hg 80	1.44 Tl 81	1.50 Pb 82	1.51 Bi 83	1.68 Po 84	2.2 At 85	1.99 Rn 86
Fr 87	2.20 Ra 88	Lr 103															
1.69 La 57	1.65 Ce 58	1.64 Pr 59	1.64 Nd 60	1.63 Pm 61	1.62 Sm 62	1.65 Eu 63	1.62 Gd 64	1.61 Tb 65	1.60 Dy 66	1.58 Ho 67	1.58 Er 68	1.58 Tm 69	1.70 Yb 70				
2.0 Ac 89	1.65 Th 90	1.43 Pa 91	1.43 U 92	1.43 Np 93	1.43 Pu 94	1.43 Am 95	1.43 Cm 96	1.43 Bk 97	1.43 Cf 98	1.43 Es 99	1.43 Fm 100	1.43 Md 101	1.43 No 102				

# 3. Chemical affinity Factor

- The greater the chemical affinity of two metals, the more restricted their solubility is their solid solubility.
- When their chemical affinity of two metals is great, two metals tend to form an intermediate phase rather than a solid solution.
- Generally, the farther apart the elements are in the periodic table the greater the chemical affinity.

- If the elements have **similar electronegativity, they will make a solid solution,**
- **if they have a different electronegativity, a intermetallic compound**



# 4. Relative valence Factor

- Consider a two atoms, one with large valence electrons and the other with small number of valence electron.
- It has been found that high valence can dissolve only a small amount of a lower valence metal, while the lower valence metal may have good solubility for higher valence metal.

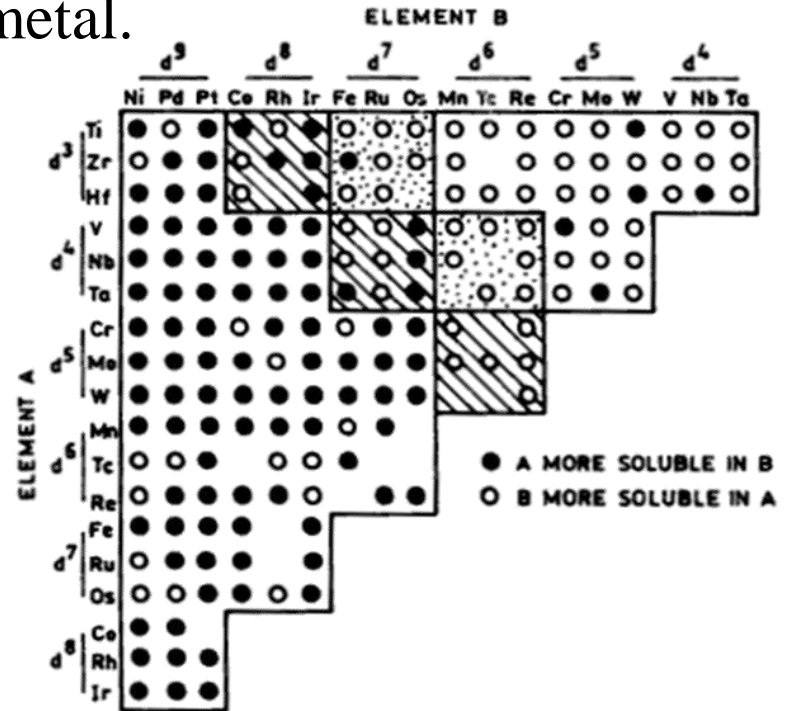


Fig. 1.5. Experimental relative solubilities in transition-metal alloys. The dotted region indicates systems where the d-bands of the constituents are equally far from half-filled; the hatched region indicates a diagonal boundary region in which no clear bias appears in the relative solubilities. (Redrawn after Watson *et al.*)

**Solidification ...**

# Equilibrium Phase Diagram

- A diagram that depicts **existence of different phases** of a system under equilibrium is termed as phase diagram.
- It is actually a **collection of solubility limit curves**. It is also known as equilibrium or constitutional diagram.
- Equilibrium phase diagrams represent there **relationships between temperature, compositions and the quantities of phases** at equilibrium.
- These diagrams do not indicate the dynamics when one phase transforms into another.

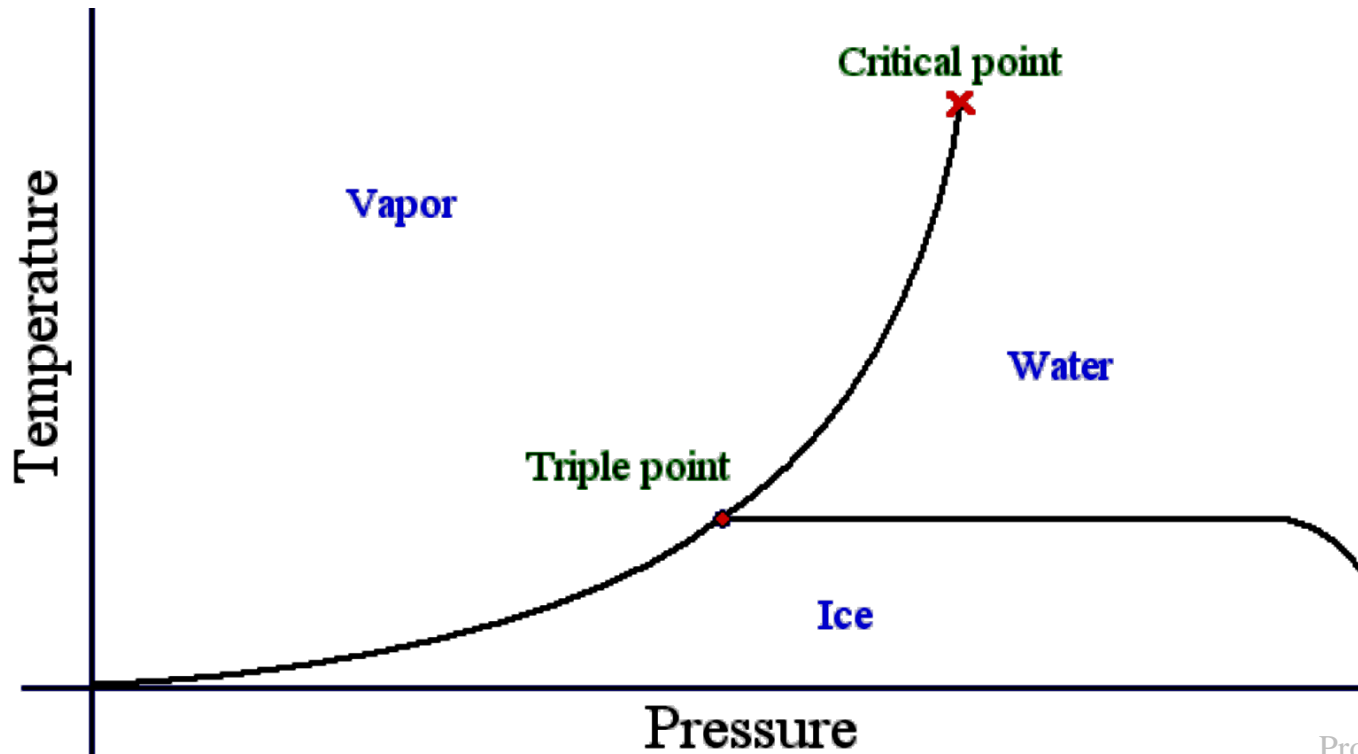
# Equilibrium Phase Diagram

- Important information, useful in materials development and selection, obtainable from a phase diagram.
- It shows **phases present at different compositions and temperatures** under slow cooling (equilibrium) conditions.
- It indicates equilibrium solid solubility of one element / compound in another.
- It **suggests temperature at which an alloy starts to solidify** and the range of solidification.
- It signals the temperature at which different phases **start to melt**.
- Amount of each phase in a two-phase mixture can be obtained



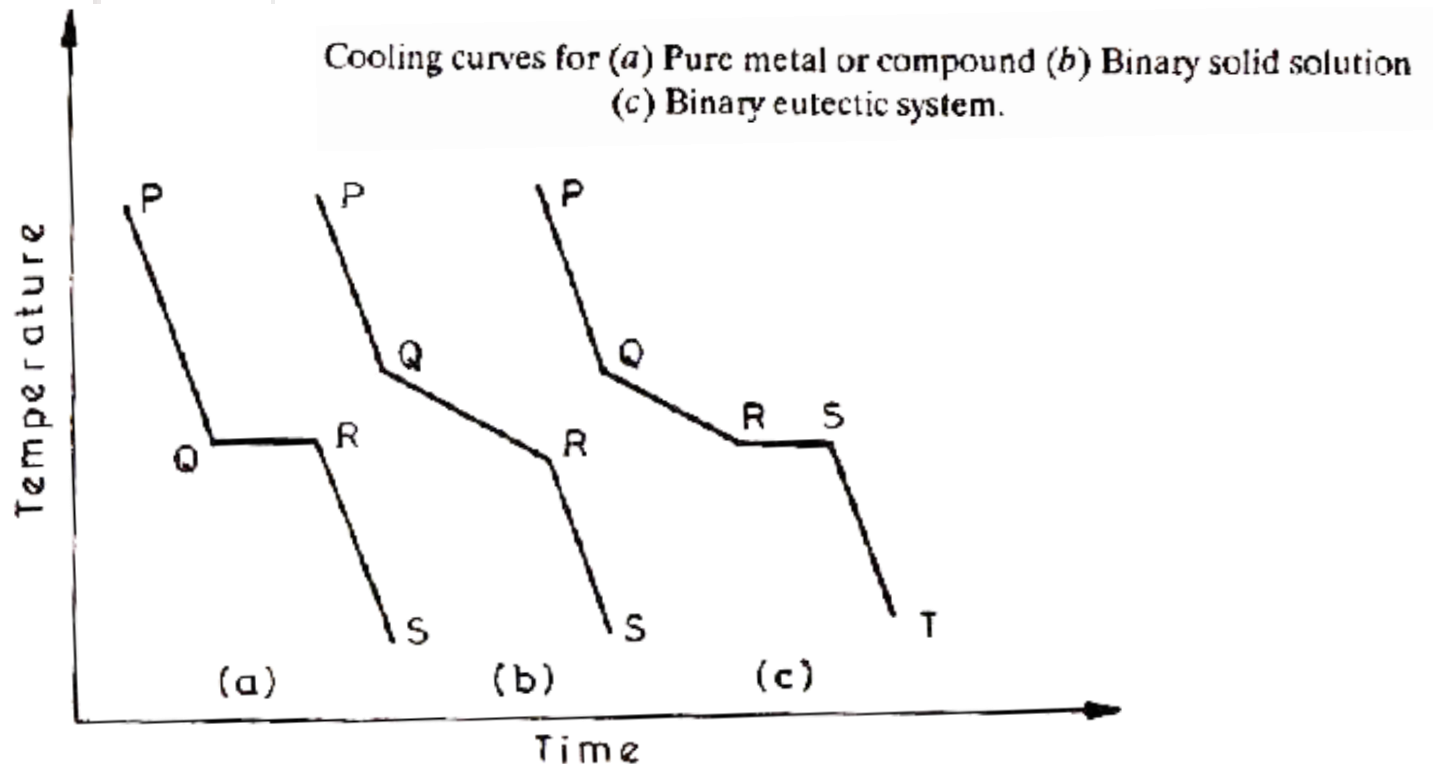
# Unary phase diagram

- If a system consists of **just one component**(e.g.:water), equilibrium of phases exists depicted by unary phase diagram. The component may exist in different forms, thus variables here are—temperature and pressure.



# Cooling Curves

- A method, to determine the temperatures at which phase changes (liquid  $\rightleftharpoons$  solid) occur in an alloy system, consists of following the temperature as a function of time as different alloys in the system are very slowly cooled.



# Cooling Curves

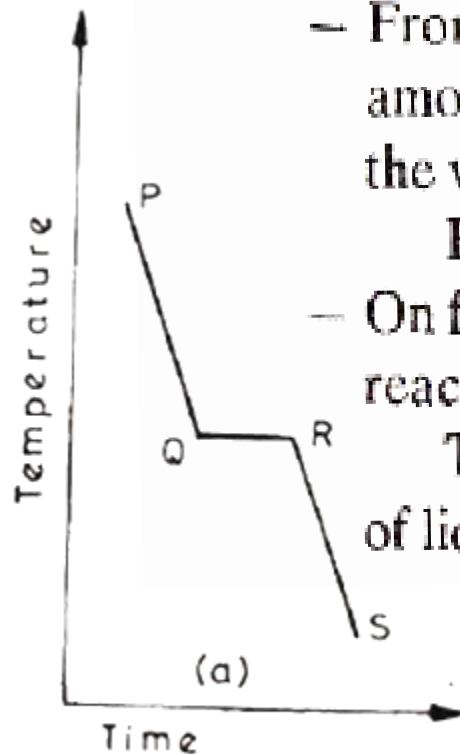
## (a) Cooling curve of pure metal or compound

- Liquid metal cools from  $P$  to  $Q$ . First crystals begin to form at point  $Q$ .
- From  $Q$  to  $R$ , the melt liberates latent heat of fusion in such amounts that the temperature from  $Q$  to  $R$  remains constant, until the whole mass has entirely solidified (at point  $R$ ).

Between  $Q$  and  $R$ , the mass is partly liquid and partly solid.

- On further cooling from  $R$  to  $S$ , the solid metal cools and tends to reach room temperature.

The slopes of  $PQ$  and  $RS$  lines depend upon the specific heats of liquid and solid metals respectively.

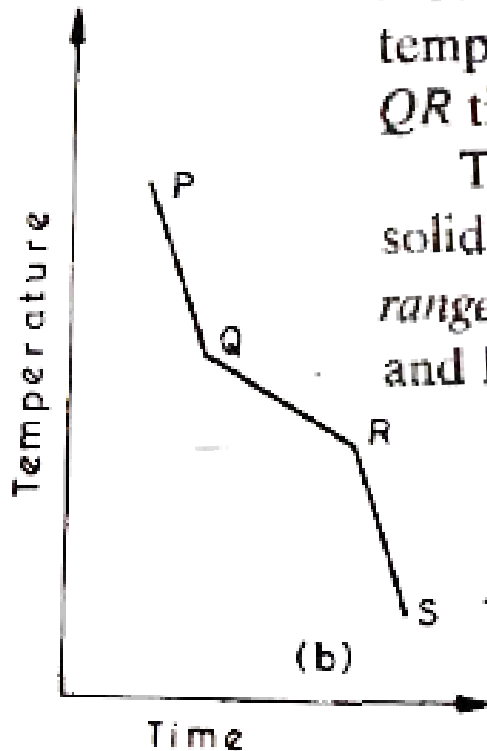


Cooling curves for (a) Pure metal or compound

# Cooling Curves

## (b) Cooling curve of a binary solid solution

- Curve portion  $PQ$  is similar no matter it is for a pure metal or for a binary system consisting of two metals forming a solid solution.
- However, in a binary system, during freezing (i.e.,  $QR$ ) period, the temperature does not remain constant, rather it drops along line  $QR$  till, the whole mass is solid at point  $R$ .



The dropping trend of  $QR$  indicates that the alloy does not solidify at constant temperature, rather, it possesses a *freezing range*\* which is due to the changes in the composition of the solid and liquid phases which naturally result in variable freezing (or melting) points, [for further details refer section 24.4 on Equilibrium (phase) diagrams].

- The solid cools along  $RS$  to attain the room temperature.

(b) Binary solid solution

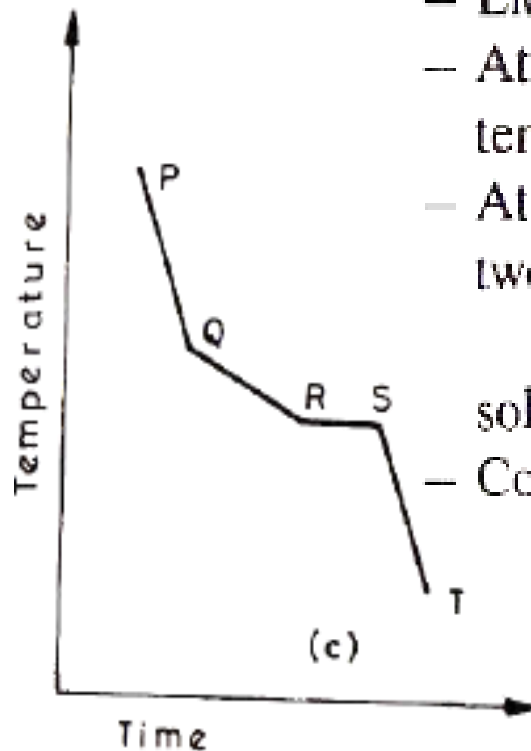
# Cooling Curves

(c) *Cooling curve of a binary eutectic system [Fig. 39.1 (c)]*

- In this system, the two components are completely soluble in the liquid state but entirely insoluble in the solid state.
- Liquid cools along  $PQ$  until temperature  $Q$  is reached.
- At  $Q$ , one component that is in excess will crystallize and the temperature will drop along  $QR$ .
- At point  $R$  the liquid composition has been reached at which the two components crystallize simultaneously from the solution.

The temperature remains constant until the whole mass is solid.

- Cooling from  $S$  to  $T$  is as usual.

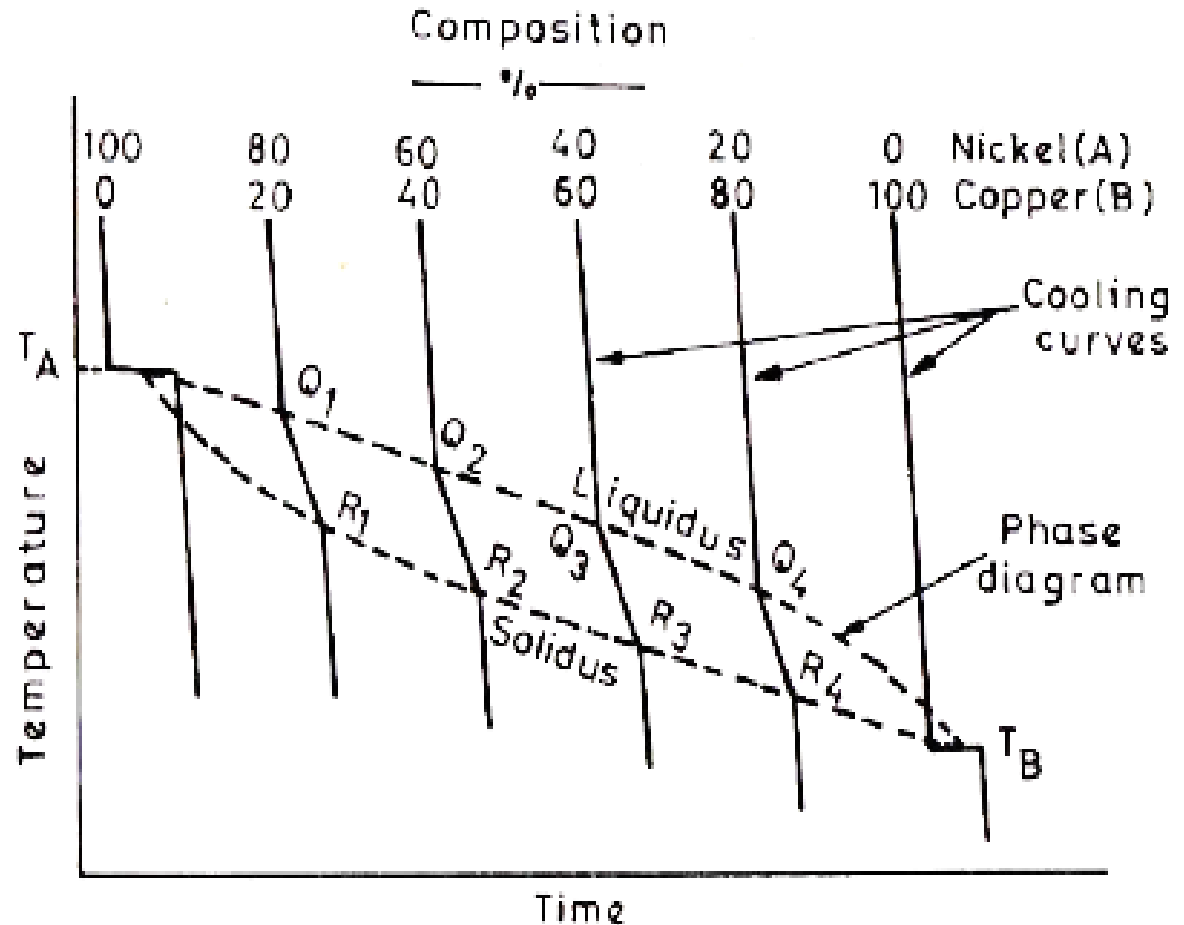


(c) Binary eutectic system.

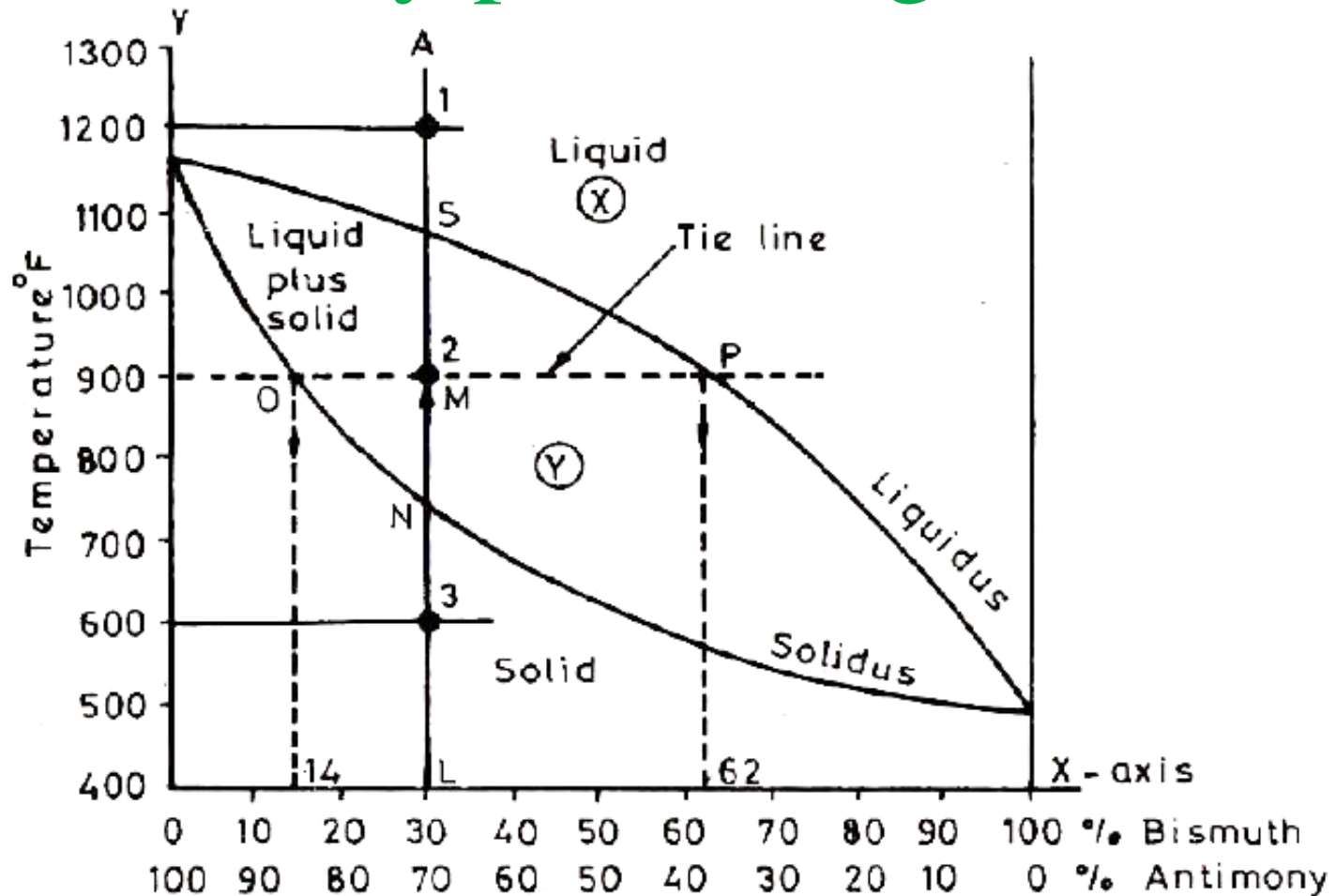
# Binary phase diagram

If a system consist soft components, equilibrium of phases exist is depicted by binary phase diagram. Pressure is constant, thus in dependently variable parameters are— temperature and composition.

- Two component systems are classified based on extent of mutual solid solubility
- completely soluble in both liquid and solid phases (isomorphous system)
- completely soluble in liquid phase where as solubility is limited in solid state.



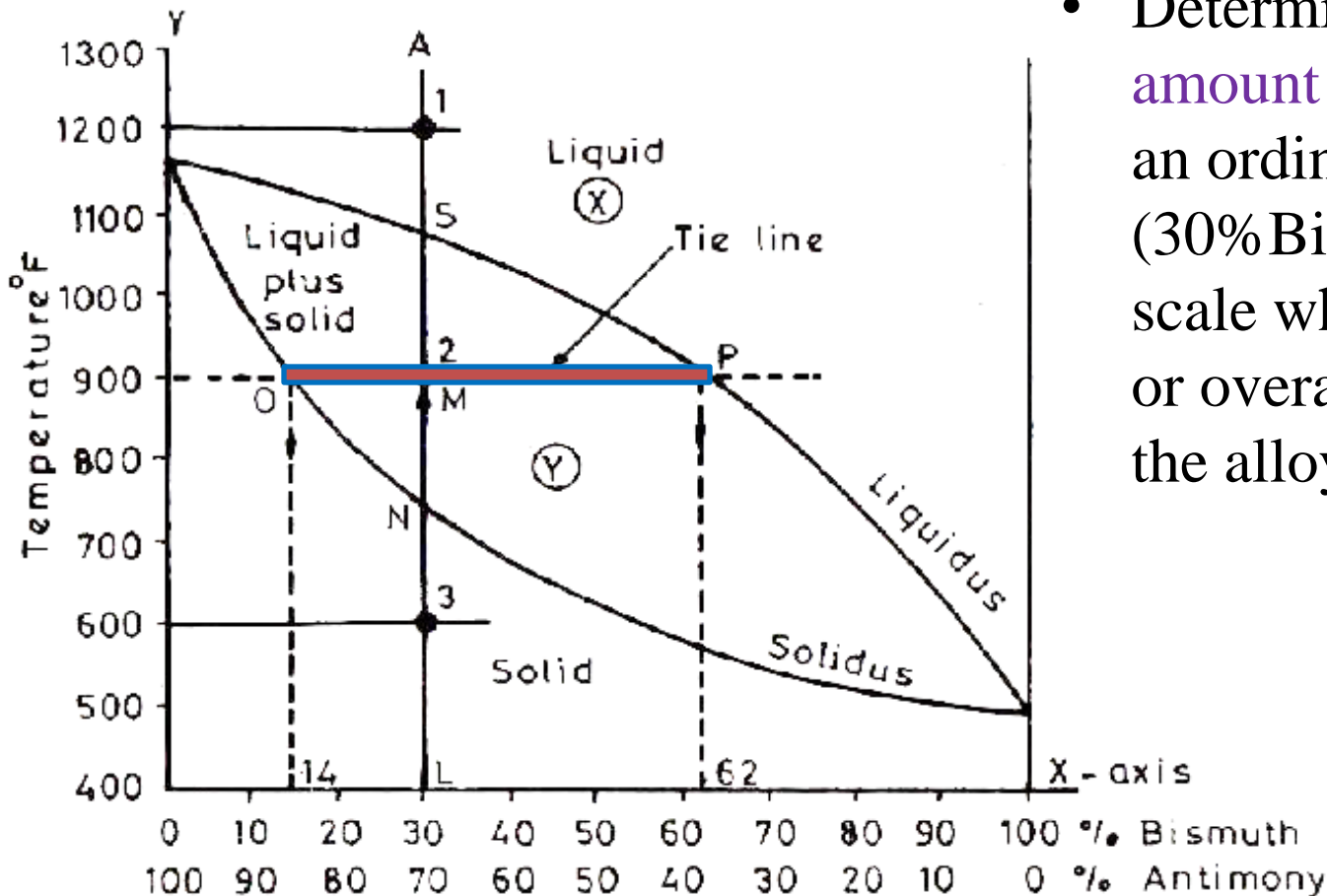
# Binary phase diagram



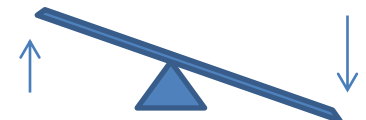
- Point 1: With 30% Bi — 70% Sb alloy at 1200°F, only one phase, *i.e.*, the liquid solution is present.
- Point 2: With the same alloy, but at 900°F, two phases are present, *i.e.*, liquid solution and solid solution
- Point 3: With the same alloy, but at 600°F, only one phase, *i.e.*, the solid solution is present.

# Lever Arm Principle

- Proportion of co-existing phase at any given temperature.



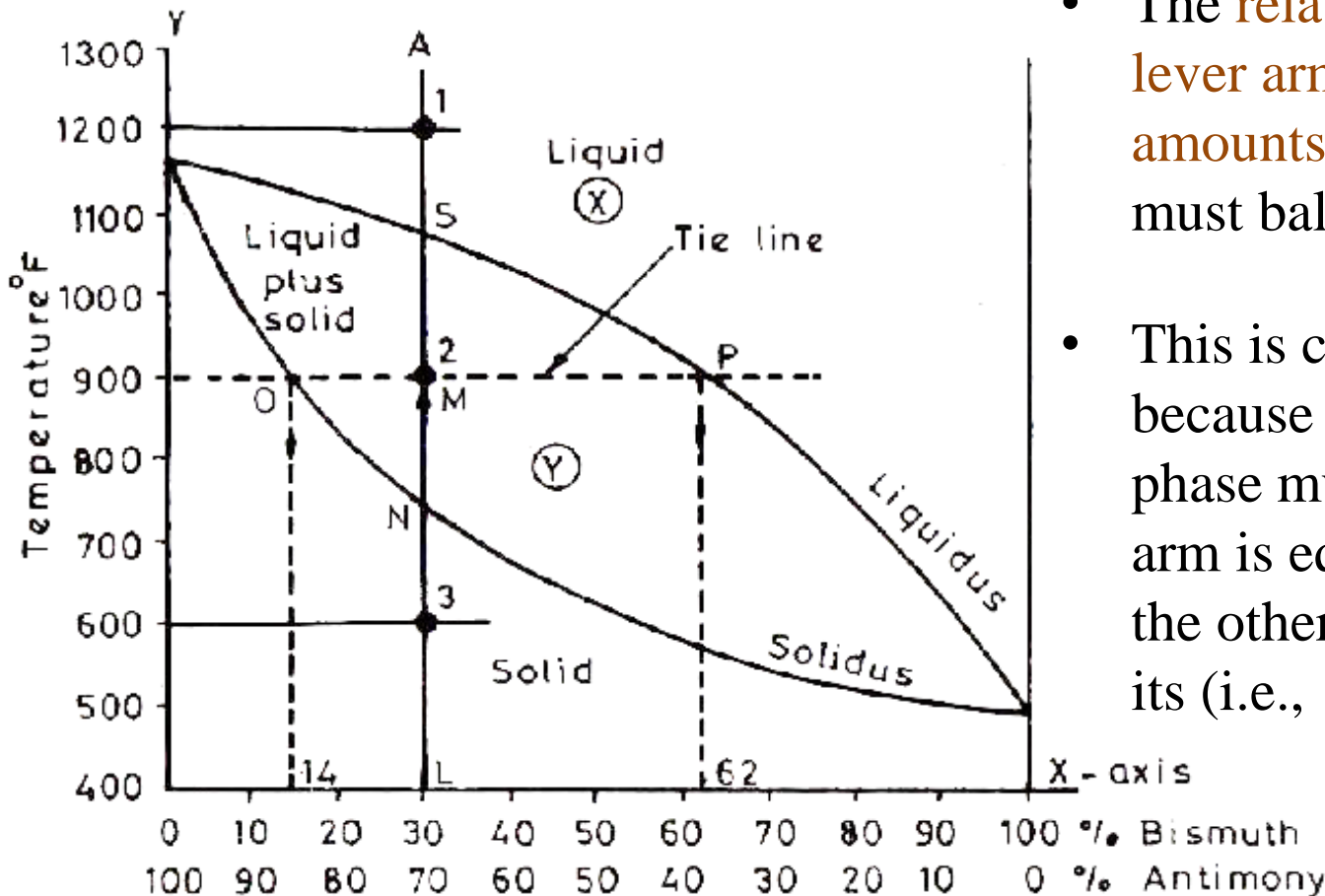
- Determine the **relative amount of two phases**, erect an ordinate at a point (30% Bi) on the composition scale which gives the total or overall composition of the alloy.





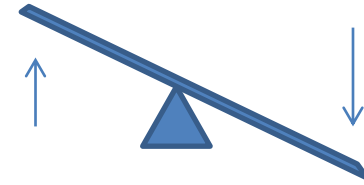
# Lever Arm Principle

- The intersection of this composition vertical (AL) and a given isothermal line OP (i.e., point M is the fulcrum of a simple lever system and OM and MP are two lever arms.)

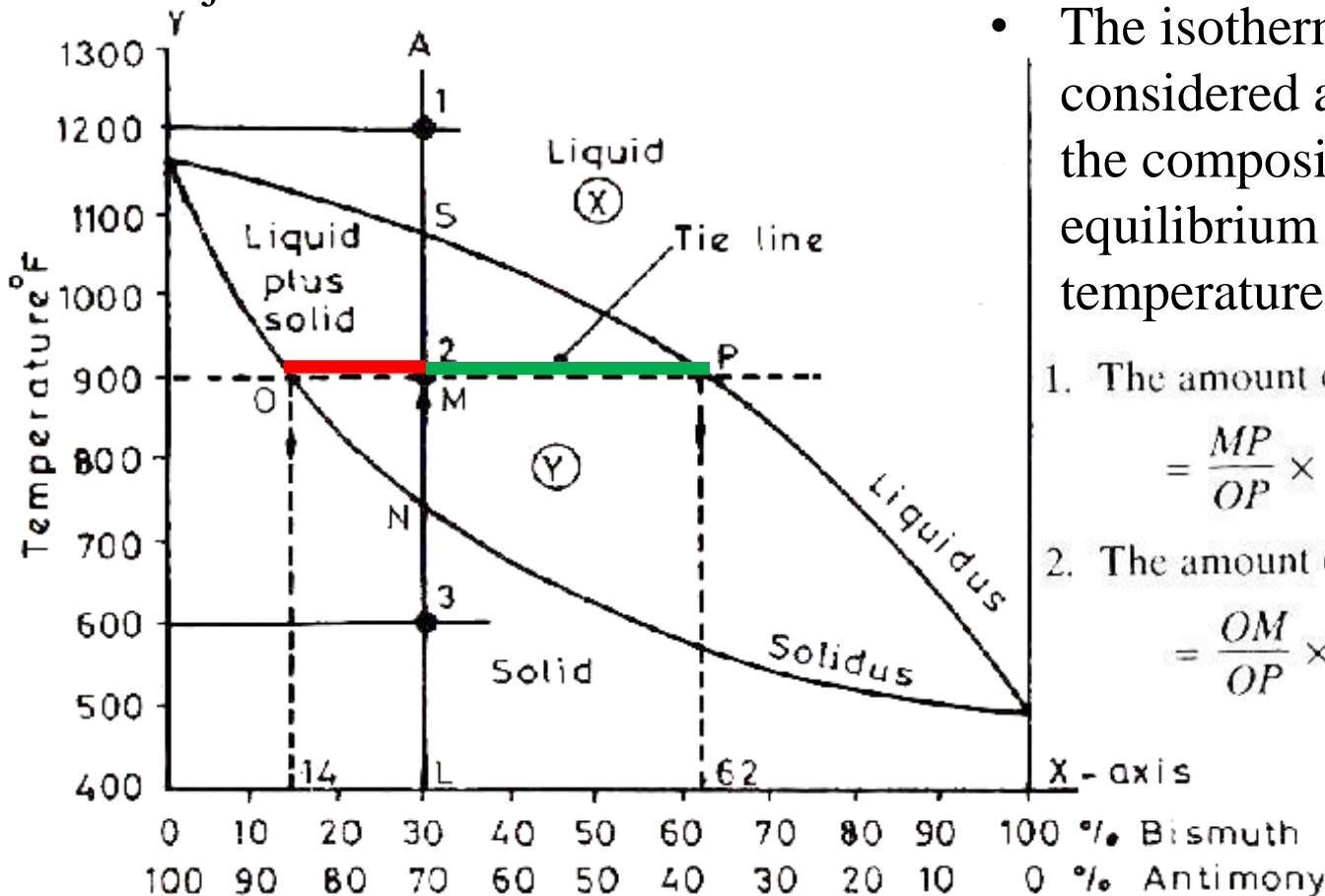


- The relative lengths of the lever arms multiplied by the amounts of the phase present must balance.
- This is called the lever rule because the amount of a given phase multiplied by its lever arm is equal to the amount of the other phase multiplied by its (i.e., other) lever arm.

# Lever Arm Principle



- It can also be seen that the proportion of solid corresponds to the length of the segment adjacent to liquidus line, whereas the fraction of liquid corresponds to the length of segment adjacent to the solidus line.



- The isotherm (line OMP) can be considered as a tie line, since it joins the composition of two phases in equilibrium at a specific temperature.

1. The amount of solid phase

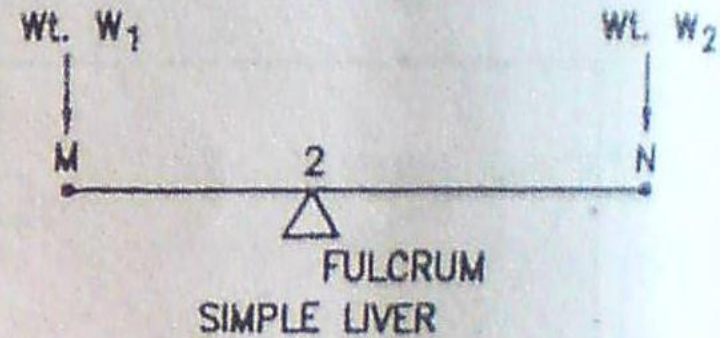
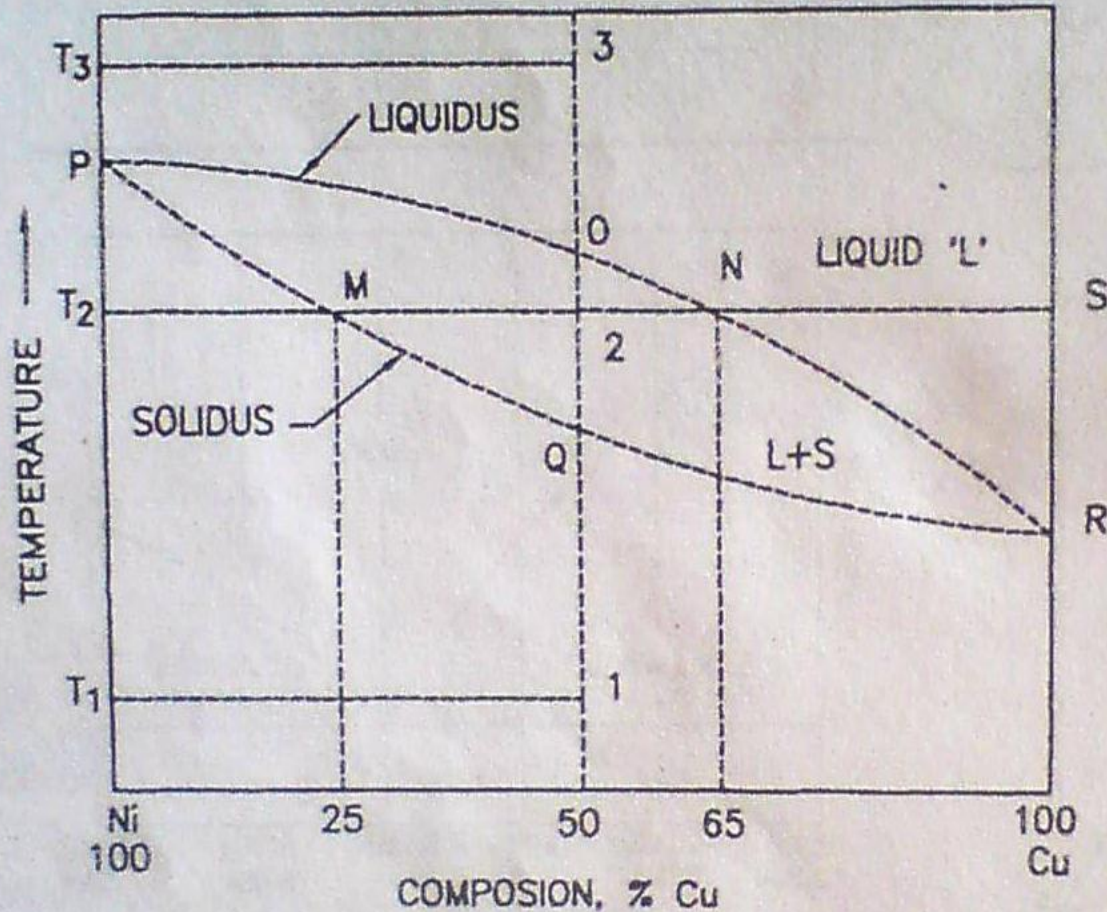
$$= \frac{MP}{OP} \times 100 = \frac{(62 - 30)}{(62 - 14)} \times 100 = 66\frac{2}{3}\%$$

2. The amount of liquid phase

$$= \frac{OM}{OP} \times 100 = \frac{30 - 14}{62 - 14} \times 100 = 33\frac{1}{3}\%$$

## Relative amount of each phase

- % Liquid =  $(M2/MN) \times 100 = [(50-25)/(65-25)] \times 100 = 62.5\%$
- % Solid =  $(2N/MN) \times 100 = [(65-50)/(65-25)] \times 100 = 37.5\%$



LEVER RULE

$$W_2 \times N_2 = W_1 \times M_2$$

= MUST BALANCE

# Gibbs's Phase Rule

- The Phase Rule, known as Gibbs Phase Rule, establishes the **relationship between** the number of degrees of freedom (F), the number of components (C) and the number of phases (P). It is expressed mathematically as follows:

$$\mathbf{P + F = C + 2}$$

- where, P is the number of phases (e.g., solid, liquid etc.)
- F is the number of degrees of freedom or the number of physical ' variables (pressure, temperature and concentration) that **can be independently changed without altering the equilibrium**, i.e., **without causing disappearance of a phase or the formation of a new phase in the system.**
- C is the number of components in the system (for example, Pb and Sn are the components of Pb-Sn equilibrium diagram.

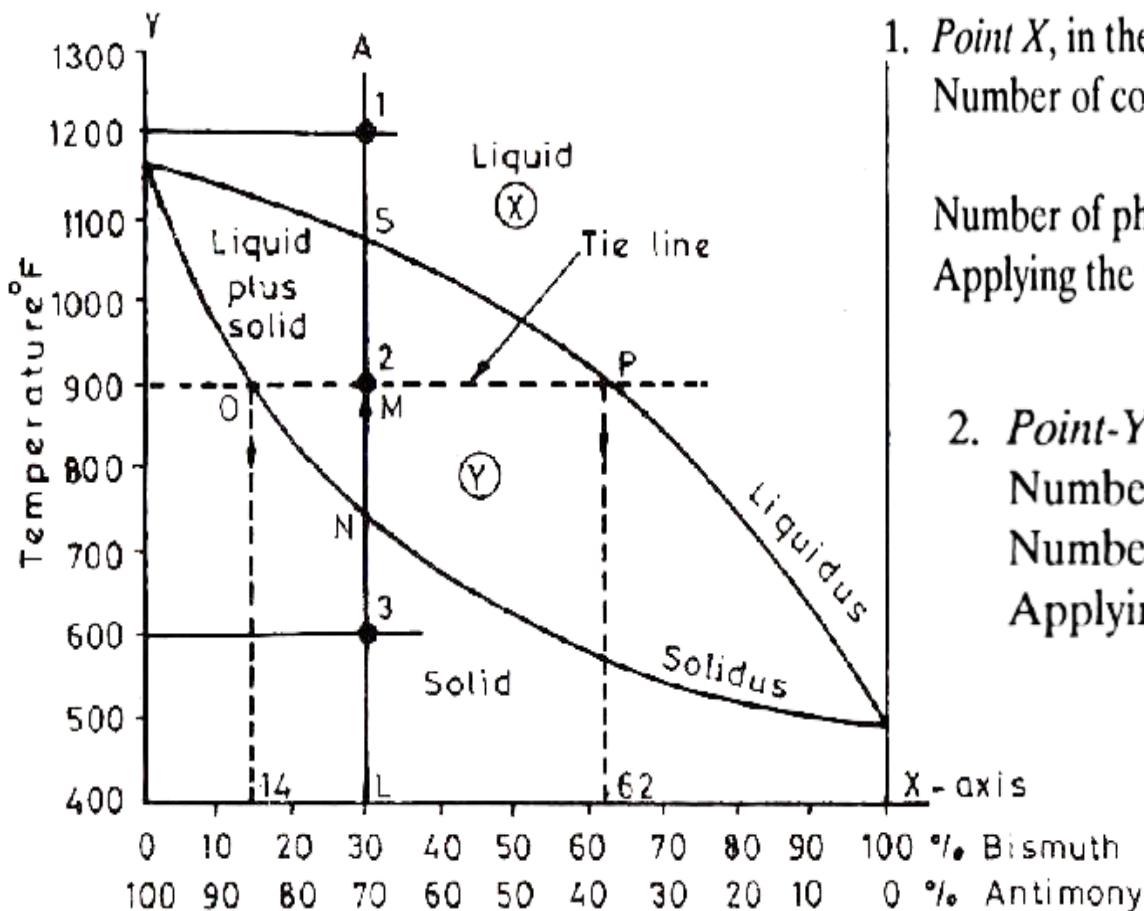
# Gibbs's Phase Rule

- “Provided the equilibrium between any no. of phases is not influenced by gravity or electrical forces or magnetic forces or surface tension, and **influenced only by the temperature, pressure and concentration** then the no. of degrees of freedom (F) of the system is related to no. of components (C) and phases (P) can be related by the phase rule equation.  $F = C - P + 2$
- In studying the chemical equilibrium, temperature and pressure are considered as external factors determining the state of the system. Therefore in the phase rule equation, the digit 2 stands for these two variables – temperature and pressure.
- In applying the Gibb's phase rule to the metal systems, the pressure is considered as remaining fixed at one atmosphere. Thus, the effect of pressure is neglected, leaving only one variable factor i.e. temperature.
- The phase rule equation then simplifies to  $F = C - P + 1$
- since the degrees of freedom F cannot be less than zero
- $C + 1 - P \Rightarrow 0$ , OR  $P \leq C + 1$  which means the **number of Phases can not exceed the number of component plus one.**

# Gibbs's Phase Rule

Therefore in a Binary system having value of  $C = 2$ , not more than  $(2 + 1 = ) 3$  phases may be in equilibrium.

– Considering points  $X$  and  $Y$  in Fig. 39.4, it is required to determine the number of degrees of freedom using the phase rule.



- Point X*, in the region above the liquidus  
 Number of components ( $C$ ) = 2, Since it is a binary system of Bi and Sb,  
 Number of phases ( $P$ ) (liquid) = 1  
 Applying the rule,  $F = C + 2 - P = 2 + 2 - 1 = 3$  degrees of freedom.
- Point-Y*, between the liquidus and solidus  
 Number of components ( $C$ ) = 2  
 Number of phases ( $P$ ) (liquid and solid) = 2  
 Applying the rule,  $F = C + 2 - P = 2 + 2 - 2 = 2$  degrees of freedom.

# Gibbs's Phase Rule

- In equilibrium, all factors have definite (non-zero) values. Therefore, all degrees of freedom cannot be less than zero. Mathematically,  
$$F > 0 \Rightarrow C - P + 1 > 0 \Rightarrow C + 1 > P$$
- This means that the no. of phases in a system cannot exceed the no. of components in a system plus one.
- For, a Binary alloy (2 metal alloy) system, no. of components  $C = 2$
- ✓ Now, if
  - $P = 1 \Rightarrow F = 2 - 1 + 1 = 2$  This is called Bi-variant System
  - $P = 2 \Rightarrow F = 2 - 2 + 1 = 1$  This is called Mono-variant System
  - $P = 3 \Rightarrow F = 2 - 3 + 1 = 0$  This is called Non-variant System
- ✓ Now, if
  - $F = 2 \Rightarrow$  Both temperature and pressure can be varied independently
  - $F = 1 \Rightarrow$  Only one out of temperature and pressure can be varied independently
  - $F = 0 \Rightarrow$  Neither temperature nor pressure can be varied independently.

# Reactions

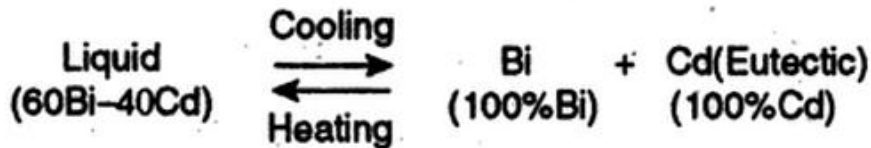
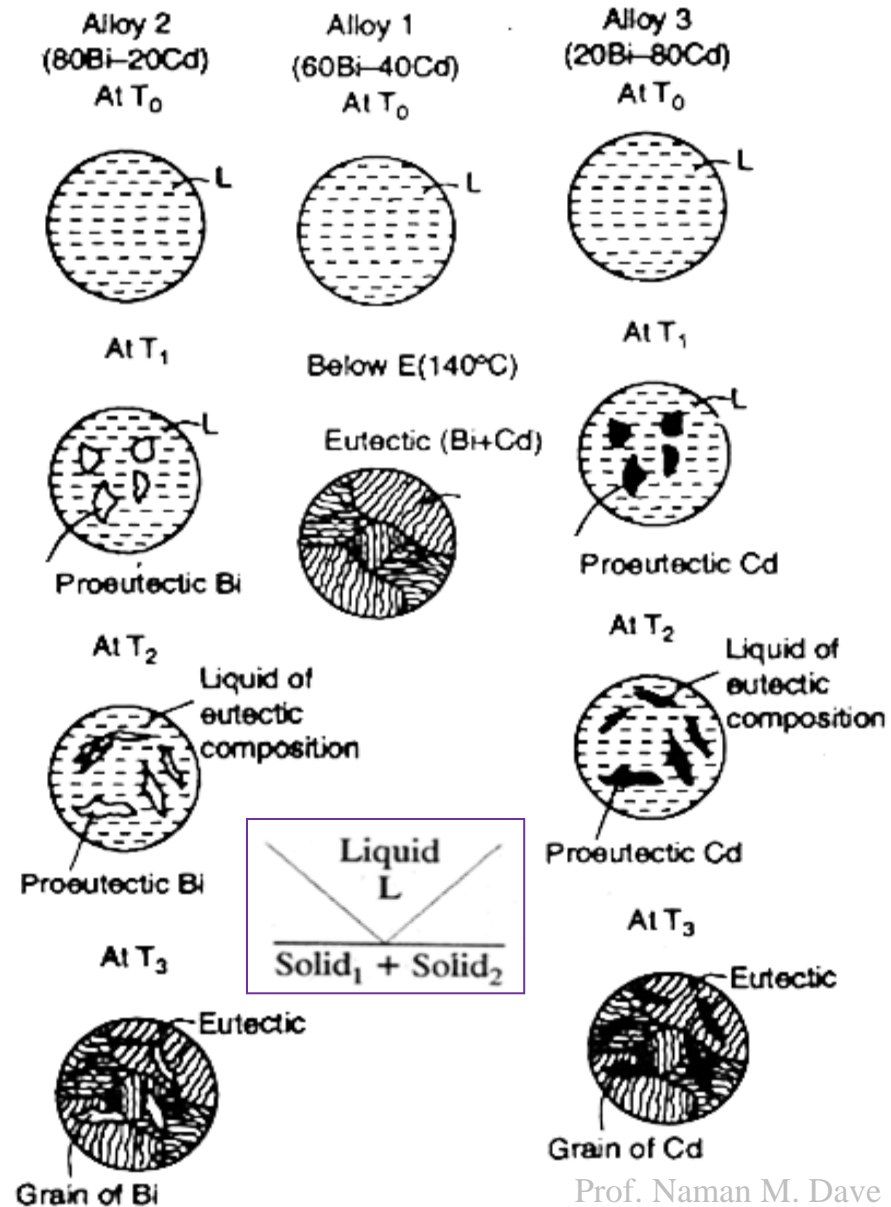
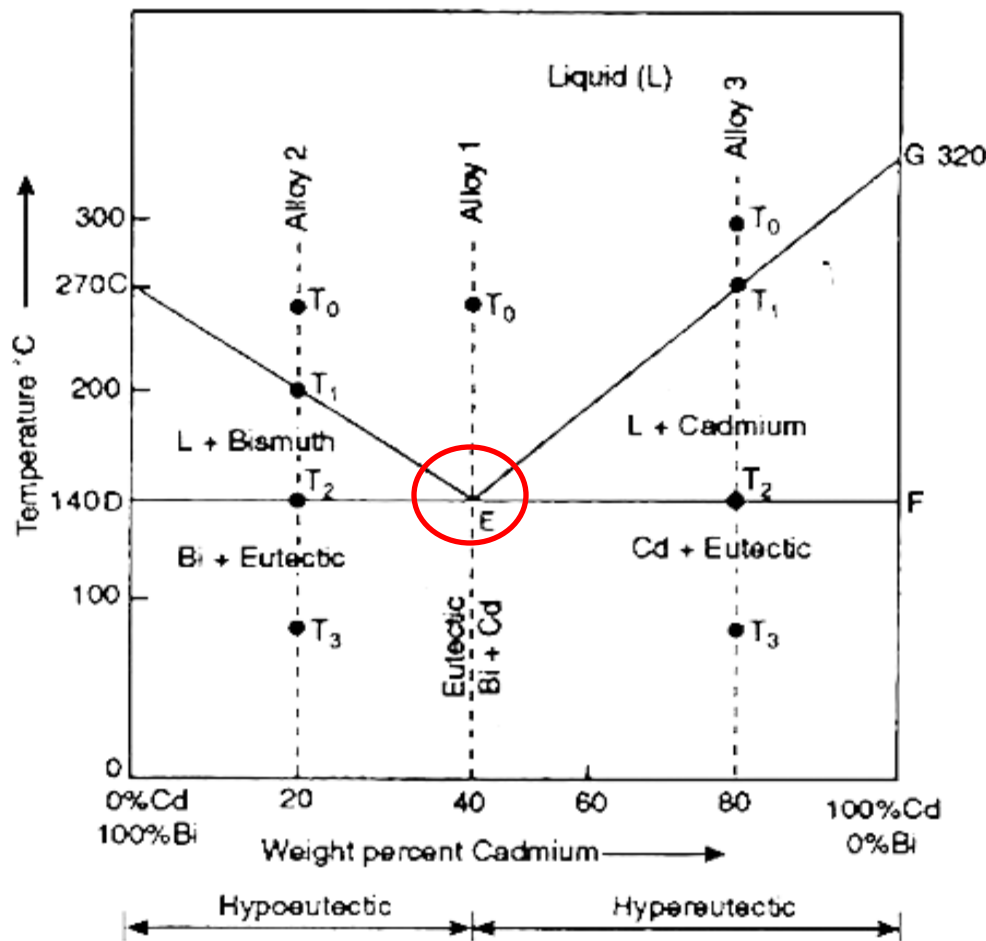
## CLASIFICATION OF EQUITIBRIUM DIAGRAMS

- An equilibrium diagram has been defined as a plot of the composition of phases is function of temperature in any alloy system under equilibrium conditions
- Equilibrium diagrams may be classified according to the relation of the component in the liquid and solid states as follows:

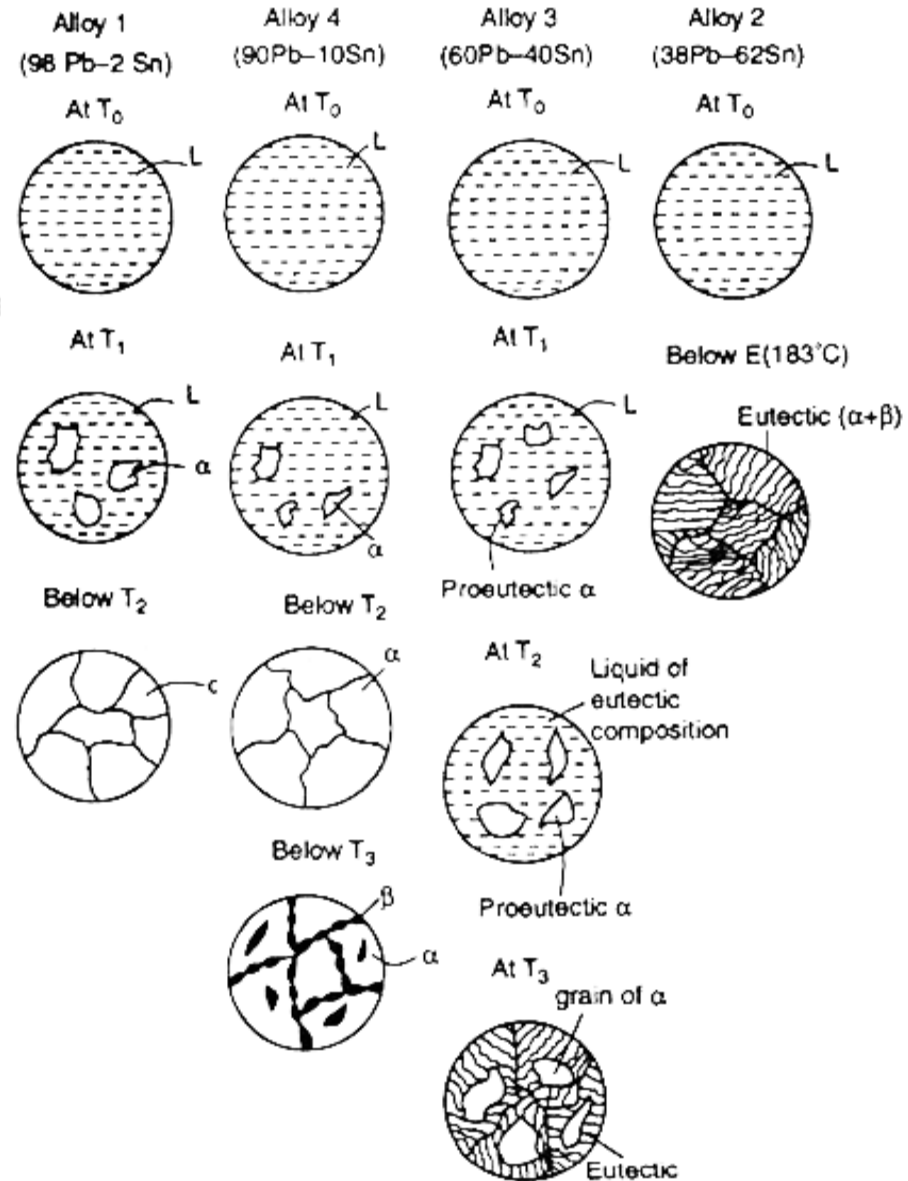
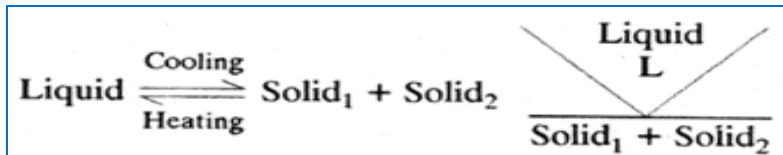
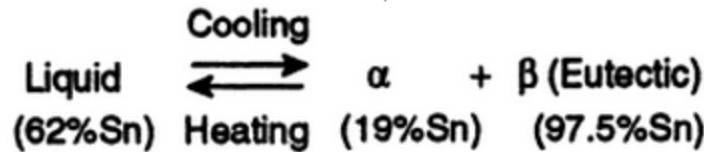
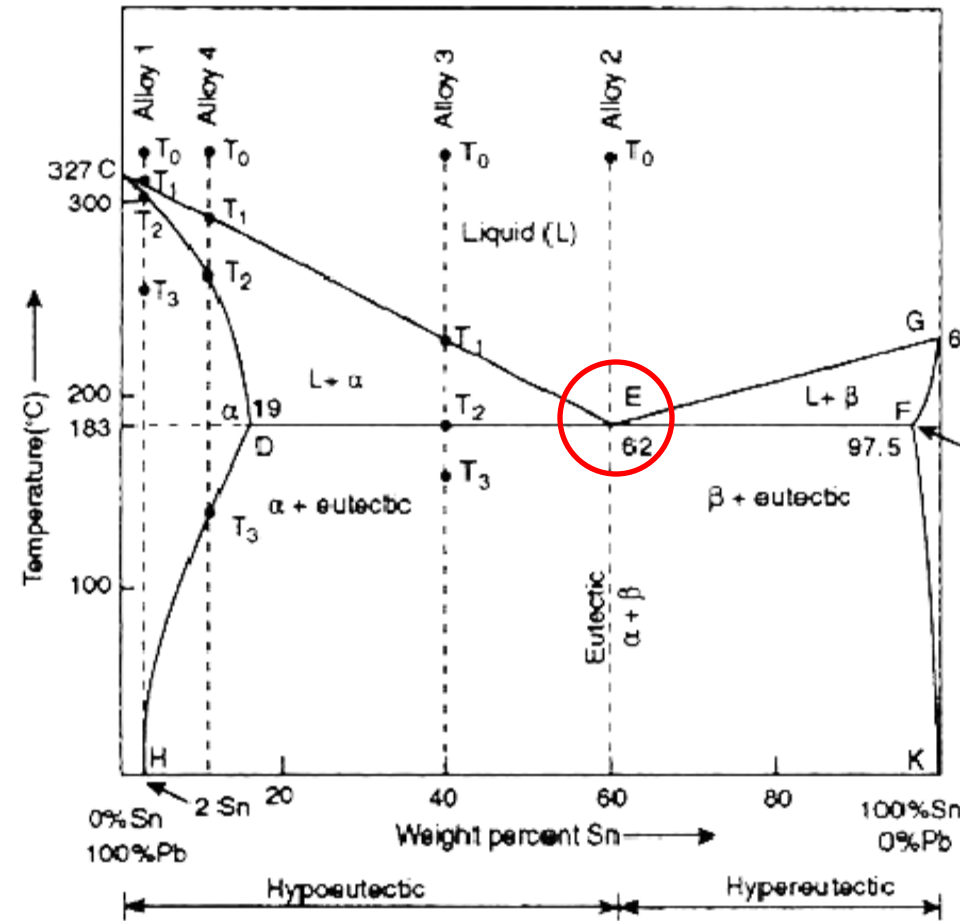
- ❑ Components completely soluble in the liquid state,
  - and also completely soluble in the solid state,
  - but partly soluble in the solid state (EUTECTIC REACTION Type I).
  - but insoluble in the solid state (EUTECTIC REACTION Type II)
  - The PERITECTIC Reaction
- ❑ Transformation in solid state
  - Eutectoid reaction
  - Peritectoid reaction
- ❖ Types of reactions in binary phase diagrams
  - Eutectic Reaction
  - Peritectic Reaction
  - Eutectoid reaction
  - Peritectoid reaction



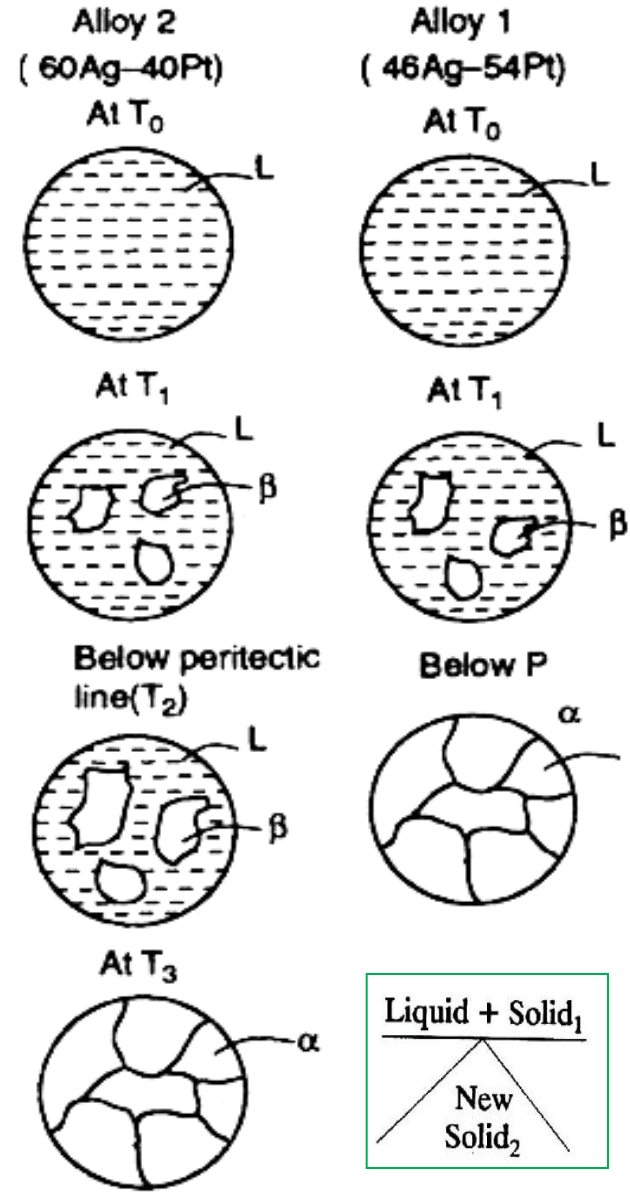
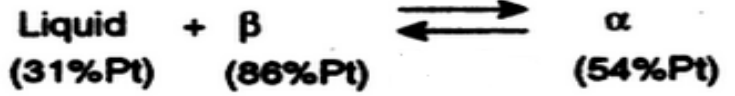
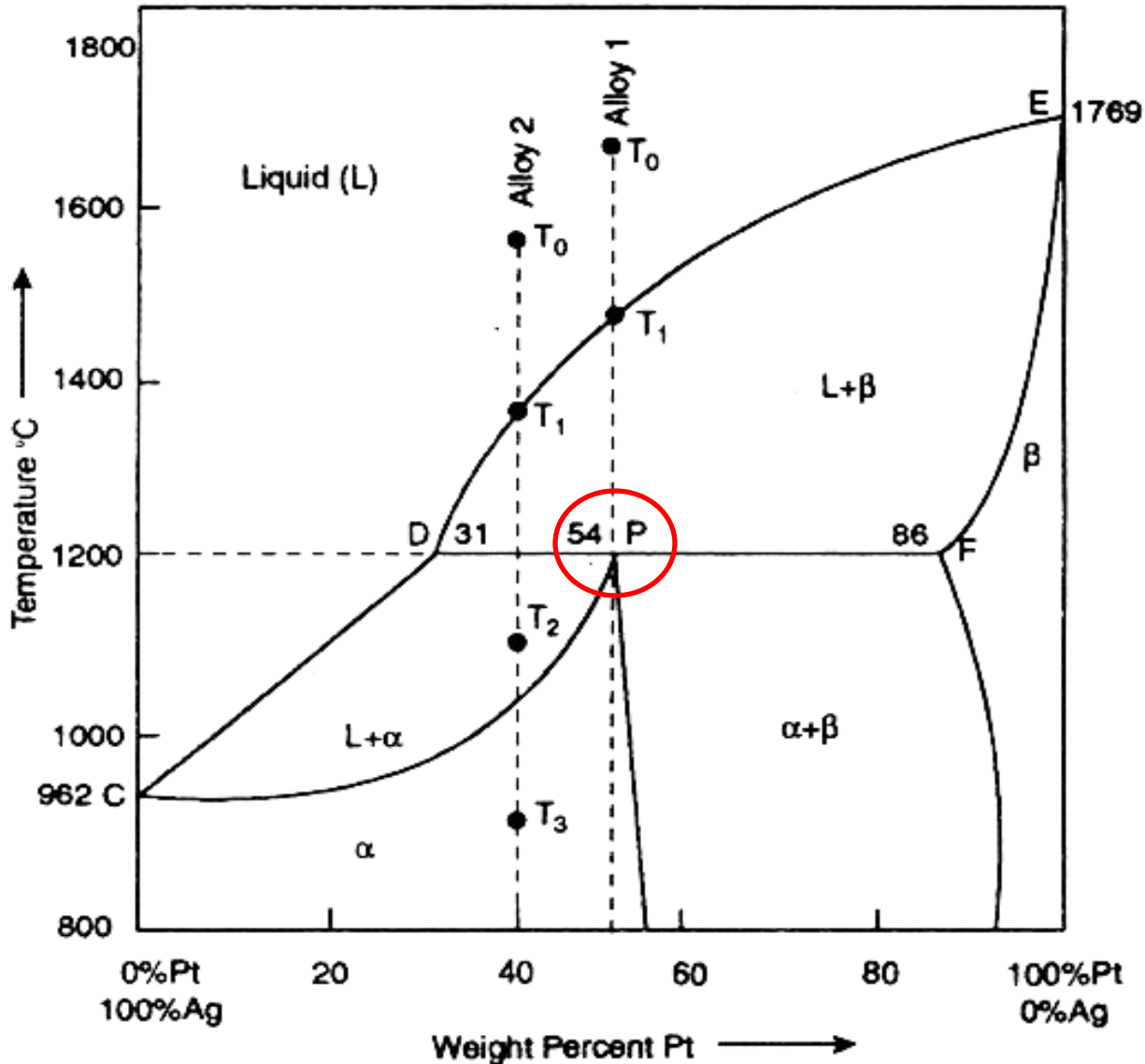
# Eutectic Reaction I-Type



# Eutectic Reaction II-Type

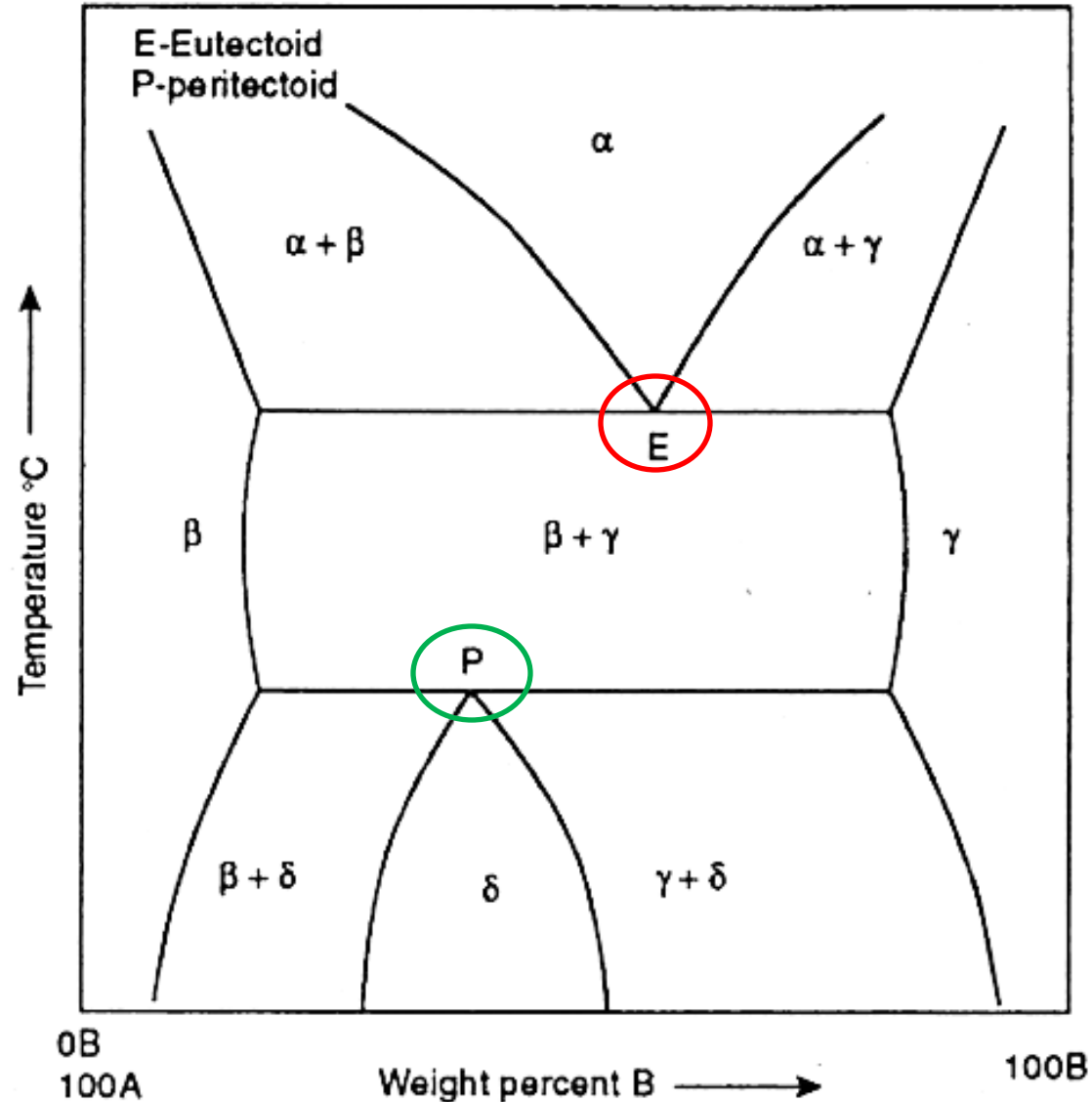
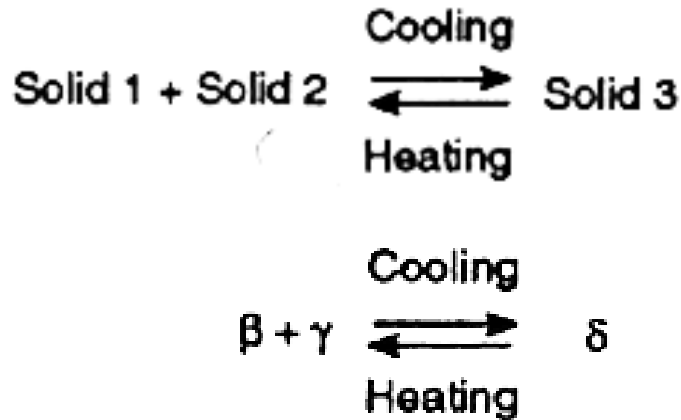
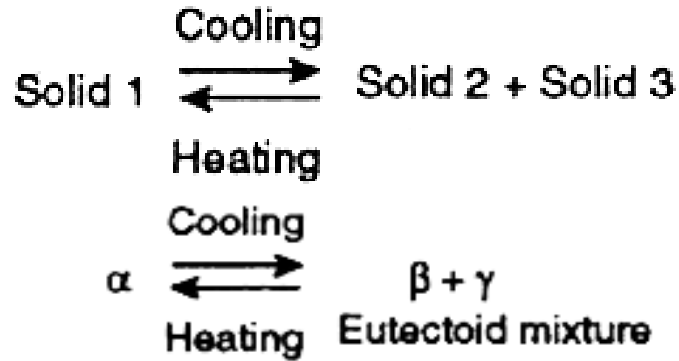


# Peritectic Reaction



# Eutectoid reaction

# Peritectoid reaction



# Types of reactions in binary phase diagrams

Name of reaction	Equation	Phase diagram characteristic
Eutectic	$L \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \alpha + \beta$	
Peritectic	$\alpha + L \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \beta$	
Eutectoid	$\alpha \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \beta + \gamma$	
Peritectoid	$\alpha + \beta \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \gamma$	

