

## Binary Phase Diagrams

- A binary phase is a two component system. Temperature & Composition are the usual variables in binary phase diagrams.
- Pressure changes often have little effect on the equilibrium of solid phases. Hence, binary phase diagrams are usually drawn at 1 atmosphere pressure.
- Binary phase diagrams are most commonly used in alloy designing.
- The Gibbs phase rule is reduced to  $F = C - P + 1$ . (1 is for T).
- Fe-Ni, Cu-Ni, Ag-Au,  $Al_2O_3 - Cr_2O_3$ , Pb-Sn and Fe-Fe C are the examples for a

two-component system.

### Classification of binary phase diagrams

- These have been classified based on:
  - Two metals Complete Solubility in both liquid & solid states- Isomorphous binary alloy system.
  - Partial Solubility in solid state-Eutectic system
  - Phase diagram containing three phase reactions

### The tie-line Rule-the Lever Rule

A tie-line is a horizontal line drawn in a two-phase region of a binary phase diagram, to determine the composition of two phases.

Consider the phase

diagram of metal A (Cu) and metal B (Ni). The composition is plotted on X-axis and temperature on Y-axis. Let  $x$  be the alloy composition of interest and  $T$  be the temperature of interest.

### Simple procedure to find the equilibrium compositions of the two phases

- A tie line is constructed across the two-phase region at the temperature of the alloy.
- The intersections of the tie line and the phase boundaries on either side are noted.
- Vertical lines are dropped from these intersections to the horizontal composition axis, from which the composition of each of the respective phases is determined.
- The opposite arms of the lever are proportional to the fraction of the solid and liquid phases present (this is the lever rule).

$$W_L = \frac{LO}{LS}$$

And

$$W_S = \frac{OS}{LS}$$

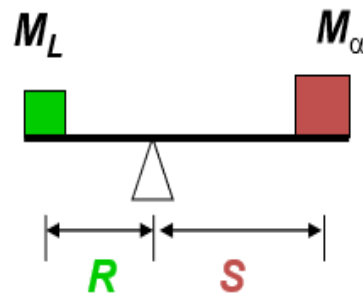
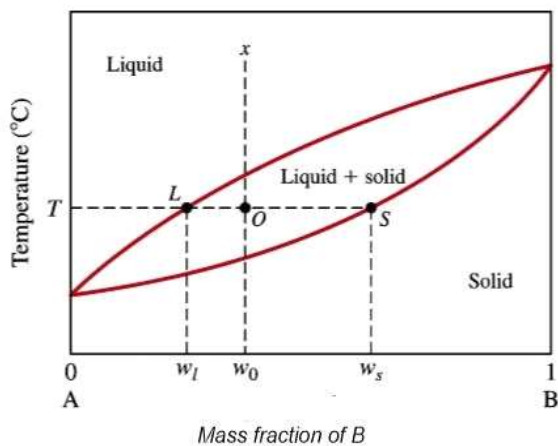


Figure.1.9 Tie line and lever rule

### Lever Rule

The lever rule is used to find the fractions of liquid phase and solid phase in the binary alloy in the two-phase state at equilibrium.

The rule can be obtained by using the law conservation of mass.

Let  $W_L$

be the weight fraction of liquid phase and

$W_S$  be the weight fraction of solid

phase in the binary alloy in the state B.

Then

$$W_L + W_S = 1 \dots \dots \dots (1)$$

The mass fraction of Ni in the liquid phase + the mass fraction of Ni in the solid phase

must be equal to the mass fraction of Ni in the  $S + L$  phase.

The mass fraction of Ni in the liquid phase of mass fraction  $W_L = C_L W_L$

The mass fraction of Ni in the solid phase of mass fraction  $W_S = C_S W_S$

The mass fraction of Ni in the  $(S + L)$  phase =  $C_o$

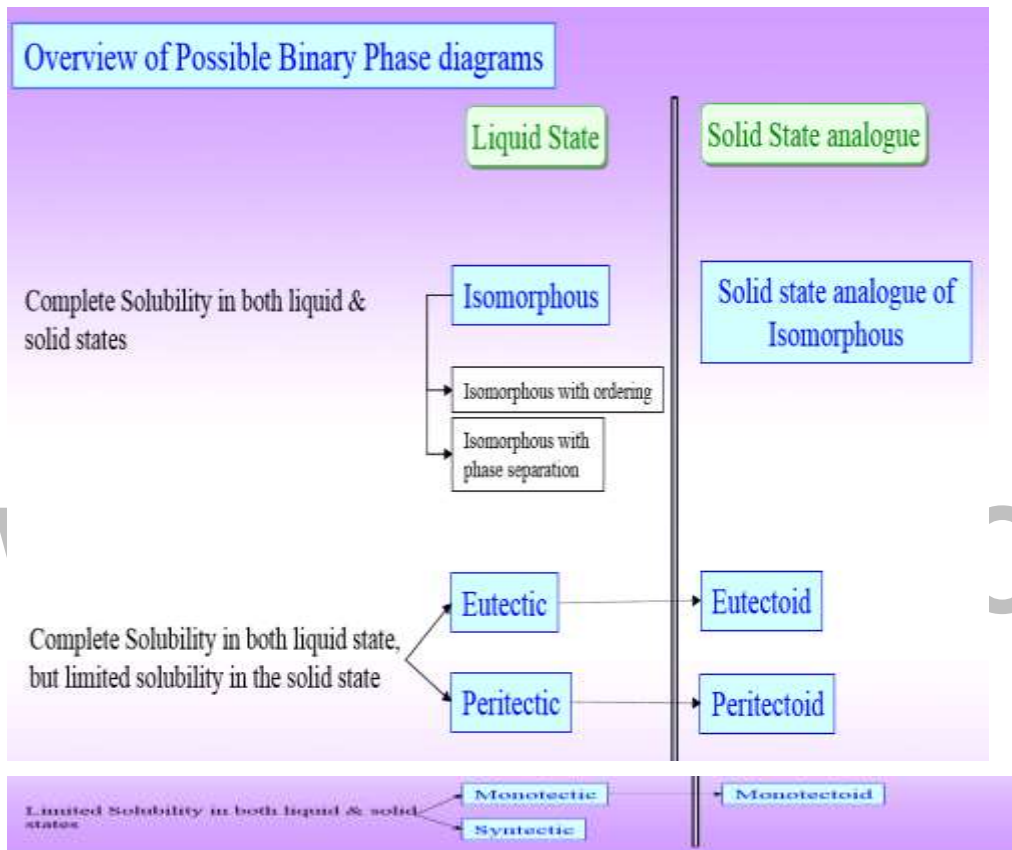
$$\text{So } C_L W_L + C_S W_S = C_o \dots \dots \dots (2)$$

From equations (1) and (2)

$$W_L = \frac{C_S - C_o}{C_S - C_L} \text{ and } W_S = \frac{C_o - C_L}{C_S - C_L}$$

Thus one can find the composition of liquid phase and solid phase in the two- phase system and also the composition of the constituents in the liquid phase and the solid phase, using the phase diagram.

### Overview of Possible Binary Phase diagrams



### Isomorphous binary alloy system

In some binary metallic systems, the two elements completely soluble in each other in both the liquid and solid state. In these systems, only a single type of crystal structure exists for all compositions of the components, and therefore they are called isomorphous systems.

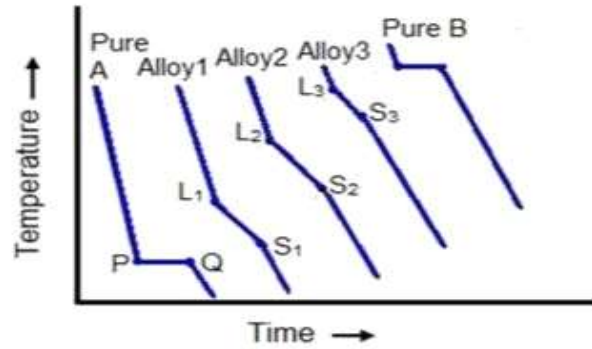
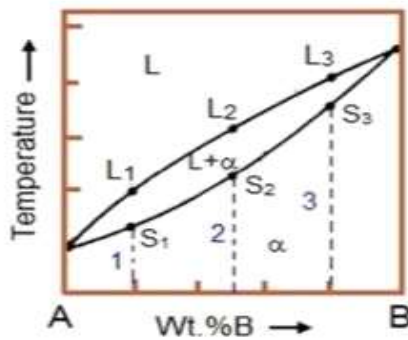
- An important example of an isomorphous binary alloy system is the copper–nickel system.
- Temperature is plotted along the ordinate, and the abscissa represents the composition of the alloy.
- The composition ranges from 0 wt% Ni (100 wt% Cu) on the left horizontal extremity to 100 wt% Ni (0 wt% Cu) on the right.
- Three different phase regions appear on the diagram, a solid ( $\alpha$ ) field, a liquid ( $L$ ) field, and a two-phase ( $\alpha + L$ ) field.
- The solid ( $\alpha$ ) phase is a substitutional solid solution consisting of both Cu and Ni atoms, and having an FCC crystal structure.
- The liquid  $L$  is a homogeneous liquid solution composed of both copper and nickel.
- This complete solubility is explained by the fact that both Cu and Ni have the same crystal structure (FCC), nearly identical atomic radii and electronegativities, and similar valences.
- **Liquidus** line is the line or boundary that separates liquid and liquid + solid phase regions. The liquid phase is present at all temperatures and compositions above this line. **Solidus line** is the line or boundary that separates solid and solid + liquid phase regions. The line below which solidification completes is called solidus line.
- The intermediate region between liquidus and solidus lines is the two-phase region where liquid and solid coexists. It can be noted that the two metals are soluble in each other in the entire range of compositions in both liquid and solid state. This kind of system is known as ‘Isomorphous’ system.

- The copper–nickel system is termed **isomorphous** because of this complete liquid and solid solubility of the two components.
- The melting temperatures of pure copper and nickel are 1085°C and 1453°C, respectively. At temperatures below about 1085°C, copper and nickel are mutually soluble in each other in the solid state for all compositions.

For example, upon heating an alloy of composition 50 wt% Ni–50 wt% Cu (Figure 9.3a), melting begins at approximately 1280°C (2340°F); the amount of liquid phase continuously increases with temperature until about 1320°C (2410°F), at which the alloy is completely liquid.

### Cooling curves

- Upon cooling from liquid state, the temperature of the pure metal (A or B) drops continuously till melting point at which solidification starts.
- Solidification happens at a constant temperature (line PQ) as  $F = 0$  ( $F = 1 - 2 + 1 = 0$ ). The temperature drops again on completion of solidification.
- For any alloy (1, 2, 3 etc.) temperature drops till the liquidus ( $L_1, L_2, L_3$ ). However, in this case, solidification proceeds over a range of temperature as  $F = 1$  ( $2 - 2 + 1 = 1$ ).
- Once solidification completes at the solidus ( $S_1, S_2, S_3$ ) the temperature drops again.



## INTERPRETATION OF PHASE DIAGRAMS

For a binary system of known composition and temperature that is at equilibrium, at least three kinds of information are available:

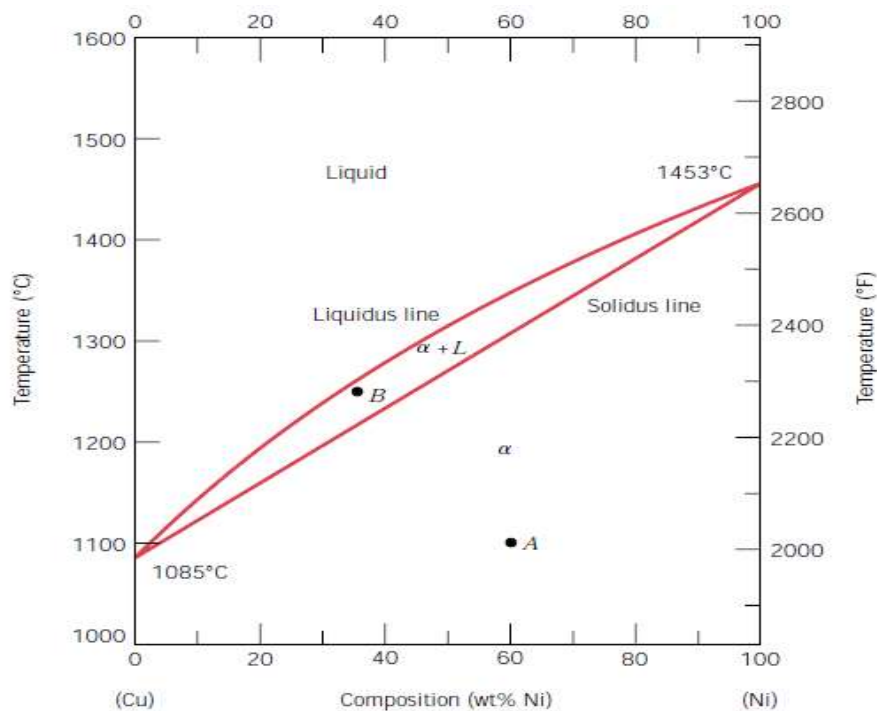
- the phases that are present,
- the compositions of these phases, and
- the percentages or fractions of the phases.

### Phases Present

- An alloy of composition 60 wt% Ni–40 wt% Cu at 1100°C would be located at point A in Figure 9.3a; because this is within the solid ( $\alpha$ ) region, only the single  $\alpha$  phase will be present. The Gibbs phase rule is reduced to  $F = C - P + 1$ . Here  $C=2$  and  $P=1$   $\therefore F = 2 - 1 + 1 = 2$
- On the other hand, a 35 wt% Ni–65 wt% Cu alloy at 1250 °C (point B) will consist of both solid and liquid phases at equilibrium. Here  $C=2$  and  $P=2$   $\therefore F = 2 - 2 + 1 = 1$

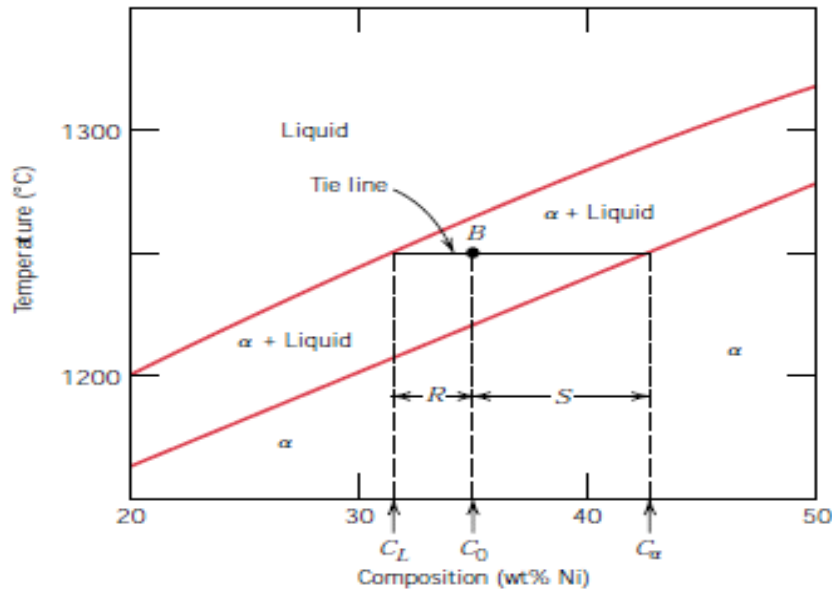
### Determination of Phase Compositions

- For an alloy having composition and temperature located in a two-phase region, the situation is more complicated. To compute the equilibrium concentrations of the two phases, the following procedure is used.
  - A tie line is constructed across the two-phase region at the temperature of the alloy.
  - The intersections of the tie line and the phase boundaries on either side are noted.
  - Vertical lines are dropped from these intersections to the horizontal composition axis, from which the composition of each of the respective phases is determined.



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**Figure 1.10** Isomorphous binary alloy system and its phase composition

Overall composition  $C_o = 35$  wt% Ni–65 wt% Cu alloy at 1250 °C, located at point  $B$

Liquid composition  $C_L = 31.5$  wt% Ni–68.5 wt% Cu  
 Solid composition  $C_\alpha = 42.5$  wt% Ni–57.5 wt% Cu.

### Determination of Phase Amounts

- The relative amounts (as fraction or as percentage) of the phases present at equilibrium may also be computed with the aid of phase diagrams. Then we have to apply the **lever rule**.

From figure,

$$C_o = 35 \text{ wt\% Ni} \quad C_L = 31.5 \text{ wt\% Ni} \quad C_\alpha = 42.5 \text{ wt\% Ni}$$

$$W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{42.5 - 35}{42.5 - 31.5} = 0.68 = 68\%$$

and

$$W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L} = \frac{35 - 31.5}{42.5 - 31.5} = 0.32 = 32\%$$

- Thus, the lever rule may be employed to determine the relative amounts or fractions of phases in any two-phase region for a binary alloy if the

temperature and composition are known and if equilibrium has been established

### $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ binary alloy system

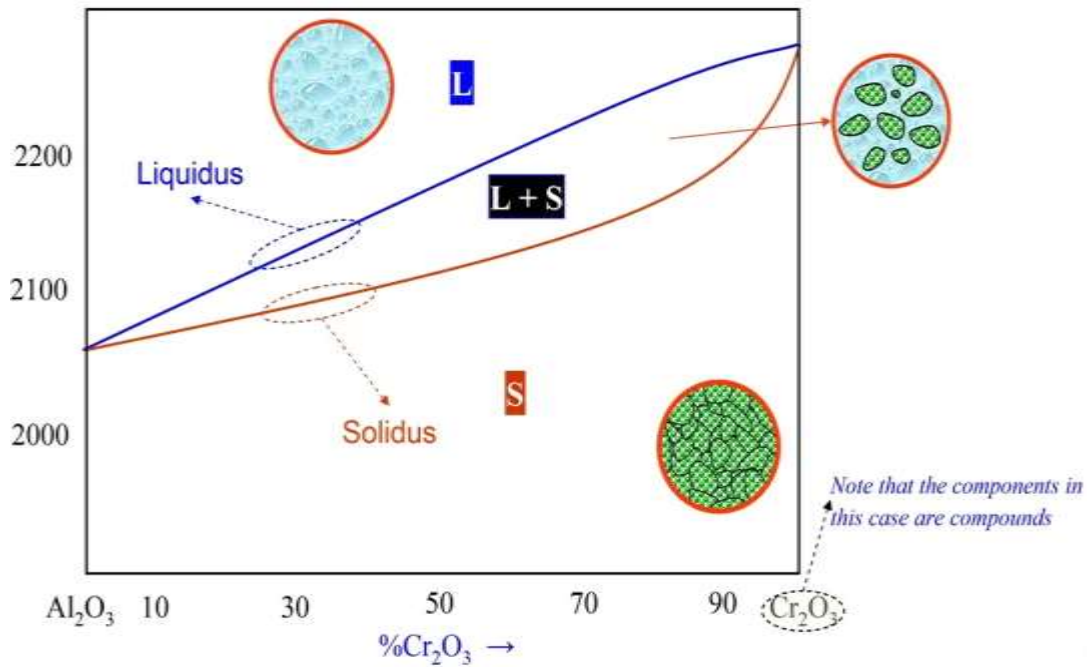


Figure.1.11  $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$  binary alloy system

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## Eutectic system

- The term EUTECTIC means Easy Melting → The alloy of eutectic composition freezes at a lower temperature than the melting points of the constituent components.
- **Liquid ( $L$ )  $\leftrightarrow$  solid solution-1 ( $\alpha$ ) + solid solution-2( $\beta$ )**
- A eutectic reaction is defined as the one which generates two solids from the liquid at a given temperature and composition.
- Examples: Cu-Ag, Pb-Sn and Al-Cu system.

## Eutectic phase diagram

- A phase diagram in which constituents exhibit complete solubility in liquid state and partial solubility in solid state is known as partial eutectic phase diagram.
- First of all, there are three single phase regions, namely liquid phase ( $L$ ),  $\alpha$  and  $\beta$  solid solution phases. There also exist three two phase regions:  $L+\alpha$ ,  $L+\beta$  and  $\alpha+\beta$  are found on the eutectic phase diagram.
- The  $\alpha$  phase is a solid solution in which elements of metal A (solvent) is more than that of metal B (solute). The  $\beta$  phase is a solid solution in which elements of metal B (solvent) is more than that of metal A (solute). The regions of limited solid solubility at each end of a phase diagram are called **terminal solid solutions ( $\alpha$  and  $\beta$ )** as they appear at ends of the diagram.
- **Liquidus** line is the line or boundary that separates liquid and liquid + solid phase regions. The line „**cdg**’ is known as liquidus line.
- **Solidus line** is the line or boundary that separates solid and solid + liquid phase regions. The line „**cbdfg**’ is known as **solidus line**.

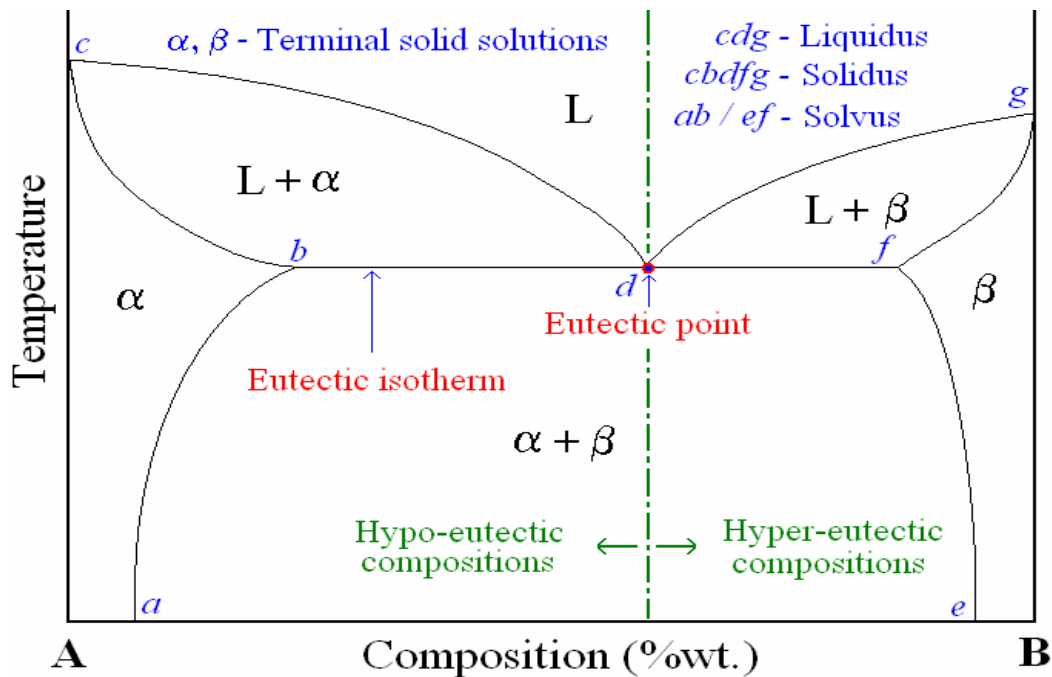


Figure.1.4. Typical phase diagram for a binary eutectic system.

- **Solvus lines** separate single phase solid regions from two phase solid regions. It also denotes the maximum solubility limits of metal A in B and of metal B in A respectively. The lines „ab“ and „ef“ are **solvus lines**.
- The introduction of metal B decreases the melting temperature of metal A along the liquidus line „cd“. Similarly the addition of metal A decreases the melting temperature of metal B along the liquidus line „gd“.
- These two liquidus lines met at the point, „d“ on the phase diagram. The point is known as **eutectic point**. Eutectic point is the lowest freezing point of the alloy. At this point three phases (L,  $\alpha$  and  $\beta$ ) are in equilibrium with each other.

The phase rule for a binary alloy

$$F = C - P + 1$$

Here  $C=2$  and  $P=3$  Hence degrees of freedom

$$F = 2 - 3 + 1 = 0$$

- The corresponding temperature and composition on the phase diagram is called

**eutectic temperature** and **eutectic composition** respectively.

- Eutectic temperature is the minimum temperature at which a binary system is melted completely.
- When the liquid of eutectic composition is cooled, at or below eutectic temperature this liquid transforms simultaneously into two solid phases (two terminal solid solutions, represented by  $\alpha$  and  $\beta$ ). This transformation is known as *eutectic reaction* and is written symbolically as:

**Liquid (L)  $\leftrightarrow$  solid solution-1 ( $\alpha$ ) + solid solution-2 ( $\beta$ )**

- This eutectic reaction is called invariant reaction as it occurs under equilibrium conditions at a specific temperature and specific composition which can not be varied. Thus, this reaction is represented by a thermal horizontal arrest in the cooling curve of an alloy of eutectic composition.
- Compositions that are on left-hand-side of the eutectic composition are known as **hypo-eutectic compositions** while compositions on right-hand-side of the eutectic composition are called **hyper-eutectic compositions**. The phase that forms during cooling but before reaching eutectic temperature is called **pro- eutectic phase**.

**Microstructural Changes on cooling**

- Development of micro-structure and respective cooling curves for eutectic alloys are shown in *figure* for different compositions.
  - The three two phase regions are separated by horizontal line corresponding to the eutectic temperature. Below the eutectic temperature, the material is fully solid for all compositions. Compositions and relative amount of the phases can be determined using tie-lines and lever rule.
  - While cooling a hypoeutectic alloy from the liquid state, the temperature drops continuously till liquidus point, a, at which crystals of proeutectic  $\alpha$  begins to form.
  - On further cooling the fraction of  $\alpha$  increases. At any point, b, in the two-phase region the  $\alpha$  fraction is given by the lever rule. Solidification of proeutectic  $\alpha$  continues till the eutectic temperature is reached.
  - The inflection in the cooling curve between points a and e is due to evolution of the latent heat. At the eutectic point (e) the solidification of eutectic mixture ( $\alpha + \beta$ ) begins through the eutectic reaction and proceeds at a constant temperature as  $F = 0 (2 - 3 + 1)$ .
- The cooling behavior in hypereutectic alloy is similar except that proeutectic  $\beta$  forms below the liquidus.
- For a eutectic composition, the proeutectic portion is absent and the cooling curve appears like that of a pure metal.
  - Any composition left of point c or right of point d ( $\alpha$  and  $\beta$  single phase regions respectively) will cool and solidify like an isomorphous system.

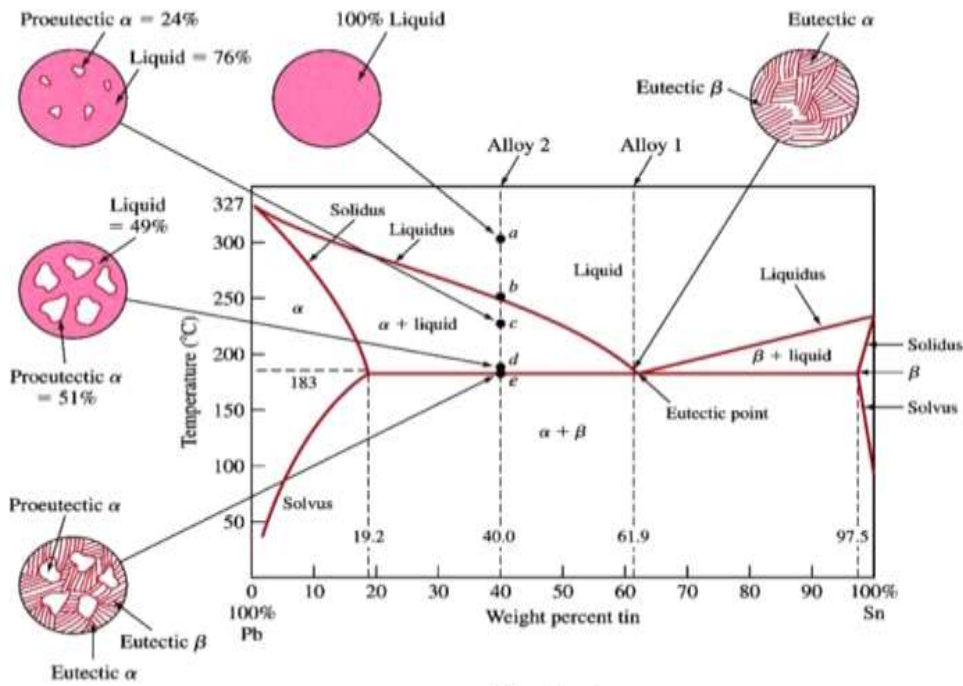


Figure.1.5.Cooling curve and micro-structure development for eutectic alloy

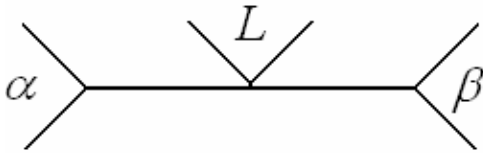
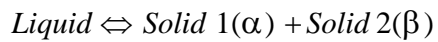
### Invariant reactions:

- Invariant means that there are zero degrees of freedom. That is, the reaction occurs with a fixed composition at a fixed temperature. There are many types of reaction that occur in binary equilibrium diagrams. Some of the important reactions that are found generally in different phase diagrams are:

- Eutectic reaction 2. Peritectic reaction 3. Eutectoid reaction 4. Peritectoid reaction

### Eutectic reaction

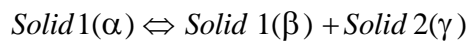
- Eutectic reaction is the reversible, isothermal reaction of a liquid phase  $L$ , transforms into two different solids phases ( $\alpha$  and  $\beta$ ) upon cooling. Eutectics are found in many metallic and ceramic systems- Fe-C, Al-Si, Ag-Au, Sn-Pb.



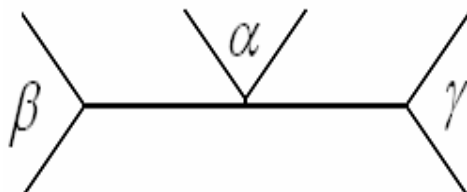
Schematic of eutectic invariant reaction

### Eutectoid reaction

- Eutectoid reaction is the reversible, isothermal reaction of a solid phase ( $\alpha$ ) transforms into two different solids phases ( $\beta$  and  $\gamma$ ) upon cooling.



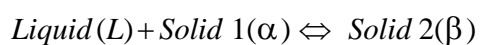
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Eutectoid reaction is found in many systems such as Cu-Al, Cu-Sn, Al-Mn

### Peritectic reaction

- Peritectic reaction is the reversible, isothermal reaction of a solid phase ( $\alpha$ ) reacts with a liquid phase to produce a new solid phase upon cooling.



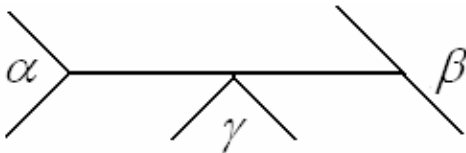
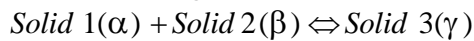




Peritectic reaction is found in Sb-Sn and Pt-Ag systems.

### Peritectoid reaction

- Peritectoid reaction is the reversible, isothermal reaction in which two solid phases ( $\alpha$  and  $\beta$ ) transform into a single new solid phase ( $\gamma$ ) upon cooling.



Peritectoid reaction is found in many systems such as Ni-Zn, Ni-Mo, Fe-Nb

### Monotectic reaction

- Monotectic reaction is an invariant reaction in which a liquid phase transforms into a solid phase and a liquid phase of different composition.

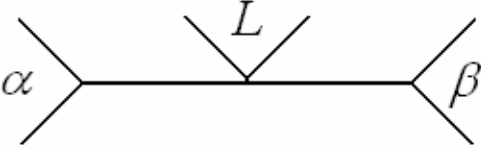
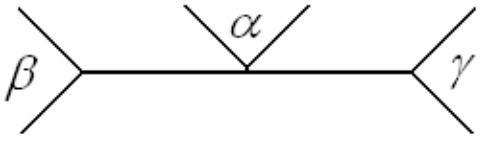
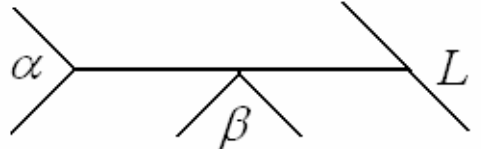

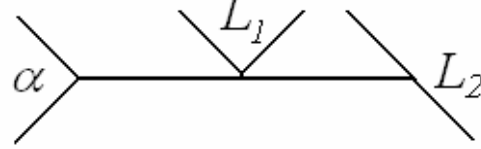
### Monotectoid reaction

- Monotectoid reaction is an invariant reaction in which a solid phase transforms to produce two solid phases of different compositions.

### Syntectic reaction

- Another notable invariant reaction that is associated with liquid immiscibility is **syntectic reaction** in which two liquid phases react to form a solid phase.

- All the invariant reactions are summarized in the table-1 showing both symbolic reaction and schematic part of phase diagram.

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \leftrightarrow \alpha + \beta$		Fe-C, 4.27%  C, 1147° C
Eutectoid	$\alpha \leftrightarrow \beta + \gamma$		Fe-C, 0.80%  C, 723° C
Peritectic	$L + \alpha \leftrightarrow \beta$		Fe-C, 0.16 % C, 1495° C
Peritectoid	$\alpha + \beta \leftrightarrow \gamma$		Ni-Zn, Ni-Mo, Fe-Nb
Monotectic	$L_1 \leftrightarrow L_2 + \alpha$		Fe-C, 0.51%  C, 1495° C

Summary of invariant reactions in binary systems

## Peritectic Phase Diagram

Like the eutectic system, the peritectic reaction is found in systems with complete liquid solubility but limited solid solubility.

- Peritectic reaction is the reversible, isothermal reaction of a solid phase ( $\alpha$ ) reacts with a liquid phase to produce a new and different solid phase upon cooling.

*Liquid (L) + Solid*

$1(\alpha) \leftrightarrow$

*Solid 2( $\beta$ )*

- Peritectic reaction is found in Sb-Sn and Pt-Ag systems.
- The melting points of the two components are quite different.

### Pt-Ag system

- Let us consider silver-platinum as an example for peritectic phase diagram. Silver melts at  $961^\circ\text{C}$  and platinum melts at  $1769^\circ\text{C}$ . The melting points of the components differ more than  $800^\circ\text{C}$ . In this system, the peritectic reaction  $L + \alpha \leftrightarrow \beta$  occurs at 42.4% Ag and  $1186^\circ\text{C}$ . Since the solid  $\beta$  forms at the interface between the L and the solid( $\alpha$ ), further reaction is dependent on solid state diffusion.
- The region marked „liquid“ above the liquidus line shows the binary alloy present in complete liquid phase.
- The region marked “ $\alpha$ ” below the solidus line shows the presence of alloy in pure  $\alpha$  which is a solid solution phase rich in Ag.

- The region marked “ $\beta$ ” below the solidus line shows the presence of alloy in pure  $\beta$  which is a solid solution phases rich in Pt.
- The region marked “ $L+\beta$ ” between the solidus line and liquidus line shows the presence of alloy as a mixture liquid and solid phase  $\beta$ .
- The region marked “ $L+\alpha$ ” between the solidus line and liquidus line below peritectic isotherm shows the presence of alloy as a mixture liquid and solid phase  $\alpha$ .
- $T_P$  is the peritectic temperature. The isotherm passing through peritectic temperature is called peritectic isotherm.
- The region marked “ $\alpha+\beta$ ” is formed below the peritectic isotherm and a heterogeneous solid consisting of a mixture of  $\alpha$  and  $\beta$  is present.
- A liquid phase reacts with the solid phase to form a new and different solid phase is called peritectic reaction.

*Liquid (L) + Solid*  
 $1(\alpha) \Leftrightarrow$

*Solid 2( $\beta$ )*

- The peritectic horizontal is the tie-line which defines the composition of the liquid phase and the  $\beta$  phase at the peritectic temperature.
- At peritectic temperature, three phases namely liquid,  $\alpha$  and  $\beta$  are in equilibrium with each other.

$$\text{Hence phase rule } F = C - P + 1 = 2 - 3 + 1 = 0$$

- In some peritectic reactions (e.g. the Pt-Ag system), the (pure)  $\beta$  phase is not

stable below the peritectic temperature ( $T_P = 1186$  splits into a mixture of  $(\alpha + \beta)$  just below  $T_P$ .

C for Pt-Ag system) and

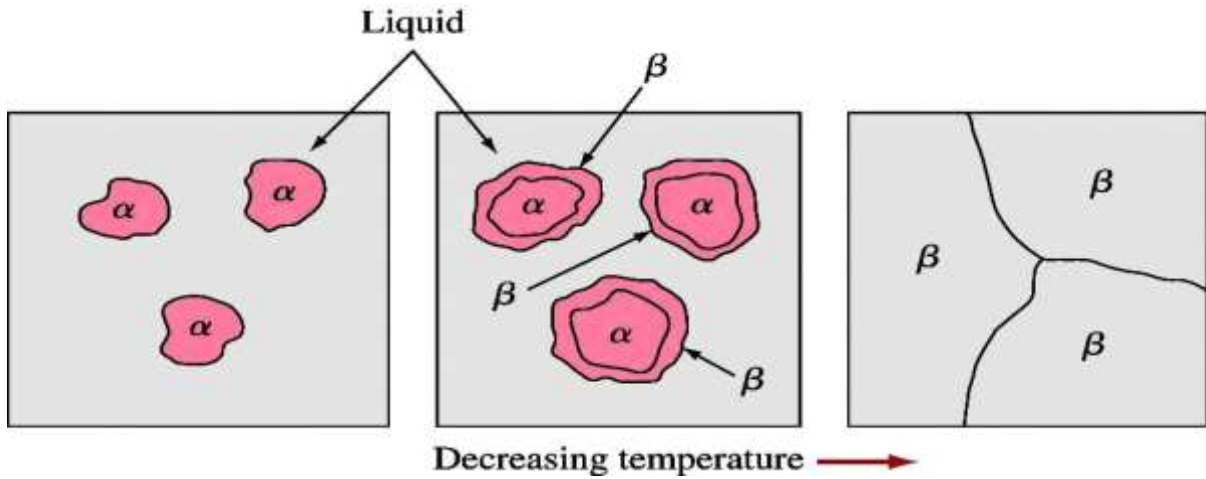
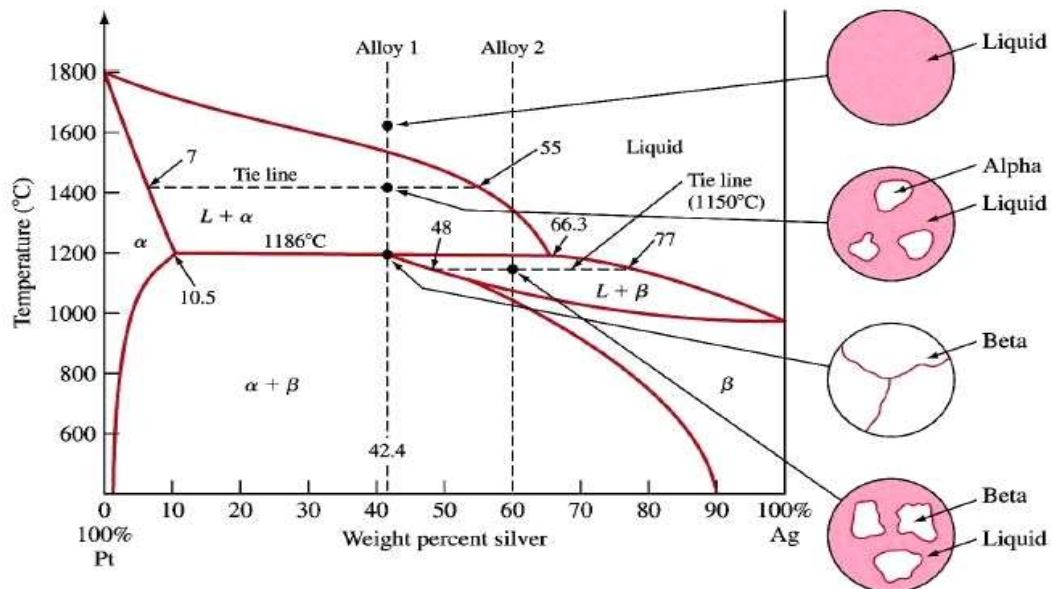


Figure.1.6. Schematic representation of the progressive development of  $L + \alpha \leftrightarrow \beta$

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Figure.1.7. Pt-Ag peritectic phase diagram



## Free energy composition curves for binary systems

- A binary phase diagram is a map which indicates the equilibrium phases present at a given temperature and composition. Free energy is a measure of a system's internal energy which gives the entropy of the system. For any phase, the Gibbs free energy is a function of pressure, temperature, and composition.

### Step (I)

- Let's construct a binary phase diagram for the simplest case: A and B components are mutually soluble in any amounts in both solid (**isomorphous system**) and liquid phases, and form ideal solutions.
- We have 2 phases – liquid and solid.
- Let's consider Gibbs free energy curves for the two phases at different Temperature.
- $T_1$  is above the equilibrium melting temperatures of both pure components:  $T_1 > T_m(A) > T_m(B)$ . At temperature  $T_1$ , the liquid phase will be the stable phase for any composition, because of its low Gibbs free energy.

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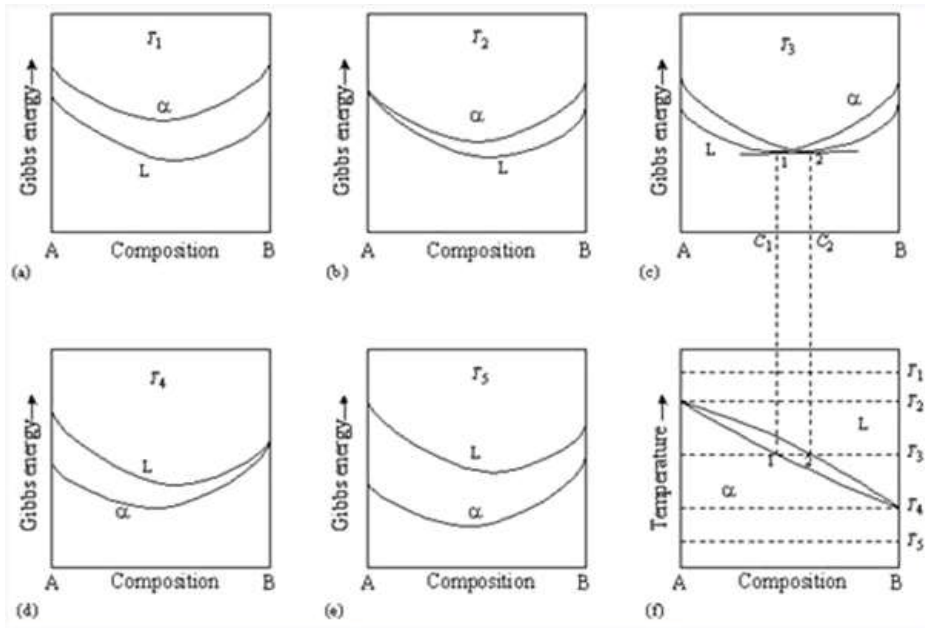


Figure.1.8 Free energy composition curves for binary systems

### Step (II)

At temperature  $T_2$ , component A begins to melt. The liquid and solid phases are equally

liquid

stable only at a composition of pure A i.e.,  $G^A$

$$= G$$

<sup>A</sup>  
solid

### Step (III)

- At temperature  $T_3$ , the Gibbs free energy curves for the liquid and solid phases will cross each other.

### Step (IV)

- At temperature  $T_4$ , the component begins to melt as it is the melting temperature of component B.

### Step (V)

- At lower temperature Gibbs free energy of the solid phase is lower than the G of the liquid phase ( $G_s < G_L$ ), so that solid phase is more stable at  $T_5$ .

### **Construction of Phase diagram of components with complete solubility**

- The isomorphous phase diagrams having completely soluble components can be constructed from Gibbs free energy curves.
- At temperature  $T_3$ , the Gibbs free energy curves for the liquid and solid phases will cross each other.
- The common tangent construction can be used to show the compositions of two phases in equilibrium.
- The two-phase field consists of a mixture of a mixture of liquid and solid phases.
- The compositions of the two phases in equilibrium at temperature  $T_3$  are given as  $C_1$  and  $C_2$ .
- The points of tangency, 1 and 2, are called solidus and liquidus respectively.
- The horizontal isothermal line meeting points 1 and 2 at temperature  $T_3$ , is called tie-line.
- Similar tie-lines meet the coexisting phases throughout all two phase field in binary system.

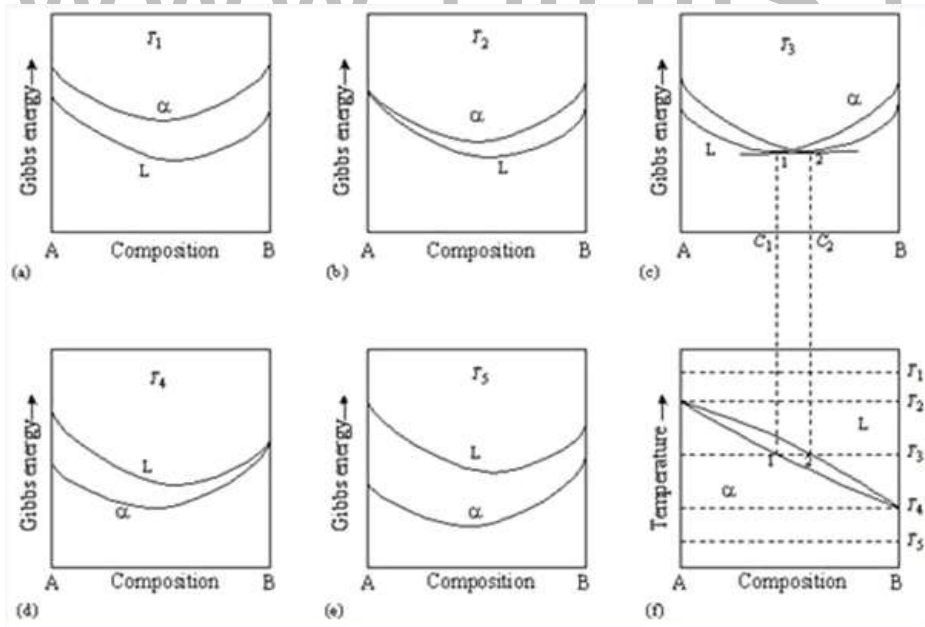


## Free energy composition curves for binary systems

- A binary phase diagram is a map which indicates the equilibrium phases present at a given temperature and composition. Free energy is a measure of a system's internal energy which gives the entropy of the system. For any phase, the Gibbs free energy is a function of pressure, temperature, and composition.

### Step (I)

- Let's construct a binary phase diagram for the simplest case: A and B components are mutually soluble in any amounts in both solid (**isomorphous system**) and liquid phases, and form ideal solutions.
- We have 2 phases – liquid and solid.
- Let's consider Gibbs free energy curves for the two phases at different Temperature.
- $T_1$  is above the equilibrium melting temperatures of both pure components:  $T_1 > T_m(A) > T_m(B)$ . At temperature  $T_1$ , the liquid phase will be the stable phase for any composition, because of its low Gibbs free energy.



Free energy composition curves for binary systems

### Step (II)

At temperature  $T_2$ , component A begins to melt. The liquid and solid phases are equally

liquid

stable only at a composition of pure A i.e.,  $G^A = G$

<sup>A</sup>  
solid

### Step (III)

- At temperature  $T_3$ , the Gibbs free energy curves for the liquid and solid phases will cross each other.

### Step (IV)

- At temperature  $T_4$ , the component begins to melt as it is the melting temperature of component B.

### Step (V)

- At lower temperature Gibbs free energy of the solid phase is lower than the  $G$  of the liquid phase ( $G_s < G_L$ ), so that solid phase is more stable at  $T_5$ .

### Construction of Phase diagram of components with complete solubility

- The isomorphous phase diagrams having completely soluble components can be constructed from Gibbs' free energy curves.
- At temperature  $T_3$ , the Gibbs free energy curves for the liquid and solid phases will cross each other.
- The common tangent construction can be used to show the compositions of two phases in equilibrium.
- The two-phase field consists of a mixture of a mixture of liquid and solid phases.
- The compositions of the two phases in equilibrium at temperature  $T_3$  are given as  $C_1$  and  $C_2$ .

- The point of tangency, 1 and 2, are called solidus and liquidus respectively.
- The horizontal isothermal line meeting points 1 and 2 at temperature  $T_3$ , is called tie-line.
- Similar tie-lines meet the coexisting phases throughout all two phase field in binary system.

### Microstructural Change during Cooling

- In any binary system (isomorphous, eutectic, and peritectic), the microstructure of the elements change during cooling.
- Let us consider the copper–nickel system. In this system temperature is plotted along the Y-axis, and the X-axis represents the composition of the alloy.
- For example, specifically an alloy of composition 35 wt% Ni–65 wt% Cu as it is cooled from  $1300^\circ\text{C}$ .
- At  $1300^\circ\text{C}$ , point *a*, the alloy is completely liquid (of composition 35 wt% Ni–65 wt% Cu) and has the microstructure represented by the circle inset in the figure.
- As cooling begins, no microstructural or compositional changes will be realized until it reaches the liquidus line (point *b*,  $\sim 1260^\circ\text{C}$ ). At this point the first solid  $\alpha$  begins to form, which has a composition dictated by the tie line drawn at this temperature [i.e., 46 wt% Ni–54 wt% Cu, noted as ( $\alpha$  -46 %Ni)]. With continued cooling, both compositions and relative amounts of each of the phases will change. The compositions of the liquid and  $\alpha$  phases will follow the liquidus and solidus lines, respectively. Furthermore, the fraction of the  $\alpha$  phase will increase with continued cooling.
- At  $1250^\circ\text{C}$ , point *c* in Figure 9.4, the compositions of the liquid and  $\alpha$  phases are 32 wt% Ni–68 wt% Cu [ $L(32\text{ Ni})$ ] and 43 wt% Ni–57 wt% Cu [ $\alpha(43\% \text{ Ni})$ ], respectively.

- The relative amounts (as fraction or as percentage) of the phases present at equilibrium may also be computed with the aid of phase diagrams. Then we have to apply the **lever rule**.

From figure,

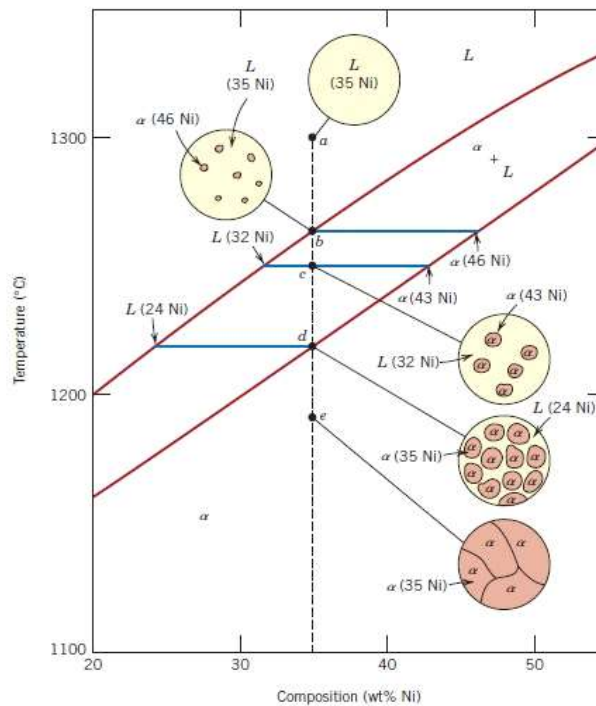
$$C_o = 35 \text{ wt\% Ni} \quad C_L = 32 \text{ wt\% Ni} \quad C_\alpha = 43 \text{ wt\% Ni}$$

$$W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{42.5 - 35}{42.5 - 31.5} = 0.68 = 68\%$$

and

$$W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L} = \frac{35 - 31.5}{42.5 - 31.5} = 0.32 = 32\%$$

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Schematic representation of the development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy.

- At point *d*: The solidification process is virtually completed at about  $1220^{\circ} C$ . At the point *d*; the composition of the solid  $\alpha$  is approximately 35 wt% Ni–65 wt% Cu (the overall alloy composition), whereas that of the last remaining liquid is 24wt% Ni–76 wt% Cu.
- At point *e*: Upon crossing the solidus line, the remaining liquid solidifies; the final product then is a polycrystalline  $\alpha$ -phase solid solution that has a uniform 35 wt% Ni–65 wt% Cu composition. Subsequent cooling will produce no microstructural or compositional alterations.

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## UNIT- I PHASE DIAGRAMS

9

Solid solutions - Hume Rothery's rules – the phase rule - single component system - one-component system of iron - binary phase diagrams - isomorphous systems - the tie- line rule - the lever rule - application to isomorphous system - eutectic phase diagram - peritectic phase diagram - other invariant reactions – free energy composition curves for binary systems - microstructural change during cooling.

### Learning Objectives

- Learn solid solutions based on Hume Rothery's rules.
- Discuss the phase rule for unary and binary phase diagrams.
- Explain binary isomorphous systems based on tie-line rule and the lever rule
- Compare eutectic phase diagram and peritectic phase diagram
- Analyze the importance of invariant reactions.
- Describe the free energy composition curves for binary systems.
- Learn the microstructural change during cooling.

### Introduction

A solution (liquid or solid) is phase with more than one component; a mixture is a material with more than one phase. Solute 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! A pure substance, under equilibrium conditions, may exist as either of a phase namely vapor, liquid or solid, depending upon the conditions of temperature and pressure

## Basic terms used in phase diagrams

### System

- A portion of the universe that has been isolated so that its properties can be studied. System may also refer to a specific body of material under consideration.

### Components

- Macroscopic basic unit of a material is called component. It refers to an independent chemical species. The components of a system may be elements, ions or compounds. Component is either pure metal and/or compounds of which an alloy is composed. A component can exist in many phases.
- In **brass** the main components are Cu and Zn. In **carbon steel** the main components are Fe and C. A **binary alloy** contains two components. A **ternary alloy** contains three; a **quaternary alloy**, four, etc.
- E.g.: Water exists as ice, liquid water, and water vapor. Carbon exists as graphite and diamond.

### Composition

- Alloys are defined by their composition – i.e. the concentrations of the components in weight % (wt.%) or atom % (at%).

### Mixtures

- Processing of metallic alloys (which are mixtures of elements) leads to microstructures in which the component elements are distributed in a number of ways. In the liquid state for metals, more or less everything dissolves completely, therefore forming a single phase. But in the solid state, things are more complex

– for example, in a binary alloy (i.e. a mixture of two components) the solid microstructure usually takes one of three forms:

- A single solid solution (one phase);
- Two separated solid solutions (two phases);
- A chemical compound (phase 1), with a separated solid solution (phase 2).

### **Alloys**

- A metallic alloy is a mixture of a metal with other metals or non-metals.
- The element which is present in the largest portion is called the base metal, and other elements present are called alloying elements.
- For example: **Brass**: a mixture of Copper (Cu) and Zinc (Zn).

**Carbon steel**: based on Iron (Fe) and Carbon (C).

**Spinel**: a ceramic alloy made of Magnesia (MgO) and Alumina (Al<sub>2</sub>O<sub>3</sub>).

### **Equilibrium:**

- A system is at equilibrium if its free energy is at a minimum. Characteristics of the system do not change with time, i.e., the system is stable. If you change the temperature, pressure, or composition, the free energy will change.

### **Phase**

- Physically distinct, chemically homogenous and mechanically separable region of a system.

### **Phase diagram**

- A phase diagram is a type of graph used to show the equilibrium conditions between the thermodynamically-distinct phases; or to show



what phases are present in the material system at various temperature, pressure and compositions

## **Phase transformation**

Phase Transformation is the change of one phase into another.

- E.g.: Water → Ice

## **Classification of Phase diagrams**

- Phase diagrams are classified based on the number of components in the system.
  - Single component systems have unary diagrams
  - Two-component systems have binary diagrams
  - Three-component systems are represented by ternary diagrams, and so on

## **Phase diagram – Useful information**

- It is actually a collection of solubility limit curves. It is also known as equilibrium or constitutional 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.
- Useful terminology related to phase diagrams are liquidus, solidus, solvus, terminal solid solution, invariant reaction, intermediate solid solution, inter-metallic compound, etc.

## One component system

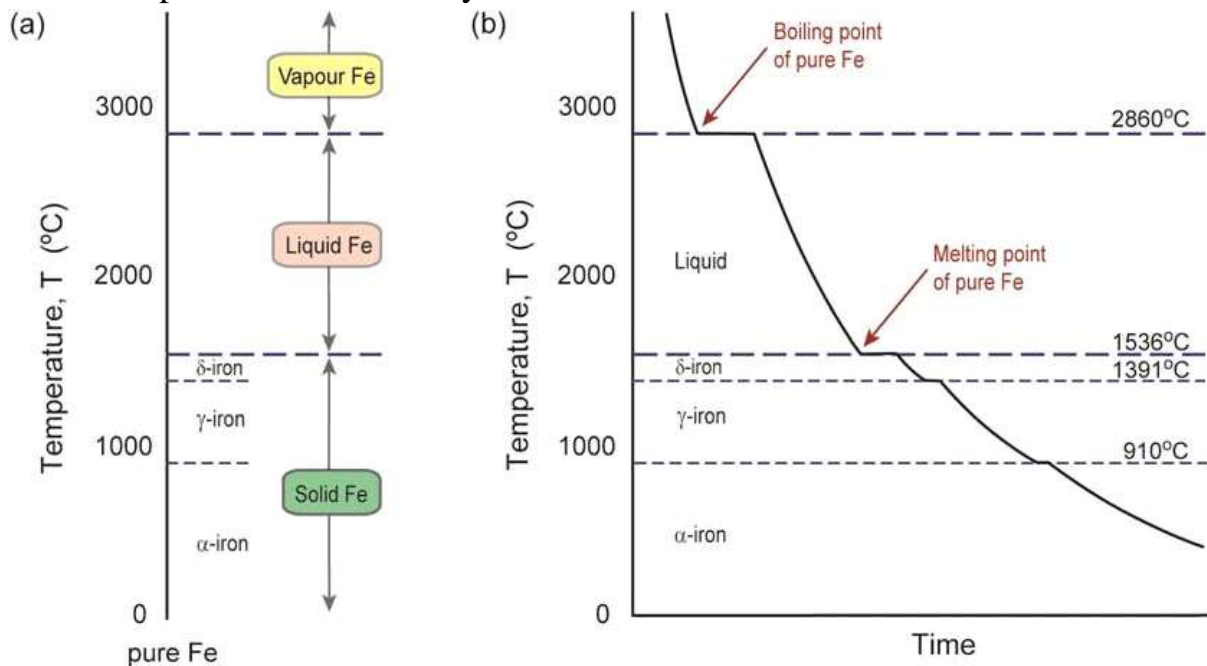
- A single component system is one which has no composition variable.
- It is also known as pressure-temperature or P-T diagram.
- The simplest phase diagram is the water which is a one component system.

## Single component phase diagrams

### (Unary)One component system of

### iron

- Consider first a pure material is heated from the solid state. The melting temperature is the unique temperature at which the phase change to the liquid state occurs, and solid and liquid can co-exist in equilibrium. Similarly, liquid changes to vapour at a unique (higher) temperature, the boiling point.
- Pure iron (Fe) is a single component system and there is no composition variable. The pressure is plotted on the X-axis and temperature on the Y-axis. Therefore this phase diagram is called PT unary phase diagram. Apart from the liquid and gaseous phases many solid phases ( $\alpha, \gamma$ , and  $\delta$ ) are possible based on crystal structure.



: (a) one-dimensional phase diagram for pure iron; (b) Cooling curve of a pure iron

The Gibbs phase rule for one component system is

- Let us first consider the single phase regions on the diagram such as gas, liquid and several crystal forms of iron. Here  $C=1$  and  $P=1$  and phase rule becomes

$$F = C - P + 2 = 1 - 1 + 2 = 2. \quad \text{(Two degrees of freedom)}$$

- This result tells that there is two degrees of freedom, and thus two variables (T and P) can be changed independently and the system will remain a single phase.
- When two phases are in equilibrium,  $C=1$  and  $P=2$ . Thus from Gibbs phase rule,

$$F = C - P + 2 = 1 - 2 + 2 = 1 \quad \text{(One degree of freedom)}$$

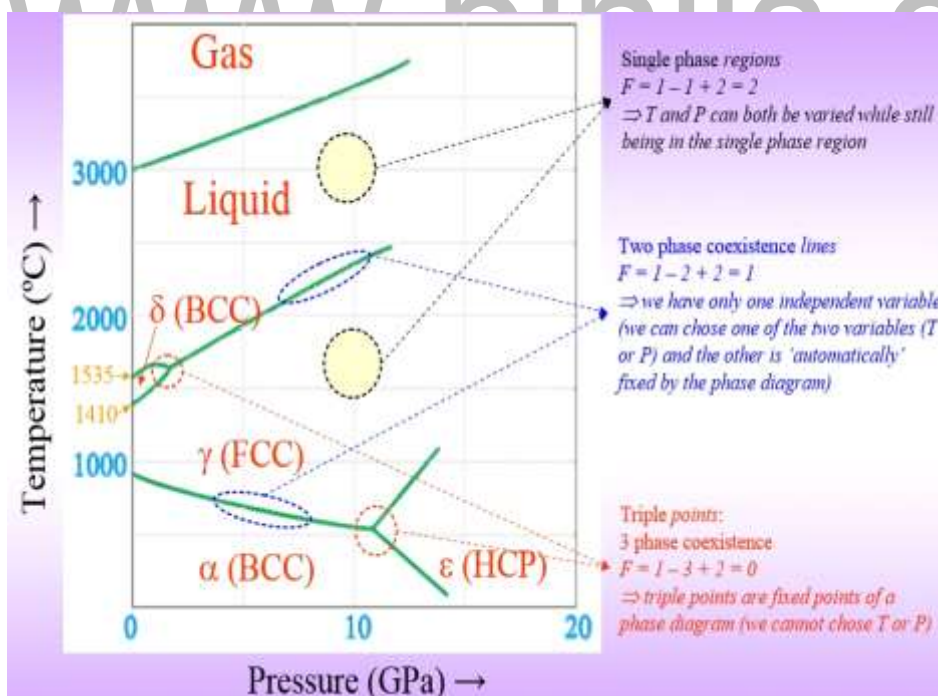
- This result reveals that there is one degree of freedom, and thus one variable (T or P) can be changed independently and still maintain a system with two coexisting phases (phase boundaries).
- At the triple point, three phases coexist in equilibrium, and since there is one component in the system (iron), the number of degrees of freedom is given by

$$F = C - P + 2 = 1 - 3 + 2 = 0 \quad \text{(Zero degrees of freedom)}$$

- At only one particular combination of pressure and temperature, three phases will coexist. If we change pressure or temperature from the fixed triple point value, one or two phases will appear.
- First, we consider pure iron. Figure 2.5a shows the phases found in pure iron. The low temperature form of iron is called *ferrite* (or  $\alpha$ -iron), which has a body-centred cubic (BCC) lattice. On heating pure iron changes to *austenite* (or  $\gamma$ -iron) at  $910^\circ\text{C}$ , and switches to a face-centred cubic (FCC) lattice. Pure austenite is

stable up to 1391°C, when it changes back to BCC  $\delta$ -iron, before melting at 1536°C, and boiling at 2860°C.

- Above 1536°C, pure iron is in molten form (melting point). It solidifies initially to BCC  $\delta$ -iron, but undergoes further solid-state phase transformations on cooling, first to FCC  $\gamma$ -iron at 1391°C, and then back to BCC  $\alpha$ -iron at 910°C. At 910°C, another phase occurs from FCC non-magnetic  $\alpha$ -iron into BCC non-magnetic  $\alpha$ -iron. Finally at 768°C,  $\alpha$ -iron becomes magnetic without a change in lattice structure.
- When pressure is increased, the  $\alpha \rightarrow \gamma$  transition temperature is lowered, whereas the  $\gamma \rightarrow \delta$  transition temperature is increased. If applied pressure of 15 GPa at room temperature, the BCC  $\alpha$ -iron transforms to the HCP  $\epsilon$ -iron phase. The cooling for pure iron showing allotropic changes is shown in figure 2.6.



One-component system of iron

### Phase diagram- $H_2O$ system

- Let us consider the application of Gibbs phase rule to the PT phase diagram of water. The temperature is plotted on the X-axis and pressure on the Y-axis. There three phases in  $H_2O$  system namely solid, liquid and gas. At the triple point, three phases coexist in equilibrium, and since there is one component in the system (water), the number of degrees of freedom is given by

$$F = C - P + 2 = 1 - 3 + 2 = 0 \quad \text{(Zero degrees of freedom)}$$

- Since none of the variables (temperature or pressure) can be changed and still keep the three phases in balance, the triple point is called **invariant point**.
- Consider next a point along the liquid-solid freezing curve of water system at any point along this line two phases will coexist. Thus from Gibbs phase rule,

$$F = C - P + 2 = 1 - 2 + 2 = 1 \quad \text{(One degrees of freedom)}$$

- This result reveals that there is one degree of freedom, and thus one variable (T or P) can be changed independently and still maintain a system with two coexisting phases.

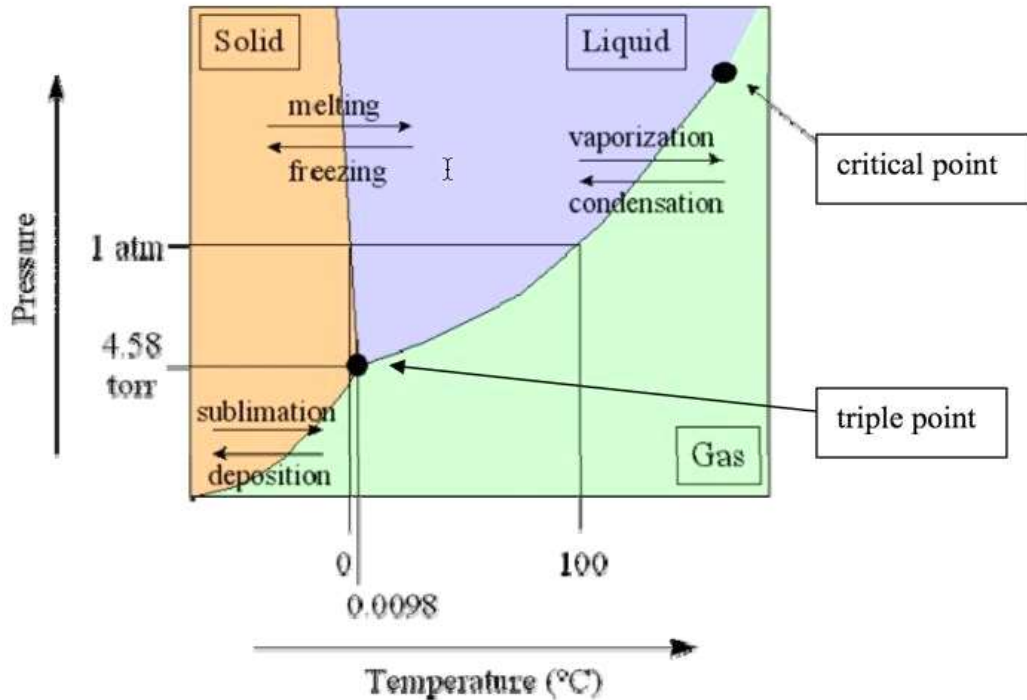


Figure 1.2. Phase diagram of water system

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- For a third case, consider a point on the water PT phase diagram inside a single phase. Then there will be only one phase present ( $P=1$ ), and substituting into the phase-rule gives

$$F = C - P + 2 = 1 - 1 + 2 = 2 \quad \text{(Two degrees of freedom)}$$

- This result tells that there is two degrees of freedom, and thus two variables (T and P) can be changed independently and the system will remain a single phase.
- The **triple point** of a substance is the temperature and pressure at which gas, liquid, and solid coexist in thermodynamic equilibrium.
- Above the critical pressure and temperature, there is no distinction between the liquid phase and the gas phase. Basically, they merge into one phase that is called the **super critical fluid phase (SCF)**.

- It is used on a large scale for the decaffeination of green coffee beans, the extraction of hops for beer production, and the production of essential oils and pharmaceutical products from plants.

### **Phase diagram of sugar- Water solution**

- Let us first consider the phase diagram of sugar- water solution. The composition of sugar in water in wt.% is plotted on the X-axis and temperature on the Y-axis.
- The phase diagram consists of only two sections.
- The curve that divides the two sections represents the solubility limit. When sugar is added to water, sugar solution (syrup) is formed which is a homogeneous solution. This is the single phase system which is shown on the left side of this curve. On the right side of this curve the system exists in equilibrium as a two- phase system, syrup + sugar.
- From the diagram, the solubility limit of sugar at various temperatures can be read, e.g. at  $20^{\circ}C$  the maximum solubility of sugar in water is 65 wt%.
- Beyond this concentration the solution is saturated; the sugar that is added remains as solid sugar in the liquid syrup. But now if the temperature is raised to about  $60^{\circ}C$ , the sugar dissolves because the solubility limit is 70 wt.% at this temperature.

**Solubility limit** – for almost all alloy systems, at a specific temperature, a maximum of solute atoms can dissolve in solvent phase to form a solid solution. The limit is known as solubility limit. In general, solubility limit changes with temperature. If solute available is more than the solubility limit that may lead to formation of different phase, either a solid solution or compound.

- Changing T can change the no of phases: path A to B
- Changing Co can change the no of phases: path B to D

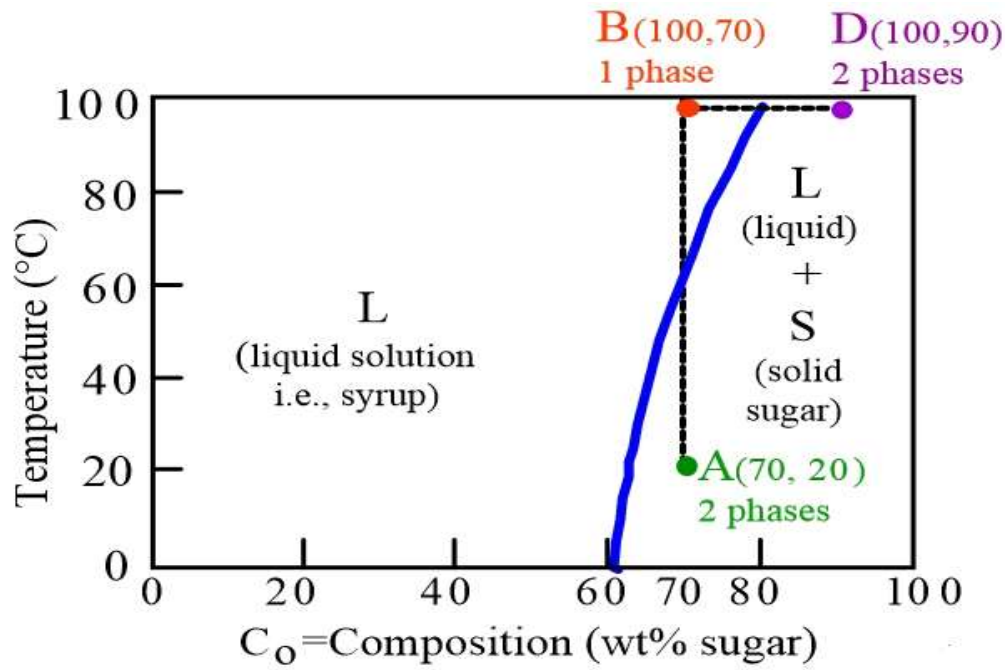


Figure.1.3. Phase diagram of sugar-Water solution

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## Solid Solution

- A solid solution is formed when two metals are completely soluble in liquid state and also completely soluble in solid state. In other words, when homogeneous mixtures of two or more kinds of atoms (of metals) occur in the solid state, they are known as **solid solutions**.

## Solvent and Solute

- The more abundant atomic form is referred as **solvent** and the less abundant atomic form is referred as **solute**.

## Types of Solid Solution

- Solid solutions are of two types. They are
  - Substitutional solid solutions.
  - Interstitial solid solutions.

## Substitutional Solid Solution

- If the atoms of the solvent or parent metal are replaced in the crystal lattice by atoms of the solute metal then the solid solution is known as **substitutional solid solution**.
- For example, copper atoms may substitute for nickel atoms without disturbing the F.C.C. structure of nickel
- In the substitutional solid solutions, the substitution can be either disordered or ordered.
- Figure 1.1 shows disordered substitutional solid solution. Here the solute atoms have substituted disorderly for the solvent atoms on their lattice site.

- Fig.1.1 shows an ordered substitutional solid solution. Here the solute atoms have substituted in an orderly manner for the solvent atoms on their lattice site.

### Interstitial Solid Solutions

- In interstitial solid solutions, the solute atom does not displace a solvent atom, but rather it enters one of the holes or interstices between the solvent atoms. An excellent example is iron-carbon system which is shown in Fig 1.1.
- In this system the carbon (solute atom) atom occupies an interstitial position between iron (solvent atom) atoms. Normally, atoms which have atomic radii less than one angstrom are likely to form interstitial solid solutions.
- Examples are atoms of carbon ( $0.77 \text{ \AA}$ ), nitrogen ( $0.71 \text{ \AA}$ ), hydrogen ( $0.46 \text{ \AA}$ ), Oxygen ( $0.60 \text{ \AA}$ ) etc.

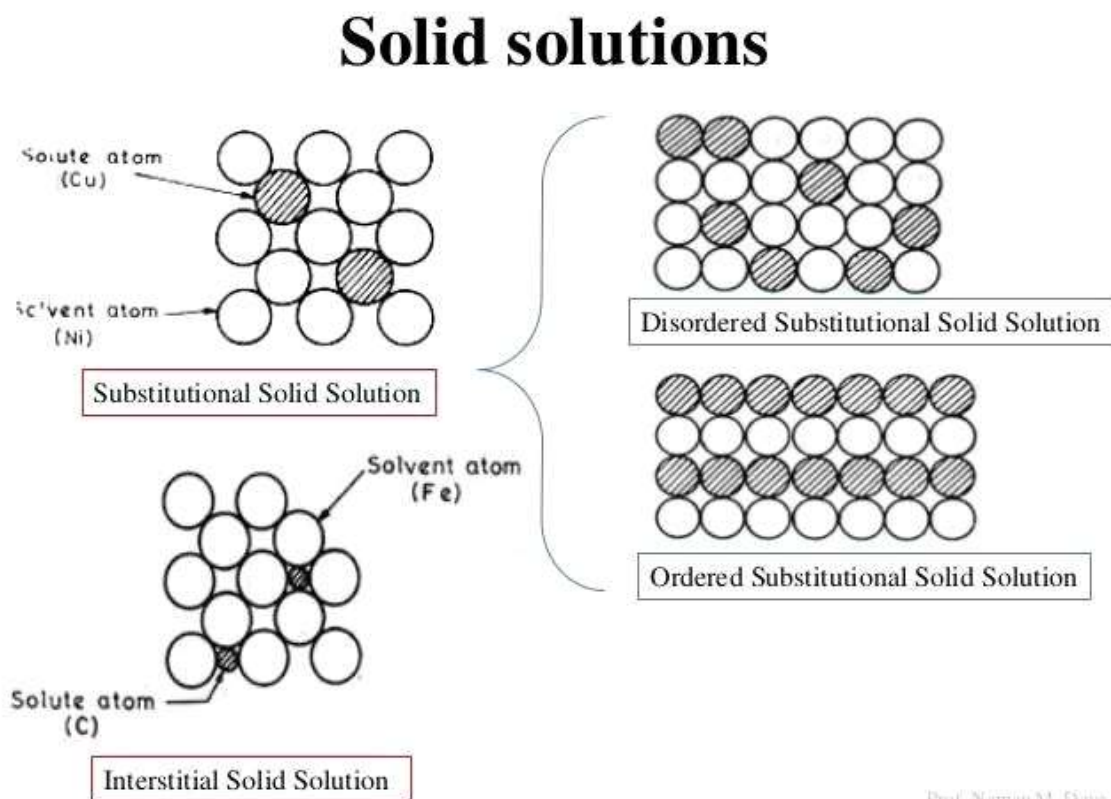


Figure 1.1 solid solution and its types

## Hume Rothery rules for the formation of substitutional solid solutions

- By studying a number of alloy systems, Hume Rothery formulated certain rules which govern the formation of substitutional solid solutions.

These are:

- Crystal structure factor:
  - ***For complete solid solubility, the two elements should have the same type of crystal structure i.e., both elements should have either F.C.C. or B.C.C. or H.C.P. structure.***
- Relative size factor:
  - As the size (atomic radii) difference between two elements increases, the solid solubility becomes more restricted. ***For extensive solid solubility the difference in atomic radii of two elements should be less than about 15 percent.*** If the relative size factor is more than 15 percent, solid solubility is limited. For example, both silver and lead have F.C.C. structure and the relative size factor is about 20 percent. Therefore the solubility of lead in solid silver is about 1.5 percent and the solubility of silver in solid lead is about 0.1 percent. Copper and nickel are completely soluble in each other in all proportions. They have the same type of crystal structure(F.C.C.) and differ in atomic radii by about 2 percent.

Comparing the atomic radii of solids that form solid solutions, the empirical rule given by Hume-Rothery is given as:

- Chemical affinity factor:
  - ***Solid solubility is favoured when the two metals have lesser chemical affinity.*** If the chemical affinity of the two metals is greater then greater is the tendency towards compound formation. Generally, if the two metals are separated in the periodic table widely then they possess

greater chemical affinity and are very likely to form some type of compound instead of solid solution.

- Relative valence factor:
  - A metal of higher valency can dissolve a small amount of lower valency metal. *The solute and solvent atoms should typically have the same valence in order to achieve maximum solubility.*
  - For example in aluminium-nickel alloy system, nickel (lower valence) dissolves 5 percent aluminium but aluminium (higher valence) dissolves only 0.04 percent nickel.

### Gibbs phase rule

- Gibbs' phase rule describes the possible no of degrees of freedom (F) in a closed system at equilibrium, in terms of the number of separate phases (P) and the number of chemical components (C) in the system.
- Thermodynamically derived *Gibbs phase rule*:

$$F = C - P + 2$$

- Where, F is no of degrees of freedom or variance

### Degree of freedom F

- Degree of freedom (or variance) F is the number of variables (Temperature, pressure, and composition) that can be changed independently without changing the phases of the system.

### Component

- Component is the minimum no of species necessary to define the composition of the system.
- Example H<sub>2</sub>O C=1

$$(i) P=1, F=2; \quad (ii) P=2, F=1; \quad (iii) P=3, F=0$$

### Condensed Gibbs phase rule (Reduced phase rule)

- In practical conditions for metallurgical and materials systems, pressure can be treated as a constant (1 atm.).
- $F = C - P + 1$
- Thus Condensed Gibbs phase rule is written as