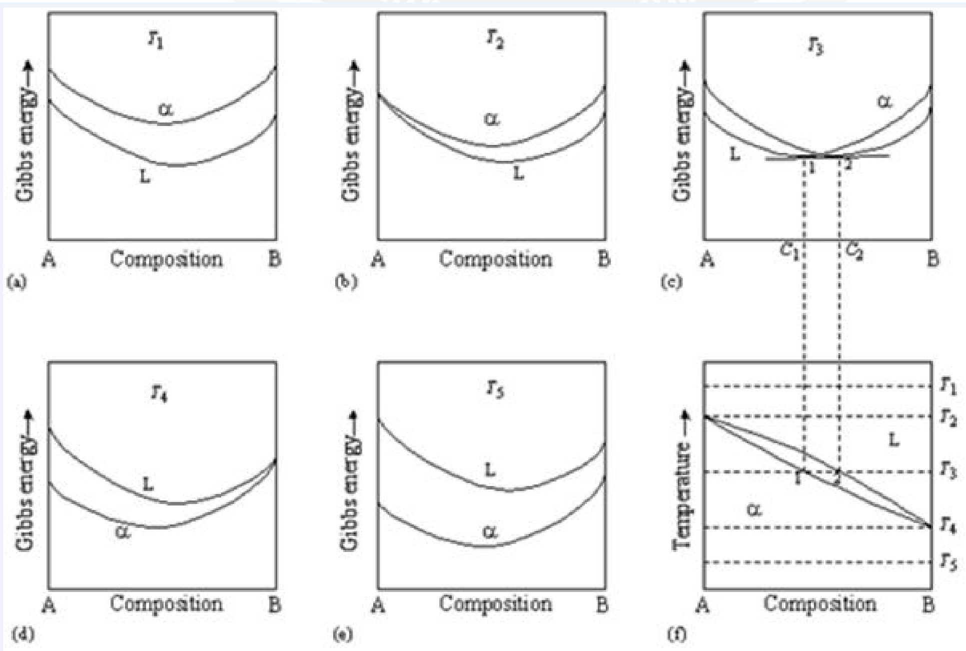
Free energy composition curves for binary systems

- 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 Gibb's 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 Gibb's free energy.



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Step (II)

At temperature T_2, component A begins to melt. The liquid and solid phases are equally stable only at a composition of pure A i.e., $G_{liquid}^{A} = G_{solid}^{A}$

Step (III)

- ❖ At temperature $\mathbf{T_3}$, 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 Gibb's 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 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 $1300^{\circ}C$.

- At $1300^{\circ}C$, 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*, ~$1260^{\circ}C$). At this point the first solid α 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 (α -46 %Ni)]. With continued cooling, both compositions and relative amounts of each of the phases will change. The compositions of the liquid and α phases will follow the liquidus and solidus lines, respectively. Furthermore, the fraction of the α phase will increase with continued cooling.

- At $1250^{\circ}C$, point *c* in Figure 9.4, the compositions of the liquid and α phases are 32 wt% Ni–68 wt% Cu [*L*(32 Ni)] and 43 wt% Ni–57 wt% Cu [α (43% Ni)], respectively.

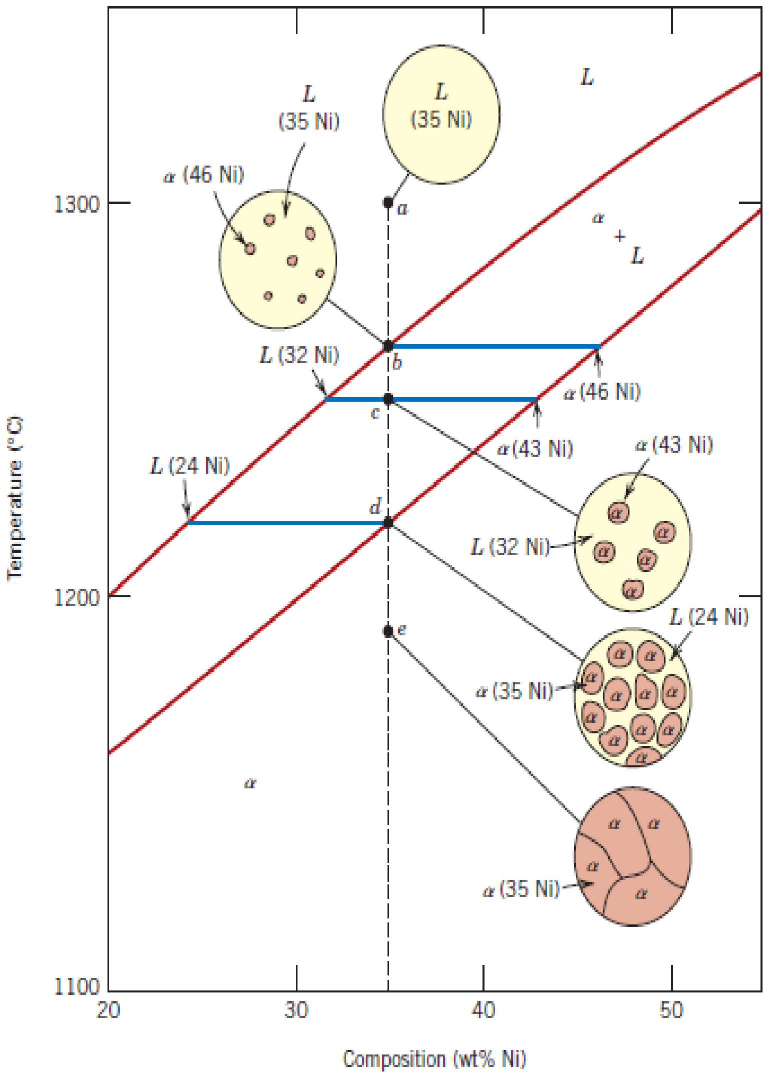
- The relative amounts (as fraction or as percentage) of the phases present at equilibrium may also be computed with the aid of phase diagrams. Then we have to apply the **lever rule.**

From figure,

C_o = 35 wt% Ni C_L = 32 wt% Ni C_α =43 wt% Ni

$$W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{43-35}{43-32} = 0.72 = 72\%$$ and

$$W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L} = \frac{35-32}{43-32} = 0.28 = 28\%$$



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 α is approximately 35 wt% Ni–65 wt% Cu (the overall alloy composition), whereas that of the last remaining liquid is 24 wt% Ni–76 wt% Cu.

- At point e: Upon crossing the solidus line, the remaining liquid solidifies; the final product then is a polycrystalline α-phase solid solution that has a uniform 35 wt% Ni–65 wt% Cu composition. Subsequent cooling will produce no microstructural or compositional alterations.