LECTURE-24

FREE ENERGY COMPOSITION DIAGRAM FOR BINARY ALLOYS SYSTEMS: The free energy of each of phase's presents on a phase diagram can be plotted as a function of composition at a series of temperature. The phases co-exist in equilibrium are those correspond to the lowest free energy of the system.

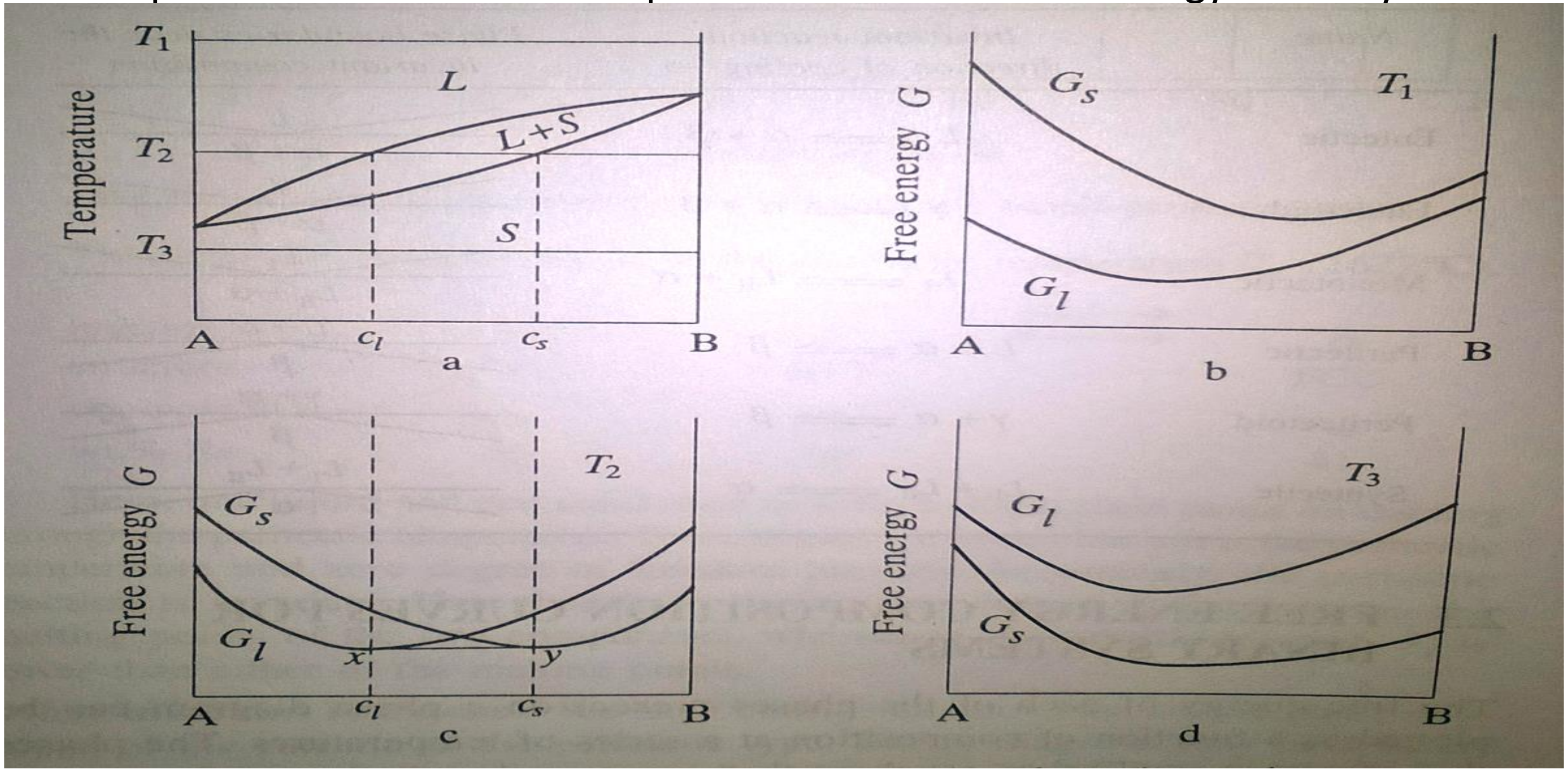

Fig. Free energy – composition relationships for an isomorphous system at three temperatures, Ref-Raghavan, V. (2012). *Physical metallurgy: principles and practice*. PHI Learning Pvt. Ltd.

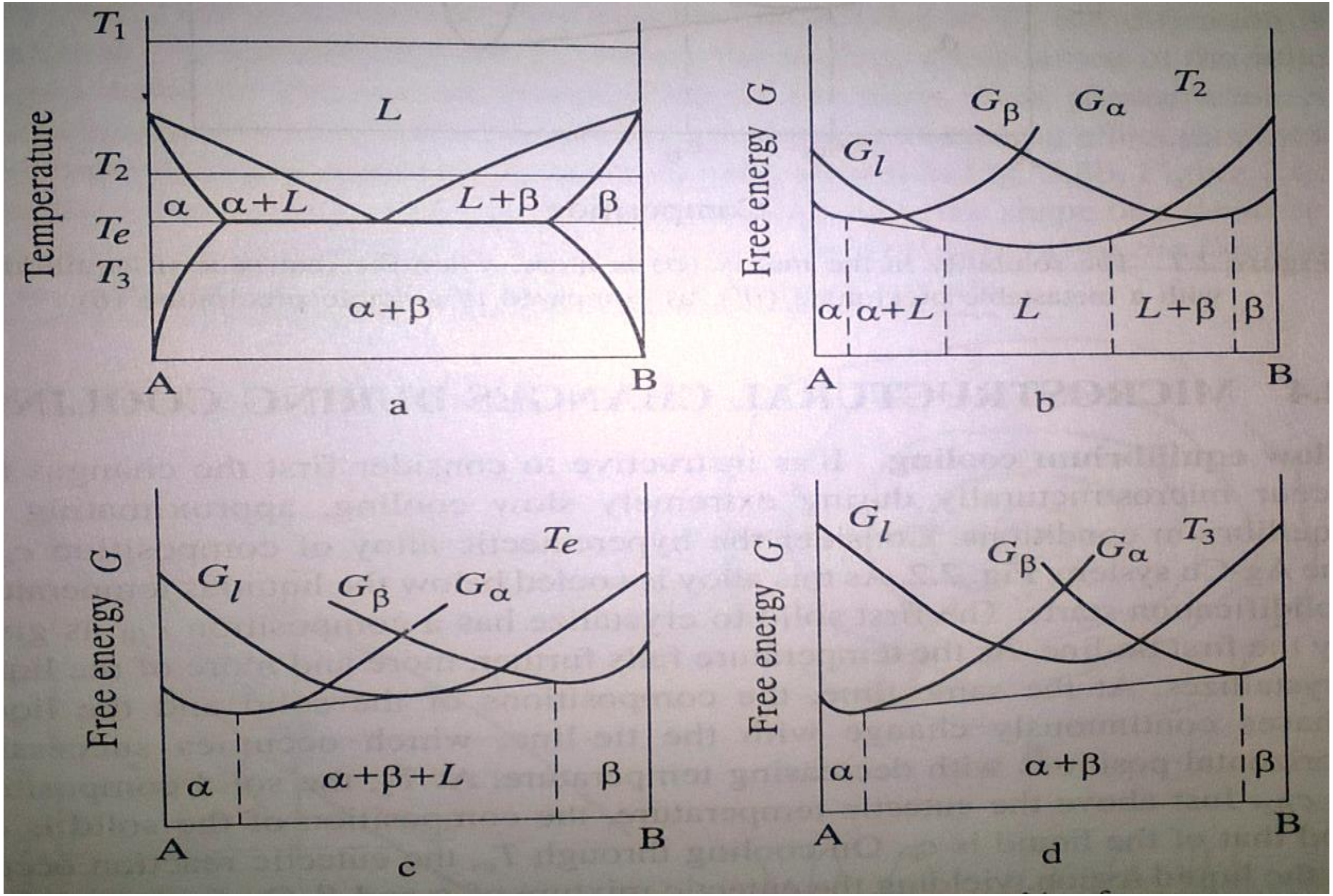

Fig. - Free energy vs. composition relationships for a simple eutectic system at different temperature,

Ref-Raghavan, V. (2012). *Physical metallurgy: principles and practice*. PHI Learning Pvt. Ltd.

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<u>Binary Phase Diagram:</u> The most commonly used phase diagrams are those that depict the equilibrium between two components. These are known as binary phase diagrams.

<u>Example:</u> (Fe-Fe3C) phase diagram, (Cu – Ni) phase diagram.

For graphical representation of the binary phase prelateships, we need a map with three axes corresponding to temperature, pressure & composition. For binary phase diagrams, we ignore the pressure variable & the vapor phase. As one of the variables has been arbitrarily omitted the phase rule for condensed phases (i.e. liquid & solids) only is written as

$$\mathrm{F} = \mathrm{C} - \mathrm{P} + 1 \qquad (276)$$

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<u>Isomorphous system:</u> An Isomorphous system defined as the simplest binary phase diagram for a system that exhibiting complete liquid as well as solubility.

<u>Example:</u> Cu – Ni phase diagram

M. pt of Cu → 1083 ^{0}C, M. pt of Ni → 1455 ^{0}C

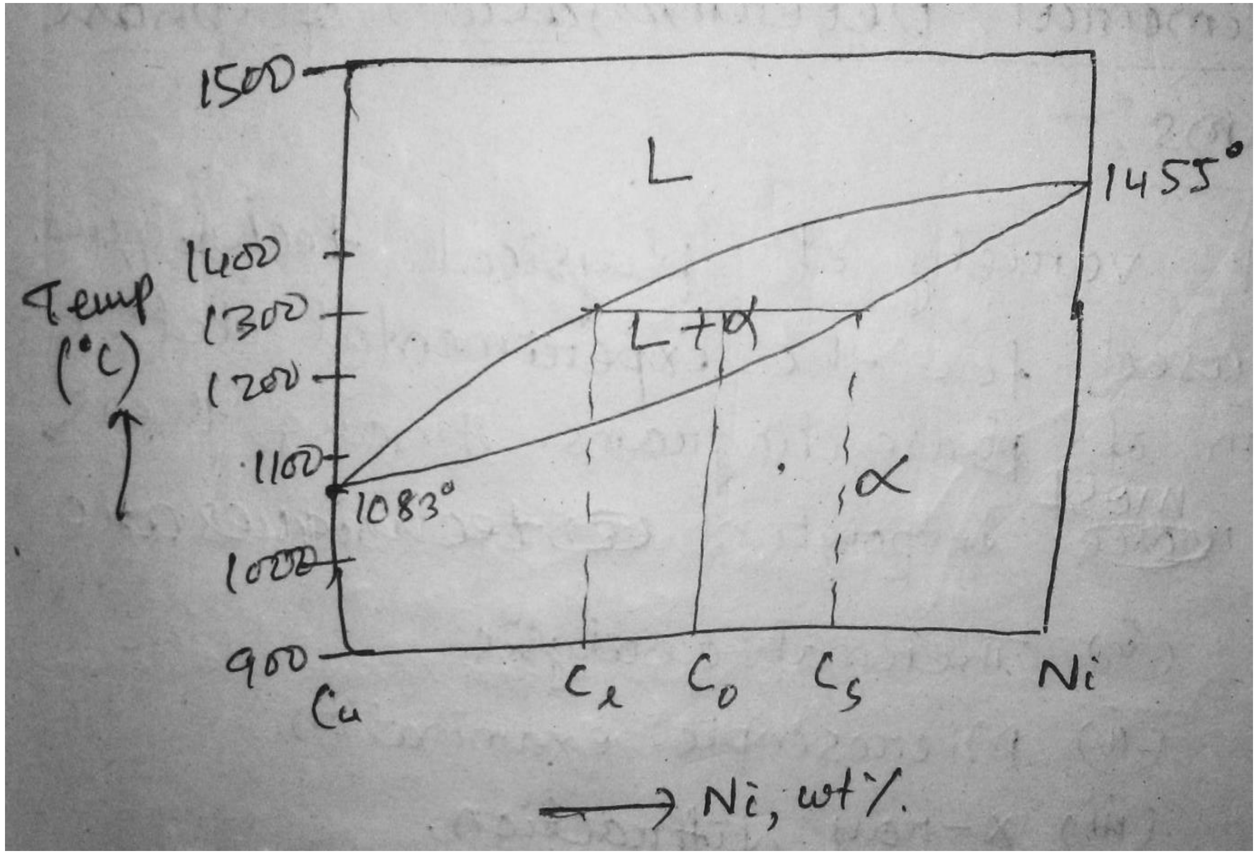

Fig-The Copper-Nickel phase diagram, showing complete solubility both in the liquid and in the solid states.

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- The liquid & solid regions are separated by a two-phase region, where both the phase co-exists.
- The boundary between two-phase region & the liquid is called liquidous line. The boundary between the two-phase region & the solid is called solidus line.
- **Solvus Line:** It is the solid-state phase boundary between the terminal solid solution & the two-phase region.

EXPERIMENTAL DETERMINATION OF PHASE DIAGRAMS: A variety of physical techniques are used for the experimental determination of phase diagrams. Among these the most important techniques are

1. Thermal analysis.
2. Microscopic examination.
3. X-ray diffraction.

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Determination of Liquidus and Solidus:

- Thermal analysis is the most important method for determination of the liquid-solid transformations
- This method based on evolution or absorption of heat occurs during a phase change
- When the temperature of an alloy sample is plotted as a function of time during heating or cooling, abrupt changes in slope of plot occur at points corresponding to the start or finish of a phase change

Cooling Curves: Curves of single composition for different conditions using thermal analysis explained below.

Case – I: ***[For pure metal without super cooling]*** In this case, evolution of latent heat due to start of solidification is equal to heat loss due to surroundings (refer fig. (a)). **Example:** Pure metals like Fe, Cu, Ni etc.

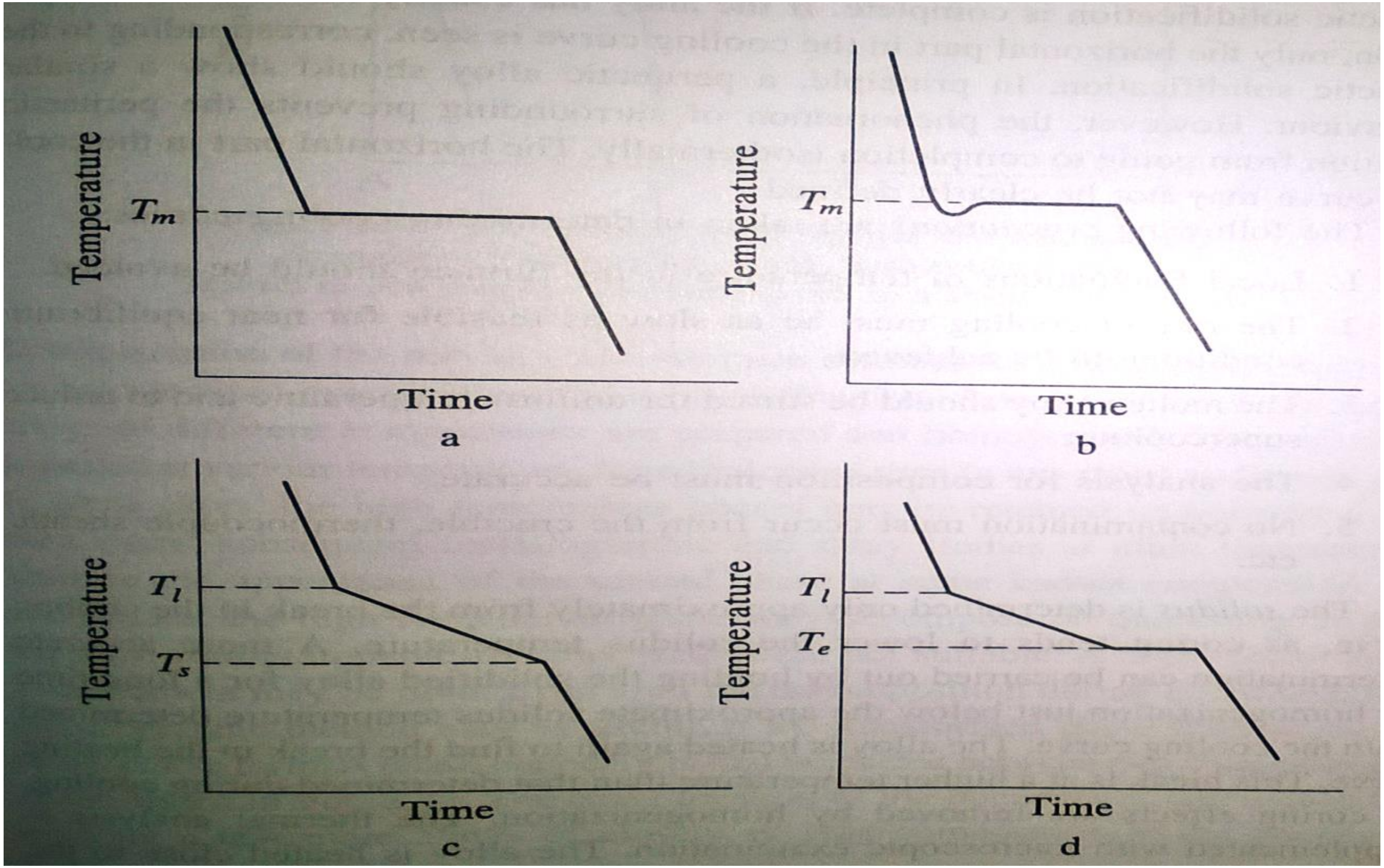

Fig-Thermal analysis. Cooling curves (a) for a pure metal without supercooling, (b) for a pure metal with supercooling, (c) for a solid solution alloy, (d) for a hypoeutectic alloy, **Ref-**Raghavan, V. (2012). *Physical metallurgy: principles and practice*. PHI Learning Pvt. Ltd.

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Case – II*: [For a pure metal with super-cooling]*

- In this case, evolution of latent heat due to the solidification less than heat lost to the surroundings and this process is known as Super-cooling (refer fig. (b)).
- Once Solidification starts heat evolution raise the sample temperature back to freezing point

Case – III: ***[For a solid solution alloys]***

- From fig. (c) we have, first arrest indicating abrupt decrease in the cooling rate occurs as the liquidus temperature T_l is crossed. Since, over a range of temperature the solidification occurs. So there is no horizontal part.
- The second arrest is observed at the solidus temperature T_S, when the cooling rate starts to increase again.

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<u>**Case – IV:**</u> ***[For a hypothetical alloy or pro-eutectic binary alloy]***

- From fig. (d) we have, Peritectic alloy also shows the similar behavior as pro-eutectic or hyper-eutectic alloy.
- First arrest occurs at the liquidus temperature & the cooling rate decreases.
- At the eutectic temperature T_e, the cooling curve becomes horizontal as invariant eutectic reaction occurs isothermally. The cooling rate increases again when the eutectic solidification is complete.

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Following precautions are taken to determining cooling curves

- Local fluctuations of temperature in the furnace should be avoided.
- For the achievement of near equilibrium conditions, the rate of cooling must be slow as feasible.
- To reduce super cooling, the molten alloy should be stirred for uniform temperature.
- Composition analysis must be accurate.
- No contamination must occur from the crucible, thermocouple sheath etc.

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- Solidus is determined by approximate lines in cooling curve, as coring tends to lower the solidus temperature.

- A more accurate determination can be carried out by holding the solidified alloy for a long time for homogenization just below the approximate solidus temperature determined from cooling curve.

- The alloy heated again to find the breaking in the heating curve. This break is at a higher temp then that determined during cooling as coring effects are removed by homogenization.

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Coring: Above solidus temperature same liquid remains without transfer to solid is known as coring.

- Thermal analysis can be replaced with microscopic examination; the alloy is heated close to the solidus & quenched to ascertain microscopically the appearance of the first chilled liquid.

- Using the break in the cooling & heating curves for a series of compositions covering the entire binary range, the liquidus & solidus boundaries can be fully determined.

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Determination of the Solvus:

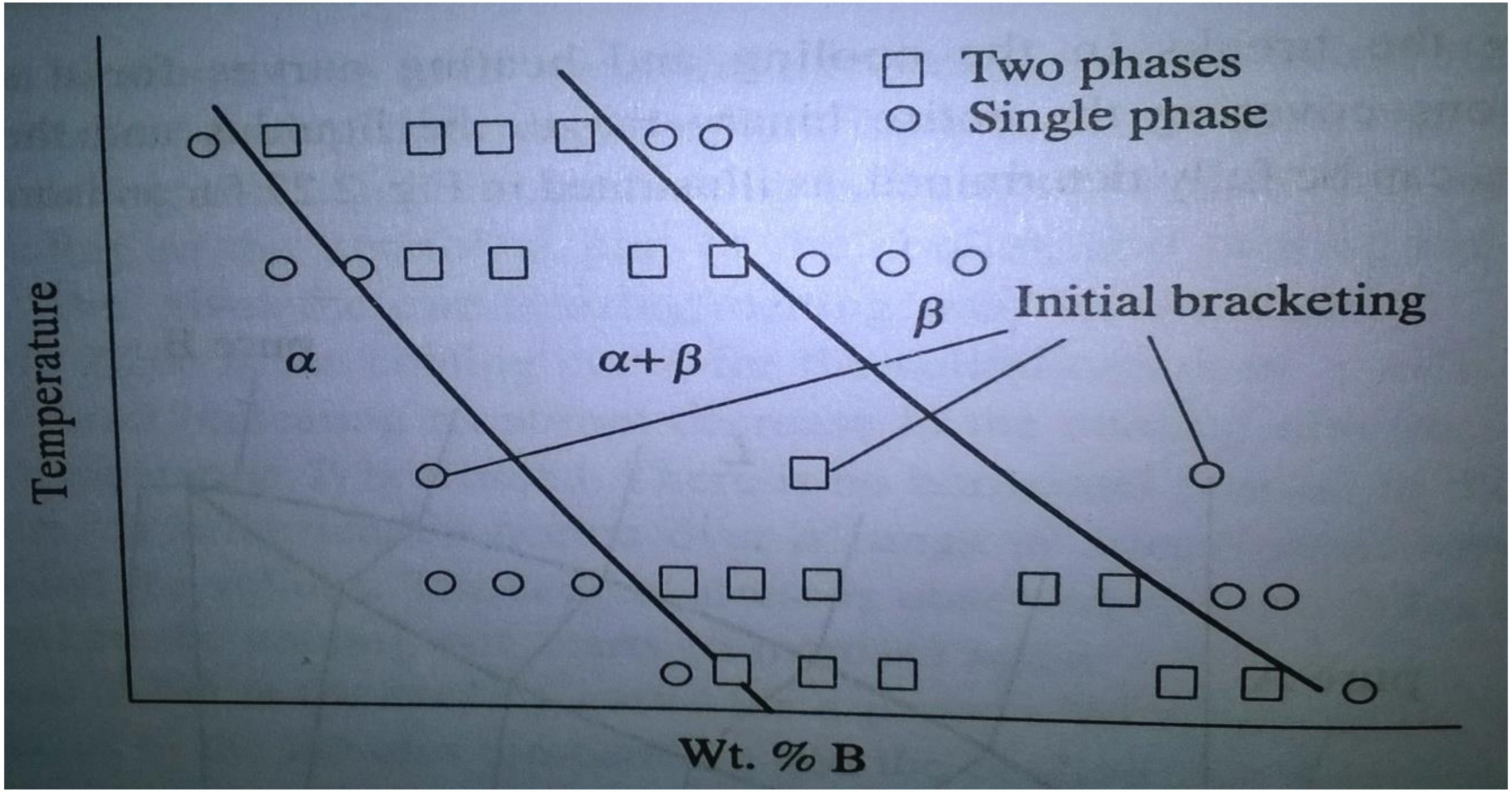

Fig-Determination of Solvus boundaries by the metallographic & X-ray methods, Ref-

Raghavan, V. (2012). *Physical metallurgy: principles and practice*. PHI Learning Pvt. Ltd.

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- The common methods for determining the Solvus are microscopic examination & X-ray diffraction.
- A series of small ingots of alloys of different compositions are prepared and homogenized. They are then annealed at various temperatures for prolonged time (a few days) and quenched.
- In such cases, subsequent metallographic and X-ray studies at room temperature disclose the appearance of second phase at some known composition.
- In other cases, at high temperature phase may decompose on quenching, If this happens room temperature, X-ray studies are not suitable. So a high temperature X-ray camera used.
- But even after the decomposition during quenching the metallographic method may be useful, if the transformed phase is in an easily recognizable form.
- A phase boundary is first bracketed between two compositions and then exact location of boundary is determined by studying a few more alloys of closely varying composition in the boundary region.