Lecture 24

Application of Thermodynamics in Phase Diagrams

The Free Energy – Composition Diagrams

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Today's Topics

- Free energy – composition (G-X) diagrams for binary systems
- Examples of G-X diagrams for common binary phase diagrams

Free Energy – Composition Diagrams

- The most useful tool to obtain connections between the phase diagrams and their underlying thermodynamics principles.

- The fundamental principles of G-X diagrams are:

  For a system of definite composition at constant P and T,

  1. The stable phase has the lowest free energy, G.
  2. The free energy is the same for coexisting phases.

G-X Diagrams for Ideal Solutions

- The molar free energy of ideal binary solutions:

$$\Delta G^S = \Delta G_1 + \Delta G^M \quad (1)$$

where, ΔG^M, the molar free energy of mixing of component 1 and 2, is:

$$\Delta G^M = \Delta H^M - T\Delta S^M = RT\,(X_1 \ln X_1 + X_2 \ln X_2) \quad (2)$$

and ΔG_1, the molar free energy of unmixed solution is:

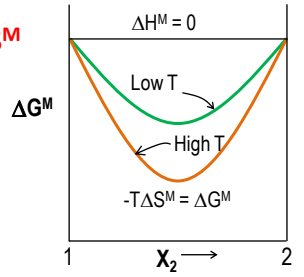
$$\Delta G_1 = X_1 G^0_1 + X_2 G^0_2 = G^0_1 + (G^0_2 - G^0_1)X_2 \quad (3)$$

- Combining eq.(1) and eq.(3), we get,

$$\Delta G^S = G^0_1 + (G^0_2 - G^0_1)\, X_2 + \Delta G^M \quad (4)$$

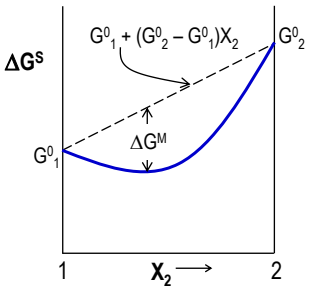
$\Delta G^M = RT (X_1 \ln X_1 + X_2 \ln X_2) = \Delta H^M - T\Delta S^M$

- The $\Delta G^M - X$ plot shows that:
  - The curve is symmetrical at X_2=0.5 and has a vertical slope at X_1=1 and X_2=1.
  - The curve has a minimum value of –RT ln2 at X_2=0.5. This magnitude increases linearly with T.



$\Delta G^S = G^0_1 + (G^0_2 - G^0_1) X_2 + \Delta G^M$

- Since, throughout the curve, ΔG^M is –ve and ΔG^S is less than ΔG_1, components 1 and 2 prefer to form a solution.



- Thus, for a given phase of the solution, G-X diagram is a plot of the molar Gibbs free energy of mixing, ΔG^M, versus the mole fraction of component B, X_B, at a fixed P and T.
- Each existing phase in a system has its own G-X curve.
- The competition for domains of stability of the phases and interactions that produce two and three phase fields that separate them can be visualised by comparing the G-X curves for all the phases in the system.
- For such a comparison of free energies of mixing to be valid, it is absolutely essential that the energies of each component in all the phases be referred to the same reference state.

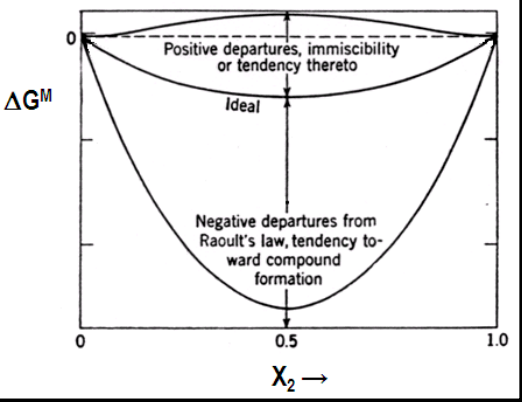
G-X Diagrams for Non-ideal Solutions

- The form of G-X curve for non-ideal or real solution is given by the equation

$$\Delta G^M = RT (X_1 \ln a_1 + X_2 \ln a_2)$$

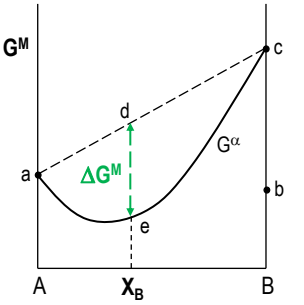
$$\Delta G^M = \Delta G^{ex} + RT (X_1 \ln X_1 + X_2 \ln X_2)$$

where the excess free energy of mixing, ΔG^{ex}, can be positive or negative depending on the type of deviation from ideality.

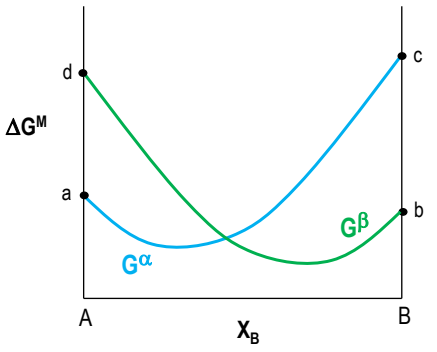


- To produce G-X curves for non-ideal binary solutions of components A and B, the following steps can be followed:

- Let the stable forms of pure A and B at the given T and P be α (fcc) and β (bcc), respectively.
- The molar free energies of fcc A and bcc B are shown as point **a** and **b** in the figure.
- To draw the free energy curve of the fcc α phase, convert the stable bcc arrangement of B atoms into an unstable fcc arrangement. This requires an increase in free energy, **bc**.
- Construct the free energy curve for the α phase now be by mixing fcc A and fcc B as shown in the figure. The distance **de** will give ΔG^M for such solution of composition X_B.



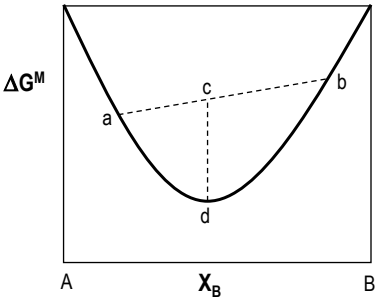
- A similar procedure produces the molar free energy curve for the β phase.
- In the following figure, G-X diagrams for both α and β phases are constructed in a single plot for comparison.



Comparing Free Energy of Solutions with that of its Unmixed Components

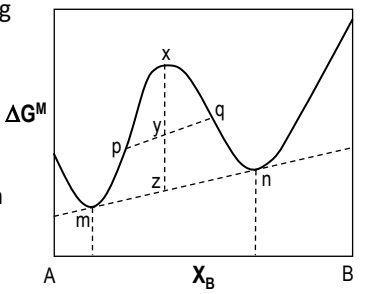
G-X curves "convexing downwards"

- Consider mixing of two separate solutions of A and B, marked by the points **a** and **b**.
- The free energy of unmixed solutions is given by the point **c**.
- The free energy of mixed homogeneous solution will be represented by the point **d**, which is lower than that of point **c**.
- Thus, the resultant single-phase solution is stable relative to any two unmixed portions.
- This is true for any single phase region in which the G-X curve is **"convex downwards."**



G-X curves "convexing upwards"

- The two separated solutions represented by point **p** and **q** have a free energy corresponding to point **y**, which is lower than that for the single homogeneous solution represented by point **x**.

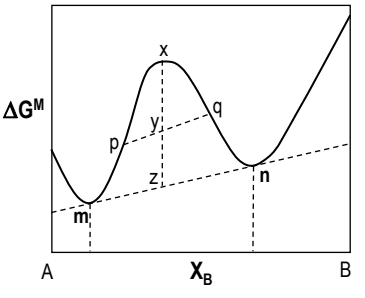


- The configuration with the lowest free energy for this composition is obviously the point **z** on the line **mn**, where two separate solutions of compositions **m** and **n** are in equilibrium with each other.

- Thus, the stable system with compositions
  - from X_B=0 to X_B=m are composed of a single solution
  - from X_B=m to X_B=n consists of a mixture of two solutions of compositions m and n
  - from X_B=n to X_B=1 the stable system is again composed of a single solution.

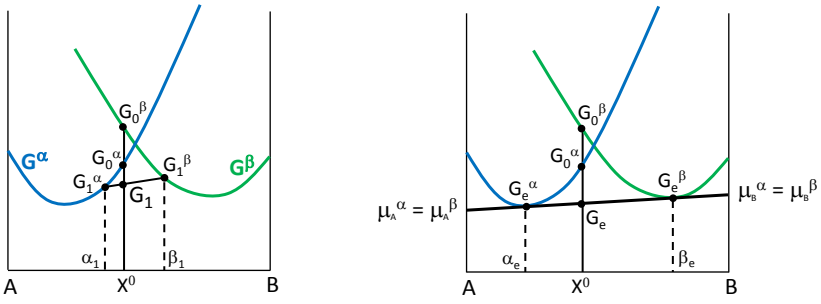
- Single phase solutions from X_B=m to X_B=n are **metastable** with respect to the un-mixed two-phase system.

- This situation is typical for systems exhibiting **a miscibility gap** in the phase diagram and is associated with sufficiently great positive deviation from the ideal behaviour.



System Consisting Two or More Separate Phases

- Similar kind of miscibility may occur.
  - The A-rich alloys will have the lowest free energy as a homogeneous α phase and B-rich alloys as β phase.
  - For alloys with compositions near the cross-over in the G curves, the total free energy can be minimised by the atoms separating into two phases.



Construction of a tangent line common to two (G-X) curves for a pair of phases identifies the compositions of those two phases that coexist in equilibrium at the indicated temperature and pressure.

Examples of Some Common G-X Diagrams

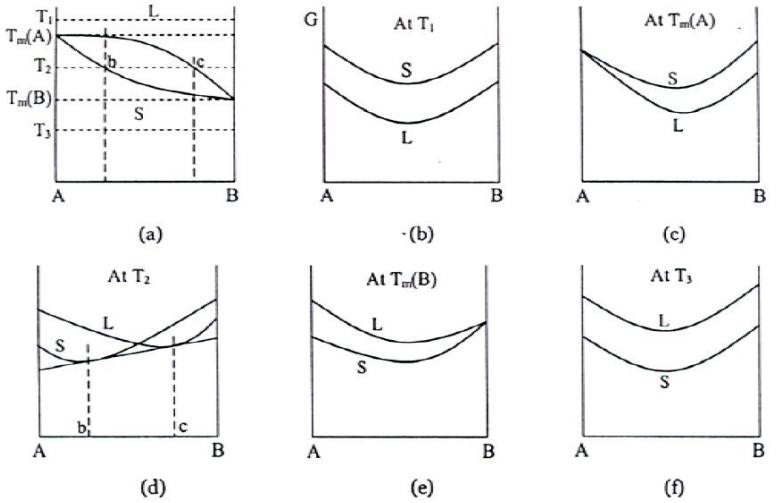


FIGURE 7.19
Free energy– composition curves (b - e) for the completely miscible binary A-B phase diagram (a) at five indicated temperatures.

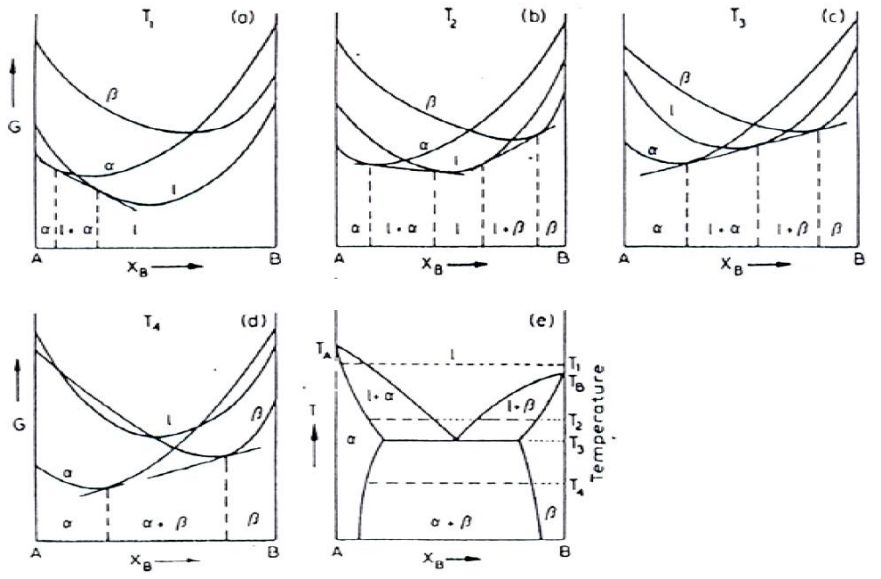


FIGURE 7.22
The free energy – composition diagram of a simple eutectic phase diagram having solids of different crystals with limited solubility at the indicated temperatures.

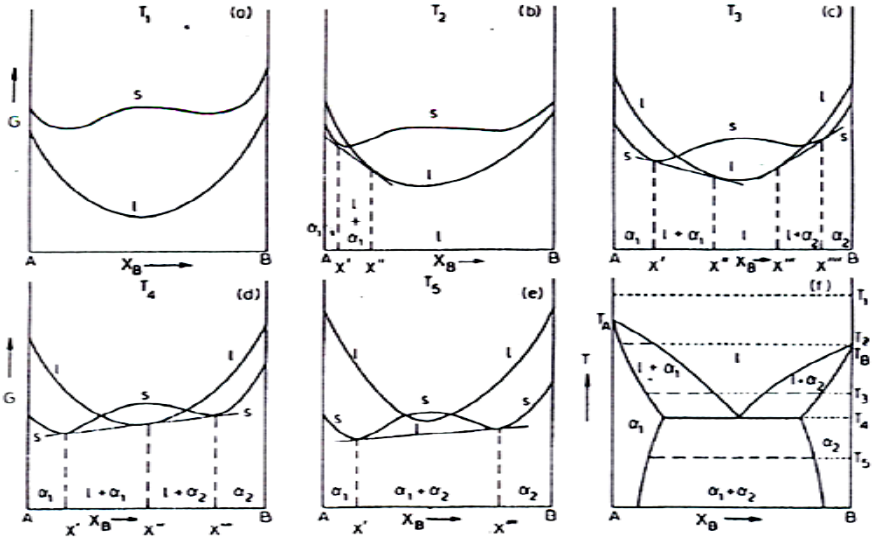


FIGURE 7.21
The free energy – composition diagram of a simple eutectic phase diagram having solids of similar crystals with limited solubility at the indicated temperatures.

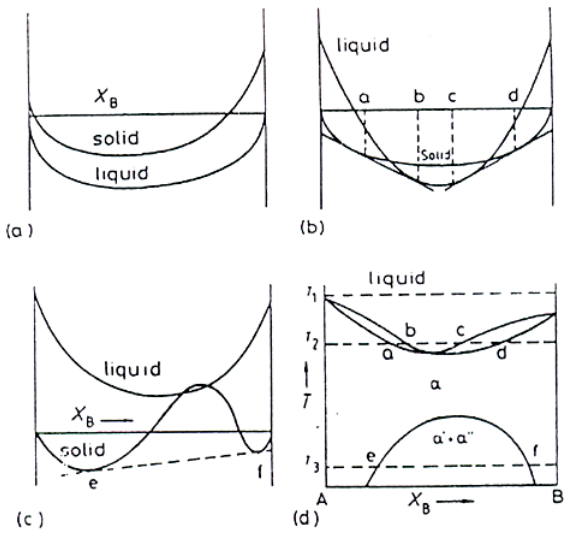


FIGURE 7.20
The free energy-composition curves for (a) T_1, (b) T_2, and (c) T_3 temperatures for (d) the phase diagram showing a miscibility gap where $\Delta H_S^M > \Delta H_L^M = 0$.

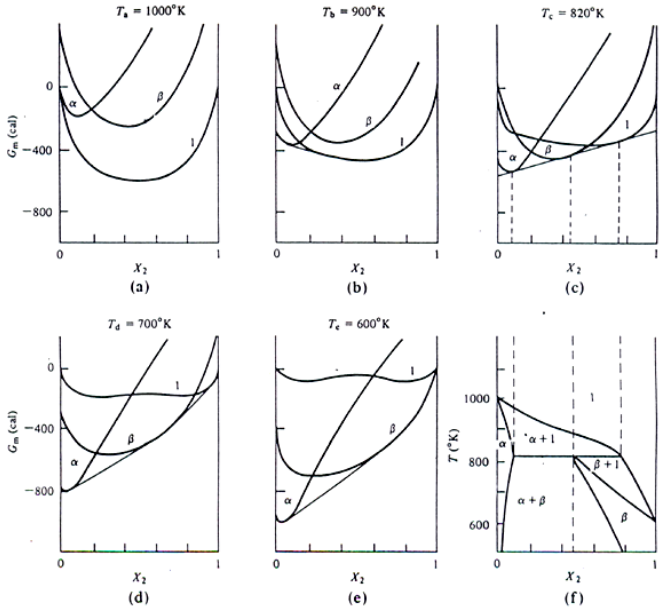


FIGURE 7.23
The free energy – composition diagram of a simple peritectic type phase diagram having solids of different crystals with limited solubility at different temperatures.

Next Class

Lecture 25

Application of Thermodynamics in Phase Diagrams

Problem Solving