

Part I : Preliminaries (Thermodynamics and Kinetics)

Module 3. G versus x_B curves and phase diagrams

4.1 Motivation

It is fairly well known that higher the temperature of water, higher is the salt that you can dissolve in it. Given a temperature, how do I know how much salt I will be able to dissolve? Also, can I cool some salty water (say, sea water) and remove excess salt from it and extract less salty (or even pure) water?

4.2 Free energy versus composition diagrams

Phase diagrams are a concise way to indicate the stable (and metastable) phases in any system; typical phase diagrams that we consider in these course notes are diagrams of composition and temperature; unless stated otherwise, we assume that the pressure is constant (and equals atmospheric pressure).

As we noted earlier, at constant pressure and temperature, equilibration demands that the Gibbs free energy of the system is a minimum. We have also noted that the transformation temperature is the one at which the phases co-exist in equilibrium. Hence, if we know the Gibbs free energy as a function of composition at various temperatures, then, using them, one can construct the phase diagrams.

4.2.1 Mechanical mixtures and solutions

In the previous section, we have seen that systems with a concave curvature in the G versus x_B curves tend to undergo unmixing. In such cases, a mechanical mixture is preferred over a solution. Consider a concave section of the G versus x_B curve as shown in Fig. 10. When unmixing takes place in such a system, what are the compositions of the phases that form the mechanical mixture? This question is answered by the so-called common tangent construction [1]. This is because, as shown in Fig. 11, if we consider two phases with molar free energies G_1 and G_2 , then the free energy of the mechanical mixture lies on the straight line connecting them; that is, a mechanical mixture of f_1 moles of G_1 and f_2 moles of G_2 will have a free energy $G = f_1G_1 + f_2G_2$. Hence, as shown in Fig. 12, a common tangent that replaces the concave part will give the lowest possible free energy for a mechanical mixture of the two end compositions; depending on the overall composition of the alloy, the mole fractions are given by the so called lever rule: see Fig. 12.

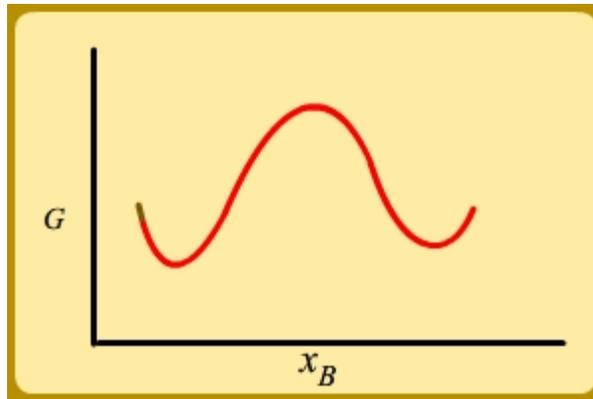


Figure 10: Free energy with a concave curvature.

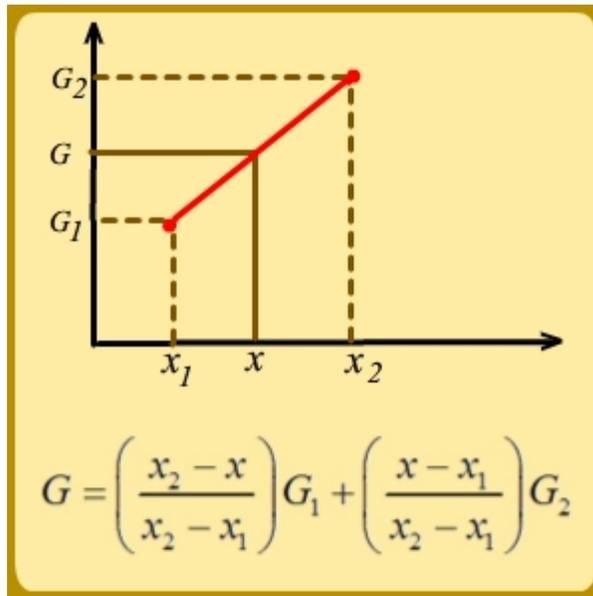


Figure 11: Free energy of a mixture and lever rule for the calculation of mole fraction.

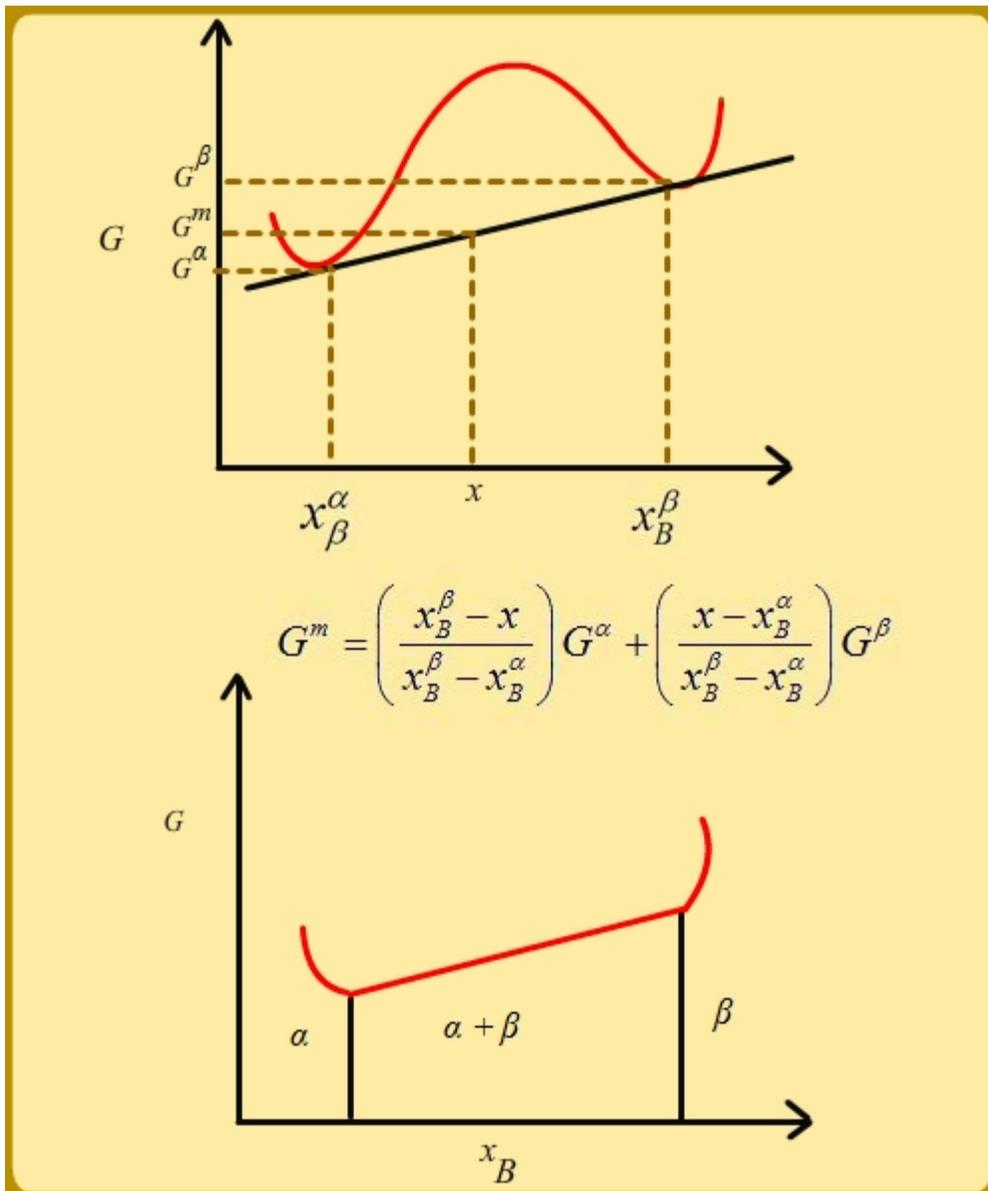


Figure 12: Replacing the concave portion of free energy with a straight line corresponding to a mechanical mixture; note the common tangent construction to identify the composition of the phases that make up the mechanical mixture.

4.3 A simple phase diagram

Consider a phase diagram which is as shown in Fig. 13. It shows complete miscibility in both the solid and liquid phases. In such a case, the G versus x_B curves at the five different temperatures marked T_1 through T_5 are as shown in Fig. 14.

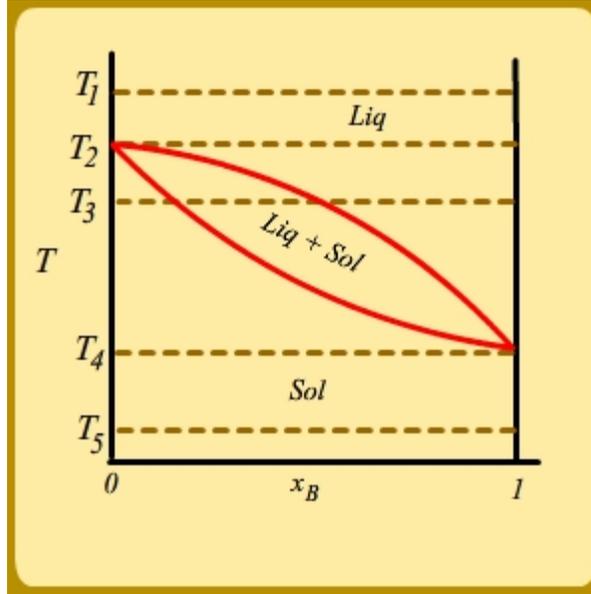


Figure 13: A simple phase diagram.

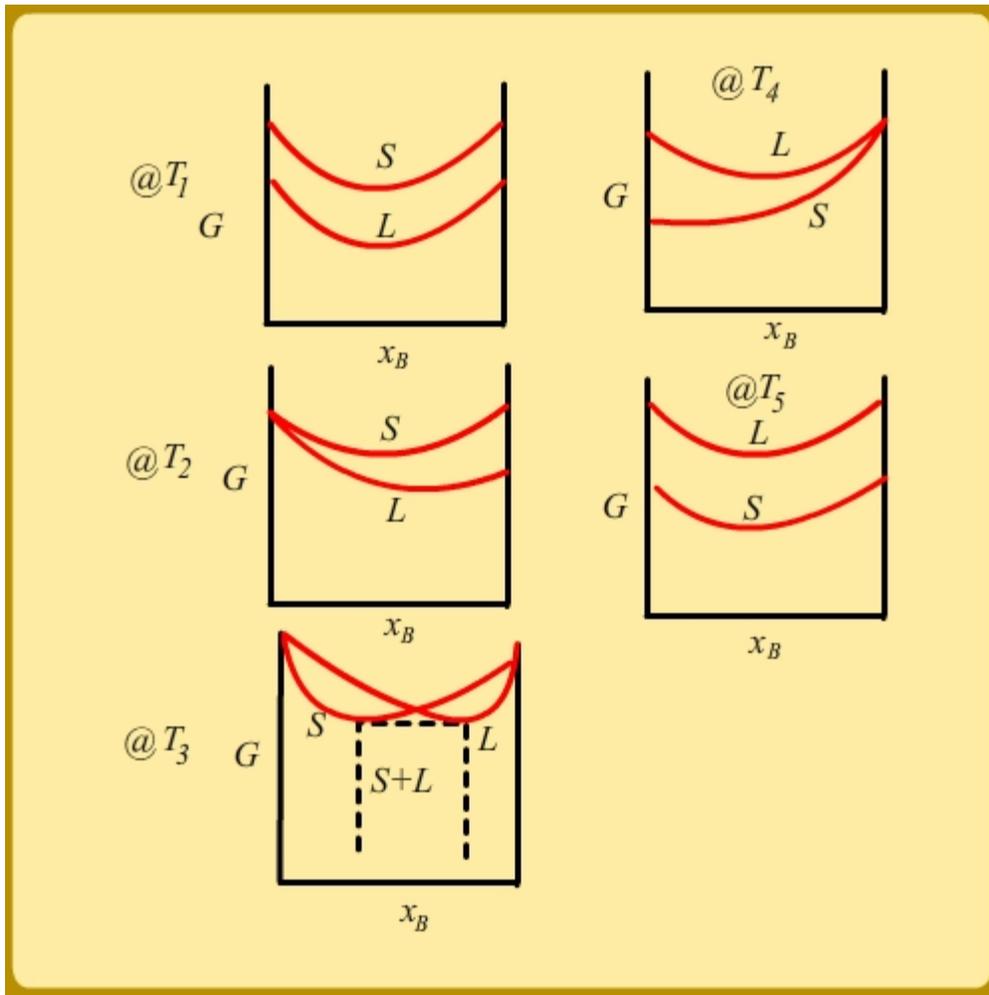


Figure 14: Free energy versus composition diagrams for the simple phase diagram.

4.3.1 Gibbs phase rule

In this simple phase diagram shown in Fig. 13, there are two single phase regions, namely, above the liquidus where the system is in liquid state and below the solidus where the system is in solid state. In these two regions, it is possible to choose both temperature (T) and the composition x_B as independent components; that is, it is possible to prepare systems which are at equilibrium at any given temperature with any given composition. However, in the lens like two phase region, the number of degrees of freedom is reduced to one; here, if the temperature is chosen, the lever rule determines the composition of the phases that form the mechanical mixture; or, if the composition of one of the phases is decided, that automatically fixes the temperature. The Gibbs phase rule summarises these observations: $P + F - C - 1 = 0$, where P is the number of phases, F is the degrees of freedom, C is the number of components (2 in this case since we are dealing with binary alloys). The number unity is added because we have used only T as the independent variable and fixed the pressure P ; if P is also allowed to change, the phase rule is modified as $P + F - C - 2 = 0$. Thus, in a binary alloy, $P + F = C + 1 = 2 + 1 = 3$. Hence, as we saw, if the number of phases is unity, the number of degrees of freedom is two; if the number of phases is two, the number of degrees of freedom reduces to unity.

4.4 An eutectic phase diagram

Consider a phase diagram which has an eutectic point as shown in Fig. 15. Eutectic point is a point of co-existence of three phases. Hence, the number of degrees of freedom is zero; that is both the compositions of the phases that make up the mechanical mixture (that forms from the given liquid) and temperature of the eutectic point is fixed. Hence, the line indicating the eutectic reaction in the phase diagram is known as invariant line. In Fig. 16, we show the G versus x_B lines at the four temperatures T_1 through T_4 marked on the phase diagram.

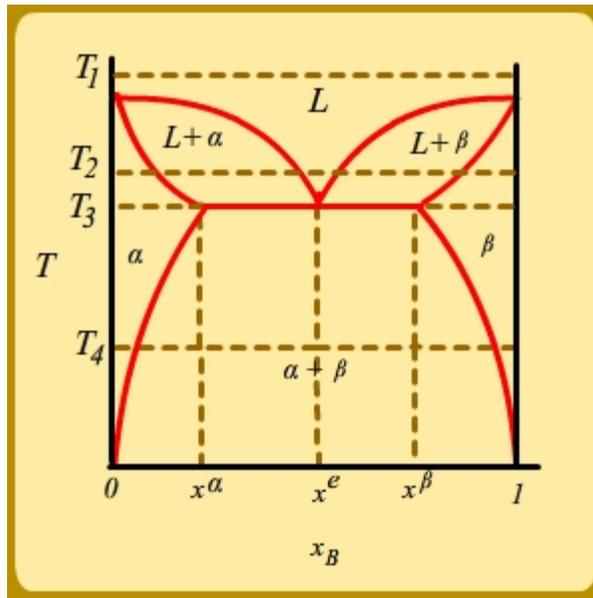


Figure 15: An eutectic phase diagram.

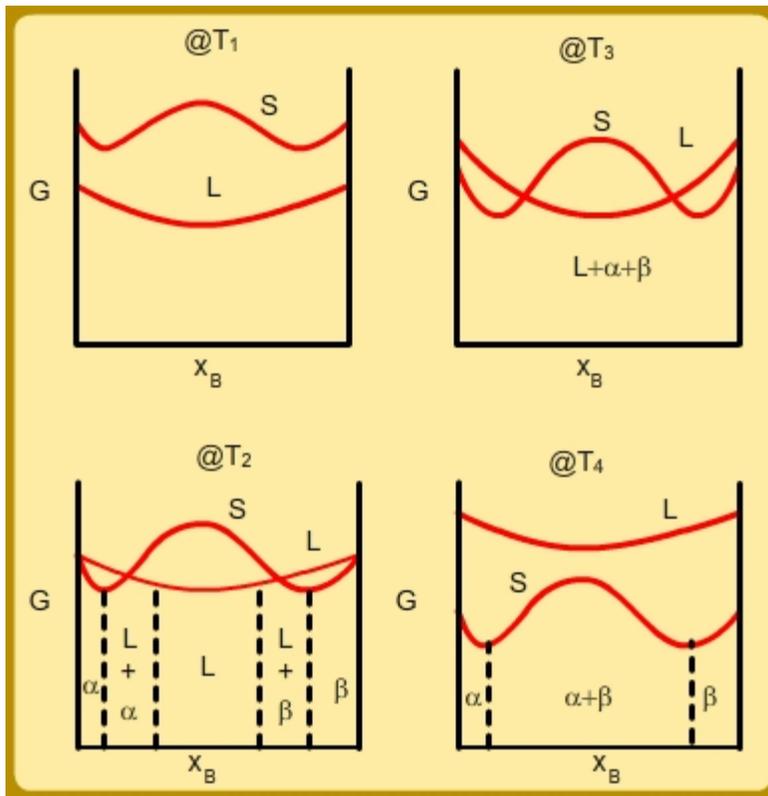


Figure 16: Free energy versus composition plots for a system with an eutectic phase diagram. Note that we have assumed that the phases that make up the eutectic mixture have the same structure.

4.5 Tutorial problems and questions

1. Shown in Fig. 17 is the water-salt phase diagram. As is clear from the figure, there is an eutectic reaction at -21°C where pure ice and pure salt are formed. Thus, given the sea water contains 3.5% salt, it is possible to extract pure water from the same by cooling it just below -21°C . Calculate the amount of pure water that you can extract from sea water by cooling it?

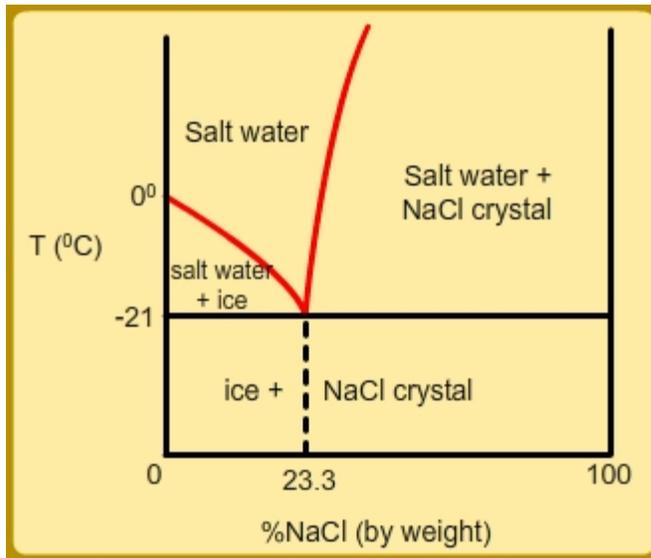


Figure 17: Water-salt phase diagram.

Answer

We use the Lever rule. Since the overall composition is 3.5%, and the eutectic composition is 23.3%, we get the ice fraction as $\frac{23.3-3.5}{23.3-0.0} = 0.85$. So, one can extract about 85% of pure water from the sea water by cooling just below the eutectic line.

2. Shown in Fig. 18 is a simple phase diagram which has a miscibility gap at low temperatures. Show the G versus x_B diagram at the temperatures T_1 and T_2 marked on the phase diagram.

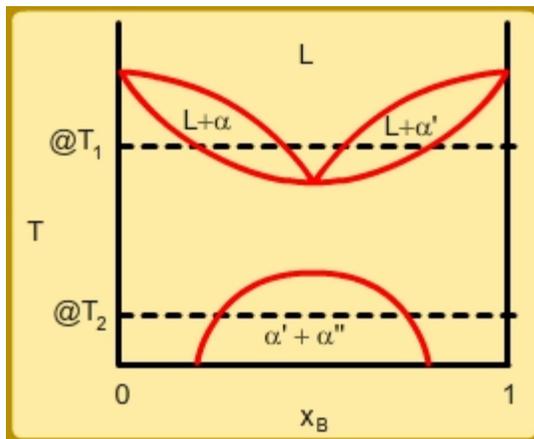


Figure 18: Phase diagram with a miscibility gap at low temperatures.

Answer

See Fig. 19.

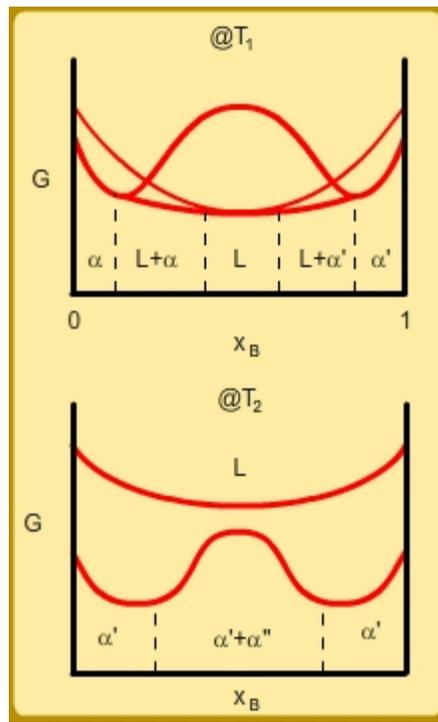


Figure 19: Solution to problem 2 above

3. Consider a binary alloy in which P is also allowed to change; how many phases can be at equilibrium in such a system?

Answer

Since $P + F = C + 2 = 2 + 2 = 4$, and since at best $F = 0$, the number of phases that can be at equilibrium in such a system is 4.

Supplementary information

Calculating the phase diagrams numerically using thermodynamic data is beyond the scope of these notes. Phase diagrams in ternary systems are also important in many important industrial alloys. However, unlike binary alloys, they can only be represented in 3D; in 2D, one can only show different sections of the 3D phase diagram. Again, phase diagrams in ternary alloys is beyond the scope of these notes. We refer the interested reader to [1] and [2] (and references therein).