Lecture 31

Solution Thermodynamics

Last Time

Other Types of Phase Diagrams

Models for Solutions

Limiting Behavior for Dilute and nearly Pure Solutions

Ternary Phase Diagrams

Phase diagrams have been constructed for the case of one component (P-T diagrams for a pure material), and for two component systems (T-X_B diagrams drawn at constant pressure). Each time a new component is added, another intensive variable must be held constant if the phase diagram is to be drawn in two-dimensions.

For ternary systems, there are three components. Let the three components be denoted by R, G, and B. Because, $X_R + X_G + X_B = 1$, the system can be represented by two components, say X_R, and X_G, and the phase diagram could be represented in the following coordinate system:

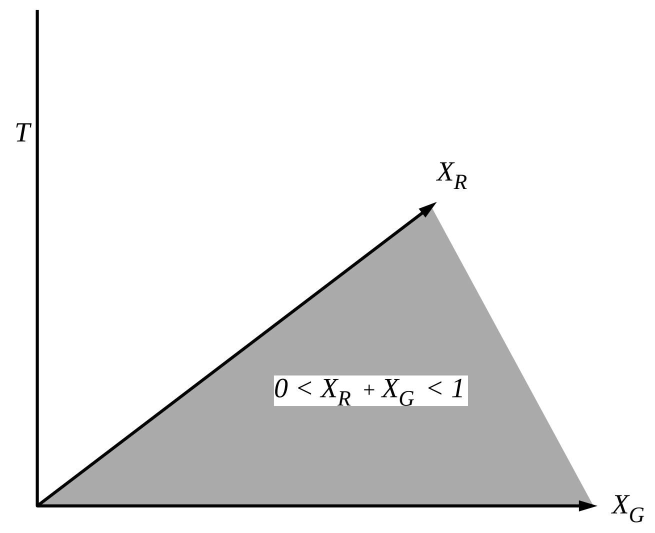

Figure 31-1: Possible way to draw a ternary phase diagram at constant pressure. It would be difficult to interpret such diagrams.

Question: what is the maximum number of phases that can be in equilibrium at one point in Figure 31-1?

It may be possible to represent such a diagram in two dimensions by taking slices at constant composition, for instance:

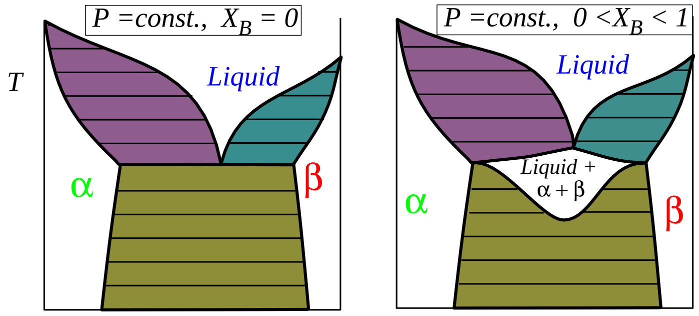

Figure 31-2: Pseudo-binary slices of a ternary phase diagram at constant pressure. The figure on the left is a true binary phase diagram and has the same corresponding rules for the degrees of freedom.

Ternary phase diagrams are traditionally drawn at constant pressure and temperature—and the following scheme is used to represent all three components:

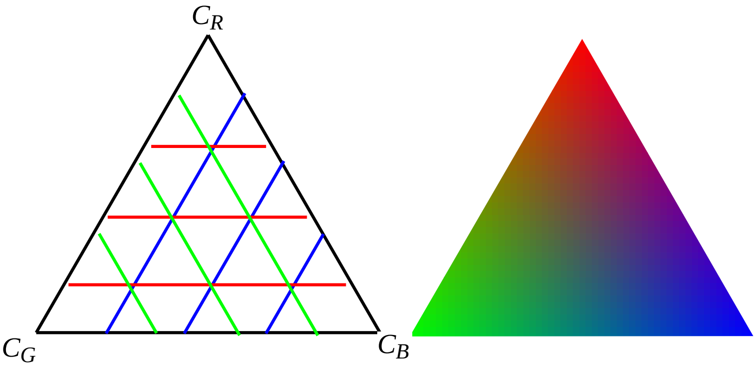

Figure 31-3: Representation of three components at constant pressure and temperature. Each triangle vertex corresponds to a pure component. Each triangle side corresponds to: 1) a system with *none* of the component from the opposite vertex; 2) a binary alloy with none of the third component represented by the opposite vertex.

For example, a ternary phase diagram may look something like this:

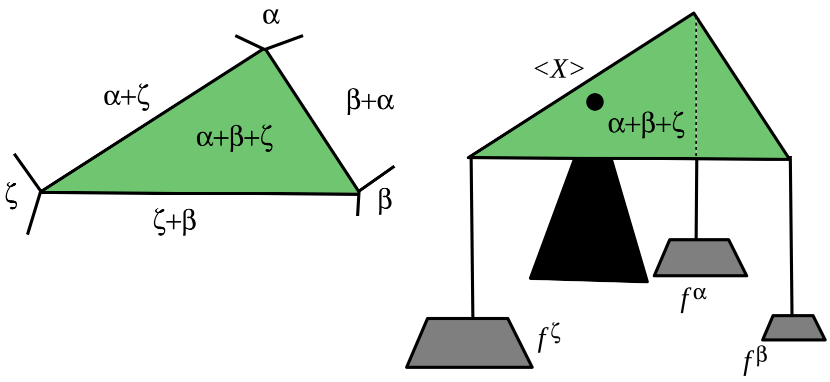

Figure 31-4: An example of a ternary phase diagram. Three phase regions become triangles where the limiting composition of each co-existing phase is given by the vertices of the triangle. The sides of the triangle are the limits of the tie-lines from an abutting two phase region. The lever rule in three phase region is graphically illustrated by the weighted phase fractions distributed about the average composition.

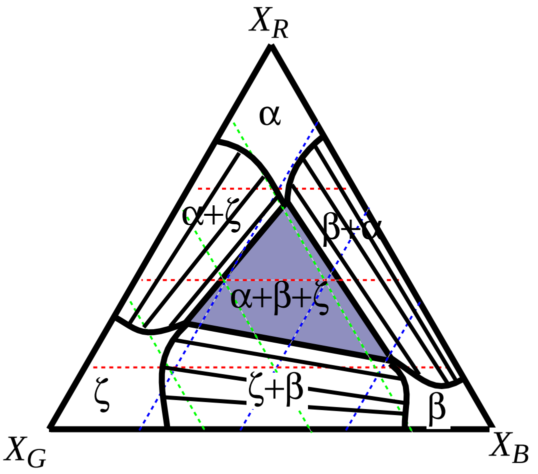

Figure 31-5: Example of a simple ternary phase diagram at constant P and T.

Solution Free Energies that Generate Phase Diagrams

For the construction of phase diagrams, plausible forms of the free energy of solution have been utilized without discussion of their derivation. For instance,

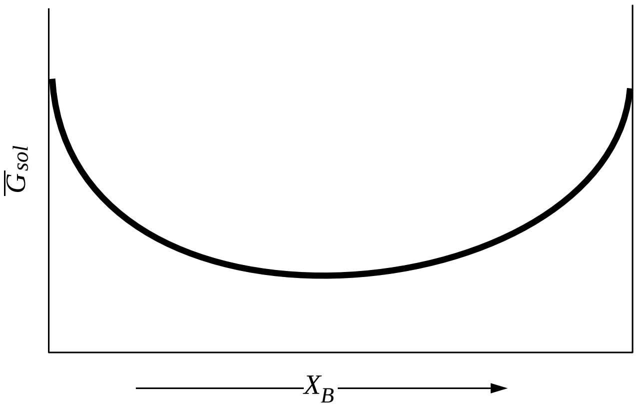

Figure 31-6: Prototype of the Molar Gibbs Free Energy of Solution.

Previously, the *ideal solution* was defined for the case where the chemical potential of *each* component is a linear function of the log of its mole fraction:

$$\mu_i{}^{\mathcal{IS}}(T, P, X_i) = \mu_{i_\circ}{}^{\mathcal{IS}}(T, P) + RT \log X_i \tag{31-1}$$

which implies that:

$$
\begin{aligned}
\overline{G^{\text{total}^{\mathcal{IS}}}}(T,P) &= \sum_{i=1}^{C} X_i \; {\mu_i}_{\circ}^{\mathcal{IS}}(T,P) - (-R)T \sum_{j=1}^{C} X_j \log X_j \\
&= \overline{H^{\text{total}^{\mathcal{IS}}}} - T\overline{S^{\text{total}^{\mathcal{IS}}}}
\end{aligned}
\tag{31-2}
$$

which does give the qualitative features that are drawn in Figure 31-6.

One might wonder why such a simple form of the molar Gibbs free energy of solution would be used for condensed phases, since this is the form that was derived from ideal gases.

One condition of equilibrium is that the chemical potential in each phase must be equal. Therefore if the vapor phase above a condensed phase is in equilibrium then:

$$\mu_i^{sol} = \mu_i^{vap}$$

Considering an ideal gas as the vapor (another assumption):

$$ {\mu_i}_{\circ}^{\mathcal{IS}}(T,P) + RT \log X_i = {\mu_i}_{\circ}^{\mathcal{IG}}(T) + RT \log P_i \tag{31-3}$$

The second term it is what we derived for the ideal solution:

$$ \frac{P_i}{X_i} \equiv {\gamma_i}^{\mathcal{IS}} = e^{-\left[\frac{{\mu_i}_{\circ}^{\mathcal{IG}}(T) - {\mu_i}_{\circ}^{\mathcal{IS}}(T,P)}{RT}\right]} \tag{31-4}$$

where γ^{IS} is independent of X_i.

Limiting Solution Behavior

It can be shown that the ideal solution represents the limiting behavior of very dilute solutions. The question may be posed: "In what cases can we expect the activity to depend only on composition?"

Consider a very dilute solution of B in A:

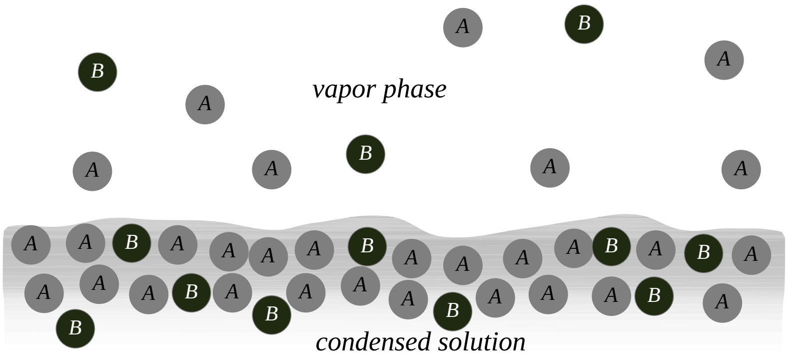

Figure 31-7: An atomic idealization of a dilute condensed solution of B dissolved in A in equilibrium with its vapor.

Each time an A comes out of solution, it does so mostly without any influence of B. It is as if it does so as in a pure solution.

Each time a B comes out of solution, it does so entirely under the influence of the surrounding A atoms; it is as if it does so from pure A.

So one can expect very concentrated, or very dilute solutions to behave ideally.

Typically, the data look like the following:

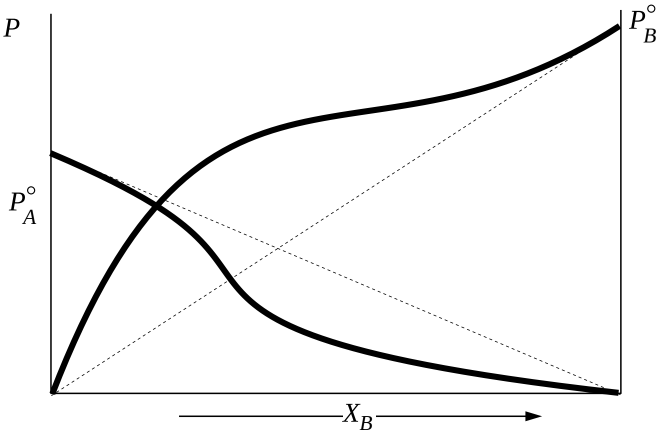

Figure 31-8: Typical data for the behavior of solutions.

One gets as limiting behavior:

Raoult's Law:[30]

$$\gamma_i \rightarrow 1 \quad \text{as} \quad X_i \rightarrow 1 \quad \text{(Raoult's Law)} \tag{31-5}$$

and Henry's law:

$$\gamma_i \rightarrow \gamma_i^{\mathcal{IS}} = \text{constant} \quad \text{as} \quad X_i \rightarrow 0 \quad \text{(Henry's Law)} \tag{31-6}$$

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[30] Raoult's = really pure = really simple