

CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 24: Binary phase diagrams

References

1. Levine, *Physical Chemistry*, Sections 9.1, 9.3, 9.5–9.6

Key Concepts

- For an ideal, binary solution the free energy of mixing can be written as:

$$\bar{G}_{mixed} = X_A\mu_A + X_B\mu_B = X_A\mu_A^\circ + X_B\mu_B^\circ + RT(X_A \ln X_A + X_B \ln X_B)$$

- The change in free energy upon mixing is given by:

$$\Delta\bar{G}_{mixing} = \bar{G}_{mixed} - \bar{G}_{unmixed} = RT(X_A \ln X_A + X_B \ln X_B)$$

For an ideal solution, this free energy change will always be negative meaning that two ideal components will always mix in all compositions.

- We can understand this mixing by considering the enthalpy and entropy of mixing. The entropy of mixing is:

$$\Delta\bar{S}_{mix} = - \left(\frac{\partial \Delta\bar{G}_{mix}}{\partial T} \right) = -R(X_A \ln X_A + X_B \ln X_B)$$

The entropy of mixing of two ideal components is always positive, which agree with the previous case we considered for just ideal gases. The enthalpy of mixing can be found as well:

$$\Delta\bar{G}_{mix} = \Delta\bar{H}_{mix} - T\Delta\bar{S}_{mix}$$

$$\Delta\bar{H}_{mix} = 0$$

So for an ideal solution, the driving force for mixing is the entropy change and there is no enthalpy change upon mixing. This makes sense when we take into account that for the ideal case we assumed no chemical interactions.

- To understand the stability of phases in a binary system, we need to use the tangent construction to determine the chemical potential of each component at a particular composition. We can do this graphically as shown in class.
- To map out the stability of phase we need to consider how the free energy curves for the phases of interest (for example solid and liquid) move relative to each other as we change temperature. The phase(s) with the lowest free energy is(are) stable.
- For a generic ideal system of A & B we found the following different behaviors as we changed the temperature:
 1. Above the melting temperature of both components, the system will be in the liquid phase since it has a lower free energy at all compositions.
 2. At the melting temperature of B ($T_m(B)$) but above that of A ($T_m(A)$) we found that for pure B we would expect solid and liquid to be in equilibrium (just like the unary case). However, in a mixture of A and B we would still expect the system to be in the liquid phase (it has the lowest free energy).

We did not get past this point, but I have included this material, which we will cover next time.

3. At a temperature between $T_m(A)$ and $T_m(B)$ we would expect three different behaviors. It is easiest to think of these as we start from pure B and move towards pure A:

- (a) As we start at pure B the system will be in the single-phase solid state.
 - (b) Once we reach the common tangent line between the solid and liquid free energy curve, the system can actually lower its free energy by forming a two phase mixture of the solid and liquid phase.
 - (c) This two phase region continues until the tangent point on the liquid free energy curve is reached. Beyond this point, the system exists as a single phase liquid.
- If we put all of these curves together on a plot of temperature versus X_B we can construct a map of phase stability or a binary phase diagram that tells us what phases we would expect to be stable at equilibrium.
 - Ideal binary phase diagrams are often called lense diagram due to the shape of the two-phase region.