**SIMPLE SOLID – LIQUID PHASE EQUILIBRIA**

An understanding of solid liquid phase equilibria is required to describe and calculate phase diagrams of interest in both fundamental materila science and applications such as crystallizer design. A very simple phase diagram is shown below. For this system the two solid phase do not mix (form intercallated crystals) or form solid compounds. This is what we see in many cases for binary systems for which the materials are very similar chemically. Here we plot the temperature versus the mole fraction of species A in an A – B binary. This diagram can depend on pressure as well but it takes large pressure changes (100 bar or more) to cause signifacant variation.
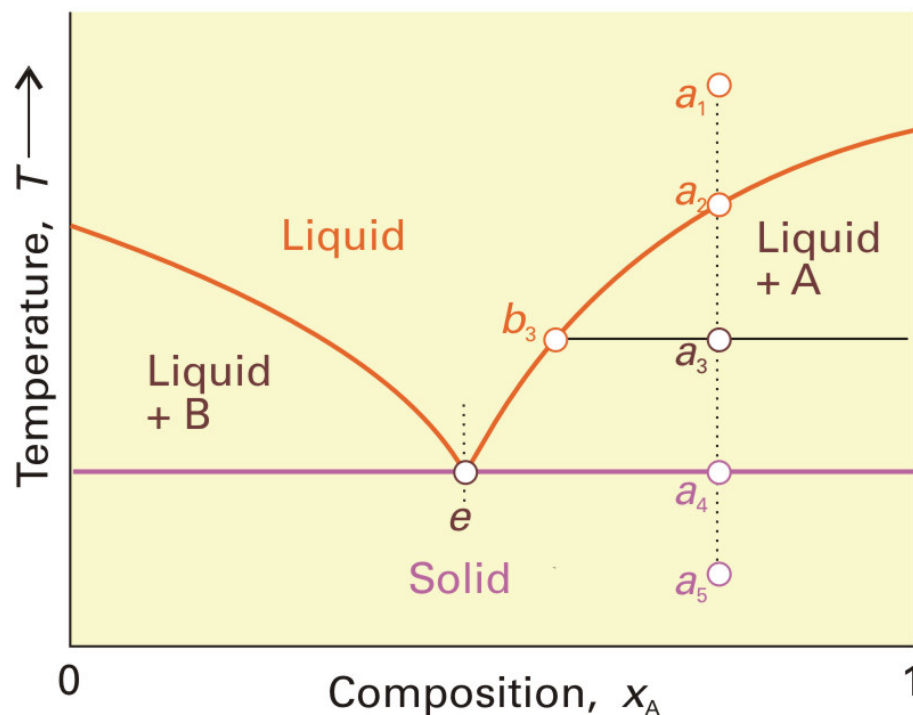
The point labeled e is known as an eutectic point. Notice that for x_A values less than those for point A systems that are cooled from high temperature will separate into mixtures that are liquid and pure solid B. Foe compositions of A greater than the eutectic composition, like the line shown in the figure, the solid phase that forms is pure A. The lines separating the liquid region from the two phase regions are termed liquidus lines. The line that runs from the pure component B melting point to the eutectic point is defined by

$$f_B^S(T,P) = \hat{f}_B^L(T,P,x_A)$$

The other liquidus line, that runs from the melting point of pure A to the eutectic point is given by

$$f_A^s(T,P) = \hat{f}_A^L(T,P,x_A)$$

The intersection of these two lines defines the eutectic point. This behavior is simpler than what is typically seen in metallic systems where mixed solids and alloys form.

Separation process based on this phenomena are not totally effective as the solid that is formed always has some liquid attached that will be at the equilibrium liquid composition. This is why many crystallizers are high speed rotary devices designed to remove as much attached liquid as possible.

The typical approach for solution of such problems is shown below.

Solid Solubility Calculation

We wish to consider the problem of the solubility of a solid in a solvent. Here we will label the solid as species 1 and the solvent as species 2. At equilibrium we have the phase equilibrium relationship

$$f_1^s(T,P) = \hat{f}_1^l(T,P,x_1)$$

This is the condition that the fugacity of the pure solid species 1 at the temperature and pressure of interests is the same as the fugacity of species 1 in the liquid mixture. If we use the standard approach for calculation of liquid state fugacities this can be written as

$$f_1^s = x_1\gamma_1 f_1^l$$

Here we write the fugacity of the species in solution in terms of the liquid reference state fugacity f_1^l using the activity coefficient.

Rearrange this leads to

$$x_1\gamma_1 = \left(\frac{f_1^s}{f_1^l}\right)$$

The benefit of this approach is two fold: first, the fugacity ratio on the right is not dependent on composition, it depends only on T and P and the pressure dependence is almost always neglected as this is a ratio of properties for a solid and a liquid, neither of which depends strongly on pressure, and second we can construct a thermodynamic path that allows use to calculate this ratio based on measurable properties.

If we realize that for a pure component the fugacity and the molar Gibbs Free Energy are related by

$$dG = RTd\ln(f)$$

the fugacity ratio term above can be written as

$$RT\ln\left(\frac{f_1^s}{f_1^l}\right) = (H_1^s - H_1^l) - T(S_1^s - S_1^l)$$

We perform similar calculations for both the enthalpy and entropy differences using a thermodynamic path. We calculated the difference in either the enthalpy or entropy using a three step path.

$$liquid\ at\ T \rightarrow liquid\ at\ T_M \rightarrow solid\ at\ T_m \rightarrow solid\ at\ T$$

For the enthalpy we have

$$H_1^s - H_1^l = (H_1^s(T,P) - H_1^s(T_m,P)) + (H_1^s(T_m,P) - H_1^l(T_m,P)) + (H_1^l(T_m,P) - H_1^s(T,P))$$

This can be written as

$$H_1^s - H_1^l = \int_{T_m}^{T} C_P^s dT + \Delta H_{fus}(T_m) + \int_{T}^{T_m} C_P^l dT$$

If we assume that the heat capacity terms for both phases can be treated as constants then this result can be written as

$$H_1^s - H_1^l = \Delta C_p(T - T_m) + \Delta H_{fus}(T_m)$$

Where ΔC_p is the difference between the heat capacity of the solid and the liquid for species 1 and $\Delta H_{fus}(T_m)$ is the heat of fusion for species 1 at the melting temperature.

Performing a similar analysis we find the entropy difference can be calculated as

$$S_1^s - S_1^l = \Delta C_p \ln\left(\frac{T}{T_m}\right) - \frac{\Delta H_{fus}(T_m)}{T_m}$$

If we combine the initial phase equilibrium relationship with these calculations for the enthalpy and entropy changes we come to

$$\ln(x_1\gamma_1) = \frac{\Delta H_{fus}}{RT_m}\left(1 - \frac{T}{T_m}\right) + \frac{\Delta C_p}{R}\left(1 - \frac{T_m}{T} + \ln\left(\frac{T_m}{T}\right)\right)$$

In many cases the heat capacity difference is small enough that it can be neglected. What this means is that the difference in the heat capacity is a small number relative to the ratio of the heat of fusion to the melting temperature. This leads to the useful expression for non-ideal liquid solutions

$$\ln(x_1\gamma_1) = \frac{\Delta H_{fus}}{RT_m}\left(1 - \frac{T}{T_m}\right)$$

If we can also assume the liquid phase is ideal we obtain the ideal solubility equation

$$\ln(x_1) = \frac{\Delta H_{fus}}{RT_m}\left(1 - \frac{T}{T_m}\right)$$

You should compare this to the freezing point depression equation that you see in a typical Pkysical Chemistry book.

Class Problem Assigned for HW#3 in ECH 3418 (Separation Processes) Spring 2018

#4 A fundamental problem of interest in Materials Science is the calculation of solid – liquid phase diagrams. Many systems of similar compounds form simple eutectic solutions. The phase diagram for such a system and the equations that describe the phase transition lines are shown in our class notes. In our laboratory we have used a differential scanning calorimeter to measure the melting points and heats of fusion for both palmitic acid and stearic acid.

   a. Use the data given in the table below to develop the solid-liquid phase diagram for this system.
   b. If a mixture that is 95 % stearic acid is cooled down from 350 K, at what temperature would the first solid form?
   c. If a mixture that is 95% palmitic acid is cooled to 330 K what fraction of the palmitic acid would be solidified?

Species	T_f (K)	DH_f (kJ/mole)
Palmitic Acid	335.85	51.85
Stearic Acid	341.97	51.68