

CHEM 3410: Physical Chemistry I — Fall 2009

November 2, 2009

Lecture 26: Eutectic phase diagrams

## References

1. Levine, *Physical Chemistry*, Sections 12.1, 12.5–12.9

## Key Concepts

- In a solution with repulsive interactions between the components, we observe a competition between the entropy of mixing (which usually favors mixing) and the enthalpy of mixing (which in this case are repulsive and favor separation).

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

At high temperatures, entropy dominates while at lower temperature the enthalpic contribution becomes more significant.

- If the interactions between A & B are repulsive, that is, A and B don't like to be together then you get phase separation or immiscible phases. (Think: ouzo and water)
  1. If you start with pure A at some temperature T and begin to add B, initially the B will go into solution and there will be a single phase.
  2. At some concentration of B, you can't get any more into A, and you form a second B-rich phase. This is the two phase region.
  3. If you continue to add B, you just move across the two-phase region until you reach the other side of the *miscibility gap*.
  4. You can now dissolve the small amount of A present into B, yielding a single-phase solution of B with some A dissolved.
- If we now turn on interactions in the liquid and the solid phase we can get more complicated diagrams with new types of transitions.
- A eutectic diagram is a special type of binary diagram that has one composition where there is a direct transition from a liquid to two solid phases ( $L \rightarrow \alpha + \beta$ ). All the rules and ideas we discussed for ideal binary diagrams still apply.
- In a eutectic, there is one temperature ( $T_E$ ) where three phases can exist simultaneously (L and two solid phases). This is similar to the triple point on a unary diagram, but it is a line on a binary because of the additional composition variable.
- Another special feature of a eutectic system is that if you have a the eutectic composition ( $X_e$ ), there will be a direct transition from the liquid phase to the solid phases ( $L \rightarrow \alpha + \beta$ ). At this composition we would observe a thermal arrest at the eutectic temperature where this direct transformation takes place.
- We can construct free energy ( $\bar{G}$ ) versus composition curves by using the phase diagram to determine what phases are stable at a particular temperature. In a single phase region, the stable phase has the lowest free energy. In a two-phase region, a common tangent can be constructed yielding a mixture of two phases which have a lower free energy than either phase individually.