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CHEM 3410: Physical Chemistry I — Fall 2008

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Lecture 25: Regular solutions & 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).

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

  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 imiscible 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 dissolve.

- 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 ($\mathrm{L} \rightarrow \alpha + \beta$). 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 ($\overline{G}$) 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.