

CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 25: Non-ideal binary systems

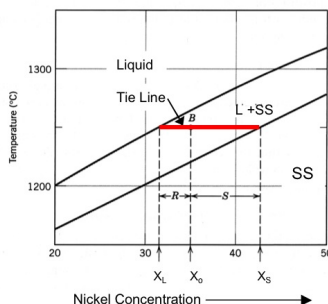
### References

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

### Key Concepts

- The behavior of a single component or unary system is much different than that of a binary system when we looked at cooling curves for each case. Unary systems have a well defined melting point while binary systems melt over a range of temperatures.
- Phase diagrams act as a map and can give us three useful pieces of information if we know the overall composition of the solution:
  1. What phases we expect to be present — Read off diagram
  2. What the composition of each phase should be (i.e. is one phase enriched in a particular component) — Read off diagram. In two-phase regions at a fixed temperature, the composition of each phase is fixed by the tie line.
  3. How much of each phase is present at equilibrium — Two Phase Region = Lever Rule
- The Lever Rule allows you to calculate the amount of each phase in a two phase region. Using the diagram for Cu-Ni shown below, the phase fractions can be found as follows:

$$f_L = \frac{S}{R+S} = \frac{X_S - X_o}{X_S - X_L}$$
$$f_S = \frac{R}{R+S} = \frac{X_o - X_L}{X_S - X_L}$$



This will work in any two-phase region: Liquid/Solid, Liquid/Liquid, Solid/Solid, Liquid/Vapor

- In two-phase regions, different overall compositions in this range lead to the composition of the phases remaining the same, but the **relative** amounts change of each phase change as predicted by the lever rule.
- If we now turn on interactions between the two components, we can get more interesting behavior like *phase separation, miscibility gaps, compound formation*.
- We wrote for a general system that:

$$\mu_B = \mu_B^\circ + RT \ln a_B$$

For a non-ideal system, the activity a component is not necessarily equal to the mole fraction of that component. The activity coefficient ( $\gamma$ ) takes into account the non-ideal behavior.

- For a positive deviation from ideality, the chemical potential (and activity) of a component is greater than predict in the ideal case. This means that repulsive interactions are dominating since mixing the two component raises the chemical potential, i.e. makes it less stable.
- For a negative deviation from ideality attractive forces dominate, making the chemical potential of a component in the mixture less than predict in the ideal case. This means the solution or mixed state is more stable than in the ideal case.
- In the concentrated limit,  $X_B \rightarrow 1$  (B is the solvent), component B will act close to ideally, which is called Raoultian behavior ( $a_B \approx X_B$  as  $X_B \rightarrow 1$ ).
- In the dilute limit,  $X_B \rightarrow 0$  (B is the solute), component B will not be ideal but will have a constant activity coefficient ( $\gamma^\circ$ ). This simple linear behavior is called Henrian.
- A “simple” model for real binary systems is the regular solution model, which accounts for all interactions in a single parameter,  $\Omega$ . For a non-ideal system,  $\Delta H_{mix}$  is non-zero and is accounted for in this model by  $\Omega$ .

$$\Delta \bar{G}_{mix}^{regular} = RT(X_A \ln X_A + X_B \ln X_B) + \Omega X_A X_B$$

- $\Omega$  takes into account the difference between the energy of the A-B interactions ( $E_{AB}$ ) and the average AA and BB interactions ( $E_{AA}, E_{BB}$ )

$$\Omega = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})$$

- If  $\Omega > 0$ , this means that the  $E_{AB} > \frac{1}{2}(E_{AA} + E_{BB})$  and AB interactions are higher energy than AA and BB. This means the system will favor separation, i.e. A and B being near each other is higher energy than AA or BB interactions.
- If  $\Omega < 0$ , this means that the  $E_{AB} < \frac{1}{2}(E_{AA} + E_{BB})$  and AB interactions are lower energy than AA and BB. This means the system will favor mixing, i.e. A and B being near each other is lower energy than AA or BB interactions.
- This leads to a competition between the entropy of mixing (which usually favors mixing) and the enthalpy of mixing (which can either be attractive and favor mixing or be 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 dissolve.