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CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 19: Phase equilibrium

References

1. Levine, *Physical Chemistry*, Sections 7.1–7.3

Key Concepts

- At equilibrium, the free energy is minimized. Therefore, the phase with the lowest chemical potential will be stable.
- For a single component system, $\mu = \frac{G}{n} = \overline{G}$.
- The key question is how μ depends on T and P. We can find this dependence by writing $d\mu$ ($d\overline{G}$ for a single component system) out in two different ways:

$$d\overline{G} = d\mu = -\overline{S}dT + \overline{V}dP$$

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_P dT + \left(\frac{\partial \mu}{\partial P}\right)_T dP$$

which gives us:

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -\overline{S} \quad \text{and} \quad \left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V}$$

- We can now see how μ varies with T and P by comparing the molar entropy and volume of different phases.
- The molar entropy of a gas phase is much greater than the molar entropy of a solid or liquid phase. This is due to the large number of different ways to arrange molecules in the gas phase (i.e. the vast number of configurations leads to high entropy. Using a similar argument, the molar entropy of the solid phase will be the smallest since there are a much more limited number of possible configurations, leading to a low entropy phase.
- So, in a plot of μ versus T, a curve for the gas phase will have the steepest negative slope, while a solid phase will have a much shallower negative slope.
- If we polt μ versus T at a fixed pressure, the most stable phase at a particular temperature is the phase with the lowest μ. If the chemical potential of two phases is equal, the two phase coexist at that temperature and pressure, i.e. they are in equilibrium.
- To determine the effect of pressure on the stability of phases, we need to examine the differences the molar volume ($\overline{V}$) of each phase. Gases typically have the largest molar volumes, so changing the pressure would have a large impact on the chemical potential of a gas phase, while it is a much smaller impact when dealing with a condensed phase, such as a liquid or solid.
- If we want to capture both the temperature and pressure dependence of the stability of phases we can plot P versus T and generate a phase diagram for the single component system. The phase diagram is a map that indicates which phase(s) is(are) most stable under particular T and P conditions.
- When we construct these single-component or unary phase diagrams, we will see regions when single phases are stable, lines where two phases are in equilibrium, and one single point (the triple point) where all three phases are in equilibrium.