Lecture 23  Chapt 14  Phase diagrams and Phase Equilibria

Announcements:

Exam 2 will cover chapters 10-14, homeworks 6-9
If you haven’t already be sure to send me an email TODAY about exam time.

Wed will be exam review – no quiz this week.

Outline:

Phase Transitions
Phase Diagrams
\[ \left( \frac{\partial G}{\partial T} \right)_p = -S \]
\[ \left( \frac{\partial G}{\partial p} \right)_T = V \]

Clapeyron Equation
\[ \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H}{T \Delta V} \]

Clausius – Clapeyron Equation
\[ \frac{1}{p} \frac{dp}{dT} = \frac{\Delta_{\text{trans}} H}{nRT^2} \]
\[ \ln(p) = -\frac{\Delta_{\text{trans}} H}{RT} + \text{constant} \]

Review

We used \( \Delta G^0 = -RT \ln K \) and \( \Delta \Gamma G^0 = \Delta \Gamma R H^0 - T \Delta \Gamma R S^0 \) to derive the van’t Hoff equation,
\[ \frac{d \ln K}{dT} = \left( \frac{\Delta \Gamma R H^0}{RT^2} \right) \]
or in a different form that is sometimes more convenient:
\[ \frac{d \ln K}{d(1/T)} = -\left( \frac{\Delta \Gamma R H^0}{R} \right) \]

which we integrated to give
\[ \ln K_2 = -\frac{\Delta \Gamma R H^0}{R} \frac{1}{T_2} + \left( \ln K_1 + \frac{\Delta \Gamma R H^0}{RT_1} \right) \]

Thus, measuring K as a function of T gives us \( \Delta G^0, \Delta \Gamma R H^0, \) and \( \Delta \Gamma R S^0 \)
Getting back to partition functions we used the example of H$_2$ + I$_2$ $\rightarrow$ 2 HI

$$K_c(T) = \left( \frac{q_{HI}}{V} \right)^2 = \frac{q_{HI}}{q_{H_2}q_{I_2}}$$

This gave us that long expression (similar to example 13.2 in Dill)

$$K_c(T) = \left( \frac{m_{HI}^2}{m_{H_2}m_{I_2}} \right)^{3/2} \left( \frac{4\Theta_{rot}^{H_2}\Theta_{rot}^{I_2}}{(\Theta_{rot}^{HI})^2} \right) (1 - e^{-\Theta_{rot}^{H_2}/T}) (1 - e^{-\Theta_{rot}^{I_2}/T}) e^{\frac{2D_{H_2}^2 - D_{HI}^2 - D_{I_2}^2}{RT}}$$

translational    rotational    vibrational    electronic

$T$ dependence still in Vib term, but also now in Electronic term

Okay then, let’s move into chapter 14, where we get into phase equilibria. I will not be describing his liquids lattice model today, but we will be using it in the future. So, please please please read through it carefully. It is a little long, but he explains things thoroughly I think.

**Phase Diagrams**

Phase Diagrams Summarize Solid-Liquid-Gas Behavior of a Substance

**Let’s start by defining a phase:** form of matter that is uniform throughout in chemical composition and physical state.

**Phase transition:** the spontaneous conversion of one phase to another that occurs at a well-defined temperature – the transition temperature

said another way, the **transition temperature** is the temperature at which the Gibbs free energies for both phases are? equal (remember that the system is seeking the minimum Gibbs free energy).

We can explain transition temperatures by understanding how the Gibbs energy changes with temperature:
Recall that $G$ is a function of $p$ and $T$, so then the total derivative is?

$$dG = \left( \frac{\partial G}{\partial p} \right)_T dp + \left( \frac{\partial G}{\partial T} \right)_p dT \quad \text{ (from definition of total derivative for } dG \text{)}$$

But, we also know from our fundamental equation for $G$?:

$$dG = Vdp - SdT$$

As we have done three times before, you guys can quickly fill in?
\( \left( \frac{\partial G}{\partial p} \right)_T = V \) and \( \left( \frac{\partial G}{\partial T} \right)_p = -S \) (equating coefficients in expressions for \( \text{d}G \))

Therefore, if we plot \( G \) vs. \( T \), what is the slope? negative of the (molar) entropy

Show diagram. How do you expect the entropies of the phases to vary? \( S_g > S_l > S_s \). Gases have the highest entropy and therefore the steepest dependence of \( G \) on temperature (then liquids and then solids). Where are the transition temperatures? the intersections of the \( G \) vs. \( T \) lines for each phase.

Note that the above \( G \) vs. \( T \) plot gives us two points on a \( p-V \) phase diagram.

If we repeat for many pressures, then we can build up a full phase diagram – a \( P \) vs. \( T \) plot showing regions of thermodynamic stability. We have a generic one below:

Notice the following characteristics of phase diagrams:

**Phase boundaries or phase coexistence curves**: shows the pressure, temperature pairs where two phases coexist in equilibrium. These boundaries are important as they indicate such important quantities as the freezing and boiling temperatures as a function of pressure.
**Vapor pressure:** the pressure of a vapor in equilibrium with its condensed phase at a specified temperature. For example, the vapor pressure for water at 25 C is about 25 Torr, while the vapor pressure for mercury at 25 C is ~ 0.01 Torr. The value of the vapor pressure is directly related to the intermolecular forces that govern the properties of the liquid (mercury has a greater attraction for itself than does water).

**Normal boiling temperature:** this is a special pressure, temperature point on the liquid-gas phase boundary because it is defined for a pressure of 1 atm. In a microscopic sense, all of the molecules now have sufficient energy to push the atmosphere out of the way and escape as a gas. Note that for equilibrium conditions, the boiling and condensation temperatures are the same.

**Critical point:** the temperature at which there is no longer any difference between the liquid and gas phases. As the temperature is increased in a closed system, more and more of the liquid is vaporized, leading to an increased density of the gas. **Where does this lead?** Eventually, a high enough temperature is reached so that $\rho_{\text{liquid}} = \rho_{\text{gas}}$. Another way to put this is that $\Delta H_{\text{vap}}$ decreases as $T$ increases until, at the critical point, $\Delta H_{\text{vap}}$ equals zero.

Thus, the two phases are indistinguishable. Of course, there is a corresponding **critical pressure** at the **critical temperature**. For water, the critical temperature is 647 K and the corresponding critical pressure is 218 atm!

**Normal melting temperature:** this is another special pressure, temperature point on the solid-liquid phase boundary. It is also defined for a pressure of 1 atm. Note that for equilibrium conditions, the melting and freezing temperatures are the same.

**Triple point:** this is a very special pressure, temperature point. It lies at the intersection of the gas-liquid and liquid-solid phase boundaries. At this point only, all three phases can coexist. For water, the triple point is 273 K and 4.58 Torr.

**Dependence on phase stability on the conditions**

It is generally true that at low temperatures that the most stable phase is the solid. However as we saw earlier, because the rate of change of the free energy with temperature is different for each phase, eventually the liquid and gas phases become the most thermodynamically stable as the temperature is raised. **How does $G$ vary with $T$?**

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

This shift in stability comes about because of the difference in the way the free energy of each phase depends on pressure. Let’s look more closely at this pressure dependence. **Recall how $G$ varies with $p$?**

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$
Thus, the slope of a $G$ vs. $p$ plot is the volume (usually molar $V$ and molar $G$). For most things how does molar $V$ depend on phase? $V_g > V_l > V_s$

Note that for water $V_s > V_l$ so things are a little different

Let’s look at phase transitions a little more quantitatively.

**Equilibrium:** $\Delta G$ must be 0, so between two phases, $\alpha$ and $\beta$: $\mu_\alpha(p,T) = \mu_\beta(p,T)$
Therefore, there is no thermodynamic driving force for change

We can use this equality to get an equation for the phase boundary.

If $p$ and $T$ are changed infinitesimally in a way that the two phases $\alpha$ and $\beta$ remain in equilibrium. Then

\[
\mu_\alpha = \mu_\beta \quad \text{before the change}
\]
\[
\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta \quad \text{after the change}
\]
and therefore

\[
d\mu_\alpha = d\mu_\beta \quad \text{(or equivalently for two phases of a pure substance)}
\]

\[
dG_{\alpha,m} = dG_{\beta,m}
\]

plug in (fundamental equation?) $dG_m = -S_mdT + V_mdp$ for each phase:

\[
-S_{\alpha,m}dT + V_{\alpha,m}dp = -S_{\beta,m}dT + V_{\beta,m}dp \quad \text{and this rearranges}
\]
\[
(V_{\beta,m} - V_{\alpha,m})dp = (S_{\beta,m} - S_{\alpha,m})dT
\]

For measurable changes, this expression becomes the **Clapeyron Equation**:

\[
\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}
\]

Notice that this is a total derivative and applies for any phase change for any pure substance.

Let’s see a quick example:
How does the vapor pressure for water change as its temperature is changed?

$H_2O$ at 25 °C has a vapor pressure of 24 Torr (β is gas, α is liquid)

\[
\Delta S_m = \Delta_{\text{trans}}S_m = S_m(\beta) - S_m(\alpha) = 188.8 \text{ J K}^{-1} \text{ mol}^{-1} - 69.9 \text{ J K}^{-1} \text{ mol}^{-1} = 118.9 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
\Delta V_m = \Delta_{\text{trans}}V_m = V_m(\beta) - V_m(\alpha) \sim V_m(\beta) = RT/p = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} / 24 \text{ Torr} = 103 \text{ J mol}^{-1} \text{ torr}^{-1}
\]
\[
\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{118.9 \text{JK}^{-1}\text{mol}^{-1}}{103 \text{Jmol}^{-1}\text{Torr}} = 1.15 \text{TorrK}^{-1}
\]

So at 10 °C, the vapor pressure is 24 Torr + 1.15 Torr K\(^{-1}\) x (-15 K) = 6.75 Torr

**Molecular explanation for why \(dp/dT\) is always positive?**: higher T means more energy available for molecules to escape attractive forces in liquid

**What is vapor pressure at 1 °C?** 25 torr + 1.15 torr/K (-24 K) = -3.6 torr.

**What is wrong?** You can’t use this expression very far from the reference temperature (298 K in this case) because the \(\Delta S/\Delta V\) ratio changes with temp.

For two phases at equilibrium we can change the Clapeyron eq by noting:

\[
G_\alpha = G_\beta
\]

\[
H_\alpha - TS_\alpha = H_\beta - TS_\beta
\]

\[
T(S_\beta - S_\alpha) = H_\beta - H_\alpha
\]

\[
T\Delta_{\text{trans}} S = \Delta_{\text{trans}} H
\]

\[
\Delta_{\text{trans}} S = \Delta_{\text{trans}} H / T \quad (This should look familiar… when \(\Delta_{\text{trans}} H = q\))
\]

We then can rewrite the Clapeyron equation:

\[
\frac{dp}{dT} = \frac{\Delta_{\text{trans}} H}{T\Delta_{\text{trans}} V}
\]

If we make two assumptions:
1) \(\Delta_{\text{trans}} V = V_{\text{gas}} - V_{\text{liquid}} \approx V_{\text{gas}}\) (volume of liquid or solid is negligible)
2) \(V_{\text{gas}} = nRT/p\) (ideal gas)

\[
\frac{dp}{dT} = \frac{p\Delta_{\text{trans}} H}{nRT^2} \quad \text{we know how to solve this. Rearranging to get common variables on the same side of the equation}
\]

\[
\frac{dp}{p} = \frac{\Delta_{\text{trans}} H_m}{R} \times \frac{dT}{T^2}
\]

This is one form of the Clausius-Clapeyron eq.

If we integrate both sides indefinitely

\[
\int \frac{dp}{p} = \frac{\Delta_{\text{trans}} H_m}{R} \times \int \frac{dT}{T^2}
\]
\[ \ln p = \frac{\Delta_{\text{trans}} H_m}{R} \left( \frac{-1}{T} \right) + \text{constant} \]

Second form of the Clausius-Clapeyron eq.

Thus, this tells us that a plot of \( \ln p \) vs \( 1/T \) is linear with slope \( = -\Delta_{\text{trans}} H_m/R \)

**what do we assume here?** That \( \Delta_{\text{trans}} H_m \) is constant

If instead, we do the integral definitely (from \( p_1, T_1 \) to \( p_2, T_2 \)):

\[
\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta_{\text{trans}} H_m}{R} \times \int_{T_1}^{T_2} \frac{dT}{T^2}
\]

\[
\ln \left( \frac{p_2}{p_1} \right) = -\frac{\Delta_{\text{trans}} H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Yet a third form of the Clausius-Clapeyron eq.