

8.2: Entropy is the Reason Phase Changes Occur

In Sec. 5.3.3, we showed you that, at constant pressure, Gibbs energy always decreases with temperature. We will derive that again here, starting with the change in Gibbs energy per mole which is the chemical potential:

$$\partial G_m = \partial \mu = -S_m \partial T + V_m \partial P$$

Taking the derivative with respect to temperature at constant pressure results in:

$$\left(\frac{\partial \mu}{\partial T} \right)_P = -S_m \quad (8.2.1)$$

The relationship above reveals that $\left(\frac{\partial \mu}{\partial T} \right)_P$ is always negative because entropy per mole is always positive. Thus, the chemical potential of a particular phase of a substance decreases with temperature in proportion to that phase's entropy. Consequently, heating causes the chemical potential of a liquid decreases faster than a solid. Likewise, the chemical potential of a gas decreases faster than the liquid. This is important because, at very low temperatures, the solid phase has the lowest chemical potential. If you doubt this, we remind you that all chemicals are solids at very low temperatures. As the temperature increases, the liquid's chemical potential eventually becomes lower than the solid's, and thus we observe a phase transition (melting) at that temperature. As the temperature increases further, eventually the gas phase's chemical potential becomes lower than the liquid's which is why we observe boiling. This is all represented in Figure 8.3 (left-most figure); note that chemical potential is shown decreasing linearly with temperature but this is just an approximate representation.

As for the effect of pressure at constant temperature, we use the change in Gibb's energy: $\partial G_m = \partial \mu = -S_m \partial T + V_m \partial P$ to show that:

$$\left(\frac{\partial \mu}{\partial P} \right)_T = V_m \quad (8.2.2)$$

Equation 8.2.2 is always positive because volume per mole can only be positive. And usually a solid is denser than the liquid, both of which are always denser than the gas. When we combine these effects in Figure 8.3, we can start to map out the pressure and temperature points of coexistence between two phases on a P vs. T phase diagram.

We hope the discussion thus far has aided your understanding of phase transitions; however, we can't actually use equations 8.2 or 8.3 to define the boundaries in a phase diagram such as that shown in Figure 8.1. This can be accomplished by numerically calculating the chemical potentials of all phases over the full range of pressures and temperatures in the graph and determining where they are equal. And since we never know what the absolute energies are, we must always use relative formation energies ($\Delta_f G_m$) when performing thermochemical calculations. The $\Delta_f G_m$'s are chemical potentials, and we must adjust the standard state values from a data table for other pressures and temperatures. To this end we use the many tools discussed in Chapter 6 that provided for us the following:

$$\mu(P, T) = \Delta_f G_m(P, T) = \Delta_f H_m(P, T) - T \times \Delta_f S_m(P, T)$$

where:

$$\Delta_f H_m(P, T) = \Delta_f H_m^\circ + \int_{298.15K}^T C_{P,m}(T) \partial T$$

and:

$$\Delta_f S_m(P, T) = \Delta_f S_m^\circ + \int_{298.15K}^T \frac{C_P(T)}{T} \partial T - \int_{1bar}^P \frac{V_m}{T} \partial P$$

The phase boundaries occur where $\mu^{solid} = \mu^{liquid}$, $\mu^{liquid} = \mu^{gas}$ and $\mu^{solid} = \mu^{gas}$. Furthermore, the phase present is the one with the lowest chemical potential for any given P and T in the phase diagram. This approach is demonstrated for water in Figure 8.4, where we have made 2-dimensional plots of the chemical potential surfaces of each water phase including projections where the energies cross onto the P vs. T planes. These clearly mark the boundaries between phases with considerable accuracy. As shown in Figure 8.4 A, the solid – liquid chemical potentials are equal at 0 °C at 1 bar pressure, and the equilibrium is left-sloping with increasing pressure due to the lower density of ice compared to the liquid. Figure 8.4 B shows that the liquid water – steam

boundary begins at 373 K at 1 bar pressure and has a boiling temperature that rises with pressure. Unfortunately, calculations of this nature are extremely labor intensive, and require accurate knowledge of the temperature dependence of the heat capacities of all the phases. One can get lost in all the equations and calculations, making it difficult to discern if there are simple reasons for why a phase diagram appears the way it does. This prompts us to use a more simple approach.

8.2.1 The Clausius-Clapeyron Relation

In our discussion above we calculated where two phases α and β are in equilibrium by finding the pressure and temperature points where their chemical potentials are equal: $\mu^\alpha = \mu^\beta$. Another rule of thermodynamics requires that the derivatives of the chemical potentials are also equal at equilibrium: $\partial\mu^\alpha = \partial\mu^\beta$. In a constant pressure and temperature world this means:

$$-S_m^\alpha \partial T + V_m^\alpha \partial P = -S_m^\beta \partial T + V_m^\beta \partial P$$

Collecting like terms:

$$V_m^\alpha \partial P - V_m^\beta \partial P = S_m^\alpha \partial T - S_m^\beta \partial T$$

Next we factor the change in pressure and temperature and divide the results:

$$\begin{aligned} (V_m^\alpha - V_m^\beta) \partial P &= (S_m^\alpha - S_m^\beta) \partial T \\ \frac{\partial P}{\partial T} &= \frac{(S_m^\alpha - S_m^\beta)}{(V_m^\alpha - V_m^\beta)} = \frac{\Delta S_m}{\Delta V_m} \end{aligned} \quad (8.2.3)$$

Since we don't like to work with changes in entropy due to the complexity of entropy in general, we can make a clever substitution. Since enthalpy represents a heat exchange with the outside ($\partial H = \partial q$), and given the definition of a change in entropy ($\partial S = \frac{\partial q}{T}$), we can substitute $\frac{\Delta H_m}{T}$ for ΔS_m to show:

$$\frac{\partial P}{\partial T} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \cdot \Delta V_m} \quad (8.2.4)$$

This is the Clausius-Clapeyron equation that can help predict where different phases co-exist on a P vs. T phase diagram. Below, we use equation 8.5 to directly map out the lines between solid-liquid, solid-gas, and liquid-gas boundaries in a phase diagram.

8.2.1.1. Solid-Liquid

We will begin by analyzing the relationship between the solid and liquid phases, which allows us to determine melting temperature of a substance at different pressures. Since we are discussing the process of melting ΔH_m in Equation 8.2.4 is specifically the enthalpy of fusion:

$$\Delta H_m = \Delta_{fus} H_m = \Delta_f H_{m,liquid} - \Delta_f H_{m,solid}$$

Likewise:

$$\Delta V_m = \Delta_{fus} V_m = V_{m,liquid} - V_{m,solid}$$

To derive the P vs. T lines of equilibrium, we take the Clausius-Clapeyron relation (Equation 8.2.4) and “juggle” the partials as so:

$$\partial P = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \frac{\partial T}{T}$$

Note that we can make the approximation that neither the enthalpy nor the density are temperature dependent, which is not correct. However, inclusion of the temperature dependence of these properties creates a nightmarish calculus scenario, so we will approximate that there is no temperature dependence. As a result, the integration of the above is simple:

$$\int_{P_1}^{P_2} \partial P = P_2 - P_1 = \int_{T_1}^{T_2} \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \frac{\partial T}{T} = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \int_{T_1}^{T_2} \frac{\partial T}{T} = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \ln\left(\frac{T_2}{T_1}\right)$$

Here we see that a starting point on the phase diagram, (P_1, T_1) must be known before we can determine the pressure and temperature of the solid-liquid line of coexistence at a different condition (P_2, T_2) . Clearly the triple point is a good choice, and

thus $P_1 = P_t$ and $T_1 = T_t$. We will simply call P_2 and T_2 as P and T in our simplification of the above equation:

$$P = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \ln\left(\frac{T}{T_t}\right) + P_t \quad (8.2.5)$$

Equation 8.2.5 gives us a formula for a line that delineates between the liquid and solid phases in a phase diagram.

Does Equation 8.2.5 conform with the experimental data? First note that natural logarithms are fairly linear, and as a result Equation 8.2.5 is like a line with a slope of $\frac{\Delta_{fus} H_m}{\Delta_{fus} V_m}$. Concerning the slope, the numerator $\Delta_{fus} H_m$ (the input of energy required to melt the solid) is usually a rather large, positive value. At the same time, the difference in the densities of solids and liquids is very small and as a result the slope of the solid-liquid line $\frac{\Delta_{fus} H_m}{\Delta_{fus} V_m}$ is huge. Concerning the right or leftwards slant of Figures 8.1 and 8.2, respectively, $\Delta H_{m,fus}$ doesn't play a role since it is always positive. In contrast, the volume per mole in the denominator is generally greater for a liquid than a solid. This makes $\Delta V_{m,fus}$ likewise positive, which is why the P vs. T line between the solid and liquid phases is to the right in Figure 8.1. The notable exception is water, which has a denser liquid than the solid (remember ice cubes float) and thus $\Delta V_{m,fus}$ is negative. As a result, water's solid-liquid line is to the left as seen in Figure 8.2.

8.2.1.2. Solid-Vapor

A solid can evaporate directly into the vapor phase, which is the process of sublimation. Here we use the Clausius-Clapeyron relation as previously to define the solid-vapor boundary:

$$\partial P = \frac{\Delta_{sub} H_m}{T \cdot \Delta_{sub} V_m} \partial T$$

where $H_{m,sub} = H_{m,vap} - H_{m,solid}$ and $\Delta V_{m,sub} = V_{m,vap} - V_{m,solid}$. We will assume that enthalpy is independent of temperature, but we cannot do the same for $\Delta V_{m,sub}$ as a gas's volume is highly dependent on the temperature. In fact, we can deal with this temperature dependence by making a minimal approximation whereby the difference in molar volume (gas – solid) can be assumed to just be the molar volume of the gas: $\Delta V_{m,sub} \approx V_{m,vap}$ and thus $\partial P = \frac{\Delta_{sub} H_m}{T \cdot V_{m,vap}} \partial T$

This works because the volume of a gas is always significantly greater than that of the solid. We can make another substitution into the above by inserting the perfect gas law $V_m = \frac{RT}{P}$ to substitute $V_{m,vap}$:

$$\partial P = \frac{\Delta_{sub} H_m}{T \left(\frac{RT}{P}\right)} \partial T = \frac{P \cdot \Delta_{sub} H_m}{RT^2} \partial T$$

The pressure factor must be moved from the left side before integration, and as before we will assume that the initial pressure and temperature are those of the triple point:

$$\int_{P_t}^P \frac{\partial P}{P} = \ln\left(\frac{P}{P_t}\right) = \int_{T_t}^T \frac{\Delta_{sub} H_m}{RT^2} \partial T = \frac{-\Delta_{sub} H_m}{R} \left(\frac{1}{T} - \frac{1}{T_t}\right)$$

Some rearrangement makes this easier to look at:

$$\ln(P) = \frac{-\Delta_{sub} H_m}{RT} + C \quad (8.2.6)$$

where the constant is $C = \frac{\Delta_{sub} H_m}{RT_t} + \ln(P_t)$. Equation 8.2.6 looks like an exponential rise in a graph of P vs. T , which is exactly how the solid-vapor line appears in the phase diagram examples shown in Figure 8.1 and 8.2.

8.2.1.3. Liquid-Vapor

The development of the liquid-vapor line is identical to the above, except the process is vaporization rather than sublimation:

$$\ln\left(\frac{P}{P_t}\right) = \frac{-\Delta_{vap} H_m}{R} \left(\frac{1}{T} - \frac{1}{T_t}\right)$$

which as before can be rearranged into: $\ln(P) = \frac{-\Delta_{vap} H_m}{RT} + C$ where $C = \frac{\Delta_{vap} H_m}{RT_t} + \ln(P_t)$. As in the previous example, the liquid-vapor line appears as an exponential rise starting from the triple point just as seen in Figures 8.1 and 8.2.

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