

CHAPTER OVERVIEW

8: Phase Changes

Phase diagrams show under what conditions that one or more chemical substances exist in the solid, liquid or vapor state. There are multiple ways to express this information, although usually such diagrams take the form of 2D graphs where different phases appear as interior regions and thermodynamic variables are along the axes. Shown in Figure 8.1 is a common and rather generic example of a pressure vs. temperature phase diagram for a single chemical. We will start to develop our understanding of phase equilibria as a function of pressure and temperature because these are intensive variables that define equilibrium. We also assume that phase diagrams always represent systems at equilibrium, although you should know that it is possible to have chemicals exist in a non-equilibrium phases albeit for a short period of time. For example, the present record on the coldest temperature of liquid water is $-45\text{ }^{\circ}\text{C}$!

The phase diagram in Figure 8.1 shows the usual players: solid, liquid and gas, as well as an additional curious thing called the “supercritical”. This is a phase that is like a combination of liquid and gas. There are broad areas that represent each phase, lines that delineate between them, and a single triple point between all three phases. There can be other triple points, and these may occur in the solid phase region area. This is possible because there can be more than one solid phase as defined by different crystallographic structures. For example, water is known to have 9 different solid phases. There is of course only one gas and liquid phase with one exception, that being the case of helium that can have two liquid phases due to the formation of a “Bose-Einstein condensate”, which is an esoteric quantum mechanical phenomenon. As shown in Figure 8.1, the liquid-solid line slopes to the right, which means that if you increase the pressure of a solid then it will melt at a higher temperature. This is because most things have a denser solid phase compared to the liquid, so the application of high pressure inhibits the expansion of the solid into the liquid phase. Water is a notable exception due to the fact that it has a less dense solid phase. You know this already because you are well aware that ice floats in water. As a result, the phase diagram of Figure 8.1 does not apply to water, which is shown in Figure 8.2.

As discussed in the previous chapter on colligative properties, a phase diagram is more information rich than it initially appears. For example, in Figure 8.1 we plot a point at 1 bar pressure at $25\text{ }^{\circ}\text{C}$ where we see that this chemical is a liquid. A line runs parallel along the x-axis (temperature) to the left and right of that point and is constant along the y-axis (1 bar pressure). The line crosses the solid-liquid boundaries, and where this crossing occurs can be used to read off the melting point (T_{fus}) and boiling point (T_{vap}). Looking back at the point at 1 bar, $25\text{ }^{\circ}\text{C}$ in Figure 8.1 we see a line that points straight down and intersects the liquid-gas boundary. This point provides the pure partial vapor pressure of this substance in equilibrium with the liquid as measured at 1 bar pressure. We used this value in our Raoult’s Law calculations in the previous chapter.

The phase diagram of water in Figure 8.2 shows a solid-liquid line that slopes to the left due to the unusual lower density of the solid state compared to the liquid. This phase diagram also demonstrates why you have to cook Raman noodles longer at higher altitudes; if you go up in altitude and experience a lower atmospheric pressure, then the boiling temperature decreases. For example, water boils at $94.6\text{ }^{\circ}\text{C}$ in Albuquerque, New Mexico.

[8.1: The Gibbs Phase Rule](#)

[8.2: Entropy is the Reason Phase Changes Occur](#)

[8.3: Other Examples of Phase Changes](#)

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