

## 8.3: Other Examples of Phase Changes

Talking about ice melting is about as fun as watching paint dry, which is itself a phase change. However, there are many interesting things about phase changes once one realizes how many different types of phase changes exist. For example, surfactants such as phospholipids can lie flat on the surface of water, until they are pressurized upon which they stand up. This is important for living cells that are coated with phospholipids. Solid state materials have different magnetic phases; another example of a phase change is cooling a ceramic to the electrically superconducting state. We know that these are legitimate phase changes by noting discontinuities with thermodynamic variables such as heat capacity upon heating, as energy is inputted with no observable change in temperature. In the next few sections we review some other examples of interesting phase diagrams for multicomponent systems, which explain why solder (i.e. wire glue) melts at a relatively low temperature.

### Multicomponent Phase Diagrams, pressure vs. composition

Mapping the phases of solutions is important for understanding many processes such as separation via distillation, an example we will study in this section. Distillation requires us to understand the liquid-vapor phase diagram, and we will stipulate that the vapor originates from a liquid that is an ideal solution. The phase diagram itself reveals the liquid and vapor phases as a function of pressure (y axis) and composition (x axis, in the form of the mole fraction). To create this phase diagram we will make a plot of total pressure vs. liquid phase composition using Raoult's Law, Equation 7.2 from the previous chapter. If you don't recall, Raoult's Law relates a component's vapor partial pressure to its mole fraction in the liquid state; for example:  $P_B = \chi_B P_B^*$  where  $P_B^*$  is the pure partial pressure for the B component. We must use this information to determine the net pressure P, which we can do simply by adding the individual partial pressures:

$$P = P_A + P_B = \chi_A P_A^* + \chi_B P_B^*$$

Since  $\chi_A = 1 - \chi_B$  and:

$$P = P_A + P_B = (1 - \chi_B) P_A^* + \chi_B P_B^*$$

then:

$$P = P_A^* + \chi_B (P_B^* - P_A^*)$$

This relationship is plotted in Figure 8.5, which is clearly a simple line. Now, we must determine the total pressure as a function of the composition of the vapor phase using the mole fractions of the vapors  $v_A$  and  $v_B$  (note we use  $\chi$ 's to refer to the liquid, and  $v$ 's for the vapors). It may seem odd that we are introducing a new variable for the vapor phase mole fractions; afterall doesn't Raoult's Law mean  $\chi_A = v_A$  and  $\chi_B = v_B$ ? No, it doesn't; this is because Raoult's Law relates a component's liquid mole fraction to its vapor partial pressure, not the contribution to the total pressure. For example, imagine that the pure partial pressure of a liquid is 0 Pa. In this case, the mole fraction of the liquid ( $\chi$ ) doesn't have any effect on the total pressure and is thus unrelated to the vapor's  $v$ ! To demonstrate using equations, first note that the mole fraction of a vapor is related to the pressure and pure partial pressure via Dalton's Law:  $P_B = v_B P$  which rearranges to:

$$v_B = \frac{P_B}{P} = \frac{P_B}{P_A^* + \chi_B (P_B^* - P_A^*)} = \frac{\chi_B P_B^*}{P_A^* + \chi_B (P_B^* - P_A^*)}$$

where we used the fact that  $P = P_A^* + \chi_B (P_B^* - P_A^*)$  and  $P_B = \chi_B P_B^*$ . A similar derivation for component "A" yields:

$$v_A = \frac{\chi_A P_A^*}{P_B^* + \chi_A (P_A^* - P_B^*)}$$

From here we see that, if  $P_B^* = P_A^*$ , then  $v_B = \chi_B \frac{P_B^*}{P_A^*}$  and  $v_A = \chi_A \frac{P_A^*}{P_B^*}$ . Consequently, it is immediately obvious that the mole fractions in the liquid and vapor phases are not exactly equal; furthermore, these relationships are even more complex if  $P_B^* \neq P_A^*$ .

To complete a pressure vs. composition phase diagram, we have to determine the total pressure as a function of the vapor mole fractions  $v_A$  and  $v_B$ . First, we solve the liquid mole fractions as functions of the vapor mole fractions using the relationships above, which are:

$$\chi_A = \frac{v_A P_B^*}{P_A^* - v_A (P_A^* - P_B^*)} = \frac{v_A P_B^*}{P_A^* - (1 - v_B) (P_A^* - P_B^*)} = \frac{v_A P_B^*}{P_B^* - v_B (P_B^* - P_A^*)}$$

where we used  $v_A = (1 - v_B)$ , and:

$$\chi_B = \frac{v_B P_A^*}{P_B^* - v_B (P_B^* - P_A^*)}$$

When we plug these into the expression for total pressure  $P = P_A + P_B = \chi_A P_A^* + \chi_B P_B^*$  we find:

$$P = \frac{v_A P_B^* P_A^*}{P_B^* - v_B (P_B^* - P_A^*)} + \frac{v_B P_B^* P_A^*}{P_B^* - v_B (P_B^* - P_A^*)} = \frac{(v_A + v_B) P_A^* P_B^*}{P_B^* - v_B (P_B^* - P_A^*)} = \frac{P_A^* P_B^*}{P_B^* - v_B (P_B^* - P_A^*)}$$

This behavior is illustrated in Figure 8.6 for the case of  $P_B^* \gg P_A^*$ .

With the total pressure expressed as a function of the liquid and vapor mole fractions (Figures 8.5 and 8.6), we can now generate the multicomponent liquid-vapor phase diagram by the simple superimposition of these two graphs as shown in Figure 8.7. This multicomponent phase diagram has a single y axis (total pressure) yet two simultaneous x axes, that being  $\chi_B$  and  $v_B$ . Instead of a line between the liquid and vapor (gas) phase found in a single component phase diagram (Figures 8.1 and 8.2), we see instead a liquid + vapor region. The reason that the equilibrium between these phases has gone from a line in a single component phase diagram to an area in the multicomponent one is because there are two degrees of freedom as verified by the Gibbs Phase rule  $f = 2 + c - p = 2 + 2 - 2 = 2$ . Recall that there is only one degree of freedom in a single component diagram.

To understand the data presented in Figure 8.7, we will study the same diagram over a closer range with points defined within each region as shown in Figure 8.8. The first point,  $x_1$ , is at high pressure. Here, the system is in a single liquid state with a composition that can be read off the x-axis as  $\chi_B = 0.6$  (obviously this makes  $\chi_A = 0.4$ ). This is the “boring” part of the diagram; however, if we decrease the total pressure we arrive at point  $x_2$  which is more interesting as two phases are present. Each phase, liquid and vapor, has its own compositions that are determined by drawing tie lines to the left and right of the  $x_2$  point to the liquid line (blue) and vapor line (red), respectively, as seen in Figure 8.8. This shows that the vapor is composed of mostly “B” ( $v_B = 0.7$ ,  $v_A = 0.3$ ) and likewise the liquid is mostly “A” ( $\chi_B = 0.33$ ,  $\chi_A = 0.67$ ). The reason that the compositions of the vapor and liquid differ within the liquid + vapor region of Figure 8.8 is because component “B” vaporizes more readily than “A” due to the former’s higher vapor pressure. And since “B” has been removed from the liquid, the remainder is richer in component “A”. If we lower the pressure further to arrive at  $x_3$  the pressure is low enough such that both liquids have fully vaporized.

### 8.3.1.1. The Lever Rule

The multicomponent phase diagram in Figure 8.8 is more information rich than it appears and imparts an interesting lesson on degrees of freedom. Imagine that the system is in a state described by point  $x_2$ . Next, you add a small additional amount of liquid “B” and allow the system to re-equilibrate; what do you think is different? Probably you believe that the percentage of “B” in the liquid’s composition has increased. However, this is not the case, mostly because addition or subtraction of a small quantity of a component isn’t an available degree of freedom. This is because at point  $x_2$  there are  $f = 2 + c - p = 2 + 2 - 2 = 2$  degrees of freedom which are the temperature and pressure. As a result, the addition of a small quantity of “B” cannot change the composition of either the liquid or vapor in the system. In fact, given that temperature is constant the only way to increase the “B” in the liquid phase’s composition is to raise point  $x_2$ , i.e. increase the pressure. To summarize, if the pressure and temperature are unaltered after adding or removing a small quantity of either “B” or “A”, then the compositions of the liquid and vapor phases are unaltered.

So in this example where did the extra “B” go? The answer is that the excess “B” must be accounted for by an increase in the phase rich in “B”, which is the vapor. Thus, when you poured in more liquid “B” into the system, it reached equilibrium by creating more vapor. This allows the system to absorb the mass yet leave the compositions of both the liquid and vapor phases unaltered. The phase diagram is even capable of quantifying the relative amounts of liquid and vapor using the following method. At point  $x_2$ , we already discussed how tie lines to the left and right allow us to determine the phases’ compositions. If we call the length of the tie lines  $I_{liq}$  and  $I_{vap}$ , then the relative masses of liquid and vapor are related via:

$$\frac{I_{liq}}{I_{vap}} = \frac{m_{vap}}{m_{liq}}$$

where  $m_{liq}$  and  $m_{vap}$  is the mass of “A” and “B” in the liquid and vapor phases, respectively. Consequently, one can see that if more “B” is poured into the system at state  $x_2$ , then point  $x_2$  would shift to the right resulting in a larger  $I_{liq}$ , smaller  $I_{vap}$ , and thus a greater amount of vapor. As in our initial discussion on single component phase diagrams, it appears that there is much greater information “hidden” in these diagrams than initially appears!

### 8.3.1.2. Temperature vs. composition, distillation and azeotropes. The case of vapor-liquid phase diagrams

It is possible to create multicomponent phase diagrams as a function of temperature at a constant pressure. In fact, these are more practical because they help us understand such processes as distillation. Shown in Figure 8.9 is a temperature vs. vapor + liquid mole fraction diagram for a mixture of water and ethylene glycol at a constant pressure of 100 kPa ( $\sim 1/3$  an atm). The graph makes it clear that there is only a vapor at a high temperature while only one liquid phase exists at a low temperature, as is sensible. Also, the pure liquid boiling points can be read off the right and left sides of the graph, and we sensibly see that water's boiling point is lower than 100 °C given the reduced pressure. Most importantly, the graph reveals the existence of a mixed phase state at intermediate temperatures.

To understand how to use the multicomponent phase diagram fully we examine Figure 8.9 starting at point  $x_1$ . Here, there is a single liquid phase composed of 50% / 50 % ethylene glycol and water. If we raise the temperature to point  $x_2$ , there remains a liquid with a composition of  $\sim 93\%$  ethylene glycol and a vapor that is  $\sim 30\%$  water. The vapor and liquid are of course the same temperature, and the reason that the vapor has more water is because  $H_2O$  has a lower boiling point than ethylene glycol. Now imagine that the vapor could be collected and cooled back into a liquid, and re-vaporized again. If we did so we would be at point  $x_3$ , then the vapor would nearly be pure water. If we repeat this cycle several more times, it seems that we could capture nearly pure water via the vapor phase while leaving behind a pure ethylene glycol liquid phase, given that all the water eventually vaporizes out. This process is distillation as guided by the large arrows in Figure 8.9.

Two phase diagrams of azeotropic liquid mixtures are shown in Figures 8.10. An azeotrope is made from a non-ideal liquid mixture, imparting a strikingly different phase behavior compared to the previous example. In Figure 8.10 A we see an example of a positive azeotrope, methanol and chloroform, that has a lower boiling point when mixed compared to either individual liquid. A negative azeotrope such as formic acid in water has a higher boiling point as a mixture as shown in Figure 8.10 B. As part of an exercise at the end of the chapter, you will demonstrate that these systems cannot be fully purified via distillation.

#### 8.3.1.4. Liquid-liquid phase diagrams

It may surprise you to know that not all liquids mix, and as a result there is such a thing as liquid + liquid multicomponent phase diagrams. Examples are shown in Figure 8.11. We will learn to use them by example; for instance, in the case of aniline and hexane shown in Figure 8.11A at point  $x_1$  we have a single liquid phase with a 50% / 50% composition of the two components. Next, upon cooling the solution to point  $x_2$  one observes a liquid-liquid phase separation. Using a tie line at that point reveals that one layer is rich in hexane ( $\sim 70\%$ ) and the other has more aniline. Surprisingly, it is possible to observe the opposite- liquids that are mixed at a low temperature that separate upon heating. An example included trimethylamine in water. One of the most unusual observations is for nicotine in water as shown in Figure 8.11 B, which has both properties. The components can mix at low and high temperature, but not in between!

#### 8.3.1.4. Liquid-solid and solid-state phase diagrams

Multicomponent phase diagrams may also incorporate the solid state. Shown in Figure 8.12A is the liquid + solid phase diagram of sodium and rubidium. At the high temperature point of  $x_1$  there is a single liquid phase composed of 40% Rb and 60% Na. A solid will precipitate once we cool the liquid to point  $x_2$ . Using the tie lines we can read off the diagram that the liquid is composed of 60% Rb and the solid floating in the liquid is made of pure sodium. Upon further cooling to point  $x_3$  we form a solid solution, which is a single mass containing segregated microdomains of sodium and rubidium. Generally one needs a microscope to discern this fact. There is one other interesting feature in this figure, which is the  $-4.5$  °C “eutectic point” composed of  $\sim 80$  % Rb 20 % Na. This represents the lowest temperature at which a liquid can be observed in the phase diagram and is useful for preparing liquid metals at room temperature. This is the principal by which solder works, whereby wires can be bonded to substrates using an alloy of 60% tin / 40% lead that melts at 190 °C. This is a relatively low temperature that can be safely applied to electronic circuit boards using a soldering iron.

Phase diagrams can become extremely complex as shown in the solid + solid + liquid example in Figure 8.12B, which is a “reactive” phase diagram between sodium and potassium. The high temperature point  $x_1$  describes a fully liquid system. Solid particles form upon cooling to point  $x_2$  leaving the liquid with a greater percentage of potassium. The solids are not pure metallic sodium, rather  $Na_2K$  which is a distinct chemical compound. This is why this phase diagram is labeled as “reactive” as the intermediates found in these systems can have distinct properties. An extreme example can be found in the gallium and arsenic phase diagram, where the two metals combine to form GaAs which is a semiconductor. Concerning sodium and potassium, the compound  $Na_2K$  continues to exist even as the liquid component solidifies upon cooling from point  $x_2$  to  $x_3$  where we find a solid

~94% potassium alloy. This phase diagram also provides an example of “incongruent melting” for the solid compound  $\text{Na}_2\text{K}$ . If we have the pure compound at point  $x_4$  and heat it to the liquid + solid region at point  $x_5$ , you don’t get a liquid with the same stoichiometry. Rather it loses its distinct chemical identity as the liquid that forms is a combination of sodium + potassium with a solid that is mostly pure sodium.

**Conclusion.** In this chapter we have used chemical potential to define the boundaries between phases of state. This was difficult if we attempted to calculate the chemical potentials of all phases over a range of temperatures and pressures, which is why we used the Clausius-Clapeyron equation. This allowed us to define the various phase boundaries so long as we had some data as to the location of the triple point. Multicomponent phase diagrams are, in essence, multiple diagrams that overlap which allows for the determination of the compositions of the various phases as a function of either temperature or pressure. Such representations become complex if the components react to form distinct compounds.

## References

1. Goy, C.; Potenza, M. A. C.; Deder, S.; Tomut, M.; Guiller, E.; Kalinin, A.; Voss, K. O.; Schottelius, A.; Petridis, N.; Prosvetov, A.; Tejada, G.; Fernandez, J. M.; Trautmann, C.; Caupin, F.; Glasmacher, U.; Grisenti, R. E. Shrinking of Rapidly Evaporating Water Microdroplets Reveals Their Extreme Supercooling. *Physical Review Letters* 2018, 120. doi:10.1103/PhysRevLett.120.015501.
2. Kim, K. H.; Spah, A.; Pathak, H.; Perakis, F.; Mariedahl, D.; Amann-Winkel, K.; Sellberg, J. A.; Lee, J. H.; Kim, S.; Park, J.; Nam, K. H.; Katayama, T.; Nilsson, A. Maxima in the Thermodynamic Response and Correlation Functions of Deeply Supercooled Water. *Science* 2017, 358, 1589-+. doi:10.1126/science.aap8269.

---

This page titled [8.3: Other Examples of Phase Changes](#) is shared under a [CC BY-NC 4.0](#) license and was authored, remixed, and/or curated by [Preston Snee](#).