


1.4: Phase Transitions

Under certain temperature and pressure conditions real gas equations can predict very odd behavior. We will use CO₂ as an example because it has interesting properties that makes it useful for a large number of industrial applications. The phase diagram of CO₂ is shown in Figure 1.4, where a “critical point” is marked with a red “X”. This is where the distinction between the liquid and gas phases comes to an end. Furthermore, above the critical temperature it is impossible for the gas to be liquefied even if you pressurize the system considerably. This high pressure and temperature supercritical region should be considered a separate phase because it can have unique properties that are not observed for either the gas or liquid phases. For example, supercritical CO₂ is a very good solvent; in fact, it is used to extract the caffeine out of coffee beans.

The van der Waals equation predicts critical behavior. Shown in Figure 1.5 are van der Waals P vs. V_m isotherms, where each line represents the pressure at a single temperature (the top line is 70.9 °C and the bottom one is -8.9 °C). Do you see how the green line at 30.9 °C flattens out near 73 atm? Now look back at Figure 1.4- that’s the critical point! In fact, we can mathematically define the critical point because it’s clear that the line is flat, i.e. $\frac{\partial P}{\partial V_m} = 0 \text{ atm} \cdot \text{mol}/L$. In fact, it’s true that the double derivative is also flat: $\frac{\partial^2 P}{\partial V_m^2} = 0 \text{ atm}^2 \cdot \text{mol}^2/L^2$. Setting these two derivatives equal to 0 provides two equations that can be used to solve the two unknowns, which are the critical pressure $P_c = \frac{a}{27b^2}$ and per molar critical volume $V_{c,m} = 3b$. Several examples are provided in Table 1.0. When we plug P_c and $V_{c,m}$ into the van der Waals equation we determine that $T_c = \frac{8a}{27Rb}$.

Now let’s look at the P vs. V_m isotherms in Figure 1.5 further, because at temperatures below T_c there is some odd behavior circled with “?”s. Specifically, it appears that an increase in volume results in an *increase in pressure*- how could this possibly be true? Do you think if you were to pull on a piston that it would suddenly fly out toward at you? No, this would never happen. Thus, it appears that the van der Waals has some certain pressure, volume, and temperature points where it does not describe gases correctly. To understand what is happening, imagine that we have a container filled with CO₂ at a set of P, V_m and T in the circled region of Figure 1.5. If we peer through a window into this container we would make a startling observation - the CO₂ is a liquid! So, of course the real gas equation doesn’t make sense anymore because CO₂ isn’t a gas to begin with!

 Perhaps we can use this fact to determine at what pressures and temperatures that the gas liquifies and check that against the phase diagram? To do so we need to be able to define the positions in the P vs. V_m isotherms that the gas is expected to liquify. This is possible by the creation of a “Maxwell construction”, which is meant to blot out the offending increasing P vs. V_m behavior with a straight line. An example is shown in the inset of Figure 1.5, where the Maxwell construction is the thick green line that cuts through the weird part of the van der Waals isotherm at -8.9 °C. To understand, imagine that we have a container at -8.9 °C, the V_m is 0.073 L/mol, and the pressure is 40.6 atm (the furthest left-hand point of the Maxwell construction in Figure 1.5 inset). If we decrease the volume further the pressure increases dramatically. It turns out that the reason for this is that the CO₂ is a liquid. Of course it takes extremely high pressure to compress a liquid! Now let’s move right of this point by increasing the volume, and as we do so the Maxwell construction dictates that the pressure remains a constant 40.6 atm. This is happening because the liquid inside the container is turning into a gas, which maintains the pressure despite the increasing volume. This goes on until we reach V_m=0.36 L/mol, the furthest right-hand point of the Maxwell construction in Figure 1.5 inset. Here, the liquid has completely vaporized, and so if we keep increasing the volume then the pressure drops just like a normal gas.

For a given isotherm there is one line that defines the Maxwell construction. This corresponds to a single pressure because the construction is a straight line. The pressure of the Maxwell construction is unique for each isotherm shown in Figure 1.5 as it is defined such that the areas of the van der Waals isotherm above and below the line are equal. These are the grey shaded areas in the inset of Figure 1.5. We determined a set of temperatures and corresponding pressures and plotted them as the green circles in Figure 1.4. The critical point is dead on, and clearly the other data track the liquid / vapor line decently well. Nay Sayers may note how the points are not perfect; let me remind you that the van der Waals equation is for gases. Yet it predicts the formation of the liquid phase, and the predictions in Figure 1.4 are pretty good! And did your Nobel-winning real gas equation do better?

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