

## 7.1: Partial Vapor Pressure

You have to do very little to understand the thermodynamics of a pure liquid like a cup of water, or a solid substance such as a teaspoon of salt. There are data tables with all the relevant information ( $\Delta_f H_m^\circ$ ,  $\Delta_f G_m^\circ$ ,  $S_m^\circ$ , etc., see Table 6.1); you can simply look them up. You can also sit down and watch the cup of water, but probably there isn't much to see (and the teaspoon of salt is doing even less!). It's all, rather... boring.

Let's do something much more fun! Take the teaspoon of salt and add it to the water, and start answering some questions- does it dissolve? Does the water get warm, cold, or stay the same? Does the energy of the water and salt change? Now we are getting somewhere, and to begin we probably need a way to determine how the energies of things change when they are mixed. As you can imagine, this could be extremely complicated. Initially the water molecules interacted with each other via hydrogen bonds, and this is still true after adding salt except for the fact that the water is also interacting with the salt. Also salt tends to dissociate into ions ( $\text{Na}^+$  and  $\text{Cl}^-$  for example); surely there are energetic and entropic consequences for that although we also have to consider that not all the salt may dissolve. Overall, this seems like a very complicated system to analyze due to the enthalpy of water interacting with the dissolved ions and the increase in entropy due to the salt dissociating. In fact, all of this is so complex that we are going to avoid directly analyzing the liquid solution altogether.

Fortunately, there is a much easier way to study the thermodynamics of condensed phases and processes such as mixing. To this end we examine the vapors that are in equilibrium with the liquid. Recall in Ch. 6 that we determined that the intensive variables of substances in equilibrium are all equal. These include temperature, pressure, as well as the chemical potentials which are the most important. Concerning the mixing of salt and water, we know that the chemical potential of water drops due to the addition of salt. Since the water vapor and liquid water are assumed to always be in equilibrium, the vapor experiences *the exact same change in chemical potential!* Consequently, measuring the very complex interactions due to mixing in the liquid phase is equivalent to measuring the thermodynamic changes in the vapor (i.e. gas) phase, which is great because we have learned in previous chapters exactly how to do that!

As it applies to mixing, we have to determine what properties of the vapor change when the liquid (i.e. the equilibrium partner) mixes with something like salt, and how those changes perturb the vapor's chemical potential. Using liquid water at room temperature and pressure as an example, we know that having a cup of water in a very dry room will result in evaporation. This continues until the partial water vapor pressure reaches 3,200 Pa ( $\sim 0.03$  atm), as this is the equilibrium vapor pressure under standard conditions. If salt is added to the bath, some of the water vapor will return to the liquid to "dilute" the salt that sullied the pure water; you might recognize this as Le Chatelier's principle that describes how a system resists change. Thus, the partial pressure of water vapor will decrease. It is this decrease in the vapor's partial pressure that allows us to calculate  $\Delta_{mix} \mu$  for the liquid.

There is another way to view this dynamic as shown in Figure 7.1. While water will vaporize off the surface of a cup of the pure liquid as shown in the left, it will do so to a lesser extent if salt is present as shown on the right. Here, we can think of the salt as forming a barrier at the surface of the liquid, which hinders water from vaporizing off of it. Perhaps the ions "hold down" the water molecules, which prevents them from flying off into the vapor state? Regardless, the vapor pressure from a saturated aqueous NaCl solution has been measured to be  $\sim 2,700$  Pa, which is about a 15% less than the vapor pressure of pure liquid water.

Chemical potential is the per molar Gibbs energy, and we need to know how the Gibbs energy of a vapor changes due to a drop in its partial pressure at a constant temperature. This is very easy as we determined in Chapter 5 that the  $\Delta G$  of a gas is equal to reversible work:  $\Delta G = -nRT \cdot \ln\left(\frac{V_2}{V_1}\right)$ , with initial volume  $V_1$  and final volume  $V_2$ . As we are concerned with pressure rather than volume, we insert the perfect gas law to show:

$$\Delta G = -nRT \cdot \ln\left(\frac{V_2}{V_1}\right) = -nRT \cdot \ln\left(\frac{\frac{nRT}{P_2}}{\frac{nRT}{P_1}}\right) = nRT \cdot \ln\left(\frac{P_2}{P_1}\right)$$

where  $P_2$  is the vapor pressure of the salted water and  $P_1$  is from pure water. When we divide by the number of moles  $n$  we now have an equation for the change in chemical potential:  $\frac{\Delta G}{n} = \Delta \mu = RT \cdot \ln\left(\frac{P_2}{P_1}\right)$

Some notational changes are needed because we are discussing mixtures. Specifically, we state  $P_2 = P_i$ , where  $P_i$  is the partial pressure of substance "i" in the mixed state (we must keep track of what is what using the "i" subscript because there must be

two or more chemical substances when making a solution). If we assume that the initial pressure is derived from the pure liquid, then we call it  $P_i^*$  which is the pure partial pressure of liquid "i". Inserting these notational differences:

$$\mu_i = \mu_i^\circ + \Delta\mu_i = \mu_i^\circ + RT \cdot \ln\left(\frac{P_i}{P_i^*}\right) \quad (7.1.1)$$

The equation above represents a way to determine the change in a vapor's chemical potential via an alteration of its partial pressure. A drop in the partial pressure would likely result from dilution of the source liquid by addition of salt, or anything else for that matter. And the  $\Delta\mu_i$  of the vapor is exactly the same as the  $\Delta\mu_i$  of the liquid, assuming that the vapor and liquid are in equilibrium.

---

This page titled [7.1: Partial Vapor Pressure](#) is shared under a [CC BY-NC 4.0](#) license and was authored, remixed, and/or curated by [Preston Snee](#).