Henry's Law

Last time, we discussed Raoult's law and the ideal solution. We also saw that many mixtures will deviate, sometimes significantly, from Raoult's law behavior. However, in the limit that the solution is dilute, we again observe behavior that we can easily model. Let's look at the vapor pressure of one of the components of a mixture as the concentration is changed. In the region of pure component B, we see that the Real curve approaches the line given by Raoult's law. Look also at the dilute limit, where \( x_B \) approaches zero. Here we also observe the Real curve approaching a straight line.

William Henry, an English chemist, found that for real solutions at low solute concentrations, the vapor pressure of the solute was proportional to the mole fraction. However, the constant of proportionality was not the vapor pressure of the pure material, but a different value. He wrote this observation as

\[
p_B = x_B K_B
\]

where \( K_B \) is an empirical constant with units of pressure. This is known as Henry's Law and describes the behavior of the solute in the limit of a dilute solution. The Henry's law constant is often written in terms of the molality \( b \) of the solute

\[
p_B = b_B K_B
\]

We won't do this here, but it can be shown that if the solute obeys Henry's law, then the solvent must obey Raoult's law. Such a system is called an ideal-dilute solution. It should be noted that Henry's law constants must be determined for a given solute in each individual solvent.

Molecular Description of Ideal-Dilute Solutions

If the solution is ideal-dilute, then the solvent is behaving practically the same as the pure material. This makes sense from a molecular standpoint, because most of the solvent molecules only see other solvent molecules. The solute molecules, however, only see solvent molecules and rarely see other solute molecules. Thus, the solute molecules are in a very different environment from the pure solute material. The Henry's law constant is an extrapolation of what the vapor pressure of the pure solute would be if the pure material behaved like the solute behaves in solution.
Colligative properties

Now that we have discussed how the chemical potential varies with composition, let's go back to our phase transitions and see what effect composition has on them. We call these colligative properties, because they depend on the collection of the system. All colligative properties depend on changes in the chemical potential of the liquid phase. As we have seen, we can write the chemical potential of the liquid phase of an ideal mixture as

\[ \mu_A = \mu^*_A + RT \ln x_A \]

The \( * \) denotes the pure liquid. Because the mole fraction is always between 0 and 1, the \( \ln \) term is always negative. Thus, the addition of solute lowers the chemical potential of the liquid relative to the pure liquid. The chemical potential of the pure solid and pure gas do not change, so we can graphically represent the changes as shown in the plot. We can readily see from this plot that a lowering of the chemical potential of the liquid results in a lowering of the melting point and an increase of the boiling point. Let's look at this more quantitatively.

**Boiling point elevation** – Boiling occurs when the chemical potential of the liquid equals that of the pure gas, assuming the solute is nonvolatile. This also means the vapor pressure of the solvent equals the ambient pressure. If the solvent obeys Raoult's law, we have

\[ \mu^*_A(g) = \mu^*_A(l) + RT \ln x_A \]

The change of Gibbs energy for vaporization for the pure liquid is

\[ \Delta_{vap} G = \mu^*_A(g) - \mu^*_A(l) = RT \ln x_A \]

or

\[ \ln x_A = \frac{\Delta_{vap} G}{RT} \]

Now, we want to know how this changes with temperature, so we differentiate this expression with respect to \( T \) and use the Gibbs-Helmholtz equation

\[ \frac{d \ln x_A}{dT} = \frac{1}{R} \frac{d}{dT} \left( \frac{\Delta_{vap} G}{T} \right) = -\frac{\Delta_{vap} H}{RT^2} \]

Now, to determine the boiling point at a given composition, we need to integrate this expression. To do so, we will assume that \( \Delta_{vap} H \) is constant over a narrow temperature range

\[ \int_0^{\ln x_A} d \ln x_A = -\frac{\Delta_{vap} H}{R} \int_{T_1}^{T} \frac{1}{T^2} dT \]
Our lower limit is the pure solvent, so \( x_A = 1 \) and \( \ln x_A = 0 \). The lower limit of temperature is \( T^\ast \), the normal boiling point. This can be rewritten as

\[
\ln x_A = \ln \left( 1 - x_B \right) = \frac{\Delta v_{ap} H}{R} \left( \frac{1}{T} - \frac{1}{T^\ast} \right)
\]

Now, we will make some assumptions. If \( x_B \ll 1 \), we can write \( \ln \left( 1 - x_B \right) \approx -x_B \). For the temperature, we can write

\[
\frac{1}{T} - \frac{1}{T^\ast} = \frac{T^\ast - T}{T T^\ast} \approx -\frac{\Delta T}{T^\ast^2}
\]

this only holds if \( T \approx T^\ast \)

We can plug these approximations into our expression and we have

\[
x_B = \frac{\Delta v_{ap} H \Delta T}{RT^\ast^2} \quad \text{or} \quad \Delta T = K x_B \quad \text{with} \quad K = \frac{RT^\ast^2}{\Delta v_{ap} H}
\]

All the constants in \( K \) are properties of the solvent, so it shouldn't matter what the solute is. Often, we write this expression in terms of the molality of the solute

\[
\Delta T = K_b b
\]

where \( K_b \) is the boiling-point constant of the solvent. So long as the concentration is relatively low, it doesn't matter what the solute is.

*Freezing point depression* – We can go through a similar analysis for the freezing point. The equilibrium is between pure solid solvent and a solution. The freezing point depression of a solution can actually be used to determine the molar mass of the solute, however we have much better ways to do that these days.

**Osmosis**

Let's consider the situation in the figure. We have two sides to our system, separated by a semipermeable membrane. The membrane lets solvent through, but not solute. What will happen? The chemical potential on the solution side is lower than that of the pure solvent. Pure solvent will flow from the left side to the right side, which makes the solution more dilute and raises the chemical potential of the solution. Applying additional external pressure to the solution raises the chemical potential. If we apply enough pressure, we can bring the chemical potential of the solution back up to that of the pure liquid and stop the flow of solvent across the membrane.
We designate the additional pressure as $\Pi$. We write the equilibrium expression as

$$\mu^*_A(p) = \mu_A(x_A, p + \Pi)$$

Let's look at the right side of the equation and take the effect of the solute into account

$$\mu^*_A(x_A, p + \Pi) = \mu^*_A(p + \Pi) + RT \ln x_A$$

Now we can take the pressure increase into account as follows

$$\mu^*_A(p + \Pi) = \mu^*_A(p) + \int_p^{p+\Pi} \tilde{V} \, dp$$

When we combine these expressions, we have

$$\mu^*_A(p) = \mu^*_A(p) + \int_p^{p+\Pi} \tilde{V} \, dp + RT \ln x_A$$

or

$$-RT \ln x_A = \int_p^{p+\Pi} \tilde{V} \, dp$$

Recall that $x_A = 1 - x_B$, and $\ln (1 - x_B) = -x_B$ for $x_B << 1$. Using this lets us write

$$RT x_B = \tilde{V} (p + \Pi - p) = \Pi \tilde{V}$$

If the solution is dilute, then $n_A >> n_B$, and $x_B$ is about equal to $n_B / n_A$. Likewise, the volume of the solution is basically the volume of the solvent, or $\tilde{V} \approx \frac{V}{n_A}$. This lets us write

$$RT n_B = \Pi \tilde{V}$$

or

$$\Pi = RT \left[ B \right]$$

where [B] is the molar concentration $n_B / V$. This is known as the van 't Hoff equation. Does the form of it look familiar?

The van 't Hoff equation really only works in very dilute solutions. To account for the non-ideality of the solutions, we can do a virial-like expansion on the van 't Hoff equation and write

$$\Pi = [J] RT [1 + B [J] + C [J]^2 + \ldots]$$

Here we are using [J] for the concentration of solute, rather than [B]. B in the above expression is the second osmotic virial coefficient.

**NOTE** A final note on what we have done here. We have made certain assumptions: the solvent behaves ideally, the enthalpies don't change with $T$, etc. To the extent that these assumptions are valid, the expressions we derived can be applied to real situations. For other systems, such as solubilities of ionic solids, mixtures of water and volatile liquids, these assumptions may not hold, and we have to derive more complicated expressions. The expressions we have done are often the limiting case expressions.
The general approach in science is to start with some assumptions and see where that leads us and what we can do with it. If the assumptions are good, then why do something more complicated? Once the assumptions don't hold, then we have to do more work. We can either develop a more sophisticated molecular model, or tabulate the data of real systems and attempt to fit that data to an empirical model.