

7.4: Henry's Law, Activity, and Ideal-Dilute Solutions

We learned from the previous section that the mixing of ideal solutions is an entropically driven process. However, not every combination of two liquids can be ideal as we know that many liquids don't mix at all! Take for example water and ethanol, the data for which in Figure 7.2 B reveal that they do not follow Raoult's Law. Mixing the two results in a temperature increase, and there is always a negative excess mixing volume; all of these data confirm the non-ideality of the water and ethanol interactions. Our intuition should be good enough to suspect that this is due to the disruption of water's hydrogen bonding by ethanol.

In this section we will study the limits of the ideal approximations as expressed by Raoult's Law, and what properties of liquid mixtures result in non-ideality. We will also study how to incorporate non-ideality into our thermodynamic analyses beginning with Henry's Law. In 1803, William Henry published a paper on the dissolution of gases in water, most notably CO_2 as well as "oxygeneous" and "azoitic" gases. Henry's Law can be used to determine the partial pressure of a vapor of a solution's solute, where the solute is defined as a highly diluted component of a liquid mixture ($\chi_{\text{solute}} \rightarrow 0$). Mathematically Henry's Law is:

$$P_i = K \cdot \chi_i \quad (7.4.1)$$

where K is the Henry's Law constant of substance "i". Figure 7.4 reveals more clearly how this works, as it can be seen that Henry's Law constant acts as a replacement for the pure partial pressure in Raoult's Law. Hence, it is simply an empirical "fix" for Raoult's equation when it doesn't work for a diluted component in a solution. In a mixture where the solvent follows Raoult's Law and the solute Henry's, we refer to such as an ideal-dilute solution.

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### 7.4.1 Activity

Thus far we have shown how the chemical potential of component "i" of a solution, which is exactly  $\mu_i = \mu_i^\circ + RT \cdot \ln\left(\frac{P_i}{P_i^*}\right)$ , can be approximated using Raoult's Law:  $\mu_i = \mu_i^\circ + RT \cdot \ln(\chi_i)$  for an ideal solution or Henry's Law:  $\mu_i = \mu_i^\circ + RT \cdot \ln\left(\frac{K \cdot \chi_i}{P_i^*}\right)$  for the solute of an ideal-dilute solution. However, as we see in Figure 7.4 neither Henry's nor Raoult's laws are especially accurate for a non-ideal solution near the center of the graph. As a result, there is an ultimate empirical "fix" to calculate the chemical potential whereby the ratio of the measured partial pressure to the pure partial pressure of a component  $\left(\frac{P_i}{P_i^*}\right)$  is simply called the activity " $a_i$ " of that component. The value of the unitless activity is exactly equal to  $\left(\frac{P_i}{P_i^*}\right)$ , which means that its inclusion into the equation for chemical potential:

$$\mu_i = \mu_i^\circ + RT \cdot \ln(a_i)$$

makes the expression work perfectly. The activity of a component changes as a function of solution composition, which makes the use of activity somewhat silly because it is simply another way to express the ratio  $\left(\frac{P_i}{P_i^*}\right)$  that has to be measured for every solution concentration. To preserve a relationship to the mole fraction in a liquid mixture, activity can be expressed as:

$$a_i = \left(\frac{P_i}{P_i^*}\right) = \gamma_i \chi_i \quad (7.4.2)$$

where  $\gamma_i$  is a correction factor that forces the liquid mole fraction  $\chi_i$  to return the correct activity. As a result, the mixing excess Gibbs energy for a binary mixture of "A" and "B" is:

$$\begin{aligned} \Delta_{\text{mix}} G &= nRT \cdot (\chi_A \cdot \ln(\gamma_A \cdot \chi_A) + \chi_B \cdot \ln(\gamma_B \cdot \chi_B)) \\ \Delta_{\text{mix}} G &= nRT \cdot (\chi_A \cdot \ln(\gamma_A) + \chi_B \cdot \ln(\gamma_B) + \chi_A \cdot \ln(\chi_A) + \chi_B \cdot \ln(\chi_B)) \end{aligned} \quad (7.4.3)$$

Calculating activities requires measuring all the partial pressures of all the components of a solution, which is what we were trying to avoid using the concepts of ideal and ideal-dilute solutions. However, this approach may be necessary because Henry's and Raoult's Laws are really just approximations.

#### 7.4.1.1 Excess Enthalpy and Activity

Activity can be used to understand what makes a solution non-ideal, which we already have shown means that  $\Delta_{\text{mix}} H$  is not equal to 0. In other words, a solution becomes warm or cold after mixing the components. To this end we will create a phenomenological

model for a non-zero  $\Delta_{mix}H$  and use that to understand activity and thus the deviations from Raoult's Law. First, we take into account that, for a solution composed of "A" and "B", the enthalpy must be proportional to the total mass of solution  $n$ . Also, if the total mass is composed of only "A" or "B", then there is no mixing and thus no excess enthalpy. Furthermore, our model must have units of energy. An equation such as:  $\Delta_{mix}H = nRT \cdot \chi_A \chi_B$

combines these effects. However, we must allow both the sign and magnitude of the excess enthalpy to change. As a result, we multiply this phenomenological relationship by " $\beta$ ", a fix-it factor, to yield:

$$\Delta_{mix}H = \beta \cdot nRT \cdot \chi_A \chi_B \quad (7.4.4)$$

If we insert the above into the expression for the change in Gibb's energy, Equation 7.7:  $\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$  we find that:

$$\Delta_{mix}G = \beta \cdot nRT \cdot \chi_A \chi_B + nRT \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B))$$

where we used Equation 7.10 for  $\Delta_{mix}S$ . Now we do some factoring and multiply  $\beta \cdot nRT \cdot \chi_A \chi_B$  by  $(\chi_A + \chi_B)$ , which doesn't change anything since the sum of the mole fractions is equal to 1.0:  $\Delta_{mix}G = nRT \cdot (\beta \cdot \chi_A \chi_B (\chi_A + \chi_B) + \chi_A \ln(\chi_A) + \chi_B \ln(\chi_B))$

The reason this is done is to create four different terms as shown below:

$$\Delta_{mix}G = nRT \cdot (\chi_A \cdot \beta \cdot \chi_B^2 + \chi_B \cdot \beta \cdot \chi_A^2 + \chi_A \ln(\chi_A) + \chi_B \ln(\chi_B))$$

When compared to our previous relationship for  $\Delta_{mix}G$  based on activity, Equation 7.12, we see that:

As the circled terms must be equal, it must be true that:  $\ln(\gamma_A) = \beta \cdot \chi_B^2$  and:  $\ln(\gamma_B) = \beta \cdot \chi_A^2$ , or upon simplification:

$$\gamma_A = e^{\beta \chi_B^2} \text{ and } \gamma_B = e^{\beta \chi_A^2}$$

This reveals how the excess enthalpy  $\beta$  factor accounts for Henry's Law from Equation 7.11. To see how, let's say that "A" is our solute and that  $P_A = K \cdot \chi_A$ . If we divide by  $P_A^*$  we find an equation for the activity:  $a_A = \left(\frac{P_A}{P_A^*}\right) = \frac{K}{P_A^*} \chi_A$ , which is equal to  $a_A = \gamma_A \cdot \chi_A = e^{\beta \chi_B^2} \cdot \chi_A$  according to Equation 7.12 and the fact that  $\gamma_A = e^{\beta \chi_B^2}$ . Consequently,  $\frac{K}{P_A^*} \chi_A = e^{\beta \chi_B^2} \cdot \chi_A$  which can be simplified to  $K = P_A^* e^{\beta \chi_B^2}$ . If we assume  $\chi_B \approx 1$  (since "B" is the solvent) then the Henry's Law constant for the solute is:

$$K = P_A^* \cdot e^{\beta}$$

Thus, the excess enthalpy modulates the effective pure partial pressure of solution component "A" when it is in the form of a dilute solute. For the solvent "B", a similar derivation shows  $a_B = e^{\beta \chi_A^2} \cdot \chi_B$ . However, since  $\chi_A^2 \approx 0$ , then  $e^{\beta \chi_A^2} \approx e^0 = 1$  and the above reduces to:  $a_B = \frac{P_B}{P_B^*} = \chi_B$ , which is Raoult's Law. Thus, solvents always follow Raoult's Law.

**To summarize**, the chemical potential of a solution can be known from the same of the vapors in equilibrium. It is tempting to estimate the chemical potential from the composition of the solution. To this end Raoult's Law seems intuitive and sensible, but generally it is a poor approximation. Henry's Law is nothing more than a simple empirical fix to Raoult's Law for highly dilute solutes. Deviations from the ideal or ideal-dilute cases is due to excess enthalpy that either warms or cools a solution after mixing.

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