

## 7.3: Excess Functions and Ideal Solutions

Raoult's Law gives us a starting point to analyze the thermodynamics of mixtures in much the same way that the perfect gas law did in Chapter 1. We will use it to define several new thermodynamic variables for liquid mixtures; these are called "excess functions" and we will begin with the excess volume  $\Delta_{mix} V$ . To describe it we have to define a few terms; first, the volume per mole of liquid "A" in its pure form is  $V_{m,A}$ . This is defined such that if we have a glass full of liquid "A" and add one more mole of "A" to it, then the volume will increase by  $V_{m,A}$ . When expressed mathematically this is  $V_{m,A} = \left( \frac{\partial V}{\partial n_A} \right)_{P,T}$ , which is called a pure partial molar volume. You are actually quite familiar with this concept; if you add a mole (18 g) of water to water, the volume increases by  $\sim 18$  mL because the density of water is exactly 1.0 g/mL. Thus,  $V_{m,H_2O} = 18 \text{ mL/mol}$ . However, if we were to add 1 mole of water to a large quantity of ethanol, then the total solution volume would only increase by  $\sim 14$  mL! It is this difference that represents the excess volume of mixing.

To generalize, we state that if a glass contains liquid "B", the volume increase that occurs after the addition of a mole of "A" is:

$$\underline{V}_A = \left( \frac{\partial V}{\partial n_A} \right)_{P,T,n_B \neq n_A}$$

where the subscript " $n_B \neq n_A$ " means that we are studying a solution that has more than one component. In the water + ethanol example  $\underline{V}_{H_2O} = 14 \text{ mL/mol}$  in eq  $V_{m,H_2O}$ . In this situation there is a non-zero excess mixing volume ( $\Delta_{mix} V$ ), which is defined as:

$$\Delta_{mix} V = n_A \left( \underline{V}_A - V_{m,A} \right) + n_B \left( \underline{V}_B - V_{m,B} \right) \quad \text{\label{7.3}}$$

where  $n_A$  and  $n_B$  are the total number of moles of "A" and "B" in the resulting solution. Of course we had to add in the volume for component "B" into Equation 7.3 for  $\Delta_{mix} V$ , after all we can't make a solution just out of liquid "A"! In the case of a water + ethanol solution the excess volumes  $\underline{V}_{H_2O}$  and  $\underline{V}_{EtOH}$  are shown in Figure 7.3, where it can be seen that they are continuously changing functions of the composition of the liquid.

It is important to understand that the excess solution volume, Equation 7.3, is not the same as the total solution volume. For example, adding water to water makes  $\Delta_{mix} V = 0 \text{ mL/mol}$ . To find  $\Delta_{mix} V$  for the addition of water to a very large quantity of ethanol we look at Figure 7.3 to find  $\underline{V}_{H_2O} = 14.1 \text{ mL/mol}$ , while the partial molar volume of ethanol is the same as the pure partial volume,  $\underline{V}_{EtOH} = V_{m,EtOH} = 58.7 \text{ mL/mol}$ . Thus the excess mixing volume upon addition of 1 mol water to a large excess of ethanol is:  $\Delta_{mix} V = 1 \text{ mol} \cdot (14.1 - 18.0) \text{ mL/mol} + 0 \text{ mL} = -3.9 \text{ mL}$ . To check your understanding, perform the same calculation on the addition of ethanol to a large volume of water, where the partial molar volume of ethanol is  $\underline{V}_{EtOH} = 54.9 \text{ mL/mol}$  (you should find  $\Delta_{mix} V = -3.8 \text{ mL}$ ). One last item of interest is the fact that the partial molar volume data shown in Figure 3.7 are nearly mirror images of each other. This is no accident and is explained by a Gibbs-Duhem equation discussed in the extra information section.

There are excess functions for all thermodynamic variables, which are listed below:

$$\Delta_{mix} U = \sum_{i=1}^{\alpha} n_i (\underline{U}_i - U_{m,i}) \quad (7.3.1)$$

$$\Delta_{mix} H = \Delta_{mix} U + P \cdot \Delta_{mix} V = \sum_{i=1}^{\alpha} n_i (\underline{H}_i - H_{m,i}) \quad (7.3.2)$$

$$\Delta_{mix} S = \sum_{i=1}^{\alpha} n_i (\underline{S}_i - S_{m,i}) \quad (7.3.3)$$

$$\Delta_{mix} G = \Delta_{mix} H - T \cdot \Delta_{mix} S = \sum_{i=1}^{\alpha} n_i (\underline{G}_i - G_{m,i}) \quad (7.3.4)$$

In these equations  $\alpha$  number of components in the solution; generally we will use  $\alpha = 2$  (for example, water and ethanol) for simplicity.

With the excess functions are defined we can examine what makes a solution "ideal". Specifically, the components "A" and "B" of an ideal solution obey Raoult's Law and have the following properties:

1. The partial volumes of the components in solution are identical to their pure partial volumes.
2. The components of an ideal solution interact the same way with their mixing partner as they do with each other.

The first property states that  $\Delta_{mix} V = 0 \text{ m}^3$  for all ideal solutions. The consequence of the second property is that the internal energy of molecule “A”, when in its pure form, is the same as when mixed with molecule “B”. This means that  $\Delta_{mix} U = 0 \text{ J}$ . Combining these properties allows us to determine the enthalpy of mixing (Equation 7.5):

$$\Delta_{mix} H = \Delta_{mix} U + \Delta_{mix} (PV) = \Delta_{mix} U + V \cdot \Delta_{mix} P + P \cdot \Delta_{mix} V = \Delta_{mix} U + P \cdot \Delta_{mix} V$$

The  $V \cdot \Delta_{mix} P$  is removed because we assume the pressure is constant; furthermore,  $\Delta_{mix} U = 0 \text{ J}$  and  $\Delta_{mix} V = 0 \text{ m}^3$  due to the fact that we are describing an ideal solution. As a result  $\Delta_{mix} H = 0 \text{ J}$ , which demonstrates that an ideal solution neither warms nor cools when “A” and “B” are mixed. As an example, let’s recall that toluene and benzene obey Raoult’s Law as seen in Figure 7.2A. Our chemical intuition tells us that these two aromatic molecules likely interact with each other and among themselves via  $\pi$ - $\pi$  interactions; furthermore, they have similar volumes. As a result we can conclude that toluene and benzene form an ideal solution.

Let’s study why ideal solutions mix, which must mean that  $\Delta_{mix} G$  is negative. According to Equation 7.7:

$$\Delta_{mix} G = \Delta_{mix} H - T \cdot \Delta_{mix} S$$

and since  $\Delta_{mix} H = 0 \text{ J}$ , then  $\Delta_{mix} G = -T \cdot \Delta_{mix} S$ . Consequently entropy is entirely responsible for ideal solution mixing. For  $\Delta_{mix} G$  to be negative then  $\Delta_{mix} S$  must be positive which we will prove in the following derivation. In Sec. 7.1 we determined that the Gibbs energy change for component “A” in a mixture is:  $\Delta G_A = n_A RT \cdot \ln\left(\frac{P_2}{P_1}\right)$ , where the initial pressure is the pure partial pressure ( $P_1 = P_A^*$ ) and the final pressure is the partial pressure in the mixed state ( $P_2 = P_A$ ). As a result  $\Delta G_A = n_A RT \cdot \ln\left(\frac{P_A}{P_A^*}\right)$ , which can be further simplified by insertion of Raoult’s Law:  $P_A = P_A^* \cdot \chi_A$ :

$$\Delta G_A = n_A RT \cdot \ln\left(\frac{P_A^* \cdot \chi_A}{P_A^*}\right) = n_A RT \cdot \ln(\chi_A)$$

Since there must be at least two species to form a mixture, we must add in the change in chemical potential of species “B” to calculate the total change:

$$\Delta_{mix} G = \Delta G_A + \Delta G_B = n_A RT \cdot \ln(\chi_A) + n_B RT \cdot \ln(\chi_B) \quad (7.3.5)$$

As the chemical potential is Gibbs energy per mole, we divide Equation 7.8 by total number of moles  $n = n_A + n_B$ :

$\Delta_{mix} G_m =$

 **ParseError: invalid DekiScript** ([click for details](#))

$\Delta_{mix} G_m = \Delta_{mix} \mu = \Delta \mu_A + \Delta \mu_B$

$$\begin{aligned} &= \frac{n_A}{n} RT \cdot \ln(\chi_A) + \frac{n_B}{n} RT \cdot \ln(\chi_B) \\ &= RT \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \end{aligned} \quad (7.3.6)$$

Given the  $\Delta_{mix} G_m = -T \cdot \Delta_{mix} S_m$  relationship derived earlier, we can see that:  $\Delta_{mix} S_m = -R \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B))$

which is always a positive quantity, and reveals that ideal solutions always mix due to the increase in entropy. The size extensive forms of the change in entropy is simply the per molar form multiplied by the total number of moles:

$$\Delta_{mix} S = -nR \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \quad (7.3.7)$$

This page titled [7.3: Excess Functions and Ideal Solutions](#) is shared under a [CC BY-NC 4.0](#) license and was authored, remixed, and/or curated by [Preston Snee](#).