Announce:
- HW due next Monday
- We’ll go over exams on Wednesday

Outline:

Partial molar volumes
\[ V_j = \left( \frac{\partial V}{\partial n_j} \right)_{p,T,n'} \]
\[ V_{tot} = n_A V_A + n_B V_B \]

Mixing of ideal solutions
\[ \Delta H_{mix} = 0 \]
\[ \Delta S_{mix} = - n_{tot} R \left( X_A \ln X_A + X_B \ln X_B \right) \]
\[ \Delta G_{mix} = n_{tot} RT \left( X_A \ln X_A + X_B \ln X_B \right) \]

Mixing of non-ideal solutions
\[ \Delta H_{mix} \neq 0 \]
\[ \Delta G_{mix} \] could be anything

Liquid/gas equilibria
\[ \mu_A (l) = \mu_A^* (l) + RT \ln \left( \frac{p_A}{p_A^*} \right) \]

Review

Remember last lecture when Brian played bartender and mixed up our giant Scotch and Water.

Rule 1? Scotch should be served neat.

Observations?
1) Volumes don’t add up. **What does this say about molecular interactions?** ethanol and water must be more attracted to each other than they are to themselves.

2) Temperature increases. **What does this say about \( \Delta_{mix}H \)?** We measured a negative \( \Delta_{mix}H \). **Internal energy of mixture vs. individual components?** Lower.

We’ll get to these in a minute.
Recall that for gases, we used Dalton’s law ($p_i = X_i p_{tot}$) to calculate the \textbf{partial} pressures. This is valid for mixtures that behave ideally. Clearly, molecules are obviously interacting with each other in the liquid phase, can we use something similar to Dalton’s law for liquid mixtures?

To deal with the first observation, let’s introduce the concept of the \textbf{partial molar volume}, which is similar to Dalton’s law of partial pressures.

\textbf{Show diagram for water - ethanol at 298K}. We started with 500 ml or 500 g (27.7 moles) of water and 500 ml or 395 g (8.6 moles) of ethanol.

Note that pure water normally 18 mL/mol and ethanol 58 mL/mol

Let’s operate in terms of ethanol:

\[ M_{\text{ethanol}} = 8.6 \text{ mol}/V_{\text{tot}} \text{ (depends on T, because } V \text{ depends on T)} \]

\[ 8.6/0.95 = 9.05 \text{ M or } 8.6/0.90 = 9.56 \text{ M} \]

\[ m_{\text{ethanol}} = 8.6 \text{ mol EtOH}/0.5 \text{ kg solvent (H}_2\text{O)} = 17.2 \text{ mol kg}^{-1} = 17.2 \text{ mol/kg (independent of T)} \]

\textbf{(What happens to } M \text{ and } m \text{ for dilute aqueous solutions? } M \approx m) \]

\[ X_{\text{ethanol}} = 8.6 \text{ mol}/36.3 \text{ mol} = 0.25 \]

\[ w_{\text{ethanol}} = 395 \text{ g}/895 \text{ g} = 0.44 \]

Look on diagram for $X_{\text{ethanol}} = 0.25 \rightarrow V_{\text{ethanol}} = 58 - 2.5 = 55.5 \text{ ml mol}^{-1} \]

and $V_{\text{water}} = 18 - 0.5 = 17.5 \text{ ml mol}^{-1}$. 


More generally, we would like to know how \( V \) depends on individual components. For a binary mixture (with components A and B), we can define a total derivative for \( V \):

\[
dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B
\]

Not surprisingly, we will define molar volume as

\[
\bar{V} = \left( \frac{\partial V}{\partial n} \right)_{p,T,n'}
\]

This gives us

\[
dV = \bar{V}_A dn_A + \bar{V}_B dn_B
\]

Finally we can integrate this expression to get the total volume \( V \)

\[
V_{\text{tot}} = n_A V_A + n_B V_B \quad \text{(of course you knew this from unit conversion)}
\]

Finally, then for our gigantic Scotch and water:

\[
V = 8.6 \text{ mol} \times 55.5 \text{ ml mol}^{-1} + 27.7 \text{ mol} \times 17.5 \text{ ml mol}^{-1} = 962 \text{ ml}
\]

As we experimentally determined, the total volume for the mixture is less than the summed volume of the two components!

**Thermodynamics of Mixing**

Let’s think of the lattice model in the book – simulates a liquid of two different things. There are \( N \) total sites each filled with either an A or a B molecule. (sketch lattice)

\[
N = N_A + N_B
\]

Let’s think about the entropy of the situation.

What are the number of arrangements?

\[
W = N! / N_A!N_B! \quad \text{What about A and B before mixing?}
\]

\[
W_A = N_A! / N_A! \quad W_B = N_B! / N_B!
\]

(so we can ignore these contributions)

\[
\Delta S_{\text{Mix}} = k \ln W - k \ln W_A - k \ln W_B = k \ln \frac{W_A W_B}{W} = -k [N \ln N - N_A \ln N_A - N_B \ln N_B]
\]

\[
= k \left[ N_A \ln N - N_A \ln N_A - N_B \ln N_B \right]
\]

\[
= k \left[ N_A \ln N + N_B \ln N - N_A \ln N_A - N_B \ln N_B \right]
\]

\[
= k \left[ N_A (\ln N - \ln N_A) + N_B (\ln N - \ln N_B) \right]
\]

\[
= -k [N_A (\ln X_A) + N_B (\ln X_B)]
\]

\[
= -k N [X_A (\ln X_A) + X_B (\ln X_B)]
\]
or

\[ \Delta S_{\text{mix}} = -n_{\text{tot}}R \left( X_A \ln X_A + X_B \ln X_B \right) \]

Now it turns out this is true for gasses or liquids or whatever. What about enthalpy if we had ideal gasses?

\[ \Delta H_{\text{mix}} = \] zero, because there are no interactions between the gases

So, then it is easy to get \( \Delta G_{\text{mix}} \)

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} = n_{\text{tot}}RT \left( X_A \ln X_A + X_B \ln X_B \right) \]

\( \Delta G_{\text{mix}} \) is ALWAYS negative if no interactions (called an ideal mixture)
In other words, ideal mixing is always spontaneous

But, back to our big Scotch and water, \( \Delta T \neq 0 \), so \( \Delta_{\text{mix}}H \neq 0 \)
Obviously, not an ideal mixture. How do we deal with this? (This is great stuff by the way, we are learning about molecular interactions \( \rightarrow \) chemistry!)

We’ll do this a bit differently than the textbook, so please read the book and think about this from both points of view.

 Dependence of chemical potential on composition for liquids

Let’s pretend we have two things in a closed system at equilibrium. Noting that \( \mu_{\text{liquid}} = \mu_{\text{gas}} \) because we are at equilibrium

<table>
<thead>
<tr>
<th>( A(g) + B(g) )</th>
<th>( \mu_A(g) = \mu_A(l) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A(l) + B(l) )</td>
<td>( \mu_B(g) = \mu_B(l) )</td>
</tr>
</tbody>
</table>

For now, define substance A as the solvent and substance B as the solute.

Let’s divert for a minute to think about just pure substance
\[ \mu_A^*(g) = \mu_A^*(l) \]

Note * notation for pure substance

Thinking back to chapter 11, the chemical potential for a gas is:

\[ \mu = \mu^\varphi + RT \ln \left( \frac{p}{p^\varphi} \right) \]  

(we gave this before using G)

Because we have a liquid and vapor at equilibrium, \( \mu_s \) must be equal and \( p \) must be the vapor pressure

\[ \mu_A^*(l) = \mu_A^\varphi + RT \ln \left( \frac{p_A^*}{p_A^\varphi} \right) \]

If we now allow for the presence of another substance (solute), we replace the pure quantities in the above expression:

\[ \mu_A(l) = \mu_A^\varphi + RT \ln \left( \frac{p_A}{p_A^\varphi} \right) \]

By equating these two relations through the standard chemical potential \( \mu_A^\varphi \), we can eliminate the dependence on the standard chemical potential:

\[ \mu_A(l) = \mu_A^*(l) + RT \ln \left( \frac{p_A^*}{p_A^\varphi} \right) \]

if \( p_A < p_A^* \), then \( \mu_A(l) < \mu_A^*(l) \) (mixing lowers the chemical potential)

Therefore, the chemical potential for the liquid substance A in a mixture is dependent on the chemical potential for the pure substance plus a factor that is dependent on the ratio of the vapor pressures (of \( p \) in mixture to \( p \) of pure substance).

**Raoult’s Law**

Let’s simplify this last relationship that connects chemical potential with ratio of vapor pressures. We can use the experimental result that (for similar liquids) the mole fraction of the substance A in the mixture is approximately \( p_A/p_A^* \), or the ratio of the partial vapor pressures of each component in a mixture to its vapor pressure as a pure liquid:
\[ p_A = X_A p_A^* \] (Raoult’s law)

We can see (since the mole fraction is always less than 1) that the vapor pressure is always reduced for a substance when additional substances are added to the mixture. The reason for this can be understood simply by considering that only molecules near the surface of the liquid may easily escape.

So, it makes sense that the mole fraction in the mixture should directly affect the vapor pressure. Raoult’s law is valid for similar substances – this is because then interactions with other substance will closely mimic those with the pure substance.

We can use Raoult’s law to write the equation for the chemical potential of the liquid A:

\[ \mu_A (l) = \mu_A^* (l) + RT \ln X_A \]

This equation is valid only for ideal solutions (similar interactions, \( \Delta_{\text{mix}} H = 0 \)). Remember that \( \Delta_{\text{mix}} H = 0 \) does not mean that there are no interactions, it means that the interactions in the mixture are the same as those in either pure substance.
Even for non-ideal solutions **under what conditions might Raoult’s law be obeyed?** When the mole fraction of a substance approaches one. In this case, the solvent obeys Raoult’s law.

The molecular explanation for this limiting behavior is that each of the molecules will have only molecules identical to itself in its next-neighbor sphere.

and the solute obeys Henry’s law

\[ p_B = X_B K_B \]  
(Henry’s law)

Notice here that while the vapor pressure is proportional to the mole fraction (as is the case for Raoult’s law), the constant of proportionality is not the vapor pressure of the pure substance. This constant \( K_B \) is chosen to be tangent to the experimentally determined curve at \( X_B = 0 \). **Show diagram for transition from Henry’s law regime to Raoult’s law regime.**

**Ideal-dilute solutions:** are those that behave as above – non-ideal mixtures for which the solvent obeys Raoult’s law and the solute obeys Henry’s law.

Henry’s law constants are inversely proportional to the solubility (vapor pressure is inversely proportional to solubility). Right? If something is very soluble then we would expect it to not escape into the vapor phase.

Sample Henry’s law constants for aqueous solutions (298 K) (from Tinoco)

<table>
<thead>
<tr>
<th>Solute</th>
<th>( K_B ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>( 131 \times 10^3 )</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>( 86 \times 10^3 )</td>
</tr>
</tbody>
</table>
As we saw before for non-ideal gas behavior, more electrons lead to greater intermolecular attraction, and in this case, greater solubility. **Why?** Larger dispersive interactions – it is easy to induce dipoles.