Announce:
- Chem club meeting

Outline:
- Raoult’s Law
- Henry’s Law
- Ideal-dilute solutions
- Positive/negative deviations
- Activity
- Real $\Delta G_{\text{mix}}$ and $\Delta H_{\text{mix}}$

Review

Partial molar volumes

$$V_j = \left( \frac{\partial V}{\partial n_j} \right)_{p,T,n}$$

$$V_{\text{tot}} = n_A V_A + n_B V_B$$

(remember we can do partial molar anything)

Gibbs-Duhem Eq.

$$\sum_j n_j \mu_j = 0$$

(so the chemical potentials of everything are linked)

Mixing of ideal solutions

$$\Delta H_{\text{mix}} = 0$$

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

$$\Delta G_{\text{mix}} = n_{\text{tot}} R T \left( X_A \ln X_A + X_B \ln X_B \right)$$

Mixing of non-ideal solutions

$$\Delta H_{\text{mix}} \neq 0$$

$$\Delta G_{\text{mix}}$$ could be anything

Liquid/gas equilibria

$$\mu_A (l) = \mu_A^* (l) + R T \ln \left( \frac{p_A}{p_A^*} \right)$$

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, \( \Delta_{mix} H = 0 \)). Note that \( \Delta_{mix} H = 0 \) 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>
<tr>
<td>CO</td>
<td>( 57 \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.

**Example**

**Origin of “the bends” in deep-sea diving.** The bends are caused by bubbles of \( N_2 \) gas that form in the bloodstream as the diver rises too quickly from a dive. Let’s calculate the solubility for \( N_2 \) at sea level and 100 m below the surface. Assume blood is basically an aqueous solution.

Mercury is 13.6 times more dense than water, so we can convert depth to pressure in torr. So, 100m gives:

\[
\frac{100,000 \text{ mm water}}{13.6} = 7350 \text{ mm Hg} = 9.67 \text{ atm}
\]

This is just from depth, must add atmospheric pressure

\[\text{total } P = 10.67 \text{ atm.}\]

\[X_{N_2} = \frac{P_{N_2}}{K_{N_2}}\]

**At 100m depth:**

\[X_{N_2} = 10.67 \text{ atm} / 86 \times 10^3 \text{ atm} = 1.24 \times 10^{-4}\]

to convert to molarity, use: 55.6 moles of water per liter

\[[N_2] = X_{N_2} \times 55.6 \text{ moles/L} = 6.9 \times 10^{-3} \text{ M}\]

**At sea level:**

\[X_{N_2} = 1.00 \text{ atm}/86 \times 10^3 \text{ atm} = 1.16 \times 10^{-5}\]

\[[N_2] = X_{N_2} \times 55.6 \text{ moles/L} = 6.5 \times 10^{-4} \text{ M}\] So, the blood can hold 10 x less – causes \( N_2 \) to come out of solution as depth decreases.

**Real Mixtures**

**Show acetone-chloroform pressure vs. mole fraction diagram** (from Levine)
We can see that at very low mole fractions, both acetone and chloroform obey Henry’s law and that at high mole fractions they obey Raoult’s law. **What kind of behavior is this?** Ideal-dilute

However, at intermediate mole fractions the mixture deviates from ideality – the vapor pressure for each substance is less than that predicted by Raoult’s law (negative deviation). **Why negative?** This is because acetone and chloroform have more attraction for each other than they do themselves.

**Show acetone-carbon disulfide diagram**
Here is a case of even stronger non-ideality, although here we can see that the deviation is positive. Why positive? acetone and carbon disulfide have less attraction for each other relative to their attraction for themselves. Note that they don’t necessarily repel each other – just attract less.

Let’s back up a second. Remember our focus here is intermolecular interactions.

How do we quantify the intermolecular interactions in:
- gaseous mixtures? no interactions
- liquid mixtures? similar in mixture compared to pure components

Thus, our reference state for a liquid mixture is the intermolecular interactions in the pure solutions.

In yet another duplication of notation, use \( u \) for intermolecular interactions.

**What should \( u \) be for an ideal solution?**

\[ u_{A-B} = \frac{u_{A-A} + u_{B-B}}{2} \]

Alternatively, we can define \( w \) as the non-ideality

\[ w = 2u_{A-B} - u_{A-A} - u_{B-B} \]

\( w = 0 \) for ideal
\( w < 0 \) for stronger attraction
\( w > 0 \) for weaker attraction/repulsion

In the case of benzene-toluene we saw this mixture was ideal, so \( w = 0 \)
In the case of acetone-chloroform we saw that the A-B interactions were stronger (more attractive) and the cause of the observed non-ideality.

$$u_{A-B} < \frac{u_{A-A} + u_{B-B}}{2} \quad \text{(more negative, } w < 0)$$

On the other hand, for acetone-carbon disulfide we saw that the A-B interactions were weaker (more repulsive) and caused non-ideal behavior of opposite sign to that the acetone-chloroform case.

$$u_{A-B} > \frac{u_{A-A} + u_{B-B}}{2} \quad \text{(less negative, } w > 0)$$

It is possible for real solutions that $\Delta_{\text{mix}} G > 0$ (either because of enthalpy increases or entropy decreases upon mixing) such that the components of the mixture separate. Example: oil and water

**Activities**

For an ideal solution, Raoult’s law is obeyed and we can write the chemical potential:

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

When the solution does not obey Raoult’s law, the form of the above expression can be retained by substituting the activity for the mole fraction:

$$\mu_A (l) = \mu_A^* (l) + RT \ln a_A$$

The activity is an “effective” mole fraction for non-ideal solutions just as fugacity is an “effective” pressure for non-ideal gases. (We didn’t do fugacity in lecture, but Chapt 8 talks about it.)

By comparison to our general equation for the chemical potential of a mixture, we can see that $a_A = \frac{p_A}{p_A^*}$. Therefore, the activity can simply measured as the ratio of the vapor pressure of component in $A$ in a mixture and its vapor pressure as a pure substance.
Solvent activity

Since all substances obey Raoult’s law as the $X_A \rightarrow 1$, we can say:

as $X_A \rightarrow 1$, then $p_A \rightarrow p_A^*$ and therefore $a_A \rightarrow X_A$

We can define a new term called the **activity coefficient** for substance A ($\gamma_A$):

$$a_A = \gamma_A X_A \quad (\gamma_A \text{ is not constant}!!)$$

**It follows then that?**

$X_A \rightarrow 1$, $\gamma_A \rightarrow 1$ and therefore $a_A \rightarrow X_A$ as it should

The chemical potential for a solvent in a **non-ideal** solution is therefore:

$$\mu_A = \mu_A^* + RT \ln X_A + RT \ln \gamma_A$$

Notice that the second two terms are zero for $X_A = 1$, so:

as $X_A \rightarrow 1$, $\mu_A \rightarrow \mu_A^*$

**Can we quantify non-ideality**

Remember that $\Delta G_{mix} = n_{tot}RT (X_A \ln X_A + X_B \ln X_B)$ for ideal solutions

Keeping in mind that $\mu_A = \mu_A^* + RT \ln X_A + RT \ln \gamma_A$

then **what might $\Delta G_{mix}$ be for our non-ideal case?**

$$\Delta G_{mix} = n_{tot}RT (X_A \ln X_A + X_B \ln X_B + X_A \ln \gamma_A + X_B \ln \gamma_B)$$

**ideal mixing**

**excess Gibbs energy**

**of mixing**

$$\Delta G_{mix} = \Delta G_{ideal} + \Delta G_{excess}$$

This is great stuff – allows us to quantify the intermolecular interactions!