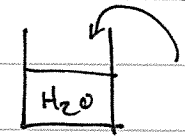
Let's talk about mixtures

mole fractions: $\frac{n_A}{n} = X_A$ $\frac{n_B}{n} = X_B$

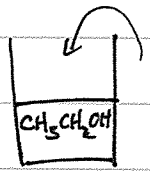
for a binary mixture: $X_A + X_B = 1$

Suppose we have some flasks of liquids



let's dump in 1 mol of H_2O

$\Delta V = 18\,cm^3$

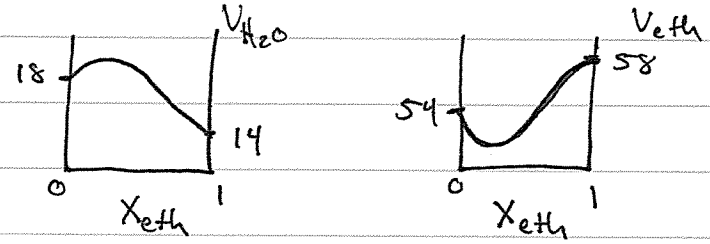


let's dump in 1 mol of H_2O

$\Delta V = 14\,cm^3$

Why the difference? Because the volume of a molecule of H_2O depends on the molecules that surround it!

We can do the experiment as a function of $X_{ethanol}$:



The partial molar volume of each component changes with the composition because of the changing environment: We can try to quantify this:

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{P,T,n'}$$

$\leftarrow$ Hold P, T and moles of everything else constant

$\uparrow$ change in volume due to a change in moles of substance J

Now let's do a mixture

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

change in volume to solution

$$dV = V_A\, dn_A + V_B\, dn_B$$

So, if we have good values for the partial molar volumes at a T, P, and composition, we know the volume at any composition

$$V = V_A n_A + V_B n_B$$

Volume is an easily-visualized concept, but the same thing works for free energies as well:

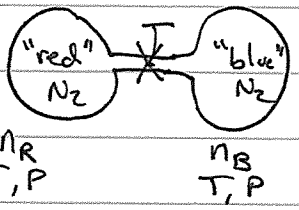
$$G = \mu_A n_A + \mu_B n_B$$

μ_A is called the "chemical potential" and it just measures how G changes with 1 mole of A.

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B}$$

μ = "Gibbs energy per mole"

Let's think about a simple case of mixing "red" and "blue" N_2 molecules



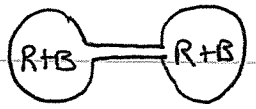
don't feel any different about each other. Their chemical environments are identical.

Opening the valve lets each gas expand into the space of the other.

What can change? T? No, both are at same T

P? No, they're both at same P

After



← same T & P as before, but the partial pressures have changed

$$P_{red} = P_R = \frac{n_R}{n_R+n_B} P \qquad P_B = \frac{n_B}{n_R+n_B} P$$

$$P_R = X_R P \qquad P_B = X_B P$$

Because the mixing is spontaneous, the gibbs free energy must also be negative.

Before: $G_i = n_R RT \ln P + n_B RT \ln P$

↕ only partial pressure changes

After: $G_f = n_R RT \ln P_R + n_B RT \ln P_B$

$$\Delta G_{mix} = G_f - G_i = n_R RT \ln \frac{P_R}{P} + n_B RT \ln \frac{P_B}{P}$$

But $P_R = X_R P$, so:

$$\Delta G_{mix} = n_R RT \ln X_R + n_B RT \ln X_B$$

We also have a relationship between n_R & X_R

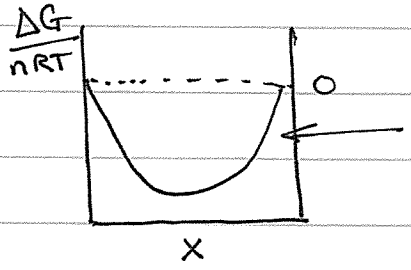
$n_R = X_R\, n$, so:

$$\Delta G_{mix} = RT\left(X_R \ln X_R + X_B \ln X_B\right)$$

Σ free energy for mixing 2 gases that don't feel any different about their new neighbors

(Any time you see an $x \ln x$ expression, you can be pretty sure entropy is driving the process....)

Applet Demo

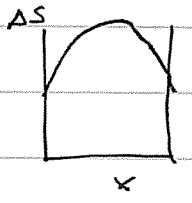
So: 

ΔG is always negative for ideal mixtures!

In this experiment, the Red & Blue N_2 molecules don't feel any changes in their local environment so $\Delta H = 0$

Since $\Delta G = \Delta H - T\Delta S$, so

$$\Delta S_{mix} = -R\left(X_R \ln X_R + X_B \ln X_B\right)$$



The entropy of mixing is always ⊕

Now, suppose Red & Blue are chemically distinct

(R) + (R) = meh

(B) + (B) = meh

(R) + (B) = woo hoo!!! ← energetic benefit for mixing

ΔH_{mix} is negative

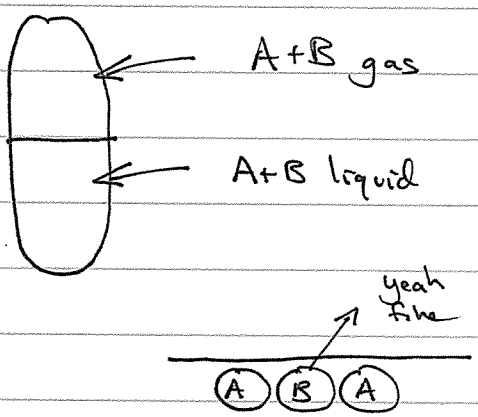
(R)+(R) = woo hoo!

Or: (B)+(B) = woo hoo!

(R)+(B) = yuck ← Red and Blue pay an energetic penalty for mixing

ΔH_{mix} is positive

Now, on to the gases above a solution



If A & B are chemically indifferent to the identity of their neighbors, they are equally willing to enter the vapor phase, so the only thing that governs the vapor pressure is how much stuff there is in the liquid:

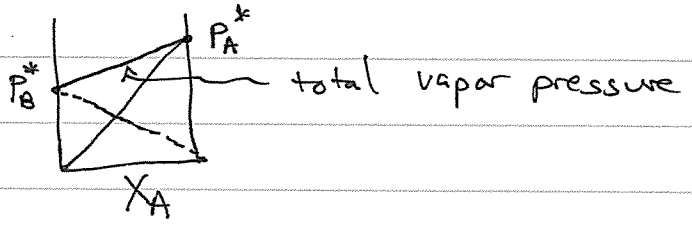
$$P_A = X_A P_A^*$$

P_A: vapor pressure of A in mixture above liquid

X_A: mol fraction of A in the liquid

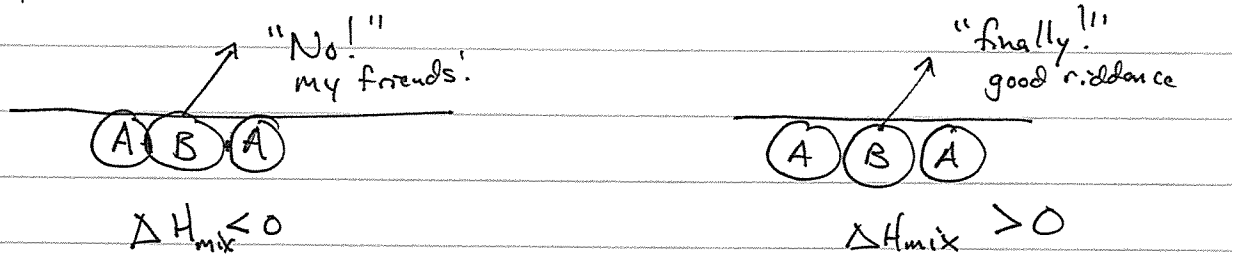
P_A^*: vapor pressure of pure liquid A

This case for ideal solutions is called Raoult's law. No one really cares what the name is, just remember that it only works for ideal solutions (ones where A & B are equally attracted to each other & themselves)

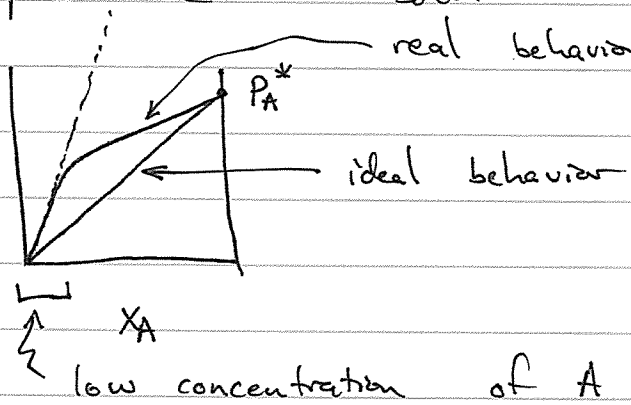


Non-ideal solutions (i.e. everything)

Now A & B have an energetic bias to stay together (or leave):



We get deviations from linear behavior for any solution where the solute has greater or lesser preference for solute than for itself:



The low concentration region has a linear slope if we get close enough to 0

$$P_A = X_A K_A$$

← "Henry's" law constant for deviations in "ideal-dilute" solutions

Why is this a big deal?

Henry's law governs the solution composition of sea water:

- If P_{CO_2} goes up in the air the amount we can solubilize in the water, X_{CO_2} depends on K_{CO_2}
- The temperature behavior of K_{CO_2} is massively important

Also gaseous (inhaled) anesthetics have a really narrow range of $X_{anesthetic}$ where they knock you out (before causing calcium channels to fail).

$P_{anesthetic} = X_{anesthetic} K_{an}$ ← knowing this might be the difference between a good outcome and a not good one.