Mixing – one more time!

First, a word about "perfect" vs. "ideal":

For a perfect solution: $\mu_i(P,T,x_i) = \mu_i^*(P,T) + RT\ln x_i$
in which $\mu^*(P,T)$ is the chemical pot. of the i^{th} component at $P + T$ <u>when it is pure</u>

For an ideal solution: $\mu_i(P,T,x_i) = \mu_i^0(P,T) + RT\ln x_i$
in which $\mu_i^0(P,T)$ is the chemical pot. of the <u>reference</u> state of the ith component at $P+T$. The only thing special about this reference state is that $\mu^0(P,T)$ is a constant for a given $P+T$, which are typically 1 bar and 298K

All solutions are ideal for $x_i \approx 0$ just as all gases are ideal for $P \approx 0$

To deal with the non-ideality that creeps in as x_i gets larger, we substitute x_i with a_i, the activity, which can be expressed $\gamma_i x_i$, in which γ_i is the activity coefficient.

Now, $\bar{G}$ (mixing) of a "perfect" solution is just the sum of the chemical potentials:

Don't forget the x_i's

$$\bar{G}_{mix} = \sum_i x_i\mu_i(P,T,x_i) = \sum_i x_i\mu_i^*(P,T) + RT\sum_i x_i\ln x_i$$

the first sum is just the G before mixing. The second sum is the effect of mixing, i.e. ΔG_{mix}

Interestingly, there is no ΔH_{mix}. In effect, the heating is zero. The same is true for ΔU, ΔV, etc

(This is only true for perfect solutions, not ideal)

For non-ideal solutions, we use activity:

$$\Delta G_{mix} = RT \sum_i x_i \ln \underbrace{\gamma_i x_i}_{a_i}$$

The difference between ideal + non-ideal is the excess ΔG_{mix}

$$\Delta G_{Excess} = RT \sum_i x_i \ln \gamma_i$$

One can also calculate ΔH_{Excess}, etc.

$\underbrace{\Delta G_{Excess}}_{E}$ is made up of $\Delta H_{Excess} - T\Delta S_{Excess}$, so:

1. when $\Delta G_E \approx \Delta H_E$, γ_i is proportional to $1/T$
2. when $\Delta G_E \approx T\Delta S_E$, γ_i is independent of T

case 1 is a "thermal" solution → "bonds" btwn molecules
case 2 is an "athermal" solution → no new "bonds"

the derivations of $\gamma \propto 1/T$, etc. will not be tested