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 \( \mu_i^*(p, T) \) is the chemical pot. of the \( i \)th component at \( P + T \) when it is pure.

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 reference state of the \( i \)th component at \( P + T \).

The only thing special about this reference state is that \( \mu_i^0(p, T) \) is a constant for a given \( P + T \), which are typically 1 bar and 298 K.

All solutions are ideal for \( x_i \to 0 \) just as all gases are ideal for \( p \to 0 \).

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 as \( x_i a_i \), in which \( a_i \) is the activity coefficient.

Now, \( G_{\text{mix}} \) (mixing) of a perfect solution is just the sum of the chemical potentials:

\[ G_{\text{mix}} = \sum_i \mu_i(p, T, x_i) = \sum_i \mu_i^*(p, T) + RT \sum_i x_i \ln x_i \]
The first sum is just the $G$ before mixing. The second sum is the effect of mixing, i.e. $\Delta G_{\text{mix}}$.

Interestingly, there is no $\Delta H_{\text{mix}}$. In effect, the heating is zero. The same is true for $\Delta U, \Delta V$, etc. (This is only true for perfect solutions, not ideal.)

For non-ideal solutions, we use activity:

$$
\Delta G_{\text{mix}} = RT \sum \chi_i \ln \chi_i
$$

The difference between ideal and non-ideal is the excess $\Delta G_{\text{mix}}$:

$$
\Delta G_{\text{Excess}} = RT \sum \chi_i \ln \chi_i
$$

One can also calculate $\Delta H_{\text{Excess}}$, etc.

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

1. When $\Delta G = \Delta H$, $\chi_i$ is proportional to $\sqrt{T}$
2. When $\Delta G = T \Delta S$, $\chi_i$ is independent of $T$

Case 1 is a "thermal" solution ⇒ bonds between molecules
Case 2 is an "athermal" solution ⇒ no new "bonds"

The derivatives of $\chi_i \sqrt{T}$, etc. will not be tested.