

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: $\mu_i(p, T, x_i) = \mu_i^{\circ}(p, T) + RT \ln x_i$
 in which $\mu_i^{\circ}(p, T)$ 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 $\mu_i^{\circ}(p, T)$ 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

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

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:

$$\Delta G_{\text{mix}} = RT \sum_i x_i \ln \frac{\gamma_i x_i}{a_i}$$

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

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

One can also calculate ΔH_{Excess} , etc.

ΔG_{Excess} is made up of $\Delta H_{\text{Excess}} - T\Delta S_{\text{Excess}}$, 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 \rightarrow "bonds" b/w molecules
 case ② is an "athermal" solution \rightarrow no new "bonds"

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