Chemical potentials of mixtures

Previously showed how chemical potentials (partial molar Gibbs Free Energies) govern phase equilibria.

Now we will look more at how these depend on concentration of multiple components (mixtures & reactions)

Difference between phases & reactions

\[
\text{G} = n_1 \mu_1 + n_2 \mu_2 + (\text{interfacial})
\]

\[
\approx n_1 \mu_1^* + n_2 \mu_2^* \quad \text{for all } n_1, n_2
\]

where \( \mu^* \) is chemical potential of pure material
\[ A \nRightarrow B \]

\[ G = n_1 \mu_1 + n_2 \mu_2 \quad \text{but} \]
\[ \mu_1 \neq \mu_1^* \quad \mu_2 \neq \mu_2^* \quad \text{except at } \theta = \theta_1 \text{ and } \theta = \theta_2 \]

2 contributions to non ideality:
\[ \mu_i = \bar{H}_i - T \bar{S}_i \]

\( ^\wedge \) energy changes due to interactions and change in structure

S changes b/c minimized in pure states

Need to compute these contributions relative to some known value
Concentration Scales (see also, worksheet)
Reference concentrations can be measured different ways and different ones are useful for different situations.

All concentration scales are intensive (doubling system keeps same)

Species normalized scales:
- Mole fraction \( X_i = n_i/n \)
- Molality \( M_i = n_i/1000\omega_s \cdot W_s = X_i/1000\omega_s X_s \)

\( W_s = \) molecular weight solvent (eg water = 18 g/mol)

\( \sum \omega_i = 1 \)

\( \sum m_i = \frac{1}{1000\omega_s X_s} \)
Volume normalized

• Molarity $M_i = [i] = \frac{n_i}{V_t} = \frac{n_i}{\Sigma n_i \bar{V}_i} = \frac{x_i}{\Sigma x_i \bar{V}_i}$

$$\Sigma M_i = \frac{n_i}{V_t} = \Sigma \text{everything}$$

• Partial density $\rho_i = \frac{n_i \bar{w}_i}{V_t} = \frac{x_i \bar{w}_i}{\Sigma x_i \bar{V}_i}$

$$\Sigma \rho_i = \rho_{\text{everything}} = \frac{\text{mass total}}{\text{volume total}}$$

[Do water on worksheet]

• Partial pressure (for gas)

$$p_T = \Sigma p_i \Rightarrow p_i = p_T - \Sigma p_j$$

Ideal gas $= \frac{RT n_i}{V} = RT M_i$
Return to concentration def of \( \mu_i \):

Previously, G-D relation:

\[
\sum n_i d\mu_i = U dp - S dT
\]

\[\text{since } U = \sum n_i \bar{U}_i, \text{ & } S = \sum n_i \bar{S}_i\]

\[
\text{\( \nu \) & \( \bar{\nu} \) equations: } d\mu_i = \bar{V}_i dp - \bar{S}_i dT
\]

\[
p = \sum p_i \Rightarrow dp = \sum dp_i
\]

for const \( T \) & \( P_j \neq i\)

\[d\mu_i = \bar{V}_i dp_i\]

Consider ideal gas \( \bar{V} = RT/p \)

\[
\Rightarrow \int_{\mu_i} d\mu_i = \int_{p_i} \frac{RT}{p} dp
\]

\[
\Rightarrow \mu_i = \mu_i^0 - RT \ln \left( \frac{p_i}{p_i^0} \right)
\]

What is \( \text{ref?} \) for gas choose \( p_i = \text{atm} \)

& \( \mu_i = \mu_i^0 \text{ at atm} \)
Can choose other standard states
\[ X_i^* = 1 \] already discussed (high conc mixtures)
\[ \Gamma_i^0 = 1 \text{ mol} \text{l} \text{ (low conc mixture)} \]

Note, it is possible to have
\[ P_A = P_B = P_C = \ldots = \text{latm} \]
\[ \& \ [A] = [B] = [C] \ldots = 1 \text{ mol} \text{l} \text{ (to some limit)} \]
but not \[ X_A^* = X_B^* = 1 \]

Also \[ \mu_A \neq \mu_B \text{ in general} \]

Chemical potentials for liquid mixtures
Liquid & vapor are in eq
\[ \mu_i^{\text{liq}} = \mu_i^{\text{gas}} = \mu_i^* + RT \ln \left( \frac{?i}{p_i} \right) \]
assuming gasses behave ideally

This \( p_i \) is a property of the liquid called the vapor pressure
But how does this help us determine $\mu_i$ as a function of species concentrations?

Raoult's Law (ideal solution approximation)

$$P_i = \chi_i \pi_i^*$$

This doesn't mean $A&B$ don't interact, it means $AA$, $AB$, $BB$ interactions all very similar.

Eg:

$$\text{Ethylene dibromide}$$

$$\text{Propylene dibromide}$$

$$(\text{Dibromo ethene})$$