Statistical Molecular Thermodynamics

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Video 10.9

Regular Solution Theory
Molecular Model of Non-ideal Soln’s

Assume molecules are randomly mixed (i.e., entropy of mixing is the ideal entropy of mixing). Then, any excess Gibbs free energy of mixing must be associated with some enthalpy (ultimately, potential energy) component.

\[ U = N_{11} \varepsilon_{11} + N_{12} \varepsilon_{12} + N_{22} \varepsilon_{22} \quad \text{potential energy of the solution} \]

where: \( N_{ij} \) is the number of interactions between molecules \( i \) and \( j \)
\( \varepsilon_{ij} \) is the energy of interaction between molecules \( i \) and \( j \)
(interactions assumed to be only between nearest neighbors)

Total number of type 1 neighbors (of any given molecule): \( z \chi_1 \)

Total number 1-1 neighboring pairs: \( N_{11} z \chi_1 / 2 \)

eliminates double counting

Total number 1-2 neighboring pairs: \( N_{11} z \chi_2 = N_{22} z \chi_1 \)

(coordination number (here, 6, assumed same for both components, for purpose of simplicity)}
**Isolating Non-ideal Interactions**

\[ U = N_{11} \varepsilon_{11} + N_{12} \varepsilon_{12} + N_{22} \varepsilon_{22} \]  

potential energy of the solution

Using the derived numbers of interactions as a function of \( z \):

\[ U = \frac{N_1 z x_1}{2} \varepsilon_{11} + N_1 z x_2 \varepsilon_{12} + \frac{N_2 z x_2}{2} \varepsilon_{22} \]

Now taking the definition of mole fraction \( x_n = \frac{N_n}{N_1 + N_2} \)

\[ U = \frac{N_1^2 z}{2(N_1 + N_2)} \varepsilon_{11} + \frac{N_1 N_2 z}{N_1 + N_2} \varepsilon_{12} + \frac{N_2^2 z}{2(N_1 + N_2)} \varepsilon_{22} \]

Now define a new variable \( w = 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} \)

\[ U = \frac{z \varepsilon_{11} N_1}{2} + \frac{z \varepsilon_{22} N_2}{2} + \frac{zw N_1 N_2}{2(N_1 + N_2)} \]

In an ideal solution, all molecular interaction energies are equal, in which case, \( w = 0 \)
**Zooming in on Non-ideality**

\[ U = \frac{z\varepsilon_{11} N_1}{2} + \frac{z\varepsilon_{22} N_2}{2} + \frac{zwN_1 N_2}{2(N_1 + N_2)} \]

\[ G_{\text{sol}} = G_{\text{ideal}} + \frac{zwN_1 N_2}{2(N_1 + N_2)} \]

using \( \frac{N_i}{N_A} = n_i \)

\[ G_{\text{sol}} = G_{\text{ideal}} + \frac{zwN_A n_1 n_2}{2(n_1 + n_2)} \]

\[ \mu_1 = \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2} = \left( \frac{\partial G_{\text{ideal}}}{\partial n_1} \right)_{T,P,n_2} + \frac{zwN_A}{2} \left( \frac{\partial n_1 n_2/(n_1 + n_2)}{\partial n_1} \right)_{n_2} \]
\[ \mu_1 = \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2} = \left( \frac{\partial G_{\text{ideal}}}{\partial n_1} \right)_{T,P,n_2} + \frac{zwN_A}{2} \left( \frac{\partial n_1 n_2 / (n_1 + n_2)}{\partial n_1} \right)_{n_2} \]

\[ \left( \frac{\partial n_1 n_2 / (n_1 + n_2)}{\partial n_1} \right)_{n_2} = \frac{n_2 (n_1 + n_2) - n_1 n_2}{(n_1 + n_2)^2} = \frac{n_2}{(n_1 + n_2)} \left( 1 - \frac{n_1}{n_1 + n_2} \right) \]

\[ = x_2 (1 - x_1) = x_2^2 \]

So, \[ \mu_1 = \mu_1^* + RT \ln x_1 + \frac{zwN_A x_2^2}{2} \]

Defining yet another variable: \[ u = \frac{zwN_A}{2} \]

Behold, the activity!

we arrive at: \[ \mu_1 = \mu_1^* + RT \ln \left( x_1 e^{ux_2^2/RT} \right) \]
**Effect of Non-ideality**

\[ \mu_1 = \mu_1^* + RT \ln \left( x_1 e^{ux_2^2/RT} \right) \]

\[ a_1 = \frac{P_1}{P_1^*} = x_1 e^{ux_2^2/RT} \]

Note that \( u \) is positive when 1,2 interactions are less favorable than 1,1 and 1,2 interactions, and negative when 1,2 interactions are more favorable than 1,1 and 1,2 interactions.

\[ u = \frac{z(2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22})N_A}{2} \]

Plotted for \( u = -1, 0, 1 \)
Excess Free Energy of Mixing Again

\[ \Delta_{mix} \bar{G} = x_1 \mu_1^{sol} + x_2 \mu_2^{sol} - x_1 \mu_1^* - x_2 \mu_2^* \]

Using now:

\[ \mu_1 = \mu_1^* + RT \ln x_1 + u x_2^2 \quad \mu_2 = \mu_2^* + RT \ln x_2 + u x_1^2 \]

Substitution provides:

\[ \Delta_{mix} \bar{G} = RT \left( x_1 \ln x_1 + x_2 \ln x_2 \right) + x_1 u x_2^2 + x_2 u x_1^2 \]

\[ = \Delta_{mix} \bar{G}_{\text{ideal}} + u x_1 x_2 \left( x_2 + x_1 \right) = \Delta_{mix} \bar{G}_{\text{ideal}} + u x_1 x_2 \]

\[ \bar{G}^E = u x_1 x_2 \quad \bar{H}^E = u x_1 x_2 \quad \bar{S}^E = 0 \]

Note that if \( u \) is negative, the free energy of mixing is even more favorable than for an ideal solution. But, what if \( u \) is positive?
Free Energy of Mixing vs Composition

\[
\frac{\Delta_{\text{mix}} G}{u} = \frac{RT}{u} \left(x_1 \ln x_1 + x_2 \ln x_2 \right) + x_1 x_2
\]

Plotted for \( RT / u = 0.4, 0.5, 0.6 \)
Finding Preferred Compositions

Using the equation below, we can solve for maxima and minima in the free energy of mixing at different temperatures. While \( x_1 = 0.5 \) is always a stationary point, when \( RT / u < 0.5 \), two other roots occur (and they are minima). It is these roots that correspond to the compositions of the two separate phases in equilibrium.

\[
\left( \frac{\partial \Delta_{\text{mix}} \bar{G} / u}{\partial x_1} \right) = \frac{RT}{u} \left[ \ln x_1 - \ln(1 - x_1) \right] + (1 - 2x_1) = 0
\]

\[
\frac{RT}{u} = 0.4, \quad x_1_{\text{min}}(\Delta_{\text{mix}} \bar{G} / u) = 0.145, 0.855
\]

To build a temperature composition diagram, one repeats this for a range of temperatures.
Temperature-Composition Diagrams Redux

Critical points in composition as a function of $RT/\mu$

- One phase for $RT/\mu > 0.5$
- Two phases for $RT/\mu < 0.5$

Phenol and water

$c.f.$ last slide of video 10.7
$dU = \delta q + \delta w$

Next: Review of Module 10