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.

$$U = N_{11}\varepsilon_{11} + N_{12}\varepsilon_{12} + N_{22}\varepsilon_{22}$$

potential energy of the solution

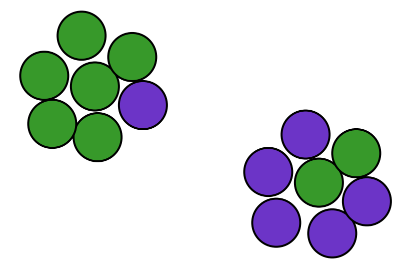
where: N_{ij} is the number of interactions between molecules i and j
ε_{ij} is the energy of interaction between molecules i and j
(interactions assumed to be only between nearest neighbors)

Total number of type 1 neighbors (of any given molecule): zx_1

Total number 1-1 neighboring pairs: $N_1 z x_1 / 2$

eliminates double counting

Total number 1-2 neighboring pairs: $N_1 z x_2 = N_2 z x_1$



z

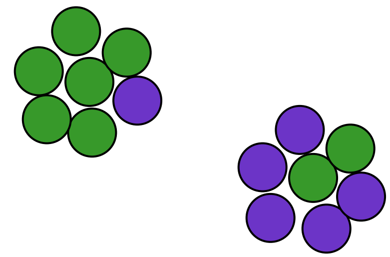
coordination number (here, 6, assumed same for both components, for purpose of simplicity)

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 $x_n = N_n / (N_1 + N_2)$

$$U = \frac{N_1^2 z}{2(N_1 + N_2)}\varepsilon_{11} + \frac{N_1 N_2 z}{N_1 + N_2}\varepsilon_{12} + \frac{N_2^2 z}{2\left(N_1 + N_2\right)}\varepsilon_{22}$$

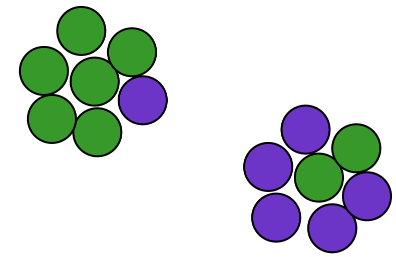
now define a new variable $w = 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}$

$$U = \frac{z\varepsilon_{11}N_1}{2} + \frac{z\varepsilon_{22}N_2}{2} + \frac{zwN_1N_2}{2(N_1 + N_2)}$$

In an ideal solution, all molecular interaction energies are equal, in which case, $w = 0$

Zooming in on Non-ideality

$$U = \frac{z\varepsilon_{11}N_1}{2} + \frac{z\varepsilon_{22}N_2}{2} + \frac{zwN_1N_2}{2(N_1 + N_2)}$$



using $\frac{N_i}{N_A} = n_i$

$$G_{sol} = G_{ideal} + \frac{zwN_1N_2}{2(N_1 + N_2)} \qquad G_{sol} = G_{ideal} + \frac{zwN_An_1n_2}{2(n_1 + n_2)}$$

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial G_{ideal}}{\partial n_1}\right)_{T,P,n_2} + \frac{zwN_A}{2}\left(\frac{\partial\, n_1n_2/(n_1 + n_2)}{\partial n_1}\right)_{n_2}$$

Zooming in on Non-ideality 2

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

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

$$= x_2(1-x_1) = x_2^2$$

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

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

we arrive at: $$\mu_1 = \mu_1^* + RT\ln\left(x_1 e^{ux_2^2/RT}\right)$$

Behold, the activity!

Effect of Non-ideality

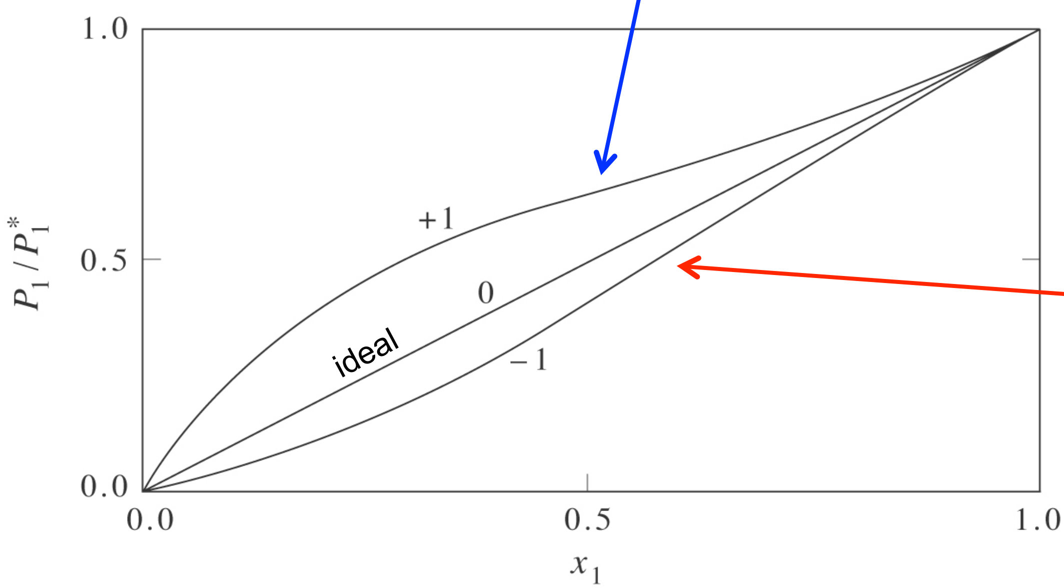
$$\mu_1 = \mu_1^* + RT\ln\left(x_1 e^{ux_2^2/RT}\right)$$

$$u = \frac{z\left(2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}\right)N_A}{2}$$

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

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*

positive deviation from Raoult's Law behavior



negative deviation from Raoult's Law behavior

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:

$$\mu_1 = \mu_1^* + RT\ln x_1 + ux_2^2 \qquad \mu_2 = \mu_2^* + RT\ln x_2 + ux_1^2$$

cf. 2 slides ago

Substitution provides:

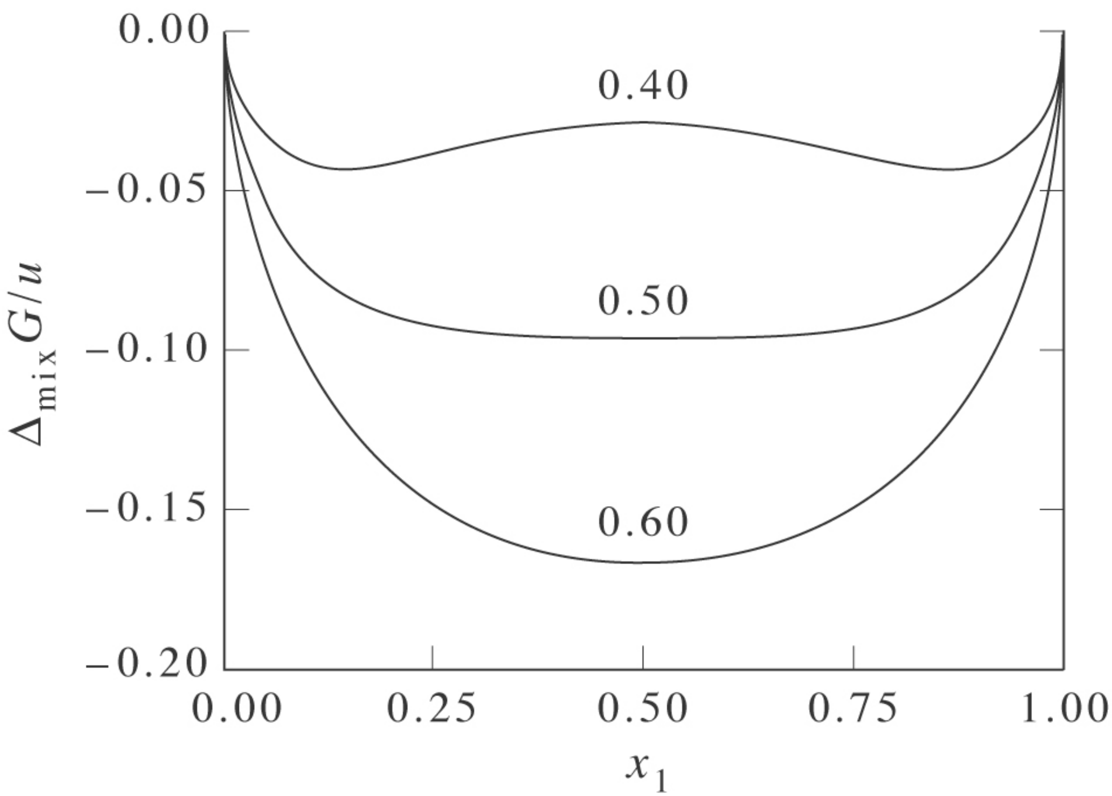
$$\begin{aligned}\Delta_{mix}\bar{G} &= RT\left(x_1\ln x_1 + x_2\ln x_2\right) + x_1ux_2^2 + x_2ux_1^2 \\ &= \Delta_{mix}\bar{G}_{\text{ideal}} + ux_1x_2\left(x_2 + x_1\right) = \Delta_{mix}\bar{G}_{\text{ideal}} + ux_1x_2\end{aligned}$$

$$\bar{G}^{\mathrm{E}} = ux_1x_2 \qquad \bar{H}^{\mathrm{E}} = ux_1x_2 \qquad \bar{S}^{\mathrm{E}} = 0$$

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

$$\frac{\Delta_{\text{mix}}\overline{G}}{u} = \frac{RT}{u}(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2$$



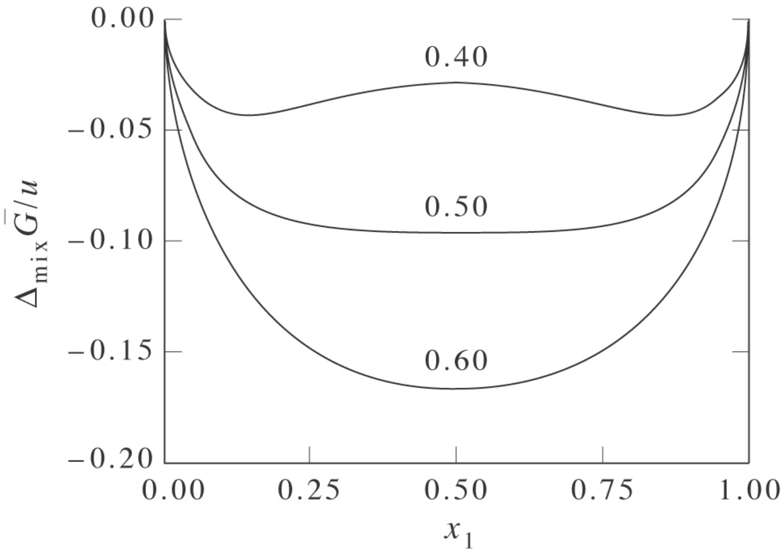
plotted for $RT/u = 0.4, 0.5, 0.6$

$\frac{RT}{u} < 0.5$ unstable region

$\frac{RT}{u} = 0.5$ at critical temp

$\frac{RT}{u} > 0.5$ stable region

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.

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

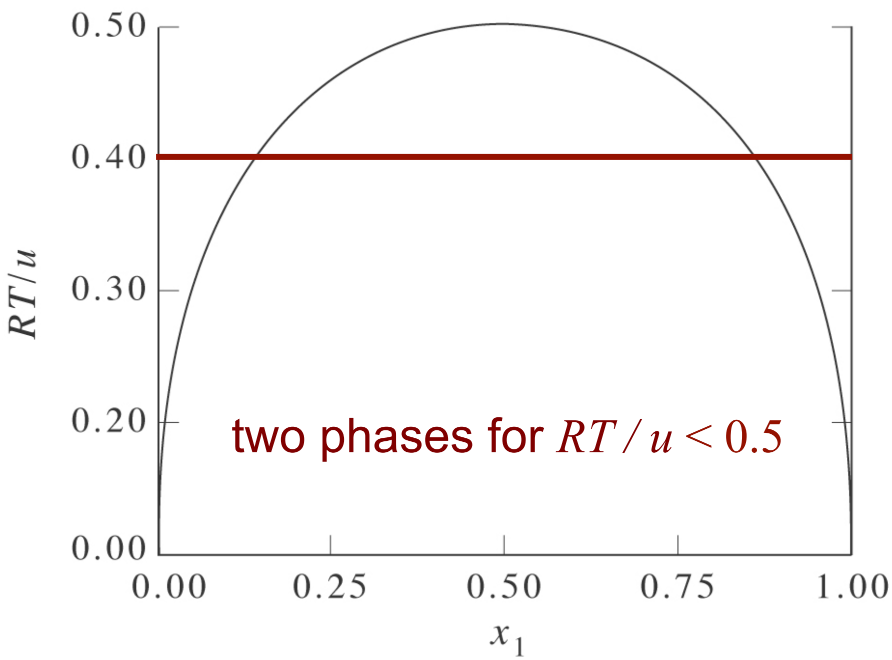
$$\frac{RT}{u} = 0.4,\ \ x_1 \underset{\min\left(\Delta_{mix}\overline{G}/u\right)}{=} 0.145, 0.855$$

To build a temperature composition diagram, one repeats this for a range of temperatures

Temperature-Composition Diagrams Redux

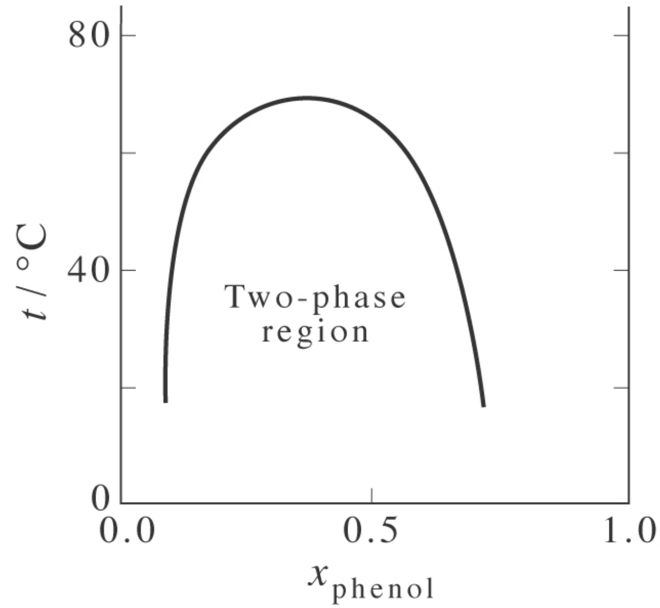
Critical points in composition as a function of RT/u

one phase for $RT/u > 0.5$



two phases for $RT/u < 0.5$

phenol and water



(b)

cf. last slide of video 10.7

Next: Review of Module 10