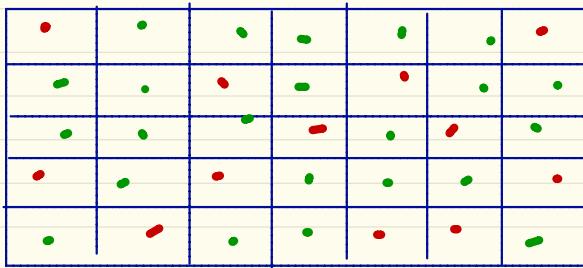


Liquid mixtures

Develop a microscopic model of solutions
Lattice model



N lattice sites that are filled by either species A or B.

$$N = N_A + N_B$$

Suppose all configurations are the same energy

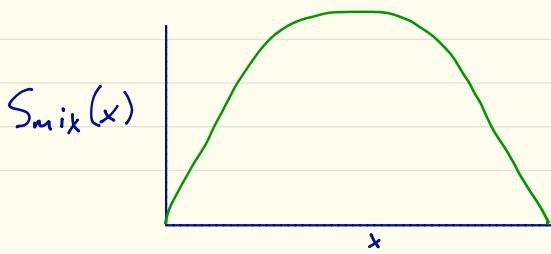
$$\Omega = \frac{N!}{N_A! N_B!} \text{ Arrangements}$$

isomorphic to 2 state problem

$$S_{\text{mix}} = k \ln \Omega = -k \left(N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} \right)$$

$$S_{\text{mix}} = -k \left(x \ln x + (1-x) \ln (1-x) \right)$$

Same result we derived for an ideal gas mixture



If the interactions of A-A, B-B, A-B all the same, then free energy determined only by this S^{mix} .

$$N_A + N_B \rightarrow N_A/N_B$$

$$\Delta U^{\text{mix}} = 0 \quad \Delta V^{\text{mix}} = 0$$

$$\Delta F^{\text{mix}} = \Delta U^{\text{mix}} - T\Delta S^{\text{mix}} = -T\Delta S^{\text{mix}} \quad \text{from above}$$

Any mixture that obeys these rules is an ideal mixture (or Lewis mixture)

$$F(N_A, N_B) = F_A(N_A) + F_B(N_B) - k_B T \Delta S_{\text{mix}}$$

$$\mu_A = \left(\frac{\partial F(N_A, N_B)}{\partial N_A} \right)_{N_B} = f_A + k_B T \ln x_A$$

$$= \mu_A^\circ(T) + k_B T \ln x_A$$

chem pot'l of pure liquid A

(4)

Why do substances form mixtures?

To maximize entropy/minimize (free) energy.

Usually interested in constant T, P situations, so usually think about Gibbs energy

How to characterize a mixture?

Have to indicate amounts of each component in the mixture, N_i . Most conventional to do in terms of mole fractions, although (many) other conventions possible.

N components $\rightarrow N-1$ independent composition variables

$$x_i = \frac{N_i}{N} \quad x_n = 1 - \sum_{i=1}^{n-1} x_i$$

How do properties of mixtures relate to constituent parts?

Might naively think that extensive properties are simple linear combinations of independent elements. Generally not true

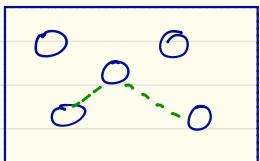
$$v(T, p, x_1, \dots, x_{n-1}) \neq \sum_{i=1}^{n-1} x_i v_i(T, p)$$

similarly for G, S, F, ...

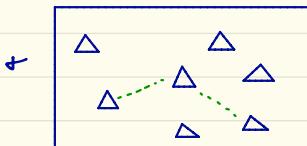
What are microscopic driving forces?

Entropic - mixing things Always (?) increases the configurations available to a system

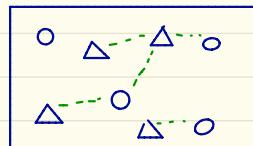
Energetic - A + B may like to be next to each other more (or less) than A with A and B with B



A-A interactions



B-B interactions



A-B interactions

Partial molar properties

In single component system, have molar $j = \frac{J}{N}$

In multicomponent, "molar" properties depend on composition.

$$\bar{J}_i = \left(\frac{\partial J}{\partial N_i} \right)_{T, P, N_j \neq i}$$

Eg, $V = V(T, P, N_1, N_2, \dots)$ 1st order homogeneous

$$dV = \left(\frac{\partial V}{\partial T} \right)_{P, N_i} dT + \left(\frac{\partial V}{\partial P} \right)_{T, N_i} dP + \sum_i \left(\frac{\partial V}{\partial N_i} \right)_{T, P, N_j \neq i} dN_i$$

Define "partial molar volume"

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i} \right)_{T, P, N_j \neq i}$$

How volume changes when an infinitesimal splash of i is added to a mixture at a given composition.

Identical to what we did in

$$U(S, V, N) \rightarrow dU = \left(\frac{\partial U}{\partial S} \right) dS + \left(\frac{\partial U}{\partial V} \right) dV + \left(\frac{\partial U}{\partial N} \right) dN$$

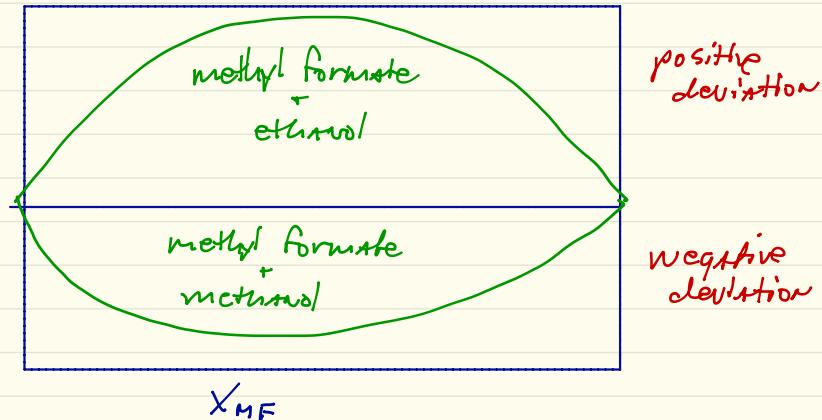
Euler relation:

Because V is homogeneous of order 1, must have

$$V = \sum_i \bar{V}_i N_i , \quad v = \sum_i \bar{v}_i x_i$$

Thus knowing \bar{v}_i permits calculation of total v by addition.

Define $\Delta V_{\text{mix}}(x_i) = \sum_i \bar{v}_i x_i - \sum_i x_i v_i(T, p)$



An "ideal" mixture would have $\Delta V_{\text{mix}} = 0$. Non-ideality can happen in either direction.

Similar rules for all other partial molar quantities

$$H = \sum_i \bar{h}_i N_i \quad h = H/N = \sum_i \bar{h}_i x_i$$

$$C_p = \sum_i \bar{C}_{p,i} N_i \quad c_p = C_p/N = \sum_i \bar{C}_{p,i} x_i$$

Further, all relations that hold on thermodynamic

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potentials and derivatives hold:

$$\bar{h}_i = \bar{u}_i + p\bar{v}_i \quad \bar{f}_i = \bar{u}_i - T\bar{s}_i$$

$$\text{Eg. } H = U + PV \rightarrow \left(\frac{\partial H}{\partial N_i} \right)_{T, P, N_j} = \left(\frac{\partial U}{\partial N_i} \right)_{T, P, N_j} + P \left(\frac{\partial V}{\partial N_i} \right)_{T, P, N_j}$$

$$= \bar{u}_i + P\bar{v}_i$$

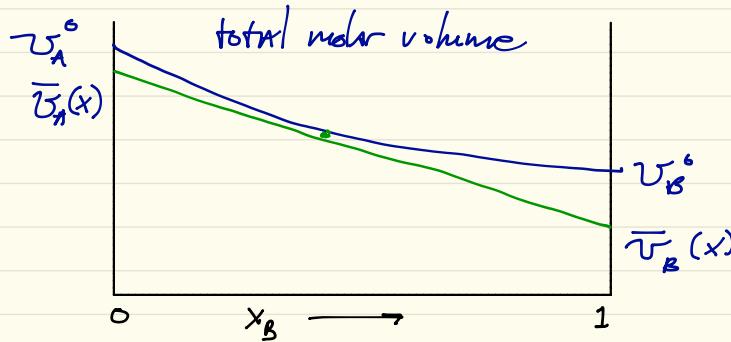
$$\text{Similarly, } d\bar{g}_i = -\bar{s}_i dT + \bar{v}_i dP + \sum_m \left(\frac{\partial \bar{g}_i}{\partial N_m} \right) dN_m$$

Gibbs-Duhem like relationship: @ const T, P

$$dV = \sum_i \bar{v}_i dN_i + \sum_i N_i d\bar{v}_i = \sum_i \bar{v}_i dN_i \rightarrow \boxed{\sum_i N_i d\bar{v}_i = 0}$$

Partial molar quantities not independent

Suppose we could measure volume as a function of composition. What are partial molar quantities?



Consider tangent to volume line:

$$dV = \bar{V}_A dx_A + \bar{V}_B dx_B \quad dx_A + dx_B = 0$$

$$\Rightarrow \frac{dV}{dx_A} = \bar{V}_B - \bar{V}_A \quad \text{slope}$$

$$\text{But } V = \bar{V}_B x_B + \bar{V}_A (1-x_B)$$

1st order homogeneous property

Combining, can show intercept $x_B=1 \rightarrow \bar{V}_B$ intercept +
 " $x_B=0 \rightarrow \bar{V}_A$

If we were to plot ΔV_{mix} rather than V_{mix} , would get intercepts to be $\bar{V}_i - V_i$.

Knowing 1 intercept gives the other. Could use Gibbs-Duhem to get 1 from the other.

More modern approach would be to fit mixture data to a model, eg Redlich-Kister expansion:

$$\Delta V_{\text{mix}} = x_1 x_2 \sum_{k=0}^n a_k (x_1 - x_2)^k$$

Property goes to zero in pure (x_1 or $x_2 = 1$) limits.

Can fit data to models like this and analytically extract \bar{V}_i .

In general, we get partial molar differential quantities by differentiating extensive quantities.

Non-ideal liquid mixtures

What makes solutions not ideal? Different interactions amongst components

Suppose interactions can be described by local interaction energies

$$\begin{array}{ll} U_{AA} & \text{1 NN A-A} \\ U_{BB} & \text{1 NN B-B} \\ U_{AB} & \text{1 NN A-B} \end{array}$$

For a given configuration, the total energy

$$U = m_{AA} U_{AA} + m_{BB} U_{BB} + m_{AB} U_{AB}$$

where m_{ij} count the number of interactions.

If a cell has z sides ($z=6$ for a cubic lattice), there are Nz/z intersections, because each face is shared. Each interaction is either A-A or A-B or B-B.

$$(N_A + N_B) z/2 = m_{AA} + m_{BB} + m_{AB}$$

$$N_A z/2 = m_{AA} + \frac{1}{2} m_{AB} \quad \text{all A-A} + \frac{1}{2} A-B$$

$$N_B z/2 = m_{BB} + \frac{1}{2} m_{AB} \quad \text{ditto}$$

\Rightarrow rearrange $m_{AA} = \frac{1}{2}(zN_A - m_{AB})$

$$m_{BB} = \frac{1}{2}(zN_B - m_{AB})$$

$$U = \frac{1}{2}(zN_A - m_{AB}) U_{AA} + \frac{1}{2}(zN_B - m_{AB}) U_{BB} + m_{AB} U_{AB}$$

$$= \frac{1}{2} z N_A U_{AA} + \frac{1}{2} z N_B U_{BB} + \underbrace{(U_{AB} - \frac{U_{AA} + U_{BB}}{2})}_{\text{difference in bond energy}} m_{AB}$$

In general, would need some Monte Carlo technique to count m_{AB}

Bragg-Williams / mean field approximation
Assume particles randomly distributed

If I'm an A, the average number of B neighbors I have is $\frac{N_B}{N} \cdot z$

$$\text{Thus } m_{AB} = N_A \cdot \left(\frac{N_B}{N}\right) z = z N_A (1-x)$$

$$U = \frac{1}{2} z N_A U_{AA} + \frac{1}{2} z N_B U_{BB} + z \left(U_{AB} - \frac{U_{AA} + U_{BB}}{2} \right) \frac{N_A N_B}{N}$$

$$= \frac{1}{2} z N_A U_{AA} + \frac{1}{2} z N_B U_{BB} + k_B T \chi_{AB} \frac{N_A N_B}{N}$$

$$\chi_{AB} = \frac{z}{k_B T} \left(U_{AB} - \frac{U_{AA} + U_{BB}}{2} \right)$$

dimensionless "exchange" parameter
 energy/kT to swap A and B between pure A + B
 Typically $\chi_{AB} > 0$

Can write down free energy of mixture

$$F(N_A, N_B) = \frac{z}{2} \left(N_A U_{AA} + N_B U_{BB} \right) + \chi_{AB} \frac{N_A N_B}{N} k_B T + k_B T \left(N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} \right)$$

$$\Delta F_{\text{mix}} = F(N_A, N_B) - F(N_A, 0) - F(0, N_B)$$

$$= N k_B T \left[x \ln x + (1-x) \ln (1-x) + \chi_{AB} x (1-x) \right]$$

This is called the Hildebrand regular solution model.

Can extract chemical potentials:

$$\mu_A = \left(\frac{\partial F(N_A, N_B)}{\partial N_A} \right)_{T, N_B} = \underbrace{\frac{z U_{AA}}{2}}_{=} + \chi_{AB} (1-x_A)^2 k_B T + k_B T \ln x_A$$

$$\text{Ditto } \mu_B = \mu_A^* \quad \begin{matrix} \text{chem potl of pure A} \\ \neq \mu_A^\circ \end{matrix}$$

Liquid-liquid phase equilibria

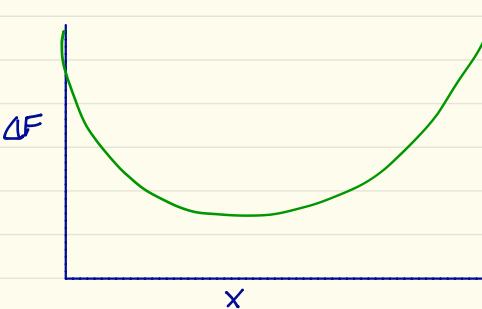
$$\text{Go back to } \Delta F_{\text{mix}} = F(N_A, N_B) - F(N_A, 0) - F(0, N_B)$$

$$= N k_B T [x \ln x + (1-x) \ln (1-x) + \chi_{AB} x (1-x)]$$

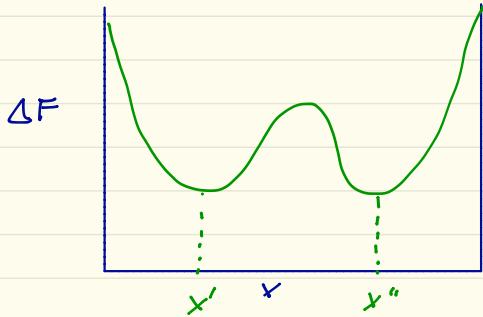
$$\chi_{AB} \propto 1/T$$

How does this behave w/T?

T large, χ_{AB} small



T low, χ_{AB} large

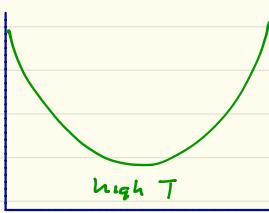
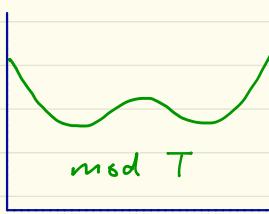
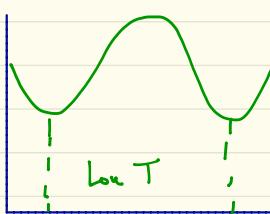


Free energy always convex
Mixture stable at all compositions.
"miscible"

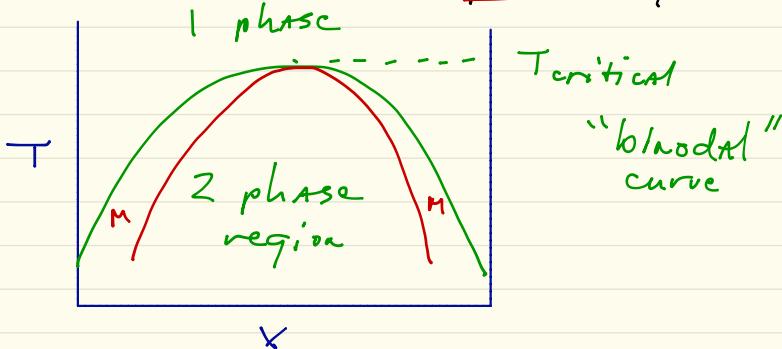
Free energy curve violates
stability criterion in
intermediate region.
"phase separation"

In latter case, common
tangent construction shows that any composition
between x' and x'' is unstable to separating
into these two.

Make this construction for lots of different T's



Connect coexistence points to get phase diagrams



Simple lattice model gives symmetric 2 phase region — consequence of simple pair-wise interaction

Real materials more likely have asymmetric binodal curves.

How would we find x', x'' ?

$$\left(\frac{\partial \Delta F_{\text{mix}}}{\partial x} \right) = 0 \rightarrow N k_B T \left[\ln \left(\frac{x}{1-x} \right) + \chi_{AB} (1-2x) \right] = 0$$

transcendental

How to find amounts of two phases?

Lever rule:

f_A : fraction of A-rich phase

f_B : fraction of B-rich phase

$$f_A + f_B = 1$$

x' : composition of A-rich phase

x'' : " " " B- " "

$$x_0 = \frac{N_B}{N_A + N_B} \quad \text{Mass-balance on B:}$$

$$x_0 = f_A \cdot x' + (1-f_A)x''$$

$$= x'' + f_A (x' - x'')$$

$$f_A = \frac{x_0 - x''}{x' - x''}$$

Closer x_0 is to x' , more x' you get!!

Recall local stability criterion, $\left(\frac{\partial^2 F}{\partial x^2}\right) > 0$

There is a meta-stable spinodal region within the 2-phase region. See M region Above.

Evaluate by taking 2nd derivative of ΔF , setting to zero, and solving for x's.

Critical pt is point at which distinct phases disappear
Binodal + spinodal curves merge here.

The binodal lines given by $\left(\frac{\partial F}{\partial x}\right) = 0$,

spinodal " " " $\left(\frac{\partial^2 F}{\partial x^2}\right) = 0$

As these approach each other, must have

$$\left(\frac{\partial^3 F}{\partial x^3}\right) = 0$$

All this looks very similar to the boiling transition, with the exception that the composition order parameter x is replaced by volume v.

What's missing in this model?

If A-B is attractive/repulsive, B-W under/over estimates interaction #'s. Still...

quasi-chemical

ch 11 of Teller + Modell

Assumes internal free energy of A + B are the same in pure and mixture states.
 μ_i° is same in two states. Doesn't have to be so.

activity?