

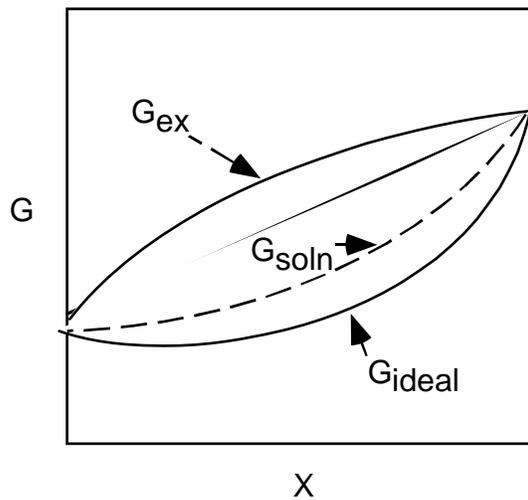
12.480 Handout #2

Non-ideal solutions

Reading Thompson (1967) *Researches in Geochem*, v.2., 340-361.

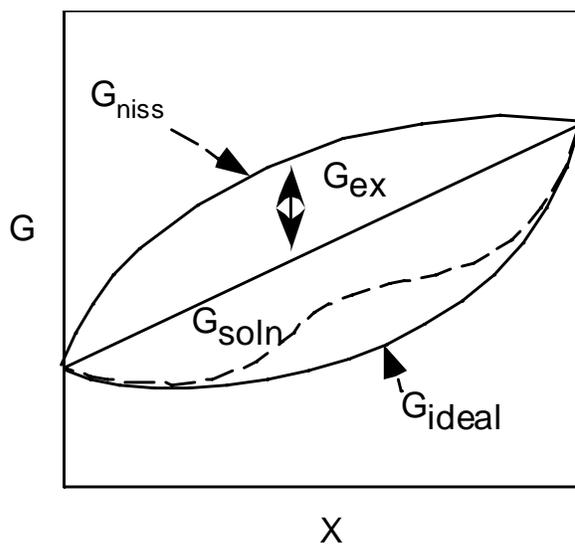
Solutions for which $\Delta H_{\text{mix}} > 0$

Depending on the contribution from ΔH_{mix} , we can have one of two general cases.



I. Solution is stable over entire composition range.

II. Contribution from ΔH is such that solution is stable only near the end members and we have phase separation for intermediate compositions.



In general, we will separate out an excess free energy of mixing term. G_{ex}

then

$$G_{\text{soln}} = \sum_i X_i G_i - T\Delta S_{\text{mix}} + G_{\text{ex}}$$

and we allow

$$G_{\text{ex}} = E_{\text{ex}} - PV_{\text{ex}} - TS_{\text{ex}}$$

Another way of rationalizing G_{ex} is that it is the contribution to free energy left over after the ideal and standard state free energy contributions are subtracted out.

Representations of G_{ex}

There are many ways of representing G_{ex} , and we'll talk about one representation here and about some other examples later.

We will use Margules' power series expansion in terms of the solution components. The choice of a power series as the mathematical representation is a matter of convenience. Some of the criteria are: 1) The method be useful in prediction. 2) Should account for variations in data using the minimum number of fitting parameters, 3) The model should be consistent with mineral site symmetry constraints or molecular constraints. The Margules' expression represents G_{ex} as the third power of composition.

To obtain values for the coefficients of this power series we need to define another expression: G_{niiss}

$$G_{\text{niiss}} = G_{\text{soln}} + T\Delta S_{\text{mix}} = \sum X_i G_i + G_{\text{ex}} = A + BX_2 + CX_2^2 + D X_2^3$$

G_1^* and G_2^* are the hypothetical excess free energies implied by Henry's law behavior. G_2^* is obtained by extrapolating the behavior of component 2 (the solute) in a solvent consisting dominantly of component 1 to a hypothetical state of behavior where the concentration is pure component 2. G_1° and G_2° are the standard state free energies for phases consisting of pure component 1 or 2, respectively. We will derive an expression for G_{ex} that expresses the deviation from ideal behavior as the difference between these two end member standard states ($G_2^* - G_2^\circ$).

First, we'll look at the values of these coefficients in the limits as $X_2 \rightarrow 0$

$$G_{\text{ex}} + X_1 G_1^\circ + X_2 G_2^\circ = A + BX + CX^2 + DX^3$$

$$\text{as } X_2 \rightarrow 0, G_{\text{ex}} \rightarrow 0$$

$$\text{so } G_{\text{ex}} + G_1^\circ = A \text{ and } A = G_1^\circ$$

as $X_2 \rightarrow 1$, $G_{ex} \rightarrow 0$

and $G_1^\circ + B + C + D = G_2^\circ$

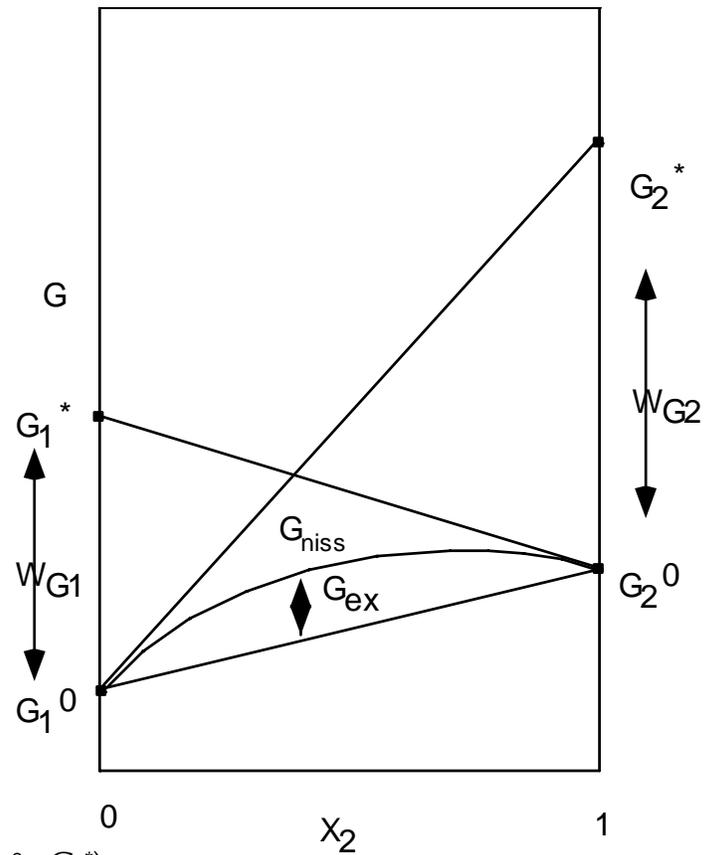
Now take the derivative of G_{si}

$$\partial G_{niss} / \partial X_2 = B + 2CX_2 + 3DX_2^2$$

So, we'll evaluate these in the limits of "infinite dilution"

This is the well known Henry's Law behavior exhibited by solutions.

as $X_2 \rightarrow 0$ $\partial G_{si} / \partial X_2 = B = (G_2^* - G_1^\circ)$



as $X_2 \rightarrow 1$ $\partial G_{si} / \partial X_2 = B + 2C + 3D = (G_2^\circ - G_1^*)$

Therefore,

$$(G_2^* - G_1^\circ) + 2C + 3D = (G_2^\circ - G_1^*)$$

(expression for $\partial G_{niss} / \partial X_2$)

$$G_1^\circ + (G_2^* - G_1^\circ) + C + D = G_2^\circ$$

(Expression for G_{niss})

multiply second expression by 2 and subtract

$$-G_1^\circ - G_2^* + D = -G_2^\circ - G_1^*$$

$$D = (G_2^* - G_2^\circ) - (G_1^* - G_1^\circ)$$

plug back and solve for C

$$C = G_2^\circ - G_2^* - (G_2^* - G_2^\circ) + (G_1^* - G_1^\circ)$$

$C = (G_1^* - G_1^\circ) - 2(G_2^* - G_2^\circ)$
 plug back into G_{niss} and collect terms

$$G_{\text{si}} = G_1^\circ + (G_2^* - G_1^\circ)X_2 + [(G_1^* - G_1^\circ) - 2(G_2^* - G_2^\circ)]X_2^2 \\ + [(G_2^* - G_2^\circ) - (G_1^* - G_1^\circ)]X_2^3$$

if we define $W_{G1} = (G_1^* - G_1^\circ)$

$$W_{G2} = [(G_2^* - G_2^\circ)]$$

$$C = W_{G1} - 2W_{G2}$$

$$D = W_{G2} - W_{G1} \quad (\text{error in JBT})$$

No we are ready to plug in for G_{niss} and simplify

$$G_{\text{si}} = X_1G_1^\circ + X_2G_2^\circ + W_{G2}X_2 + [W_{G1} - 2W_{G2}]X_2^2 \\ + [W_{G2} - W_{G1}]X_2^3$$

$$G_{\text{si}} = \sum X_i G_i^\circ + W_{G2}X_2(1-2X_2 + X_2^2) + W_{G1}X_2^2(1-X_2)$$

$$G_{\text{si}} = \sum X_i G_i^\circ + W_{G2}X_2(X_1)^2 + W_{G1}X_2^2(X_1)$$

$$\text{So, } G_{\text{ex}} = W_{G2}X_2(X_1)^2 + W_{G1}X_2^2(X_1)$$

and the total free energy of the solution can be expressed by plugging G_{niss} in the ideal contribution to the free energy from the existence of a solution. This gives us G_{soln} .

Since $\mu_i^\circ = G_i^\circ$ we can write G_{soln} in the following way

$$G_{\text{soln}} = X_1\mu_1^\circ + X_2\mu_2^\circ + nRT(X_1 \ln X_1 + X_2 \ln X_2) + (W_{G1}X_2 + W_{G2}X_1)X_1X_2$$

$$\text{recall } \mu_1 = G_{\text{soln}} + X_2 \partial G_{\text{soln}} / \partial X_2 \quad P, T = \text{constant}$$

$$\text{and } \mu_2 = G_{\text{soln}} + (1-X_2) \partial G_{\text{soln}} / \partial X_2 \quad P, T = \text{constant}$$

$$\partial G_{\text{soln}} / \partial X_2 = (\mu_2^\circ - \mu_1^\circ) + RT \ln X_2 / X_1 + W_{G1} X_2 (3X_1 - 1) - W_{G2} X_1 (3X_2 - 1)$$

then plug in & simplify:

$$\mu_1 = \mu_1^\circ + nRT \ln X_1 + X_2^2 (W_{G1} + 2(W_{G2} - W_{G1})X_1)$$

The observed departure of a solution from ideal behavior for component 1 is given by the term:

$$X_2^2 (W_{G1} + 2(W_{G2} - W_{G1})X_1)$$

This term can be thought of as μ_1^{ex} and

$$\mu_1^{\text{ex}} = nRT \ln \gamma_1$$

The γ term is a way of expressing the deviation of a solution from ideal behavior through the activity of a component in a phase.

$$a_i = \gamma_i X_i$$

and

$$\mu_1 = \mu_1^0 + nRT \ln a_1$$

$$RT \ln a_1 = RT \ln X_1 + RT \ln \gamma_1$$

Therefore,

$$nRT \ln \gamma_1 = X_2^2 (W_{G1} + 2(W_{G2} - W_{G1})X_1)$$

and

$$\gamma_1 = \exp[X_2^2 (W_{G1} + 2(W_{G2} - W_{G1})X_1) / nRT]$$

Symmetric solutions

We call solutions obeying this power series relation asymmetric solutions. There is a special case called a symmetric solution where $W_{G2} = W_{G1}$ and our expressions reduce to:

$$G_{\text{ex}} = W_G X_1 X_2$$

$$G_{\text{soln}} = X_1 \mu_1^\circ + X_2 \mu_2^\circ + nRT (X_1 \ln X_1 + X_2 \ln X_2) + X_1 X_2 W_G$$

And

$$\mu_1 = \mu_1^\circ + RT \ln X_1 + (1-X_1)^2 (W_G)$$

The G_1^* and G_2^* in our expressions are related to the Henry's law chemical potential. They are the chemical potential of component 1 in a physically unattainable state - that is in pure component 2.

We used Margules (1895) power series and we truncated the power series and obtained a 2 parameter fit. Originally this expression was used in gas-liq systems to describe vapor pressure of a component in a binary solution.

Other expressions for excess free energy

(1) Van laar equations

$$\log \gamma_1 = \frac{A_{12}}{[1 + (A_{12}X_1 / A_{21}X_2)]^2}$$

(2) Redlich-Kister or Guggenheim equation

$$\Delta G_{\text{ex}} / RT = X_1(1-X_1) B + C(2X_1-1) + D(2X_1-1)^2 + \dots$$

an infinite series - again truncated.

(3) Wilson Equation

$$\Delta G_{\text{ex}}/RT = \sum_i X_i \ln \left(\sum_j X_j \Lambda_{ij} \right)$$