

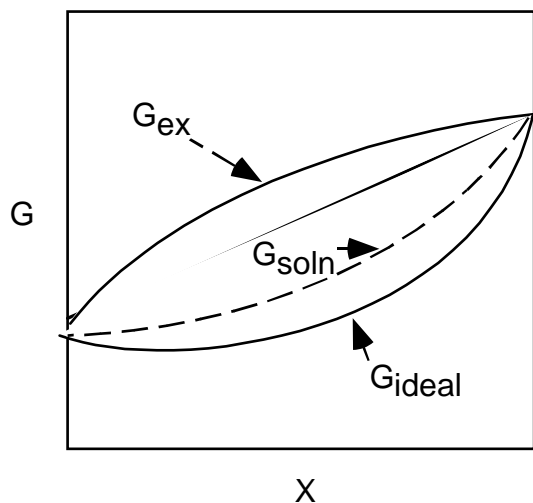
## 12.480 Handout #2

### Non-ideal solutions

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

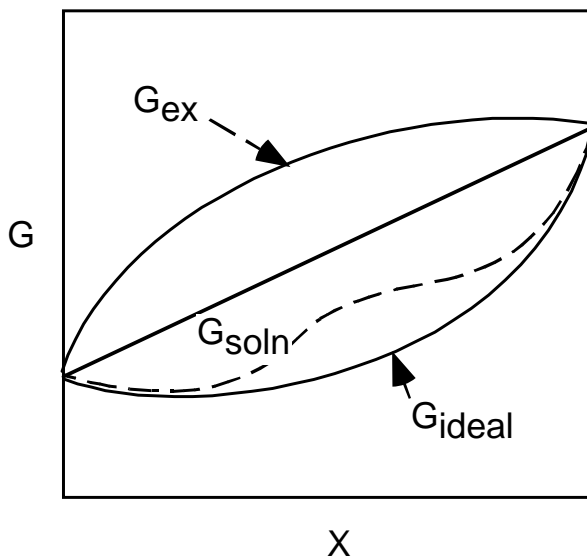
Solutions for which  $\Delta H_{\text{mix}} > 0$

Depending on the contribution from  $\Delta H_{\text{mix}}$ , we can have one of two general cases.



I. Solution is stable over entire composition range.

II. Contribution from  $\Delta H$  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.  $G_{\text{ex}}$

then  $G_{\text{soln}} = \sum X_i G_i - T\Delta S_{\text{mix}} + G_{\text{ex}}$   
and we allow  $i$

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

Another way of rationalizing  $G_{\text{ex}}$  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 $G_{\text{ex}}$*

There are many ways of representing  $G_{\text{ex}}$ , 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  $G_{\text{ex}}$  as the third power of composition.

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

$G_1^*$  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.  $G_1^\circ$  and  $G_2^\circ$  are the standard state free energies for phases consisting of pure component 1 or 2, respectively. We will derive an expression for  $G_{\text{ex}}$  that expresses the deviation from ideal behavior as the difference between these two endmember standard states ( $G_2^* - G_2^\circ$ ).

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

$$G_{\text{ex}} + X_1 G_1^\circ + X_2 G_2^\circ = A + BX_2 + CX_2^2 + DX_2^3$$

$$\text{as } X_2 \rightarrow 0$$

$$\text{as } G_{\text{ex}} + G_1^\circ = 0 \text{ and } A = G_1^\circ$$

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

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

$$\frac{\partial G_{si}}{\partial X_2} = B + 2CX + 3DX_2^2$$

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

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

Therefore,

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

(expression for  $\frac{\partial G_{si}}{\partial X_2}$ )

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

(Expression for  $G_{si}$ )

multiply second expression by 2 and subtract

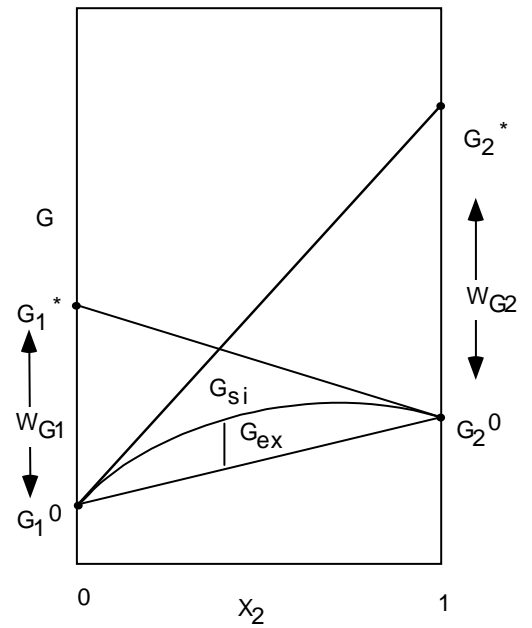
$$-G_1^\circ - G_2^* + D = -G_2^\circ - G_1^*$$

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

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  $G_{si}$  and collect terms

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

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

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

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

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

plug in for  $G_{si}$  and simplify

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

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

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

and the total free energy of the solution can be expressed by plugging in the ideal contribution to the free energy from the existence of a solution. is

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

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

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

then plug in & simplify:

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

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  $\mu_1^{\text{ex}}$  and

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

The  $\gamma$  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

$$\mu_1 = \mu_1^\circ + RT \ln a_1$$

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

Therefore,

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

and

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

*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:

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

$$G = X_1\mu_1^\circ + X_2\mu_2^\circ + nRT (X_1\ln X_1 + X_2\ln X_2) + X_1X_2W_G$$

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

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

(2) Redlich-Kister or Guggenheim equation

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

an infinite series - again truncated.

(3) Wilson Equation

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