Simple (Ideal) Ternary Solution

Binary:

$$\bar{G} = X_A\mu_A^o + X_B\mu_B^o \qquad\qquad + \alpha RT(X_A \ln X_A + X_B \ln X_B)$$

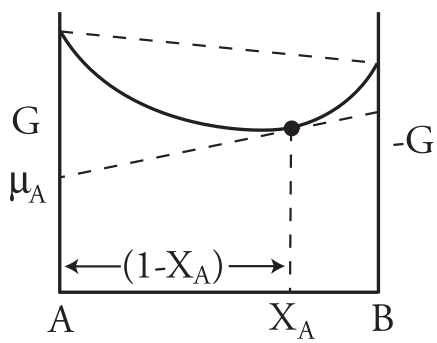
Ternary:

$$\bar{G} = X_A\mu_A^o + X_B\mu_B^o + \underline{X_C\mu_C^o} + \alpha RT(X_A \ln X_A + X_B \ln X_B + \underline{X_C \ln X_C})$$

Notes:

1. $X_C < 1$, so $\ln X_C < 0$. Therefore, adding component C increases $\bar{S}_{config.}$, and so makes G more negative.
2. $\sum_{i=A}^{C} X_i\mu_i^o$ defines a <u>triangular plane</u>: mechanical mixing.

Like a binary, we evaluate μ's (say, μ_A) by "correcting" $\bar{G}$ at the compotition of interest towards composition A:
Binary:

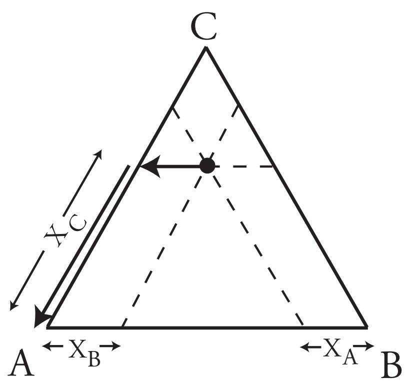


$$\mu_A = G - (1 - X_A)\frac{dG}{dX_A}$$

or

$$= G + (1 - X_A)\frac{dG}{dX_A}$$

Ternary:

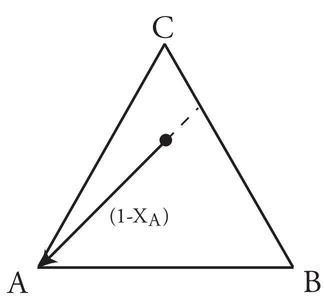


$$\mu_A = G + X_B \left(\frac{\partial G}{\partial X_A}\right)_{X_C} + X_C \left(\frac{\partial G}{\partial X_A}\right)_{X_B}$$

or

$$\mu_A = G + (1 - X_A) \left(\frac{\partial G}{\partial X_A}\right)_{X_B/X_C}$$

where X_B/X_C is a constant ratio.



Symmetrical Ternary

Assume G_{ex} is a polynomial of degree 2 in X_2 and X_3.

$$G_ex = A + BX_2 + CX_3 + DX_2^2 + EX_2X_3 + FX_3^2$$

$$\text{as } X_1 \to 1,\ G_{ex} \to 0 = A$$

$$\text{as } X_2 \to 1,\ G_{ex} \to 0 = B + D$$

$$D = -B$$

$$\text{as } X_3 \to 1,\ G_{ex} \to 0 = C + F$$

$$F = -C$$

$$G_{ex} = BX_2 + CX_3 - BX_2^2 + EX_2X_3 - CX_3^2$$

Reintroducing X_1

$$G_{ex} = BX_2X_1 + CX_3X_1 + (B + C + E)X_2X_3$$

$$W_{G_{12}} = B$$

$$W_{G_{23}} = B + C + E$$

$$W_{G_{13}} = C$$

$$G_{ex} = W_{G_{12}}X_2X_1 + W_{G_{13}}X_3X_1 + W_{G_{23}}X_2X_3$$

$$\alpha RT \ln \gamma_1 = W_{12}X_2^2 + W_{13}X_3^2 + X_2X_3(W_{12} + W_{13} - W_{23})$$

Asymmetrical Ternary

Assume G_{ex} is a polynomial of degree 3 in X_2 and X_3.

$$G_{ex} = A + BX_2 + CX_3 + DX_2^2 + EX_2X_3 + FX_3^2 + GX_2^3 + HX_2X_3^2 + IX_2^2X_3 + JX_3^3$$

$$\text{as } X_1 \to 1,\ G_{ex} \to 0 = A$$

$$\text{as } X_2 \to 1,\ G_{ex} \to 0 = B + D + G$$

$$B = -D - G$$

$$\text{as } X_3 \to 1,\ G_{ex} \to 0 = C + F + J$$

$$C = -F - J$$

$$G_{ex} = D(X_2^2 - X_2) + EX_2X_3 + F(X_3^2 - X_3) + G(X_2^3 - X_2) + HX_2X_3^2 + IX_2^2X_3 + J(X_3^3 - X_3)$$

$$\begin{aligned} G_{ex} = {} & X_1^2X_2(-D - G) + X_1X_2^2(-D - 2G) + X_1^2X_3(-F - J) + X_1X_3^2(-F - 2J) \\ & + X_2^2X_3(-D + E - F - 2G + I - J) + X_2X_3^2(-D + E - F - G + H - 2J) \\ & + X_1X_2X_3(-2D + E - 2F - 2G - 2J) \end{aligned}$$

$$G_{ex} = W_{G_{12}}X_1^2X_2 + W_{G_{21}}X_2^2X_1 + W_{G_{13}}X_1^2X_3 + W_{G_{31}}X_3^2X_1 + W_{G_{23}}X_2^2X_3 + W_{G_{32}}X_3^2X_2$$

And setting

$$W_{12} \equiv -D - 2G$$

$$W_{21} \equiv -D - G$$

$$W_{13} \equiv -F - 2J$$

$$W_{31} \equiv -F - J$$

$$W_{23} \equiv -D + E - F - G + H - 2J$$

$$W_{32} \equiv -D + E - F - 2G + I - J$$

$$W_{123} \equiv G - \frac{1}{2}H - \frac{1}{2}I + J$$

We obtain

$$G_{ex} = W_{12}(X_1X_2)(X_2 + \frac{1}{2}X_3) + W_{21}(X_1X_2)(X_1 + \frac{1}{2}X_3) + W_{13}(X_1X_3)(X_3 + \frac{1}{2}X_2)$$
$$+W_{31}(X_1X_3)(X_1 + \frac{1}{2}X_2) + W_{23}(X_2X_3)(X_3 + \frac{1}{2}X_1) + W_{32}(X_2X_3)(X_2 + \frac{1}{2}X_1)$$
$$+W_{123}(X_1X_2X_3)$$

Ternary Solutions

$$G_{ex} = \alpha RTX_1 \ln \gamma_1 + \alpha RTX_2 \ln \gamma_2 + \alpha RTX_3 \ln \gamma_3$$

$$\left(\frac{\partial G_{ex}}{\partial X_1}\right)_{X_3} = \alpha RT \ln \gamma_1 - \alpha RT \ln \gamma_2$$

$$\left(\frac{\partial G_{ex}}{\partial X_1}\right)_{X_2} = \alpha RT \ln \gamma_1 - \alpha RT \ln \gamma_3$$

Obtain G_{ex} as a function of the partials and γ_1 only.

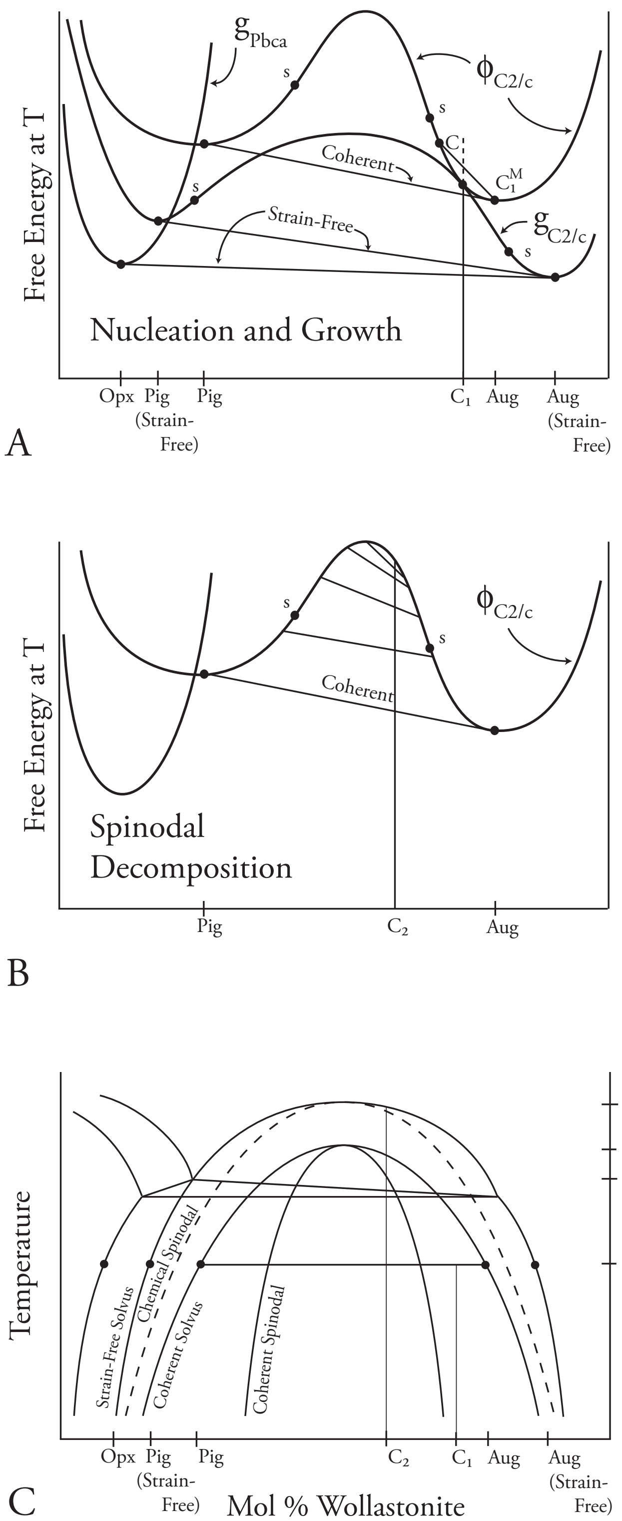
$$G_{ex} = \alpha RTX_1 \ln \gamma_1 - X_2 \left(\frac{\partial G_{ex}}{\partial X_1}\right)_{X_3} + \alpha RTX_2 \ln \gamma_1 - X_3 \left(\frac{\partial G_{ex}}{\partial X_1}\right)_{X_2} + \alpha RTX_3 \ln \gamma_1$$

$$\alpha RT \ln \gamma_1 = G_{ex} + X_2 \left(\frac{\partial G_{ex}}{\partial X_1}\right)_{X_3} + X_3 \left(\frac{\partial G_{ex}}{\partial X_1}\right)_{X_2}$$

$$\alpha RT \ln \gamma_2 = G_{ex} + X_1 \left(\frac{\partial G_{ex}}{\partial X_2}\right)_{X_3} + X_3 \left(\frac{\partial G_{ex}}{\partial X_2}\right)_{X_1}$$

$$\alpha RT \ln \gamma_3 = G_{ex} + X_1 \left(\frac{\partial G_{ex}}{\partial X_3}\right)_{X_2} + X_2 \left(\frac{\partial G_{ex}}{\partial X_3}\right)_{X_1}$$

Unmixing Mechanisms for Non-Ideal Solutions



Above: Free-energy versus composition and temperature versus composition diagrams illustrating the exsolution mechanisms of nucleation and growth and of spinodal decomposition. (A) shows free-energy curves g_{Pbca} and $g_{C2/c}$ for the strain-free phases, and $\phi_{C2/c}$ for the strained phases, at temperature T. The compositions of the two coexisting pairs of strain-free phases indicated by the common tangents (labeled strain-free), are "Opx" and "Aug (strain-free)," and "Pig (strain-free)" and "Aug (strain-free)." The compositions of the coexisting pair of coherent phases, indicated by the common tangent (labeled coherent), are given by the position of "Pig" and "Aug." (B) shows a free-energy curve for $C2/c$ phases strained by coherency. (C) shows the pseudobinary phase diagram. The coherent spinodal and chemical spinodal are curves defined by the loci of the inflection points (s), on the free-energy curves $\phi_{C2/c}$ and $g_{C2/c}$, respectively, as a function of temperature. The coherent solvus and strain-free solvus are curves defined by the loci of the common-tangent points of free-energy curves $\phi_{C2/c}$ and $g_{C2/c}$, respectively. The orthopyroxene-augite strain-free solvus (outermost curves) is defined by the common-tangent points on free-energy curves g_{Pbca} and $g_{C2/c}$.