12.480 Handout #3

Reading

Stormer (1975) Am.Mineral 60, 667-674.

Whitney and Stormer (1977) Am.Mineral 62, 687-691.

Andersen and Lindsley (1981) GCA 45, 847-853.

Two feldspar thermometry-barometry

The use of coexisting plagioclase and alkali feldspars to predict temperature and pressure of equilibration was first proposed by Barth (1951) who used natural phase assemblages to calibrate a thermometer. Whitney and Whitney and Stormer subsequently develop a simple thermodynamic model for treating feldspar equilibria. The important assumptions for this model were:

1.) Use one of the conditions of equilibrium.

$$\mu_{Ab}^{AF} = \mu_{Ab}^{PF}$$

where AF = alkali feldspar and PF = plagioclase feldspar.

2.) Assume that Or content in PF has no effect on a_{Ab}^{PF} and that An content in AF has no effect on a_{Ab}^{AF}.

The equilibrium condition can be written

$$\mu_{Ab}^{AF} = \mu_{Ab}^{oAF} + RT\ln a_{Ab}^{AF}$$
$$\mu_{Ab}^{PF} = \mu_{Ab}^{oPF} + RT\ln a_{Ab}^{PF}$$

3.) Assume that the standard state chemical potential for pure Ab in both phases was the same.

Then

$$0 = RT\ln \frac{a_{Ab}^{AF}}{a_{Ab}^{PF}}$$

$$= RT\ln \frac{\gamma_{Ab}^{AF}\; X_{Ab}^{AF}}{\gamma_{Ab}^{PF}\; X_{Ab}^{PF}}$$

4.) Assume $\gamma_{Ab}^{PF} = 1$

$$\text{so } \ln \frac{X_{Ab}^{AF}}{X_{Ab}^{PF}} = \ln\gamma_{Ab}^{AF}$$

$$\ln \gamma_{Ab}^{AF} = \frac{1}{RT}(2W_{GOr} - W_{GAb})X_{Or}^{AF\,2} + 2(W_{GAb} - W_{GOr})\, X_{Or}^{AF\,3}$$

Several of the simplifications of the Whitney and Stormer thermometer have been dealt with in subsequent models of feldspar equilibria, and some have not.

<u>First assumption:</u>

The μ^{o}'s are not equal and we require two sets of W's!

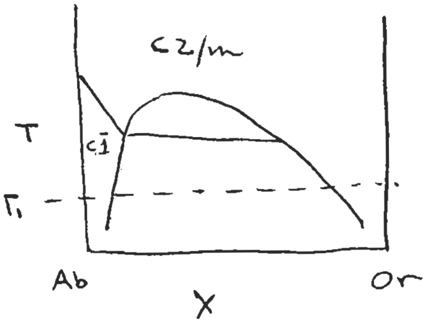
$$\text{so } \mu_{Ab}^{AF} = \mu_{Ab}^{PF}$$

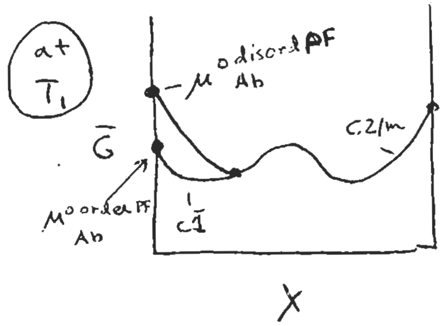
$$\mu_{Ab}^{AF} = \mu_{Ab}^{o\,\text{disordAF}} + RT\ln \gamma_{Ab}X_{Ab}$$

where W's were appropriate to disordered 0.

$$\mu_{Ab}^{PF} = \mu_{Ab}^{o\,\text{ordered plag}} + RT\ln\gamma_{Ab}X_{Ab}$$

potentially we also need W's for a different solution.





Second Assumption

A ternary soln. model would be more appropriate.

$$RT\ln\gamma_1 = W_{G12}X_1^2X_2 + W_{G21}X_2^2X_1$$
$$+ W_{G13}X_1^2X_3 + W_{G31}X_3^2X_1$$
$$+ W_{G23}X_2^2X_3 + W_{G32}X_3^2X_2$$

Margules formulations for ternary and quaternary solutions were developed by Wohl (1946, 1953).

Lindsley and Anderson (1981) go through the exercise of deriving an expression for a ternary asymmetric model. These models, like the ones for binary systems assume that a polynomial of degree 2 (symmetric) or degree 3 (asymmetric) in component 2 and 3 are adequate models of the excess free energy of mixing.

Ghiorso (1984) Contrib Mineral Petrol 87:282-296.
Fuhrman and Lindsley (1988) Amer. Mineral. 73:201-215.
Elkins and Grove (1990) Amer. Mineral. 75: 544-559.

Wen and Nekvasil (1994) Comp Geosci 20: 1025-1040.
Kroll et al. (1993) Contrib Mineral Petrol 114: 510-519.
Green and Udansky (1986) Amer. Mineral. 71:1100-1108.
Stormer and Whitney (1985) Amer. Mineral. 70:52-64.
Brown and Parsons (1981) Contrib Mineral Petrol 76:369-377.
Johannes (1979) Contrib Mineral Petrol 68:221-230.
Seck (1971a)Neues Jahrb. Mineral. Abh. 115:315-345.
Seck (1971b) Contrib Mineral Petrol 31:67-86

Ghiorso (1984)

In this paper Ghiorso expanded the Al-avoidance configurational entropy model of Kerrick and Darken (1975) and Newton et al. (1980) to ternary feldspars. The Kerrick and Darken approach is intended to provide an approximation of the ideal part of the activity when mixing takes place with charge balance constraints. We know this as coupled substitution. These moels for the ideal part of the activity give larger negative values to the entropy of mixing term ($-T\Delta S_{mix}$).

Ghiorso used the constraints from all three equilibria to estimate equilibration temperature.

Ghiorso's analysis of Seck's (1971) experimental data resulted in a negative W_s term for the W_{oran} excess parameter.

Green and Udansky (1986)

In this paper Seck's 1, 5 and 10 kbar data were used to derive a Wv term for the An-Or excess free energy term. The magmitude of this term was large and led Green and Udansky and others to suggest a pressure sensitivity to feldspar equilibria. Therefore, coexisting feldspars might serve as a barometer and a thermometer.

Stormer and Whitney (1985) estimated a pressure for the Fish Canyon tuff of 8 to 9 kbar (24-27 km depth). They cite a pressure dependence of 18 ^oC/kbar on feldspar equilibria. This pressure dependency comes from Brown and Parsons (1981) CMP 76:369-377. B&P fit a pressure dependency to the Ab-Or solvus using a variety of experimental data, and derive this pressure dependency.

Fuhrman and Lindsley (1988)

In response to the G&U and S&W papers, F&L remodeled the Seck 1 kbar experimental data. Their contribution to evolution of these models was to fit x-ray data for ternary feldspars to derive an expression for W_v. They also evaluate critically the utility of two feldspar thermometry and provide a calculation procedure for estimating two-feldspar temperatures.

Elkins and Grove (1990)

New experimental data on coexisting ternary feldspars and a model for excess free energy that uses the simpler XlnX formulation for $-T\Delta S_{mix}$.

$$\bar{G}^{xs} = (A) + BX_2 + CX_3 + DX_2^2 + EX_2X_3 + FX_3^2 + GX_2^3 + HX_2X_3^2 + IX_2^2X_3 + JX_3^3 \qquad (2)$$

where the third-degree terms (with coefficients G, H, I, J) account for ternary asymmetry. Setting X_1, X_2, and X_3 successively to 1, we find

$$A = 0; \quad B = -D - G; \quad C = -F - J.$$

Substituting these values, and noting that, since

$$X_1 + X_2 + X_3 = 1,$$
$$X_2^3 = X_2(1 - X_1 - X_3)(1 - X_1 - X_3),$$

we obtain:

$$\begin{aligned}
\bar{G}^{xs} &= (-D - G)X_2 + (-F - J)X_3 + DX_2^2 \\
&\quad + EX_2X_3 + FX_3^2 + G(X_2 - 2X_1X_2 \\
&\quad - 2X_2X_3 + X_1^2X_2 + 2X_1X_2X_3 + X_2X_3^2) \\
&\quad + HX_2X_3^2 + IX_2^2X_3 + J(X_3 - 2X_1X_3 \\
&\quad - 2X_2X_3 + X_1^2X_3 + 2X_1X_2X_3 + X_2^2X_3) \\
&= D(X_2^2 - X_2) + (E - 2G - 2J)X_2X_3 \\
&\quad + F(X_3^2 - X_3) - 2GX_1X_2 - 2JX_1X_3 \\
&\quad + (H + G)X_2X_3^2 + (I + J)X_2^2X_3 \\
&\quad + GX_1^2X_2 + JX_1^2X_3 + (2G + 2J)X_1X_2X_3
\end{aligned}$$

Since

$$X_2^2 - X_2 = X_2(X_2 - 1) = X_2(-X_1 - X_3)$$

and

$$X_3^2 - X_3 = X_3(X_3 - 1) = X_3(-X_1 - X_2),$$

$$\begin{aligned}
\bar{G}^{xs} &= D(-X_1X_2 - X_2X_3) + (E - 2G - 2J)X_2X_3 \\
&\quad + F(-X_1X_3 - X_2X_3) - 2GX_1X_2 \\
&\quad - 2JX_1X_3 + (H + G)X_2X_3^2 + (I + J)X_2^2X_3 \\
&\quad + GX_1^2X_2 + JX_1^2X_3 + (2G + 2J)X_1X_2X_3.
\end{aligned}$$

Next multiply each of the first five terms by $(X_1 + X_2 + X_3)$:

$$\begin{aligned}
\bar{G}^{xs} &= D(-X_1^2X_2 - 2X_1X_2X_3 - X_1X_2^2 - X_2^2X_3 \\
&\quad - X_2X_3) + (E - 2G - 2J) \\
&\quad \times (X_1X_2X_3 + X_2^2X_3 + X_2X_3^2) \\
&\quad + F(-X_1^2X_3 - 2X_1X_2X_3 - X_2^2X_3 \\
&\quad - X_1X_3^2 - X_2X_3^2) - 2G(X_1^2X_2 + X_1X_2^2 \\
&\quad + X_1X_2X_3) - 2J(X_1^2X_3 + X_1X_2X_3 \\
&\quad + X_1X_3^2) + (H + G)X_2X_3^2 + (I + J)X_2^2X_3 \\
&\quad + GX_1^2X_2 + JX_1^2X_3 + (2G + 2J)X_1X_2X_3.
\end{aligned} \qquad (3)$$

Now that all composition terms are of third degree, we collect terms and simplify:

$$\begin{aligned}
\bar{G}^{xs} &= X_1^2X_2(-D - G) + X_1X_2^2(-D - 2G) \\
&\quad + X_1^2X_3(-F - J) + X_1X_3^2(-F - 2J) \\
&\quad + X_2^2X_3(-D + E - F - 2G + I - J) \\
&\quad + X_2X_3^2(-D + E - F - G + H - 2J) \\
&\quad + X_1X_2X_3(-2D + E - 2F - 2G - 2J)
\end{aligned} \qquad (4)$$

Asymmetrical Ternary – assume G^{ex} is a polynomial of degree 3 in X_2 and X_3

This is similar to our eqn (1) where $W_{21} = -D - G$, etc., and $W_{123} = -2D + E - 2F - 2G - 2J$. Note, however, that in this formulation W_{123} is partly a function of the second-degree (*symmetric*) coefficients D, E, and F, and is independent of H and I, two of the third-degree (asymmetric) coefficients! Thus, setting W_{123} to zero in eqn (1), as done deliberately by ANDERSEN and LINDSLEY [1979, eqn (15), p. 499] and implicitly by THOMPSON (1967), requires a relation between second- and third-degree coefficients

$$[2G + 2J = -2D + E - 2F]$$

that appears unlikely.

A better approach is to collect terms in eqn (3) in such a way that the coefficient of $X_1X_2X_3$ contains only G, H, I, and J—the asymmetric ternary coefficients of the power series. To do so, we must distribute the second-degree portions of the coefficient over the binary terms, and thus obtain:

$$\begin{aligned}
\bar{G}^{xs} &= (-D - G)(X_1^2X_2 + \tfrac{1}{2}X_1X_2X_3) \\
&\quad + (-D - 2G)(X_1X_2^2 + \tfrac{1}{2}X_1X_2X_3) \\
&\quad + (-F - J)(X_1^2X_3 + \tfrac{1}{2}X_1X_2X_3) \\
&\quad + (-F - 2J)(X_1X_2^2 + \tfrac{1}{2}X_1X_2X_3) \\
&\quad + (-D + E - F - 2G + I - J) \\
&\quad \times (X_2^2X_3 + \tfrac{1}{2}X_1X_2X_3) \\
&\quad + (-D + E - F - G + H - 2J) \\
&\quad \times (X_2X_3^2 + \tfrac{1}{2}X_1X_2X_3) \\
&\quad + (G - \tfrac{1}{2}H - \tfrac{1}{2}I + J)(X_1X_2X_3)
\end{aligned} \qquad (5)$$

and setting

$$\begin{aligned}
W_{12} &\equiv -D - 2G; \\
W_{21} &\equiv -D - G; \\
W_{13} &\equiv -F - 2J; \\
W_{31} &\equiv -F - J; \\
W_{23} &\equiv -D + E - F - G + H - 2J; \\
W_{32} &\equiv -D + E - F - 2G + I - J; \\
W_{123} &\equiv G - \tfrac{1}{2}H - \tfrac{1}{2}I + J;
\end{aligned}$$

we obtain

$$\begin{aligned}
\bar{G}^{xs} &= W_{12}(X_1X_2)(X_2 + \tfrac{1}{2}X_3) + W_{21}(X_1X_2) \\
&\quad \times (X_1 + \tfrac{1}{2}X_3) + W_{13}(X_1X_3)(X_3 + \tfrac{1}{2}X_2) \\
&\quad + W_{31}(X_1X_3)(X_1 + \tfrac{1}{2}X_2) + W_{23}(X_2X_3) \\
&\quad \times (X_3 + \tfrac{1}{2}X_1) + W_{32}(X_2X_3)(X_2 + \tfrac{1}{2}X_1) \\
&\quad + W_{123}(X_1X_2X_3)
\end{aligned} \qquad (6)$$

where the bold terms show the differences from eqn (1). Equation (6), although cumbersome, is more appropriate than eqn (1), because the W_{123} term now contains only third-degree (asymmetric) coefficients. By setting $G = H = I = J = 0$ (hence, $W_{123} \equiv 0$ and $W_{12} = W_{21}$, etc.), we find that eqn (6) reduces to the symmetric ternary expression. Likewise, it reduces to the asymmetric binaries if we set each mole fraction successively to zero.

Simple (ideal) Ternary solution

Binary $\quad \bar{G} = X_A \mu_A^\circ + X_B \mu_B^\circ \quad + \alpha RT(X_A \ln X_A + X_B \ln X_B)$

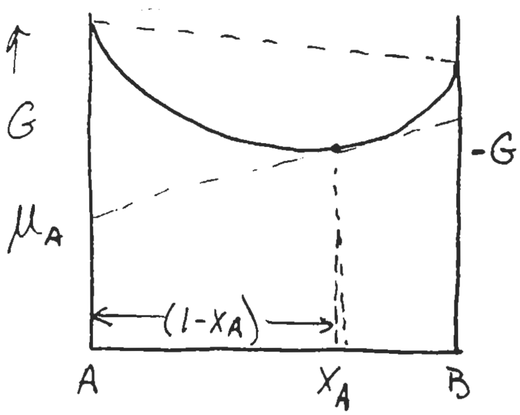
Ternary $\quad \bar{G} = X_A \mu_A^\circ + X_B \mu_B^\circ + \underline{X_C \mu_C^\circ} + \alpha RT(X_A \ln X_A + X_B \ln X_B + \underline{X_C \ln X_C})$

Notes: 1. $X_C < 1$, so $\ln X_C < 0$. Therefore, adding component C increases $\bar{S}_{config}$, and so makes G more negative.

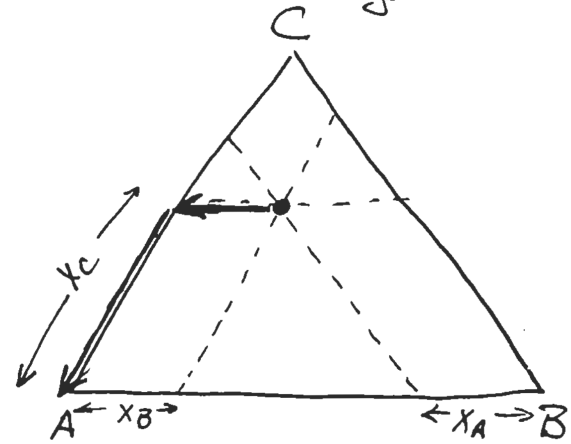
2. $\sum_{i=A}^{C} X_i \mu_i^\circ$ defines a triangular plane: mechanical mixing

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

Binary:



Ternary:



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

or

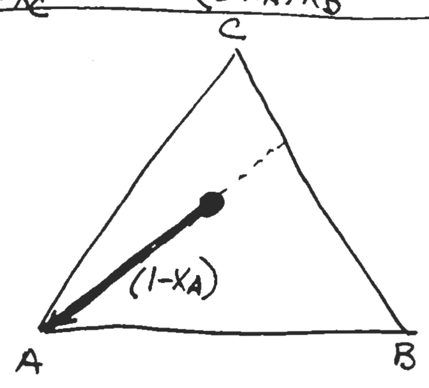
$$= G + (1-X_A)\frac{\partial G}{\partial X_A}$$

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

or

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

constant ratio



Ternary solutions

$$G_{ex} = \alpha RT X_1 \ln \gamma_1 + \alpha RT X_2 \ln \gamma_2 + \alpha RT X_3 \ln \gamma_3$$

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

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

obtain G_{ex} as a fnc. of the partials & γ_1 only

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

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

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

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