L.M. Barron

THERMODYNAMIC MULTICOMPONENT SILICATE EQUILIBRIUM PHASE CALCULATIONS

Dept. of Geology Ph.D.

ABSTRACT

Phase equilibria of solution phase - solution phase and pure phase - solution phase type in binary and ternary systems are calculated by computer assuming zero excess entropy of mixing. The multicomponent activities are calculated with a thermodynamically consistent equation. Input data are heats of fusion and partial excess chemical potentials of mixing derived from binary phase diagrams. The system Quartz - Fayalite - Leucite has a calculated internal immiscibility field at liquidus temperatures above 1100°C. The solid solution liquidus is calculated for the Granite system and Diopside - Albite - Anorthite with an accuracy of ± 8°C, ± 5% composition of liquid and ± 2% of crystal. Isocons of the coexisting solid solution phase (icophases) are contoured on the ternary liquidus. An empirical multicomponent correction free energy with n independent parameters is suggested to adjust calculated results to experiments using one (eutectic minimum) or two (cotectic line) points. The calculations can be used to guide experiments.

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Multicomponent Silicate Equilibrium Phase Calculations

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A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy.

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July, 1970

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Phase equilibria of solution phase - solution phase and pure phase - solution phase type in binary and ternary systems are calculated by computer assuming zero excess entropy of mixing. The multicomponent activities are calculated with a thermodynamically consistent equation. Input data are heats of fusion and partial excess chemical potentials of mixing derived from binary phase diagrams. The system Quartz - Fayalite - Leucite has a calculated internal immiscibility field at liquidus temperatures above 1100°C. The solid solution liquidus is calculated for the Granite system and Diopside - Albite - Anorthite with an accuracy of ± 8°C, ± 5% composition of liquid and ± 2% of crystal. Isocons of the coexisting solid solution phase (icophases) are contoured on the ternary liquidus. An empirical multicomponent correction free energy with n independent parameters is suggested to adjust calculated results to experiments using one (eutectic minimum) or two (cotectic line) points. The calculations can be used to guide experiments.

SYMBOLS

$\overset{x}{V}$	superscript x for excess thermodynamic function V
$\overset{k}{V}$	superscript k for correction thermodynamic function V
V_i^A	superscripts A, B, crystal, liquid, for function V of phases
V_i^A	subscripts i, k, 1, 2, for function V of components
R	gas constant
μ	chemical potential
G	Gibbs free energy
H	enthalpy
S	entropy
T	absolute temperature
X	mole fraction
N	number of moles, stoichiometric constants
a	activity
γ	activity coefficient
T_i	temperature of fusion of a solid phase pure in component i
ΔH_i°	heat of fusion of a solid phase pure in component i
$\Delta H_i'$	superscript ' used for the value of ΔH_i° estimated from a liquidus in binary ij
W_{ij}	regular or subregular solution model interaction energy parameter
$\overset{x}{G}_{ij}$	actual value of excess free energy of mixing across the binary ij
Z_{ij}	normalized mole fraction of component i in binary ij
θ_{ij}	slope of $\overset{x}{G}_{ij}$ at Z_{ij}
n	number of components in the system
C_p	an arbitrary constant with $2 \leq p \leq n$

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CLAIM TO ORIGINAL WORK

1) Formulation of asymmetric n - component excess free energy of mixing model and corresponding formulas for n - component activity coefficients.

2) Computerized derivation of general binary partial excess chemical potentials from phase diagrams of simple eutectic type and solid solution type.

3) Computerized method for calculating tie lines between solution phase one - solution phase two:

   I ternary immiscible liquid one - ternary immiscible liquid two

   II binary crystal (ie. plagioclase) - ternary liquid

   The process can be generalized to more than three components.

4) Formulation of empirical n - component correction free energy model with n independent parameters for adjusting calculated results to experimental results using a few selected key experimental points such as:

   Phase invariant points, two points on cotectic lines, three points on cotectic surfaces.

   If compositions of the coexisting solid solution minerals are known, one point is sufficient.

ACKNOWLEDGEMENTS

I would like to acknowledge the financial assistance of the National Research Council for three years support on Grant number 1560. In addition I would like to mention the debt owed to Dr. A.R. Philpotts for his encouragement and continuing support with regard to the degree. Helpful questions and criticisms came also from Dr. D.M. Carmichael and Dr. G.M. Anderson, and from fellow students M. Marchand, N. Gray and Y. Lamontagne. The topic was originally a subject prepared for a seminar in "Current Problems in Petrology" supervised by Dr. E.H. Kranck and Dr. A.R. Philpotts of the Department of Geological Sciences, McGill University. Often interesting and highly informative discussions on many topics resulted from these open seminars. I would like to also thank Sandy Conway (the typist) for her patience and fast delivery.

1. INTRODUCTION

Theories of Non - Ideal Liquids and Methods of Calculating Immiscibility

The development of theories of non - ideal liquids dates back to Margules (1895), Hildebrande (1929), and Scatchard (1935). However, in increasing relevance to the development of the dissertation, important treatments begin with Blander (1964), who developed and derived formulae for the theoretical properties of a molecular scale model of a non - ideal liquid. This required complex equations with a large number of poorly known parameters, especially if the model was extended past a first order approximation. Calculated results compared satisfactorily with experimental determinations only on certain molten salt systems. Darken and Gurry (1953) presented a more empirical approach that was applied to a few metal alloy systems while Lumsden (1966) used a similar but more detailed approach to treat and discuss in detail almost four hundred molten salt systems. He included as well, excess entropy corrections which strongly reduced errors of a first order approximation. These treatments were for binary systems only. Thompson (1967), in a very informative paper, derived easily handled expressions for non - ideality from macroscopic considerations. The expressions included two orders of approximation.

Bowen (1928) briefly studied non - ideal liquidus surfaces in petrologic systems and used the cryoscopic equation:

$$\ln(a_i) = \frac{\Delta H_i}{R}\left(\frac{1}{T_{oi}} - \frac{1}{T}\right)$$

where ΔH_i is molar enthalpy of fusion of component i and T_{oi} is the temperature of fusion of pure i, and a_i is the activity of i in liquid, to generate partial excess differential free energies of mixing for systems with a simple binary eutectic and no solid solution. Other techniques for obtaining binary excess chemical potentials have been studied indirectly through phase diagrams and by direct experimental measurements. For instance, Thompson (1967) derived a formula for calculating two non - ideality constants from a known immiscibility field in a binary system. Muan, Masse and Rosen (1966) used a gaseous side reaction to buffer iron and cobalt activities to determine isothermal non - ideality in the solid solution of Fe_2SiO_4 and Co_2SiO_4. Pelton and Flengas (1969) developed a computer handled analytical technique for treating non - ideality calculations in a ternary system. He showed how activity coefficients of all three components could be calculated if twenty or more isothermal partial excess free energies for component one were available to be fitted to a fifteen parameter surface by the method of least squares. The method is general and extremely useful, but requires coverage of the ternary with activity data for component one. Experiments on vapour pressures, volatility data, chemical reactivity in gaseous side-reaction or crystallization point depression can provide this ternary data, but the most accessible type of data (phase diagrams with isotherms) is the most difficult to use. This is because the primary liquidus coexisting with crystalline "A" is terminated at the ternary eutectic and does not cover the whole compositional field.

Darken and Gurry (1953), Blander (1964), Lumsden (1966), and Thompson (1967) and Thompson and Waldbaum (1969a, 1969b) used one, two or three parameters to fit by least squares the excess free energies and excess entropy across the binary interval from x=0 to x=1. However, the methods developed in this dissertation allow use of the actual excess free energy values and when the rest of the non - ideal theory is transformed in the same fashion, nonlinear simultaneous equations describing a phase set can be solved by computer. While Bowen's approach and use of the cryoscopic equation was immediately usable, it was necessary to alter slightly Thompson's approach to solving for immiscibility and derive methods of interpreting three additional types of common behavior:

solid solution-liquid equilibria (plagioclase-liquid)
solid solution-solid solution (ortho-clinopyroxene)
incongruent melting of solids (orthoclase to leucite+liquid)

Excess free energies for two component pairs can now be calculated from binary phase data for all types of behavior. Ternary excess free energies can be estimated at any point by a combination of the binary excess free energies. It is not difficult to estimate n-ternary excess free energies (and consequently activity coefficients) from a combination of the binaries but it becomes difficult to solve the equations of a specific phase set unless a specific distribution of the fourth and higher components is assumed (ie. constant 4% H_2O in all non-aqueous phases in a system containing three or more components as well as water).

The main qualitative methods of predicting immiscibility have been presented in papers in the Journal of American Ceramic Society. Levin and Block (1957-1967) in a series of four papers, reviewed and developed various methods based on molecular models for determining the extent of miscibility gap. The methods are based on coordination and structural studies, oxygen volume relationships, and additive cell density studies. When applied to a large number of ceramic oxide systems, these methods gave reasonable estimates of the compositional limits of binary and some ternary immiscibility fields (two points for a binary, three points for a ternary), but neither the temperature dependence nor the thermal maximum could be calculated. As a result the calculations are valid only for systems where the immiscibility volumes show little variation with temperature. Using thermodynamics, Kadik and Khitarov (1963) discussed the role of various thermodynamic properties in affecting the topology of immiscible water-silicate melt equilibria. Charles and Wagstaff (1967, 1968) studied two types of systems: the alkali metal oxide-silica systems (R_2O-SiO_2) and the $B_2O_3-SiO_2$ system in an attempt to calculate the extent of metastable immiscibility. Liquidus data close to R_2O were not available, so that volatility data and Knudsen cell data were used to generate excess free energies for these regions while the cryO-scopic equation was used close to SiO_2 and throughout the $B_2O_3-SiO_2$ system. The immiscibility fields were determined by graphical construction from a series of isothermal plots of total free energy versus composition. Experimental results roughly verified Charles and Wagstaff's calculated metastable immiscibility regions. The much larger discrepancies in the R_2O-SiO_2 systems were probably due in part to the mixed source of activity data. Christie (1968) used a similar graphical construction to discuss the spinodal mechanism of exsolution in the alkali feldspars. Mueller (1964b), Thompson (1967) and Kern and Weisbrod (1967) demonstrated the theory of calculating or determining graphically a binary immiscibility field by solving the so-called immiscibility equations, which are set up with one or two fixed non - ideality parameters. Olson (1965) calculated a ternary liquidus and developed a repeat graphical construction technique for positioning the <u>extension</u> of a regular binary immiscibility field into a regular ternary solution, providing the approximate orientation of the tie lines are known. The calculations ignored excess entropy of mixing. Blander (1968) studied molten salt systems and derived an equation involving binary regular solution parameters for calculating the maximum immiscibility temperature in a ternary. The relationship between immiscibility in reciprocal systems and some additive ternary systems was demonstrated for salts. The effects of melting temperatures, enthalpies of fusion, and total free energies on the topology of molten ternary salt systems is discussed very well by Blander. For every binary a single non - ideality parameter is calculated from the experimental eutectic temperature and composition. Then these parameters were used to calculate liquidus temperatures in the ternary systems of the reciprocal type. The results compared very well in surface details with the known liquidus, although the error in the ternary eutectic was larger than possible experimental error. In addition the calculated diagram violated the Alkemade theorem. Excess entropy of mixing was not considered, and <u>All</u> calculated non-ideality parameters were negative ie. the mixtures show negative departures from ideality (towards compound formation) as opposed to the positive departures (towards immiscibility) so common in silicate liquids. There were no calculations done of liquidus surfaces in ternary systems where there was any positive deviations shown in the binaries.

The procedures developed in this dissertation allow direct calculation of points on an immiscibility field for two and three component systems. Excess entropy of mixing is not included in the treatment. A comparison of calculated liquidus temperatures with immiscibility temperatures distinguishes between stable and metastable immiscibility fields and fixes the curve of intersection of a stable immiscibility field and a liquidus surface. In addition points on the liquidus extending into ternary systems from a binary or ternary solid solution phase can be calculated by a similar process to calculating immiscibility tie-line. Isocons of coexisting solid solution phase were contoured on the liquidus, making it possible to construct all types of crystallization paths accurately. Empirical correction free energies, that can be calculated by comparison of calculated results with 1, 2 or 3 experimental points, permit adjustment of calculations to experimental results.

2. DERIVATION OF ACTIVITY COEFFICIENT EXPRESSIONS

2.I Partial and Total Excess Free Energy, the Operator D( ) and the Regular Solution Model

The original definition of the excess quantities can be extended to chemical potentials (Thompson 1967) so that for component I

$\underset{REAL}{\mu_i} \equiv \underset{IDEAL}{\mu_i} + \underset{EXCESS}{\overset{x}{\mu}_i}$ where the superscript ^{x} indicates an excess quantity.

However, $\underset{REAL}{\mu_i} = \mu_i^\circ + RT\ln a_i$ where γ_i is an activity coefficient.

$= \mu_i^\circ + RT\ln X_i + RT\ln\gamma_i$

Since $\underset{IDEAL}{\mu_i} = \mu_i^\circ + RT\ln X_i$ it follows that $\overset{x}{\mu}_i = RT\ln\gamma_i$. Like other partial molar quantities, $\overset{x}{\mu}_i$ satisfies

$$\overset{x}{\mu}_i = \overset{x}{G} - (1-N_i)\,\frac{\partial(\overset{x}{G})}{\partial(1-N_i)} \qquad \text{Moore (1963)}$$

$$= \overset{x}{G} + (1-N_i)\,\frac{\partial(\overset{x}{G})}{\partial(N_i)} \qquad \underline{2\text{-}1}$$

$$\overset{x}{G} = \sum_{i=1}^{n} \overset{x}{\mu}_i N_i \qquad \underline{2\text{-}2}$$

The symbols used in (2-1,2) are the excess free energy $\overset{x}{G}$ and the number of moles N_i of component I. It is more convenient in later developments to use the mole fraction X_i rather than N_i . The partial differential ∂N_i means that all other $N_j (j \neq i)$ are to be held constant and hence the internal ratios of $\frac{N_j}{N_k}\ (i \neq j \neq k)$ are constant. If the total number of moles is N_T , it follows that $\frac{N_j}{N_T} \Big/ \frac{N_k}{N_T}\ (i \neq j \neq k)$ are also constant. Since $X_j = \frac{N_j}{N_T}$ then ∂N_i can be replaced by dX_i where the differential dX_i is constrained to a path so that the internal ratios of $\frac{X_j}{X_k}\ (i \neq j \neq k)$ are constant. This path lies in the line joining $X_i = X_i$ and $X_i = 1$. This method of differentiation will be referred to by the operator $\frac{D(\ )}{D(\ )}$ and (2-1) is redefined as

$$\overset{x}{\mu}_i = \overset{x}{G} + (1-X_i)\,\frac{D(\overset{x}{G})}{D(X_i)} \qquad \underline{2\text{-}3}$$

The regular solution model as used by Kern and Weisbrod (1967) and others is based on the nearest neighbour approximation followed by assumptions of randomness and negligible excess volume of mixing. Consider an n - component system (I,J,K,...) in the volume V that contains one mole total. All state functions of the system are hence molar quantities. The nearest neighbour first order approximation is that the only important interactions are independently bimolecular of the well defined form I - I or I - J, and that the resulting internal energies of association E_{I-J} are fixed independent of the matrix. In terms of relative numbers, the number of interactions of type I - J is X_iX_j and the number of interactions of type I - I is X_iX_i . Summing over all pairs of components, the total number of interactions of all acceptable types is

$$\sum_{i=1}^{n} X_i^2 + \sum_{i=1}^{n} \sum_{j\neq i}^{n} X_iX_j = \sum_{i=1}^{n} X_i^2 + 2\sum_{i=1}^{n} \sum_{j>i}^{n} X_iX_j$$
$$= \left(\sum_{i=1}^{n} X_i\right)^2 = 1$$

Thus the relative numbers are also the normalized occupation numbers of the various internal energy levels of association E_{I-J} . For the exchange association of components I, J according to

$$(I-I) + (J-J) \rightleftharpoons 2(I-J)$$

the excess internal energy per association I - J is

$$\omega_{I-J} = E_{I-J} - \tfrac{1}{2}\left(E_{I-I} + E_{J-J}\right)$$

The total molar excess internal energy $\overset{x}{e}$ in volume V is the sum of the products of normalized occupation number and the excess internal energy level value (Moore 1963, Laidler 1965)

$$\overset{x}{e} = 2\sum_{i=1}^{n} \sum_{j>i}^{n} X_iX_j\,\omega_{I\cdot J}$$
$$= \sum_{i=1}^{n} \sum_{j>i}^{n} X_iX_j\,W_{I\cdot J} \qquad \text{where } W_{I\cdot J} \equiv 2\,\omega_{I\cdot J}$$

The terms involving X_i^2 drop out as $\omega_{I\cdot I}=0$. If we now make use of the assumptions of randomness $(\overset{x}{s}=0)$ and negligible excess volume of mixing then

$$\overset{x}{G} = \overset{x}{h} - T\overset{x}{s} = \overset{x}{h} = \overset{x}{e} + P\overset{x}{v}$$
$$= \overset{x}{e} = \sum_{i=1}^{n} \sum_{j>i}^{n} X_iX_j\,W_{I\cdot J} \qquad \underline{2-4}$$

Applying (2-4) to a binary, $\overset{x}{G} = x_1 x_2 W_{12} = X_1(1-X_1)W_{12}$ and (2-3)

$$\overset{x}{\mu}_1 = \overset{x}{G} + (1-X_1)\frac{D(\overset{x}{G})}{D(X_1)} = X_1(1-X_1)W_{12} + (1-X_1)(1-2X_1)W_{12}$$

$$= W_{12}(1-X_1)(X_1+1-2X_1)$$

$$= (1-X_1)^2 W_{12}$$

Similarly $\overset{x}{\mu}_2 = (1-x_2)^2 W_{12}$ and as a check of (2-2)

$$X_1\overset{x}{\mu}_1 + X_2\overset{x}{\mu}_2 = X_1(1-X_1)^2 W_{12} + X_2(1-X_2)^2 W_{12}$$

$$= W_{12} X_1 X_2 (1-X_1+1-X_2)$$

$$= X_1 X_2 W_{12}$$

$$= \overset{x}{G}$$

2.II The Asymmetric Model Defined by Extension of the Regular Solution Model and Derivation of Equations for $\overset{x}{\mu}$.

Consider the n-component regular solution model where

$$\overset{x}{G} = \sum_{i=1}^{n}\sum_{j>i} X_i X_j W_{IJ} \tag{2-4}$$

Each binary pair ij contributes $X_i X_j W_{IJ}$ to the total $\overset{x}{G}$. This can be interpreted as

$$X_i X_j W_{IJ} = \left[\left(\frac{X_i}{X_i+X_j}\right)\left(\frac{X_j}{X_i+X_j}\right)W_{IJ}\right]\boldsymbol{\left(X_i+X_j\right)^2}$$

The term in square brackets is the value of $\overset{x}{G}$ in the binary ij at composition $\left(\frac{X_i}{X_i+X_j}\right)$ and the term in heavy parentheses is the DILUTION FACTOR by which the binary excess free energy is multiplied by to take it into the n-component system. Making $\overset{x}{G}_{ij}$ the value of the excess free energy in the binary ij at $\left(\frac{X_i}{X_i+X_j}\right)$ then $\overset{x}{G}$ becomes

$$\overset{x}{G} = \sum_{i=1,n}^{n}\sum_{j>i}^{n} (X_i+X_j)^2\, \overset{x}{G}_{ij} \tag{2-5}$$

This is the asymmetric model and makes use of the actual values of $\overset{x}{G}_{ij}$ that occur in the binaries. It is necessary to use (2-3) on (2-5) to derive consistent expressions for $\overset{x}{\mu}_i$. Now the double summation (2-5) **for**

the purposes of considering component 1, can be broken into $\sum_{j\neq 1}^{n} (x_j + x_1)^2 \overset{x}{G}_{1j}$ and $\sum_{i\neq 1}^{n} \sum_{j>i} (x_i + x_j)^2 \overset{x}{G}_{ij}$. To allow use of the $D(\ )$ operator, $\frac{x_3}{x_2} = C_3$, $\frac{x_4}{x_2} = C_4$ and $\frac{x_P}{x_2} = C_P$ where P is an integer $2 \leqslant P \leqslant n$.
Since $\sum_{i=1}^{n} x_i = 1$ then $x_1 + x_2 \left(\sum_{2}^{n} C_P \right) = 1$
Rearranging $x_2 = \frac{(1-x_1)}{\sum_2 C_P}$ and using $x_P = x_2 C_P = \frac{C_P (1-x_1)}{\sum_2 C_P}$
Thus $\frac{C_P}{\sum_2 C_P} = \frac{x_P}{(1-x_1)}$. Using operator $D(\ )$ on these relations 2-6

$$D(x_2) = - \frac{D(x_1)}{\sum_2 C_P} \qquad \text{and} \qquad D(x_P) = - \frac{C_P D(x_1)}{\sum_2 C_P} \tag{2-7}$$

Considering terms from $\sum_{j\neq 1}^{n} (x_1 + x_j)^2 \overset{x}{G}_{1j}$

$$\frac{D\left((x_1+x_j)^2 \overset{x}{G}_{1j} \right)}{D(x_1)} = 2 (x_1 + x_j) \overset{x}{G}_{1j} \left(1 + \frac{D(x_j)}{D(x_1)} \right) + (x_1 + x_j)^2 \frac{D\left(\overset{x}{G}_{1j} \right)}{D\left(\frac{x_1}{x_1 + x_j} \right)} \frac{D\left(\frac{x_1}{x_1+x_j} \right)}{D(x_1)}$$

Defining $\theta_{ij} \equiv \frac{D\left(\overset{x}{G}_{ij} \right)}{D\left(\frac{x_i}{x_i + x_j} \right)}$ and using (2-7) followed by (2-6) then

$$\frac{D\left((x_1+x_j)^2 \overset{x}{G}_{1j} \right)}{D(x_1)} = 2 (x_1 + x_j) \overset{x}{G}_{1j} \left(1 - \frac{C_P}{\sum_2 C_P} \right) + (x_1 + x_j)^2 \theta_{1j} \left[\frac{x_1 + x_j - x_1 \left(1 - \frac{C_j}{\sum_2 C_P} \right)}{(x_1 + x_j)^2} \right]$$

$$= 2 \frac{(x_1 + x_j) \overset{x}{G}_{1j} (1 - x_1 - x_j)}{(1 - x_1)} + \theta_{1j} \left[x_1 + x_j - \frac{x_1 (1 - x_1 - x_j)}{(1 - x_1)} \right]$$

$$= \left(\frac{1}{1 - x_1} \right) \left[2 (x_1 + x_j) \overset{x}{G}_{1j} \left(1 - (x_1 + x_j) \right) + x_j \theta_{1j} \right]$$

Since the result is independent of the C_P , then this holds for all $j \neq 1$.
Considering terms from $\sum_{i\neq 1}^{n} \sum_{j>i}^{n} (x_i + x_j)^2 \overset{x}{G}_{ij}$,

$$\frac{D\left((x_i+x_j)^2 \overset{x}{G}_{ij} \right)}{D(x_1)} = 2 (x_i + x_j) \overset{x}{G}_{ij} \left(\frac{-[C_i + C_j]}{\sum_2 C_P} \right)$$

Since $\frac{x_i}{x_j}$ is some sort of constant, then $Z = \left(\frac{x_i}{x_i + x_j} \right)$ is also constant and thus $\overset{x}{G}_{ij}$ as found at Z in the binary is also fixed independent of x_1 .

Hence $\overset{x}{G}_{ij}$ is treated as a constant to $D(x_1)$ in the above differentiation.

Using (2-6)

$$\frac{D\left((x_i+x_j)^2\overset{x}{G}_{ij}\right)}{D(x_1)} = -2\,(x_i+x_j)\,\overset{x}{G}_{ij}\,\frac{(x_i+x_j)}{(1-x_1)}$$

$$= -2\,\frac{(x_i+x_j)^2}{(1-x_1)}\overset{x}{G}_{ij}$$

This is independent of choice of $\mathcal{G}$ and hence is true for all $(i \neq j \neq 1)$.

From (2-3) then $\overset{x}{u}_1 = \overset{x}{G} + (1-x_1)\frac{D(\overset{x}{G})}{D(x_1)}$ so

$$\overset{x}{u}_1 = \sum_{j \neq 1}^{n} \overset{x}{G}_{1j}[x_1+x_j][2(1-x_1-x_j)+x_1+x_j] + \sum_{j \neq 1}^{n} x_j\,\theta_{1j} - \sum_{i \neq 1}^{n}\sum_{j>i}^{n} (x_i+x_j)^2\overset{x}{G}_{ij}$$

$$= 2\sum_{j \neq 1}^{n}(x_1+x_j)\overset{x}{G}_{1j} + \sum_{j \neq 1}^{n} x_j\,\theta_{1j} - \overset{x}{G}$$

The general formula then must be

$$\overset{x}{u}_i = 2\sum_{j \neq i}^{n}(x_i+x_j)\overset{x}{G}_{ij} + \sum_{j \neq i}^{n} x_j\,\theta_{ij} - \overset{x}{G} \qquad \underline{2\text{-}8}$$

As a check of (2-2)

$$\sum_{i=1}^{n} x_i\,\overset{x}{u}_i = 2\sum_{i=1}^{n}\sum_{j \neq i}^{n} x_i(x_i+x_j)\overset{x}{G}_{ij} + \sum_{i=1}^{n}\sum_{j \neq i}^{n} x_i x_j\,\theta_{ij} - \overset{x}{G}\sum_{i=1}^{n} x_i$$

The coefficients of $\overset{x}{G}_{ij}$ are

$x_i(x_i+x_j)+x_j(x_i+x_j) = (x_i+x_j)^2$

because $\overset{x}{G}_{ij} = \overset{x}{G}_{ji}$

The coefficients of θ_{ij} are $x_i x_j - x_j x_i = 0$ because $\theta_{ij} = -\theta_{ji}$.

Making use of these properties

$$\sum_{i=1}^{n} x_i\,\overset{x}{u}_i = 2\sum_{i=1}^{n}\sum_{j>i}^{n}(x_i+x_j)^2\overset{x}{G}_{ij} - \overset{x}{G}$$

$$= 2\overset{x}{G} - \overset{x}{G}$$

$$= \overset{x}{G}$$

Applying the general formula (2-8) for three components

$$\overset{x}{\mu}_1 = 2\left[(X_1+X_2)\overset{x}{G}_{12} + (X_1+X_3)\overset{x}{G}_{13}\right] + X_2\,\theta_{12} + X_3\,\theta_{13} - \overset{x}{G}$$

$$\overset{x}{\mu}_2 = 2\left[(X_2+X_1)\overset{x}{G}_{12} + (X_2+X_3)\overset{x}{G}_{23}\right] - X_1\,\theta_{12} + X_3\,\theta_{23} - \overset{x}{G} \qquad \underline{2\text{-}9}$$

$$\overset{x}{\mu}_3 = 2\left[(X_3+X_1)\overset{x}{G}_{13} + (X_3+X_2)\overset{x}{G}_{23}\right] - X_1\,\theta_{13} - X_2\,\theta_{23} - \overset{x}{G}$$

where $\overset{x}{G} = (X_1+X_2)^2\overset{x}{G}_{12} + (X_1+X_3)^2\overset{x}{G}_{13} + (X_2+X_3)^2\overset{x}{G}_{23}$

The form of $\overset{x}{G}_{ij}$ and θ_{ij} in (2-8) is completely unspecified. This is an advantage, for now if we wish to specify a certain model, say the n-component regular solution model, then (2-8) can be used to generate the corresponding general $\overset{x}{\mu}$. Defining $Z_{ij} \equiv \left(\frac{X_i}{X_i+X_j}\right)$ then from (2-4) $\overset{x}{G}_{ij} = Z_{ij}(1-Z_{ij})W_{ij}$ so that $\theta_{ij} = \frac{D(\overset{x}{G}_{ij})}{D(Z_{ij})} = (1-2Z_{ij})W_{ij}$.

Reintroducing X_i and X_j results in $\overset{x}{G}_{ij} = \frac{X_i X_j}{(X_i+X_j)^2}W_{ij}$ and

$$\theta_{ij} = \left(1 - \frac{2X_i}{(X_i+X_j)}\right)W_{ij} = \left(\frac{X_j - X_i}{X_i+X_j}\right)W_{ij}$$

Then by (2-8) we have

$$\overset{x}{\mu}_i = 2\sum_{j\neq i}^{n} \frac{X_i X_j W_{ij}}{(X_i+X_j)} + \sum_{j\neq i}^{n} \frac{X_j(X_j - X_i)W_{ij}}{(X_i+X_j)} - \overset{x}{G}$$

$$= \sum_{j\neq i}^{n} \frac{W_{ij}}{(X_i+X_j)}\left[2X_iX_j - X_j^2 - X_iX_j\right] - \overset{x}{G}$$

$$\overset{x}{\mu}_i = \sum_{j\neq i}^{n} X_j W_{ij} - \overset{x}{G} \qquad \underline{2\text{-}10}$$

For a more complex type of $\overset{x}{G}$, it is not necessary to generate the explicit equations for $\overset{x}{\mu}_i$. A general computer routine which uses (2-8) with the appropriate substitutitons is also valid. Consider for example, Thompson's (1967) formulation of

$$\overset{x}{G} = \sum_{i=1}^{n} \sum_{j>i} X_i X_j (Z_{ij} W_{ji} + Z_{ji} W_{ij})$$ where $W_{ij} \neq W_{ji}$. Now

for use of (2-8) $\overset{x}{G}_{ij} = Z_{ij}(1-Z_{ij})(Z_{ij} W_{ji} + (1-Z_{ij}) W_{ij})$

and then $$\Theta_{ij} \equiv \frac{D(\overset{x}{G}_{ij})}{D(Z_{ij})} = W_{ij}(1-3Z_{ij})(1-Z_{ij}) + W_{ji} Z_{ij} (2-3Z_{ij})$$

The general routine then becomes, with the symbols defined as

GT ≡ $\overset{x}{G}$
X(I) ≡ X_i
W(I,J) ≡ W_{ij}
TH(I,J) ≡ Θ_{ij}
RTLG(I) ≡ α_i

```
C  ROUTINE CALCULATES N-COMPONENT RTLG(I) AT (X1,X2,X3,...,XN)
      GT=0
      DO 20 I=1,N
      RTLG(I)=0
      I1=I+1
      DO 10 J=I1,N
      IF(J.EQ.N+1)GO TO 10
      Z=X(I)/(X(I)+X(J))
11    G(I,J)=Z*(1.-Z)*(Z*W(J,I)+(1.-Z)*W(I,J))
12    TH(I,J)=W(I,J)*(1.-3.*Z)*(1.-Z)+W(J,I)*Z*(2.-3.*Z)
      GT=GT+G(I,J)*(X(I)+X(J))**2
      RTLG(I)=RTLG(I)+2.*G(I,J)*(X(I)+Y(J))+X(J)*TH(I,J)
10    CONTINUE
20    CONTINUE
      DO 30 I=1,N
30    RTLG(I)=RTLG(I)-GT
```

If a different formulation were used, this routine would function properly if statements 11 and 12 were changed accordingly. While the problem of solution of phase equilibria has not yet been solved for more than three components, the awkardness of the formulae, as noted by Thompson (1967), has been completely removed for any multicomponent formulation of $\overset{x}{G}$.

To conclude then, the general formulae for activity coefficients are:

1) Symmetric non-ideality $\overset{x}{G}_{ij} = Z_{ij} Z_{ji} W_{ij}$ and $\overset{x}{G} = \sum_{i=1}^{n} \sum_{j>i} X_i X_j W_{ij}$

then $$\overset{x}{\mu}_i = \sum_{j \neq i}^{n} x_j w_{ij} - \overset{x}{G} \qquad \underline{2-10}$$

2) Asymmetric non-ideality $$\overset{x}{G} = \sum_{i=1}^{n} \sum_{j > i} (x_i + x_j)^2 \overset{x}{G}_{ij} \qquad \underline{2-5}$$

$$\overset{x}{\mu}_i = 2 \sum_{j \neq i}^{n} (x_i + x_j) \overset{x}{G}_{ij} + \sum_{j \neq i}^{n} x_j \, \theta_{ij} - \overset{x}{G} \qquad \underline{2-8}$$

where $\theta_{ij} \equiv \dfrac{D(\overset{x}{G}_{ij})}{D(Z_{ij})}$ where $Z_{ij} \equiv \left(\dfrac{x_i}{x_i + x_j}\right)$

The influence of an n-component mixture on the activity coefficient of i is made up of two types of contributions:

1) The term $\overset{x}{G}$ is from all ${}^{n}C_{2}$ binaries, including those exclusive of i .

2) The other terms involve only binaries with component i .

Thus all ${}^{n}C_{2}$ binary excess free energies influence the activity coefficient of component i .

2.III <u>Validity Tests for Partial and Excess Free Energies</u>

During this investigation, a collection of tests was made to check the consistency of activity coefficient functions with respect to a specific formulation of $\overset{x}{G}$. They are

<u>2-11</u> $\underset{n+1\ \text{components}}{\overset{x}{\mu}_i}$ must approach $\underset{n\ \text{components}}{\overset{x}{\mu}_i}$ as number of components is reduced by one.

<u>2-12</u> $\sum_{i=1}^{n} x_i \overset{x}{\mu}_i = \overset{x}{G}$, a restatement of (2-2)

<u>2-13</u> $\overset{x}{\mu}_i = \overset{x}{G} + (1 - x_i)\dfrac{D(\overset{x}{G})}{D(x_i)}$, a restatement of (2-3)

2-14 $\overset{x}{\mathcal{U}}_i$ (asymmetric) must reduce to $\overset{x}{\mathcal{U}}_i$ (symmetric) when the symmetric relations are substituted for the asymmetric.

2-15 $\overset{x}{\mathcal{U}}_i$ as expressed in terms of summations must be consistently interchangeable in i, j, k .

Tests (2-11, 12, 15) are usually the easiest to apply, but test (2-13) by derivation is the only absolutely certain method of validity testing. All five relations hold for a correct formulation of $\overset{x}{\mathcal{U}}_i$ from a specified formulation of $\overset{x}{G}$. Conversely if one condition does not hold then the expressions are not valid.

To illustrate with an example where the formulation of $\overset{x}{\mathcal{U}}_i$ was incorrect with respect to a $\overset{x}{G}$ definition consider the paper by Sryvalin **and Esin** (1959); page 109

> "The simplest formulation of the influence of the energetic non-equivalence of different sites for like atoms leads to the appearance of two energy effects in the expression for the heat of mixing:
>
> $$\Delta E = Q_{12}X_1X_2 + q_{12}X_1X_2^2 + Q_{13}X_1X_3 + q_{13}X_1X_3^2 + Q_{23}X_2X_3 + q_{23}X_2X_3^2$$
>
> One of these Q, as for regular solutions, represents the interaction energy, while the other q represents deviations from regular mixtures due to structural peculiarities of the solution. Assuming further that the entropy of mixing is the same as for ideal solutions, we have the following expressions for the activity coefficients of components in the ternary systems:

$$\overset{x}{\mathcal{U}}_1 = Q_{12}X_2(1-X_1) + q_{12}X_2^2(1-2X_1) + Q_{13}X_3(1-X_1) + q_{13}X_3^2(1-2X_1) - Q_{23}X_2X_3 - 2q_{23}X_2X_3^2$$

$$\overset{x}{\mathcal{U}}_2 = Q_{12}X_1(1-X_2) + 2q_{12}X_1X_2(1-X_2) - Q_{13}X_1X_3 - 2q_{13}X_1X_3^2 + Q_{23}X_3(1-X_2) + q_{23}X_3^2(1-2X_2)$$

$$\overset{x}{\mathcal{U}}_3 = -Q_{12}X_1X_2 - 2q_{12}X_1X_2^2 + Q_{13}X_1(1-X_3) + 2q_{13}X_1X_3(1-X_3) + Q_{23}X_2(1-X_3) + q_{23}X_2X_3(1-X_3)$$

End of quote.

Although condition (2-12) holds: $\sum x_i \overset{x}{u}_i = \overset{x}{G}$, it is easily seen that condition (2-15) does not hold in the terms g_{ij}. Hence the asymmetry in the binaries has not been properly taken into the ternary. Closer examination also shows that condition (2-11) is also not satisfied. It appears that the expressions for $\overset{x}{u}_i$ were manufactured so as to satisfy conditions (2-12, 14).

3. EQUILIBRIUM PHASE SETS : EQUATIONS

3.I Liquid with Pure Crystalline Solid

The cryoscopic equation used by Bowen (1928) is

$$\ln(a_i) = \frac{\Delta H_i}{R}\left(\frac{1}{T_{0i}} - \frac{1}{T}\right) \tag{3-1}$$

where ΔH_i is the heat of fusion at T_{0i} for the crystalline solid i pure in component i, and a_i is the activity of component i in the liquid phase at T with reference state crystal i pure in i at T. Rearranging yields

$$\overset{x}{u}_i = RT\ln\gamma_i = \Delta H_i\left(\frac{T}{T_{0i}} - 1\right) - RT\ln X_i \tag{3-2}$$

where γ_i is the activity coefficient of i at X_i and T. Using (3-2) and liquidus data from a simple binary phase diagram a $\overset{x}{u}_i$ curve for component i in the liquid phase can be calculated for the composition range between $X_i = 1$ and the simple eutectic composition, but not on the other side of the eutectic. Three methods were developed to convert these incomplete $\overset{x}{u}_i$ curves to completed excess free energies of mixing: a repeat graphical construction, numerical solution of the associated first order differential equation, and, the method used herein, a classical Gibbs-Duhem integration. The other two methods gave similar results but required more data sets within a binary. The methods are described in detail in Appendix A.

Rearrangement of (3-1) also yields

$$T = -T_{0i}\,\frac{(\overset{x}{u}_i + \Delta H_i)}{(RT_{0i}\ln X_i - \Delta H_i)} \tag{3-3}$$

so that knowing $\overset{x}{u}_i$, a general liquidus surface away from $X_i = 1$, $T = T_{0i}$ can be calculated. Since $\overset{x}{u}_i$ is affected by binary pairs jk $(j \neq k \neq i)$

as well as by binary pairs $ij\ (j \neq i)$, then the liquidus surface away from i is also affected by binary pairs $jk\ (j \neq k \neq i)$.

3.II Solution Phase A with Solution Phase B

From Kern and Weisbrod (1967)

$$\mu_1^A = \mu_1^{\circ A} + RT \ln a_1^A$$

$$\mu_1^B = \mu_1^{\circ B} + RT \ln a_1^B$$ 3-4

The standard states are the end members of phases A and B being pure in component 1 or 2.

Since $\mu_1^A = \mu_1^B$ at equilibrium so $RT \ln\left(\frac{a_1^B}{a_1^A}\right) = \mu_1^{\circ A} - \mu_1^{\circ B} = \Delta G_1^{\circ B \to A}$.

but $\Delta G_1^{\circ B \to A} = \Delta H_1^{\circ B \to A} - T \Delta S_1^{\circ B \to A}$ and at T_{o_1} , the transition temperature,

then $\Delta G_1^{\circ B \to A} = 0$ and $\Delta S_1^{\circ B \to A} = \frac{\Delta H_1^{\circ B \to A}}{T_{o_1}}$ for pure component 1.

Since $\overset{x}{\mu}_1 = RT \ln \gamma_1 = RT \ln a_1 - RT \ln X_1$

then $\overset{x}{\mu}_1^B - \overset{x}{\mu}_1^A = RT \ln\left(\frac{X_1^A}{X_1^B}\right) + \Delta H_1^{\circ B \to A}\left(1 - \frac{T}{T_{o_1}}\right)$

and similarily $\overset{x}{\mu}_2^B - \overset{x}{\mu}_2^A = RT \ln\left[\frac{(1-X_1^A)}{(1-X_1^B)}\right] + \Delta H_2^{\circ B \to A}\left(1 - \frac{T}{T_{o_2}}\right)$ 3-5

where the temperature dependence of $\Delta H_i^{\circ B \to A}$ is taken to be zero. The development is completely general for all solution phase-solution phase equilibria that satisfy $B \to A$ at T_{o_i} where binary phases B and A have the same end member composition but different structures. Hence both solid solution-liquid solution (plagioclase-liquid) and solid solution-solid solution (clinopyroxene-orthopyroxene) behavior can be treated if $\overset{x}{\mu}_i$ are known for both phases, both components. In the case of the alkali feldspar solid solution series, there is a temperature minimum where $X_1^A = X_1^B$ and so (3-5) reduces to $\overset{x}{\mu}_1^A \neq \overset{x}{\mu}_1^B$ and $\overset{x}{\mu}_2^A \neq \overset{x}{\mu}_2^B$. In general this will be true for any two phases: different phases have different excess free energies.

Equation (3-1) also follows from (3-5) when $X_1^A = 1, \overset{x}{\mu}{}_1^A = 0$.

3.III Application of Solution Models to Generate $\overset{x}{G}$, $\overset{x}{\mu}$ From Binary Equilibria Involving Two Solution Phases

For phases A and B, components 1 and 2, the regular solution model can be added to (3-5), using $W_A \equiv W_{12}$ for phase A, $\overset{x}{G}_A \equiv \overset{x}{G}_{12}$ in phase A, $X_A \equiv X_1^A$ and $\Delta H_1 \equiv \Delta H_1^{\circ\, B \to A}$. Since $\overset{x}{\mu}{}_1^A = (1 - X_A)^2 W_A$ by (2-4), then by (3-4)

$$(1 - X_B)^2 W_B - (1 - X_A)^2 W_A = RT \ln\left(\frac{X_A}{X_B}\right) + \Delta H_1 \left(1 - \frac{T}{T_{D_1}}\right)$$

$$X_B^2 W_B - X_A^2 W_A = RT \ln\left[\frac{(1 - X_A)}{(1 - X_B)}\right] + \Delta H_2 \left(1 - \frac{T}{T_{D_2}}\right) \tag{3-6}$$

Solving simultaneously where

$$\phi(1) = \Delta H_1 \left(1 - \frac{T}{T_{D_1}}\right) + RT \ln\left(\frac{X_A}{X_B}\right)$$

$$\phi(2) = \Delta H_2 \left(1 - \frac{T}{T_{D_2}}\right) + RT \ln\left[\frac{(1 - X_A)}{(1 - X_B)}\right]$$

$$W_B = \frac{[X_A^2\, \phi(1) - (1 - X_A)^2\, \phi(2)]}{(X_A + X_B - 2X_A X_B)(X_A - X_B)}$$

$$W_A = \frac{[X_B^2\, W_B - \phi(2)]}{X_A^2} \tag{3-7}$$

Program W1XLIQ is designed,using equation (3-7),to calculate W_{CRYST}, W_{LIQ} from a set of T-X_{LIQ}-X_{CRYST} data from a solid solution binary. The minimum and maximum values for the error envelope about $\overset{x}{\mu}_i$ are obtained by combination of reasonable errors in T, X_{LIQ}, X_{CRYST}. The errors are errors in reading points off the curve of the phase diagram. A smooth curve for $\overset{x}{\mu}_i, X_i \geqslant .5$ is drawn and the Gibbs - Duhem integration is used to generate $\overset{x}{\mu}_i, X_i < .5$. The curve should be smooth at $X_i \doteq .5$ but if it is not then it must be adjusted to be smooth within the limits of the error envelopes. If this is not possible, then $\overset{x}{G}$ cannot be closely represented by $X_i X_j W_{ij}$

and instead a two or three parameter $\overset{x}{G}$ must be tried. For Thompson's (1967) model using two parameter $\overset{x}{G}$

$$\overset{x}{G}_A \equiv X_A(1-X_A)[W_{12}^A(1-X_A)+W_{21}^A X_A] \quad \text{where} \quad W_{12}^A \neq W_{21}^A \quad \text{and}$$

$$\overset{x}{\mu}_1^A = (1-X_A)^2[W_{12}^A(1-2X_A)+2X_A W_{21}^A] \tag{3-8}$$

Exchanging subscripts 1, 2 and using $X_2^A = 1 - X_1^A$, $X_A \equiv X_1^A$

results in $$\overset{x}{\mu}_2^A = X_A^2[W_{21}^A(1-2[1-X_A]) + W_{12}^A 2(1-X_A)]$$

$$= X_A^2[W_{12}^A(1-X_A)2 + W_{21}^A(2X_A-1)] \tag{3-8}$$

There are four unknowns: $W_{12}^A, W_{21}^A, W_{12}^B, W_{21}^B$ but there are only two equations of (3-5) for each temperature. It is necessary to use data at two temperatures, and generate four simultaneous equations which can be reduced to the form $\sum_{i=1}^{4} A_i Y_i = G_j$ where $Y_1 = W_{12}^A, Y_2 = W_{21}^A, Y_3 = W_{12}^B, Y_4 = W_{21}^B$. These four equations are solved by a general subroutine rather than as specific formulae as are presented by (3-7). This model is built into program WWXLIQ using equation (3-6). If the $\overset{x}{\mu}_i$ curves of only one of the two phases is valid, the $\overset{x}{\mu}_i$ of the other phase can be generated from the $\overset{x}{\mu}_i$ data of the first phase by use of the solid solution equation (3-4). This is the function of program OLCAL.

As a check of the methods, points from the calculated system Orthoclase-Albite (Thompson and Waldbaum 1969a-partIV) were used to generate $\overset{x}{\mu}_{UQ}$ curves which compare very well (figure E-1) with Thompson's $\overset{x}{\mu}_{UQ}$ curves. Since Thompson's W's are temperature dependent, the curves will not compare exactly. There does not appear to be any absolute method of generating a general $\overset{x}{\mu}_i$ curve from the data without this method of curve smoothing.

Concerning immiscibility, an additional statement can be made to (3-4) as shown by Kern and Weisbrod (1967): $\mu_1^{oA} = \mu_1^{oB}$. This is equivalent to $\Delta H_1^{o\,B\to A} = 0$ where $T_{o1} \neq 0$. 3-9

Thus the same equations in (3-6, 7) can be used to obtain $\overset{x}{G}$ from binary immiscibility fields with the additional restrictions: $\Delta H_i^{o} = 0$ for $T_{oi} = 0$.

Further simplifications for immiscibility can be made if with the first model $W^A = W^B$ or with the second model $W_{12}^A = W_{12}^B$. Note that these simplifications are permitted only because $\Delta H_1^{o\,B\to A} = 0$ and would not be allowed otherwise: as stated for the case the alkali feldspar minimum, where $X_A = X_B$, $\overset{x}{\mu}{}_1^A \neq \overset{x}{\mu}{}_1^B$ and thus $W_A \neq W_B$. Then instead of (3-7) where $W = W_A = W_B$ and 3-10

$$\overset{x}{\mu}{}_1^A = (1 - X_1^A)^2 W$$

$$W = \frac{RT \ln\left(\frac{X_A}{X_B}\right)}{\left[(1-X_A)^2 - (1-X_B)^2\right]} \qquad \text{3-11}$$

Thompson demonstrated for his model

with $\phi(1) = \frac{1}{2} \frac{(X_A + X_B)}{(X_A - X_B)} \ln\left(\frac{X_A}{X_B}\right)$

and $\phi(2) = \frac{1}{2} \frac{[2 - (X_A + X_B)]}{(X_A - X_B)} \ln\left[\frac{(1 - X_A)}{(1 - X_B)}\right]$

then
$$\frac{W_{12}}{RT} = \frac{\phi(1)}{(X_A + X_B)} + \frac{\phi(2)}{[2 - (X_A + X_B)]} + \frac{[\phi(2) - \phi(1)][2 - 3(X_A + X_B)]}{(X_A - X_B)^2}$$

$$\frac{W_{21}}{RT} = \frac{W_{12}}{RT} + 2\,\frac{[\phi(2) - \phi(1)]}{(X_A - X_B)^2}$$

The $\overset{x}{\mu}$ and $\overset{x}{G}$ are calculated from these W using $W_A = W_B$ AND (3-8).

4. ASSOCIATION - DISSOCIATION IN LIQUIDS

Particle Interactions that Affect $\overset{x}{\mu}_i$, Liquidus Curves and the Estimation of Heats of Fusion

The $\overset{x}{\mu}_i$ are determined as the excess quantity that is necessary to bring an experimental liquidus to its ideal ($\gamma=1$, no association or dissociation) curve defined by $\Delta H_i, T_{0i}$ and the cryoscopic equation (3-1). If ΔH_i has not been determined calorimetrically (as is true for many silicates), it can be estimated, as will be shown, by the freezing point depression method using the cryoscopic equation. However, association and/or dissociation causes the estimate of ΔH_i to be incorrect ($\Delta H_i'$), so that $\overset{x}{\mu}_i$ calculated using $\Delta H_i'$ will also be incorrect. Association and dissociation are particle interactions (a non ideality) and as such, should be included completely in $\overset{x}{\mu}_i$ (not in an incorrect ΔH_i). This is especially important when activity matching is attempted: in a multicomponent system with coexisting liquid phases A and B, in general $\overset{x}{\mu}_i^A - \overset{x}{\mu}_i^B = f(\Delta H_i - \Delta H_i')$ so that $X_i^A - X_i^B = f(\Delta H_i - \Delta H_i')$. However, the effect on calculating an n-component liquidus temperature for i tends to cancel out if $\overset{x}{\mu}_i'$ and $\Delta H_i'$ are used in equation (3-3). It is thus necessary to consider carefully the use of the cryoscopic equation in estimating heats of fusion.

Since (3-1) is $\ln a_i = \frac{\Delta H_i}{R}\left(\frac{1}{T_{0i}} - \frac{1}{T}\right)$ then

by replacing a_i by X_i and ΔH_i by $\Delta H_i'$ (an estimate of ΔH_i) then

$\ln X_i = \frac{\Delta H_i'}{R}\left(\frac{1}{T_{0i}} - \frac{1}{T}\right)$, resulting in $\lim_{X_i \to 1} (\Delta H_i') = \Delta H_i$ so that a plot of

$\Delta H_i' = \frac{R \ln X_i}{\left(\frac{1}{T_{0i}} - \frac{1}{T}\right)}$ versus X_i then has a limiting value of ΔH_i. The shape of 4-1 this curve as extrapolated to $X_i=1$ is undefined, so consider $\Delta H_i'$ as $X_i \to 1 : \ln X_i \to 0, \left(\frac{1}{T_{0i}} - \frac{1}{T}\right) \to 0$. Hence $\Delta H_i'$ has the indeterminate limiting form of $\frac{0}{0}$. Using L'Hopital's Rule on indeterminate limits

$$\lim_{X_i \to 1} (\Delta H_i') = \frac{\lim_{X_i \to 1}\left[\frac{d(R \ln X_i)}{d(X_i)}\right]}{\lim_{X_i \to 1}\left[\frac{d\left(\frac{1}{T_{0i}} - \frac{1}{T}\right)}{d(X_i)}\right]} = \lim_{X_i \to 1}\left[\frac{\frac{R}{X_i}}{\frac{1}{T^2}\frac{dT}{dX_i}}\right] = \frac{R T_{0i}^2}{\left(\frac{dT}{dX_i}\right)_{X_i=1}} = \Delta H_i$$

Thus $\left(\frac{dT}{dX_i}\right)_{X_i=1} = \frac{R T_{0i}^2}{\Delta H_i}$ and the limiting liquidus slope at $X_i=1$ defines <u>4-2</u>

the heat of fusion. In the region close to $X_i=1$, $\frac{R T_{0i}^2}{\Delta H_i}$ will approximate $\left(\frac{dT}{dX_i}\right)_{X_i \to 1}$ so $\lim_{X_i \to 1} (\Delta H_i') = \frac{\frac{R}{X_i}}{\frac{1}{T^2}\frac{R T_{0i}^2}{\Delta H_i}} = \frac{\Delta H_i}{T_{0i}^2}\left(\frac{T^2}{X_i}\right) = C\frac{T^2}{X_i}$ where C is constant. <u>4-3</u>

A plot of $\Delta H_i'$ versus $\frac{T^2}{X_i}$ should be linear near $X_i=1$.

Association or dissociation in the liquid affects these methods of estimating ΔH_i . Assuming component I to dissociate completely into two particles in liquid component J then the actual concentration of particles of component I is $X_i = \frac{2N_i}{(N_j+2N_i)}$ where N = moles, so that the actual mole fraction of J is $X_j = \frac{N_j}{(N_j+2N_i)}$. <u>4-4</u>

Calculating a mole fraction ignoring dissociation $X_j' = \frac{N_j}{(N_j+N_i)}$ so $N_i = \frac{N_j}{X_j'} - N_j$ and substituting in (4-4) then $X_j = \frac{N_j}{\left[N_j + 2\left(\frac{N_j}{X_j'}\right) - 2N_j\right]} = \frac{X_j'}{[2-X_j']}$

Thus $dX_j = \frac{[(2-X_j')+X_j']\,dX_j'}{(2-X_j')(2-X_j')}$

$= 2dX_j'$ as $X_j' \to 1$ and $X_j \to 1$.

Hence $\left(\frac{dT}{dX_j'}\right)_{X_j \to 1} = 2\left(\frac{dT}{dX_j}\right)_{X_j \to 1} = \frac{2RT_{0j}^2}{\Delta H_j} = \frac{RT_{0j}^2}{\Delta H_j'}$ where $\Delta H_j' = \frac{\Delta H_j}{2}$. <u>4-5</u>

Complete dissociation of I into two particles causes $\Delta H_j'$ to be an incorrect estimate of ΔH_j by a factor of two. In a similar fashion complete dissociation of J into two particles causes $\Delta H_j' = 2\Delta H_j$ while association of J into half as many particles causes $\Delta H_j' = \frac{\Delta H_j}{2}$.

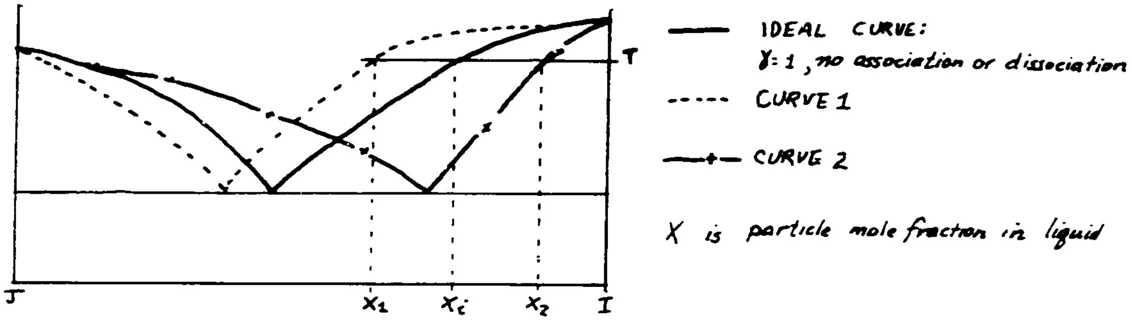


Figure 4-1
Liquidus Variation Due to Interactions

A more diagramatic approach is to consider figure 4-1 at temperature T:

1) if I dissociates it takes a smaller amount of I to make X_i at T, i.e. $X_i' < X_i$ and curve 1; $X_i' \equiv X_1$

2) if I associates it takes a larger amount of I to make X_i at T, i.e. $X_i' > X_i$ and curve 2; $X_i' \equiv X_2$

So then if I dissociates it raises its liquidus and $\Delta H_i'$ and drops J's liquidus and $\Delta H_J'$. The reverse is true for association of I.

A method of protecting against these problems is to analyse liquidus data of component J with several different types of component I (tectosilicate, sorosilicate, orthosilicate). If I dissociates in a melt of J, a tectosilicate I should give a different number of particles than a sorosilicate I, and hence $\Delta H_j'$ should change with the type of silicate structure of component I. Calculations on both Gehlenite - Anorthite and Gehlenite - Akermanite resulted in $\Delta H_{GEHL}'$ = 20 kcal. The conclusion is that neither Akermanite nor Anorthite dissociate or associate in liquid Gehlenite. Since Gehlenite is similar in structure and physical properties to Akermanite, it should also not undergo such particle interactions and hence $\Delta H_{GEHL} = \Delta H_{GEHL}'$ = 20 kcal. In contrast to gehlenite, pyroxene type components behave much differently, showing very high $\Delta H_{PX}'$.

Possibly some. dissociation takes place in the pyroxene structure at the same time as a lot of association of the other components. Pyroxene dissociation would be loss of simple cations , as opposed to extensive modification of the chain like structure - Chipman 1942 , while the pyroxene like liquid causes added components to polymerize.

I have attempted to characterize a liquidus surface by using as a model a scheme of incomplete dissociation/association of a component where the equilibrium constants of the interactions are temperature dependent. This differs from the models of Flood (1968), Bradley (1964) and Cochran (1967), where the interactions are assumed to be complete and temperature independent, which is equivalent to very large or small equilibrium constants of the order $ABS[\mathrm{Log}_{10}(k)]>2$. Lacy (1965) discussed the problem of statistical models for silicate melts and came to the conclusion that polymerization/depolymerization interactions generally do not go to completion. In the present scheme ten constants are given assumed values, where 1 and 2 are components:

for fusion (f)

$$\left\{\begin{array}{l} \Delta H_1^f , T_{o1}^f \\ \Delta H_2^f , T_{o2}^f \end{array}\right.$$

4-6

for interaction equilibria $(\leftrightarrow)$

$$\left\{\begin{array}{l} \overset{\leftrightarrow}{N}_1 , \overset{\leftrightarrow}{N}_2 \\ \ln \overset{\leftrightarrow}{k}_1 = \dfrac{\Delta \overset{\leftrightarrow}{H}_1}{RT} - \dfrac{\Delta \overset{\leftrightarrow}{S}_1}{R} \\ \ln \overset{\leftrightarrow}{k}_2 = \dfrac{\Delta \overset{\leftrightarrow}{H}_2}{RT} - \dfrac{\Delta \overset{\leftrightarrow}{S}_2}{R} \end{array}\right.$$

N is the stoichiometry of interaction

The interaction equilibria interfere with each other the way an inert gas displaces a chemical reaction that has a different number of moles products than reactants (Moore 1963). It becomes necessary to solve three simultaneous interdependent non linear equations with three unknowns.

This is quite difficult to do, but then if such a model is fitted to a liquidus, the constants of the interaction equilibria also become unknowns, two of which are exponents. However, this sort of model is very realistic, and if the techniques are perfected, it should provide a theoretical basis for applying statistics to picking the best possible liquidus through experimental points.

Association/dissociation equilibria introduces a type of nonideality similar to that of element partitioning between an ideal single site phase and an ideal double site phase. Calculations (Barron 1970 unpublished) show that regular solution partitioning curves can be duplicated very accurately (but not exactly : 1% mole fraction) by single site phase - double site phase partitioning with temperature dependent equilibrium constants. The reverse though, is not generally true: once the regular solution model W is given a value, the values and temperature dependence of the two equilibrium constants are fixed. In a similar manner the interaction model will generally approximate a regular solution model, but results can be obtained from the interaction model that cannot be fitted to the regular solution model. The $\overset{x}{\mathcal{U}}_i$ curves for the interaction model should thus only be used with an approach similar to that of this dissertation.

5. RESULTS OF A THREE COMPONENT $\overset{x}{G}$ AND VALIDITY OF THE EMPIRICAL CORRECTION FREE ENERGY $\overset{K}{G}$

The $\overset{x}{G}$ developed in this dissertation does not take into account excess entropies of mixing. In general the sign of $\overset{x}{S}$ need not be the same as the sign of $\overset{x}{G}$ (Lupis 1966). When several calculated ternary systems are compared with the experimental ones it is found:

1) if $\overset{x}{G}_{ij} > 0$ in binaries, temperature surfaces calculated are higher than experimental determinations.

2) if $\overset{x}{G}_{ij} < 0$ in binaries, the calculated temperatures were lower than experimental.

3) mixed value $\overset{x}{G}_{ij}$ in binaries resulted in temperatures both greater and less than experimental temperatures.

The deviations in the calculations consistently reflect the sign of the binary excess free energies, and thus are not likely to be caused by excess entropies. Instead they must be explained in terms of some ternary interaction factor. Such an effect would require a change in the dilution factor (2-5): $(X_i + X_j)^2$. From the relationship of sign of $\overset{x}{G}_{ij}$ in binaries to the sign of T calculated - T experimental, it is necessary that the dilution factor get smaller faster than $(X_i + X_j)^2$. This way the absolute value of a ternary $\overset{x}{\mu}_i$ would get closer to zero (i.e. γ_i closer to one) so the calculated temperatures would be raised if $\overset{x}{G}_{ij} < 0$ and lowered if $\overset{x}{G}_{ij} > 0$. The form of the ternary effect is completely unspecified. In fact it may have a molecular interpretation no more important than a homogenizing of the environment around each species. In the complete formulation of $\overset{x}{G}_{ij}$ approach, species are not treated and hence the use of an Empirical Correction Free Energy $\overset{K}{G}$ is justified if the model seems to work where results can be checked.

An n-component correction free energy model should satisfy the following preliminary restrictions:

<u>5-1</u> $\overset{K}{G} \to 0$ as any $(x_i + x_j) \to 1$

<u>5-2</u> $\overset{K}{\mu}_i \to 0$ as $x_i \to 1$ and $(x_i + x_j) \to 1$

<u>5-3</u> It should have at least n independent adjustable parameters so that in the case of an (n+1) phase minimum (i.e. a ternary eutectic), the n liquidus surfaces can all be raised to the eutectic temperature and composition.

Various models tried were:

i $\overset{k}{G} = \sum_{i=1}^{n} \sum_{j>i}^{n} (1 - x_i - x_j) k_{ij}$ which doesn't satisfy (5-1) for $n > 2$

ii $\overset{k}{G} = \sum_{i=1}^{n} \sum_{j>i}^{n} (1 - x_i - x_j)(x_i + x_j) k_{ij}$ but $\overset{k}{\mu}_i \not\to 0$ as $x_i + x_j \to 1$ for $n > 3$

iii $\overset{k}{G} = \left(\prod_{i=1}^{n} x_i \right) \sum_{i=1}^{n} x_i k_i$ which yields $\overset{k}{G} = 0$ for any $x_i = 0$ for $n > 2$

iv $\overset{k}{G} = \left[\prod_{i=1}^{n} \prod_{j>i}^{n} (1 - x_i - x_j) \right] \sum_{i=1}^{n} x_i k_i$ which seems to satisfy (5-1, 2, 3) <u>5-4</u>

Developing model iv

$$\overset{k}{G} = \left[\prod_{i=1}^{n} \prod_{j>i}^{n} (1 - x_i - x_j) \right] \sum_{i=1}^{n} x_i k_i = \left[\prod_{j \neq 1}^{n} (1 - x_1 - x_j) \right] \left[\prod_{i \neq 1}^{n} \prod_{j>i}^{n} (1 - x_i - x_j) \right] \sum_{i=1}^{n} x_i k_i$$

and using $d \ln x = \frac{1}{x} dx$ then $\overset{k}{G} \frac{D(\ln \overset{k}{G})}{D(x_1)} = \frac{D(\overset{k}{G})}{D(x_1)}$

so
$$\ln \overset{k}{G} = \sum_{j \neq 1}^{n} \ln (1 - x_1 - x_j) + \sum_{i \neq 1}^{n} \sum_{j>i}^{n} \ln (1 - x_i - x_j) + \ln \left[\sum_{i=1}^{n} x_i k_i \right]$$

$$\frac{D(\ln \overset{k}{G})}{D(x_1)} = \sum_{j \neq 1}^{n} \frac{(x_j - 1)}{(1 - x_1 - x_j)(1 - x_1)} + \sum_{i \neq 1}^{n} \sum_{j>i}^{n} \frac{(x_i + x_j)}{(1 - x_i - x_j)(1 - x_1)} + \frac{\left[k_1 - \frac{\sum_{i \neq 1}^{n} x_i k_i}{(1 - x_1)} \right]}{\left(\sum_{i=1}^{n} x_i k_i \right)}$$

$$(1 - x_1) \frac{D(\ln \overset{k}{G})}{D(x_1)} = \sum_{j \neq 1}^{n} \frac{(x_j - 1)}{(1 - x_1 - x_j)} + \sum_{i \neq 1}^{n} \sum_{j>i}^{n} \frac{(x_i + x_j)}{(1 - x_i - x_j)} + \frac{k_1}{\left(\sum_{i=1}^{n} k_i x_i \right)} - 1$$

Now $\overset{k}{\mu}_1 = \overset{k}{G} + (1-X_1)\frac{D(\overset{k}{G})}{D(X_1)} = \overset{k}{G} + (1-X_1)\overset{k}{G}\frac{D(\ln\overset{k}{G})}{D(X_1)} = \overset{k}{G}\left[1 + (1-X_1)\frac{D(\ln\overset{k}{G})}{D(X_1)}\right]$

so that $\overset{k}{\mu}_1 = \overset{k}{G}\left[\sum_{j\neq 1}^{n}\frac{(X_j - 1 + X_1 - X_1)}{(1-X_1-X_j)} + \sum_{i\neq 1}^{n}\sum_{j>i}^{n}\frac{(X_i+X_j)}{(1-X_i-X_j)} + \frac{K_1}{\sum_{i=1}^{n} X_i K_i}\right]$

Rearranging and using $\overset{K}{G} = L\sum_{i=1}^{n} X_i K_i$ where $L = \prod_{i=1}^{n}\prod_{j>i}^{n}(1-X_i-X_j)$ 5–5

so $\overset{k}{\mu}_1 = L\sum_{i=1}^{n} X_i K_i\left[\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{(X_i+X_j)}{(1-X_i-X_j)} - \sum_{i\neq 1}^{n}\frac{(X_1+1)}{(1-X_1-X_i)} + \frac{K_1}{\sum_{i=1}^{n} X_i K_i}\right]$

Using $XS = \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{(X_i+X_j)}{(1-X_i-X_j)}$ which does not change with the choice of **component** 1 and $XS1 = \sum_{j\neq 1}^{n}\frac{(X_1+1)}{(1-X_1-X_j)}$ which does depend on the choice of component 1,then 5–6

$$\overset{k}{\mu}_1 = L\sum_{i=1}^{n} X_i K_i\left[XS - XS1 + \frac{K_1}{\sum_{i=1}^{n} X_i K_i}\right]$$

$$= L\left[K_1X_1(XS - XS1 + 1) + K_2X_2(XS - XS_1) + \dots K_nX_n(XS - XS1)\right]$$

The general formula is then

$$\overset{k}{\mu}_i = L\left[K_iX_i(XS - XS_i + 1) + (XS - XS_i)\sum_{j\neq i}^{n} X_jK_j\right]$$

$$= L\left[(XS - XS_i)\sum_{j=1}^{n} X_jK_j + X_iK_i\right] \qquad \text{5–7}$$

Formulating $RT\ln a_i = RT\ln X_i + \overset{x}{\mu}_i + \overset{k}{\mu}_i$ where $\overset{k}{\mu}_i$ is the correction to be calculated and using the freezing point depression equation results in 5–8

$$\overset{k}{\mu}_i = \Delta H_i\left(\frac{T}{T_{0_i}} - 1\right) - RT\ln X_i - \overset{x}{\mu}_i \qquad \text{5–9}$$

At an n – solid phase point, by knowing $T, X_i\ (i=1,n)$, using binary data to estimate $\overset{x}{\mu}_i$, then n values of $\overset{k}{\mu}_i$ can be calculated from (5-9). These are used in the n equations of the form of (5-7), solved simultaneously to give n independent values of K_i. These K_i are then used over the whole region, modifying the n-component activities. When one binary of a ternary system forms a solid solution the situation becomes more difficult. One additional unknown is introduced (X_i in crystal) and two nonlinear equations associated with solid solution are introduced (3-5). Consider for example a correction of Diopside - Albite - Anorthite, with reference to figure 5-1 and diagram 7-2 .

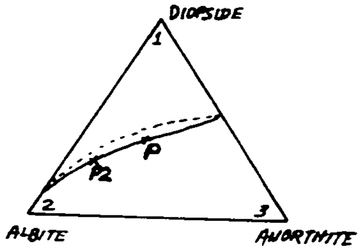


Figure 5-1
Compositions for $\overset{K}{\mathcal{U}}_i$

____experimental cotectic

----calculated cotectic

P, P2: Centrally chosen points with experimental T, X_i known.

For Diopside $\overset{K}{\mathcal{U}}_1 = \Delta H_1\left(\frac{T}{T_{01}} - 1\right) - RT\ln X_1 - \overset{X}{\mathcal{U}}_1$ by (5-9).

For the Plagioclase - Liquid equilibria we have by (3-5), (5-8)

$$RT\ln \underset{LIQUID}{a_2} = \underbrace{\overset{K}{\mathcal{U}}_2 + RT\ln X_2 + \overset{X}{\mathcal{U}}_2}_{LIQUID} = RT\ln \underset{CRYSTAL}{a_2} + \Delta H_2\left(\frac{T}{T_{02}} - 1\right)$$

or

$$\underset{LIQUID}{\overset{K}{\mathcal{U}}_2} = RT\ln \underset{CRYSTAL}{a_2} + \Delta H_2\left(\frac{T}{T_{02}} - 1\right) - \underbrace{RT\ln X_2 - \overset{X}{\mathcal{U}}_2}_{LIQUID}$$

and similarly for component 3 5-10

$$\underset{LIQUID}{\overset{K}{\mathcal{U}}_3} = RT\ln \underset{CRYSTAL}{a_3} + \Delta H_3\left(\frac{T}{T_{03}} - 1\right) - \underbrace{RT\ln X_3 - \overset{X}{\mathcal{U}}_3}_{LIQUID}$$

The first two terms on right hand side of $\overset{K}{\mathcal{U}}_2, \overset{K}{\mathcal{U}}_3$ are independent of X_i^{LIQUID} and at fixed T are nonlinear functions of $X_2^{CRYSTAL}$.

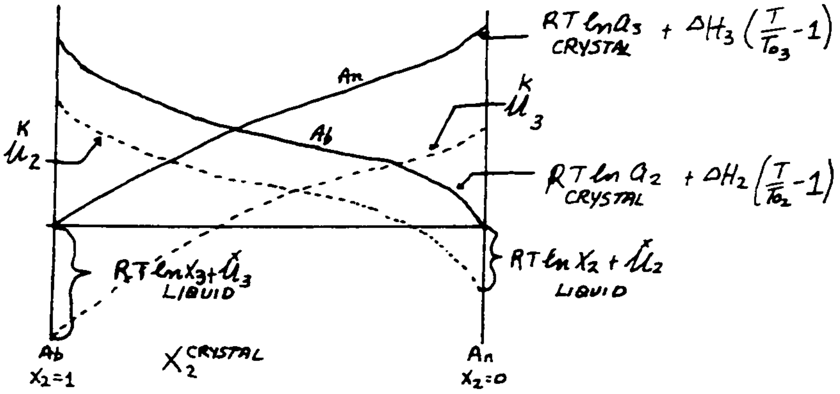


Figure 5-2
$\overset{K}{\mathcal{U}}_i$ as a Function of $X_2^{CRYSTAL}$

The next two terms are fixed independent of $X_2^{CRYSTAL}$ so the resultants are two curves of μ_2^k, μ_3^k as functions of $X_2^{CRYSTAL}$, figure 5-2. Obviously if $X_2^{CRYSTAL}$ is known then μ_2^k, μ_3^k are defined, and the three linear equations are solved for k_1, k_2, k_3. However if $X_2^{CRYSTAL}$ is not known then there exists corresponding curves for k_1, k_2, k_3 as a function of $X_2^{CRYSTAL}$ (figure 5-3).

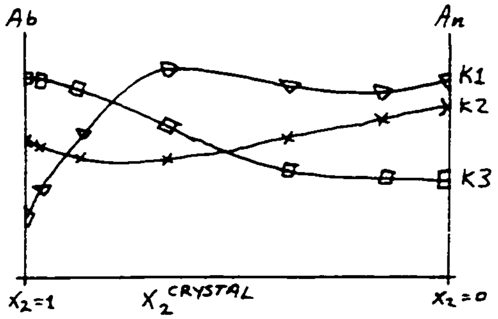


Figure 5-3
k_i From X_2Crystal

There is no unique solution so that a second composition P2 on the cotectic is needed. First a trial $X_2^{CRYSTAL}$ is taken for composition P, yielding values for k_1, k_2, k_3 using (5-10, 7). The values for μ_i^k at composition P2 can then be calculated with these K_i. With μ_i^k, (5-8) and program GAPMIS, the temperature (T_{calc}) at composition P2 is calculated. This procedure is repeated for several trial values of $X_2^{CRYSTAL}$ at composition P to obtain a plot of Tcalc — T experiment for composition P2 versus $X_2^{CRYSTAL}$ at composition P. There is a unique solution where Tcalc = T experiment which yields the desired $X_2^{CRYSTAL}$ at compositions P and P2.

6. GENERAL CRITICISMS

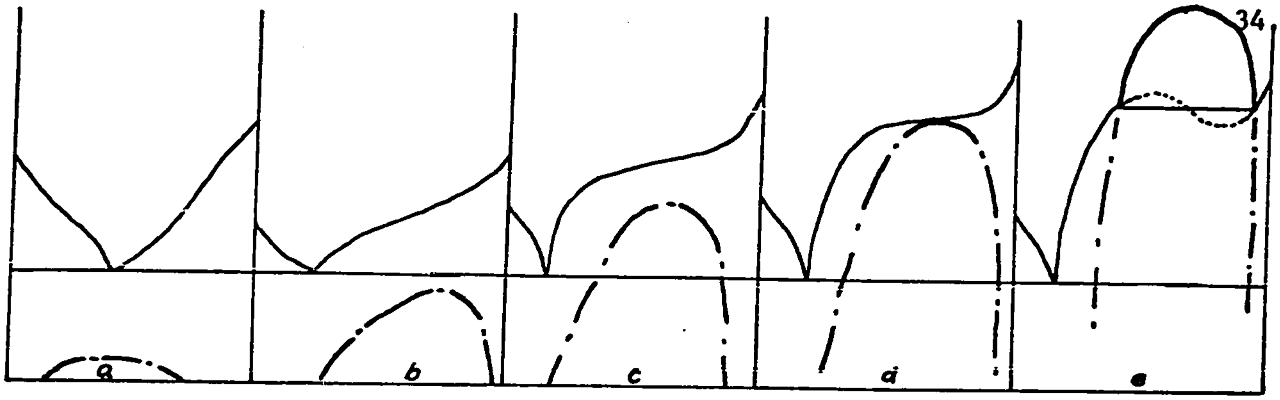
6.I Usage of the Total Function Versus Statistically Determined Two or Three Parameter

Use of a complete or total function $\overset{x}{G}$ rather than a one or two parameter $\overset{x}{G}$ has not been justified from a basis of a statistical evaluation of the original liquidus data. However, some systems require at least a three parameter $\overset{x}{G}$. For example, systems like Fayalite-Silica, Forsterite-Silica have strongly non-centered immiscibility fields with both sides being very steep. Thompson and Waldbaum (1969b) demonstrated the shape of a two parameter $\overset{x}{G}$ immiscibility field for NaCl-KCl: the maximum temperature is displaced off $X = 0.5$, and the short side is much steeper than the other. Hence for Fayalite-Quartz, Forsterite-Quartz at least a three parameter $\overset{x}{G}$ is required to describe the shape of the binary immiscibility field. The ternary $\overset{x}{\mu}_i$ for a three parameter $\overset{x}{G}$ contains nine different terms whereas the complete formulation of $\overset{x}{G}$ requires only six terms in the ternary $\overset{x}{\mu}_i$. Just to include the necessary number of parameters in $\overset{x}{G}$ causes the formulation of $\overset{x}{\mu}_i$ to increase in complexity.

A statistical study of possible liquidus curves through a series of T-X^{uo} points is not wise unless very careful consideration is given to the required result. Several authors have discussed various types of ionizing models to explain anomalous freezing point depression curves (Flood, 1968; Bradley, 1964; Cochran, 1967). The results indicate that the liquidus surface is very sensitive to anything displacing the degree of association or dissociation. A statistical treatment assumes that the errors are random and should average out. If errors in temperature were caused by impurities, then the thermodynamically best liquidus would be the upper limit of the possible curves because additional components lower the liquidus by Alkemade's Rule (unless there is appreciable ideal solid solution of an impurity component that melts at a higher temperature). Statistics can only be applied if there is a valid model of the phase. For example, Green (1970) recently published information on the statistically fitted quasi-chemical model which explained the calorimetric non-ideality in solid NaCl-KCl better than a statistically determined two parameter $\overset{x}{G}$ (Thompson 1969). Inherent in the use of the quasi-chemical model is the partition energy functions of the existing particles. For liquids this would require detailed knowledge of the species present. The interaction model described in section (4-6) could be used to statistically pick a best liquidus, but with at least six unknowns, twenty to thirty sets of data are required. The use of the complete formulation of $\overset{x}{G}$ effectively avoids these problems by not attempting to analyse the cause of non-ideality, and hence not constraining the liquidus curve or the $\overset{x}{\mathcal{U}}$ curves to a special type of curve. There is, at present, no thermodynamically sound way to put a best general liquidus through experimental points. The only true restrictions are that the curve be smooth and within the possible experimental error of the experimental points. Arbitrarily, a polynomial might be fitted to the liquidus data so that analytically the curve is well defined. Dr. W.C. Luth made just such a general point in a conversation at the spring 1970 annual meeting of the AGU.

6.II $\overset{x}{\mathcal{U}}$ as Obtained in Forsterite-Quartz and Fayalite-Quartz

Consider a liquidus surface as it approaches the top of a metastable immiscibility field:



Figures 6-1
Interaction of Liquidus and Liquid Immiscibility

It is of interest in figure 6-1e, where the two liquid field breaks through the liquidus, to consider what the metastable liquidus looks like. Assuming a liquidus to be a smooth curve, it must have some shape like the dotted curve of figure 6-1e. This then should be the liquidus curve used to generate $\overset{x}{\mu}_i$ for the metastable liquidus, not the apparent flat liquidus at constant temperature which was used in the calculations in this dissertation. In order to realistically specify the shape of the metastable liquidus it is necessary to have control on the shape of the stable liquidus close to the immiscibility field in figure 6-1e. With the immiscibility in these silicate systems, this control has not been demonstrated experimentally (Bowen 1928). As a result there are unknown errors in the $\overset{x}{\mu}_i$ curves of both components, since the Gibbs-Duhem integration is used. How these errors affect the calculated results in Quartz-Fayalite-Leucite is completely unknown. Perhaps (3-12) can be used to estimate the two parameters for Thompson's immiscibility model, which then are used to generate the metastable liquidus. The technique can only be approximate since the shape of the immiscibility field suggests that $\overset{x}{G}$ for the liquids involved requires at least three parameters.

6.III Incongruent Melting, Non Binary Behaviour, Minor Solid Solution

Many of the binaries treated contained incongruent melting substances. The metastable portions of the liquidus were drawn by eye and used as acceptable if the resulting $\overset{x}{\mu}_i$ curves were smooth. Some binaries were estimated by extrapolation from ternary diagrams: Anorthite-Orthoclase was attempted from Quartz-Anorthite-Orthoclase. The metastable liquidus was modified in the region of the extrapolated binary eutectic so that the $\overset{x}{\mu}_i$ curves were smooth (Figure E-2)

Most of the calculations of $\overset{x}{\mu}_i$ from binaries have ignored small amounts of solid solution. Calculations on Gehlenite-Akemanite, Albite-Orthoclase and Anorthite-Albite indicate that in the liquid phase $\overset{x}{\mu}_{GEHL}$, $\overset{x}{\mu}_{Or}$, $\overset{x}{\mu}_{An}$ are almost independent of the solid composition if the solid is greater than 85-90% pure (mole fraction). Non binary behaviour in general was ignored in because of lack of information on the compositions of the phases involved. However, such behaviour causes the albite liquidus in Albite-Leucite to be lowered (Levin et al 1964) and the albite liquidus in Albite-Diopside to be raised to a humped maximum (Morse 1968) not shown in Bowen's (1928) diagrams. The only experimental points in Bowen's Diopside-Albite-Anorthite which violate the calculated results are two compositions close to the cotectic near $X_{An}^{LIQUID}=.12$. The calculated feldspar liquidus is too high. Since the Diopside-Albite liquidus used for the calculations is that of Bowen, the calculated liquidus of plagioclase in Diopside-Albite and in Diopside-Albite-Anorthite close to $X_{An}^{LIQUID}=0$ is below what it should be according to the data of Morse (1968). If the calculated liquidus had been too low, then non binary behaviour would be an explanation, but this is not the case, so some other effect must be present.

7. CONCLUSIONS

The calculated systems Quartz-Fayalite-Leucite, Diopside-Albite-Anorthite and Quartz-Albite-Orthoclase are shown in diagrams 7-1, 2, 3. The sources of liquidus-solidus data for these systems are presented in table 7-1.

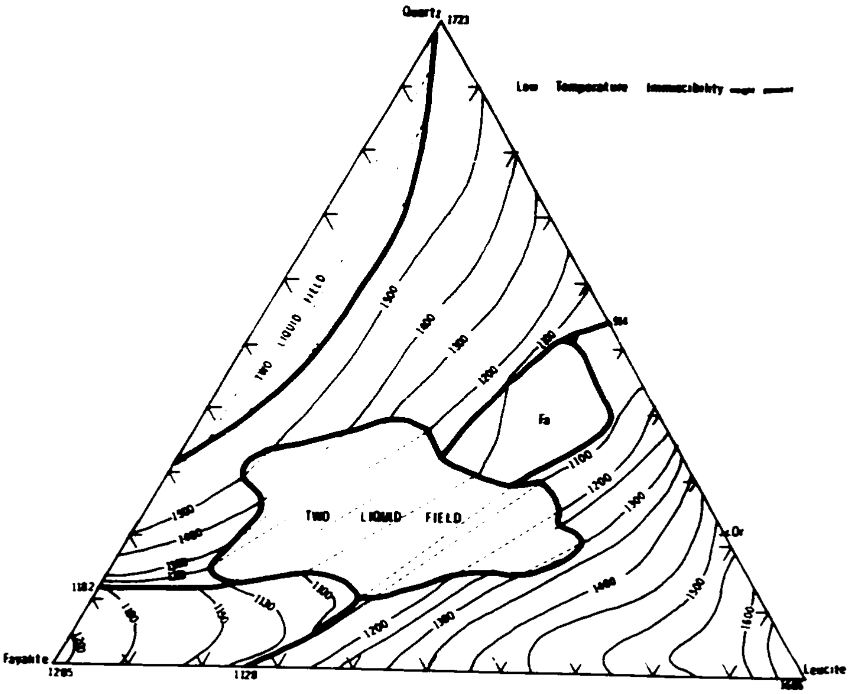
TABLE 7-1

THERMODYNAMIC DATA SOURCES

SYSTEM	SOURCE
Quartz-Fayalite-Leucite	Roedder (1951)
Diopside-Albite-Anorthite	Bowen (1928)
Quartz-Albite-Orthoclase	J. Schairer in Levin et al. (1964) fig. 786, Krauskopf (1967) fig. 14-1.
Quartz-Fayalite	Levin et al. (1964). 586, 682, 696
Quartz-Forsterite	Levin et al. (1964) fig. 598, 682, 803 Turner (1960) page 126
Forsterite-Leucite	op cit fig. 803, 811
Fayalite-Leucite	$\check{\mu}_i$ from Forsterite-Leucite
Leucite-Quartz	op cit fig. 412, 795, 803, Turner (19600 page 107
Quartz-Albite	Luth (1966-67)
Quartz-Orthoclase	Luth (1966-67)
Orthoclase-Anorthite	Levin et al. (1964) fig. 795, 799
Diopside-Albite	Bowen (1928)
Diopside-Anorthite	Bowen (1928)
Albite-Orthoclase	Thompson (1969) part IV
Albite-Anorthite	Deer et al. (1966)

Molecular weights and heats of fusion are from Waldbaum (1968), except the heat of fusion of Leucite which was estimated to be 6770 cals/mole from the systems Leucite-Quartz and Leucite-Forsterite.

The procedures developed give reasonable results in terms of general topography. There are differences, however, which are mainly due to the calculated temperatures being higher than the experimental ones. In the system Quartz-Fayalite-Leucite (diagram 7-1) the calculated immi-



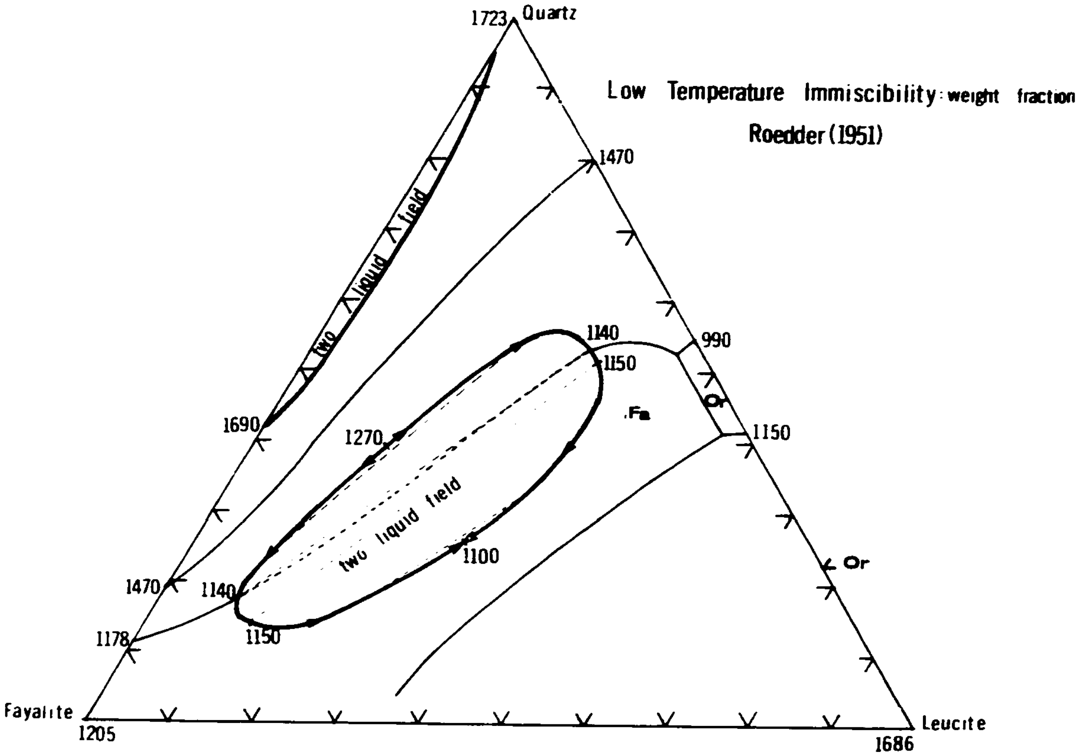


Figure 7-1
The system Quartz - Fayalite - Leucite

scibility fields are considerably larger than the experimental ones. The minimum temperature of immiscibility is about 1090 ± 10°C in both cases. The calculated internal immiscibility field completely cuts across the field of crystallization of fayalite and encroaches 250°C into the field of Leucite. Actually, the line Orthoclase-Fayalite crosses the immiscibility field between 1290 and 1320°C and is cut by the immiscibility tie-lines in this area. This means that a critically undersaturated liquid below the line Orthoclase-Fayalite could exsolve a liquid above the line which would eventually fractionate to free quartz, orthoclase and fayalite. If a few more components were added it is entirely possible that this trend of immiscibility could occur in systems close to natural rock systems. Philpotts (1970) has recently found field evidence that liquids of quartz syenite composition show immiscibility phenomena with liquids of a feldspathoidal basalt composition in the Monteregian province of Quebec.

The shape of the calculated immiscibility field is quite irregular although smooth. Perhaps in an experimental system this could be due to preferred structures in the liquid increasing the immiscibility gap as was suggested by Dr. Philpotts in a conversation. It is certainly reasonable that an immiscibility field should be elongated or stretched towards binary compositions that support the liquid structures causing immiscibility. If there are three such structures then an irregular immiscibility field would result with the additional possibility of a three liquid field occuring if the non-ideality is large enough. Disordered forms of at least three solid silicate structures occur in liquid silicates: inosilicates (Philpotts, private communication), orthosilicate and tectosilicate. Significant differences are found in

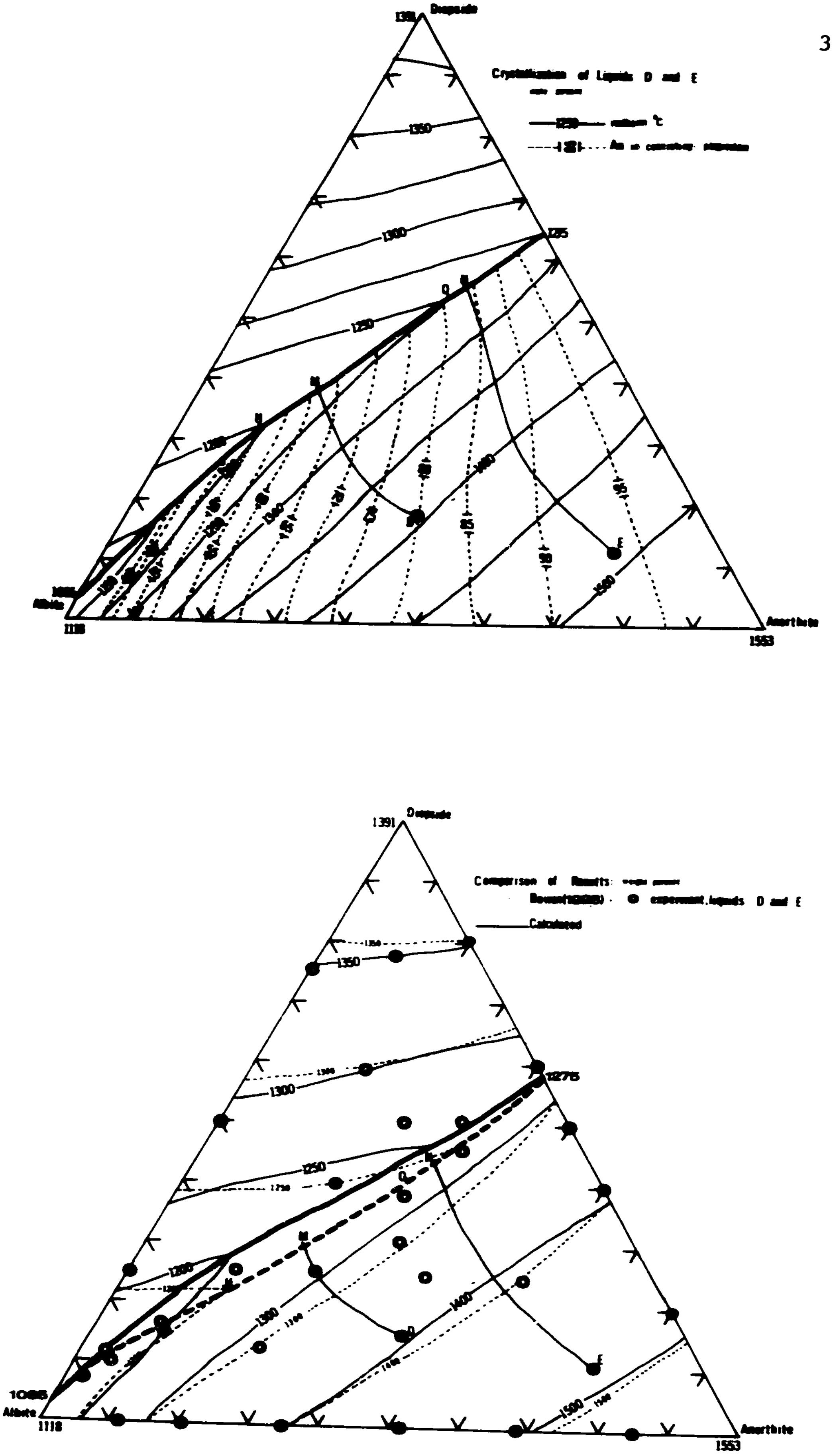


Figure 7-2
The System Diopside Albite - Anorthite

viscosity, density and electrical conductivity between two liquid silicates with a different predominant structure. This means the liquid structures are fairly well-defined and hence irregularly shaped immiscibility fields should occur in ternary silicate liquids. Silicate immiscibility fields are inevitably shown with smooth regular isotherms and liquidus intersections but perhaps this is assumed rather than proven experimentally. McTaggart, in Levin et al. (1964) fig. 783, studied the system TiO_2-ZrO_2-SiO_2 and mapped out an immiscibility field extending from the binary TiO_2-SiO_2 at 1765°C into the ternary to 40% ZrO_2 at 1680°C, with a sudden drop of 85° to 1680°C taking place at 4% ZrO_2. This is an immiscibility field that suddenly rises just before it gets to the binary, but still the liquidus intersection at the sudden rise is shown as a regular curve with no change in curvature. This is not likely to be the case. On the other hand Levin et al. (1964), fig. 559, extrapolated the line of maximum immiscibility temperatures in SiO_2-B_2O_3-BaO through to BaO-SiO_2 from 10% $B_2O_3$and got estimates of metastable immiscibility which were supported by electron microscope studies of glasses in SiO_2-BaO. Evidently some silicate immiscibility fields have regular surfaces, but the regularity must be demonstrated both in temperature and compositions before it is taken to be the case.

The calculated system Diopside-Albite-Anorthite (diagram 7-2) compares very well with Bowen's (1928) experimental results. In general the ternary liquidus calculated is high by 2-15°C with an average of 8°C. Bowen's results from the equilibrium crystallized liquids D and E permit the checking of temperatures and crystal compositions calculated from a similar path mapped out using figure 7-2 and the techniques developed in appendix D. Table 7-2 shows the correspondence, with data source 3 resulting from carefully plotting Bowen's quoted compositions on his diagram, and interpolating temperatures using the isotherms. In four cases this changed temperatures by as much as 4-5°C. This is not a criticism of the quoted values since the isotherms have an error possibility similar to individual readings.

TABLE 7-2

EQUILIBRIUM CRYSTALLIZATION IN DIOPSIDE-ALBITE-ANORTHITE

Mole percent variation in plagioclase

source data	liquid	mole % Dio/Ab/An	first crystal	T	X	first Diopside	T	X	last liquid	T	X
1	D	18	D	1375	80	M	1216	66	H	1200	50
2	D	41	D	1385	80	M	1215	62	H	1199	50
3	D	41	D	1380	80	M	1220	66	H	1200	50
1	E	13	E	1480	95	N	1245	85	0	1237	82
2	E	16	E	1480	94	N	1255	84	0	1251	82
3	E	71	E	1480	95	N	1249	85	0	1241	82

sources 1: Bowen (1928), 2: calculated, 3: Bowen (1928)

The compositions of crystals at H and O are fixed by the bulk composition only so here the temperatures are the things to compare.

The exercise in working out a crystallizing path using the isocons of the coexisting plagioclase immediately indicates the usefulness of the isocons. Further details are provided in appendix D, but in general it can be stated that <u>any</u> type of crystallization path can be constructed easily and quickly using the isocons. Much important information can be obtained from these paths, but they can only be defined by extensive careful experimentation or by the simpler use of the isocons. Therefore a new term for this type of contour is proposed by the author. The contours are <u>lines on the liquidus of constant composition of the coexisting solid solution phase</u>. The term suggested is ICOPHASE, I for equal composition and COPHASE for the coexisting phase. In addition, where the coexisting phase is specifically to be understood, the new terms ICOCRYST (the coexisting phase is crystalline) and ICOLIQ (the coexisting phase is a liquid) are proposed. In this sense, the contours on figures 7-2, 3 are ICOCRYSTS. Plotting of immiscibility relations using ICOLIQS will allow one extra degree of freedom in displaying results. To summarize, the definitions of the new terms are:

ICOPHASE	isocon of a component in a coexisting solution phase.
ICOCRYST	isocon of a component in a coexisting solid solution phase.
ICOLIQ	isocon of a component in a coexisting liquid phase.

As a suggestion it would be worthwhile if simplified systems of geologic importance were redone experimentally with the purpose of obtaining icocrysts of the main minerals that are solid solutions. The solvus of feldspars in An-Or-Ab would require two sets of icocrysts as the solid solution is ternary. Graphical construction of crystallization paths can be replaced by computer construction if the information contained in the icocrysts is fitted to a polynomial function of the liquid composition.

The calculations done on the granite system (diagram 7-3) yield slightly higher temperatures than the experimental results. Table 7-3 shows the results on the ternary minimum.

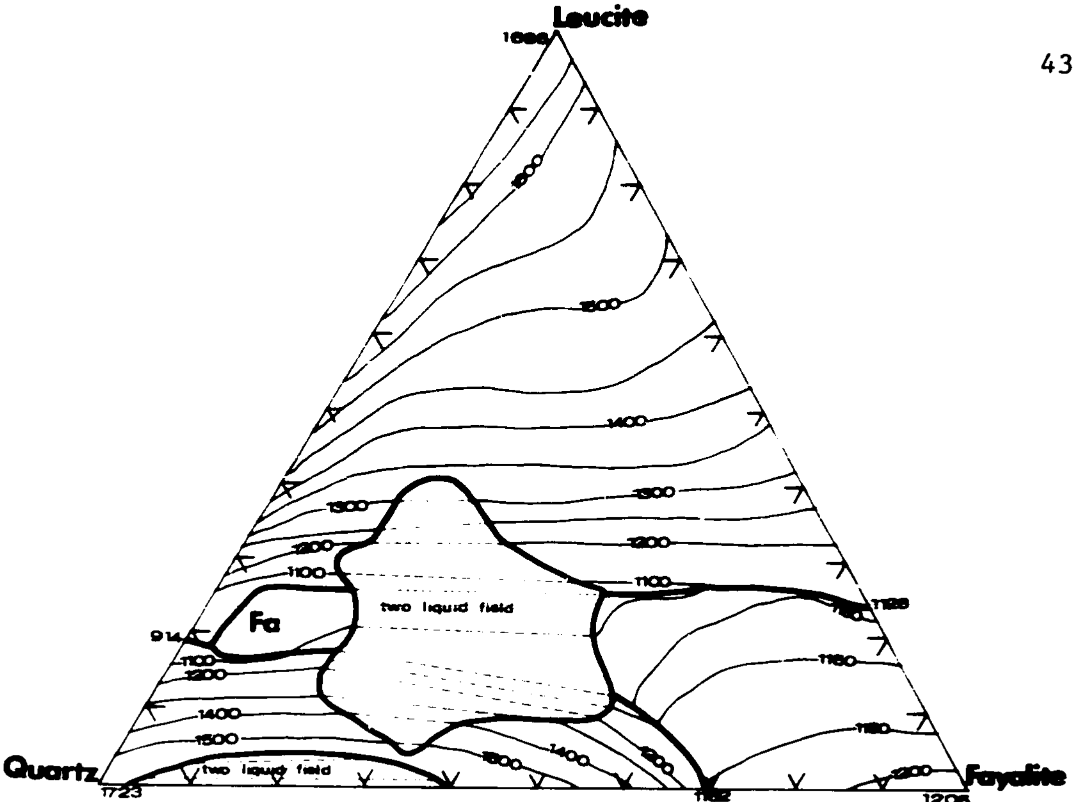
TABLE 7-3

TERNARY MINIMUM IN THE GRANITE SYSTEM

	composition	weight		temperature
Source	quartz	Ab	Or	cent.
Calculated	29.5	34.0	36.5	988
Experiment	35.0	27.0	38.0	975*

*Krauskopf(1967)

The quoted accuracy of the binary eutectic in Quartz-Orthoclase is 990 ± 20°C so that the ternary minimum might only be depressed one or



LOW TEMPERATURE IMMISCIBILITY
MOLE PERCENT

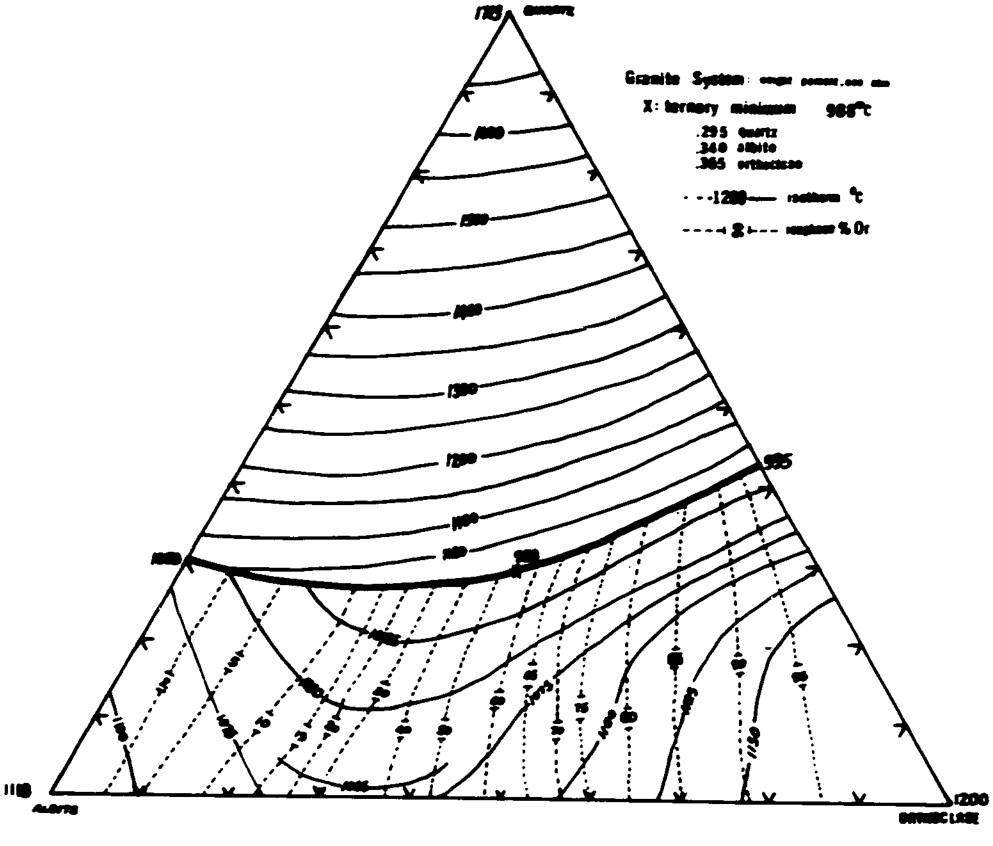


Figure 7-3
The Systems Quartz - Fayalite - Leucite
and Quartz - Albite - Orthoclase

two degrees below the eutectic in Quartz-Orthoclase. If the experimental ternary minimum is correct, the calculations would suggest that the eutectic in Quartz-Orthoclase is near 992°C. One important fact shown by the calculated results in diagram 7-3 is that the compositions of the alkali feldspars change quite rapidly in the region of the minimum, especially on the cotectic line towards albite. A change along the cotectic of 10% Ab in the liquid changes the composition of the coexisting alkali feldspar by as much as 25% Or. A strange thing also happens if liquids close to Ab-Or are fractionally crystallized, for it appears to be possible for the coexisting crystal to first get poorer in Or, but then as the liquid swings and approaches the minimum from Ab, the crystal will then increase in Or. The same composition of alkali feldspar can crystallize at two different temperatures along the same crystallization path. It would be interesting to see if this could be demonstrated in the field.

The n-component correction free energy model is introduced to the dissertation only for the purpose of clarifying and demonstrating how the time and expense of detailed experimentation can be reduced by correcting the calculated results to a few experimental points. A testing of the form of the model by application is beyond the scope of the dissertation and will be saved for further work in the future.

8. SUGGESTIONS FOR FURTHER WORK

8.I Ternary Solid Solution - Liquid Equilibria

For the liquidus extension of a binary solid solution series into a ternary, the activities in the ternary liquid and binary fused crystal were matched only for the two components in the binary solid solution. For a ternary solid solution series, it is necessary to include the matching of activities for all three components. Considering the feldspar system Ab-An-Or, there is data for the crystalline and liquid states in Ab-Or (Thompson and Waldbaum 1969b), An-Ab (Deer et al 1966), and by extrapolation and curve smoothing for the liquid in Or-An (this research). The only thermodynamic data required is for the solid phases in Or-An. From chemical analyses of feldspars it is possible to obtain a minimum estimate of the mutual solid solubility limits of orthoclase and anorthite. By Deer et al (1966), this is about 4-5%, so using the regular solution model at the extrapolated eutectic temperature, a $W_{Or\text{-}An}$ for the crystal phase can be calculated by (3-11) as:

$$W_{Or\text{-}An} = \frac{RT \ln\left(\frac{X_1^A}{X_1^P}\right)}{\left[(1-X_1^A)^2 - (1-X_1^P)^2\right]}$$

$$= \frac{1.987 * 1443 \ln\left(\frac{.95}{.05}\right)}{(.95^2 - .05^2)}$$

$$= 9400 \text{ cals/mole}$$

where T is the eutectic temperature, X_1 is mole percent Or, A is alkali feldspar, P is plagioclase

The liquidus surface would be contoured with two sets of icocrysts, one for the mole percent of Or and the other for the mole percent An. Crystallization paths could easily be deduced using the icocrysts as shown in Appendix D. Next, by calculating the shape of the ternary solvus a plot of some ratio (R) versus temperature would yield a geothermometer.

For example $R = \dfrac{\text{normalized Ab in Alkali feldspar}}{\text{normalized Ab in Plagioclase}}$

would be an acceptable R. There is no unique curve for this such as the one used by Barth (1951) because the mutual solubility of alkali feldspar and Plagioclase is temperature-dependent, but a series of curves of R at constant A_x in Alkali feldspar would provide a unique solution for the temperature.

8. II Pressure and Temperature Dependence of $\overset{x}{G}$

It is evident from Lindsley's work published in the volume "Symposium on Anorthosites" (Isachsen, 1970) that the shifting of the Diopside-Anorthite eutectic towards anorthite at higher pressures cannot be accounted for simply on the basis of raised melting temperatures, plus the same $\overset{x}{\mu}$ curves. The eutectic is shifted so quickly that the non-ideal properties must be pressure dependent. That is to say, the excess volume of mixing is not zero. Thompson (1969) calculated a moderate pressure dependence for his two non-ideality parameters in solid Albite-Orthoclase. In terms then of generality, all excess thermodynamic free energies are pressure dependent. Assuming the $\overset{x}{G}$ is temperature independent, a phase diagram done at two pressures will yield two $\overset{x}{G}$ curves and since $\frac{\partial G}{\partial P} = \overset{x}{V}$ then $\overset{x}{V} = \frac{(\overset{x}{G}_P - \overset{x}{G}_{1atm})}{(P-1)}$, figure 8-1.

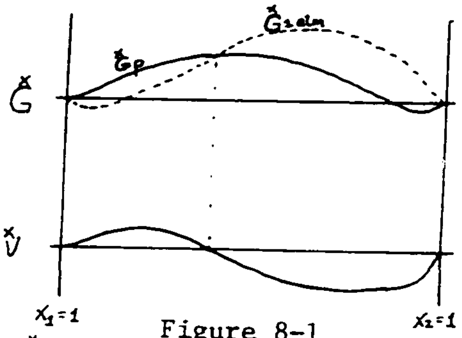


Figure 8-1
$\overset{x}{G}$ and $\overset{x}{V}$ of Two Pressures

This calculated $\overset{x}{V}$ can then be used to get $\overset{x}{G}$ for pressures between 1-atm and P and for moderate extrapolation to higher pressures as

$$\overset{x}{G}_P = \overset{x}{G}_{1\,atm} + (P-1)\cdot\overset{x}{V}$$

Using Lindsley's data on Albite-Anorthite at successive pressures, $\overset{x}{V}$-liquid and $\overset{x}{V}$-solid can be obtained, and with similar data for Diopside-Albite, Diopside-Anorthite, the pressure shifting of the Diopside-Plagioclase cotectic line could be calculated.

Thompson and Waldbaum (1969b) calculated, from a miscibility gap assuming two parameter $\overset{x}{G}$, the temperature dependence and value of $\overset{x}{G}$. The process is not simple, and implicit in the process is that at any one temperature $\overset{x}{G}$ is described accurately by $\overset{x}{G} = X_1X_2(X_1W_{21}+X_2W_{12})$. The temperature dependence of $\overset{x}{G}$ is the excess entropy $\overset{x}{S}$ as $\frac{d\overset{x}{G}}{dT} = -\overset{x}{S}$ It appears to be impossible using phase diagrams to separate the effects of a general $\overset{x}{G}$ and a general $\overset{x}{S}$. However, when the liquidus from a binary is extended into a system, the n-component eutectic minimum uses the $\overset{x}{U}$ data from the lower temperature areas of the binaries:

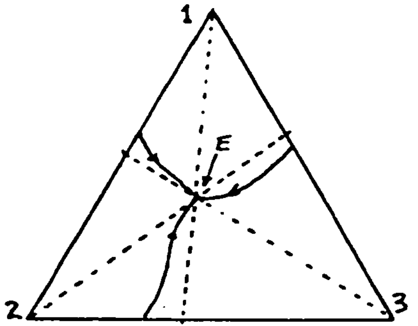


Figure 8-2
Source of $\overset{x}{U}$ for Ternary Eutectic

with reference to figure 8-2 the $\overset{x}{U}$ data for E comes from the intersection of the dotted lines with the binaries, generally cutting the binaries near the binary eutectics i.e. the lower temperatures in the binaries. The process of calculating then corrects itself for $\overset{x}{S}$ automatically to a first approximation. Thus phase diagrams done at two pressures should yield fairly accurate data on $\overset{x}{V}$.

8.III Distribution and Fractioning of Minor and Trace Elements During Crystallization and in Solid State Equilibrium

Assume or obtain equilibrium constants of partitioning of a minor element for every crystalline phase, $\ln K = A + \frac{B}{T}$ and an initial concentration for the minor element. Using the icocrysts of a calculated ternary (Diopside-Albite-Anorthite) map out a typical crystallization path and with this path and the constants derive fractionation curves of the minor element under the following assumptions:

1) Crystallization path is controlled by degree of fractional crystallization.

2) At any time, equilibrium is assumed between liquid and the crystal just crystallized. Regular zoning in crystals in major components can be modeled by fractional crystallization, but during crystallization of each zone the partitioning of the minor element is an equilibrium partitioning.

3) If minor element concentration is small then ignore its activity coefficient, but use activities for the major elements.

4) If two components contain a major element that the minor element is substituting for, it is necessary to use a collected activity for the major element. For example in liquid .70 An, .10 Ab, .20 Diop

$$\underset{\text{LIQUID}}{a_{Ca^{++}}} = \Big[\underbrace{(a_{An})^{.7}\,(a_{Diop})^{.2}}_{\text{LIQUID ACTIVITIES}}\Big]^{\frac{1}{(.7+.2)}}$$

Digital data can be taken from the crystallization path mapped out, with temperature, composition of liquid and plagioclase, activities in liquid and crystals and relative mass of plagioclase that crystallized in the last increment. This could be the input data for a program, to be developed, which moves in small increments of crystallization down the curve calculating partitioning of remaining minor element in the liquid with crystal. When diopside joins plagioclase we need a K-Diopside and the situation has to be solved so that both equilibria occur. When solidification is complete, we then need a K-Diopside-Anorthite that can be obtained from partitioning the binary Diopside-Anorthite:

$$M\cdot MgSi_2O_6 + CaAl_2Si_2O_8 \rightleftharpoons CaMgSi_2O_6 + M\cdot Al_2Si_2O_8$$

$$K_{Diop-An} = \frac{(a_{Diop})(X_M^{Plag})}{(X_M^{Diop})(a_{An}^{Plag})}$$

$a_{Diop} \doteq 1$ but a_{An}^{Plag} is dependent on T and $X_{An}^{CRYSTAL}$

Previous work has been done in this line by Neumann (1954), Mueller (1964), Ryabchikov (1960), Shimazu (1967) and Gast (1968), using assumed distribution coefficients that were temperature and composition independent. With phase data at another pressure, the $\overset{x}{\gamma}$'s can be calculated so that these element partitioning paths can be calculated at different pressures.

8.IV Testing Field Examples of Immiscibility

Collect $\overset{x}{G}$ data on major mineral pairs so that an attempt in 5 - 6 components can be made to check if activity matching does occur between two suspected immiscible liquids. This requires at least partial $\overset{x}{\mu}$ information on at least 10 binaries $({}^5C_2)$. Some experimental point in the system would be valuable to calculate $\overset{K}{G}$, the correction free energy. Then we pick a geologically reasonable temperature range and see if matching of activities can be demonstrated. Some of the liquids cannot be handled; for example, there is insufficient information on phyllosilicates, amphiboles and the effect of water pressure on crystallization. However if it can be demonstrated that these phases crystallize with the same composition in BOTH LIQUIDS, this constitutes reasonable evidence that their activities were the same. However, the $\overset{x}{G}$ for these mineral components is still required for every binary affects $\overset{x}{\mu}_i$ whether it is a binary with i or not. Possibly though, a match of activities ignoring these phases would demonstrate immiscibility.

8.V Apply Methods to Sulphide Systems, Molten Salt Systems, Metamorphic Solid State Equilibria, and Slag Systems

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APPENDIX A

Methods for Deriving $\overset{x}{\mu}$ and $\overset{x}{G}$ from a Simple Binary Eutectic System I-J with No Solid Solution

Input data: weight percent and liquidus temperature data, in order from eutectic out.

Values of $\overset{x}{\mu}_i$ on I's side of the eutectic are calculated using (3-2) $\overset{x}{\mu}_i = \Delta H_i \left(\frac{T - T_{0i}}{T_{0i}}\right) - RT \ln x_i$ and this yields an intermediate data set of the form:

I			J		
x_i	$\overset{x}{\mu}_i$	$\overset{x}{G}_{ij}$	x_j	$\overset{x}{\mu}_j$	$\overset{x}{G}_{ij}$
$x_i(1)$	$\overset{x}{\mu}_i(1)$		$x_j(1)$	$\overset{x}{\mu}_j(1)$	
$x_i(2)$	$\overset{x}{\mu}_i(2)$		$x_j(2)$	$\overset{x}{\mu}_j(2)$	
⋮	⋮		⋮	⋮	
⋮	⋮		$x_j(n_j)$	$\overset{x}{\mu}_j(n_j)$	
$x_i(n_i)$	$\overset{x}{\mu}_i(n_i)$				

← Eutectic: $X_i(1) + X_j(1) = 1$

n_i, the number of liquidus points on I's side, need not equal n_j

1) Iterative Graphical Construction of $\overset{x}{G}_{ij}$ using $\overset{x}{\mu}_i$ and $\overset{x}{\mu}_j$ with Program QCALN2

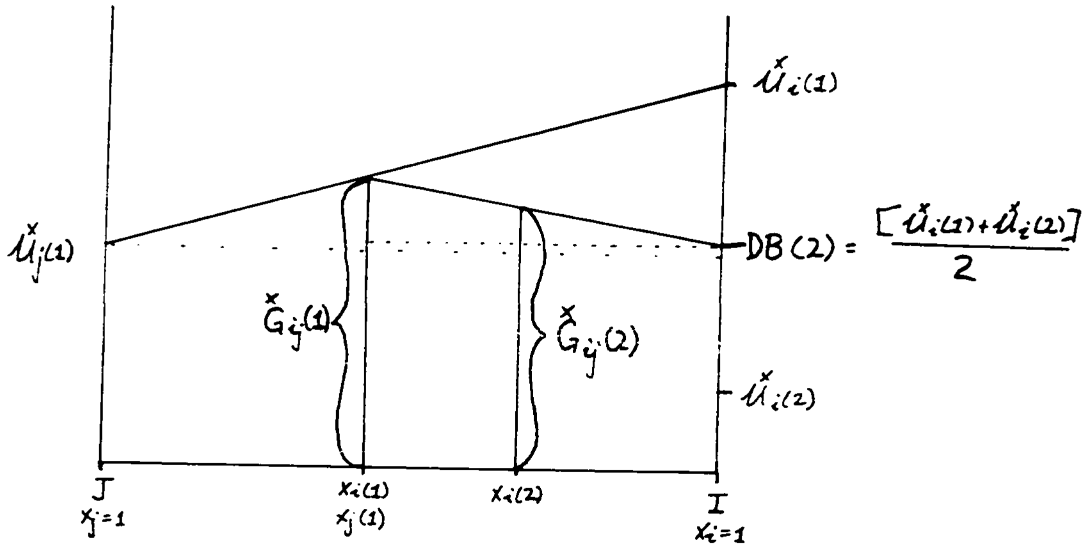


Figure A-1
Geometric Construction of $\overset{x}{G}_{ij}$

With reference to figure A-1, since $X_i(1)$ is the eutectic, with $\overset{x}{U}_i(1)$, $\overset{x}{U}_j(1)$ being the partial quantities of $\overset{x}{G}_{ij}(1)$ at $X_i(1)$, then from the geometry

$$\frac{[\overset{x}{U}_i(1) - \overset{x}{U}_j(1)]}{[1 - 0]} = \frac{[\overset{x}{G}_{ij}(1) - \overset{x}{U}_i(1)]}{[X_i(1) - 1]} \tag{A-1}$$

and hence

$$\overset{x}{G}_{ij}(1) = [1 - X_i(1)][\overset{x}{U}_j(1) - \overset{x}{U}_i(1)] + \overset{x}{U}_i(1) \tag{A-2}$$

Putting $$DB(2) = \frac{[\overset{x}{U}_i(1) + \overset{x}{U}_i(2)]}{2}$$

and solving the geometry for $\overset{x}{G}_{ij}(2)$

$$\frac{[\overset{x}{G}_{ij}(2) - DB(2)]}{[X_i(2) - 1]} = \frac{[\overset{x}{G}_{ij}(1) - DB(2)]}{[X_i(1) - 1]}$$

so

$$\overset{x}{G}_{ij}(2) = \frac{[X_i(2) - 1]}{[X_i(1) - 1]}\left[\overset{x}{G}_{ij}(1) - DB(2)\right] + DB(2) \tag{A-3}$$

Thus the general iterative formula is

$$\overset{x}{G}_{ij}(n+1) = \frac{[X_i(n+1) - 1]}{[X_i(n) - 1]}\left[\overset{x}{G}_{ij}(n) - DB(n+1)\right] + DB(n+1) \tag{A-4}$$

where $DB(n+1) \equiv [\overset{x}{U}_i(n) + \overset{x}{U}_i(n+1)]/2$.

This method requires a large number of data points (50-60) spread throughout the interval. An upper and a lower curve of $\overset{x}{G}_{ij}$ (i.e. an estimate of possible error in $\overset{x}{G}$ due to the nature of construction) can be calculated by making a curve with $DB(n) = \overset{x}{U}_i(n-1)$ and with $DB(n) = \overset{x}{U}_i(n)$. In general the difference in the curves was smaller than the accuracy of plotting if more than fifty points were used. Data for $\overset{x}{U}_j$ on I's side of the eutectic is obtained from (A-1) as $\overset{x}{U}_j = \overset{x}{U}_i + \dfrac{[\overset{x}{G}_{ij} - \overset{x}{U}_i]}{[X_i - 1]}$.

2) <u>Solution of Differential Equation for $\overset{x}{G}_{ij}$ from $\overset{x}{U}_i, \overset{x}{U}_j$ with Program QCALN3</u>

Since $\overset{x}{U}_i$ is a partial quantity of $\overset{x}{G}_{ij}$ then (2-1) holds, $\overset{x}{U}_i = \overset{x}{G}_{ij} + (1 - X_i)\dfrac{D(\overset{x}{G}_{ij})}{D(X_i)}$, and putting $X \equiv X_i$, dividing by $(1-X)^2$ yields

$\frac{1}{(1-x)}\frac{d\overset{x}{G}}{dx} + \frac{\overset{x}{G}}{(1-x)^2} = \frac{\overset{x}{\mathcal{U}}_i}{(1-x)^2}$ so that $d\left[\frac{\overset{x}{G}}{[1-x)}\right] = \frac{\overset{x}{\mathcal{U}}_i}{(1-x)^2}$

Integrating between $x(1) \equiv x_i(1)$ and $x(2) \equiv x_i(2)$

$$\frac{\overset{x}{G}(2)}{[1-x(2)]} - \frac{\overset{x}{G}(1)}{[1-x(1)]} = \int_{x(1)}^{x(2)} \frac{\overset{x}{\mathcal{U}}_i}{(1-x)^2}\,dx$$

Hence

$$\overset{x}{G}(2) = [1-x(2)]\left[\frac{\overset{x}{G}(1)}{[1-x(1)]} + \int_{x(1)}^{x(2)} \frac{\overset{x}{\mathcal{U}}_i}{(1-x)^2}\,dx\right] \qquad \text{A-5}$$

According to Darken (1953) the argument $\frac{\overset{x}{\mathcal{U}}_i}{(1-x)^2}$ is integrable as $x_i \to 1$ as a result of Raoult's Law in the neighbourhood of $x_i = 1$:

$$\lim_{x_i \to 1}\left[\frac{\overset{x}{\mathcal{U}}_i}{(1-x)^2}\right] = A$$

That is: $\overset{x}{\mathcal{U}}_i$ approaches zero as fast as $A(1-x)^2$. The integration is performed by fitting $\{\overset{x}{\mathcal{U}}_i(k), x_i(k)\}_{k=n,n+1,n+2}$ to a parabola and integrating between $x_i(n)$ and $x_i(n+1)$.

The general form is

$$\overset{x}{G}(n+1) = [1-x(n+1)]\left[\frac{\overset{x}{G}(n)}{[1-x(n)]} + \int_{x(n)}^{x(n+1)} \frac{\overset{x}{\mathcal{U}}_i}{(1-x)^2}\,dx\right] \qquad \text{A-6}$$

and (A-2) defines $\overset{x}{G}(1)$ at $x_i(1)$. Alternately $\left\{\frac{\overset{x}{\mathcal{U}}_i(k)}{[1-x_i(k)]^2}, x_i(k)\right\}_{k=n,n+1,n+2}$ could be fitted to the parabola. This simplifies the integration formula but results from both methods were within .02 percent of each other. The print out of QCALN3 uses the parabolic fit to $\overset{x}{\mathcal{U}}_i$.

3) <u>Modified Gibbs-Duhem Integration: Program DUHEM</u>

From Darken (1953), a typical Gibbs-Duhem integration takes the form

$$\ln\gamma_i = -\int_{x_i=1}^{x_i=x_i'} \frac{x_j}{(1-x_j)}\,d\ln\gamma_j \qquad \text{A-7}$$

Since $\frac{x_j}{(1-x_j)}$ becomes infinite at $x_j = 1$, the integration is difficult near $x_j = 1$ so Darken introduces the transformation $\alpha_j = \frac{\ln\gamma_j}{(1-x_j)^2}$. A-8

By the regular solution model $\check{\mathcal{U}}_i = RT\ln\gamma_i$ is temperature invariant so that $\alpha_j = RT\alpha_j'$ will be used and both sides of (A-8,7) will be multiplied by RT. This yields $\alpha_j = \frac{RT\ln\gamma_j}{(1-x_j)^2}$ and rearranging $RT\ln\gamma_j = \alpha_j(1-x_j)^2 = x_i^2\alpha_j$ A-9

so that $d(RT\ln\gamma_j) = x_i^2 d\alpha_j + 2x_i\alpha_j dx_i$. Substituting into (A-7)

$$RT\ln\gamma_i = -\int_{x_i=1}^{x_i=x_i}(1-x_i)[x_i d\alpha_j + 2\alpha_j dx_i] = -2\int_{x_i=1}^{x_i=x_i} x_j\alpha_j dx_i - \int_{x_i=1}^{x_i=x_i} x_j(1-x_j)d\alpha_j$$

Integrating the second integral by parts yields

$$\int_{x_i=1}^{x_i=x_i} x_j(1-x_j)d\alpha_j = x_i x_j\alpha_j - \int_{x_i=1}^{x_i=x_i}\alpha_j d(x_i x_j) = x_i x_j\alpha_j + \int_{x_i=1}^{x_i=x_i}\alpha_j x_i dx_i - \int_{x_i=1}^{x_i=x_i}\alpha_j x_j dx_i$$

so

$$RT\ln\gamma_i = -x_i x_j\alpha_j - \int_{x_i=1}^{x_i=x_i}[x_i\alpha_j + x_j\alpha_j]dx_i$$

and

$$\check{\mathcal{U}}_i = -x_i x_j\alpha_j - \int_{x_i=1}^{x_i=x_i}\alpha_j dx_i \qquad \text{A-10}$$

Since the input data goes from the eutectic out, the equation needs to be modified. Where $\check{\mathcal{U}}_i(n+1)$ is to be determined on J's side of eutectic at $x_j(n+1)$,

$$\check{\mathcal{U}}_i(n+1) = -x_j(n+1)[1-x_j(n+1)]\alpha_j(n+1) - \int_{x_j=0}^{x_j=x_j(n+1)}\alpha_j d(1-x_j)$$

$$\check{\mathcal{U}}_i(n) = -x_j(n)[1-x_j(n)]\alpha_j(n) - \int_{x_j=0}^{x_j=x_j(n)}\alpha_j d(1-x_j)$$

and subtracting and rearranging for the general formula

$$\check{\mathcal{U}}_i(n+1) = \check{\mathcal{U}}_i(n) + x_j(n)[1-x_j(n)]\alpha_j(n) - x_j(n+1)[1-x_j(n+1)]\alpha_j(n+1)$$
$$- \int_{x_j=x_j(n)}^{x_j=x_j(n+1)}\alpha_j d(1-x_j) \qquad \text{A-11}$$

At the eutectic $\alpha_j(1)$ is defined by (A-9). This method yields, directly, values of $\check{\mathcal{U}}_i$, $\check{\mathcal{U}}_j$ across the interval. The curve of $\check{G}_{ij}$ can be obtained by use of (A-2). Suppose inside of $x_j(n) < x_j \leq 1$, α_j remains constant.

Then using (A-11)

$$\overset{\times}{\mathcal{U}}_i(x_j=1) = \overset{\times}{\mathcal{U}}_i(n) + \alpha_j(n)\,x_j(n)\left[1-x_j(n)\right] + \alpha_j(n)\left[0-\left[1-x_j(n)\right]\right]$$

$$= \overset{\times}{\mathcal{U}}_i(n) + \alpha_j(n)\,x_j(n)\left[1-x_j(n)\right] + \alpha_j(n)\left[1-x_j(n)\right]$$

so $$\overset{\times}{\mathcal{U}}_i(x_j=1) = \overset{\times}{\mathcal{U}}_i(n) + \alpha_j(n)\left[1-x_j(n)\right]^2 \qquad \text{A-12}$$

In general all three methods gave comparable curves for $\overset{\times}{G}_{ij}$ within the plotting accuracy. One major difficulty was in recalculating accurate $\overset{\times}{\mathcal{U}}_i$, $\overset{\times}{\mathcal{U}}_j$ from segmented parabolic fitted curves of $\overset{\times}{G}_{ij}$, so that the modified Gibbs-Duhem approach was the method used to generate by direct calculation $\overset{\times}{\mathcal{U}}_i$, $\overset{\times}{\mathcal{U}}_j$. This problem of obtaining accurate $\overset{\times}{\mathcal{U}}_i$ from a segment fitted $\overset{\times}{G}_{ij}$ curve was especially bad near segment borders. Here the slope was not exactly continuous to the next segment and hence two values of $\overset{\times}{\mathcal{U}}_i$ at a border could be calculated depending on the direction of approach. But by fitting $\overset{\times}{\mathcal{U}}_i$, $\overset{\times}{\mathcal{U}}_j$ in parabolic segments, (A-2) and $\Theta_{ij} = \overset{\times}{\mathcal{U}}_i - \overset{\times}{\mathcal{U}}_j$ yielded the necessary data for the n-component activity coefficient calculations, while slope discontinuities in $\overset{\times}{\mathcal{U}}_i$ curves only appear as second derivative discontinuities in $\overset{\times}{G}_{ij}$. This is so since $\frac{d(\overset{\times}{G}_{ij})}{d(x_i)} \equiv \Theta_{ij} = \overset{\times}{\mathcal{U}}_i - \overset{\times}{\mathcal{U}}_j$ and $\frac{d^2\overset{\times}{G}_{ij}}{dx_i^2} = \frac{d\overset{\times}{\mathcal{U}}_i}{dx_i} - \frac{d\overset{\times}{\mathcal{U}}_j}{dx_i}$: $\overset{\times}{\mathcal{U}}_i$ is continuous but $\frac{d\overset{\times}{\mathcal{U}}_i}{dx_i}$ is not. An example of the problems encountered in using a segmented parabolic fit to $\overset{\times}{G}$ is shown in Figure A-2. The segmented parabolic fit to $\overset{\times}{\mathcal{U}}_i$ curves completely eliminated such difficulties and permitted calculations to be extended to ternary systems.

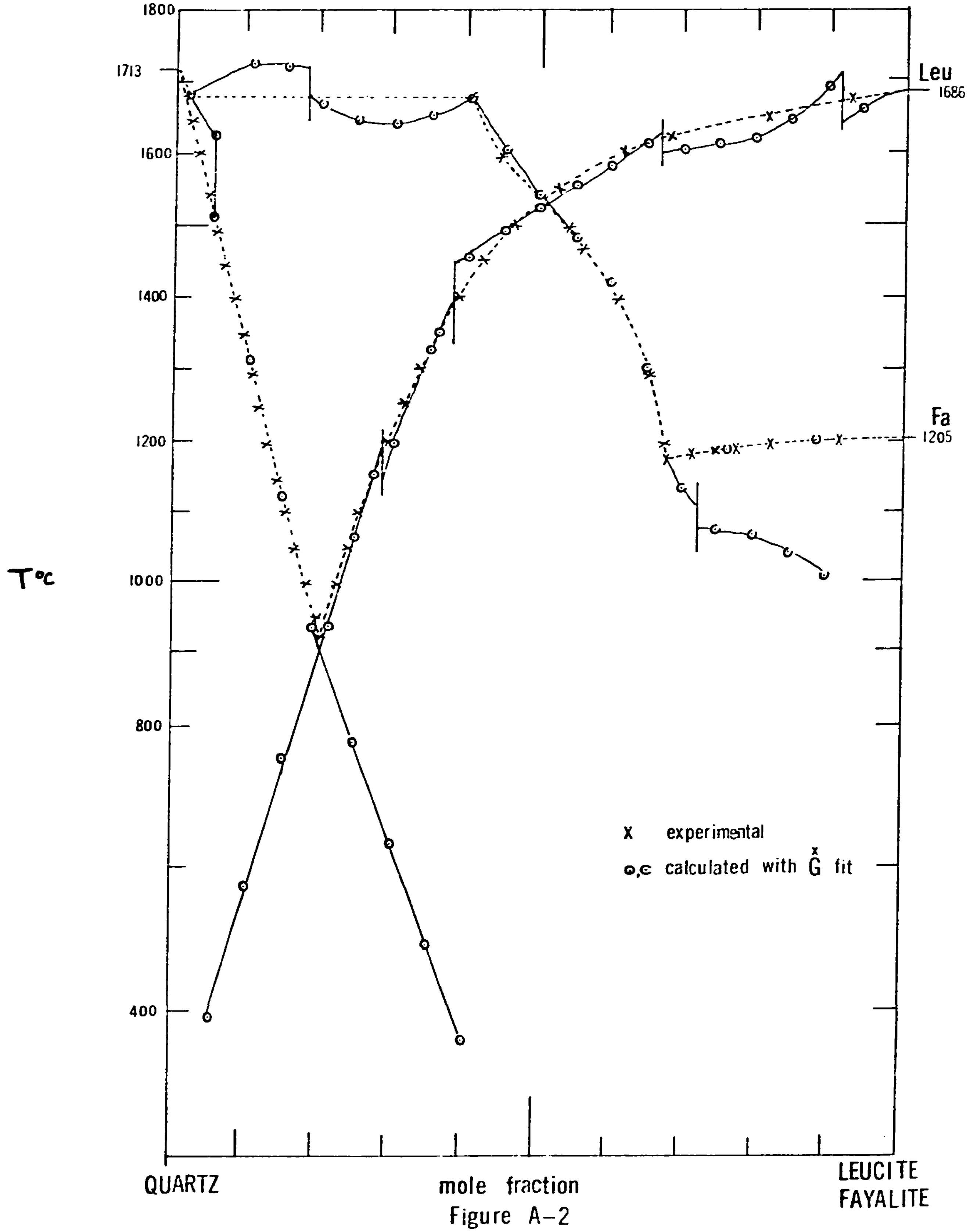


Figure A-2

Liquidus Calculated with Segmented Parabolic Fit to $\overset{x}{G}$

APPENDIX B

Methods for Generating $\overset{x}{\mu}_i$ and $\overset{x}{G}_{ij}$ from Phase Diagrams Involving Two Coexisting Solution Phases A and B: Programs W1XLIQ, WWXLIQ, OLCAL

Programs W1XLIQ: $\overset{x}{G}_{ij} = x_i x_j w_{ij}$ and WWXLIQ: $\overset{x}{G}_{ij} = x_i x_j (x_j w_{ij} + x_i w_{ji})$ use data from the binary, (3-7, 8), and calculate:no error, minimum and maximum values for $\overset{x}{\mu}_i^{LIQUID}$, $\overset{x}{\mu}_i^{CRYSTAL}$ assuming reasonable errors in $T - X_{LIQ} - X_{CRYS}$ in taking points off the phase diagram. These limits are used in conjunction with DUHEM (ITYPE =2) to see whether or not the $\overset{x}{\mu}_i$ curves can be adjusted to be smooth and satisfy the Gibbs-Duhem relation. Program OLCAL calculates $\overset{x}{\mu}_i^{A}$ from $\overset{x}{\mu}_i^{B}$ for a binary with coexisting solution phases A and B using (3-5) and the temperature and compositions:

$$\overset{x}{\mu}_i^{A} = \overset{x}{\mu}_i^{B} + RT\ln\left(\frac{X_i^{B}}{X_i^{A}}\right) + \Delta H_i^{B\to A}\,\frac{(T - T_{0i})}{T_{0i}} \qquad \underline{\text{B-1}}$$

The source of $\overset{x}{\mu}_i^{B}$ can be independent or derived from the phase diagram using programs W1XLIQ or WWXLIQ. I calculated from Nafziger's data (1968), using a least square technique, $W^{CRYSTAL}_{Fo-Fa} = 1166 \pm 128$ cals/mole with the same activity accuracy as for Nafziger's activity curves drawn to fit the data. The experiments were performed at 1100°C, so the use of OLCAL to generate $\overset{x}{\mu}_{Fo}^{LIQUID}$, $\overset{x}{\mu}_{Fa}^{LIQUID}$ curves from the phase diagram would test the assumption $W^{CRYSTAL}_{Fo-Fa} \neq f(T)$. This was tried but the relation between $\overset{x}{\mu}_{Fo}^{LIQUID}$ and $\overset{x}{\mu}_{Fa}^{LIQUID}$ did not satisfy tangency to the $\overset{x}{G}_{LIQUID}$ curve. Apparently 1100°C is too different from liquidus temperatures (1205-1890°C) and the $W^{CRYSTAL}_{Fo-Fa}$ of the crystalline olivines is temperature dependent. It was found that $\overset{x}{\mu}_i^{LIQUID}$ is insensitive to $\overset{x}{\mu}_i^{CRYSTAL}$ if the crystal is $\geq$ 85% pure, thus in some cases reliable curves for $\overset{x}{\mu}_i^{LIQUID}$ could be generated using W1XLIQ or WWXLIQ without being able to obtain suitable $\overset{x}{\mu}_i$ curves for the crystal. The $\overset{x}{\mu}_i^{CRYSTAL}$ curves can be generated using OLCAL.

Program QESTR estimates $\Delta H_i'$, the heat of fusion of I, from binary liquidus data assuming the particles of I in the melt have the same molecular weight as the crystalline end member of I. By (4-1)

$$\Delta H_i' = \frac{R \ln X_i}{\left(\frac{1}{T_{0i}} - \frac{1}{T}\right)} \quad \text{so that} \quad RT \ln X_i = \Delta H_i' \left(\frac{T}{T_{0i}} - 1\right)$$

$$= \Delta H_i' \frac{T}{T_{0i}} - \Delta H_i' \qquad \underline{\text{B-2}}$$

Thus a plot of $RT\ln X_i$ versus $\frac{T}{T_{0i}}$ has a slope of $\Delta H_i'$ which should approach ΔH_i as $X_i \rightarrow 1$. When X_i gets very close to 1, $\frac{1}{T_{0i}} - \frac{1}{T}$ is very subject to errors causing large variations in $\Delta H_i'$. The plot of $RT\ln X_i$ versus $\frac{T}{T_{0i}}$ will overlie a grid of radiating lines of constant $\Delta H_i'$ and a region for estimating ΔH_i can be outlined between $[X_i \rightarrow 1]$ and $[(\frac{1}{T_{0i}} - \frac{1}{T})$ not subject to errors$]$.

Program TMQ uses selected data from the $\check{\mu}_i$ curves generated by DUHEM, W1XLIQ, WWXLIQ, and OLCAL, and fits it in segments to parabolas and punches out on cards the resulting data in a suitable form for use with program GAPMIS.

APPENDIX C

Phase Equilibria Calculations

Program Gapmis

Input data: 1) end member reaction heats and temperatures for all components in n-component system

2) ${}^{n}C_{2}$ binary data for excess chemical potentials: boundaries of intervals and parabolic fit coefficients to μ_i^x, μ_j^x in the intervals.

3) specified temperature T and its range for computations.

4) bounding mole fractions for area (s) for computations and composition increments for calculations.

5) parameter ITYPE which defines the type of phase calculation to be performed (Table C-1).

TABLE C-1

ITYPE	Operation in area of interest at temperature T
0	immiscibility tie lines in liquid
1	immiscibility tie lines in liquid then read new T
2	a_i^x in solid solution crystal, then read new T
3	activities in liquid, then read new T
4	activities in solid solution crystal, then read new T
5	activities in fused solid solution crystal, then read new T
6	liquidus, no solid solution, away from each component
7	liquidus, then read new T
8	solid solution-liquid tie lines
9	solid solution - liquid tie lines then read new T

ITYPE Options 3,4, 5:activities at $(x_1, x_2, x_3 ,, x_n)$

Using formula (2-8) : $\overset{x}{\mu}_i = 2\sum_{j\neq i}^{n}(x_i+x_j)\overset{x}{G}_{ij} + \sum_{j\neq i}^{n} x_j\,\theta_{ij} - \sum_{i=1}^{n}\sum_{j>i}^{n}(x_i+x_j)^2\overset{x}{G}_{ij}$

with $\overset{x}{G}_{ij}$ and θ_{ij} being obtained from binary ij at $z_{ji} = \frac{x_j}{(x_i+x_j)}$.

Then

$$a_i = x_i \ \mathrm{EXP}\left(\frac{\overset{x}{\mu}_i}{RT}\right) \tag{C-1}$$

We enter the binary ij at z_{ji} as opposed to z_{ij} since the binary $\overset{x}{\mu}_1$, $\overset{x}{\mu}_2$ data is arbitrarily fitted in segmented parabolas to X_2 . Activities in the crystal can be referred to a fused state for option 5 by use of (3-5):

$$\overset{x}{\mu}_i^B - \overset{x}{\mu}_i^A = RT\ln\left(\frac{x_i^A}{x_i^B}\right) + \Delta H_i^{B\to A}\left(1 - \frac{T}{T_{0i}}\right)$$

Putting $x_i^A = x_i^B$ for fused crystal A of same composition as crystal B

then

$$\overset{x}{\mu}_i^A = \overset{x}{\mu}_i^B - \Delta H_i^{B\to A}\frac{(T_{0i}-T)}{T_{0i}} = \overset{x}{\mu}_i^B + \Delta H_i^{B\to A}\frac{(T-T_{0i})}{T_{0i}} \tag{C-2}$$

Since $\overset{x}{\mu}_i^B$ is known from the input data, then (C-1) gives the activities in the fused state from $\overset{x}{\mu}_i^B$.

Options 6,7: liquidus temperatures away from I at $(x_1, x_2, \ldots, x_n)$

With $\overset{x}{\mu}_i$, ΔH_i and T_{0i} known then by (3-3)

$$T_i = -T_{0i}\,\frac{(\overset{x}{\mu}_i + \Delta H_i)}{(RT_{0i}\ln x_i - \Delta H_i)}$$

Options 0,1: Immiscibility tie lines in three component system

In search areas A, B (figure C-1), activities a_i , b_i are calculated on the four corners of a parallelogram defined by

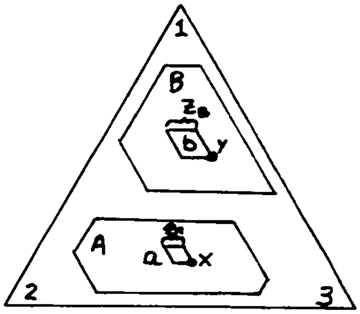


Figure C-1
The Search Parallelograms a and b
in Search Areas A and B

A	B
a: X_1, X_2, X_3	b: Y_1, Y_2, Y_3
X_1+Z_A, X_2, X_3-Z_A	Y_1+Z_B, Y_2, Y_3-Z_B
$X_1+Z_A, X_2+Z_A, X_3-2Z_A$	$Y_1+Z_B, Y_2+Z_B, Y_3-2Z_B$
X_1, X_2+Z_A, X_3-Z_A	Y_1, Y_2+Z_B, Y_3-Z_B

where Za is the search increment in area A

Then $\bar{a}_i = [\min(a_i)+\max(a_i)]/2$. with a_i being determined on each corner of a and the range of a_i from $\bar{a}_i$ is $Ra_i = [\max(a_i) - \min(a_i)]/2$.

Similarily for b:

$$\bar{b}_i = [\min(b_i)+\max(b_i)]/2$$

$$Rb_i = [\max(b_i)-\min(b_i)]/2 \qquad \underline{\text{C-3}}$$

Putting $$AB_i = [ABS(\bar{a}_i - \bar{b}_i) - (Ra_i + Rb_i)] \qquad \underline{\text{C-4}}$$

if $AB_i > 0$, then the separation between $\bar{a}_i$ and $\bar{b}_i$ exceeds the sum of their ranges so there can be no solution tie line joining points within areas a and b. However, if $AB_i \leq 0$ then the limits of a_i overlap b_i, so there is two points, one in a and one in b so that $a_i = b_i$ (activities). If it holds for all components i.e. $AB_i \leq 0$ for $i = 1,2,3$ <u>C-5</u>

then there is a solution in a and b such that

$$\text{activities in } a \left\{ \begin{array}{l} a_1 = b_1 \\ a_2 = b_2 \\ a_3 = b_3 \end{array} \right\} \text{activities in } b$$

so that the activities are matched for components 1, 2,3.

The two parallelograms can be further subdivided to refine the solution.

<u>Options 8,9: Binary Solid Solution Liquidus into System</u>

Since components outside the binary solid solution do not dissolve appreciably in the solution crystal, the activity matching (C-3,4,5) between the three component liquid and the fused crystal, is done only for the two components in the solid solution binary using (C-2,1) i.e. $AB_i \leq 0$ for i=2,3. The process and program is easily altered to handle ternary liquid solution - ternary solid solution by doing a search for $AB_i \leq 0$, i= 1,2,3.

APPENDIX D

Stepwise Construction of Crystal Fractionation Paths

A hundred percent fractionation path (F=100) is defined by constant removal of all the crystals formed in the last instant so that the bulk composition of the system is that of the liquid. As a result the liquid moves directly away from the composition of the crystallizing phase, plagioclase. This path may be constructed in incremental steps of 2.5% An in the plagioclase and icocrysts (figure D-3). For a constant bulk composition and equilibrium path (F=0), the crystal, bulk, and liquid compositions must lie on a straight line. If the crystal composition is specified as X_c, then the liquid composition is found where the line joining X_c and the bulk composition cuts the X_c icocryst. The final crystal, composition X_{c1}, is given by the bulk composition: there will only be two phases, diopside and a homogeneous plagioclase, so the plagioclase composition is given by the line Diopside-bulk composition. Thus the position of the last liquid on the cotectic is at the X_{c1} icocryst. The two paths F=0 and F=100 form the constraining boundaries for all possible types of crystallization paths excluding contamination.

Intermediate paths for $0 < F < 100$ may be modeled by removing a certain constant percentage (F) of the crystals formed in each increment of crystallization. Considering figure D-1; in order to remove F percent of the crystals, the bulk composition must be moved dY_c towards the liquid, so that $\frac{Y_c'}{L_c}$ = new amount of crystals. Thus $\frac{Y_c'}{L_c} = (1-F)\frac{Y_c}{L_c}$ so that $Y_c' = Y_c(1-F)$ since L_c remains constant. Y_c is shortened by F percent to remove F percent of the crystals.

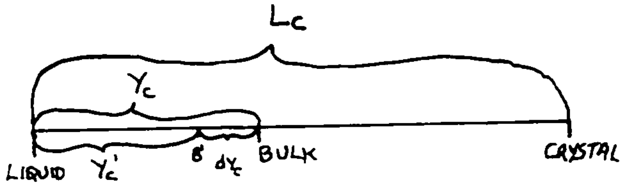


Figure D-1

Two "Component" Lever Rule for Fractionation

The bulk composition moves directly towards the liquid composition, but lags behind by Y_c' . The situation becomes more difficult when the third phase, Diopside, appears. If we assume that both Diopside and plagioclase are removed in the same proportion, then figure D-2 applies.

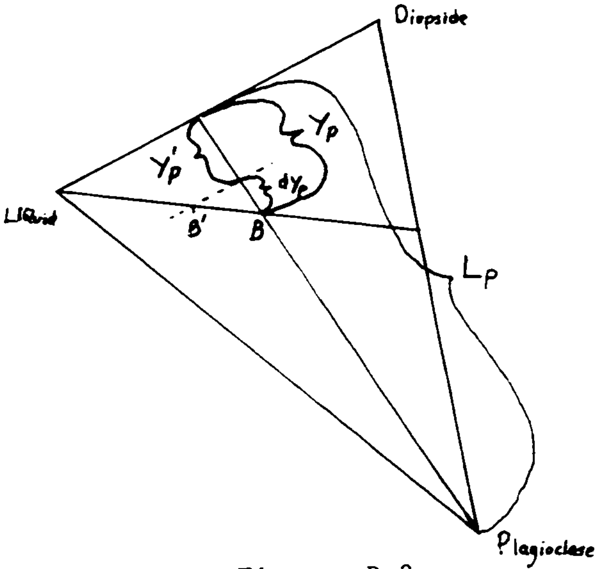


Figure D-2

Three "Component" Lever Rule for Fractionation

It is necessary to remove dY_p of P, so that the new amount of P (Y_p') is reduced by F= $\frac{dY_p}{Y_b}$ from the old amount (Y_p). A line parallel to D-LIQ through the end of Y_p' will maintain $\frac{Y_p'}{L_p}$ constant, and the new position of the bulk composition is at B'. B moves directly towards the liquid but lags behind by $L_{LIQ} - Y_p'$. If D and P are to be removed in different proportions then the construction is repeated for the line

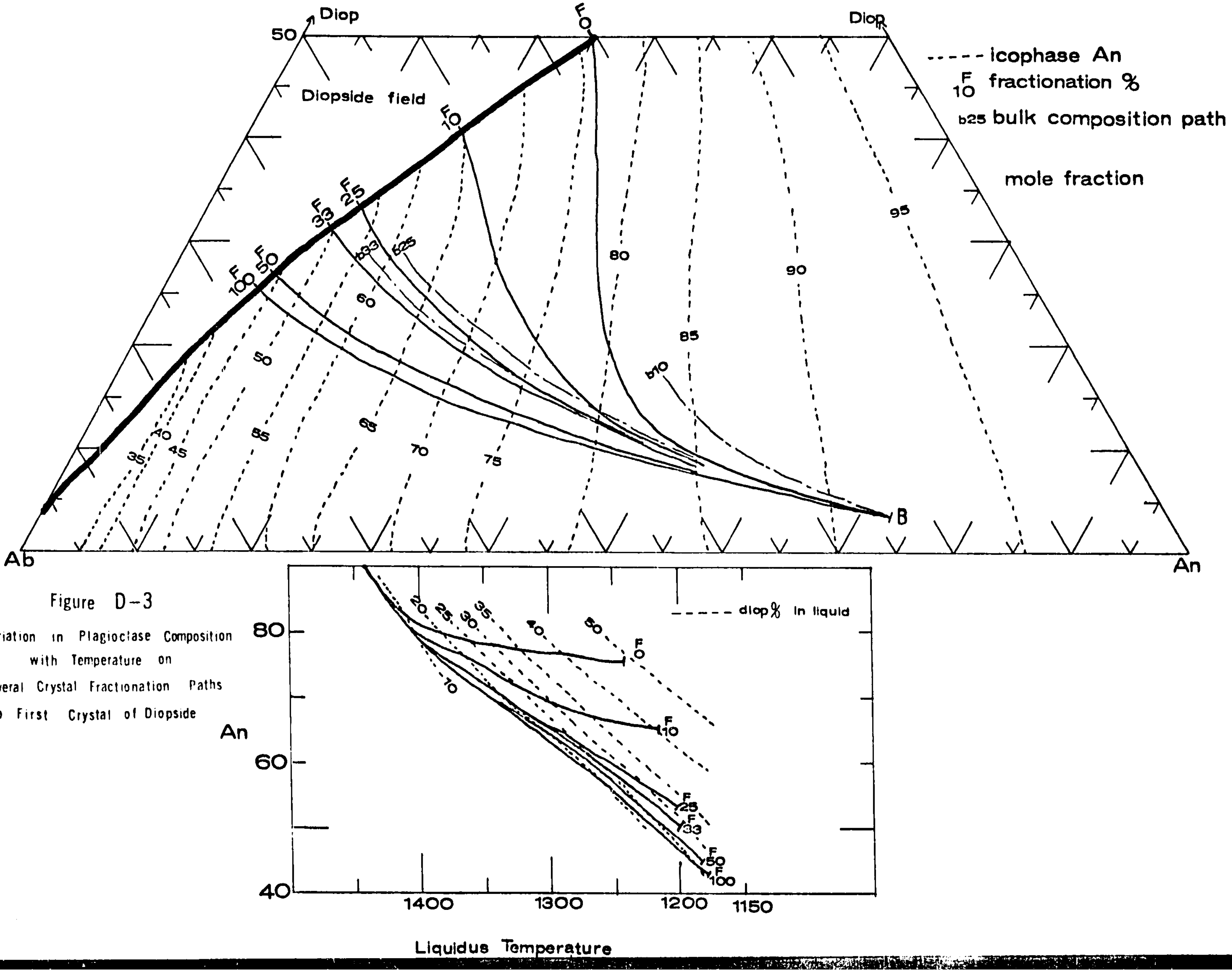


Figure D-3

Variation in Plagioclase Composition with Temperature on Several Crystal Fractionation Paths to First Crystal of Diopside

D-B and the new bulk composition occurs where the two lines of constant $\frac{Y_P'}{L_P}$ and $\frac{Y_D'}{L_D}$ intersect. In these circumstances B will not move towards the liquid.

For general crystallization, $0 < F < 100$, the path followed by the bulk composition deviates from the path followed by the liquid. As $F \rightarrow 0$ the deviation increases, until at $F=0$ the bulk composition does not move at all. Paths of $F \leq 15$ cover <u>one half</u> of the crystallization field and strongly control the composition of the coexisting plagioclase. Figure D-3 shows how small local differences in the degree of fractionation ($F=10 \pm 5$) may, <u>at the same temperature</u>, cause two quite different compositions (An ± 8%) of plagioclase to crystallize. Perhaps this provides a clue to zoning of plagioclases in igenous bodies, where computations by Jeffries (1959) indicate vertical thermal gradients as low as .3°/km for cooling with convection. Geologically reasonable values for F are probably near $F=10$ for magmas crystallizing to homogeneous gabbros on the macroscopic scale. On the other hand, for magmas separating high density minerals resulting in very sharply defined gravity stratification, the value is probably $50 < F < 100$. Furthermore, in large igneous bodies, time is approximately linearly related to temperature so that a plot of An in plagioclase versus temperature may be used with a general time sense.

If the bulk composition of B is such that the $F=0$ path does not reach the binary eutectic Diopside - Albite before complete solidification (B in figure D-3 only moves 2% Albite down the cotectic on $F=0$), then some of the lower F paths will also not reach the binary eutectic. These paths may be correctly terminated by examining to see if the moving bulk composition lies in the triangle $X_{LIQ} - An_{92} - An_{\text{ICOCRYST at } X_{LIQ}}$. This is the constraint since the "magma" is a linear combination of these three "components".

APPENDIX E

Thermodynamic Data for Data Sources

Phase diagrams and the resulting $\overset{x}{\mu}$ curves, for liquid phases and solid phases where applicable, are shown in figures E-1 to E-5. Phase diagrams which are in weight fraction are indicated with a "Wt %". All $\overset{x}{\mu}$ values are in calories per mole and the composition axis for the $\overset{x}{\mu}$ curves is in molefraction in every case. The thermodynamic data used by GAPMIS for the systems Quartz - Fayalite - Leucite and Quartz - Albite - Orthoclase is listed after figure E-5. Thermodynamic data for the system Diopside - Albite - Anorthite is listed with the program GAPMIS in Appendix F.

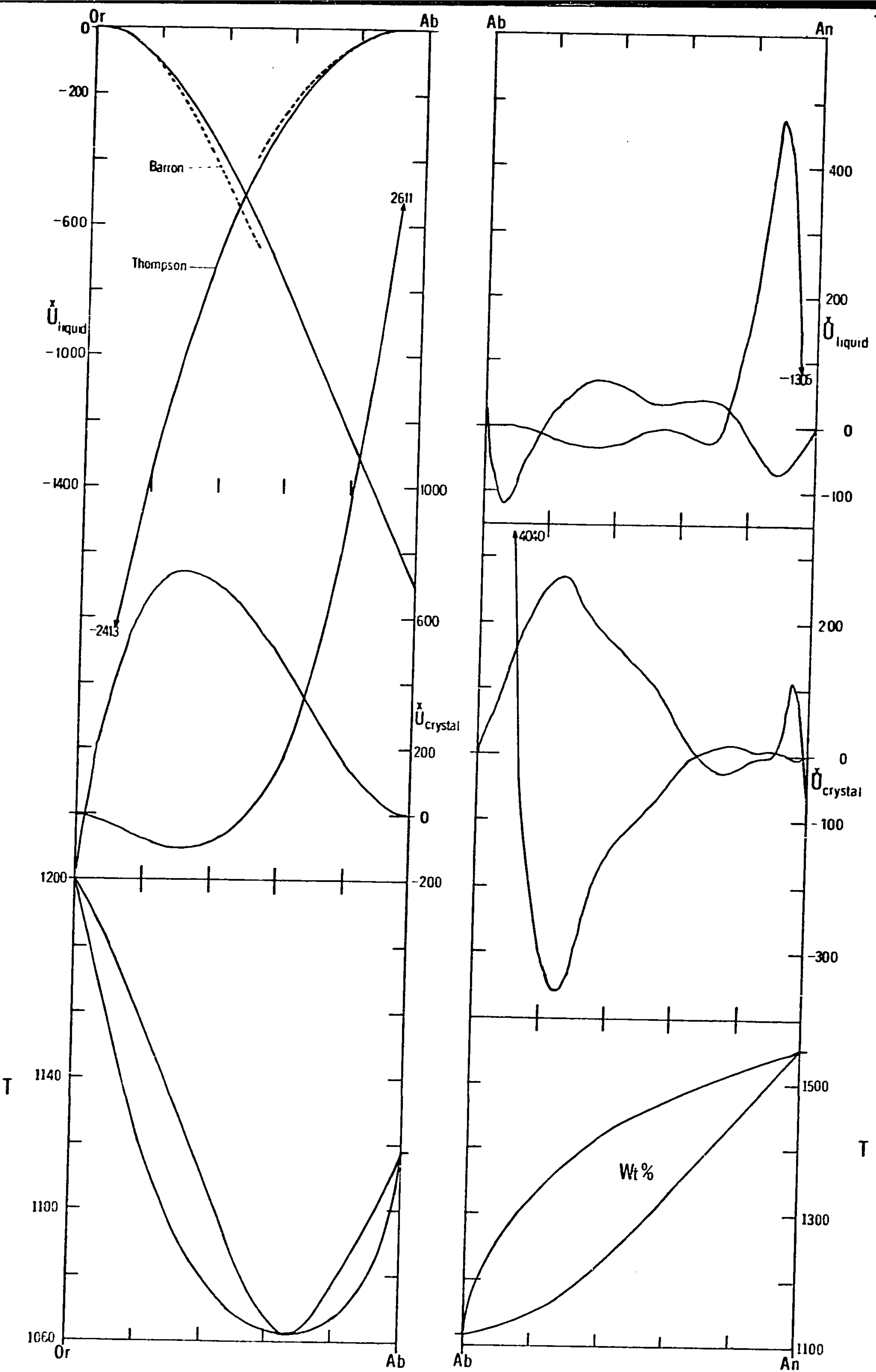

Or
Ab
0
-200
Barron
2611
-600
Thompson
$\check{U}_{liquid}$
-1000
-1400
1000
-2413
600
$\check{U}_{crystal}$
200
0
1200
-200
T
1140
1100
1060
Or
Ab
Ab
An
400
200
$\check{U}_{liquid}$
-1306
0
-100
4040
200
0
$\check{U}_{crystal}$
-100
-300
1500
T
Wt%
1300
1100
Ab
An

Figure E-1

Figure E-2

ESTIMATION OF Or – An in 1. > X_{Or} > .77 MOLE FRACTION

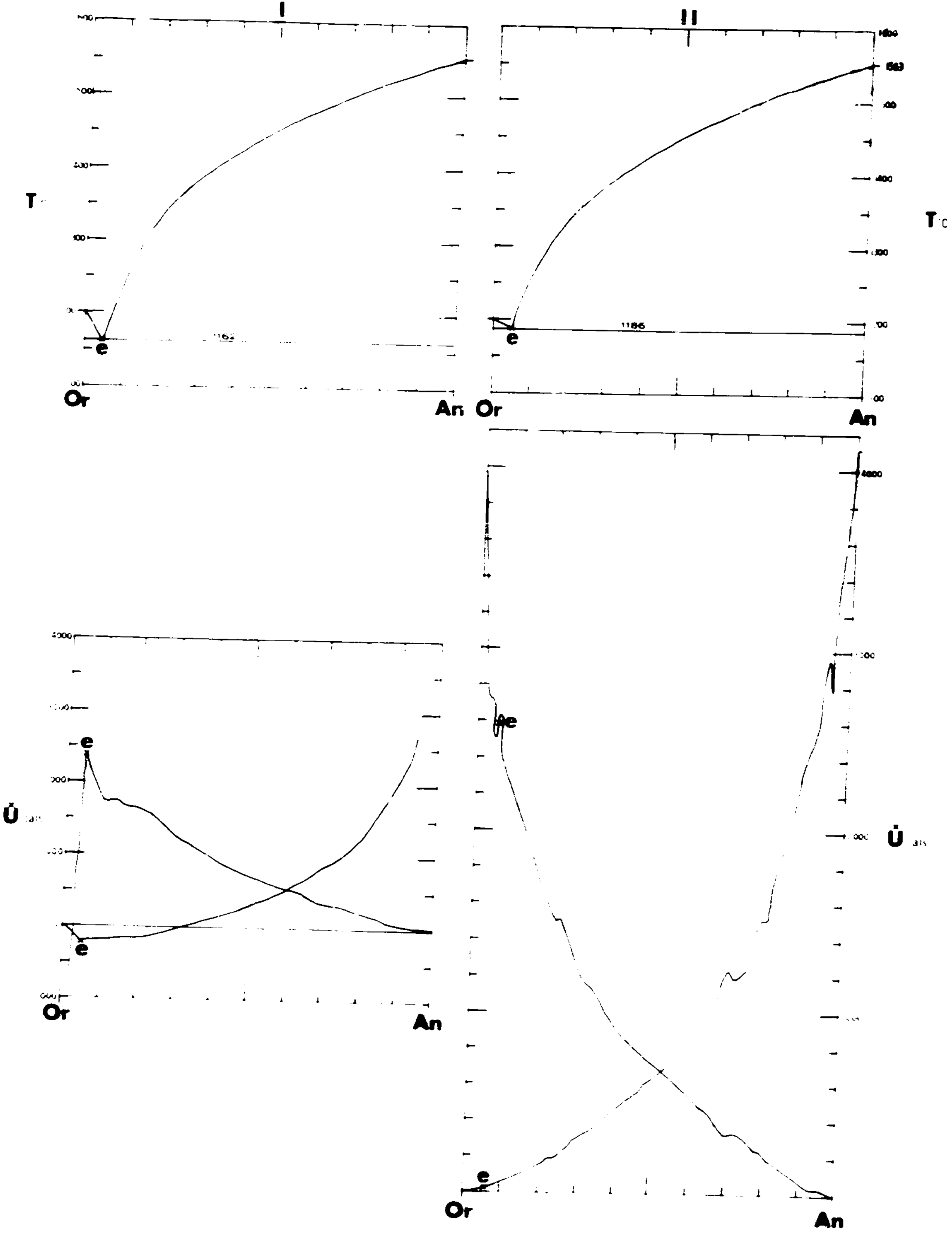
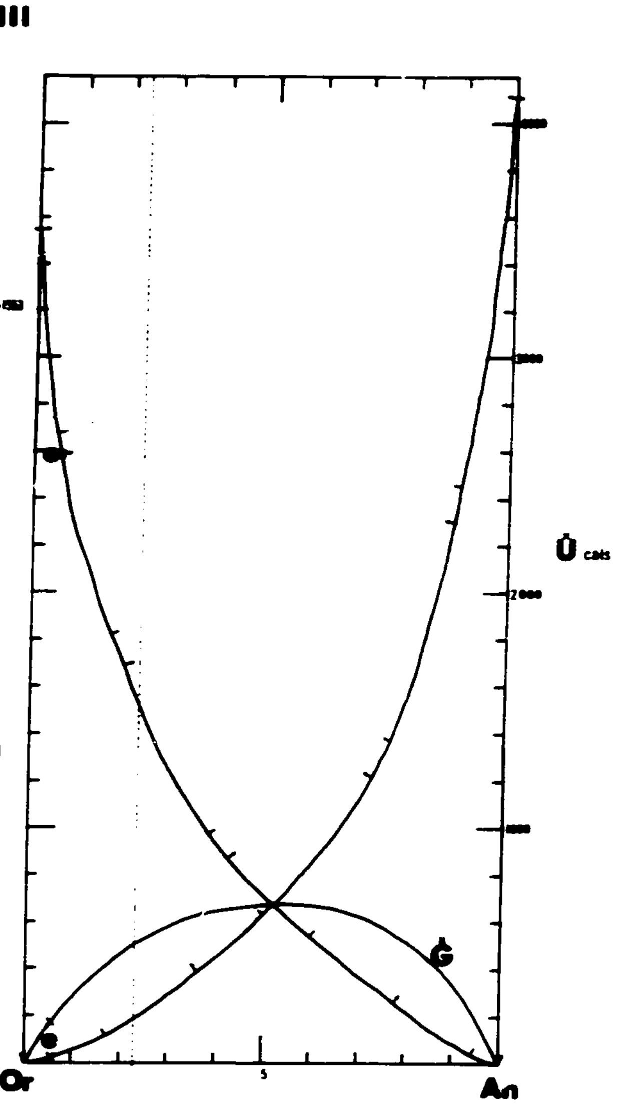
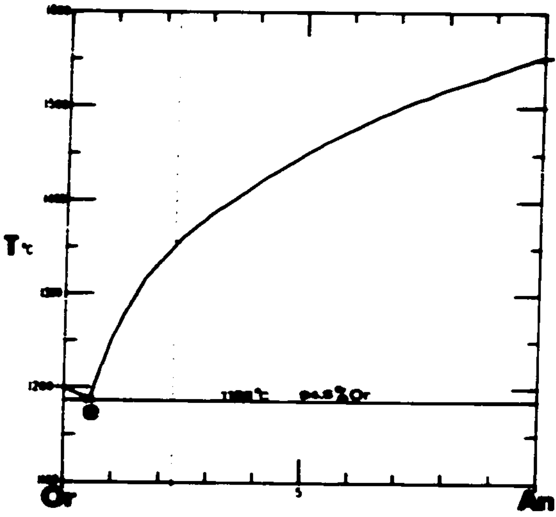


Figure E-2





data from Ǔ-X for TMQ program

```
ANOR DAN JY670
0000060022000000000   30  250
22004000580 0  250   540  860
580062008000   860   980 1680
800083009450 1680 1820 2580
945096001.00 2580 2674 3547

ANOR DOR JY670
000010001100 4114 2450 2300
110024002800 2300 1370 1200
280050006400 1200  640  380
640083001.00  380  120
```

output from TMQ ready for program GAPMIS

```
51ANOR DAN JY670
.0    .2200-0.261373E-03 0.261369E 03 0.397725E 04     0.     30.    250.
.2200.5800-0.637035E 02 0.132407E 04 0.462962E 03   250.    540.    860.
.5800.8000 0.572916E 03-0.184845E 04.0.404038E 04   860.    980.   1680.
.8000.9450 0.683992E 04-0.171647E 05 0.133934E 05  1680.   1820.   2580.
.94501.000 0.253272E 06-0.532589E 06 0.282864E 06  2580.   2674.   3547.
41ANOR DOR JY670
.0    .1100 0.411402E 04-0.181313E 05 0.149107E 05  4114.   2450.   2300.
.1100.2800 0.353787E 04-0.131324E 05 0.170815E 05  2300.   1370.   1200.
.2800.6400 0.218040E 04-0.403660E 04 0.191198E 04  1200.    640.    380.
.64001.000 0.223340E 04-0.407378E 04 0.184038E 04   380.    120.      0.
```

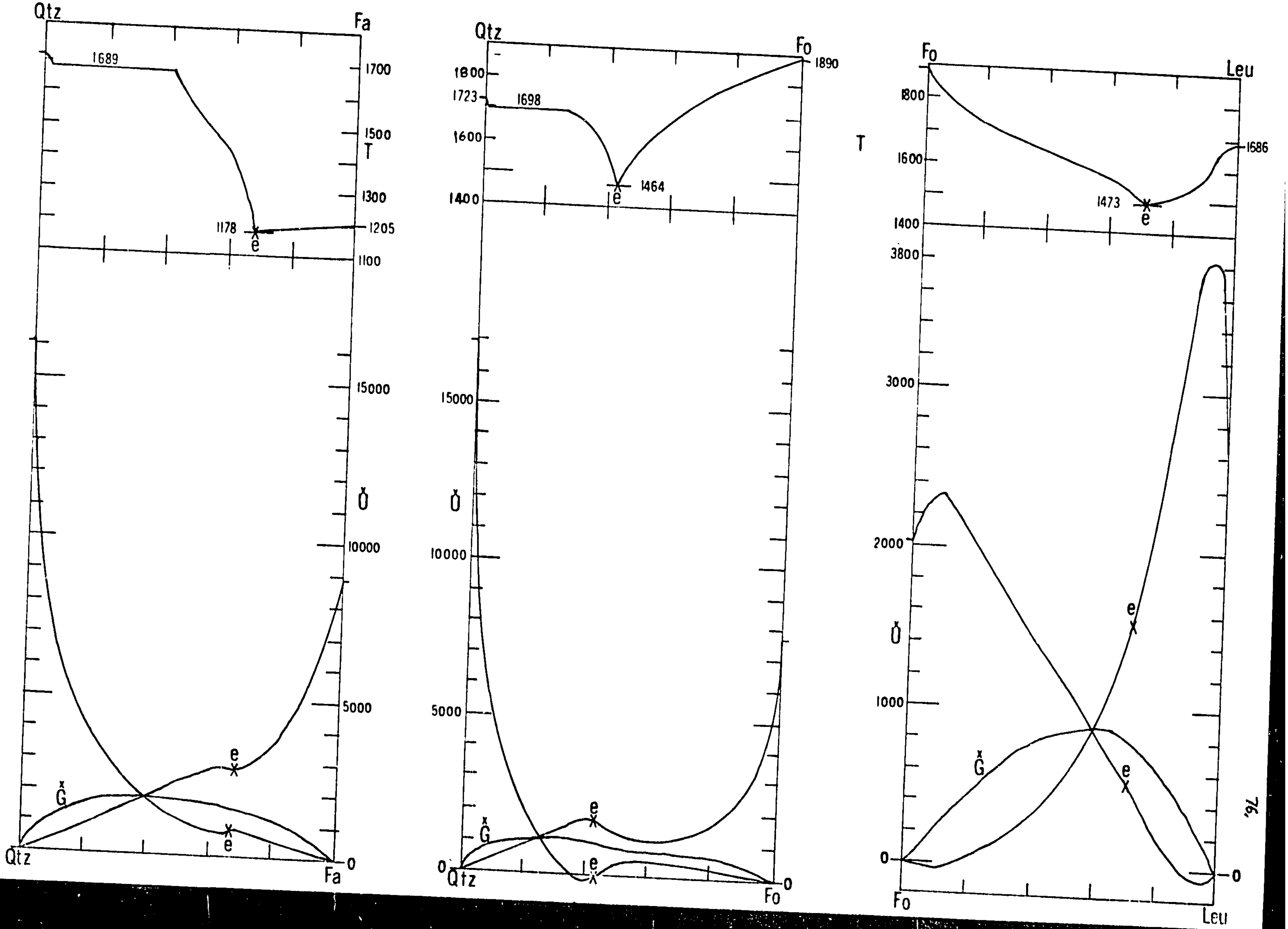

Qtz
Fa
1689
1700
1500
T
1300
1178
e
1205
1100
15000
Ǒ
10000
5000
Ǧ
e
e
0
Qtz
Fa
Qtz
Fo
1890
1800
1723
1698
1600
1464
e
1400
15000
Ǒ
10000
5000
Ǧ
e
e
0
Qtz
0
Fo
Fo
Leu
1800
T
1600
1686
1473
e
1400
3800
3000
2000
Ǒ
1000
e
Ǧ
e
0
0
Fo
Leu

Figure E - 3

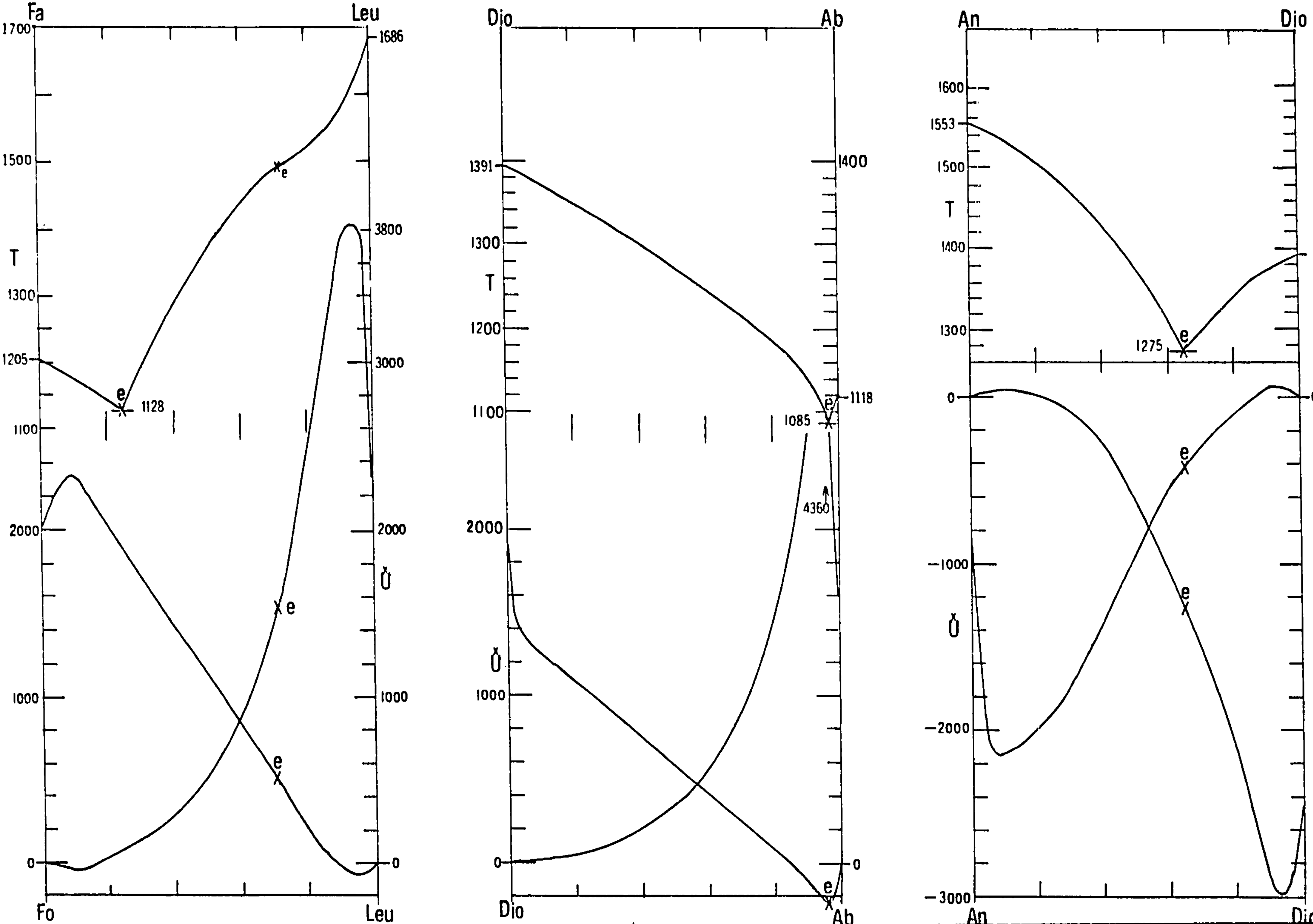

Fa
Leu
1700
1686
1500
T
1300
1205
1128
1100
2000
1000
0
3800
3000
2000
1000
0
Ǒ
e
Fo
Leu
Dio
Ab
1391
1400
1300
T
1200
1100
1118
1085
4360
2000
Ǒ
1000
0
0
e
Dio
Ab
An
Dio
1600
1553
1500
T
1400
1300
1275
0
0
−1000
Ǒ
−2000
−3000
e
An
Dio

Figure E-4

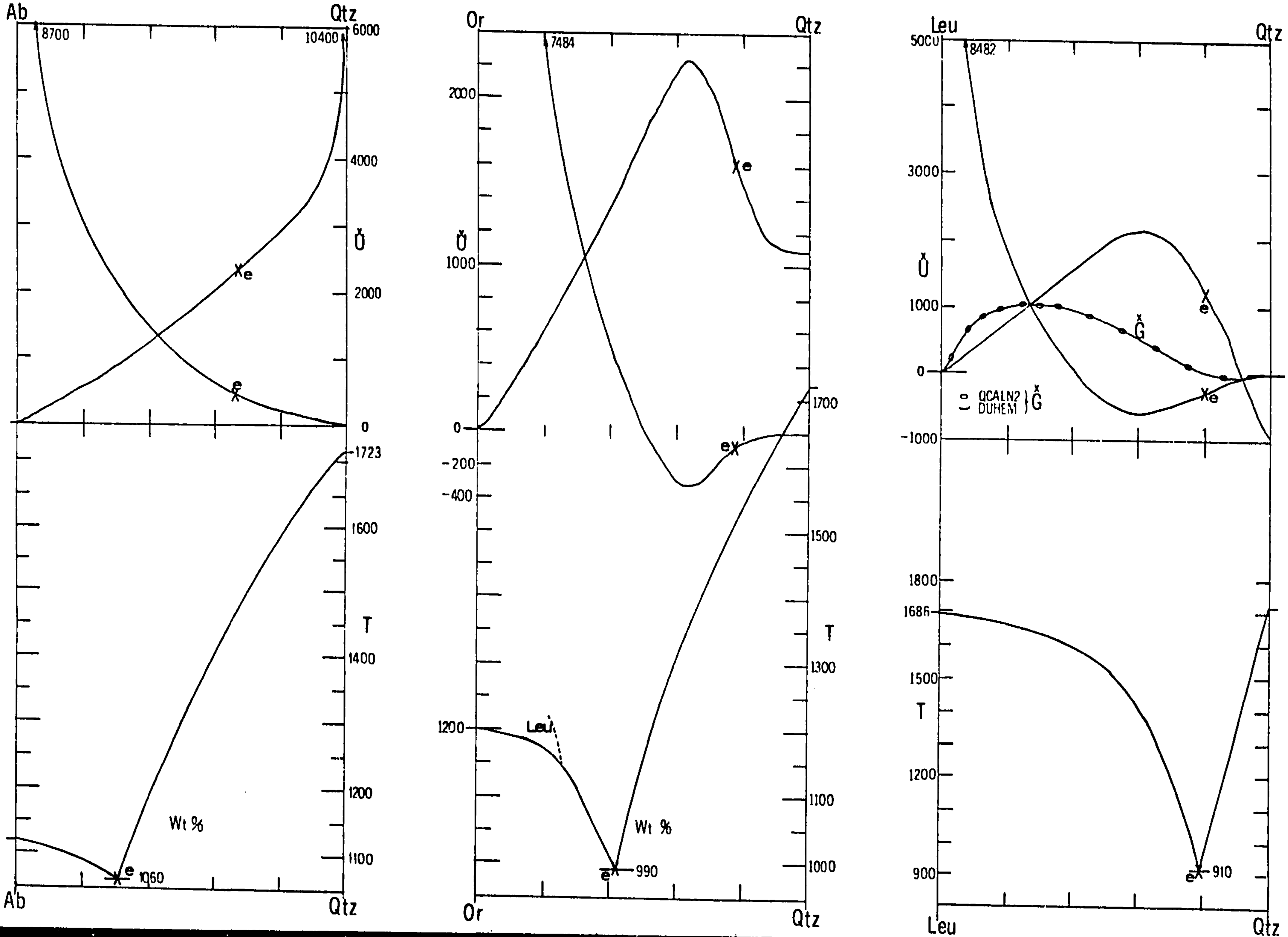

Ab
Qtz
8700
10400
6000
4000
2000
0
Ǒ
Xe
e
X
-1723
1600
T
1400
1200
1100
Wt %
e
1060
Ab
Qtz
Or
Qtz
7484
2000
1000
Ǒ
0
-200
-400
Xe
eX
1700
1500
T
1300
1200
Leu
1100
Wt %
eX
990
1000
Or
Qtz
Leu
Qtz
5000
8482
3000
Ǒ
1000
0
-1000
Ǧ
X
e
Xe
QCALN2
DUHEM
Ǧ
1800
1686
1500
T
1200
900
eX
910
Leu
Qtz

Figure E - 5

```
60.09 2030.1713.203.7914260.1205.218.26 6770.1686.140.7015350.1890.
QUARTZ,FAYALITE LEUCITE
SEG PARA FIT TO D  DEC 12,69
62    LESI DEC 19 DLE
.8222.9015-0.383621E 05 0.101144E 06-0.648458E 05
.0000.5594-0.425720E-02 0.402841E 04-0.432965E 03
.5594.6882-0.483717E 04 0.231659E 05-0.191783E 05
.6882.7941-0.909921E 04 0.371707E 05-0.305045E 05
.7941.8222 0.134969E 04 0.678045E 04-0.881802E 04
.90151.000 0.899312E 05-0.180042E 06 0.892067E 05
4LESI DEC 19 DSI
.0000.3206 0.848224E 04-0.472691E 05 0.709764E 05
.3206.5974 0.483989E 04-0.178273E 05 0.145792E 05
.5974.7745 0.250666E 04-0.105305E 05 0.890186E 04
.77451.000-0.521742E 04 0.101844E 05-0.496705E 04
61SIFA DEC 12 DSI
.0000.3067-0.183105E-02 0.354940E 04 0.334237E 04
.3067.4940-0.110571E 03 0.502249E 04-0.284924E 03
.4940.6311-0.403343E 04 0.197549E 05-0.140278E 05
.6311.6797-0.126136E 06 0.396598E 06-0.304640E 06
.6797.8118 0.936305E 04-0.237612E 05 0.206056E 05
.81181.000 0.526580E 05-0.131605E 06 0.877593E 05
6SIFA DEC 12 DFA
.0000.1370 0.174463E 05-0.195905E 06 0.808071E 06
.1370.4474 0.971254E 04-0.333153E 05 0.333305E 05
.4474.6311 0.715240E 04-0.190460E 05 0.142242E 05
.6311.6797 0.813189E 04-0.235227E 05 0.188424E 05
.6797.7942 0.439045E 03 0.305333E 04-0.359527E 04
.79421.000 0.262355E 04-0.228051E 04-0.343095E 03
61LEFO DEC 12 DFO
.0000.0992 0.154495E-03-0.165326E 03-0.975528E 03
.0992.3657-0.221070E 02-0.316588E 03 0.279567E 04
.3657.7107 0.997703E 03-0.509218E 04 0.822872E 04
.7107.9138 0.971000E 03-0.808182E 04 0.124924E 05
.9138.9707-0.104252E 05 0.286333E 05-0.139985E 05
.97071.000 0.246228E 06-0.405672E 06 0.161035E 06
6LEFO DEC 12 DLE
.0000.1000 0.200226E 04 0.743139E 04-0.395405E 05
.1000.3657 0.257688E 04-0.205467E 04-0.214215E 04
.3657.5976 0.238244E 04-0.194700E 04-0.982608E 03
.5976.7107 0.453626E 03 0.377487E 04-0.515643E 04
.7107.9363 0.675413E 04-0.134335E 05 0.658404E 04
.93631.000 0.242066E 04-0.591301E 04 0.348903E 04
51FOSI DEC 12 DSI
.0000.2691-0.318909E-02 0.367494E 04 0.309437E 04
.2691.4284-0.230340E 04 0.194497E 05-0.237182E 05
.4284.5372 0.859940E 04-0.253851E 05 0.215305E 05
.5372.7425 0.614997E 04-0.166216E 05 0.137044E 05
.74251.000 0.554009E 05-0.138838E 06 0.889728E 05
6FOSI DEC 12 DFO
.0000.1547 0.168920E 05-0.222888E 06 0.862602E 06
.1547.3662 0.789695E 04-0.384135E 05 0.459962E 05
.3662.4284 0.738777E 04-0.361219E 05 0.435148E 05
.4284.5643-0.105433E 05 0.396622E 05-0.356565E 05
.5643.7011-0.212148E 04 0.862063E 04-0.709645E 04
.70111.000 0.398344E 03 0.110433E 04-0.150269E 04
```

```
 60.09 2030.1713.278.3214702.1200.262.2213560.1118.
QUARTZ-OR-AB,IAT
SEG PARA FIT TO D M1270
52ABSI DAB M1070
.0    .1539-0.206304E-02 0.206304E 04 0.436983E 04      0.    250.   421.
.1539.4150 0.883360E 02 0.174595E 04 0.270050E 04    421.    597.  1278.
.4150.8367-0.295646E 03 0.353675E 04 0.614868E 03   1278.   2070.  3094.
.8367.9697 0.258615E 05-0.594546E 05 0.385366E 05   3094.   3434.  4445.
.96971.000 0.758811E 07-0.156109E 08 0.803371E 07   4445.   5054. 10901.
31ABSI DSI M1070
.0    .1868 0.870505E 04-0.490131E 05 0.104963E 06   8705.   3648.  3212.
.1868.6633 0.529938E 04-0.126737E 05 0.802573E 04   3212.    808.   424.
.66331.000 0.204730E 04-0.323534E 04 0.118803E 04    424.    172.     0.
62ORSI DOR M1070
.0    .2585-0.273665E-02 0.273665E 04 0.156503E 04      0.    706.   812.
.2585.4500-0.131480E 03 0.347267E 04 0.685325E 03    812.    972.  1570.
.4500.6300-0.314502E 04 0.153112E 05-0.107408E 05   1570.   2175.  2238.
.6300.8000-0.391553E 04 0.207854E 05-0.174888E 05   2238.   2160.  1520.
.8000.9000 0.244399E 05-0.506497E 05 0.274998E 05   1520.   1220.  1130.
.90001.000 0.508998E 04-0.799998E 04 0.399999E 04   1130.   1100.  1090.
51ORSI DSI M1070
.0    .2585 0.748404E 04-0.355617E 05 0.506218E 05   7484.   2005.  1674.
.2585.4300 0.547240E 04-0.189566E 05 0.164896E 05   1674.    650.   370.
.4300.6400 0.506495E 04-0.160148E 05 0.118518E 05    370.   -200.  -330.
.6400.7700 0.850704E 03-0.488073E 04 0.474356E 04   -330.   -290.   -95.
.77001.000-0.286545E 04 0.605040E 04-0.318495E 04    -95.      0.     0.
21ORAB DOR M1070 LIQ
.0    .4000 0.120003E-03-0.120001E 03-0.227500E 04      0.   -115.  -412.
.40001.000 0.285333E 03-0.156200E 04-0.453334E 03   -412.   -609. -1730.
41ORAB DAB M1070 LIQ
.0    .1000-0.241301E 04 0.618014E 04-0.600075E 04  -2413.  -1957. -1855.
.1000.3600-0.241633E 04 0.602936E 04-0.416082E 04  -1855.   -913.  -785.
.3600.6200-0.223960E 04 0.512938E 04-0.302448E 04   -785.   -282.  -222.
.62001.000-0.170637E 04 0.351632E 04-0.180994E 04   -222.    -40.     0.
52ORAB DOR M1070 XL
.0    .1600 0.716698E-04-0.716683E 02-0.158333E 04      0.    -10.   -52.
.1600.2800 0.560002E 02-0.875002E 03 0.125001E 04    -52.    -82.   -91.
.2800.6000 0.306030E 03-0.249530E 04 0.384765E 04    -91.    -47.   194.
.6000.8000 0.295328E 04-0.109916E 05 0.106548E 05    194.    340.   979.
.80001.000 0.885101E 04-0.242400E 05 0.180000E 05    979.   1615.  2611.
41ORAB DAB M1070 XL
.0    .3000-0.140006E 03 0.635562E 04-0.112964E 05   -140.    638.   750.
.3000.5800 0.544687E 03 0.149464E 04-0.270089E 04    750.    696.   503.
.5800.8000 0.141606E 04-0.156875E 04-0.946768E 01    503.    250.   155.
.80001.000 0.434640E 04-0.881066E 04 0.446426E 04    155.      9.     0.
```

APPENDIX F

Listing and Rationale of Programs

QCALN 2	Iterative geometric construction for $\overset{x}{G}$ from $\overset{x}{\mu}$
QCALN3	First order differential equation solved for $\overset{x}{G}$ from $\overset{x}{\mu}$
DUHEM	Gibbs-Duhem integration of $\overset{x}{\mu}_j$ for $\overset{x}{\mu}_i$
W1XLIQ	One parameter $\overset{x}{G}$ calculated from solid solution binary
WWXLIQ	Two parameter $\overset{x}{G}$ calculation from solid solution binary
TMQ	Segmented parabolas fitted to selected $\overset{x}{\mu}$ data
QESTE	Heat of fusion estimated from liquidus data
GAPMIS	Calculation of phase equilibria, and data for Diopside - Albite - Anorthite.

```
C     PROGRAM  QCALN2
C     GEOMETRIC CONSTRUCTION OF  G-EXCESS
      DIMENSION X(2),XX(2,100),W(2),Q(2),TO(2),T(2),D(2,100),
     1EI(2,100),N(2),E(2,100),S(15),TP(2,100),DPD(2,100),DEI(2,100),
     1DD(2,100),DPEI(2,100),A(100),B(100),C(100)
     1,R(10,10),RT(10),RA(10),RP(10),NQ(4)
     1,KA(2),KV(2)
      CALL SIGNON
 5    READ(5,10)PAIR,(W(I),Q(I),TO(I),N(I),I=1,2)
 10   FORMAT(A4,2(F6.2,F7.1,F6.1,I2))
      READ(5,1)ITYPE,(KA(I),I=1,2),(KV(I),I=1,2)
 1    FORMAT(5I1)
      J=0
      TO(1)=TO(1)+273.15
      TO(2)=TO(2)+273.15
 15   READ(5,20)(T(I),X(I),I=1,2)
 20   FORMAT(2(F4.0,F3.0))
      DO 21 I=1,2
      T(I)=T(I)+273.15
 21   X(I)=X(I)/1000.
      IF(X(1)+X(2))61,61,25
 25   J=J+1
      XX(1,J)=X(1)*W(2)/(W(1)+X(1)*(W(2)-W(1)))
      XX(2,J)=X(2)*W(1)/(W(2)+X(2)*(W(1)-W(2)))
      DO 33 I=1,2
      TP(I,J)=T(I)
      D(I,J)=Q(I)*(TP(I,J)-TO(I))/TO(I)-1.987*TP(I,J)*
     1ALOG(XX(I,J)+.00001)
 33   CONTINUE
      GO TO 15
 61   CONTINUE
      WRITE(6,130)PAIR
 130  FORMAT(1H ,A4)
      DO 104 I=1,2
      EI(I,1)=D(2,1)-(D(2,1)-D(1,1))*XX(1,1)
      N1=N(I)
      DO 104 J=1,N1
      DB=(D(I,J)+D(I,J+1))/2.
      EI(I,J+1)=EI(I,J)+(EI(I,J)-DB)
     1*(XX(I,J)-XX(I,J+1))/(1.-XX(I,J))
 104  CONTINUE
      DO 17 I=1,2
      N2=N(I)
      DO 17 J=1,N2,8
      J1=J+7
      J1=AMIN0(J1,N2)
      WRITE(6,18)(XX(I,IJ),IJ=J,J1)
 18   FORMAT(1H ,8F8.4)
      WRITE(6,19)(EI(I,IJ),IJ=J,J1)
 19   FORMAT(1H ,8F8.2)
 17   CONTINUE
      CALL SINOFF
      GO TO 5
      END
```

```
C         PROGRAM QCALN3
C     SOLVES FIRST ORDER DIFFERENTIAL EQUATION ANALYTICALLY
       DIMENSION X(2),XX(2,100),W(2),Q(2),TO(2),T(2),D(2,100),
     1EI(2,100),N(2),E(2,100),S(15),TP(2,100),DPD(2,100),DEI(2,100),
     1DD(2,100),DPEI(2,100),A(100),B(100),C(100)
 5      READ(5,10)PAIR,(W(I),Q(I),TO(I),N(I),I=1,2)
 10     FORMAT(A4,2(F6.2,F7.1,F6.1,I2))
        J=0
        TO(1)=TO(1)+273.15
        TO(2)=TO(2)+273.15
 15     READ(5,20)(T(I),X(I),I=1,2)
 20     FORMAT(2(F5.0,F4.3))
        T(1)=T(1)+273.15
        T(2)=T(2)+273.15
        IF(X(1)+X(2))61,61,25
 25     J=J+1
        XX(1,J)=X(1)*W(2)/(W(1)+X(1)*(W(2)-W(1)))
        XX(2,J)=X(2)*W(1)/(W(2)+X(2)*(W(1)-W(2)))
        DO 33 I=1,2
        TP(I,J)=T(I)
        D(I,J)=Q(I)*(TP(I,J)-TO(I))/TO(I)-1.987*TP(I,J)*ALOG(XX(I,J))
        E(I,J)=D(I,J)
 33     CONTINUE
        GO TO 15
 61     CONTINUE
        WRITE(6,130)PAIR
 130    FORMAT(1H ,A4)
        DO 104 I=1,2
        EI(I,1)=D(2,1)-(D(2,1)-D(1,1))*XX(1,1)
        TNP=EI(I,1)/(1.-XX(I,1))
        N2=N(I)-1
        DO 104 J=1,N2
        IF(J-N2)30,31,31
 30     CONTINUE
        AZ1=(XX(I,J+2)-XX(I,J+1))*(E(I,J+1)-E(I,J))
        AZ2=(XX(I,J+1)-XX(I,J))*(E(I,J+2)-E(I,J+1))
        AZ=XX(I,J+1)/2.+(XX(I,J+2)*AZ1-XX(I,J)*AZ2)/(AZ1-AZ2)
     1/2.
        BZ=(E(I,J+1)-E(I,J))/(XX(I,J+1)+XX(I,J)-2.*AZ)
     1/(XX(I,J+1)-XX(I,J))
        CZ=E(I,J)-(XX(I,J)-AZ)**2*BZ
 31     CONTINUE
        DEI(I,1)=0.
        DEI(I,J+1)=DEI(I,J)+BZ*(XX(I,J+1)-XX(I,J))-BZ*(AZ-1.)*2.*ALOG((1.-
     1XX(I,J+1))/(1.-XX(I,J)))+(BZ*(AZ-1.)**2+CZ)*(1./(1.-XX(I,J+1))-1./
     1(1.-XX(I,J)))
        EI(I,J+1)=(1.-XX(I,J+1))*(TNP+DEI(I,J+1))
 140    DPD(I,J+1)=EI(I,J+1)/XX(I,J+1)/(1.-XX(I,J+1))
 104    CONTINUE
        IN=N(2)
        WRITE(6,126)((XX(I,J),D(I,J),DEI(I,J),EI(I,J),DPD(I,J)
     1,I=1,2),J=1,IN)
 126    FORMAT(1H ,2(F5.4,F5.0,F7.0,F6.0,F7.0))
        N2=N(1)+1
        WRITE(6,126)(XX(1,J),D(1,J),DEI(1,J),EI(1,J),DPD(1,J),
     1XX(1,J+1),D(1,J+1),DEI(1,J+1),EI(1,J+1),DPD(1,J+1),
     1J=IN,N2,2)
        GO TO 5
        END
/DATA
```

PROGRAM DUHEM

MAIN

X:unnormalized weight %,XX:mole fraction,Q:heat of fusion,
W:mole weight,TO:temperature of fusion,T:liquidus temperatures,
D;E: $\dot{\alpha}_1,\alpha_1$ on 1's side of eutectic,TP:T in degrees absolute,
N:number of sets of data.

```
       DIMENSION X(2),XX(2,100),W(2),Q(2),TO(2),T(2),D(2,100),
      1EI(2,100),N(2),E(2,100),S(15),TP(2,100),DPD(2,100),DEI(2,1),
      1DD(2,100),DPEI(2,100),A(100),B(100),C(100)
      1,R%10,10<,RT%10<,RA%10<,RP%10<,NQ%4<
      1,KA(2),KV(2)
       CALL SIGNON
```

Reads name of binary, mole weight, heat of fusion, temperature of fusion and the number of data points on liquidus, then ITYPE

Normalizing factor for reducing unnormalized data.

```
5      READ(5,10)PAIR,(W(I),Q(I),TO(I),N(I),I=1,2),ITYPE
10     FORMAT(A4,2(F6.2,F6.0,F6.1,I2),I1)
       RXX=1
       J=0
```

ITYPE-1 regular T-X liquidus data from eutectic out
ITYPE=2 X- $\dot{\alpha}_1 - \dot{\alpha}_2$ data from X=.5 out.

```
       GO TO (98,99),ITYPE
99     N1=N(1)
       N(2)=N1
```

Reads molefraction component one=mole fraction component two, then $\dot{\alpha}_1$ and $\dot{\alpha}_2$ from X=.5 out.

```
81     READ(5,82)X(1),S(1),S(2)
82     FORMAT(F3.3,2F4.0)
       X(2)=X(1)
       GO TO 83
98     CONTINUE
       TO(1)=TO(1)+273.15
       TO(2)=TO(2)+273.15
```

Reads unnormalized T-X data, X(1) for component one on its side of eutectic, X(2) for component two on the other side.
Data starts at eutectic and moves outwards.

```
15     READ(5,20)(T(I),X(I),I=1,2)
20     FORMAT(2(F4.0,F3.3))
```

Normalizes X and T

```
       DO 21 I=1,2
       T(I)=T(I)+273.15
21     X(I)=X(I)/RXX
83     CONTINUE
```

A blank T-X data card causes program to operate on the data.

```
       IF(X(1)+X(2))61,61,25
25     J=J+1
```

Calculates mole fractions.

```
       XX(1,J)=X(1)*W(2)/(W(1)+X(1)*(W(2)-W(1)))
       XX(2,J)=X(2)*W(1)/(W(2)+X(2)*(W(1)-W(2)))
       DO 33 I=1,2
       TP(I,J)=T(I)
       GO TO (89,92),ITYPE
92     D(1,J)=S(1)
       D(2,J)=S(2)
       GO TO 90
89     CONTINUE
```

Calculates D- $\dot{\alpha}_1$ and E- α_1 on 1's side of eutectic.

```
       D(I,J)=Q(I)*(TP(I,J)-TO(I))/TO(I)-1.987*TP(I,J)*
      1ALOG(XX(I,J)+.00001)
90     CONTINUE
       E%I,J<#D%I,J<
      1/(1.-XX(I,J))**2
33     CONTINUE
```

Reads next data on liquidus away from eutectic or X=.5

```
       GO TO (15,81),ITYPE
61     CONTINUE
```

Writes name of binary.

TESSER performs Gibbs-Duhem integration with α_1, mole fractions, and number of data points.

```
       WRITE(6,130)PAIR
130    FORMAT(1H ,A4)
       CALL TESSER(2,XX,N,TP)
       CALL SINOFF
```

Reads new binary name.

```
       GO TO 5
       END
```

DUHEM-I

```
      SUBROUTINE TESSER(E,XX,N,TP)
      DIMENSION E(2,100),XX(2,100),N(2),B(100),C(100),D(100)
     1,XT(100),B1(100),C1(100),V(3),Z(3),T(3)
     1,TP(2,100)
      DO 104 I#1,2
      I2#I&%-1<**%I&1<
      N2#N%I2<
      B1%1<#0
      C%1<#E%I,1<*XX%I2,1<**2
      DO 25 J=1,N2
25    XT(J)=1.-XX(I2,J)
      DO 30 J#2,N2
      K1#J-1
      K2#J&1
      DO 300 J1=1,3
      KX=K1+J1-1
      V(J1)=XT(KX)
300   Z(J1)=E(I2,KX)
      IF(J-N2)27,28,28
27    CONTINUE
      CALL PARFIT(V,Z,T)
      DO 24 I1#1,3
24    T(I1)=T(I1)/FLOAT(I1)
28    CONTINUE
      DO 26 J1=1,2
      K=K1+J1-1
      R(K)=T(1)+T(2)*V(J1)+T(3)*V(J1Y**2
26    B(K)=V(J1)*B(K)
      B1%J<#B1%J-1<&B%K1<-B%J<
      C%J<#C%1<&B1%J<&XT%1<*%1.*XT%1<<*E%I2,1<-XT%J<*%1.-XT%J<<*
     $E%I2,J<
30    CONTINUE
      N3=N2+1
      C(N3)=C(N2)+XT(N2)*(1.+XX(I2,N2))*E(I2,N2)
      XX(I2,N3)=1.
      XT(N3)=0.
      N2=N3
      DO 29 J#1,N2
      TP(I2,J)=TP(I2,J)-273.15
29    D%J<#E%I2,J<*XT%J<**2
      DO 110 K1#1,2
      DO 50 J#1,N2
      IF%I-1<70,70,80
70    XT%J<#XX%I2,J<
      GO TO 90
80    XT%J<#1.-XX%I2,J<
90    IF%K1-1<91,91,92
91    C1%J<#D%J<
      GO TO 93
92    C1%J<#C%J<
93    CONTINUE
50    CONTINUE
```

TESSER
Performs Gibbs-Duhem integration on component I2, generating $\dot{\alpha}_I$ on I2's side of eutectic. Program has been proven against planimeter measured integration.

PARFIT fits E= α_{I2} for KX=J-1,J,J+1 as a parabolic function of 1.-XX(I2) where XX(I2) is mole fraction of component I2 on I2's side of the eutectic. T are the constants of the fit.

Integration of α_{I2} from K=J-1 to K=J+1 and multiplied by 1.-XX(I2) to raise the power due to integration.
B1 is the total integral from K=1 to K=J, while C is the determined value of $\check{\alpha}_I$ at XX(I2)

Calculates value of $\check{\alpha}_I$ at XX_{I2} =0 assuming α_{I2} is constant past the last data point on I2's liquidus.

Prepares $\check{\alpha}$ data for writing.

```
      DO 210 J=1,N2,8
      J1=J+7
      J1=AMIN0(J1,N2)
      WRITE(6,220)(XX(I2,IJ),IJ=J,J1)
      WRITE(6,220)(XT(IJ),IJ=J,J1)
      WRITE(6,222)(C1(IJ),IJ=J,J1)
      WRITE(6,222)(TP(I2,IJ),IJ=J,J1)
220   FORMAT(8F8.4)
222   FORMAT(8F8.2)
210   CONTINUE
100   CONTINUE
      WRITE%6,111<
111   FORMAT%///<
110   CONTINUE
104   CONTINUE
      RETURN
      END
```

Writes first the directly calculated values (from MAIN) of XX_{12} and (1 XX_{12}), θ_{12} and TP_{12} then the values of the same variables generated by the integration for 1.

Returns to calculate θ_1 for the other side of the eutectic.

```
      SUBROUTINE PARFIT(X,E,RT)
      DIMENSION X(3),E(3),A(3),RT(3)
      X1=(E(1)-E(2))*(X(2)-X(3))
      X2=(E(2)-E(3))*(X(1)-X(2))
      RT(3)=(X1-X2)/((X(2)-X(3))*(X(1)**2-X(2)**2)-(X(1)-X(2))
     1*(X(2)**2-X(3)**2))
      RT(2)=(E(1)-E(2)-RT(3)*(X(1)**2-X(2)**2))/(X(1)-X(2))
      RT(1)=E(1)-RT(2)*X(1)-RT(3)*X(1)**2
      DO 10 I=1,3
      A(I)=RT(1)+RT(2)*X(I)+RT(3)*X(I)**2
10    A(I)=A(I)-E(I)
      IF(ABS(A(1))+ABS(A(2))+ABS(A(3))-.01*ABS(E(2)))20,20,21
21    WRITE(6,25)X,E,RT
25    FORMAT(' [redacted]',3F5.4,3F7.1,3E13.6)
20    CONTINUE
      RETURN
      END
```

PARFIT

Fits parabolic curve to three sets of data then checks accuracy of the fit. Writes naughty word and data if accuracy not better then .3%.

```
/DATA
A NOR100002900015532510000147021200252
50712559
52677525
54640485
53603455
58572420
60541385
62506350
64472311
66439278
68405250
70370215
72337180
74307147
76278126
78250106
80218 90
82190 77
84164 68
86130 55
88100 47
90 73 39
92 53 28
94 37 20
96 20 10
98  9  4
```

Name of binary An-Or, mole weight, heat of fusion, temperature of fusion for components one (An) and two (Or), then IITYPE=2. The mole weights are set to 100 because X are mole fractions already.

Data is mole fraction component one × mole fraction component two, then θ_1, θ_2 from X=.5 out.

Blank card causes integration to begin.

DUHEM-3

```
ANOR278212900015534627832147021200 61
11840651184935
12070801185940
12301001188950
12571201190960
12801401193970
12981601195980
13171801193989
1332200
1345220
1357240
1366260
1373280
1380300
1389320
1398340
1404360
1410380
1417400
1423420
1430440
1437460
1442480
1449500
1454520
1460540
1465560
1470580
1475600
1480620
1484640
1489660
1491680
1495700
1501720
1507740
1510760
1513780
1518800
1520820
1524840
1527860
1530880
1534900
1538920
1541940
1544950
```

Name of binary An-Or, mole weight, heat of fusion, temperature of fusion for components one and two, then ITYPE=1.

Data is temperature, weight composition from eutectic out.

Blank card causes integration to begin.

```
      DIMENSION H(2),TO(2),X(2),X1(2),XX(2),MW(2),XO(2),W(2)
     1,U(4),UN(4),UM(4),NAME(10),IP(3,9)
      REAL H,MW
      READ(5,10)((IP(I,J),I=1,3),J=1,8)
10    FORMAT(24I1)
      DO 30 I=1,3
      IP(I,9)=0
      DO 30 J=1,8
      IF(IP(I,J))29,29,30
29    IP(I,J)=-1
30    CONTINUE
4     READ(5,11)NAME,(H(I),TO(I),MW(I),I=1,2)
11    FORMAT(10A4,/,2(F5.0,F4.0,F5.2))
      TO(1)=TO(1)+273.15
      TO(2)=TO(2)+273.15
      WRITE(6,21)NAME
21    FORMAT(10A4)
      READ(5,13)RT,RX,RX1
13    FORMAT(3F3.2)
6     READ(5,12)T1,X1(2),X1(1)
12    FORMAT(3F3.2)
      IF(X1(1)+X1(2))4,4,17
17    DO 101 IT=1,9
      T=T1+FLOAT(IP(1,IT))*.01
      X(1)=X1(1)+FLOAT(IP(2,IT))*.01
      X(2)=X1(2)+FLOAT(IP(3,IT))*.0099
      T=TO(1)+T*(TO(2)-TO(1))/RT
      X(1)=ABS(RX1-X(1))/RX
      X(2)=ABS(RX1-X(2))/RX
20    DO 15 I=1,2
15    XX(I)=X(I)/MW(1)/(X(I)/MW(1)+(1.-X(I))/MW(2))
      XO(1)=H(1)/TO(1)*(TO(1)-T)+1.987*T*ALOG(XX(2)/XX(1))
      XO(2)=H(2)/TO(2)*(TO(2)-T)+1.987*T*ALOG((1.-XX(2))/
     1(1.-XX(1)))
      W(1)=(XX(2)**2*XO(1)-(1.-XX(2))**2*XO(2))/
     1(XX(2)+XX(1)-2.*XX(2)*XX(1))/(XX(2)-XX(1))
      W(2)=(XX(1)**2*W(1)-XO(2))/XX(2)**2
      U(1)=(1.-XX(1))**2*W(1)
      U(2)=XX(1)**2*W(1)
      U(3)=(1.-XX(2))**2*W(2)
      U(4)=XX(2)**2*W(2)
      IF(IT-1)90,90,100
90    DO 91 K=1,4
      UN(K)=U(K)
91    UM(K)=U(K)
      GO TO 101
100   DO 93 K=1,4
      UN(K)=AMIN1(UN(K),U(K))
93    UM(K)=AMAX1(UM(K),U(K))
101   CONTINUE
      T=T-273.15
      WRITE(6,95)XX,T,W,(U(K),UN(K),UM(K),K=1,4)
95    FORMAT(2F5.4,F5.0,2F7.0,T42,3F7.0,/,9F7.0)
      GO TO 6
      END
/DATA
100101111110011000001010
```

WIXLIQ-1

PROGRAM W1XLIQ

MAIN

H:heat of fusion, TO:temperature of fusion,X1-S2:composition of crystal and liquid in unnormalized weight percent,XX:mole fraction composition of crystal and liquid, MW:mole weight of components,XO:0 of (3-7), W:regular solution model parameter W,UN-UM-U: $\mathcal{U}$, min-max-no error, NAME:name of binary, IP:variable which works possible error variations on T-X_{liq} -$X_{crystal}$

Reads name, ΔH, , T_o, , mole weights

Writes name of binary

Reads factors for normalizing input data of liquidus

If X_{liquid} , $X_{crystal}$ data are for component one then RX1=0, but if the data are for component two, RX1=RX and later the data are turned into mole fraction component one

Reads unnormalized liquidus data T-X_{liquid} -$X_{crystal}$ in weight percent of component 1

With blank T-X_{liquid} -$X_{crystal}$ card go to 4 to read new name and data for next binary

Normalizes T,X_{liquid} ,$X_{crystal}$ and puts on the error variations

Mole fractions are for component one

Intermediate variable 0 calculated for (3-7)

W for regular solution calculated, W(1) for crystal and W(2) for liquid.

Calculates $\mathcal{U}$, for components one and two:U(1);U(2) for crystal and U(3),U(4) for liquid.

Minimum, maximum and no error values for $\mathcal{U}$, determined

Data written in order of crystal, liquid:mole fractions of component one, temperature C, regular solution W's ($\mathcal{U}$, for no error, minimum, maximum, first for component one then for component two)

Goes to 6 to read next line of T-X_{liquid} -$X_{crystal}$ data for same binary.

DATA

Integers (IP) specifying the error combinations in T-X_{liquid} -$X_{crystal}$

Data is the same as for program WWXLIQ

```
      DIMENSION MW(2),TO(2),T(100),T1(100),X(2,100),X1(2,100)
     .,XX(2,100),NAME(10),H(2),UX(4),UN(4),UM(4),IP(3,9)
      REAL H,MW
      READ(5,1)((IP(I,J),I=1,3),J=1,8)
1     FORMAT(24I1)
4     CALL SINOFF
      READ(5,11)NAME
11    FORMAT(10A4)
      READ(5,12)(H(I),TO(I),MW(I),I=1,2),XN
12    FORMAT(2(F5.0,F4.0,F5.2),F2.0)
      N=XN
      TO(1)=TO(1)+273.15
      TO(2)=TO(2)+273.15
      WRITE(6,21)NAME
21    FORMAT(10A4)
      READ(5,13)RT,RX,RX1
13    FORMAT(3F8.2)
6     READ(5,14)(T1(K),X1(2,K),X1(1,K),K=1,N)
14    FORMAT(3F3.2)
      DO 70 J=1,N
      DO 60 IT=1,9
      K=J
76    CONTINUE
      IF(IT-9)111,112,112
111   K4=K-2*(K/2)
      K1=IP(1,IT)+K4
      K2=IP(2,IT)+K4
      K3=IP(3,IT)+K4
      T(K)=T1(K)+FLOAT((-1)**K1)*.01
      X(1,K)=X1(1,K)+FLOAT((-1)**K2)*.01
      X(2,K)=X1(2,K)+FLOAT((-1)**K3)*.0099
      GO TO 113
112   T(K)=T1(K)
      X(1,K)=X1(1,K)
      X(2,K)=X1(2,K)
113   T(K)=TO(1)+T(K)*(TO(2)-TO(1))/RT
      X(1,K)=ABS(RX1-X(1,K))/RX
      X(2,K)=ABS(RX1-X(2,K))/RX
      DO 15 I=1,2
15    XX(I,K)=X(I,K)/MW(1)/(X(I,K)/MW(1)+(1.-X(I,K))/MW(2))
40    E3=1.987*T(K)*ALOG(XX(2,K)/XX(1,K))+H(1)/TO(1)*(TO(1)-T(K))

      E4=1.987*T(K)*ALOG((1.-XX(2,K))/(1.-XX(1,K)))+H(2)/TO(2)
     1*(TO(2)-T(K))
      C1=(1.-XX(1,K))**2*(1.-2.*XX(1,K))
      C2=(1.-XX(1,K))**2*2.*XX(1,K)
      C3=(1.-XX(2,K))**2*(1.-2.*XX(2,K))
      C4=(1.-XX(2,K))**2*XX(2,K)*2.
      D1=XX(1,K)**2*2.*(1.-XX(1,K))
      D2=XX(1,K)**2*(2.*XX(1,K)-1.)
      D3=XX(2,K)**2*2.*(1.-XX(2,K))
      D4=XX(2,K)**2*(2.*XX(2,K)-1.)
      C3=-C3
      C4=-C4
      D3=-D3
      D4=-D4
      IF((K-J-1)*(K-J+1))41,42,42
41    IF(XX(1,J)+XX(2,J)-1.)54,54,53
54    K=J-3
      GO TO 55
53    K=J+3
55    CONTINUE
```

PROGRAM WWXLIQ

MAIN

MW:mole weight, TO:temperature of fusion, H:heat of fusion,T:liquidus temp., X1:unnormalized $X_{CRYSTAL} - X_{LIQUID}$ in weight percent, X:normalized $X_{CRYSTAL} - X_{LIQUID}$ with error variations in weight percent, NAME:name of binary,XX:$X_{CRYSTAL} - X_{LIQUID}$ mole fractions, UX;UN;Um; a_i no error - minimum and maximum, IP:variable causing error variations.

Reads name of binary

Reads heat of fusion, temperature of fusion, mole weight, and number of data points.

Writes name of binary.

Reads normalizing factors for T,X1. If data is component one, RX1-0

Reads unnormalized $T-X_{LIQUID} - X_{CRYSTAL}$

Program operates on successive N data points.

Sets up nine error variations.

Ninth variation is no error so go to statement 112

Error combinations are enumerated on unnormalized $T-X_{CRYSTAL} - X_{LIQUID}$ data

Normalizes $T-X_{CRYSTAL} - X_{LIQUID}$ in weight percent.

Calculates mole percent component one in crystal and liquid.

Variable multipliers for two solid solution equations;
when K=J, the first two of four and
K=J + 3, the second two of four linear equations, four unknowns.

After the variable multipliers for the last two of four equations are calculated, then go to statement 42 to solve the four equations.

If $X_{CRYSTAL} + X_{LIQUID} > 1$ mole fraction then the next pair of $T-X_{LIQUID} - X_{CRYSTAL}$ data for solution is taken from data points J and J-3.

If $X_{CRYSTAL} + X_{LIQUID} < 1$ the data points are J and J+3.

MWXL10-1

```
      E1=E3
      E2=E4
      A1=C1
      A2=C2
      A3=C3
      A4=C4
      B1=D1
      B2=D2
      B3=D3
      B4=D4
      GO TO 76
```

Variable multipliers for the first two equations (K=J) are stored then go to statement 76 to calculate those for the next two (K=J+3).

```
42    A11=B1*A2-A1*B2
      A12=B1*A3-A1*B3
      A13=B1*A4-A1*B4
      E11=B1*E1-A1*E2
      B11=D1*C2-C1*D2
      B12=D1*C3-C1*D3
      B13=D1*C4-C1*D4
      E12=D1*E3-C1*E4
      C11=D1*B2-B1*D2
      C12=D1*B3-B1*D3
      C13=D1*B4-B1*D4
      E13=D1*E2-B1*E4
      G1=B11*A12-A11*B12
      G2=A13*B11-B13*A11
      G3=B12*C11-C12*B11
      G4=B13*C11-C13*B11
      G5=E11*B11-E12*A11
      G6=E12*C11-E13*B11
```

Calculates intermediate variables in the solution of the four linear equations.

```
      V=(G5*G3-G6*G1)/(G3*G2-G1*G4)
      U=(G5-V*G2)/G1
      S=(E11-A12*U-A13*V)/A11
      R=(E1-A2*S-A3*U-A4*V)/A1
```

Calculates V and U as W's for the liquid and S and R as W's for the crystal.

```
      UX(1)=A1*R+A2*S
      UX(2)=B1*R+B2*S
      UX(3)=-(A3*U+A4*V)
      UX(4)=-(B3*U+B4*V)
```

Calculates α_i for components one and two, with UX(1), UX(2) for crystal, and UX(3), UX(4) for the liquid.

```
      IF(IT-1)190,190,200
190   DO 191 K=1,4
      UN(K)=UX(K)
191   UM(K)=UX(K)
      GO TO 60
200   DO 193 K=1,4
      UN(K)=AMIN1(UN(K),UX(K))
193   UM(K)=AMAX1(UM(K),UX(K))
```

Picks the minimum, maximum values for UX

```
60    CONTINUE
      WRITE(6,100)XX(1,J),XX(2,J),R,S,U,V,(UX(K),UN(K),UM(K),K=1,4)
100   FORMAT(2F5.4,4F7.0,T42,3F7.0,/,9F7.0)
70    CONTINUE
      GO TO 4
      END
```

Writes in order of crystal then liquid, the mole fraction for component one, Thompsons W parameters and α_i no error-min-max.
Reads new binary.

```
/DATA
10010111111001100000010 10
AB-AN DHZ P323
1 356011182622229000155327 82129
  435.00       1.0
1 125996935
1 130994900
1 135991872
1 140990849
1 145989825
1 150988803
1 160983768
1 175972721
1 185968700
```

Name of Ab-An. From Deer, Howie and Zussman (1966)
Heat of fusion, temperature of fusion and molecular weight for components one and two, the number of sets of data.
RT,TX,TX1. If data of T-X[illegible]-X[illegible] is in °C, mole fraction then make RT=TO(2)-TO(1), RX=1, and RX1=1 if data is for component two, RX=0 if data is for component one. If data is unnormalized make RT the scale length between TO(1) and TO(2), and if data is for component two, RX1=RX and RX is the scale length between X(2)=0 and X(2)=1. If data is for component one then RX1=0.
Only 9 of the full 29 sets of data points are shown.

TMQ-I

```
          DIMENSION X(3),S(3),RT(3),NAME(5)
         1,SR(8,10)
    4     READ(5,5)NAME
    5     FORMAT(5A4)
          WRITE(6,6)NAME
          N=0
    6     FORMAT(1H ,5A4)
    1     READ(5,10)X,S
   10     FORMAT(3F4.4,3F5.0)
          IF(X(3))25,25,8
    8     IF(X(1))7,7,2
    7     X(1)=1.0E-06
    2     CALL PARFIT(X,S,RT)
          N=N+1
          SR(1,N)=X(1)
          SR(2,N)=X(3)
          SR(3,N)=RT(1)
          SR(4,N)=RT(2)
          SR(5,N)=RT(3)
          SR(6,N)=S(1)
          SR(7,N)=S(2)
          SR(8,N)=S(3)
          WRITE(6,35)X(1),X(3),RT,S
   35     FORMAT(2F5.4,3E13.6,3F7.0)
          GO TO 1
   25     SR(1,1)=0
          SR(2,N)=1
          N1=N-1
          WRITE(7,400)N,NAME
  400     FORMAT(I1,'1',5A4)
          WRITE(7,401)((SR(I,J),I=1,8),J=1,N1)
  401     FORMAT(2F5.4,3E13.6,3F7.0)
          WRITE(7,402)(SR(I,N),I=1,8)
  402     FORMAT(F5.4,F5.3,3E13.6,3F7.0)
          GO TO 4
          END
          SUBROUTINE PARFIT(X,E,RT)
          DIMENSION X(3),E(3),A(3),RT(3)
          X1=(E(1)-E(2))*(X(2)-X(3))
          X2=(E(2)-E(3))*(X(1)-X(2))
          RT(3)=(X1-X2)/((X(2)-X(3))*(X(1)**2-X(2)**2)-(X(1)-X(2))
         1*(X(2)**2-X(3)**2))
          RT(2)=(E(1)-E(2)-RT(3)*(X(1)**2-X(2)**2))/(X(1)-X(2))
          RT(1)=E(1)-RT(2)*X(1)-RT(3)*X(1)**2
          DO 10 I=1,3
          A(I)=RT(1)+RT(2)*X(I)+RT(3)*X(I)**2
   10     A(I)=A(I)-E(I)
          IF(ABS(A(1))+ABS(A(2))+ABS(A(3))-4.)20,20,21
   21     WRITE(6,25)X,E,RT
   25     FORMAT(' [redacted]',3F5.4,3F7.1,3E13.6)
   20     CONTINUE
          RETURN
          END
/DATA
```

PROGRAM TMQ

MAIN

X:composition of component two corresponding to the value of $\dot{\mu}_S$, RT:roots of parabolic fit, NAME:name of binary and the name of the component considered.

Reads three values of X(in component two), then three values of $\dot{\mu}_1$ or $\dot{\mu}_2$

A blank X-$\dot{\mu}$ data card causes transfer to statement 25 for punched output of the calculated data.

PARFIT fits parabola to the three sets of data, with roots RT.

Stores all data in SR for punching on cards after blank X-$\dot{\mu}$ card.

Reads next X-$\dot{\mu}$ data point in the same binary

N1 is the number of segments in the binary.

Punches on cards the number of segments, 1, and name of binary and component considered.

Punches on cards the compositional limits of each segment in component two, the three parameters of the fit, then the three $\dot{\mu}$ data used in calculating the fit.

PARFIT

Fits parabola to three sets of X,E data of the form E=f (X), with roots RT.

Calculates intermediate variables and roots by elimination.

Checks the computed values against the input values to see if error greater than 4 for the three points. A typical value for E is 3000 calories. Writes naughty word and the data if the accuracy is not acceptable.

```
/DATA
ANOR  DAN  M1870
000007002000000000   45  215
200038006000  215  503  925
600066007200  925 1103 1327
720078008400 1327 1550 1707
840086009000 1707 1780 1900
900092009600 1900 2000 2301
960098001.00 2301 2507 2903

ANOR DOR M1870
000002000400 4409 3518 3142
040006000800 3142 2827 2612
080010001200 2612 2411 2193
120026003000 2193 1250 1090
300046005600 1090  635  453
560072007600  453  183  125
760085009000  125   60   38
900096001.00   38  1000000

DIOR DDI M1870
000012002000000000  -90  -10
200030006000  -10  200 1390
600070008600 1390 2000 3160
860091009600 3160 3870 4870
960097501.00 4870 5400 7680

DIOR DOR M1870
000002000400-1493 1650 2710
040008001300 2710 3150 3280
130017002600 3280 3100 2520
260040005000 2520 1770 1300
500070008000 1300  530  290
800090001.00  290 10000000
```

ANOR is name of binary An-Or, DAN is the $\mathring{\mu}$ for An
There are three values of mole fraction component <u>two</u> (Or)
from the segment, with the end points of the segment being two of them,
then there are three values of $\mathring{\mu}$ for An.

Blank x-$\mathring{\mu}$ card causes punching of calculated data on cards, and reading of the next binary or component.

```
      DIMENSION X(2),XX(2,100),W(2),Q(2),TO(2),T(2),D(2,100),
     1EI(2,100),N(2),E(2,100),S(15),TP(2,100),DPD(2,100),DEI(2,1),

     1DD(2,100),DPEI(2,100),A(100),B(100),C(100)
     1,R%10,10<,RT%10<,RA%10<,RP%10<,NO%4<
     1,KA(2),KV(2)
      CALL SIGNON
5     READ(5,10)PAIR,(W(I),Q(I),TO(I),N(I),I=1,2),ITYPE
10    FORMAT(A4,2(F6.2,F6.0,F6.1,I2),I1)
      RXX=1
      J=0
      TO(1)=TO(1)+273.15
      TO(2)=TO(2)+273.15
15    READ(5,20)(T(I),X(I),I=1,2)
20    FORMAT(2(F4.0,F3.3))
      DO 21 I=1,2
      T(I)=T(I)+273.15
21    X(I)=X(I)/RXX
      IF(X(1)+X(2))61,61,25
25    J=J+1
      XX(1,J)=X(1)*W(2)/(W(1)+X(1)*(W(2)-W(1)))
      XX(2,J)=X(2)*W(1)/(W(2)+X(2)*(W(1)-W(2)))
      DO 33 I=1,2
      TP(I,J)=T(I)
33    CONTINUE
      GO TO 15
61    CONTINUE
      WRITE(6,130)PAIR
130   FORMAT(1H ,A4)
      DO 400 I=1,2
      N2=N(I)
      K=0
      A(I)=0
      DO 391 J=1,N2
      E(I,J)=TP(I,J)/TO(I)
390   D(I,J)=-1.987*TP(I,J)*ALOG(XX(I,J))
      IF((D(I,J)-8340.*(E(I,J)-.88))*(D(I,J)-11666.*(E(I,J)-.94)))
     174,74,391
74    K=K+1
      A(I)=A(I)-D(I,J)*TO(I)/(TP(I,J)-TO(I))
391   CONTINUE
      A(I)=A(I)/(FLOAT(K)+.0001)
      IF(ITYPE)80,80,90
80    WRITE(6,81)A(I)
81    FORMAT(' HEAT OF FUSION',F10.2)
      GO TO 400
90    CONTINUE
      DO 210 J=1,N2,8
      J1=J+7
      J1=AMIN0(J1,N2)
      WRITE(6,220)(XX(I,IJ),IJ=J,J1)
      WRITE(6,220)(E(I,IJ),IJ=J,J1)
      WRITE(6,222)(D(I,IJ),IJ=J,J1)
220   FORMAT(8F8.4)
222   FORMAT(8F8.0)
210   CONTINUE
400   CONTINUE
      CALL SINOFF
      GO TO 5
      END
/DATA
```

QESTR

MAIN
X:unnormalized weight %,XX: mole fraction, T: liquidus temperature °C,
W:mole weight, TO:temperature of fusion, N:number of sets of data,
PAIR:name of binary, TP:successive liquidus temperatures,
A:estimate of heat of fusion in region of high plotting accuracy,

Reads name of binary, mole weight, heat of fusion, temperature of fusion, number of data points on the liquidus, and ITYPE, a print out control

Reads the normalizing factor for reducing the composition data.

Reads the T and the unnormalized X weight percent data from the liquidus for both components

Normalizes T-X

A blank T-X data card causes program to begin estimation of the heat of fusion, by transferring to statement 61.

Converts X to mole fraction of each component

DO LOOP calculates on component one's side of the eutectic, then on two's side.

A plot of D versus E lies on a series of radiating lines of contact heat of fusion, and a region can be outlined where the plotting accuracy is definite. The region is trapezohedral, and lies between TP/TO=.88 and TP/TO=.94

If D and E are in the acceptable region then D is used in estimating the heat of fusion

ITYPE=0 writes only the estimated heat of fusion while ITYPE=1 writes E,D,XX for every data point.

Reads new binary name

Data is the same as for DUHEM

```
      DIMENSION VO(4),TEX(4),ALPHA(4),QF(4),TH(4),S(4),
     1A(3),B(4),C(4),Q(4,4),QS(4,4),V(4),AH(15,15),GT(15,15),
     1GTP(15,15),G(15,15),RTLG(4),X(4),IG(15,15),Z(4),TO(4)
     1,E(4,6),NIF(12),W(4),D(4,5),NAME(10),TITLE(10)
     1,IN(4),X1(4,10),X2(4,10),AA(4,10),BB(4,10),CC(4,10)
     1,X3(4,10),X4(4,10),A1(4,10),B1(4,10),C1(4,10),INP(4),INQ(4)
     1,CAT(10,13),HEAD(10,40)
      COMMON X1,X2,IN,AA,BB,CC,X3,X4,INP,A1,B1,C1,INQ
      COMMON IB1,IB2,IB3,IB4,IB5,IB6,KB1,KB2,KB3,KB4,KB5,KB6
      EQUIVALENCE(NIF(1),IB1)
      DO 757 I=1,10
      READ(5,751)(CAT(I,J),J=1,13)
751   FORMAT(20A4)
      READ(5,751)(HEAD(I,J),J=1,40)
757   CONTINUE
481   READ(5,486)(W(I),QF(I),TO(I),I=1,4)
486   FORMAT(4(F6.2,F6.0,F5.0))
      READ(5,450)NARK,TITLE,NAME
450   FORMAT(I1,10A4,/,10A4)
      DO 488 I=1,4
488   TO(I)=TO(I)+273.
      DO 47 I=1,NARK
      READ(5,300)IN(I),INQ(I)
300   FORMAT(2I1)
      N1=IN(I)
      READ(5,45)(X1(I,J),X2(I,J),AA(I,J),BB(I,J),CC(I,J),J=1,N1)
      READ(5,300)INP(I)
      N1=INP(I)
      READ(5,45)(X3(I,J),X4(I,J),A1(I,J),B1(I,J),C1(I,J),J=1,N1)
45    FORMAT(2F5.4,3E13.6)
47    CONTINUE
21    READ(5,978)IT1,IT2,IT3
978   FORMAT(2I4,I3)
C ITYPE=0IM,1IM+T,2RTLGXL+T,3ALIQ+T,4AXL+T,5A'XL+T
C        6T,7T+T',8SS,9SS+T
22    READ(5,970)ISPACE,KSPACE,JSPACE,NIF,ITYPE
970   FORMAT(3I2,6(I2,I3),I1)
      WRITE(6,1020)ITYPE
1020  FORMAT('  ITYPE= ',I2)
      ITYP=ITYPE+1
      CALL SINOFF
      WRITE(6,752)NAME,(CAT(ITYP,IKT),IKT=1,13),TITLE
752   FORMAT(1H1,10A4,/,13A4,2X,10A4)
      WRITE(6,755)(HEAD(ITYP,IKT),IKT=1,40)
755   FORMAT(20A4)
      DO 10 I=1,12
10    NIF(I)=NIF(I)+1
      TOT=1./100.
      ITEST=0
      DO 100 IT=IT1,IT2,IT3
      T=IT+273
      WRITE(6,480)IT
480   FORMAT(' T= ',I5)
```

PROGRAM GAPMIS

MAIN

QF:heat of fusion,TO:temperature of fusion,W:mole weight,
NAME:name of ternary,TITLE:type of a_i data used, IN:number of segments on the parabolic fits to a_i of the first component in each binary, INP:same as IN for the second component, INQ:parameter which determines whether binary a_i data is backwards or not,
NIF:input data defining two search areas in triangular coordinates,
X1;X2:compositional limits of each segment in a_i data for component one,AA;BB;CC:parameters of the segmented parabolic fit to a_i for component one,X3;X4:like X1;X2 for component two, A1;B1;C1:like AA etc. for component two, CAT;HEAD:print out table headings.

Enumerated triangular coordinates of the two search areas.

These two statements cause one to one matching of values of IB1, IB2,...KB6 with NIF(1), NIF(2),...NIF(12) at all times in the execution of the program.

Reads table headings for print out

Reads mole weight, heat of fusion, temperature of fusion for the components

Reads number of pairs of a_i data to be read in (NARK), then type of a_i data, then the name of the ternary.

The parameter INQ determines whether the binary a_i is backwards or not.

Reads in a_i data for each binary in order of component one then component two. The mole fractions are for component two.

Reads temperature range and increment over which calculations are to be performed.

OPTIONS FOR CALCULATION WITH PARAMETER ITYPE. +T means after finishing the specified calculations read in a new range and increment for the temperature.A'XL means activities in fused crystal.

Reads increments for search areas one and two, refining increment, then the triangular coordinates of the two search areas and the ITYPE OPTION for calculation to be performed.

RAX library routine which prints time of execution to this point.

Writes name of ternary, type of a_i data and the table headings.

ITEST will determine the total number of points tested for the ITYPE OPTION calculations.

The temperature DO LOOP is set up.

Temperature °C is written after table h. lings.

```
      L7=ISPACE+JSPACE/5
      L6=KSPACE+JSPACE/5
      DO 100 I=IB1,IB2,ISPACE
      L1=I-L6
      L2=I+L7
961   DO 100 J=IB3,IB4,ISPACE
962   J1=103-(I+J)
      IF((IB5-J1)*(IB6-J1))963,963,100
963   V(1)=FLOAT(I-1)*TOT
      V(2)=FLOAT(J-1)*TOT
      V(3)=FLOAT(J1-1)*TOT
      ITEST=ITEST+1
      GO TO (977,977,1011,988,1011,1014,420,420,977,977),ITYP
988   CALL ACTCAL(V,B,T)
1013  GX=0
      DO 998 ITP=1,3
998   GX=GX+V(ITP)*ALOG(ABS(B(ITP)+.00001)/(V(ITP)+.00001))
      GX=1.987*T*GX
      CALL WTPER(V,W,C)
      WRITE(6,999)(V(ITP),ITP=1,3),(B(ITP),ITP=1,3),GX,(C(ITP),I
     1TP=1,3)
999   FORMAT(1H ,6F7.4,F7.1,3F7.4)
      GO TO 100
1011  CALL RTLXL(V,A,T,TO,QF,B)
      IF(ITYP-3)1016,1025,1016
1025  WRITE(6,1030)(V(ITP),ITP=1,3),(B(ITP),ITP=1,3)
1030  FORMAT(1H ,3F7.3,3F7.0)
      GO TO 100
1016  CONTINUE
      DO 1012 L=2,3
1012  B(L)=EXP(B(L)/1.987/T+ALOG(V(L)+.00001))
      GO TO 1013
1014  CALL RTLXL(V,B,T,TO,QF,A)
      GO TO 1013
420   CALL RTLGA(V,RTLG,T)
      DO 430 L=1,3
      XP=T
      A(L)=-TO(L)*(RTLG(L)+QF(L))/(1.987*TO(L)*ALOG(V(L)+.00001)
     1-QF(L))
430   A(L)=A(L)-273.
      DO 700 ITP=1,3
700   B(ITP)=RTLG(ITP)
      WRITE(6,425)(V(L),L=1,3),A,(B(L),L=1,3)
425   FORMAT(1H ,3F6.3,3F7.1,3F7.1)
      GO TO 100
977   CALL LIMS(V,S,TH,ISPACE,T,TOT,ITYP)
      L3=J-L8
      L4=J+L7
      DO 101 K=KB1,KB2,KSPACE
      DO 101 N=KB3,KB4,KSPACE
      K1=103-(K+N)
      IF((KB5-K1)*(KB6-K1))863,863,101
863   IF((K-L1)*(K-L2))864,865,865
864   IF((N-L3)*(N-L4))101,865,865
865   X(1)=FLOAT(K-1)*TOT
      X(2)=FLOAT(N-1)*TOT
      X(3)=FLOAT(K1-1)*TOT
```

DO LOOPS for compositions of components one and two for search area one
are set up.

Number of points tested is incremented by one.
Splits up to perform ITYPE OPTIONS.
ITYPE=3:calculates activities in liquid
ACTCAL calculates activities in liquid at temperature T using composition V.
Total excess free energy of mixing calculated.
WTPER calculates weight fractions (C) from mole percent.
This is a general write statement for options ITYPE=2,3,4,5

RTLXL calculates A' in crystal: activities in the fused state and μ in
crystal (B)
ITYPE=2: μ in crystal (B) at composition V

ITYPE=4:activities (B) in crystal at temperature T, composition V.

ITYPE=5:activities in fused crystal at T,V

ITYPE=6:simple eutectic liquidus temperature
RTLGA calculates μ in liquid at T as RTLG.

Formula (3-2) from text calculates liquidus.

Writes composition, temperatures and μ for components one, two, three.

LIMS calculates central value (S) and range (TH) of activities in liquid
at T in a moveable search parallelogram.
DO LOOPS for compositions of components one and two for search area number
two set up.

```
      IF(ITYP-9)750,760,760
760   CALL LIMSXL(X,B,C,KSPACE,T,TOT,TO,QF)
      GO TO 770
750   CONTINUE
      CALL LIMS(X,B,C,KSPACE,T,TOT,ITYP)
770   CONTINUE
      DO 40 I2=1,3
      IF(ABS(S(I2)-B(I2))-(TH(I2)+C(I2)))40,40,101
40    CONTINUE
      CALL REFINE(V,X,ISPACE,KSPACE,T,JSPACE,IACC,S,B,ITYP,TO,
     1QF)
      IF(IACC)100,100,160
160   CALL WTPER(V,W,TEX)
      CALL WTPER(X,W,VO)
      WRITE(6,161)(V(L),L=1,3),(X(L),L=1,3),(TEX(L),L=1,3),(VO(L
     1),L=1,3),
     1,(S(L),L=1,3),(B(L),L=1,3)
161   FORMAT(1H ,6F6.3,6F7.4,6F6.3)
      GO TO 100
101   CONTINUE
100   CONTINUE
      DO 901 I=1,12
901   NIF(I)=NIF(I)-1
      CALL SINOFF
      WRITE(6,911)ITEST,NIF,ISPACE,KSPACE,JSPACE
911   FORMAT(1H ,I5,15I4)
      GO TO (22,21,21,21,21,21,22,21,22,21),ITYP
      END
      SUBROUTINE LIMS(V,S,TH,ISPACE,T,TOT,ITYP)
      DIMENSION V(4),S(4),A(4),B(4),C(4),X(4),Y(4),TH(4)
     1,R(4),U(4)
      CALL ACTCAL(V,A,T)
      Z=FLOAT(ISPACE)*TOT
      X(2)=V(2)+Z
      X(3)=V(3)-Z
      X(1)=V(1)
      CALL ACTCAL(X,B,T)
      IF(ITYP-9)30,20,20
20    DO 35 JX=1,3
      C(JX)=A(JX)
35    U(JX)=A(JX)
      GO TO 45
30    CONTINUE
      Y(3)=X(3)
      Y(2)=V(2)
      Y(1)=1.-Y(2)-Y(3)
      CALL ACTCAL(Y,C,T)
      R(1)=V(1)+Z
      R(2)=V(2)+Z
      R(3)=V(3)-2.*Z
      CALL ACTCAL(R,U,T)
45    CONTINUE
      DO 10 I=1,3
      S(I)=AMAX1(A(I),B(I),C(I),U(I))
      TH(I)=AMIN1(A(I),B(I),C(I),U(I))
      S(I)=(S(I)+TH(I))/2.
10    TH(I)=S(I)-TH(I)
      RETURN
      END
```

ITYPE=8,9:solid solution tie line calculated at T
LIMSXL determines the central value (B) and the range (C) of activities in fused crystal in moveable search parallelogram.

LIMS for activities in liquid in second search area.

Checks to see if activities in the two moveable search parallelograms can be matched for a possible solution.

REFINE refines the possible solution to a more accurate composition.
IACC=1 means a refined solution has been found
WTPER converts V,X to weight fractions

Writes mole fractions of coexisting phases, weight fractions, and values of the matched activities.

Closes search area two.
Closes search area one.

Writes the number of points tested, the compositional limits of the two search areas and the search increments.
Reads new search areas with statement 21 and new temperature range for calculations with statement 22.
LIMS
Determines central value (S) and range (TH) of activities in liquid in the moveable search parallelogram.
The limits of the moveable search parallelogram are defined by V,X, Y,R.
The size of the parallelogram is the search increment Z.
ACTCAL calculates activities (B) in liquid at T.
Activities are calculated at each corner of the parallelogram.

ITYPE=8,9:solid solution calculations require matching of activities for only the components in the solid solution (2+3)

Determines the central value (S) and the range (TH) of activities in the parallelogram.

```
      SUBROUTINE ACTCAL(V,A,T)
      DIMENSION V(4),A(4),RTLG(4)
      CALL RTLGA(V,RTLG,T)
      DO 10 I=1,3
      A(I)=V(I)*EXP(RTLG(I)/T/1.987)
 10   CONTINUE
      RETURN
      END
      SUBROUTINE REFINE(V,X,ISPACE,KSPACE,T,JSPACE,IACC,S,B,
     1ITYP,TO,QF)
      DIMENSION V(4),X(4),S(4),TH(4),B(4),C(4)
     1,TO(4),QF(4)
      TOT=1./1000.
      CALL BOUND(V,ISPACE,IB1,IB2,IB3,IB4,IB5,IB6)
      CALL BOUND(X,KSPACE,KB1,KB2,KB3,KB4,KB5,KB6)
      DO 100 I=IB1,IB2,JSPACE
      DO 100 J=IB3,IB4,JSPACE
      J1=1003-I-J
      IF((IB5-J1)*(IB6-J1))963,963,100
 963  V(1)=FLOAT(I-1)*TOT
      V(2)=FLOAT(J-1)*TOT
      V(3)=FLOAT(J1-1)*TOT
      CALL LIMS(V,S,TH,JSPACE,T,TOT,ITYP)
      IF(ITYP-9)510,520,520
 520  KB1=1
      KB2=1
 510  CONTINUE
      DO 101 K=KB1,KB2,JSPACE
      DO 101 N=KB3,KB4,JSPACE
      K1=1003-K-N
      IF((KB5-K1)*(KB6-K1))863,863,101
 863  X(1)=FLOAT(K-1)*TOT
      X(2)=FLOAT(N-1)*TOT
      X(3)=FLOAT(K1-1)*TOT
      IF(ITYP-9)750,760,760
 760  CALL LIMSXL(X,B,C,JSPACE,T,TOT,TO,QF)
      GO TO 770
 750  CONTINUE
      CALL LIMS(X,B,C,JSPACE,T,TOT,ITYP)
 770  CONTINUE
      DO 40 I2=1,3
      IF(ABS(S(I2)-B(I2))-(TH(I2)+C(I2)))40,40,101
 40   CONTINUE
      IACC=1
      GO TO 110
 101  CONTINUE
 100  CONTINUE
      IACC=0
 110  RETURN
      END
      SUBROUTINE BOUND(V,ISPACE,I1,I2,I3,I4,I5,I6)
      DIMENSION V(4)
      I1=1000.*V(1)+11.
      I2=I1+10*ISPACE
      I3=1000.*V(2)+11.
      I4=I3+10*ISPACE
      I6=1000.*V(3)+11.
      I5=I6-20*ISPACE
      RETURN
      END
```

ACTCAL

Determines activities in liquid at T and composition V
RTLGA determines α (RTLG) in liquid at T,V.
Activities calculated

REFINE

Refines the solution found in MAIN by searching the two previous moveable search parallelograms with smaller moving search parallelograms

BOUND determines the DO LOOP limits of the two areas to be searched

Identical to the portion in the MAIN program that matches activities except the search increments are ISPACE/1000

If activities are matched the IACC=1, but IACC=0 for no solution.

BOUND

Calculates DO LOOP limits for the two moveable search parallelograms which now become refined search area one and two. They are now going to be searched with moving parallelograms with the refined increment JSPACE/100.

```
      SUBROUTINE WTPER(X,W,C)
      DIMENSION X(4),W(4),C(4)
      CT=1./(X(1)*W(1)+X(2)*W(2)+X(3)*W(3))
      DO 200 K=1,3
200   C(K)=X(K)*W(K)*CT
      RETURN
      END
      SUBROUTINE RTLGA(V,RTLG,T)
C     PROGRAM RTLGA CALCULATES RTLN(ACTIVITY COEFFICIENT)
      DIMENSION RTLG(4),V(4),Z(4),S(4),TH(4)
      Z(1)=V(3)/(V(3)+V(1)+.00001)
      CALL XHM(1,Z(1),S(1),TH(1),T)
      Z(2)=V(2)/(V(2)+V(1)+.00001)
      CALL XHM(2,Z(2),S(2),TH(2),T)
      Z(3)=V(3)/(V(3)+V(2)+.00001)
      CALL XHM('3,Z(3),S(3),TH(3),T)
140   GTX=(1.-V(2))**2*S(1)+(1.-V(1))**2*S(3)+(1.-V(3))**2*S(2)
      RTLG(1)=2.*((1.-V(3))*S(2)+(1.-V(2))*S(1))-V(2)*TH(2)-V(3)
     1*TH(1)
     1-GTX
      RTLG(2)=2.*((1.-V(3))*S(2)+(1.-V(1))*S(3))+V(1)*TH(2)-V(3)
     1*TH(3)
     1-GTX
      RTLG(3)=2.*((1.-V(2))*S(1)+(1.-V(1))*S(3))+V(1)*TH(1)+V(2)
     1*TH(3)
     1-GTX
      RETURN
      END
      SUBROUTINE XHM(I,Y,S,TH,T)
      DIMENSION X1(4,10),X2(4,10),AA(4,10),BB(4,10),CC(4,10),
     1IN(4),X3(4,10),X4(4,10),A1(4,10),B1(4,10),C1(4,10),
     1INP(4),INQ(4)
      COMMON X1,X2,IN,AA,BB,CC,X3,X4,INP,A1,B1,C1,INQ
      IF(INQ(I)-1)70,70,80
70    X=Y
      GO TO 75
80    X=1.-Y
75    CONTINUE
      N1=IN(I)-1
      DO 15 J=1,N1
      IF((X-X1(I,J))*(X-X2(I,J)))10,10,15
15    CONTINUE
      J=IN(I)
10    TH1=AA(I,J)+X*BB(I,J)+X**2*CC(I,J)
      N1=INP(I)
      DO 20 J=1,N1
      IF((X-X3(I,J))*(X-X4(I,J)))21,21,20
20    CONTINUE
      J=INP(I)
21    TH2=A1(I,J)+X*B1(I,J)+X**2*C1(I,J)
      TH=TH2-TH1
      S=TH1+X*(TH2-TH1)
      IF(INQ(I)-1)85,85,90
90    TH=-TH
85    RETURN
      END
```

WIPER
Calculates weight percent (C) from mole percent (X) with mole weights (W)

RTLGA
Calculates α in liquid

Uses the intersections in the binaries (Z) to get the binary values of ζ_{ij} and θ_{ij} using XHM

Formulae (2-8) for α in the liquid from the text.

XHM
Calculates the value of ζ_{ij} = S and θ_{ij} - TH at $Z = \left(\frac{x_i}{x_i+x_j}\right)$ in the binary ij

If INQ=2 the binary data is backwards but if INQ=1 the data is the right way around.

Determines which segmented interval that the input composition X lies in for the α data in binary ij

Calculates α_i in binary ij

Determines which segmented interval X lies in for the α_j data in binary ij

If the data is backwards the slope is reversed.

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```
      SURROUTINE LIMSXL(V,S,TH,ISPACE,T,TOT,TO,QF)
      DIMENSION V(4),C(4:,S(4),A(4),B(4),TH(4),TO(4),QF(4)
     1,X(4)
      Z=FLOAT(ISPACE)*TOT
      CALL RTLXL(V,A,T,TO,QF,X)
      C(2)=V(2)+Z
      C(3)=V(3)-Z
      CALL RTLXL(C,B,T,TO,QF,X)
      DO 10 I=2,3
      S(I)=AMAX1(A(I),B(I))
      TH(I)=AMIN1(A(I),B(I))
      S(I)=(S(I)+TH(I))/2.
10    TH(I)=S(I)-TH(I)
      TH(1)=1.E6
      S(1)=0
      RETURN
      END
```

LIMSXL

Determines the central value (S) and the range (TH) of activities in fused crystal for a moveable search interval defined by the composition V and V(2) +Z where Z is the search increment. This is done only for components <u>two</u> and <u>three</u>, the components in the solid solution phase.

RTLXL calculates activities in fused solid solution phase at T

```
      SUBROUTINE RTLXL(V,A,T,TO,QF,X)
      DIMENSION V(4),A(4),TO(4),QF(4),S(4),TH(4),X(4)
      CALL XHM(4,V(2),S(2),TH(2))
      A(2)=S(2)+V(3)*TH(2)
      A(3)=S(2)-V(2)*TH(2)
      X(2)=A(2)
      X(3)=A(3)
      DO 10 I=2,3
10    A(I)=V(I)*EXP((A(I)+QF(I)*(T-TO(I))/TO(I))/1.987/T)
      A(1)=0
      RETURN
      END
```

RTLXL

Determines activities for components two and three at T in the fused solid solution phase.
Binary name 4 called in XHM is the μ^x data for the solid solution phase

Activities in crystal referred to fused state.

```
/DATA
    IMMISCIBLE LIQUIDS AT TEMPERATURE T IN
MOLE % PHASE ONE* MOLE % PHASE TWO*  WEIGHT % ONE    * WEIGHT % TWO
*ACTIVITY
 1     2     3     1     2     3     1     2     3     1     2     3
 123-123
    IMMISCIBLE LIQUIDS AT TEMPERATURE T IN
MOLE % PHASE ONE* MOLE % PHASE TWO*  WEIGHT % ONE    * WEIGHT % TWO
*ACTIVITY
 1     2     3     1     2     3     1     2     3     1     2     3
 123-123
    EXCESS CHEMICAL POTENTIALS OF CRYSTAL IN
  MOLE % CRYSTAL     *  EXCESS CHEM POT CRYSTAL
  1      2      3      1      2      3
    ACTIVITIES OF LIQUID AT TEMPERATURE T  IN
MOLE FRACTION LIQUID*ACTIVITIES IN LIQUID*G EXCESS* WEIGHT PERCENT
  1      2      3      1      2      3    TOTAL    1      2      3
    ACTIVITIES OF CRYSTAL  AT TEMPERATURE T  IN
MOLE FRACTION CRYSTL*ACTIVITIES IN CRYSTL*G EXCESS* WEIGHT PERCENT
  1      2      3      1      2      3    TOTAL    1      2      3
    ACTIVITIES OF FUSED CRYSTAL AT TEMPERATURE T IN
MOLE FRACTION CRYSTL*ACTIVITIES IN CRYSTL*G EXCESS* WEIGHT PERCENT
  1      2      3      1      2      3    TOTAL    1      2      3
```

DATA

Headings for the tables for the different ITYPE OPTIONS. The data lines with less than 8-10 characters are a direct continuation of the preceeding line; they are actually on the same data card, but the printer width is only 70 characters.

```
   . SIMPLE EUTECTIC LIQUIDUS TEMPERATURES IN
MOLE FRACTION LIQ*LIQUIDUS TEMPERATURE*EXCESS CHEM POTENTIAL
 1     2    3      1      2      3      1      2      3
   SIMPLE EUTECTIC LIQUIDUS TEMPERATURES IN
MOLE FRACTION LIQ*LIQUIDUS TEMPERATURE*EXCESS CHEM POTENTIAL
 1     2    3      1      2.     3      1      2      3
   SOLID SOLUTION LIQUIDUS AT TEMPERATURE T  IN
MOLE % LIQUID   * MOLE % CRYSTAL  *  WEIGHT % LIQUID * WEIGHT % CRYSTL
*ACTIVITY
 1     2     3,     1     2     3     1     2     3     1     2     3
 123-123
   SOLID SOLUTION LIQUIDUS AT TEMPERATURE T  IN
MOLE % LIQUID   * MOLE % CRYSTAL  *  WEIGHT % LIQUID * WEIGHT % CRYSTL
*ACTIVITY
 1     2     3      1     2     3     1     2     3     1     2     3
 123-123
216.562550.1391.262.2213560.1118.278.2129000.1553.
4DIOP-AB-AN,1ATM
SEG PARA FIT TO D M1070
72ANDM DAN J2670
.0   .0660-0.621477E-03 0.621478E 03-0.233462E 03     0.    16.    40.
.0660.1800 0.394680E 02 0.753434E 02-0.101944E 04    40.    36.    20.
.1800.3500-0.404017E 02 0.105571E 04-0.400078E 04    20.   -21.  -161.
.3500.6420 0.513801E 02 0.113852E 04-0.498663E 04  -161.  -326. -1273.
.6420.7770-0.375841E 04 0.115747E 05-0.119990E 05 -1273. -1329. -2009.
.7770.9140 0.181383E 05-0.420840E 05 0.207907E 05 -2009. -2873. -2958.
.91401.000 0.124903E 06-0.274919E 06 0.147733E 06 -2958. -2995. -2705.
51ANDM DDI JAN2670
.0   .1060-0.855830E 03-0.326150E 05 0.195000E 06 -1572. -2159, -2122.
.1060.4120-0.215436E 04-0.326602E 03 0.596147E 04 -2122. -2020. -1277.
.4120.6420-0.415060E 04 0.908748E 04-0.512796E 04 -1277.  -571.  -430.
.6420.8950-0.389770E 04 0.794337E 04-0.395944E 04  -430.   -31.    40.
.89501.000-0.899509E 04 0.194711E 05-0.104760E 05    40.    52.     0.
51DMAB DDI J2670
.0   .5170-0.126942E-03 0.126941E 03 0.116493E 04     0.    10.   377.
.5170.8050 0.176384E 04-0.674898E 04 0.786557E 04
.8050.9170 0.253604E 05-0.676795E 05 0.471426E 05
.9170.9650-0.207293E 06 0.419067E 06-0.206985E 06  2940.  4317.  4357.
.96501.000-0.526054E 07 0.109940E 08-0.573906E 07  4357.  2960.  1831.
41DMAB DAB JAN2670
.0   .1030 0.203078E 04-0.177233E 05 0.980982E 05  1787.  1367.  1246.
.1030.6570 0.139625E 04-0.143219E 04-0.257860E 03  1246.  1047.   344.
.6570.9650 0.133286E 04-0.126987E 04-0.358064E 03   344.   130.  -226.
.96501.000 0.927823E 05-0.195621E 06 0.102839E 06  -226.  -160.     0.
```

Mole weight, heat of fusion, and temperature of fusion for components one, two and three.

Name of the ternary Diopside-Albite-Anorthite

The form of the input data is as segmented parabolic fit to $\bar{\mu}^E = D$ rather than to $\bar{\mu}$

The characters 72 ANDM DAN have the following meaning:

7	there are seven segments fitted to $\bar{\mu}^E = f(X)$
2	the binary $\bar{\mu}^E$ data is backwards so INQ=2
ANDM	the binary is An-Dio from Bowen (1928)
DAN	the data is for $\bar{\mu}^E$ of An

The characters 51 ANDM DDI are similar to those for An, only they are for Dio. The 1 is not read, as the binary is already backwards.

The order of the binary input data for $\bar{\mu}^E$ is for liquids; in Dio-An first, then for Dio-Ab, and then for Ab-An. The fourth set of $\bar{\mu}^E$ data is for the crystal phase in Ab-An.

The property of the binary $\bar{\mu}^E$ data being backwards or forwards is determined by using ITYPE options 2 and 6 in GAPMIS for binary compositions and comparing the results with the $\bar{\mu}^E$ data in the last three columns.

The first two data are the mole fraction (second component) limits of each segment, and the next three data are the parameters of the fit, while the last three data are the $\bar{\mu}^E$ values used in calculating the fit.

```
7 1ABAN LIQ DAB
.0    .1000-0.165169E-03 0.165171E 03-0.164170E 04     0.     4.     0.
.1000.3700 0.271102E 02-0.309970E 03 0.398675E 03     0.   -30.   -33.
.3700.5300-0.161343E 03 0.462498E 03-0.312498E 03   -33.   -13.    -4.
.5300.6700 0.791173E 02-0.190476E 03 0.634917E 02    -4.   -10.   -20.
.6700.8000 0.582143E 04-0.172057E 05 0.126674E 05   -20.     0.   164.
.8000.8900-0.239574E 05 0.544480E 05-0.303703E 05   164.   406.   445.
.89001.000-0.115454E 06 0.260274E 06-0.146124E 06   445.   390.  -999.
8 1ABAN LIQ DAN M770
.0    .0700 0.420049E 02-0.490614E 04 0.370256E 05    42.   -95.  -120.
.0700.1600-0.210000E 03 0.131349E 04-0.396835E 03  -120.   -95.   -10.
.1600.3300-0.204353E 03 0.157549E 04-0.225490E 04   -10.    60.    70.
.3300.4800-0.792868E 02 0.896316E 03-0.134525E 04    70.    64.    41.
.4800.5400 0.817000E 03-0.295000E 04 0.277778E 04    41.    35.    34.
.5400.7000-0.340624E 03 0.120000E 04-0.937498E 03    34.    43.    40.
.7000.8700-0.146762E 03 0.100209E 04-0.105042E 04    40.    25.   -70.
.87001.000 0.451116E 04-0.103153E 05 0.580416E 04   -70.   -72.     0.
8 2ABAN XL DAB M770
.0    .2400-0.199863E+02 0.199863E 04-0.372691E 04     0.   239.   265.
.2400.3400-0.133797E 03 0.332165E 04-0.691664E 04   265.   254.   196.
.3400.5000 0.445199E 03-0.908336E 03 0.515876E 03   196.   150.   120.
.5000.6200 0.925557E 03-0.230556E 04 0.138889E 04   120.    70.    30.
.6200.7500 0.182144E 04-0.492825E 04 0.328845E 04    30.   -17.   -25.
.7500.8700 0.384274E 03-0.118854E 04 0.857125E 03   -25.   -18.    -1.
.8700.9400 0.311606E 05-0.703701E 05 0.397151E 05    -1.    35.   105.
.94001.000-0.219796E 05 0.480386E 05-0.261109E 05   105.    50.   -52.
6 1ABAN XL DAN M770
.0    .1000 0.404007E 04-0.720669E 05 0.347762E 06  4040.   968.   311.
.1000.2500 0.205833E 04-0.226600E 05 0.518666E 05   311.  -399.  -365.
.2500.3800-0.844929E 02-0.289766E 04 0.710251E 04  -365.  -339.  -160.
.3800.7500-0.678020E 03 0.181563E 04-0.119059E 04  -160.     4.    14.
.7500.9200-0.131587E 03 0.414704E 03-0.294117E 03    14.    10.     1.
.92001.000 0.259995E 04-0.541241E 04 0.281245E 04     1.    -4.     0.

15001600 50
05081005035400801502500000040070300609
```

Do option IITYPE for 1500 to 1600°C in steps of 100°C

INCREMENTS			SEARCH AREA ONE						SEARCH AREA TWO						IYPE
1	2	REFINE	1		2		3		1		2		3		
05	08	10	05	035	40	080	15	025	00	000	42	070	30	060	9

Increment 1 is for search area one, the figures under 1 2 3 are the compositional limits for the search area, in components one, two, three.
IITYPE=9 means the calculation option to be performed is solid solution.

GAPMIS-8

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