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THERMODYNAMICS OF ROCK-FORMING CRYSTALLINE SOLUTIONS

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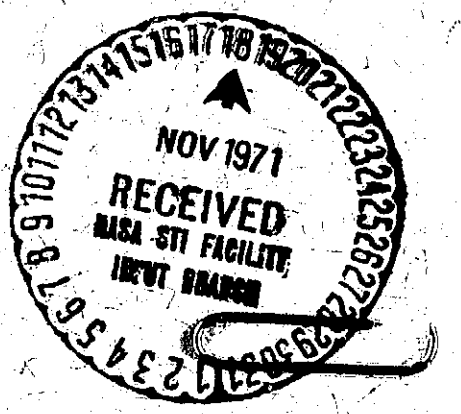

GODDARD SPACE FLIGHT CENTER
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Surendra K. Saxena

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INTRODUCTION

Today as petrologists, mineralogosts and crystallographers, we are very well equipped in our laboratories. We have refined instruments for chemical analysis such as laser probe, electron microprobe and the ion microprobe mass analyzer which can produce results within minutes, results which used to take days and weeks. Besides x-ray methods, there are several spectroscopic techiques, such as Mössbauer spectroscopy, which can be used to know the distribution of cations over the nonequivalent structural sites in a crystal. The experimental methods of synthesizing minerals assemblages in the laboratories have improved very much. There are refined techniques to control the fugacities of gases and create low to very high P and T conditions in our petrological experimentals. These technical capabilities are further enchanced by the use of computers which can take care of our numerical data and with the help of suitable thermodynamic theory tell us about the consistency or inconsistency of our experiments.

As a result of our augmented experimental capability, we have gathered a lot of phase equilibria data both from our efforts to synthesize minerals assemblages in the labortory and from our chemical analysis of natural minerals assemblages. In order to make a meaningful analysis of both these types of data, it is imperative that we have thermodynamic data on the rock-forming phases and crystalline solutions. Unfortunately the progress in obtaining these quantilies by thermochemical and calorimetric methods has been very slow and it is desirable that we consider the possibility of obtaining such quantilies by other methods.

We may consider in suitable cases of retrieving thermodynamic data from the phase diagrams themselves. These quantilies may be considered significant, if they are obtained consistently from different phase diagrams. However in the case of crystalline solutions, thermodynamic functions of mixing cannot be obtained without the use of certain solution models. Two types of phase diagrams may be considered. The first type is the diagram with the solvus or binodal curve bounding a binary two-phase region. The analytical methods have been discussed by Thompson (1967), Thompson and Waldbaum (1969) and Green (1970). These methods, however, are of limited use for rock-forming silicates, since most Fe^{2+}-Mg^{2+} crystalline solutions do not show any solvus relationship. The second type of phase diagram is the Roozeboom type figure where we plot the concentration of a component in one phase against the concentration of the same component in the a coexisting phase. Such distribution relationship, based on simple ion-exchange reactions, were discussed initially by Ramberg and De Vore (1951) followed by Kretz (1959) and Mueller (1960). It is possible to retrieve useful thermodynamic information from such distribution data in ion-exchange as collected by Nafziger and Muan (1967), Larimer (1968) Medaris (1969) and Schulien et al. (1970) among others.

Useful thermodynamic information may also be obtained by considering distribution of cations within the crystalline solution. Ghose (1961) found the interesting Fe^{2+}-Mg distribution in cummingtonite. Since then such Fe^{2+}-Mg order-disorder has been studied in several silicates by crystallographers. Theoretical framework for considering the homogeneous equilibria of intra-crystalline cation distribution has been presented in several papers by Mueller (1962), Matsui and Banno (1965), Perchuk and Ryabchikov (1968), Thompson

(1962), Matsui and Banno (1965), Perchuk and Ryabchikov (1968), Thompson (1969) and Griver and Orville (1969).

The purpose of this work is to discuss these methods of obtaining thermodynamic quanlities and discuss some aspects of partitioning of elements in coexisting phases. We do this by considering the definition of crystalline solutions, the definition of components in a silicate minerals and the definition of chemicals potentials of these components. We also consider the solution models involved. There are examples on calculating thermodynamic functions of mixing in the systems $CaWO_4$-$SrWO_4$, olivine-chloride solution, and orthropyroxene.

It is hoped that this work will generate enough interest among the experimentalists to gather useful ion-exchange data on coexisting phases and among the crystallogrphers to gather data on site-occupancies in the rock-forming silicates.

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Notations

Superscripts are generally abbreviated names of the minerals to which the thermodynamic functions is ascribed. Subscripts refer to components of the crystalline solution or the chemical system.

a_A^α Activity of component A in the phase α

A, B, C Used as a subscript denotes components A, B and C

A, B, C Energy constants used in equations describing the relation between activity and mole fractions

A_0, A_1, A_2 Energy constants in equation for excess free energy of mixing expressed as a polynomial in mole fraction

f Activity coefficient

G Molar Gibbs free energy

G_E Excess molar Gibbs free energy of mixing

G_{IM} Ideal molar Gibbs free energy of mixing ($= \sum_i RT \ln x_i$)

G_M Total molar Gibbs free energy of mixing

H Molar enthalpy

H_M Molar enthalpy of mixing

S Molar entropy

S_M Molar entropy of mixing

S_{EM} Excess molar entropy of mixing

S_{IM} Ideal molar entropy of mixing

w Energy constant or the interchange energy used in the regular solution model

W' Nw where w is independent of P and T

W Nw where w is a function of P and T as in the simple mixture model

K	Thermodynamic equilibrium constant
K_D	Distribution coefficient
M1, M2	Denotes structural sites in the crystal
N	Avogadro's number
P	Pressure
T	Absolute temperature
R	Gas constant
μ_i^{α}	Chemical potential of a component i in phase α
μ^{AM}	Chemical potential of a pure component AM
x_i	Mole fraction of a component i
opx	Orthopyroxene (Mg, Fe) SiO_3 or $(Mg, Fe)_2 Si_2O_6$
en	Enstatite $MgSiO_3$ or $MgMgSi_2O_6$
cpx	Clinopyroxene Ca Mg Si_2O_6
gar	Garnet $(Mg, Fe, Ca, Mn)_3 Al_2 Si_3O_{12}$
alm	Almandine $Fe_3Al_2Si_3O_{12}$
bi	Biotite K $(FeMg)_3 AlSi_3O_{10} (OH)_2$

Section 1

THERMODYNAMIC RELATIONS IN CRYSTALLINE SOLUTIONS

Thermodynamic relations between the concentration of a component in a solution and its chemical potential and other thermodynamic functions of mixing are presented here. The details of the simplifying assumptions and the methods of statistical thermodynamics have been given by Denbigh (1965), Guggenheim (1950, 1967), Prigogine and Defay (1954) among others. Recently Thompson (1967) also considered the properties of simple solutions. Besides presenting a summary of thermodynamic relations in binary, ternary and multicomponent solutions, we shall be particularly concerned with the difficulties encountered in their application to silicate minerals. Some of these problems such as the choice of a component and definition of its chemical potential in a silicate have been discussed by Ramberg (1952a, 1963), Kretz (1961) and Thompson (1969).

Crystalline Solutions

Crystalline solutions considered here are the rock forming silicates forming isomorphous series with one another. Such crystalline solutions have a definite structural frame work with generally two or more kinds of nonequivalent structural sites. The type of sites and the ions that occupy them vary in different crystalline solutions. The overall crystal symmetry of a solution does not change as a function of the composition, though certain microscopic details within the crystal i. e. the form and size of the individual structural sites may change with changing composition.

We may consider orthopyroxene $(Mg, Fe)_2 Si_2 O_6$ as an example. In the crystal structure there are single silicate chains parallel to the c -axis held

together by the octahedrally coordinated Mg^{2+} and Fe^{2+}. There are two kinds of structurally nonequivalent sites M1 and M2 occupied by Mg^{2+} and Fe^{2+}. The M1 octahedral space is nearly regular polyhedral but the M2 space is quite distorted. As a result of varying Mg and Fe^{2+} in the composition of the crystal, the general symmetry of the crystal does not change but there are distinct changes in M1 and M2 polyhedra. The former becomes more regular and the latter more distorted with increasing Fe/Mg ratio. Such microscopic changes at the structural sites within the same crystal framework may be regarded as continuous and the resulting energy changes a consequence of the mixing or solution of the species to form a crystalline solution.

Choice of a Chemical Component

The definition of a component in a mineral is not unique. The components in orthopyroxene may be considered to be the molecules $MgSiO_3$ and $Fe\ Si\ O_3$, or MgO, FeO, and SiO_2, or the cations Mg^{2+}, Fe^{2+}, Si^{4+} and O^{2-}. In petrological studies, the choice of a component is determined by known or postulated chemical reactions involving a mineral. In such studies, the choice of components such as $FeSiO_3$ or FeO is convenient even though there are no discrete units of this kind in the orthopyroxene crystal structure. However, while considering the thermodynamic properties of silicate crystalline solutions, it is only realistic to consider the ions as the components (see Bradley, 1962). Indeed it can be noted that if the substitution of the cation Fe^{2+} by Mg^{2+} in orthropyroxene does not induce any changes in the silicate framework or if there are any slight changes, they are directly a function of the changing Fe/Mg ratio, the alternative methods of defining $FeSiO_3$ or Fe^{2+} as a component are equivalent (see also Saxena and Ghose, 1971).

Chemical Potential and Activity of a Component in a Mineral

A solution is ideal if the chemical potential of every component is a linear function of the logarithm of its mole fraction according to the relation

$$\mu_i = \mu^i + R\,T\,\ln x_i \tag{1.1}$$

where μ_i is the chemical potential of i in a solution and μ^i is the chemical potential of pure i. μ^i is a function of P and T only. In a binary solution α, whose composition is (A, B) M where M may represent the anion group or the silicate framework, and A and B the cations which substitute for each other, there is a choice between adopting the cations A and B as components or the end member molecules AM and BM. As noted before, under certain conditions, the mole fractions may be calculated as

$$x^{\alpha}_{A} = \frac{A}{A+B} \quad \text{or} \quad x^{\alpha}_{AM} = \frac{AM}{AM+BM}$$

and these could be considered equivalent. We may write for chemical potentials

$$\mu^{\alpha}_{A} = \mu^{AM}_{A} + R\,T\,\ln x^{\alpha}_{A} \tag{1.2}$$

or

$$\mu^{\alpha}_{AM} = \mu^{AM} + R\,T\,\ln x^{\alpha}_{AM} \tag{1.3}$$

where μ^{AM}_{A} and μ^{AM} are chemical potentials of A and AM in a standard state. The standard state AM is well defined but the standard state with reference to cation A needs definition. In orthopyroxene, this is like referring to the chemical potential of Mg^{2+} in pure (Mg, Mg) Si_2O_6. The Gibbs free energy for the pure end member $MgSiO_3$ is defined and measurable experimentally but the meaning of free energy of Mg^{2+} in pure enstatite is little understood and experimental methods remain to be developed for its measurement.

However in theoretical discussion, where we are not concerned with the measured values of the potentials, the definition of chemical potential of a cation in a crystalline solution is not only permissible but also useful. Kretz (1961) defines the chemical potential of Mg in orthopyroxene as

$$\mu_{Mg} = \left(\frac{\partial G}{\partial n\, Mg}\right)_{P,T,\ n_{Fe},\ n_{Si},\ n_0} \tag{1.4}$$

where n is the number of cations in the formula.

In many crystalline solutions, when their compositions are expressed in the simplest form, there are two or more cations in one mole. Examples are olivine $(Fe, Mg)_2\ SiO_4$ and garnet $(Fe, Mg)_3\ Al_2Si_3O_{12}$. The chemical potential of a component using 'molecular' model is expressed as:

$$\mu^{ol}_{Fe_2SiO_4} = \mu^{Fe_2SiO_4} + R\ T\ \ln x_{Fe_2SiO_4} \tag{1.5}$$

$$\mu^{gar}_{Fe_3Al_2Si_3O_{12}} = \mu^{Fe_3Al_2Si_3O_{12}} + R\ T\ \ln x_{Fe_3Al_2Si_3O_{12}} \tag{1.6}$$

where the first μ is the chemical potential of the end member in the solution, the second μ is the chemical potential of the pure end member. If we choose to consider the cation Fe^{2+} as component, we have

$$\mu^{ol}_{Fe} = \mu^{Fe_2SiO_4}_{Fe} + 2\ R\ T\ \ln x^{ol}_{Fe} \tag{1.7}$$

and

$$\mu^{gar}_{Fe} = \mu^{Fe_3Al_2Si_3O_{12}}_{Fe} + 3\ R\ T\ \ln x^{gar}_{Fe} \tag{1.8}$$

where the first μ is the chemical potential of Fe^{2+} in the crystalline solution and second μ is the chemical potential of Fe^{2+} in the pure end member. The

mole fractions x are the same quantities in both the 'molecular' or 'ionic' models. It may be desirable to consider the chemical formula on one cation basis i. e. we consider olivine as (Fe, Mg) $Si_{0.5}O_2$ and garnet as (Mg Fe) $Al_{2/3}SiO_4$. In these cases we may write

$$\mu_{Fe}^{ol} = \frac{1}{2}\mu_{Fe}^{Fe_2\ SiO_4} + R\ T\ \ln x_{Fe} \tag{1.9a}$$

or

$$\mu_{FeSi_{0.5}O_2}^{ol} = \frac{1}{2}\ \mu_{Fe}^{Fe_2SiO_4} + R\ T\ \ln x_{Fe}^{ol} \tag{1.9b}$$

and

$$\mu_{Fe}^{gar} = \frac{1}{3}\mu_{Fe}^{Fe_3Al_2Si_3O_{12}} + R\ T\ \ln x_{Fe}^{gar} \tag{1.10a}$$

or

$$\mu_{FeAl_{2/3}SiO_4}^{gar} = \frac{1}{3}\mu_{Fe}^{Fe_3Al_2Si_3O_{12}} + R\ T\ \ln x_{Fe}^{gar} \tag{1.10b}$$

The usefulness of the above relations is mentioned later in connection with the composition of coexisting minerals.

We shall be mostly concerned with the activities of the components. For a binary ideal solution the activity is equal to its mole fraction. In olivine the activity of fayalite (fa) molecule is

$$a_{fa} = (x_{fa}^{ol}), \tag{1.11}$$

or for Fe^{2+},

$$a_{fe} = (x_{Fe}^{ol})^2 \tag{1.12}$$

Similarly for garnet we may have

$$a_{alm} = x_{alm}^{gar} \tag{1.13}$$

$$a_{Fe} = (x_{Fe}^{gar})^3 \tag{1.14}$$

It is desirable to consider many reactions, particularly the ion-exchange reaction, on a one cation basis i. e. consider olivine as (Fe Mg) $Si_{0.5}$ O_2 etc. Activity of a cation is then equal to its mole fraction. It is necessary to specify that although in this situation x_{Fe} (mole fraction Fe^{2+}/Fe^{2+} + Mg) is numerically the same as x_{fa} (percent of fayalite), the activities are different. x_{Fe} is equal to $(a_{Fe})^{1/2}$ in the 'ionic model' but x_{fa} is equal to a_{fa} i. e. activity of fayalite in the solution.

Non-Ideal Binary Solutions

The relation between the chemical potential of a component i and its activity in a solution is given by

$$\mu_i = \mu^i + R\,T \ln a_i \qquad (1.15)$$

ideal solution is the limiting case when a_i is equal to the mole fraction x_i. In all other cases, one may express the relation between a_i and x_i as:

$$a_i = f_i\, x_i \qquad (1.16)$$

where f_i is the activity coefficient of the component i in the solution.

The free energy of mixing G_M for a binary solution (A, B) M is given by

$$\begin{aligned} G_M &= x_A\, R\, T \ln a_A + x_B\, R\, T \ln a_B \qquad (1.17)\\ &= R\, T\, (x_A \ln x_A + x_B \ln x_B) + R\, T\, (x_A \ln f_A + x_B \ln f_B)\\ &= G_{IM} + G_{EM} \end{aligned}$$

The first term G_{IM} is the ideal free energy of mixing and the second term G_{EM} is the excess free energy of mixing arising due to the non-ideality of the system. G_{EM} is one of the functions of mixing termed 'excess functions'. Details

of the excess functions of mixing may be found in Prigogine and Defay (1954) and Thompson (1967).

Regular Solution Model

We are often required to calculate the thermodynamic properties of the crystalline solutions from compositions of mineral assemblages either obtained in experiments or occurring in rocks. In many situations the use of certain models for the activity composition relationship helps to assess such properties closely. Guggenheim's (1952) regular solution model is next in simplicity to ideal solution model.

Zeroth approximation

The excess free energy of mixing G_{EM} in a regular solution with the zeroth approximation i. e. approximation of complete disorder, is given by

$$G_{EM} = x_A \, x_B \, W' \tag{1.18}$$

where A and B are components of a solution (A, B) M and W' is equal to Nw. N is Avogadro's number. W' is often referred to as the 'interchange energy'. We shall be very much concerned with regular solutions in this work. Therefore we shall briefly discuss the parameter w. A simplified account of this parameter is presented by Denbigh (1965). It is assumed that the cations A and B are of roughly same size and can be interchanged between lattice sites without change of lattice structure and without change in the lattice vibrations. There is a certain interaction between A and B given by the energy w which is given by

$$w = (2\, w_{ab} - w_{aa} - w_{bb}) \tag{1.19}$$

where w_{aa} is the increase in potential energy when a pair of A ions are brought together from infinite distance to their equilibrium separation in the solution. Similarly w_{ab} and w_{bb} are pair potentials for A-B and B-B pairs. In spite of the interaction energy, it is assumed that the mixing of A and B is random. This means that the entropy of mixing is the same as that for an ideal solution and deviations are expressed entirely in terms of the heat of mixing.

The thermodynamic equations for the regular solution model with zeroth approximation are:

$$G_{EM} = H_{EM} = x_A \, x_B \, W' \tag{1.20}$$

$$S_{EM} = 0 \tag{1.21}$$

The 'interchange energy' W' is independent of P and T. As the excess entropy of mixing is zero, according to this model, the predictions on the excess free energy of mixing and the heat of mixing (which may often be different from the G_{EM}) are not satisfactory.

Simple mixture model

In the regular solution model W' is supposed to be independent of temperature and pressure. In Guggenheim's (1967) latest version of the lattice theory W' may be treated as an adjustable constant required to fit the experimental data to the model. Such an energy parameter with a symbol W may be called 'a cooperative free energy'. $2W$ is in a sense the free energy increase in the whole system when an AA pair and a BB pair are converted into two AB pairs. It is expected that if W is fitted to the free energy data at each temperature, the large errors usually found in the predictions of G_{EM} and H_{EM} with composition

may be at least partly eliminated. For a random mixing approximation, the various excess functions are given by

$$G_{EM} = x_A\, x_B\, \mathbb{W} \tag{1.22}$$

$$-S_{EM} = x_A\, x_B \frac{\partial\, \mathbb{W}}{\partial\, T} \tag{1.23}$$

$$H_{EM} = x_A\, x_B \left(\mathbb{W} - T \frac{\partial\, \mathbb{W}}{\partial\, T} \right) \tag{1.24}$$

The activity coefficient is related to the mole fraction as:

$$\ln f_A = \frac{\mathbb{W}}{R\,T} (x_B)^2 \tag{1.25}$$

Quasi-chemical model

The main assumptions required for this model are similar to those of the regular solution model in the preceding sections namely a) only configurational partition function of the solution is contributing to the thermodynamic excess functions and b) the intermolecular forces are central and short ranged and therefore the internal energy at 0° K may be obtained by an addition of the pair-potentials. The assumption of complete randomness is not required here. Therefore any differences found in the calculated values of the excess functions of mixing by the zeroth approximation and by the quasi-chemical approximation is due to the effect of ordering considered in the latter.

In binary solutions where the two components A and B are of similar size, the activity coefficients are given by the equations:

$$f_A = \left\{ \frac{\beta + 1 - 2\, x_B}{x_A\, (\beta + 1)} \right\}^{\frac{z}{2}} \tag{1.26}$$

$$f_B = \left\{\frac{\beta - 1 + 2 x_B}{x_A (\beta + 1)}\right\}^{\frac{z}{2}} \tag{1.27}$$

where z is the coordination number and β is given by

$$\beta = \{1 + 4 x_A x_B (e^{2W/zRT} - 1)\}^{1/2} \tag{1.28}$$

β is unity for a perfectly random mixture. $\beta > 1$ indicates a tendency for clustering and $\beta < 1$ indicates a trend for compound formation.

The excess free energy of mixing and the heat of mixing are given by

$$G_{EM} = \frac{1}{2} z R T \left\{x_A \ln \frac{\beta + 1 - 2 x_B}{x_A (\beta + 1)} + x_B \ln \frac{\beta - 1 + 2 x_B}{x_A (\beta + 1)}\right\} \tag{1.29}$$

$$H_{EM} = \frac{2}{\beta + 1} x_A x_B \left\{W - T \frac{\partial W}{\partial T}\right\} \tag{1.30}$$

The various equations of the quasi-chemical approximation may be expanded as power series in $2W/zRT$:

$$G_{EM} = W x_A x_B \left\{1 - \frac{1}{2}\left(\frac{2W}{zRT}\right) x_A x_B - \frac{1}{6}\left(\frac{2W}{zRT}\right)^2 x_A x_B (x_A - x_B)^2 + \cdots\right\} \tag{1.31}$$

$$f_A = W x_B^2 \left\{1 + \frac{1}{2}\left(\frac{2W}{zRT}\right) x_A (1 - 3 x_B) + \frac{1}{6}\left(\frac{2W}{zRT}\right)^2 x_A (1 - 11 x_B + 28 x_B^2 - 20 x_B^3) + \cdots\right\} \tag{1.32}$$

Similarly f_B may be obtained by replacing A by B in (1.32).

For molecules which are not very similar in size, we find the necessity to include a 'contact factor' (see Guggenheim, 1952 p. 186) in the above equations to take into account the size differences. The contact factors may be found roughly proportional to the molar volumes or ionic radii. The activity coefficients are given by:

$$f_A = \left[1 + \frac{\phi_B (\beta - 1)}{\phi_A (\beta + 1)}\right]^{zq_A/2} \tag{1.33}$$

$$f_B = \left[1 + \frac{\phi_A (\beta - 1)}{\phi_B (\beta + 1)}\right]^{zq_B/2} \tag{1.34}$$

where q_A and q_B are contact factors related to the contact fractions ϕ_A and ϕ_B and the mole fractions x_A and x_B by the following equations

$$\phi_A = \frac{x_A q_A}{x_A q_A + x_B q_B} \quad \phi_B = \frac{x_B q_B}{x_A q_A + x_B q_B} \tag{1.35}$$

For more details on the derivation and significance of the constants q_A and q_B and the fractions ϕ_A and ϕ_B, reference may be made to Guggenheim (1952, p. 186) and King (1969), p. 488). β in (1.33) and (1.34) is obtained by replacing x_A and x_B by ϕ_A and ϕ_B respectively in (1.28).

The other excess functions are given by

$$G_{EM} = \frac{1}{2} z R T \left\{x_A q_A \ln\left(1 + \frac{\phi_B (\beta - 1)}{\phi_A (\beta + 1)}\right) + x_B q_B \ln\left(1 + \frac{\phi_A (\beta - 1)}{\phi_B (\beta + 1)}\right)\right\} \tag{1.36}$$

$$H_{EM} = \frac{2\, x_A\, x_B\, q_A\, q_B}{(x_A\, q_A + x_B\, q_B)\,(\beta + 1)} \left(W - T \frac{\partial W}{\partial T} \right) \tag{1.37}$$

S_{EM} can be obtained by the standard equation

$$G_{EM} = H_{EM} - T\, S_{EM}.$$

Some Other Methods for Representing the Activity-Composition Relations

In the case of a binary system of components A and B, the Gibbs-Duhem equations is

$$x_A\, d \ln f_A + x_B\, d \ln f_B = 0 \tag{1.38}$$

The changes $d \ln f_A$ and $d \ln f_B$ when due to composition change dx_A at constant temperature we may write

$$x_A \left(\frac{\partial \ln f_A}{\partial x_A} \right)_T + x_B \left(\frac{\partial \ln f_B}{\partial x_A} \right)_T = 0 \tag{1.39}$$

A solution to the above equation was proposed by Margules in the form of a power series

$$\ln f_A = a_A\, x_B + b_A\, x_B^2 + c_A\, x_B^3 + d_A\, x_B^4 + \ldots \tag{1.40}$$

$$\ln f_B = a_B\, x_A + a_B\, x_A^2 + c_B\, x_A^3 + d_B\, x_A^4 + \ldots \tag{1.41}$$

when the series is terminated at x^3, the following relations exist between the coefficients a_B

$$\begin{aligned} a_A &= a_B = 0 \\ b_B &= b_A + 3\, c_A/2 + 2\, d_A + \ldots \\ c_B &= -\,(c_A + 8\, d_A/3 + \ldots) \end{aligned} \tag{1.42}$$

Using the above relations, Carlson and Colburn (1942) expressed the activity coefficients by the equations

$$\log f_A = (2B - A)(1 - x_A)^2 + 2(A - B)(1 - x_A)^3 \tag{1.43}$$

$$\log f_B = (2A - B)x_A^2 + 2(B - A)x_A^3 \tag{1.44}$$

Relations similar to these have been used by Thompson (1967) and Thompson and Waldbaum (1968, 1969).

Another two-constant equation is due to van Laar. The equation resulted from a theory based on the van der Waals equation of state. This theory is probably incorrect but van Laar's equation continues to be useful for representing the activity-composition relation. This equation is

$$\log f_A = \frac{A}{1 + \left\{\frac{A x_A}{B(1 - x_A)}\right\}^2} \tag{1.45}$$

similarly for the other component

$$\log f_B = \frac{B}{\left\{1 + \frac{B(1 - x_A)}{A x}\right\}^2} \tag{1.46}$$

For many chemical systems the van Laar's equation provides a better representation of the data than is given by the Margules two-constant equation. The relative merits of these two equations were discussed by Carlson and Colburn. It may be finally remarked that a power series expansion as (1.47 see later) for the excess free energy is now widely preferred and we shall, therefore, use only such expressions and not the equations mentioned in this section. Expressing

the excess free energy as a power series is a means of giving empirical description to deviations from ideality which is a better alternative to the power series expansions referring to individual activity coefficients mentioned above. G_{EM} expressed as a power series can be related more conveniently to the other global properties of the mixture, such as the heat and volume change of mixing than can the individual activity coefficients which represent the deviations divided up, as it were, among the components.

General Relations for Binary, Ternary and Quaternary Non-ideal Crystalline Solutions

Excess functions in non-ideal solutions may conveniently be expressed by a power series in the mole fraction. Guggenheim (1937) suggested that G_{EM} can be expressed as a polynomial in x as

$$G_{EM} = x_A\, x_B \{A_0 + A_1 (x_A - x_B) + A_2 (x_A - x_B)^2 + \ldots\} \tag{1.47}$$

where A_0, A_1 and A_2 etc. are constants. When odd terms in (1.47) vanish, the solution becomes symmetric. If A_2 and other higher terms are also zero, we have the simple mixture model with A_0 as the energy constant W in (1.22). The expressions for the activity coefficients are obtained from

$$\begin{aligned} R\,T \ln f_A &= G_{EM} + x_B \frac{\partial G_{EM}}{\partial x_A} \\ &= x_B^2 [A_0 + A_1 (3 x_A - x_B) + A_2 (x_A - x_B)(5 x_A - x_B) + \ldots.] \end{aligned} \tag{1.48}$$

$$\begin{aligned} R\,T \ln f_B &= G_{EM} - x_A \frac{\partial G_{EM}}{\partial x_B} \\ &= x_A^2 [A_0 - A_1 (3 x_B - x_A) + A_2 (x_B - x_A)(5 x_B - x_A) + \ldots.] \end{aligned} \tag{1.49}$$

Equations for other excess functions of mixing may be derived from (1.47) as:

$$-S_{EM} = x_A\, x_B \left[\partial \frac{A_0}{\partial T} + \left(\frac{\partial A_1}{\partial T}\right)(x_A - x_B) + \left(\frac{\partial A_2}{\partial T}\right)(x_A - x_B)^2 + \ldots .\right] \qquad (1.50)$$

$$H_{EM} = x_A\, x_B \left[A_0 - T\left(\frac{\partial A_0}{\partial T}\right) + \left\{A_1 - T\left(\frac{\partial A_1}{\partial T}\right)\right\}(x_A - x_B) + \left\{A_2 - T\left(\frac{\partial A_2}{\partial T}\right)\right\}(x_A - x_B)^2 + \ldots .\right] \qquad (1.51)$$

The expression for the excess free energy of mixing in a ternary system according to Redlich-Kister equation (King, 1969) is

$$\begin{aligned} G_{EM} = {} & x_A\, x_B \{b_{AB} + c_{AB}(x_A - x_B) + d_{AB}(x_A - x_B)^2 + \ldots\} \\ & + x_A\, x_C \{b_{AC} + c_{AC}(x_A - x_c) + d_{AC}(x_A - x_c)^2 + \ldots\} \\ & + x_B\, x_C \{b_{BC} + c_{BC}(x_B - x_C) + d_{BC}(x_B - x_C)^2 + \ldots\} \\ & + x_A\, x_B\, x_C (F + H_A\, x_A + H_B\, x_B) \end{aligned} \qquad (1.52)$$

where b, c and d represent A_0, A_1 and A_2 of equation (1.47). F, H_A and H_B are ternary constants and must be evaluated from ternary data. For silicate crystalline solutions such data are rare. Therefore we may consider that only the pairwise interactions are important and adopt the following empirical expression for G_{EM} for a system containing any number of components:

$$G_{EM} = \sum_{ij} x_i\, x_j\, [b_{ij} + c_{ij}(x_i - x_j) + d_{ij}(x_i - x_j)^2 + \ldots \qquad (1.53)$$

where $i \neq j$.

Section 2

THERMODYNAMIC STABILITY OF A SOLUTION

Instrinsic and Extrinsic Stability

A crystalline solution when ideal adds a certain amount of negative free energy of mixing to free energy of the system. With increasing positive deviations from ideality this contribution becomes less and less. Below a certain critical temperature of unmixing, the solution unmixes to form two or more solutions. These energetic changes obviously affect the stability of the entire system of mineral assemblage. This instability of a crystalline solution, which arises due to the positive excess free energy of mixing, may be termed intrinsic instability (see, Mueller, 1964). Ideal solutions are always intrinsically stable. A crystalline solution may also become instable if the physical-chemical conditions change in such a way that certain reaction products become a lower free energy assemblage than the crystalline solution. This instability could be considered as extrinsic. A solution may be both intrinsically and extrinsically instable. The division is essentially artificial. It, however, helps to understand and describe certain petrological reactions as shown by Mueller (1964).

Olivine $(Fe, Mg)_2 SiO_4$ and pyroxene $(Fe, Mg) SiO_3$ may be considered as ideal binary solutions at high temperature ($\sim 1100°C$). In spite of their ideal character, orthopyroxenes with more than 55 mole percent of ferrosilite were found unstable at liquidus temperatures by Bowen and Schairer (1935). The iron rich pyroxene is unstable due to the instability of ferrosilite relative to fayalite and quartz. This is the extrinsic instability.

At low temperatures ($\sim 600°C$), the situation is little different. Orthopyroxene is somewhat non-ideal and high values of G_{EM} are associated with high ferrosilite content of the solution. The extrinsic instability of the solution relative to olivine and quartz is less since iron-rich pyroxenes ($\sim$ 86 percent $FeSiO_3$) are stable in metamorphic rocks. The instability of pyroxenes with higher ferrosilite in metamorphic rocks may be both due to the extrinsic and intrinsic instability of the orthopyroxene solution.

Critical Mixing

General conditions: The conditions for critical mixing in terms of free energy of mixing G_M and the mole fraction x are

$$\partial^2 G_M / \partial x^2 = 0 \tag{2.1}$$

$$\partial^3 G_M / \partial x^3 = 0 \tag{2.2}$$

These may be expressed in terms of excess free energy of mixing G_{EM} as

$$\partial^2 G_{EM} / \partial x^2 = - R T / x (1 - x) \tag{2.3}$$

$$\partial^3 G_{EM} / \partial x^3 = - R T (2 x - 1) / x^2 (1 - x)^2 \tag{2.4}$$

Simple mixture: For a simple mixture we have

$$G_{EM} = x (1 - x) W \quad W = W (T, P) \tag{2.5}$$

By successive differentiation of (2.5), we have

$$\partial^2 G_{EM} / \partial x^2 = - 2 W \tag{2.6}$$

$$\partial^3 G_{EM} / \partial x^3 = 0 \tag{2.7}$$

By substituting (2.3) and (2.4) into (2.6) and (2.7) respectively, we have

$$-2\,\mathbb{W} = -R\,T/x\,(1-x) \tag{2.8}$$

$$0 = R\,T\,(2x-1)/x^2\,(1-x)^2 \tag{2.9}$$

These give us the critical composition as $x = 0.5$ and $2\,R\,T_C = \mathbb{W}$.

General non-ideal solution: For a binary solution which is not a symmetric solution, the excess free energy of mixing is given by

$$G_{EM} = x\,(1-x)\,[A_0 + A_1\,(1-2x) + A_2\,(1-2x)^2 + \ldots] \tag{1.47}$$

Successive differentiation of (1.47) with respect to x gives

$$\frac{\partial^2 G_{EM}}{\partial x^2} = -2A_0 - 6A_1\,(1-2x) - A_2\,[10 - 48x\,(1-x)] \tag{2.10}$$

$$\frac{\partial^3 G_{EM}}{\partial x^3} = 12A_1 + 48A_2\,(1-2x) \tag{2.11}$$

Substitution of (2.3) and (2.4) into (2.10) and (2.11) gives equations which are transcendental and cannot be solved without a computer program using an iteration method.

Formation of miscibility gaps in a ternary simple mixture: Let us consider a ternary simple mixture with components 1, 2 and 3. The $\mathbb{W}$ for the three binary systems are $\mathbb{W}_{12}$, $\mathbb{W}_{13}$ and $\mathbb{W}_{23}$. The chemical potentials of the components in the solution are given by:

$$\mu_1 = \mu_1^0\,(T,\,P) + R\,T\,\ln x_1 + R\,T\,\ln f_1,\ \text{etc.}, \tag{2.12}$$

where $R\,T\,\ln f$ may be expanded in terms of x and $\mathbb{W}$ as follows:

$$
\begin{aligned}
R\,T \ln f_1 &= (x_2)^2\, W_{12} + (x_3)^2\, W_{13} + x_2\, x_3\, (W_{12} - W_{23} + W_{13}) \\
R\,T \ln f_2 &= (x_3)^2\, W_{23} + (x_1)^2\, W_{12} + x_3\, x_1\, (W_{23} - W_{13} + W_{12}) \\
R\,T \ln f_3 &= (x_1)^2\, W_{13} + (x_2)^2\, W_{23} + x_1\, x_2\, (W_{13} - W_{12} + W_{23})
\end{aligned}
\tag{2.13}
$$

At equilibrium in the two separated coexisting phases α and β we have

$$
\mu_1^{\alpha}\,(x_2^{\alpha},\ x_3^{\alpha},\ T) - \mu_1^{\beta}\,(x_2^{\beta},\ x_3^{\beta},\ T) = 0 \tag{2.14}
$$

and similarly for u_2 and u_3. Substituting (2.12) and (2.13) in (2.14) and rearranging we have (see Kaufman & Bernstein, 1970, p. 226)

$$
\begin{aligned}
&R\,T \ln (x_1^{\beta}/x_1^{\alpha}) + W_{12}\,(x_2^{\beta^2} - x_2^{\alpha^2}) + W_{13}\,(x_3^{\beta^2} - x_3^{\alpha^2}) \\
&\qquad + \Delta W\,(x_2^{\beta}\, x_3^{\beta} - x_2^{\alpha}\, x_3^{\alpha}) = 0 \\
&R\,T \ln (x_2^{\beta}/x_2^{\alpha}) + W_{12}\,[(1 - x_2^{\beta})^2 - (1 - x_2^{\alpha})^2] + W_{13}\,(x_3^{\beta^2} - x_3^{\alpha^2}) \\
&\qquad - \Delta W\,[x_3^{\beta}\,(1 - x_2^{\beta}) - x_3^{\alpha}\,(1 - x_3^{\alpha})] = 0 \\
&R\,T \ln (x_3^{\beta}/x_3^{\alpha}) + W_{12}\,(x_2^{\beta^2} - (x_2^{\alpha})^2) + W_{13}\,[(1 - x_3^{\beta})^2 - (1 - x_3^{\alpha})^2] \\
&\qquad - \Delta W\,[x_2^{\beta}\,(1 - x_3^{\beta}) - x_2^{\alpha}\,(1 - x_3^{\alpha})] = 0
\end{aligned}
\tag{2.15}
$$

where ΔW is $W = W_{12} + W_{13} - W_{23}$

With the help of equations (2.15) compositions of coexisting phases may be calculated and the miscibility gap may be plotted on a ternary diagram. However first, we require the compositions of the coexisting phases on three binary edges.

In a binary solution, the miscibility gap can be calculated by finding the composition of the coexisting phases which together represent the minimum free energy of the system. This may be done by the "Tangent method" graphically i. e. by drawing a tangent through the two points representing the two

minima in the plot of the free energy of mixing against composition alternatively we may consider the relations

$$\mu_1^{\alpha} = \mu_1^{\beta}, \quad \mu_2^{\alpha} = \mu_2^{\beta}$$

For the binary regular solution, there is a symmetric miscibility gap and therefore

$$x_1^{\alpha} + x_2^{\alpha} = 1, \; x_1^{\beta} + x_2^{\beta} = 1 \quad \text{and also} \quad x_1^{\alpha} = x_1^{\beta}$$

and $x_2^{\alpha} = x_2^{\beta}$. We may therefore write

$$R\,T \ln (1 - x_1) + x_1^2\, W = R\,T \ln (1 - x_2) + x_2^2\, W \tag{2.16}$$

$$R\,T \ln x_1 + (1 - x_1)^2\, W = R\,T \ln x_2 + (1 - x_2)^2\, W \tag{2.17}$$

Substituting

$$x_2 = 1 - x_1$$

in (2.16) we have

$$\frac{W}{R\,T} = \frac{1}{(1 - 2\,x_1)} \ln\left\{\frac{(1 - x_1)}{x_1}\right\} \tag{2.18}$$

Equation (2.18) may be solved by an iteration method to find the miscibility gaps on the binary edges in a triangular diagram.

A computer program to solve the equations (2.15) numerically and the method to form a miscibility gap have been presented by Kaufman and Bernstein (1970). Some examples to illustrate the possible solutions of certain mineralogical problems are presented elsewhere.

Section 3

COMPOSITION OF COEXISTING PHASES

Ideal Solution Model

Distribution of a component between two ideal binary crystalline solutions

Although there are no strictly binary silicates, certain minerals such as orthopyroxene and olivine may be assumed to be quasi-binary. In view of the similarity of Fe^{2+} and Mg^{2+} in ionic charge and size, we may assume that olivine and orthopyroxene are binary ideal solutions. This assumption is re-examined later.

Ramberg and DeVore (1951) considered the following ion-exchange equilibrium between olivine and pyroxene:

$$\underset{\text{en}}{Mg\,Si\,O_3} + \frac{1}{2}\underset{\text{fa}}{Fe_2\,Si\,O_4} \rightleftharpoons \underset{\text{fs}}{Fe\,Si\,O_3} + \frac{1}{2}\underset{\text{fo}}{Mg_2\,Si\,O_4} \qquad (3a)$$

The equilibrium constant for the above reaction at a certain P and I is

$$K_{3a} = \frac{x_{Fe}^{Opx}\,(1 - x_{Fe}^{Ol})}{(1 - x_{Fe}^{Opx})\,x_{Fe}^{Ol}} \qquad (3.1)$$

The equilibrium constant K is a function of P and T only. In the present case K_{3a}, however, is not found to be constant except at high temperatures (see Olsen and Bunch, 1970).

It may be noted that (3a) is written on one cation exchange basis. We may also write

$$2\,Mg\,Si\,O_3 + Fe_2\,Si\,O_4 \rightleftharpoons 2\,Fe\,Si\,O_3 + Mg_2\,Si\,O_4 \qquad (3b)$$

The equilibrium constant for the above reaction is

$$K_{3b} = \frac{(x_{Fe}^{Opx})^2 \ (1 - x_{Fe}^{Ol})}{(1 - x_{Fe}^{Opx})^2 \ x_{Fe}^{Ol}}$$

A Roozeboom figure with such K values has been presented by Kern and Weisbrod (1967), p. 224). It is known empirically from the distribution data in several mineral assemblages, that equilibrium constants or distribution coefficients such as K_{3b} are very cumbersome to handle and inconsistent with petrological observations. One may, therefore, prefer to use the distribution data on one cation exchange basis. It is obvious that in actual calculations of the energy values, we shall be required to adjust for the activity-composition relations (such as 1.7, 1.8, 1.12 and 1.14) as discussed before.

Generally olivine and pyroxene coexist with several other minerals of fixed or variable composition. If there is no significant change in the concentration of the minor components changing the binary character of the two minerals, K_{3a} is not a function of any changes in the number or proportion or composition of other coexisting phases. This is generally true about equilibrium constants in other systems also. At a certain P and I the stability of the assemblage olivine-pyroxene is a function of the presence or absence of quartz but the value of K_{3a} itself is not affected.

Kretz (1959) used Roozeboom plots extensively to show the orderly distribution of cation between coexisting silicate minerals in rocks. If chemical equilibrium is closely approached in the distribution of a component between two binary solutions at a certain P and T, the distribution isotherm is a smooth

curve and if at the same time both the solutions are ideal, it will be of the form shown in Figure 3.1.

Coexisting ternary ideal solutions

Consider two coexisting ternary phases α and β with the formulae (A, B, C) M and (A, B, C) N. The pure components are AM, BM and CM in α and similarly AN, BN and CN in β. The chemical potentials of the components in α and β are

$$\mu^{\alpha}_{AM} = \mu^{AM} + R\,T\,\ln x^{\alpha}_{AM} \tag{3.3}$$

$$\mu^{\beta}_{AN} = \mu^{AN} + R\,T\,\ln x^{\beta}_{AN} \tag{3.4}$$

ans similarly others. The potentials of the pure components μ^{AM} etc. are functions of P and T only. We may also substitute x^{α}_{A} for x^{α}_{AM} and x^{β}_{A} for x^{β}_{AN} without altering the results (see discussion before).

The distribution of A between α and β may be represented by the ion exchanges

$$A\,\alpha + B\,\beta \rightleftharpoons B\,\alpha + A\,\beta \tag{3c}$$

$$A\,\alpha + C\,\beta \rightleftharpoons C\,\alpha + A\,\beta \tag{3d}$$

We may write the equilibrium constants as

$$K_{3C} = \frac{x^{\alpha}_{B}\,x^{\beta}_{A}}{x^{\alpha}_{A}\,x^{\beta}_{B}} \quad \text{and} \quad K_{3d} = \frac{x^{\alpha}_{C}\,x^{\beta}_{A}}{x^{\alpha}_{A}\,x^{\beta}_{C}}$$

where X_A is A/A + B + C etc.

Both K_{3C} and K_{3d} will be constants for all ratios of A: B: C. A plot of x^{α}_{A} against x^{β}_{A} will produce a symmetric ideal distribution curve.

Non-ideal Solutions

Distribution of a component between two "simple mixtures"

For the ion-exchange equation

$$A\,\alpha + B\,\beta = A\,\beta + B\,\alpha \tag{3e}$$

we have at equilibrium

$$\mu_B^{\alpha} + \mu_B^{\beta} = \mu_B^{\beta} + \mu_A^{\alpha} \tag{3.5}$$

If (A, B) α and (A, B) β are 'simple mixtures', we have

$$\mu_B^{\alpha} = \mu^{B\alpha} + R\,T \ln (1 - x_A^{\alpha}) + W\,(x_A^{\alpha})^2 \tag{3.6}$$

and similarly others.

Substituting such values (3.6) in (3.5) and rearranging we obtain

$$\ln \frac{x_A^{\beta}\,(1 - x_A^{\alpha})}{(1 - x_A^{\beta})\,x_A^{\alpha}} - \left\{ \frac{W^{\alpha}}{R\,T}\,(1 - 2\,x_A^{\alpha}) - \frac{W^{\beta}}{R\,T}\,(1 - 2\,x_A^{\beta}) \right\} = \frac{-\,\Delta\,G_a^0}{R\,T} \tag{3.7}$$

where

$$\Delta\,G_a^0 = \mu^{B\alpha} + \mu^{A\beta} - \mu^{B\beta} - \mu^{A\alpha}.$$

Or we may write

$$\ln K_{3e} = \ln K_D - \frac{W^{\alpha}}{R\,T}\,(1 - 2\,x_A^{\alpha}) + \frac{W^{\beta}}{R\,T}\,(1 - 2\,x_A^{\beta}) \tag{3.8}$$

where K_{3e} is $\exp(-\Delta G_a^0/RT)$ and K_D is the distribution coefficient.

If we can obtain a good least squares fit for the distribution data by using (3.8), it may also be found that both the minerals are close to being 'simple mixtures'.

With increasing non-ideality in one or both of the minerals, the distribution isotherms may attain different forms (see Mueller (1964). Figure 3.2 shows an example where one of the minerals α is ideal and β non-ideal. W^{β} is assumed to vary linearly with $1/T$. The values of W^{β} and K_a at 673 and 1173°K are 2.75, 1.603, 0.77 and 1.518 respectively (see Saxena, 1969a). The forms of the distribution isotherms are very different from the symmetric ideal curves.

Coexisting regular ternary solutions

The composition of two coexisting phases which obey the same equation of state is considered here as an example. These phases are products of unmixing in a ternary solution (A, B, C) M. We assume that W'_{AB}, W'_{BC} and W'_{AC} are 1500, 7000 and 9000 cal/mole respectively and W's are not a function of P, T and composition (regular solution). Figure (3.3) shows the miscibility gap in the system and the tie lines for the coexisting phases. Let the phase rich in C be denoted by α and the phase poor in C by β. For the chemical potentials we have

$$\mu_A^{\alpha} = u^{AM} + R\,T\,\ln f_A^{\alpha} x_A^{\alpha} \tag{3.3}$$

$$\mu_A^{\beta} = \mu^{AM} + R\,T\,\ln f_A^{\beta} x_A^{\beta} \text{ etc.,} \tag{3.4}$$

We may consider any one of the following ion-exchanges between α and β

$$A\,\beta + B\,\alpha \rightleftharpoons A\,\alpha + B\,\beta \tag{3f}$$

$$B\,\alpha + C\,\beta = B\,\beta + C\,\alpha$$

$$A\,\alpha + C\,\beta = C\,\alpha + A\,\beta$$

The equilibrium constant for (3f) is

$$\frac{x_A^{\alpha} x_B^{\beta}}{x_A^{\beta} x_B^{\alpha}} \cdot \frac{f_A^{\alpha} f_B^{\beta}}{f_A^{\beta} f_B^{\alpha}} = K_{3f} \tag{3.9}$$

In this particular case since α and β obey the same equation of state we have $\Delta G^0 = 0$ and K_{3f} is unity. In other cases where α and β are minerals with different crystal structures, the equilibrium constant is not unity. The f terms in equation (3.9) are functions of P, T and the A: B: C ratio and therefore K_D ($X_B^\alpha X_A^\beta / X_A^\alpha X_B^\beta$) also changes with P, T and A:B, B:C and A:C ratios.

Let A:B:C change systematically as listed in Table 3.1. We find that a plot of x_B^α against x_B^β where x is either A/A +B or A/A +B +C shows a smooth distribution curve (Figure 3.4). The form of the curve, however, is markedly different from the ideal distribution curve.

The activity coefficients are given by

$$\begin{aligned} R\,T \ln f_A &= (x_B)^2\, W'_{AB} + (x_C)^2\, W'_{AC} + x_B\, x_C\, (W'_{AB} - W'_{BC} + W'_{AC}) \\ R\,T \ln f_B &= (x_C)^2\, W'_{BC} + (x_A)^2\, W'_{AB} + x_C\, x_A\, (W'_{BC} - W'_{AC} + W'_{AB}) \\ R\,T \ln f_C &= (x_A)^2\, W'_{AC} + (x_B)^2\, W'_{BC} + x_A\, x_B\, (W'_{AC} - W'_{AB} + W'_{BC}) \end{aligned} \qquad (2.13)$$

where x_A = A/A + B + C etc. It may be checked that substitution of f values into (3.9) gives the equilibrium constant as unity.

Distribution of a Cation Between Two or More Multicomponent Minerals

Many rock-forming minerals are complex multicomponent crystalline solutions. The distribution of cations in two or more coexisting minerals in natural assemblages may still yield certain valuable informations. The method to be followed in such cases has been discussed by Kretz (1959). In silicates there are at least two types of coordination for the cations. Si^{4+}, Al^{3+}, Fe^{3+} and less commonly Ti^{4+} are in tetrahedral coordination. Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+} and Ti^{4+} are found in the octahedral coordination. Such differently

coordinated ions may be regarded as forming sub-mixtures. The distribution of Fe^{2+} or Mg^{2+} or any other octahedrally coordinated ion may be examined in two or more such sub-mixtures forming parts of different minerals. It should be noted, however, that the chemical potentials of a cation in octahedral coordination may also be a function of any chemical variation in the concentrations of the tetrahedrally coordinated ions. Such information can be usually obtained before hand by considering the chemical composition of individual minerals. For example the positive correlation between the concentration of tetrahedrally coordinated Al^{3+} in amphiboles and biotite with the Fe^{2+}/Mg ratio in the mineral is now well known (Ramberg, 1952b, Saxena, 1968a).

It may be argued that the study of the distribution of a component between only two of the coexisting minerals which are quasi-binary solutions out of an entire assemblage of five or six minerals cannot be useful. In other words, the presence or absence of a third or fourth mineral in the assemblage would affect the distribution coefficient. This is not generally true. The distribution coefficient changes only when the presence or absence of a third mineral is associated with a significant change in the concentration of one or more elements in one or both of the coexisting minerals. TiO_2 is only sparingly soluble in olivine and orthopyroxene. In such a case the chemical potential of TiO_2 may increase or decrease in the rock and rutile may be added or removed from the assemblage, K_D for the distribution of Fe^{2+} and Mg does not change. However if the change in μ_{TiO_2} changes the concentration of TiO_2 significantly in one of the two coexisting minerals, K_D may also change. Thus it is only meaningful to consider the concentrations of all the components in the two minerals and not

the presence or absence of another phase or the change in the bulk composition of the rock.

One of the important results of the study of cation partitioning is the recognition of how closely chemical equilibrium may be approached in the rocks. Irrespective of whether the minerals are ideal or not, the distribution of a component between two coexisting binary phases at a certain P and T will be represented by a smooth distribution curve provided chemical equilibrium is closely approached. If the minerals are not binary, the concentration of other components because of the diadochic or substitutional relationships may affect the orderly distribution as discussed before. In fact, the approach to chemical equilibrium can be studied with respect to each component individually. Figure 3.5 shows the distribution of Mn in coexisting minerals from charnockites (Saxena, 1968b). In other rocks as well as such orderly distribution of Mn is common. The distribution of Fe^{2+} and Mg^{2+} between coexisting olivine and orthopyroxene at 800°C and 900°C was experimentally studied by Medaris (1969). Although Medaris made repeated grinding and heating of the reaction products, Figure 3.6 shows that the distribution points both at 800 and 900°C show some scatter. The difficulties are related to the kinetics of the ion-exchange reaction as equilibrium is approached particularly when the distribution approaches 1:1 ratio in the two minerals. In contrast to these experimental results, the partitioning of Mg^{2+} and Fe^{2+} between orthopyroxene and Ca-pyroxene in metamorphic rocks as studied by Kretz (1963) is remarkably orderly. Most distribution points fall on a smooth curve (Figure 3.7) and the distribution curve representing igneous rocks is clearly separated from the distribution curve for the metamorphic rocks.

Studies of partitioning of cations between coexisting minerals in natural rocks by several petrologists such as Albee (1965), Annersten (1968), Binns (1962), Butler (1969), Mueller (1960), Kretz (1959), Gorbatschev (1969), Hietnan (1971) among many others are attempts to rationalize the concept of metamorphic facies on a mineral-chemical basis. In experimental systems similar attempts have been made by Nafziger and Muan (1967), Larimer (1968) and Medaris (1969) among others. The results of such partitioning studies have generally confirmed the usefulness of the approach and the need for more thermodynamic data on crystalline solutions.

In essence problems of phase quilibria are distribution problems and a statistical approach to such problems may be made to avoid the consideration of the thermodynamic properties of solution in individual minerals. Such approaches have been made principally by Greenwood (1967) and Perry (1972) and should be applicable in solving the petrogenetic problem of incompatible assemblages and the recognition of chemical equilibrium in natural or experimental systems.

Table 3.1

Composition of Coexisting Phases in Ternary Regular Solution

α			β					
B	A	C	B	A	C	x_B^α	x_B^β	K_D
.010	.082	.908	.043	.868	.089	.108	.047	.406
.040	.079	.881	.174	.718	.109	.336	.195	.478
.080	.071	.849	.339	.522	.140	.530	.394	.576
.100	.066	.834	.413	.431	.156	.602	.489	.632
.130	.056	.814	.512	.309	.179	.699	.624	.715
.170	.037	.793	.625	.171	.205	.821	.785	.796
.200	.020	.780	.700	.081	.219	.909	.896	.862

$$x_B = \frac{B}{B + A}, \quad K_D = \frac{x_B^\beta \, x_A^\alpha}{x_B^\alpha \, x_A^\beta}$$

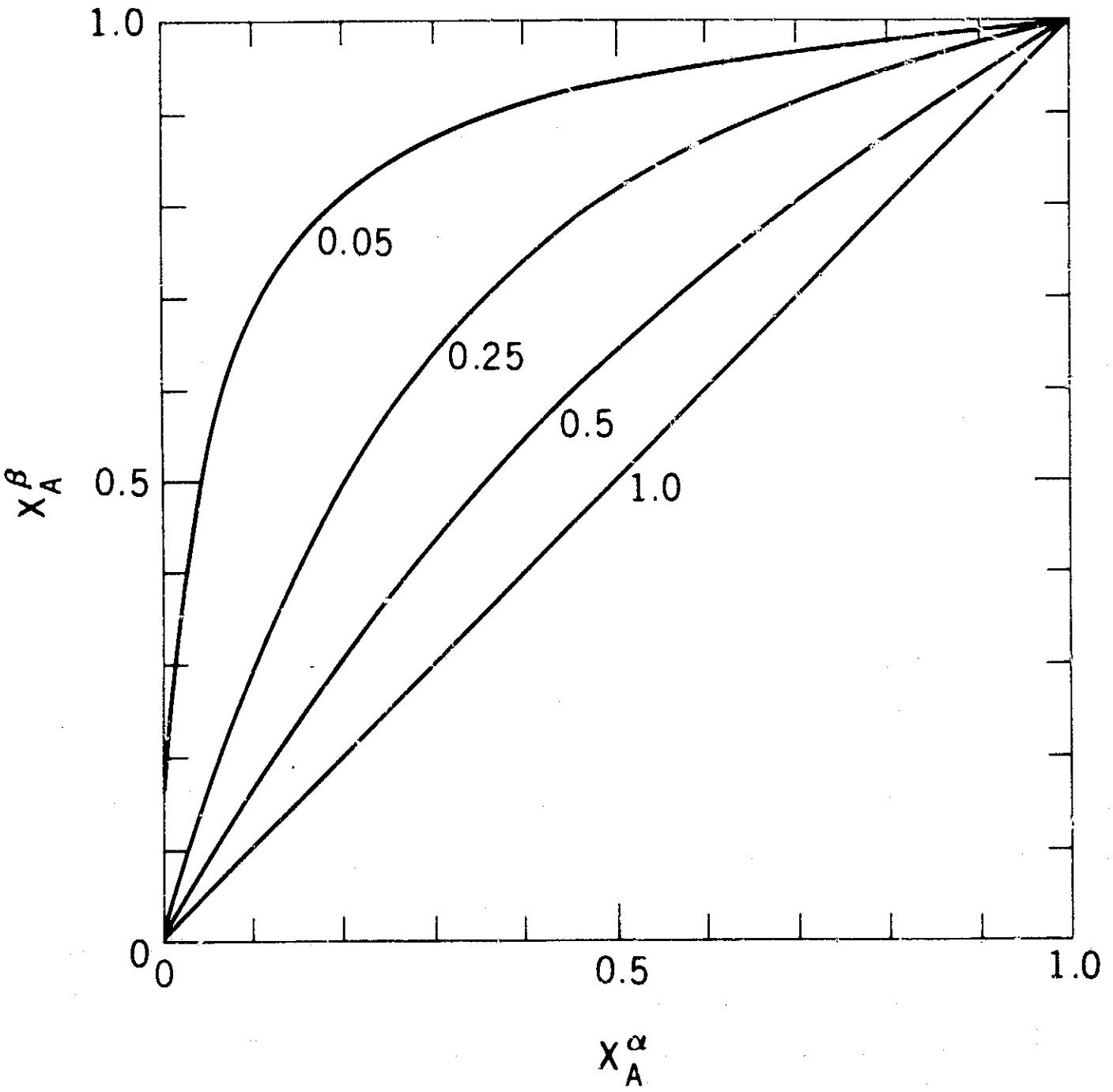

Figure 3-1. Distribution of a component A between two ideal crystalline solutions α and β. The numerical values are equilibrium constants.

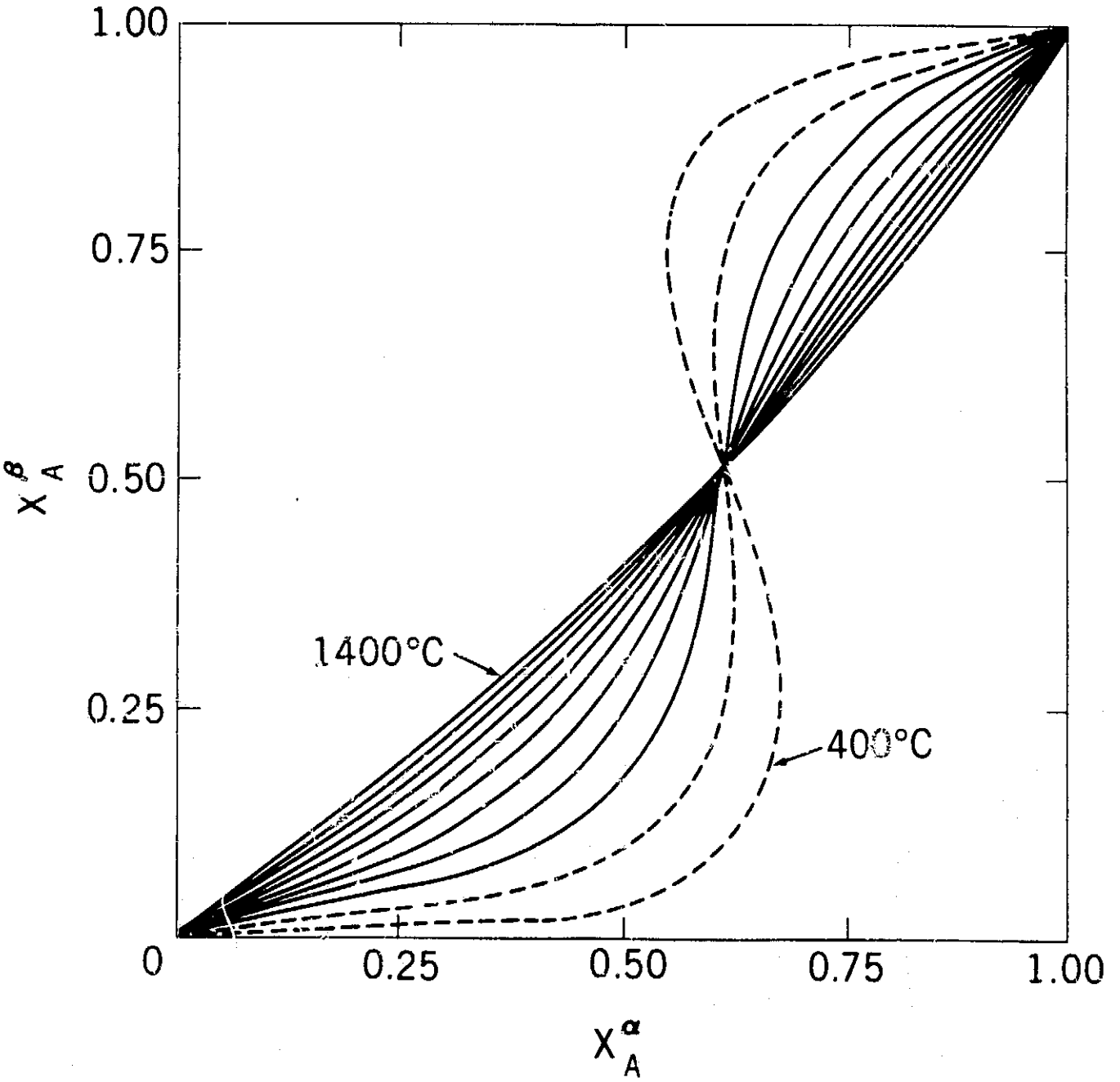

Figure 3-2. Distribution of a component A between an ideal solution α and a regular solution β. The data are

T °K	$\frac{W^\beta}{RT}$	K
673	2.75	1.60
1173	0.77	1.52

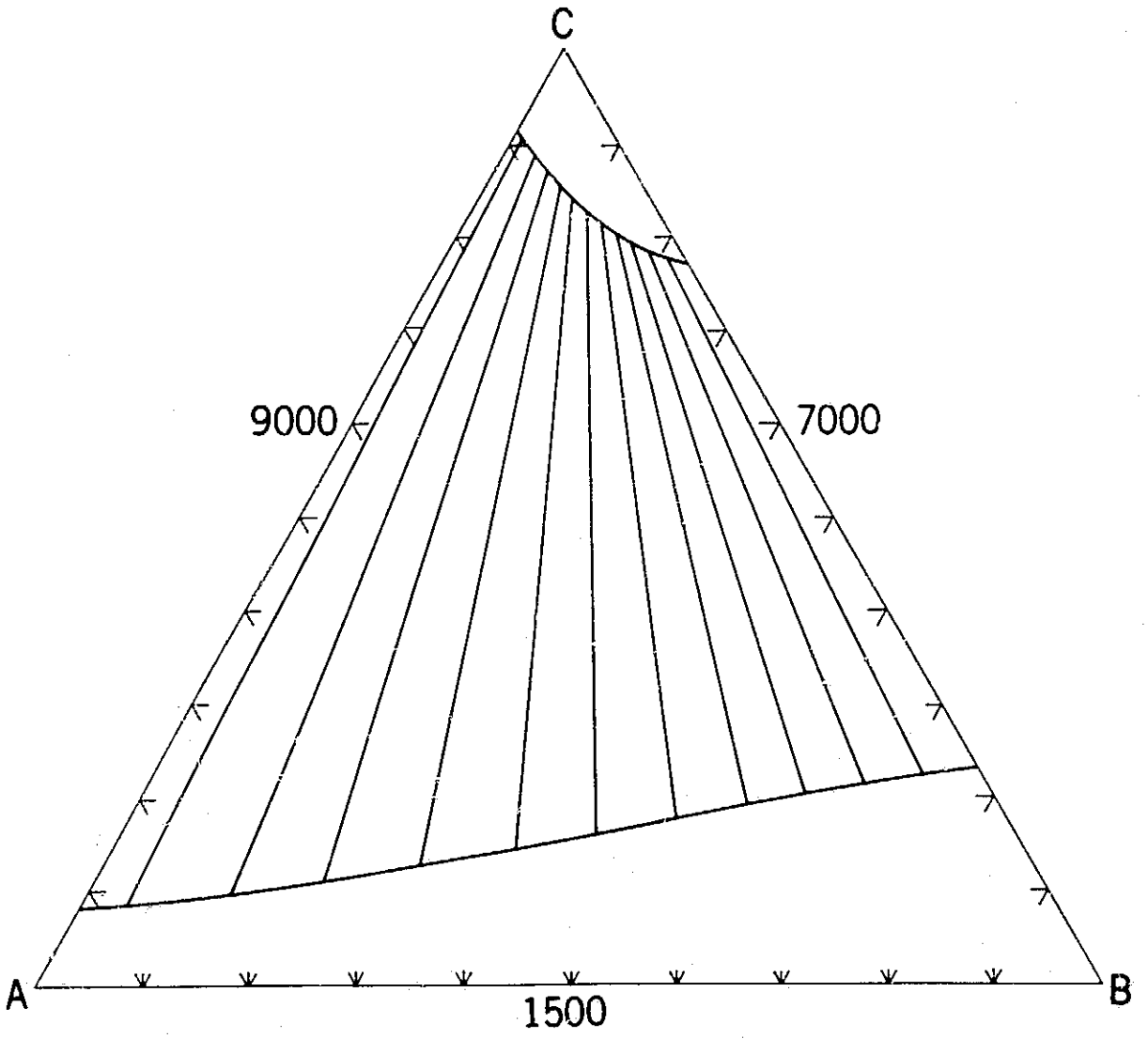

Figure 3-3. Coexisting regular ternary solutions. The components are A, B, and C. W'_{AB}, W'_{BC} and W'_{AC} are 1500, 7000 and 9000 cal/mole respectively. The temperature is assumed to be 1573°K.

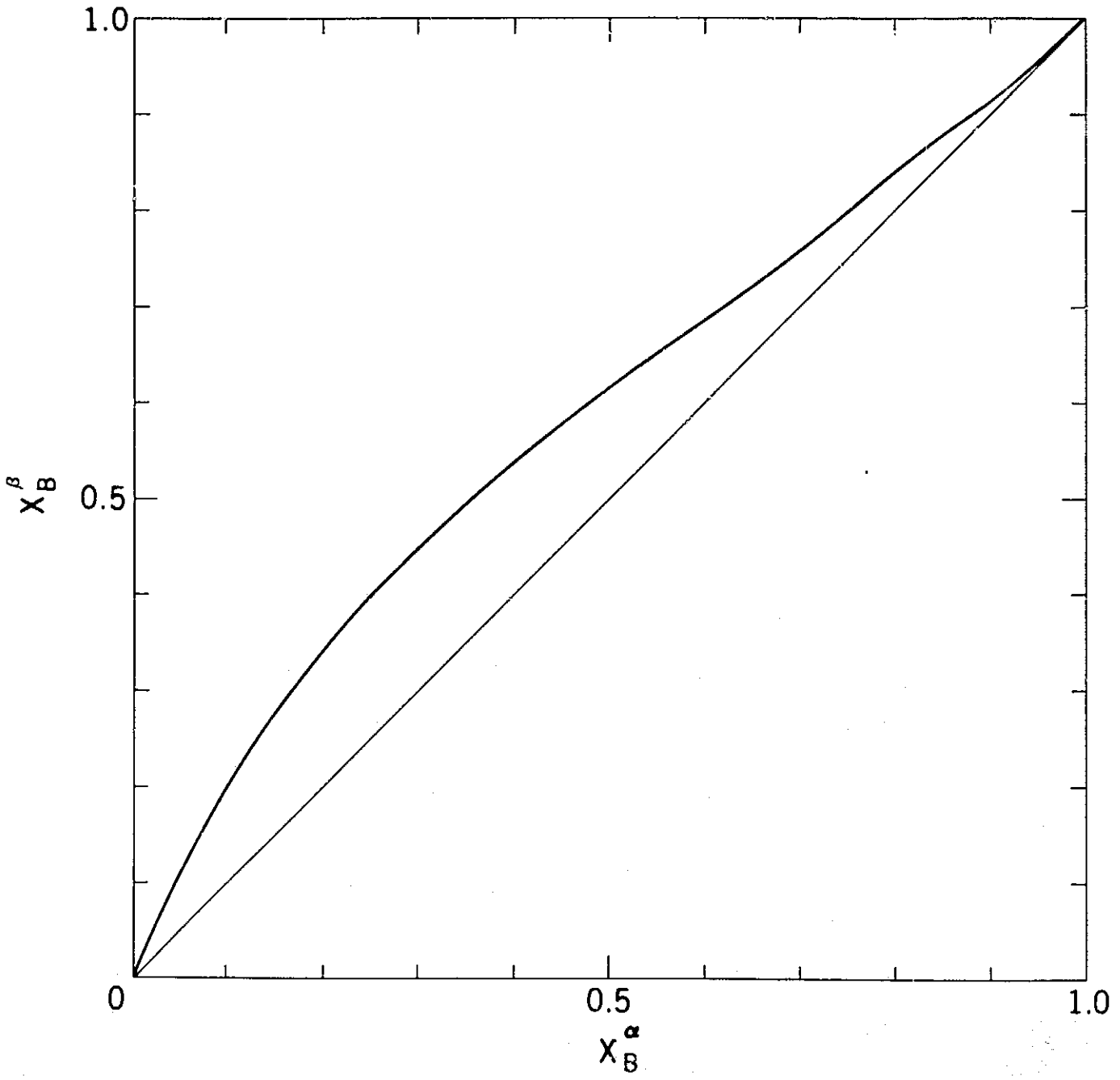

Figure 3-4. Distribution of a component B between two ternary regular solutions plotted on a Roozeboom diagram. x is B/(A + B).

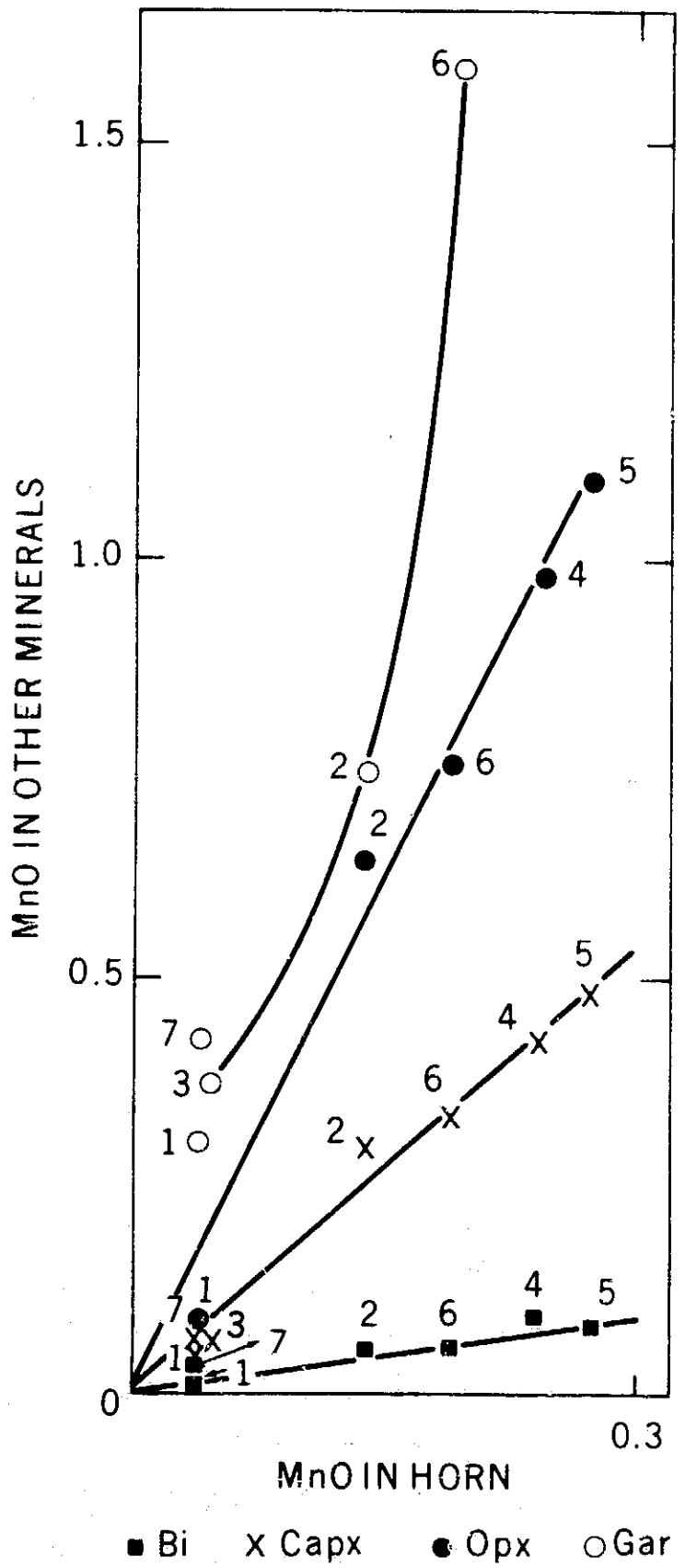

Figure 3-5. Distribution of Mn in coexisting minerals in charnockites of Varberg, Sweden (Saxena, 1968b).

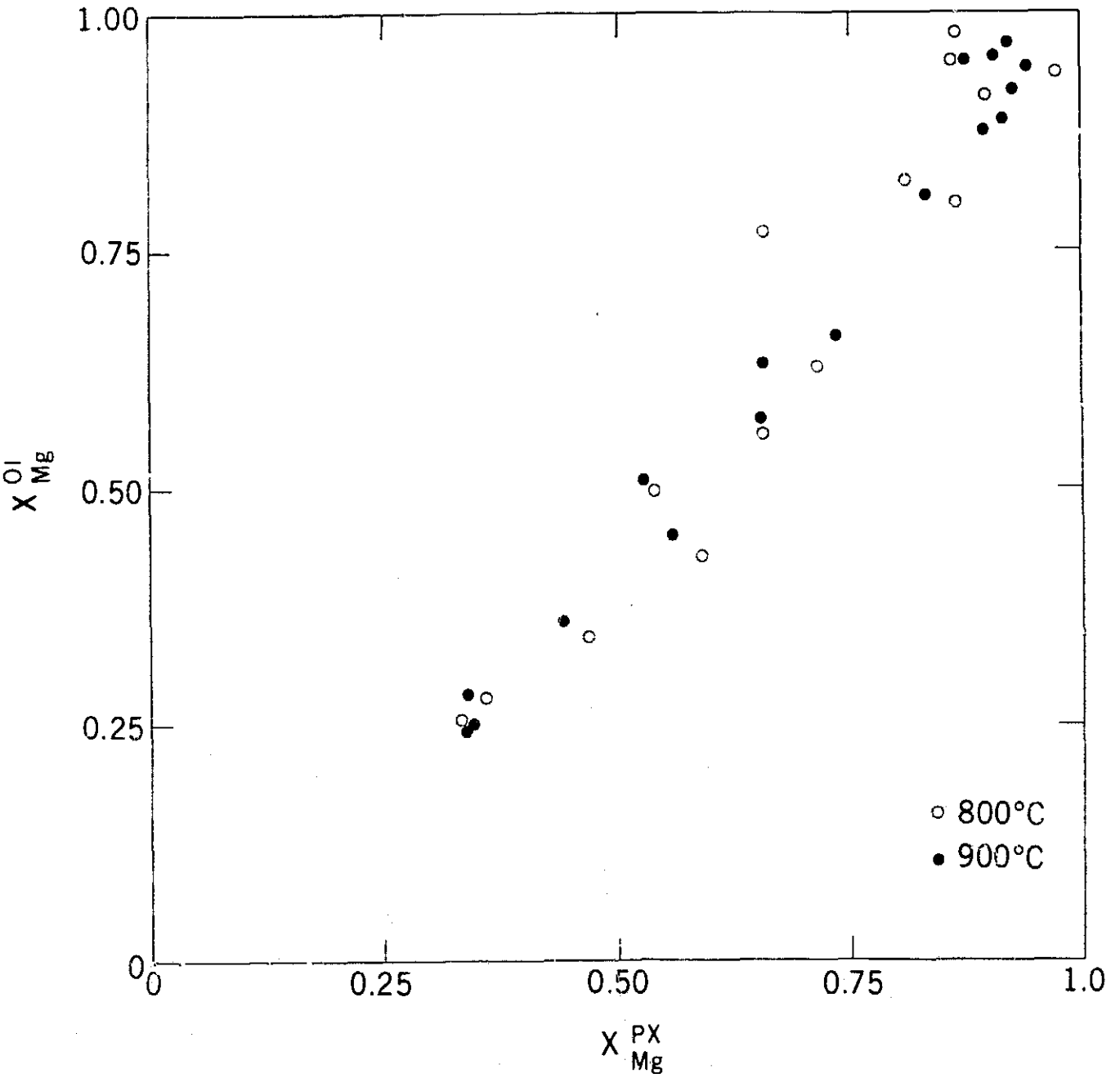

Figure 3-6. Distribution of Fe^{2+} and Mg^{2+} between synthetic olivine and pyroxene. Distribution data from Meolaris (1969).

Section 4

MEASUREMENT OF COMPONENT ACTIVITIES BY ANALYSIS OF PHASE DIAGRAMS

An experimental measurement of activities of components in a crystalline solution particularly the silicates is beset with large difficulties and the measured values are subject to large errors. Therefore, it is an attractive proposition to obtain such activity-composition relations from phase diagrams.

However, here again there is no direct method of doing this without involving some kind of a solution model. The use of a solution model brings in certain uncertainties in the activity values which depend in extent and form on the choice of the model. The attempts to obtain the thermodynamic functions of mixing through the use of various solution models is still useful. For some crystalline solutions it may be possible to experimentally determine such properties. A comparison between the experimental values and the values based on a particular model would provide a greater understanding of the interrelationship of the crystal structural parameters on which the model is based and the thermodynamics of the crystal phase. In other cases where experimental determinations cannot be made, the empirically derived functions of mixing may be tested for their physical significance by their success in application to problems of petrogenesis.

Symmetrical Mixtures

Simple mixture

The thermodynamics of a simple mixture or regular symmetric solution has been discussed before. Let us consider that the solution (A, B) M unmixes

into two coexisting solutions α rich in AM and β rich in BM. At equilibrium we have

$$\mu_A^\alpha = \mu_A^\beta \quad \text{and} \quad \mu_B^\alpha = \mu_B^\beta \tag{4.1}$$

so that according to 'simple mixture' model

$$\begin{aligned} \mu_A^{\alpha 0} + R\,T \ln x_A^\alpha + W\,(1 - x_A^\alpha)^2 \\ = \mu_A^{\beta 0} + R\,T \ln x_A^\beta + W\,(1 - x_A^\beta)^2 \end{aligned} \tag{4.2}$$

where α_0 and β_0 stand for the same pure endmember structure AM. Eliminating $\mu_A^{\alpha 0}$ and $\mu_A^{\beta 0}$ and substituting $x_A^\beta = 1 - x_A^\alpha$ we have

$$R\,T \ln x_A^\alpha + W\,(1 - x_A^\alpha)^2 = R\,T \ln (1 - x_A^\alpha) + W\,(x_A^\alpha)^2 \tag{4.3}$$

or

$$\frac{W}{R\,T} = \frac{\ln \{(1 - x_A^\alpha)/x_A^\alpha\}}{1 - 2\,x_A^\alpha} \tag{4.4}$$

This expression is similar to the one obtained by Thompson (1967). The equation for the curve of coexistence of two phases may also be written in terms of critical temperature T_c of unmixing and the mole fractions by substituting

$$W = 2\,R\,T_C$$

in (4.4)

$$T = 2\,T_C \frac{1 - 2\,x_A^\alpha}{\ln \{(1 - x_A^\alpha)/x_A^\alpha\}} \tag{4.5}$$

If we have data on the composition of coexisting phases at different temperatures and the form of the solvus is symmetric, the value of W and the activity-composition relations can be calculated.

Symmetrical mixture of higher order

Symmetrical crystalline solutions may not be simple mixtures and require a two or more constant expression for representing G_{EM} as follows:

$$G_{EM} = x_A^\alpha (1 - x_A^\alpha) \{A_0 + A_2 (1 - 2 x_A^\alpha)^2\} \tag{4.6}$$

For such a solution the relation (4.3) is

$$\begin{aligned} R T \ln x_A^\alpha + \{A_0 + A_2 (1 - 2 x_A^\alpha)^2\} (1 - x_A^\alpha)^2 \\ = R T \ln x_A^\beta + \{A_0 + A_2 (1 - 2 x_A^\beta)^2\} (1 - x_A^\beta)^2 \end{aligned} \tag{4.7}$$

Using the relation $\mu_B^\alpha = \mu_B^\beta$, we can write a similar relation as (4.7) and then solve the two equations simultaneously to obtain A_0 and A_2 and the activity-composition relation

Asymmetrical Solutions

Sub-regular model

As mentioned before the excess free energy of mixing may be expressed as a polynomial in the mole fraction x_A or x_B for the compound (A, B) M according to Guggenheim's equation:

$$G_{EM} = x_A x_B \{A_0 + A_1 (x_A - x_B) + A_2 (x_A - x_B)^2 + \ldots\} \tag{1.47}$$

If we put $A_2 = 0$ in (1.47) we have a two constant equation for an asymmetrical solution. Proceeding as in the previous sections we have

$$R T \ln x_A^\alpha + R T \ln f_A^\alpha = R T \ln x_A^\beta + R T \ln f_A^\beta \tag{4.8}$$

$$R T \ln x_B^\alpha + R T \ln f_B^\alpha = R T \ln x_B^\beta + R T \ln f_B^\beta \tag{4.9}$$

Substituting values of $R T \ln f$ from (1.48) and (1.49) we have

$$R T \ln x_A^\alpha + (x_B^\alpha)^2 \{A_0 + A_1 (3 x_A^\alpha - x_B^\alpha) = R T \ln x_A^\beta + (x_B^\beta)^2 \{A_0 + A_1 (3 x_A^\beta - x_B^\beta)\} \tag{4.10}$$

$$R\,T\,\ln x_B^{\alpha} + (x_A^{\alpha})^2\,\{A_0 + A_1\,(3\,x_B^{\alpha} - x_A^{\alpha})\} = R\,T\,\ln x_B^{\beta} + (x_A^{\beta})^2 \qquad (4.11)$$
$$\{A_0 + A_1\,(3\,x_B^{\beta} - x_A^{\beta})\}$$

The two independent relations (4.10) and (4.11) now can be solved simultaneously to yield the values of the two constants A_0 and A_1.

The method of calculation presented above is equivalent to that used by Thompson (1967) and Thompson and Waldbaum (1969). Thompson's (1967) equation for the excess free energy of mixing is

$$G_{EM} = x_A\,G_2 + x_B\,G_1 \qquad (4.12)$$

where

$$G_2 = x_A\,x_B\,W_{G2}$$

and

$$G_1 = x_A\,x_B\,W_{G1}$$

This is as if the crystalline solution is composed of x_A moles of a simple mixture with W_{G2} and x_B moles of another simple mixture with W_{G1}. We have then

$$\begin{aligned} G_{EM} &= (W_{G1}\,x_B + W_{G2}\,x_A)\,x_A\,x_B \\ &= \{W_{G1}\,(1 - x_A) + W_{G2}\,(1 - x_B)\}\,x_A\,x_B \\ &= W_{G1}\frac{(2 - 2\,x_A)}{2} + W_{G2}\frac{(2 - 2\,x_B)}{2}\,x_A\,x_B \end{aligned} \qquad (4.13)$$

substituting $1 = x_A + x_B$ in (4.13), we have

$$\begin{aligned} G_{EM} &= \left\{\frac{W_{G1}}{2}\,(1 - x_A + x_B) + \frac{W_{G2}}{2}\,(1 + x_A - x_B)\right\}\,x_A\,x_B \\ &= \left\{\frac{W_{G2} + W_{G1}}{2} + \frac{W_{G2} - W_{G1}}{2}\,(x_A - x_B)\right\}\,x_A\,x_B \end{aligned} \qquad (4.14)$$

which is of the same form as Guggenheim's equation with two constants A_0 and A_1.

Therefore

$$A_0 = \frac{W_{G2} + W_{G1}}{2} \quad \text{and} \quad A_1 = \frac{W_{G2} - W_{G1}}{2} \tag{4.15}$$

$A_0/R\,T$ and $A_1/R\,T$ would correspond to the notations B_G and C_G respectively used by Thompson (1967) following Scatchard and Hamer (1935).

For the activity coefficient, we have

$$R\,T\,\ln f_A = (x_B)^2\,[A_0 + A_1\,(3\,x_A - x_B) + \ldots] \tag{1.48}$$

Substitution of relations (4.15) in (1.48) gives

$$\begin{aligned} R\,T\,\ln f_A &= (x_B)^2 \left[\frac{W_{G2} + W_{G1}}{2} + \frac{W_{G2} - W_{G1}}{2}\,(x_A - x_B + 2\,x_A)\right] \\ &= x_B^2\left[\left\{\frac{W_{G2} + W_{G1}}{2} + \frac{W_{G2} - W_{G1}}{2}\,(x_A - x_B)\right\} + (W_{G2} - W_{G1})\,x_A\right] \\ &= x_B^2\,\{(W_{G1}\,x_B + W_{G2}\,x_A) + (W_{G2}\,x_A - W_{G1}\,x_A)\} \\ &= x_B^2\,[W_{G1}\,(x_B - x_A) + 2\,W_{G2}\,x_A] \\ &= x_B^2\,[W_{G1}\,(1 - 2\,x_A) + 2\,W_{G2}\,x_A] \\ &= x_B^2\,[W_{G1} + 2\,x_A\,(W_{G2} - W_{G1})] \end{aligned} \tag{4.16}$$

which is the same as used by Thompson (1967).

Substituting the calculated values of A_0 and A_1 in (1.47), the excess free energy of mixing can be estimated. We can then determine the solvus bounding

the two phase region by the graphical tangent method or by a suitable iteration numerical method. The calculated values of $x_A^{\alpha}, x_B^{\alpha}, x_A^{\beta}$ and x_B^{β} are then compared to the observed mole fractions to test the applicability of the model. Other excess functions of mixing may be calculated by using the relations (1.50) and (1.51).

Quasi-chemical approximation

This model has been discussed before. Green (1970) used the model to study the halite-sylvite solvus. Let us consider two coexisting phases M and N with components A and B. We have at equilibrium at a certain P and T .

$$\mu_A^M = \mu_A^N \quad \text{and} \quad \mu_B^M = \mu_B^N$$

or

$$\mu^{AM} + R\,T\,\ln x_A^M + R\,T\,\ln f_A^M = \mu^{AN} + R\,T\,\ln x_A^N + R\,T\,\ln f_A^N$$

and

$$\mu^{BM} + R\,T\,\ln x_B^M + R\,T\,\ln f_B^M = \mu^{BN} + R\,T\,\ln x_B^N + R\,T\,\ln f_B^N \qquad (4.17)$$

Since both M and N obey the same equation of state the chemical potentials of pure A in M and A in N and B in M and B in N are cancelled.

Substituting values of f_A and f_B from (1.33) and (1.34) in (4.17) we have

$$\ln x_A^M + \frac{z\,q_1}{2} \ln \left[1 + \frac{\phi_B^M (\beta - 1)}{\phi_A^M (\beta + 1)}\right] = \ln x_A^N + \frac{z\,q_1}{2} \ln \left[1 + \frac{\phi_B^N (\beta' - 1)}{\phi_A^N (\beta' + 1)}\right] \qquad (4.18)$$

$$\ln x_B^M + \frac{z\,q_1}{2} \ln \left[1 + \frac{\phi_A^M (\beta - 1)}{\phi_B^M (\beta' - 1)}\right] = \ln x_B^N + \frac{z\,q_1}{2} \ln \left[1 + \frac{\phi_A^N (\beta' - 1)}{\phi_B^N (\beta' + 1)}\right] \qquad (4.19)$$

where β and β' correspond to phases M and N respectively and along ϕ's are defined by equations (1.28 using ϕ_A instead of x_A etc.) and (1.35) presented before. q_1 and q_2 are contact factors discussed before. They are not independent and should approach unity simultaneously. Green (1970) assumed $\sqrt{q_1 q_2} = 1$. The two independent relations (4.18) and (4.19) contain two unknowns q_1/q_2 and W and can be solved by an iteration process. The ratio q_1/q_2 is a function of the geometry of the substituting chemical species and therefore may be regarded as almost independent of temperature. Substitution of q_1/q_2 back in equations (4.18) and (4.19) gives two independent values of W at each temperature. Any difference noted in the two values of W would be due to the inadequacy of the solution model to fit to the experimental data.

The solvus bounding the two phase region may as before be determined graphically by the double tangent method on a plot of free energy of mixing against mole fraction or by a numerical iteration method. The excess functions of mixing can be calculated using (1.36) and (1.37).

Calculation of Functions of Mixing Example: The System $CaWO_4$ - $SrWO_4$

Chang (1967), presented the data on the two phase regions with solvus in the binary tungstate R^{II} WO_4 type crystalline solutions. Table 4.1 shows the data on the composition of the coexisting phases α and β rich in $CaWO_4$ and $SrWO_4$ respectively. Calculated values of A_0/RT and A_1/RT according to the subregular model are listed in Table 4.2. The relationship between A_0/A_1 and T is linear and given by

$$A_0 = 22212.0 - 16.7278\ T \qquad (4.20)$$

$$A_1 = 3476.67 - 4.4379\ T \tag{4.21}$$

We may then calculate excess free energy of mixing from the relation

$$G_{EM} = x_{SrWO_4}\ x_{CaWO_4}\ \{A_0 + A_1\ (x_{SrWO_4} - x_{CaWO_4})\}$$

and the activity coefficients from the relations

$$R\ T\ \ln f_{SrWO_4} = x^2_{CaWO_4}\ [A_0 + A_1\ (3\ x_{SrWO_4} - x_{CaWO_4})]$$

$$R\ T\ \ln f_{CaWO_4} = x^2_{SrWO_4}\ [A_0 - A_1\ (3\ x_{CaWO_4} - x_{SrWO_4})]$$

Figure 4.1 shows the activity-composition relation at 800 and 1000°C. We may also plot free energy of mixing against composition and find the 'tangent method' the composition of the coexisting phases. In the present case the differences between compositions calculated by the model and the observed compositions in Table 4.1 are found to be small.

As mentioned before the activity-composition data and other thermodynamic functions as calculated from phase diagrams are sensitive to the nature of the assumptions and the model used. For the system $CaWO_4$ - $SrWO_4$, it is found by actual calculations that the use of quasi-chemical approximation predicts solvus with similar accuracy as does the sub-regular model. The use of quasi-chemical approximation requires the values of q_1, q_2 and the coordination z. z is the number of the nearest Ca or Sr ions surrounding each other. In $CaWO_4$ there are four Ca^{2+} surrounding each Ca^{2+} at distance of approximately 3.9Å. There are four more Ca^{2+} at a distance of 5 Å. We may assume 2 as 4 and solve the two equations of the quasi-chemical approximation (4.18 and 4.19) simultaneously to find q_1/q_2.

In the present case, however, we may assume either that $q_1 + q_2 = 2$ or $\sqrt{q_1 q_2} = 1$. The differences in the calculations of $\mathbb{W}$ using either of the two assumptions are small (see also, Green, 1970). A computer program now may be used which solves each of the two equations independently by using various values for q_1 and q_2 and compares the $\mathbb{W}$ values so obtained until it finds the best set of $\mathbb{W}$ values which match each other. Such values with Z as 4 are listed in Table 4.3. q_1 and q_2 are 1.20 and 0.80 corresponding to $SrWO^{2+}$ and $CaWO^{2+}$ respectively. The atomic radii (R) for Sr^{2+} and Ca^{2+} are 1.12 and 0.99 (Ahrens, 1952). We have then q_1/q_2 as 1.50 and R (Sr^{2+})/R (Ca^{2+}) as 1.13 which are not similar.

The following equation describes the relation between the calculated $\mathbb{W}$ (average of the two values listed in Table 4.3, second column) and T:

$$R\,T = 34.64 - 0.05506\,T + 0.000025\,T^2 \qquad (4.22)$$

Figure 4.2 shows a comparison of G_{EM} at 800°C calculated according to the sub-regular model and according to the quasi-chemical model. The excess free energy of mixing according to the latter is nearly twice of that calculated according to the former. Differences between the other calculated functions of mixing H_{EM} and S_{EM} are even more marked (Figure 4.2). Unfortunately we do not have data on experimentally determined H_{EM} and S_{EM} for the $CaWO_4$-$SrWO_4$ system and, therefore, no way to know which model predicts the thermodynamic functions better in this particular case.

For the system NaCl-KCl, Green (1970) provided the comparison in the thermodynamic quantities calculated by using the sub-regular model and the

quasi-chemical model and those determined by experiments. The thermodynamic quantities predicted by quasi-chemical model are closer to those measured experimentally.

A comparison of the predictions of the functions of mixing in several binary alloys by regular solution model and by the quasi-chemical model (Lupis and Elliott, 1967) shows that generally the predictions by the latter for the excess free energy are closer in agreement with experimental determinations than those by the former. The prediction for the excess entropy by the quasi-chemical model are not satisfactory. This may be in part due to the neglect of the non-configurational excess entropy in many of the binary alloys. For the halite-sylvite system, Green (1970) finds that the nonconfigurational contributions are unimportant and suggests that the positive excess entropy of mixing found in the NaCl-KCl system may result from the introduction of vacancies or other defects into a crystalline solution.

This approach of calculating thermodynamic functions of mixing by the analysis of phase diagrams is relatively new in the field of mineralogy and deserves more attention from the mineralogists and petrologists. The fact that there is no unique analysis of a solvus and two ore more solution models may be applicable to the same solvus data need not deter us from acquiring more phase data and interpreting the same with the help of various solution models. Experimental verification of many of these results may not be possible in the near future. However it may be possible to test such thermodynamic data by their application to petrogenetic problems and by getting in return some physically meaningful results.

Coexisting Phases with Different Crystal Structures

In minerals such as pyroxenes and amphiboles, one often finds a pair of minerals whose composition lies on a binary compositional join but whose structures differ more or less from each other. A case in point is the enstatite-diopside pair. The compositions in this series lie on the binary $MgSiO_3$-$CaSiO_3$ join. The solvus on this join is not comparable to the solvus for the NaCl-KCl system or for the $CaWO_4$-$SrWO_4$ system. The important difference is that enstatite and diopside do not obey the same equations of state as do the NaCl and KCl or $CaWO_4$ and $SrWO_4$. Phase equilibrium data on the enstatite-diopside solvus such as that of Boyd and Schairer (1964), therefore, cannot be used for evaluating the activity-composition relations by the methods of previous sections.

Let us consider two coexisting phases α and β with different structures but the same composition (A, B) M. We have

$$\mu^{\alpha}_{AM} = \mu^{\beta}_{AM} \tag{4.23}$$

and

$$\mu^{\alpha}_{BM} = \mu^{\beta}_{BM} \tag{4.24}$$

where

$$\mu^{\alpha}_{AM} = \mu^{AM\alpha} + R\,T\,\ln x^{\alpha}_{AM} + W\,(1 - x^{\alpha}_{AM})^2 \tag{4.25}$$

and similarly others.

Substituting relations such as (4.25) in (4.23) and (4.24), we have

$$\mu^{AM\alpha} + R\,T\,\ln x^{\alpha}_{AM} + W^{\alpha}\,(1 - x^{\alpha}_{AM})^2 = \mu^{AM\beta} + R\,T\,\ln x^{\beta}_{AM} + W^{\beta}\,(1 - x^{\beta}_{AM})^2 \tag{4.26}$$

$$\mu^{BM\alpha} + R\,T\,\ln x^{\alpha}_{BM} + W^{\alpha}\,(1 - x^{\alpha}_{BM})^2 = \mu^{BM\beta} + R\,T\,\ln x^{\beta}_{BM} + W^{\beta}\,(1 - x^{\beta}_{BM})^2 \tag{4.27}$$

Since α and β do not have the same structure and, therefore, do not obey the same equation of state generally $\mu^{AM\alpha} \neq \mu^{AM\beta}$ and $\mu^{BM\alpha} \neq \mu^{BM\beta}$. As such we need to know the values of these chemical potentials at the given P and T to be able to solve the two equations (4.26) and (4.27) simultaneously to find W^{α} and W^{β}. The free energy diagram in Figure 4.3 shows this situation. In a binary system at a given P and T, we may have two coexisting phases with compositions representing the minimum of free energy.

The enstatite-diopside system may be similar to the example shown in Figure 4.3. The binary join is (Mg, Mg) Si_2O_6 – (Ca, Mg) Si_2O_6. There are further complications here since (Ca, Mg) Si_2O_6 with orthopyroxene structure and (Mg, Mg Si_2O_6) with diopside structure are unknown.

Table 4.1

Chemical Composition of Unmixed Phases in the System $CaWO_4$-$SrWO_4$

T°C	X^{α}_{Sr}	X^{α}_{Ca}	X^{β}_{Sr}	X^{β}_{Ca}
550	0.005	0.995	0.995	0.005
600	0.010	0.990	0.980	0.020
650	0.025	0.975	0.955	0.045
700	0.035	0.965	0.905	0.095
750	0.067	0.933	0.800	0.200
800	0.120	0.880	0.630	0.370

α and β are coexixting phases rich in $CaWO_4$ and $SrWO_4$ respectively. The compositions are from Figure 3 in Chang (1967).

Table 4.2

The Calculated A_0/RT and A_1/RT in (Ca, Sr) WO_4

T °C	A_0/RT	A_1/RT
600	4.411	-.278
650	3.596	-.269
700	3.113	-.455
750	2.537	-.514
800	2.015	-.611
900*	1.106	-.743
1000*	.352	-.860

* From equations (4.20) and (4.21)

Note: An error of ±5 percent in the mole fractions (Table 4.1) results in ±200 cal/mole error in determining A_0 and A_1.

Table 4.3

$\frac{2W}{z\,R\,T}$ For the System $CaWO_4$-$SrWO_4$

T°C	z = 4, q_1 = 1.20, q_2 = 0.80	
600	5.883	5.361
650	5.173	4.821
700	4.919	4.460
750	4.495	4.301
800	4.183	4.386

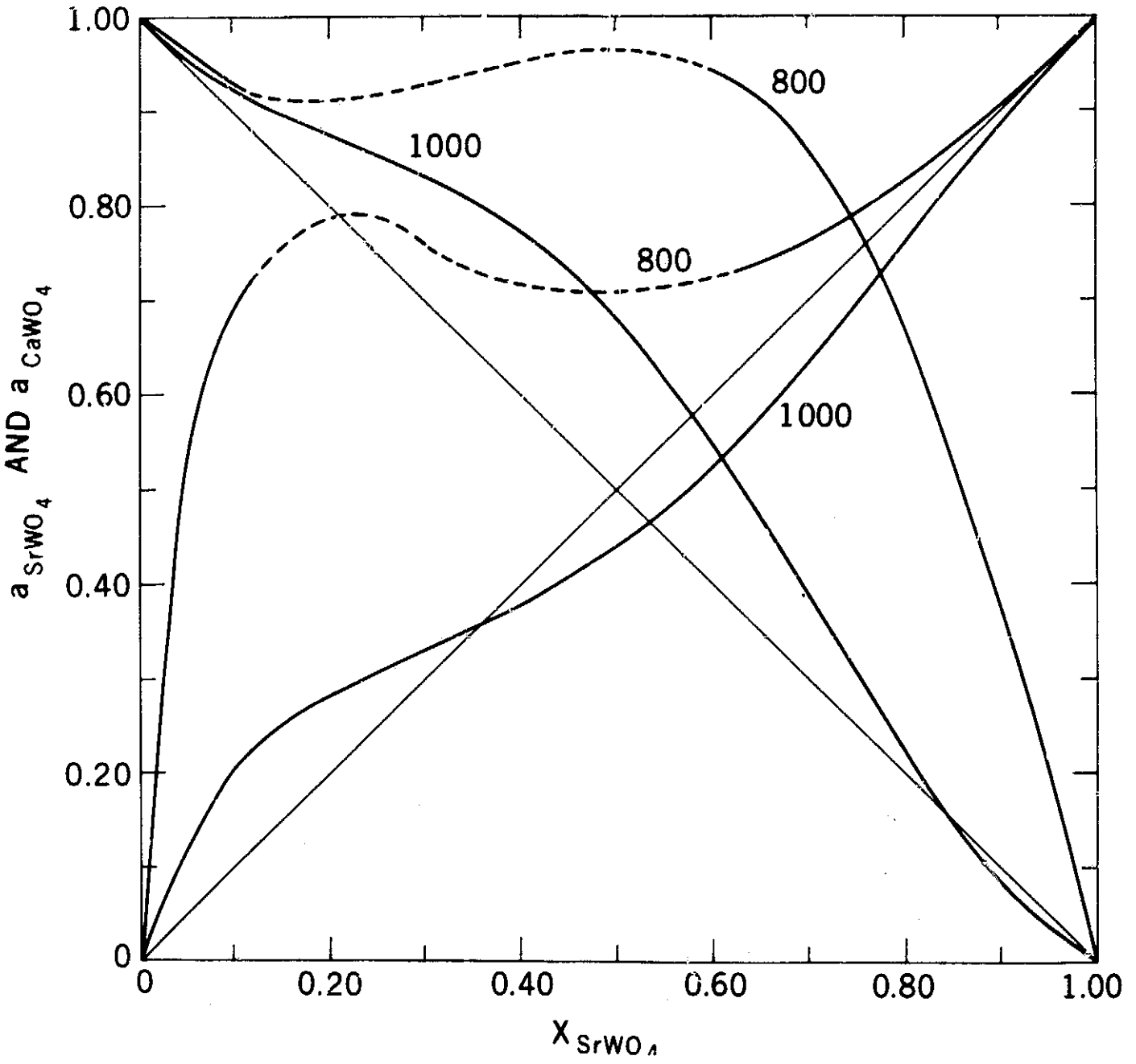

Figure 4-1. Activity-composition relation in $CaWO_4$-$SrWO_4$ crystalline solution at 800 and 1000 °C.

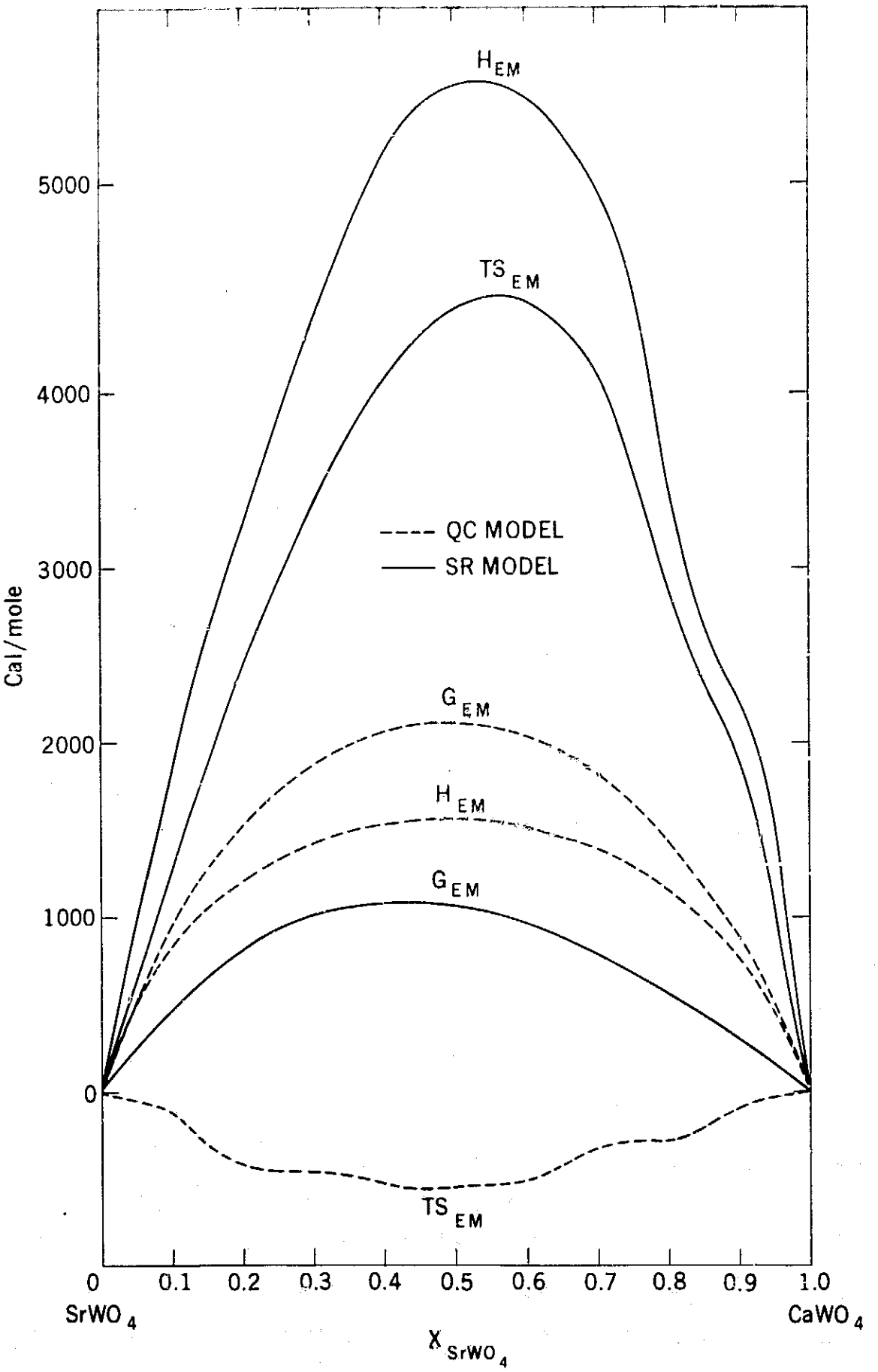

Figure 4-2. Thermodynamic excess functions of mixing in (Ca, Sr) WO_4 according to two constant asymmetric model and according to quasi-chemical approximation.

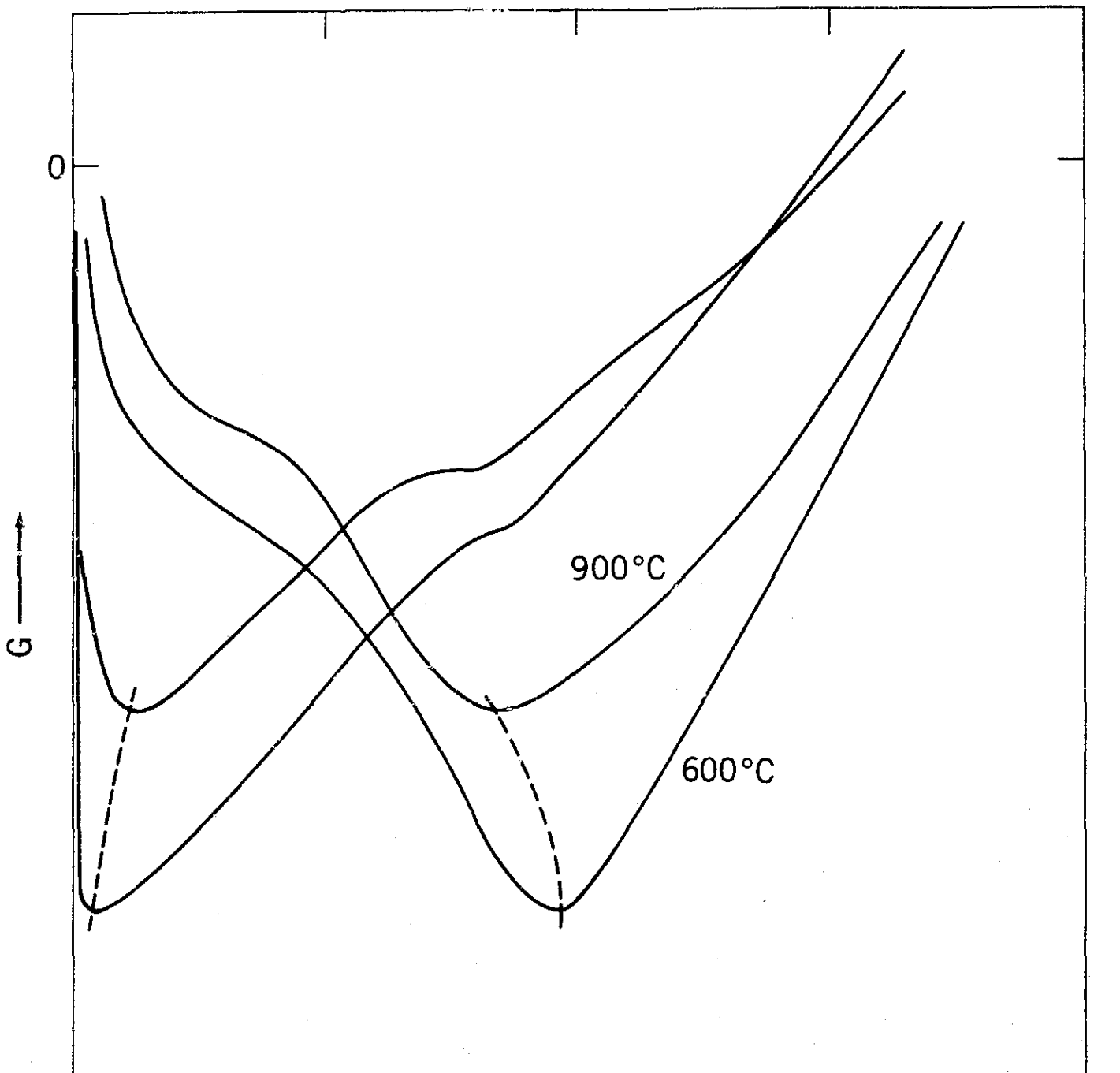

Figure 4-3. Free energy of mixing in two crystalline solutions with the same chemical components AM and BM but with different crystal structures. The enstatite-diopside system is similar in principle to this hypothetical system.

Section 5

MEASUREMENT OF COMPONENT ACTIVITY USING COMPOSITION OF COEXISTING MINERALS

Experimental data on the distribution of a component between two coexisting crystalline solutions at a fixed P and T for systems such as olivine and pyroxene have been collected by Nafziger and Muan (1967), Larimer (1968) and Medaris (1969). Distribution data are also available for natural assemblages but the P and T of their formation are indefinite. The distribution data from natural assemblages in many cases may be found to represent ion-exchange equilibrium closely. If we are not concerned with precise P and T, we may use such data to obtain useful information on the thermodynamic nature of mixing in the minerals. For this purpose, the thermodynamic equations according to various solution models for binary solutions presented in this section may be used.

The composition of coexisting phases which do not obey the same equation of states may be used to find the activity-composition relations in each phase in suitable cases. Consider α and β with chemical formulae (A, B) M and (A, B) N respectively which are in ion-exchange equilibrium at a certain P and T. We have

$$\mathrm{A}\,\alpha + \mathrm{B}\,\beta \rightleftharpoons \mathrm{B}\,\alpha + \mathrm{A}\,\beta \tag{5a}$$

The equilibrium constant K_{5a} is given by

$$K_{5a} = \left(\frac{x_{\mathrm{B}}^{\alpha}\, x_{\mathrm{A}}^{\beta}}{x_{\mathrm{A}}^{\alpha}\, x_{\mathrm{B}}^{\beta}}\right)\left(\frac{f_{\mathrm{B}}^{\alpha}\, f_{\mathrm{A}}^{\beta}}{f_{\mathrm{A}}^{\alpha}\, f_{\mathrm{B}}^{\beta}}\right) \tag{5.1}$$

The term in the first bracket is the distribution coefficient K_D. Depending on the nature of the data available, the following cases may be considered.

Compositional Data Available on a Complete Distribution Isotherm

We have the choice among simple mixture model, the two constant asymmetric model and the regular solution model with quasi-chemical approximation. As discussed before, according to simple mixture model, we have

$$\ln K_{5a} = \ln K_D - \frac{W^\alpha}{R\,T}(1 - 2\,x_A^\alpha) + \frac{W^\beta}{R\,T}(1 - 2\,x_A^\beta) \qquad (3.8)$$

A non-linear least squares fit using the data on x_A^α and x_A^β finally yields K_{5a}, W^α and W^β.

According to Redlich and Kister equations (King, 1969, p. 326) we have

$$R\,T \ln f_A = x_B^2 \{A_0 + A_1 (3\,x_A - x_B) + A_2 (x_A - x_B)(5\,x_A - x_B) + \ldots\}, \qquad (5.2)$$

$$R\,T \ln f_B = x_A^2 \{A_0 - A_1 (3\,x_B - x_A) + A_2 (x_B - x_A)(5\,x_B - x_A) + \ldots\} \qquad (5.3)$$

and therefore

$$R\,T \ln \frac{f_A}{f_B} = A_0 (x_B - x_A) + A_1 (6\,x_A\,x_B - 1) + A_2 (x_B - x_A)(1 - 8\,x_A\,x_B) \qquad (5.4)$$

Substituting the values of f_B^α/f_A^α and f_A^β/f_B^β by using (5.4) in (5.1), neglecting the constants A_2's and rearranging in logarithmic form we have

$$\ln K_{5a} = \ln K_D + \frac{A_0^\alpha}{R\,T}\,(x_A^\alpha - x_B^\alpha) + \frac{A_1^\alpha}{R\,T}\,(6\,x_B^\alpha\,x_A^\alpha - 1)$$

$$+ \frac{A_0^\beta}{R\,T}\,(x_B^\beta - x_A^\beta) + \frac{A_1^\beta}{R\,T}\,(6\,x_A^\beta\,x_B^\beta - 1) \qquad (5.5)$$

The equation (5.5) is of the form

$$N = M + A_1 x_1 + A_2 x_2 + A_3 x_3 + \cdots$$

where N and x's are known quantities. It may be solved by a numeric least squares method yielding M(= ln K_{5a}) and other constants. We must have a minimum of five distribution points.

According to the quasi-chemical approximation, f_A is given by

$$f_A = \left[1 + \frac{\phi_B\,(\beta - 1)}{\phi_A\,(\beta + 1)}\right]^{zq_A/2} \qquad (1.33)$$

and similarly f_B as in (1.34). Substituting these values of f's in (5.1) we have

$$K_D \cdot \frac{\left\{1 + \dfrac{\phi_A^\alpha\,(\beta^\alpha - 1)}{\phi_B^\alpha\,(\beta^\alpha + 1)}\right\}^{z^\alpha q_B^\alpha/2} \left\{1 + \dfrac{\phi_B^\beta\,(\beta^\beta - 1)}{\phi_A^\beta\,(\beta^\beta + 1)}\right\}^{z^\beta q_A^\beta/2}}{\left\{1 + \dfrac{\phi_B^\alpha\,(\beta^\alpha - 1)}{\phi_A^\alpha\,(\beta^\alpha + 1)}\right\}^{z^\alpha q_A^\alpha/2} \left\{1 + \dfrac{\phi_A^\beta\,(\beta^\beta - 1)}{\phi_B^\beta\,(\beta^\beta + 1)}\right\}^{z^\beta q_B^\beta/2}} = K_{5a} \qquad (5.6)$$

where β and β' are for phases α and β respectively and are given by (1.28) with x_A replaced by ϕ_A etc. q^α and q^β are contact factors for phases α and β respectively. A numerical least squares method may be used to solve (5.6).

Compositional Data Available on a Complete Distribution Isotherm And The Activity-composition Relation in One of The Two Coexisting Phases

Depending on the accuracy of the data, we may use equations (3.8), (5.5) (5.6). If necessary we may use all the three constants in equation (5.4). We may write (5.4) as

$$RT \ln \frac{f_A}{f_B} = x_B (2A_0 + 6A_1 + 10A_2) - x_B^2 (6A_1 + 24A_2) + x_B^3 (16A_2) - (A_0 + A_1 + A_2) \tag{5.7}$$

Transforming (5.1) in logarithmic form and substituting values for f_A^β / f_B^β from (5.7) we have

$$\ln K_D + \ln \frac{f_B^\alpha}{f_A^\alpha} = \left(\ln K_{5a} + \frac{A_0 + A_1 + A_2}{RT} \right) - x_B \left(\frac{2A_0 + 6A_1 + 10A_2}{RT} \right)$$

$$+ x_B^2 \left(\frac{6A_1 + 24A_2}{RT} \right) - x_B^3 \left(\frac{16A_2}{RT} \right) \tag{5.8}$$

Equation (5.8) is of the form

$$Y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots.$$

If we know the activity-composition relation in α, we may solve (5.8) by least squares analysis.

If sufficient number of distribution points are available one may use (5.5) with the third constant A_2 and compare the results with those obtained by using (5.8).

As an example of calculating the activity-composition relation in binary solutions using the distribution data, we consider the olivine-chloride solution system.

Activity-composition And G_{EM} in Olivine ($Mg_2SiO_2 - Fe_2SiO_4$)

Schulien, Friedrichsen and Hellner (1970) studied the distribution of Fe^{2+} and Mg^{2+} between a 'chloride' solution and olivine at 450 ° to 650°C. These data may be used for calculating the activity-composition in both olivine and in the 'chloride' solution. The nature of the 'chloride' solution in the experiments may not be clearly known. This need not concern us for the present and we assume that it is a homogeneous solution phase and present the ion-exchange equilibrium as done by Schulien et. al. as

$$\underset{\text{solution}}{FeCl_2} + \frac{1}{2}\underset{\text{olivine}}{Mg_2SiO_4} \rightleftharpoons \underset{\text{solution}}{MgCl_2} + \frac{1}{2}\underset{\text{olivine}}{Fe_2SiO_4} \qquad (5b)$$

The equilibrium constant is given by

$$K_{5b} = \frac{x_{Mg}^{sol}\, x_{Fe}^{ol}}{x_{Fe}^{sol}\, x_{Mg}^{ol}} \; \frac{f_{Mg}^{sol}\, f_{Fe}^{ol}}{f_{Fe}^{sol}\, f_{Mg}^{ol}}$$

We may now use one of the three methods represented by equations (3.8), (5.5) and (5.6). In the present case, it was found by actual computations that consistent thermodynamic parameters for the isotherms at 500, 550, and 650°C are given by only the 'simple mixture' model. Obviously the data accurate as they are from an experimental point of view, are not accurate enough for needing a two or more constant equation (5.5) or the quasi-chemical approximation (5.6).

W/RT values calculated by using the 'simple mixture' model are listed in Table 5.1. The data at 600°C was not considered because of several scattered points. It is noted that W/RT for olivine at 450°C is greater than 2.0 and is unrealistic. If we consider a linear relation between W^{ol} and 1/T (Figs. 5.1 and 5.2), we find that W^{ol}/RT at 450°C is 2.0 and similarly W^{sol}/RT and K_{5b} are 0.91 and 0.76 respectively.

Figure 5.3 shows the distribution isotherms calculated by using the data in Table 5.1 at 500, 550 and 650°C. The isotherm at 450°C is plotted using the linearly extrapolated values of K_{5b}, W^{ol} and W^{sol}. The model does not fit to these distribution data for the Mg-rich chloride solution and olivine. Figure 5.4 shows the activity-composition relation in olivine ($Fe_2SiO_2 - Mg_2SiO_2$) at 500 and 550°C. At 650°C olivine is close to ideal solution.

Table 5.1

Inter-change Energy W and the Standard Free Energy Change ΔG° in Olivine-chloride Solution System

T°C	$\frac{W^{sol}}{RT}$	$\frac{W^{sol}}{RT}$	$-RT/nK = \Delta G^0_{5b}$, cal/mole
450	1.86	2.32	1433
500	0.87	1.28	723
550	0.59	0.73	421
650	0.52	-0.014	181

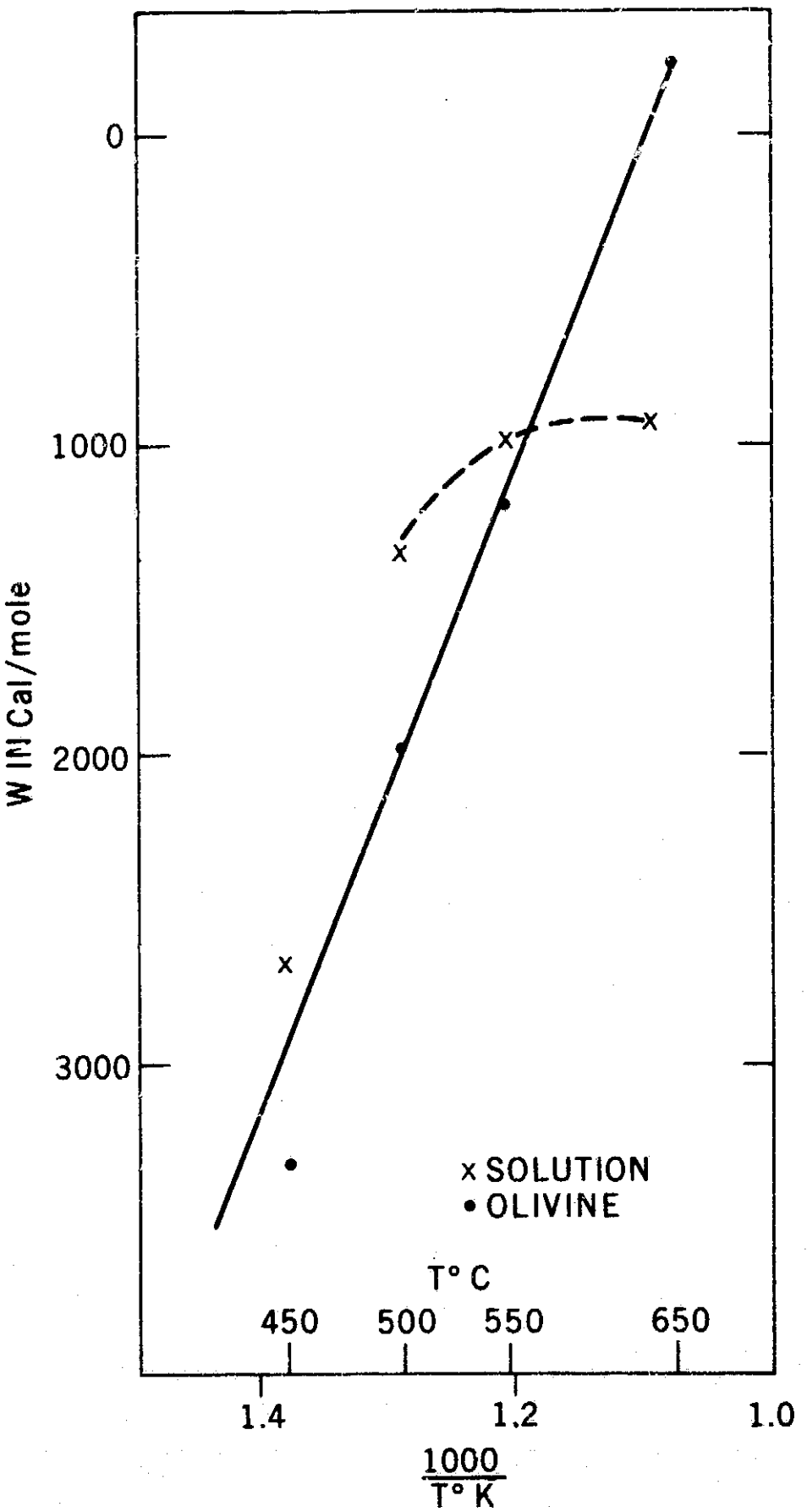

Figure 5-1. W^{ol} and W^{sol} plotted against 1/T.

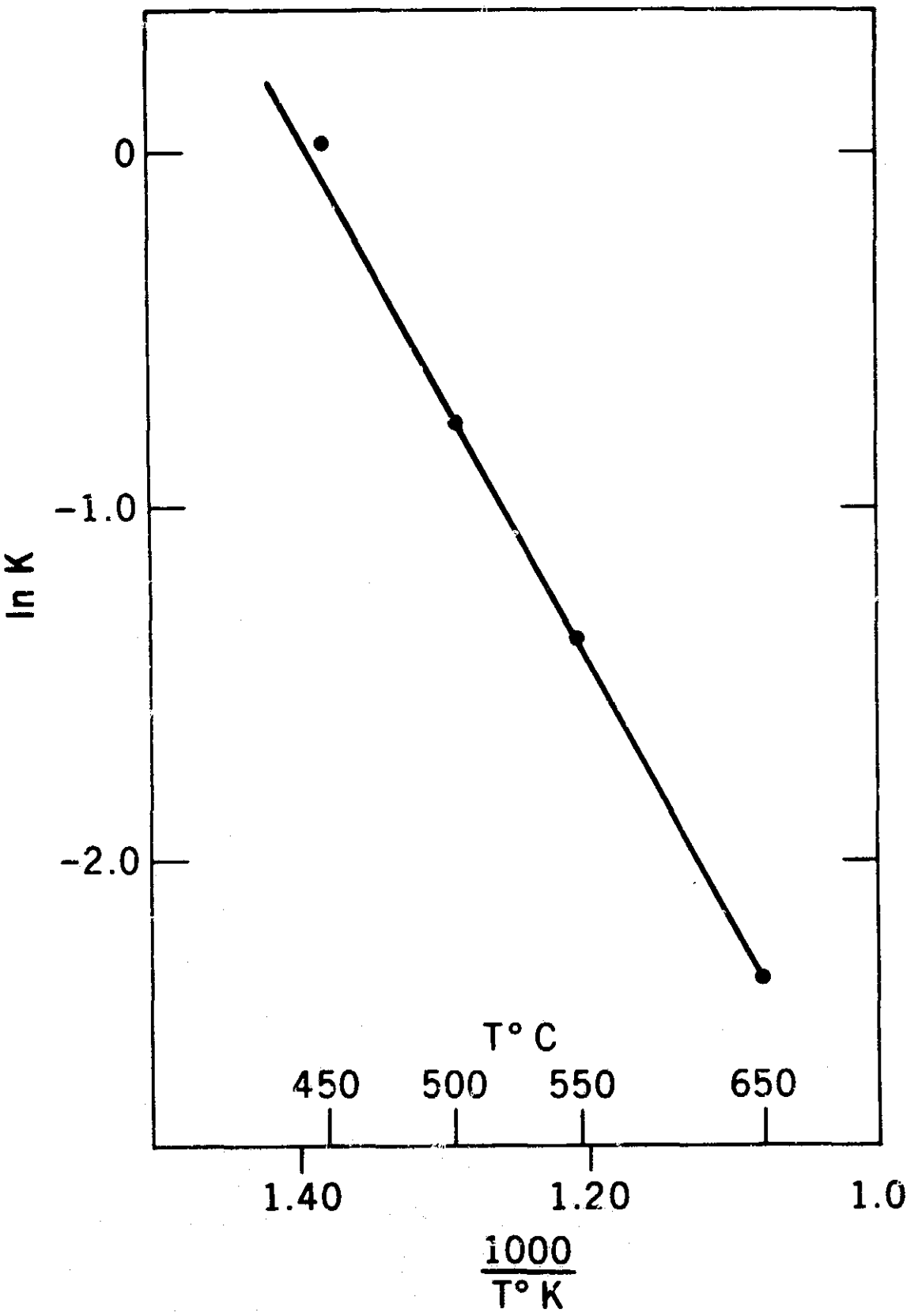

Figure 5-2. In K, for the distribution of Mg^{2+} and Fe^{2+} between chloricde solution and olivine, plotted against 1/T.

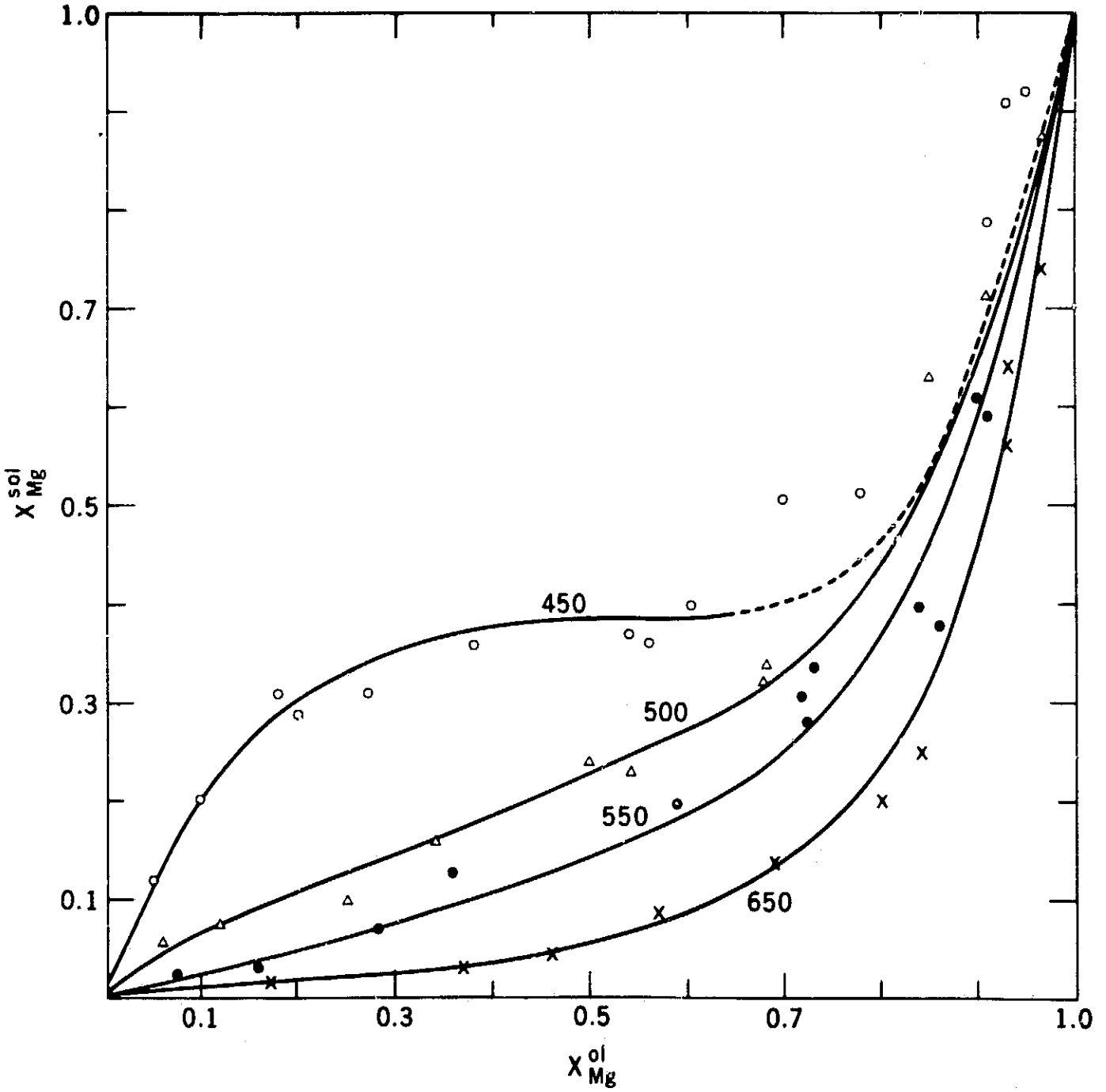

Figure 5-3. Distribution of Mg^{2+} Fe^{2+} between olivine and chloride solution. The data points are from Schulien et. al. (1970). Crosses 650 °C, solid circles 550 °C, triangles 500 °C, and open circles 450 °C. The curves are least squares curves using the 'simple-mixture' model for both the solutions.

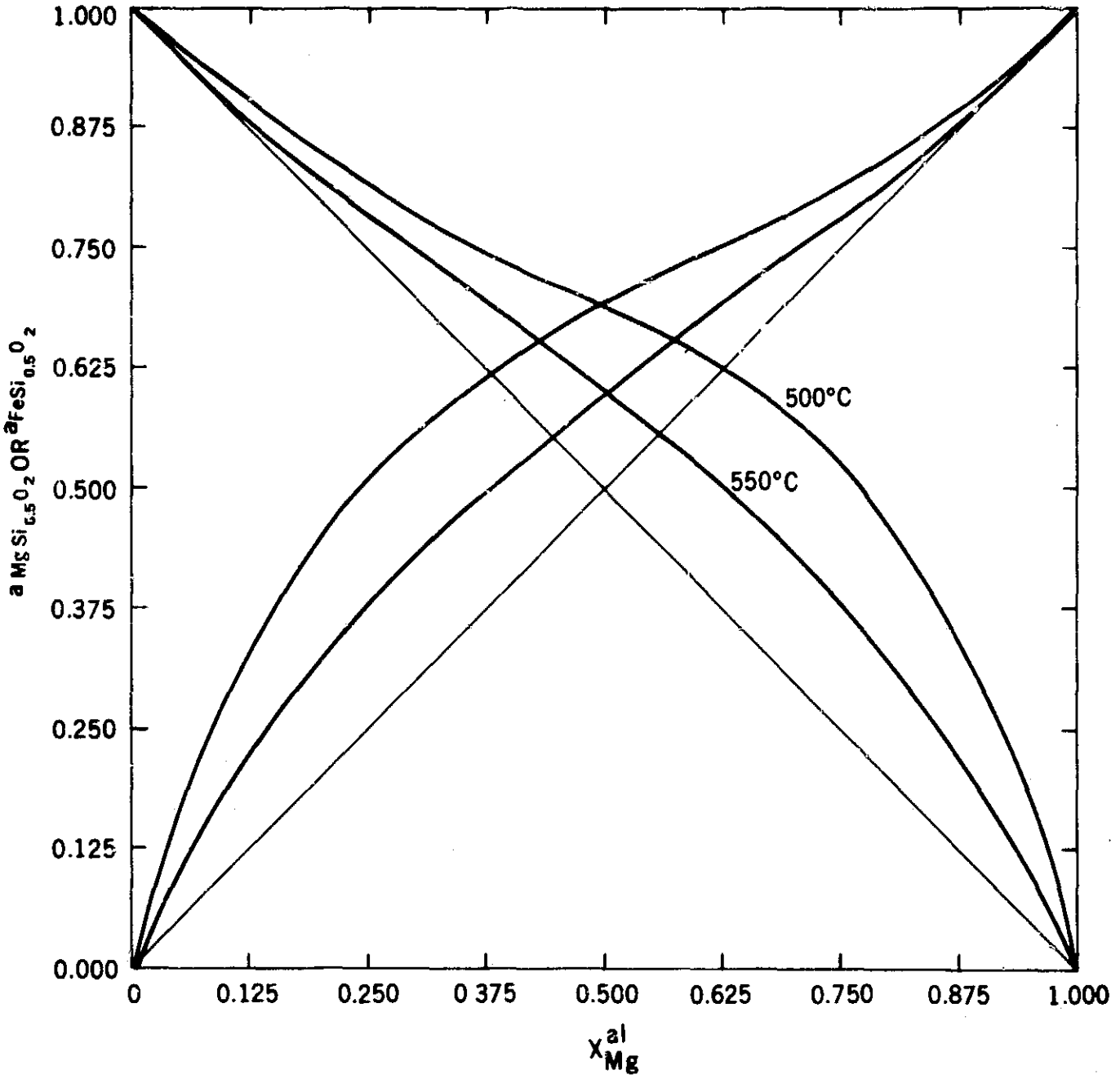

Figure 5-4. Activity-composition relation in olivine (Mg, Fe) $Si_{0.5}O_2$ at 500 and 550 °C. At 650 °C, olivine is found to be nearly ideal. Results are based on data by Schulien et al. (1970).

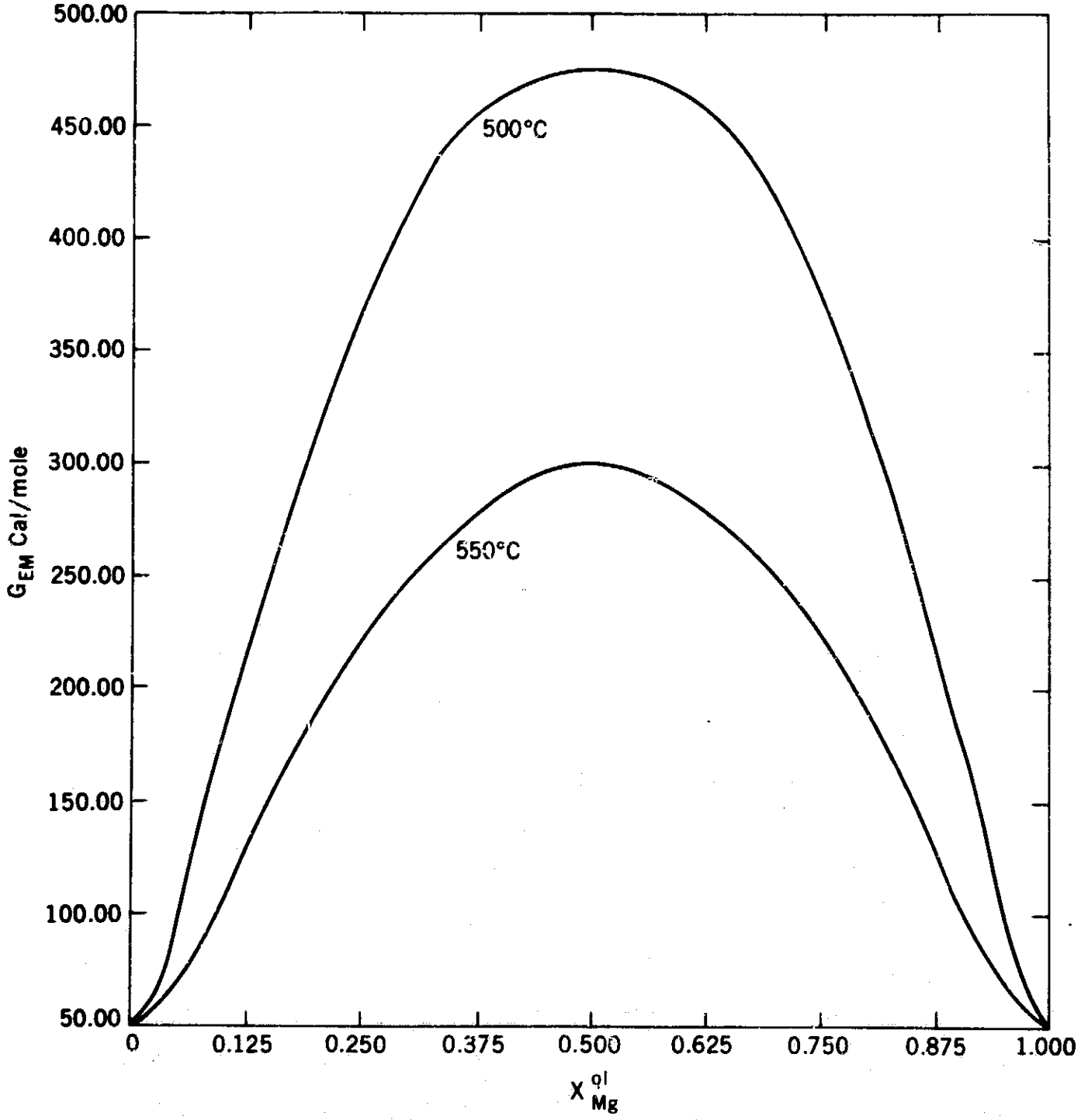

Figure 5-5. Excess free energy of mixing in olivine (Mg, Fe) $Si_{0.5}O_2$ at 500 and 550 °C.

Section 6

ORDER-DISORDER IN Fe^{2+}-Mg^{2+} SILICATES

Long-range order-disorder phenomena in ferromagnesian silicates differs from that in alloys in several important respects. First, as opposed to alloys, only a certain number of cations take part in the site exchange while the silicate framework remains more or less inert. Second usually a complete crystalline solution exists between the Mg and Fe end-members. Third since Fe^{2+} and Mg^{2+} are similar in size, charge and other characteristics, the site preference energies (corresponding to the difference in binding energy of the ion between the nonequivalent sites) are not strongly dependent on the degree of order as is usual in many binary alloys. Order-disorder or the intracrystalline cation distribution in silicates is measurable by x-ray (see Ghose, 1961) and other spectroscopic techniques. The energy of the intracrystalline ion-exchange is part of the Gibbs free energy of the crystal and is, therefore, a very useful thermodynamic quantity (see Mueller, 1969, Thompson, 1969).

Intracrystalline Ion-Exchange and Site Activities

A crystalline solution $(A_x B_{1-x})$ M may have the two cations A and B distributed between two nonequivalent sites α and β. M is the 'inert' silicate framework. Following Dienes (1955) and Mueller (1961, 1962, 1969) the disordering process may be represented by the exchange reaction

$$A\ (\alpha) + B\ (\beta) \rightleftharpoons A\ (\beta) + B\ (\alpha) \tag{6a}$$

In terms of kinetic theory the time rate of change of A in site β is given by

$$-\frac{d\, x_A^{\beta}}{dt} = K_{\beta\alpha}\, \phi_{\beta\alpha}\, x_A^{\beta}\, x_B^{\alpha} - K_{\alpha\beta}\, \phi_{\alpha\beta}\, x_B^{\beta}\, x_A^{\alpha} \tag{6.1}$$

where x refers to the mole fractions, $K_{\beta\alpha}$ and $K_{\alpha\beta}$ are rate constants and are functions only of P and T, ϕs are analogous to activity coefficient products in macroscopic chemical system and are functions of P, T and ϕ. At equilibrium we have

$$\frac{\mathrm{d}\, x_{\mathrm{A}}^{\beta}}{\mathrm{d}\, t} = 0$$

and

$$K_{6a} = \frac{K_{\beta\alpha}}{K_{\alpha\beta}} = \frac{x_{\mathrm{A}}^{\beta} f_{\mathrm{A}}^{\beta} x_{\mathrm{B}}^{\alpha} f_{\mathrm{B}}^{\alpha}}{x_{\mathrm{B}}^{\beta} f_{\mathrm{B}}^{\beta} x_{\mathrm{A}}^{\alpha} f_{\mathrm{A}}^{\alpha}} = \frac{a_{\mathrm{A}}^{\beta} a_{\mathrm{B}}^{\alpha}}{a_{\mathrm{B}}^{\beta} a_{\mathrm{A}}^{\alpha}} \qquad (6.2)$$

where f is the 'partial' activity coefficient and a the 'partial' activity. The product of the f s appear as ϕ in (6.1). The term 'partial' is used to distinguish between the activity of A on the site from the activity of A in the crystal.

The distribution coefficient is

$$K_{\mathrm{D}} = \frac{x_{\mathrm{A}}^{\beta} x_{\mathrm{B}}^{\alpha}}{x_{\mathrm{B}}^{\beta} x_{\mathrm{A}}^{\alpha}}$$

K_{D} has sometimes been referred to as the ordering parameter. The distribution coefficient, however, should not be confused with the ordering parameter S used to describe ordering in alloys. S equal to unity corresponds the highest possible order and S equal to zero to complete disorder. This is opposite in the case of K_{D}. Further K_{D} will be used to describe order-disorder in non-stoichiometric silicates forming complete crystalline solution series. In such silicates the formation of a fully ordered or disordered periodic structure is not possible. Even with the greatest tendency towards ordering some of the excess atoms of

one component must inevitably occupy sites belonging to the other which leads to a lower order or disorder. The distribution coefficient is a function of T and the varying A:B ratio in the crystal and, therefore, it is of little thermodynamic significance.

The equilibrium constant K_{6a} is a function of P and I only. However, as the volume changes involved in the ion-exchange are negligible, we ignore the dependence of K_{6a} on P and consider it only as temperature dependent.

The definition of chemical potential of a cation on a site presents certain problems (Mueller, Ghose and Saxena, 1970). One may write, as done by Grover and Orville (1969), for the chemical potential of a cation A on the sites α and β:

$$\mu_A^\alpha = \mu_A^{\alpha 0} + R\ T \ln a_A^\alpha \tag{6.3}$$

$$\mu_A^\beta = \mu_A^{\beta 0} + R\ T \ln a_B^\beta \tag{6.4}$$

where the u^0's are the standard chemical potentials, and the a's are the corresponding 'partial' activities. According to classical thermodynamics, however, it is incongruent to define two different chemical potentials for one species in a single homogeneous phase. In such a case we have:

$$\mu_A^\alpha = \mu_A^\beta \quad \text{and} \quad \mu_A^{\alpha 0} = \mu_A^{\beta 0} \tag{6.5}$$

To avoid the above difficulty Borghese (1967) regards A in site α as a distinct species from A in site β. This is somewhat analogous to speaking of the chemical potentials of O_2 and O_3 in a homogeneous gas phase. The idea of defining a new potential analogous to chemical potential called a site preference potential (Greenwood in Grover and Orville, 1970) could also be considered.

The use of a 'site preference potential' may be avoided in practice, particularly as we are rarely concerned with its quantitative use in thermodynamics.

The standard site preference energy or the intracrystalline ion-exchange energy ΔG^0 for the reaction (6a) is given by

$$\Delta G^0 = - R T \ln K_a \tag{6.6}$$

where K_a is the equilibrium constant and is a function of T only unlike K_D which is a function of both T and composition.

Thermodynamic Functions of Mixing

One of the principal aims of the study of order-disorder phenomenon is to investigate the thermodynamic properties of the crystalline solution as a whole. In case of an ideal macro-phase the activity-composition relation is given by

$$a_i = (x_i)^N \tag{6.7}$$

where N is the number of structural sites in the crystal. In the case when there are two sites we may have

$$a_i = (x_i)\ (x_i)$$

and if these sites are different we can write

$$a_i = \{(x_i^\alpha + x_i^\beta)/2\} \tag{6.8}$$

or

$$a_i = (x_i)^\alpha\ (x_i)^\beta \tag{6.9}$$

where α and β are two nonequivalent structural sites. The latter method has been generally used (Mueller, 1962, Thompson, 1969). Extending the above method to the non-ideal case, we may write

$$a_i = (a_i)^{\alpha} (a_i)^{\beta} \tag{6.10}$$

where a_i^{α} and a_i^{β} are 'partial' activities referring to the sites. In an orthopyroxene (Mg Mg Si_2O_6 - $FeFeSi_2O_6$), where we have two sites M1 and M2, the activity of Fe^{2+} in the crystal may be expressed as

$$a^{Opx}_{Fe^{2+}} = a^{M1}_{Fe^{2+}} \; a^{M2}_{Fe^{2+}} \tag{6.11}$$

If we consider the activity on one cation basis i. e. for the crystal (Mg SiO_3) Fe SiO_3) we have

$$a^{Opx}_{Fe^{2+}} = (a^{M1}_{Fe^{2+}} \; a^{M2}_{Fe^{2+}})^{1/2} \tag{6.12}$$

The 'partial' activity a_i^{α} is equal to $f_i^{\alpha} \; x_i^{\alpha}$ where f is the partial activity coefficient. At a certain temperature the atomic ratio x_i in the two sites α and β can be determined by x-ray or other resonance techniques. The next problem involves the evaluation of the 'partial' activity coefficients.

Several crystals of suitable composition (A, B) M between the endmembers AM and BM may be chosen and heated at a certain temperature for time long enough to attain equilibrium for the intra-crystalline ion exchange (6a). Several such distribution isotherms may be obtained. We shall be required to find a suitable model for interrelating the partial activity coefficient with the atomic fraction at the site. The 'simple mixture' or regular solution model may be found useful in cases where the form of the distribution isotherms do not indicate two much non-ideality of mixing A and B at α and β. We may write

$$\ln K_a = \ln K_D - \frac{W^{\alpha}}{R\,T}(1 - 2\,x_A^{\alpha}) + \frac{W^{\beta}}{R\,T}(1 - 2\,x_A^{\beta}) \tag{6.13}$$

where $\mathbb{W}$ is related to the partial activity coefficient by

$$R\ T\ \ln f_A^\alpha = \mathbb{W}\ (1 - x_A^\alpha)^2 \tag{1.25}$$

At this point certain other partial functions of mixing may be considered. The partial free energy of mixing at the sites is given by

$$G_M^\alpha = x_A^\alpha\ R\ T\ \ln a_A^\alpha + x_B^\alpha\ R\ T\ \ln a_B^\alpha \tag{6.14}$$

$$= x_A^\alpha\ R\ T\ \ln f_A^\alpha + x_B^\alpha\ R\ T\ \ln f_B^\alpha + T\ (x_A^\alpha\ R\ \ln x_A^\alpha + x_B^\alpha\ R\ \ln x_B^\alpha) \tag{6.15}$$

Substituting $S_M^\alpha \equiv -R\ (x_A^\alpha \ln x_A^\alpha + x_B^\alpha \ln x_B^\alpha)$ and (1.25) in (6.15) we have

$$= \mathbb{W}^\alpha\ x_A^\alpha\ x_B^\alpha - T\ S_M^\alpha \tag{6.16}$$

The term $\mathbb{W}^\alpha\ x_A^\alpha\ x_B^\alpha$, is also the partial excess free energy of mixing.

In a crystalline solution such as AAM - BBM the total free energy of mixing is given by

$$G_M = \left(\frac{x_A^\alpha + x_A^\beta}{2}\right) R\ T\ \ln a_A^\alpha \cdot a_A^\beta + \left(\frac{x_B^\alpha + x_B^\beta}{2}\right) R\ T\ \ln a_B^\alpha \cdot a_B^\beta \tag{6.17}$$

which can be finally shown to be

$$= \frac{x_A^\alpha - x_A^\beta}{2} R\ T\ \ln K_{6a} + G_M^\alpha + G_M^\beta \tag{6.18}$$

$$= \frac{x_A^\alpha - x_A^\beta}{2} R\ T\ \ln K_{6a} - T\ (S_M^\alpha + S_M^\beta) + \mathbb{W}^\alpha\ x_B^\alpha\ x_A^\alpha + \mathbb{W}^\beta\ x_A^\beta\ x_B^\beta \tag{6.19}$$

This is a similar expression as derived by Grover and Orville (1969) for ideal mixing at the sites. Note that the above expression K_{6a} is equilibrium constant and not the distribution coefficient as in the case of ideal mixing.

Substituting $\Delta G^0 = - R\ T \ln K_{Ga}$ in (6.19) we have

$$G_M = \frac{x_A^\beta - x_A^\alpha}{2} \Delta G^0 - T\ (S_M^\alpha + S_M^\beta) + (G_{EM}^\alpha + G_{EM}^\beta) \qquad (6.20)$$

Thus the free energy of mixing in the crystal as a whole is a result of a) energy due to the distribution of the cation between α and β sites b) entropy change due to the distribution of A and B within α and β sites and finally c) the excess energy of mixing arising due to the non-ideality of solution in α and β.

The partial excess free energy of mixing at the sites are

$$G_{EM}^\alpha = H_{EM}^\alpha - T\ S_{EM}^\alpha \qquad (6.21)$$

and

$$G_{EM}^\beta = H_{EM}^\beta - T\ S_{EM}^\beta \qquad (6.22)$$

Substituting (6.21) and (6.22) in (6.20) we have

$$G_M = \frac{x_A^\beta - x_A^\alpha}{2} \Delta G^0 + (H_{EM}^\alpha + H_{EM}^\beta) - T\ (S_I^\alpha + S_{EM}^\alpha + S_I^\beta + S_{EM}^\beta) \qquad (6.23)$$

The use of the thermodynamic relations presented in this section and before will be made in analyzing the data on site occupancies in orthopyroxene later.

Kinetics of Order-Disorder

Virgo and Hafner (1969) made an important observation that there is an apparent cut-off or transition region on the temperature scale below which no more ordering or disordering occurs.. This transition temperature in orthopyroxene was estimated to be approximately 480°C. Above this temperature the

activation energy required for diffusion to start in the direction of disordering is of the order of 20 kilocalories (Virgo and Hafner, 1969). Below this temperature the activation energy should be very high. This is confirmed from the measurement of order-disorder in metamorphic pyroxenes which cooled slowly through geological time. Figure 6.1 shows the data on the K_D values for the distribution of Fe^{2+} and Mg^{2+} between M1 and M2 sites in metamorphic orthopyroxene. From these data and the experimental results shown in Figure 8.4 later, it is noted that no orthopyroxene shows a degree of order representing temperatures lower than 450°C.

Mueller (1970) proposed a two-step mechanism for order-disorder kinetic in silicates. This involves a low temperature process with high activation energy and a high temperature process with a lower activation energy. This mechanism may be responsible for ordering characteristics distinguishing metamorphic, igneous plutonic and volcanic pyroxenes. The intracrystalline ion-exchange equilibria in igneous plutonic rocks is not ordinarily quenched in at any temperature because of slow cooling rate. The same applies to such equilibria in metamorphic rocks. However in these rocks attainment of such equilibria is possible below the transition temperature if crystallization or recrystallization occurs at these temperatures. In volcanic rocks because of rapid cooling, there is a high possibility that the intracrystalline equilibria is quenched in and the temperature indicated by order-disorder is not very much lower than the original temperature of crystallization.

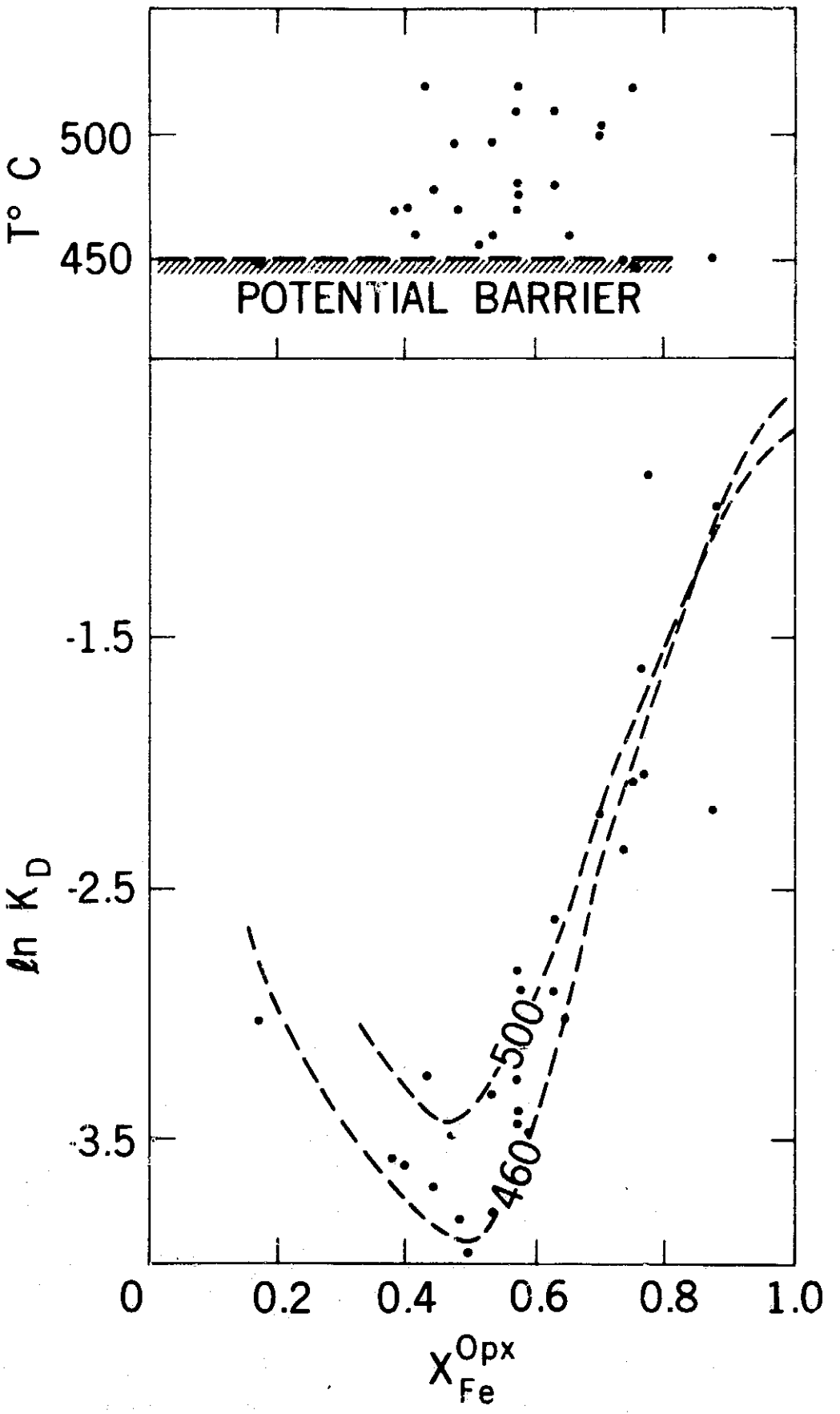

Figure 6-1. Temperature estimate of the ion-exchange equilibrium between sites in natural orthopyroxenes. 450 °C appears to be the transition temperature below which no more ordering takes place due to a potential barrier.

Section 7

ORTHOPYROXENE CRYSTALLINE SOLUTION

Orthopyroxene is one of the few important rock forming minerals which can be considered as quasi-binary without significant loss of accuracy. Usually more than 95 percent of the mineral is a crystalline solution of the endmembers enstatite ($MgSiO_3$) and ferrosilite ($FeSiO_3$). Fe^{2+} and Mg^{2+} are distributed between two nonequivalent sites M1 and M2. With the use of X-ray or Mössbauer spectroscopic technique, it is possible to determine the proportion of Fe^{2+} in the two nonequivalent sites (Evans, Ghose and Hafner, 1967). These data can be used with the help of suitable solution models to determine the thermodynamic properties of the solution (Virgo and Hafner, 1969, Saxena and Ghose, 1971).

Inter-site Ion-exchange

Thermodynamics of the intracrystalline ion-exchange was discussed in the preceding section (6). M1 and M2 sites may be regarded as two interpenetrating subsystems, each with its own thermodynamic properties of mixing. In analogy with heterogeneous ion-exchange equilibria, we may write the ion-exchange reaction as

$$Fe^{2+}\ (M2) + Mg^{2+}\ (M1) \rightleftharpoons Fe^{2+}\ (M1) + Mg^{2+}\ (M2) \qquad (7a)$$

The equilibrium constant for the above reaction at a certain P and T is

$$K_{7a} = \frac{x_{Fe}^{M1}\, f_{Fe}^{M1}\, x_{Mg}^{M2}\, f_{Mg}^{M2}}{x_{Fe}^{M2}\, f_{Fe}^{M2}\, x_{Mg}^{M1}\, f_{Mg}^{M1}} \qquad (7.1)$$

K_{7a} is mainly a function of T. P has little influence. The standard free energy for ion-exchange at a certain T is

$$\Delta G^0_{7a} = - R T \ln K_{7a} \qquad (7.2)$$

we have noted before that this energy is part of the total Gibbs free energy of the crystal and is, therefore, an important thermodynamic quantity. To determine ΔG^0_{7a} or K_{7a}, we need first, the determination of the atomic fractions x^{M1}_{Fe} and x^{M2}_{Fe} and second, the determination of the partial activity coefficients f's which are functions of T and composition. While the atomic fractions or the site occupancies can be determined quantitatively by using X-ray or Mössbauer technique, the partial activity coefficients cannot be determined without the use of a certain solution model.

Order-disorder on Individual Sites And The Choice of a Solution Model

Figure 7.1 (Figs. 1 and 2, Ghose, 1965) shows a scheme of ordering in orthopyroxone crystal as a whole. In hypersthene (Fs_{50} En_{50}) we have the possibility of complete occupation of M1 sites by Mg^{2+} and of M2 sites by Fe^{2+}. For all other compositions, one of the two ions must inevitably occupy the sites other than they normally prefer. In fact, as suggested before we except that the two ions will always show some kind of equilibrium distribution over the two sites as a function of temperature and composition. Although hypersthene has the right composition to be completely ordered, kinetics of the ion-exchange below a certain transition temperature precludes the ordered structure shown in Figure 7.1.

For considering the ion-exchange (7a) we are required to consider M1 and M2 individually as sub-systems. Complete order in the crystal as a whole as

shown in Figure 7.1 also means complete order on the sites themselves. For all other compositions, we may consider whether two neighboring M1 sites or M2 sites are both occupied by the same cations or by two different cations. We may assume that the occupancy of M1 and M2 sites by Mg^{2+} and Fe^{2+} is disordered and that the solutions at the two sites approximate to 'simple mixture' model. We shall later consider the effect of ordering on the sites by using the quasi-chemical approximation and compare the results.

Determination of Site Occupancy in Heated Orthopyroxenes

By using Mössbauer spectroscopy, Virgo and Hafner (1969) determined a distribution isotherm at 1000°C. Saxena and Ghose (1971) similarly determined isotherms between 500 and 800°C (Fig. 7.2). Orthopyroxene crystals are heated for a length of time sufficient to bring about the ion-exchange equilibrium. The samples are then quenched and the site occupancy is determined. Note that the site occupancy is averaged over all the sites present in the crystals and is a function of the changes that take place not only in the neighboring cation but also in the remaining Si-O structural framework.

Sites as Simple Mixtures

Equilibrium Constant, W^{M1} and W^{M2}

The distribution isotherms can be represented by the following equation

$$\ln K_{7a} = \ln K_D + \frac{W^{M1}}{RT}(1 - 2\,x_{Fe}^{M1}) - \frac{W^{M2}}{RT}(1 - 2\,x_{Fe}^{M2})$$

where K_D is $x_{Fe}^{M1}(1 - x_{Fe}^{M2})/x_{Fe}^{M2}(1 - x_{Fe}^{M1})$,

x_{Fe} the site occupancy and W the energy constant of the simple mixture model. A non-linear least squares program is used to calculate K_{7a}, W^{M1} and W^{M2} by simultaneous iterations on all the three unknown variables. Figure 7.3 shows a plot of ΔG^0_{7a} the standard free energy of ion-exchange (= - RT ln K_{7a}), W^{M1} and W^{M2} against $1/T$. There is a linear relation between $1/T$ and all the three variables at 600, 700 and 800°C. The equations to the three straight lines are:

$$W^{M1} = 3525 \left(\frac{10^3}{T}\right) - 1667 \qquad (7.3)$$

$$W^{M2} = 2458 \left(\frac{10^3}{T}\right) - 1261 \qquad (7.4)$$

$$\Delta G^0_a = 4479 - 1948 \left(\frac{10^3}{T}\right) \qquad (7.5)$$

The values at 500°C, however, do not fall on the straight lines. This may be due to a low degree of accuracy in determining the M1 site occupancy particularly in Mg-rich samples at 500°C. We may extrapolate and calculate the constants at 1000°C. An isotherm at 1000°C plotted with these constants is consistent for the most part with Virgo and Hafner's (1969) data.

Thermodynamic functions of mixing

The 'partial' functions of mixing in M1 and M2 may be calculated by using the following relations:

$$G^{M1}_{EM} = x^{M1}_{Fe}\, x^{M1}_{Mg}\, W^{M1} \qquad (1.22)$$

$$-S^{M1}_{EM} = x^{M1}_{Fe}\, x^{M1}_{Mg}\, \partial W^{M1}/\partial T \qquad (1.23)$$

$$H_{EM}^{M1} = x_{Fe}^{M1}\, x_{Mg}^{M1} \left(W^{M1} - \frac{\partial W^{M1}}{\partial T} \right) \qquad (1.24)$$

similarly for the M2 site.

The excess free energy of mixing for the crystal as a whole is given by

$$G_{EM}^{Opx} = R\,T\,(x_{Fe}^{Opx} \ln f_{Fe}^{Opx} + x_{Mg}^{Opx} \ln f_{Mg}^{Opx}) \qquad (7.6)$$

The values of the activity coefficients f may be obtained by

$$f_{Fe}^{Opx} = \frac{\left\{ x_{Fe}^{M1} \exp \frac{W^{M1}}{R\,T} (1 - x_{Fe}^{M1})^2 \right\}^{1/2} \left\{ x_{Fe}^{M2} \exp \frac{W^{M2}}{R\,T} (1 - x_{Fe}^{M2})^2 \right\}^{1/2}}{x_{Fe}^{Opx}} \qquad (7.7)$$

similarly for f_{Mg}^{Opx}.

It is useful to represent the excess free energy of mixing as a polynomial in x as suggested by Guggenheim (1937):

$$G_{EM}^{Opx} = x_{Fe}^{Opx}\, x_{Mg}^{Opx} \{A_0 + A_1 (x_{Fe}^{Opx} - x_{Mg}^{Opx}) + A_2 (x_{Fe}^{Opx} - x_{Mg}^{Opx})^2 + \ldots.\}$$

which may also be written as

$$G_{EM}^{Opx} / x_{Fe}^{Opx}\, x_{Mg}^{Opx} = A_0 + A_1 (x_{Fe}^{Opx} - x_{Mg}^{Opx}) + A_2 (x_{Fe}^{Opx} - x_{Mg}^{Opx})^2 + \ldots.\} \qquad (7.8)$$

Equation (7.8) is of the form

$$4 = a_0 + a_1 x_1 + a_2 x_1^2 + \ldots$$

and may be solved by a least squares program. To determine the constants A_0, A_1 and A_2, we first obtain G_{EM}^{Opx} by using (7.6) and (7.7). The constants listed in Table 7.1 are used in (7.7). These values of excess free energy are then used to calculate by using a least squares program on equation (7.8) the three constants A_0, A_1 and A_2 shown in Table 7.2. Figure 7.4 shows three curves at 600, 700 and 800°C fitted to the data on reduced excess free energy ($G_{EM}/x_{Fe}x_{Mg}$) versus ($x_{Fe} - x_{Mg}$). This method of determining A_0, A_1 and A_2 is more reliable than the Redlich and Kister method followed by Saxena and Ghose (1971).

The three constants as a function of $1/T$ (Fig. 7.5) are given by

$$A_0 = 10802 - 33862\left(\frac{10^3}{T}\right) + 35135\left(\frac{10^3}{T}\right)^2 - 11202\left(\frac{10^3}{T}\right)^3 \qquad (7.9)$$

$$A_1 = 1789 - 3612\left(\frac{10^3}{T}\right) + 2008\left(\frac{10^3}{T}\right)^2 \qquad (7.10)$$

$$A_2 = -13863 + 41051\left(\frac{10^3}{T}\right) - 40299\left(\frac{10^3}{T}\right)^2 + 13426\left(\frac{10^3}{T}\right)^3 \qquad (7.11)$$

The heat of mixing and the entropy of mixing can now be readily calculated using the following equations:

$$-S_{EM}^{Opx} = x_{Fe}^{Opx}\, x_{Mg}^{Opx}\left[\frac{\partial A_0}{\partial T} + \frac{\partial A_1}{\partial T}(x_{Fe}^{Opx} - x_{Mg}^{Opx}) + \frac{\partial A_2}{\partial T}(x_{Fe}^{Opx} - x_{Mg}^{Opx})^2 + \ldots\right] \qquad (7.12)$$

$$H_{EM}^{Opx} = x_{Fe}^{Opx}\, x_{Mg}^{Opx}\left[A_0 - T\left(\frac{\partial A_0}{\partial T}\right) + \left\{A_1 - T\left(\frac{\partial A_1}{\partial T}\right)\right\}(x_{Fe}^{Opx} - x_{Mg}^{Opx}) + \left\{A_2 - T\left(\frac{\partial A_2}{\partial T}\right)\right\}(x_{Fe}^{Opx} - x_{Mg}^{Opx})^2 + \ldots\right] \qquad (7.13)$$

The free energy of mixing is given by

$$G_M^{Opx} = H_{EM}^{Opx} - T\,S_{EM}^{Opx} + R\,T\,(x_{Fe}^{Opx}\,\ln x_{Fe}^{Opx} + x_{Mg}^{Opx}\,\ln x_{Mg}^{Opx}) \qquad (7.14)$$

It may be useful to write an expression for the free energy of mixing of the crystal as a whole in terms of partial thermodynamic functions of mixing referring to the sites. We have for (Mg, Fe) Si_2O_6 according to (6.23)

$$G_M^{Opx} = \left(\frac{x_{Fe}^{M1} - x_{Fe}^{M2}}{2}\,\Delta G_{7a}^{0}\right) + (H_{EM}^{M1} + H_{EM}^{M2}) - T\,(S_I^{M1} + S_I^{M2} + S_{EM}^{M1} + S_{EM}^{M2}) \qquad (7.15)$$

Note that $H_{EM}^{Opx} \neq (H_{EM}^{M1} + H_{EM}^{M2})$ and similarly $T\,S_{EM}^{Opx} \neq (S_{EM}^{M1} + S_{EM}^{M2})$. The expression (7.15) divides the total free energy of mixing into three terms. The term in the first bracket is the potential due to the difference in site occupancy energy. It includes both the contributions of the standard enthalpy and entropy of the exchange. The terms in the second and third brackets include the heat of mixing and the entropy of mixing respectively at the individual sites.

This division of the free energy of mixing is artificial. It may be useful in understanding the change in free energy as a function of temperature and order-disorder. Figuers 7.6 and 7.7 show a comparison of the various functions of mixing at 600 and 800°C. The values of H_{EM} and $T\,S_{EM}$ for the crystal as a whole are obtained by using equations (7.12) and (7.13). It may be noted that the first energy term

$$\left(\frac{x_{Fe}^{M1} - x_{Fe}^{M2}}{2}\,\Delta G_{7a}^{0}\right)$$

along with the entropy terms increase the negative G_M^{Opx} and make the solution stable. The negative value of the first energy term decreases somewhat with increasing temperature indicating that the disordering works against stability of the solution. This effect is, however, limited and is overridden by the positive excess heat of mixing at the sites.

At 800°C the contributions of the 'partial' energies of mixing at the sites to the energies of mixing in the crystal as a whole are somewhat asymmetric. The mixing energies H_{EM}^{Opx} and TS_{EM}^{Opx} have more or less symmetric values. With decreasing temperature, the energies of mixing at the sites increase, those for the M1 site increasing relatively more than those for the M2 site. The H_{EM}^{Opx} and S_{EM}^{Opx}, therefore, become more and more asymmetric.

Sites as Solutions With Quasi-chemical Approximation

Equilibrium constant, W^{M1} and W^{M2}

As shown in section (5), the relation among K_{7a}, W^{M1}, W^{M2} and the site occupancies may be expressed by the following equation:

$$K_D \frac{\left\{1 + \frac{\phi_{Mg}^{M1}(\beta - 1)}{\phi_{Fe}^{M1}(\beta + 1)}\right\}^{2q_{Fe}^{M1}/2} \left\{1 + \frac{\phi_{Fe}^{M2}(\beta' - 1)}{\phi_{Mg}^{M2}(\beta' + 1)}\right\}^{z'q_{Mg}^{M2}/2}}{\left\{1 + \frac{\phi_{Fe}^{M1}(\beta - 1)}{\phi_{Mg}^{M1}(\beta - 1)}\right\}^{zq_{Mg}^{M1}/2} \left\{1 + \frac{\phi_{Mg}^{M2}(\beta' - 1)}{\phi_{Fe}^{M2}(\beta' + 1)}\right\}^{z'q_{Fe}^{M2}/2}} = K_{7a} \qquad (7.16)$$

where β and β' are for M1 and M2 respectively and given by:

$$\beta = \{1 + 4\,\phi_{Fe}^{M1}\,\phi_{Mg}^{M1}\,(e^{2W^{M1}/zRT} - 1)\}^{1/2}$$

$$\beta' = \{1 + 4\,\phi_{Fe}^{M2}\,\phi_{Mg}^{M2}\,(e^{2W^{M2}/zRT} - 1)\}^{1/2}$$

ϕ's are, as before (1.35),

$$\frac{x_{Fe}\,q_{Fe}}{x_{Fe}\,q_{Fe} + x_{Mg}\,q_{Mg}},$$

z and z' are the number of neighboring cations in M1 and M2 respectively and q's are contact factors.

z and q for M1 and M2 sites

As the silicate framework does not significantly change its character as a function of temperature or Fe^{2+}/Mg^{2+} ratio, the sites M1 and M2 have definite configurations and the polyhedral geometry changes only somewhat with changing Fe^{2+}/Mg ratio. We may, therefore, assume that the number of sites which are neighbors of any one M1 site are two or four other M1 sites and q_{Mg}^{M1} is equal to q_{Fe}^{M1} and both are unity. A reference to Figure 7.1 shows that two of the four M1 sites are somewhat nearer to a central M1. It may be noted that the two inner strips with M1 sites and two outer strips with M2 sites lie more or less in a plane. Since the two M2 strips are separated by the intervening M1 sites, it is only realistic to consider that number of neighboring M2 sites to any one M2 site is only two. We may also assume that $q_{Fe}^{M2} = q_{Mg}^{M2} = 1$ and substitute in (7.16) $z = z' = 2$ and all q's as unity.

Results of calculations

The intracrystalline distribution data presented in Figure 7.2 was used to determine the quasi-chemical parameters W^{M1} and W^{M2} and the equilibrium

constant K_{7a} by using least squares analysis on equation (7.16). The distribution data at 500°C was not used and the number of data point at 700°C was not found sufficient for a satisfactory convergence. The values of W^{M1}, W^{M2} and K_{7a} at 600 and 800°C are listed in Table 7.3. Chi square values for the simple mixture model and for the quasi-chemical approximation are not significantly different.

Activity-composition relation at 600°C

We may calculate the 'partial' activity coefficients at the M1 site by using the relations

$$f_{Fe}^{M1} = \left\{1 + \frac{\phi_{Mg}^{M1}\ (\beta - 1)}{\phi_{Fe}^{M1}\ (\beta + 1)}\right\}^{zq_{Fe}^{M1}/2}$$

and similarly for f_{Fe}^{M2} and finally determine the activity-composition relation in the crystal as a whole by the equation:

$$a_{Fe}^{Opx} = (x_{Fe}^{M1}\ f_{Fe}^{M1})^{1/2}\ (x_{Fe}^{M2}\ f_{Fe}^{M2})^{1/2}$$

The results of such calculations are presented in Figure 7.8. The figure shows that there is very little difference between the activities calculated by assuming sites as 'simple mixtures' or as solutions with quasi-chemical approximation.

Unmixing

Although no data on unmixed orthopyroxenes are available, a possible unmixing can be predicted theoretically. Due to kinetic reasons, data on actual unmixing may not be available. However orthopyroxenes of suitable compositions

heated at temperatures close to the critical temperature of unmixing may show certain structural characters such as domains by the use of electron microscopy.

The conditions of critical mixing are

$$\partial^2 G^E/\partial x^2 = - R T/x (1 - x) \qquad (2.3)$$

$$\partial^2 G^E/\partial x^3 = - R T (2 x - 1)/x^2 (1 - x)^2 \qquad (2.4)$$

Successive differentiation of equation (7.10) leads to equations which are transcendental in character and cannot be solved without an iteration procedure. For the present purpose it is enough to find an approximate temperature where the activity-composition diagram shows the same activity over a small composition interval (Figure 7). From Figure 7.9 we find that the critical temperature is in the vicinity of 450°C and the critical composition is about $x_{Fe}^{Opx} = 0.83$.

At 450°C, the values of W^{M1}/RT and W^{M2}/RT are 2.23 and 1.49 respectively. For $x_{Fe}^{Opx} = 0.83$, we have $x_{Fe}^{M1} = 0.75$ and $x_{Fe}^{M2} = 0.92$.

If M1 site was an independent phase, it would have unmixed into two coexisting phases with the following compositions and proportions approximately:

M1 (Fe) 0.80	92%	M1 (Fe) 0.20	8%
M1 (Mg) 0.20		M1 (Mg) 0.80	

For the above values of x_{Fe}^{M1}, x_{Fe}^{M2} remains nearly the same and we have

Fe M1 - 0.80		M2 0.928	92%
Mg M1 0.20		M2 0.072	

Fe	M1 0.20	M2 0.92	8%
Mg	M1 0.80	M2 0.08	

The first of the above two represents the right direction towards unmixing. However, we cannot explain with above model, how a complete unmixing results at this critical temperature and composition. If the unmixing takes place via domain formation, it is obvious that the best experiments would be to examine the crystals with $x_{Fe^2}^{Opx}$ between 0.80 to 0.85 and which are heated between 450 to 500°C.

Table 7.1

Values of Equilibrium Constant K_{7a}, ΔG°_{7a} and the Constants W^{M1} and W^{M2}

		Cal/mole		
T °C	K_{7a}	W^{M1}	W^{M2}	ΔG°_{7a}
500	.279	2893	1919	1959
600	.277	2390	1577	2233
700	.273	1916	1215	2509
800	.289	1641	1057	2646
900	.298	1338	834	2818
1000	.311	1102	670	2949

Table 7.2

The Three Constants A_0, A_1 and A_2 Obtained by a Least Squares Fit to Equation (7.8). The Values in Brackets are Values Calculated by Using (7.9-7.11)

T°C	A_0	A_1	A_2
500	1542 (1544)	494 (478)	871 (867)
600	1277 (1278)	233 (287)	454 (461)
700	976 (951)	251 (199)	321 (335)
800	652 (693)	165 (168)	298 (260)
900	548 (529)	159 (170)	143 (163)

Table 7.3

Quasi-chemical Parameters W^{M1} and W^{M2} and K_{7a} as Calculated by (7.16)

T°C	K_{7a}	$\frac{W^{M1}}{RT}$	$\frac{W^{M2}}{RT}$	QC	Chi^{2*} Simple mix.
600	0.293	1.71	1.26	.027	.017
800	0.273	0.733	0.469	.007	.004

* $Chi^2 = \Sigma \frac{\{K \text{ (calculated)} - K \text{ (by least squares)}\}^2}{K \text{ (by least squares)}}$

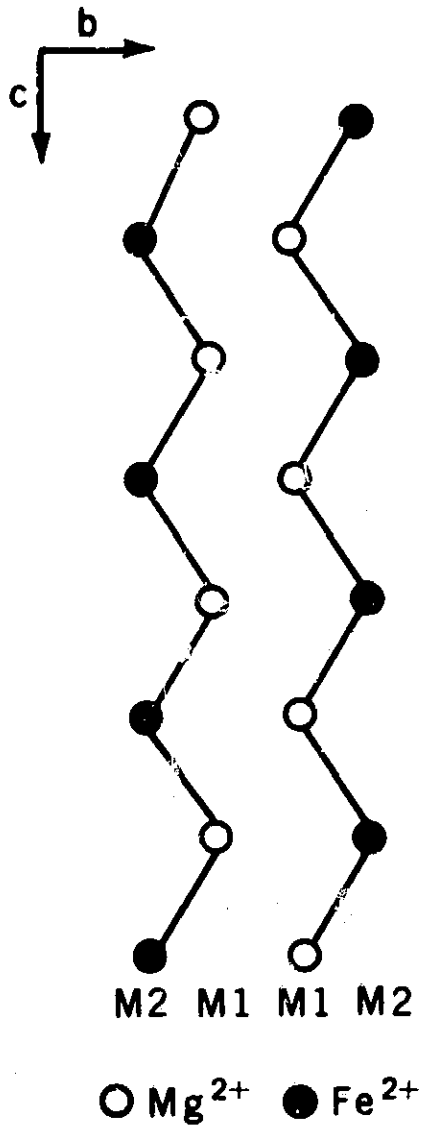

Figure 7-1. $Mg^{2+}Fe^{2+}$ ordering scheme in an orthopyroxene (Ghose, 1965).

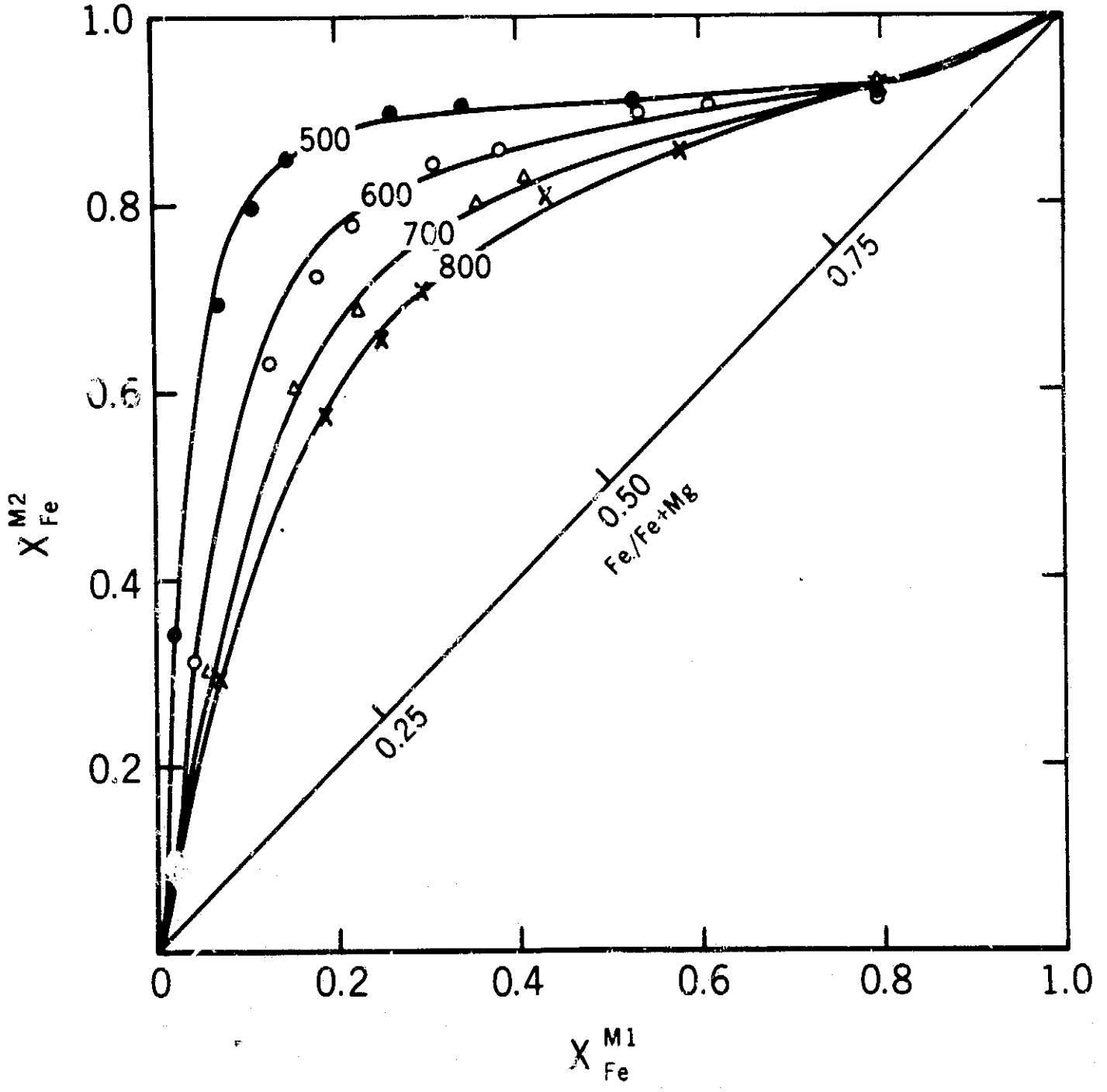

Figure 7-2. Distribution isotherms for the Mg^{2+}-Fe^{2+} partitioning between M1 and M2 sites in heated natural orthopyroxenes (Saxena and Ghose, 1971). The curves are least squares fit to the experimental data using 'simple mixture' model for the sites.

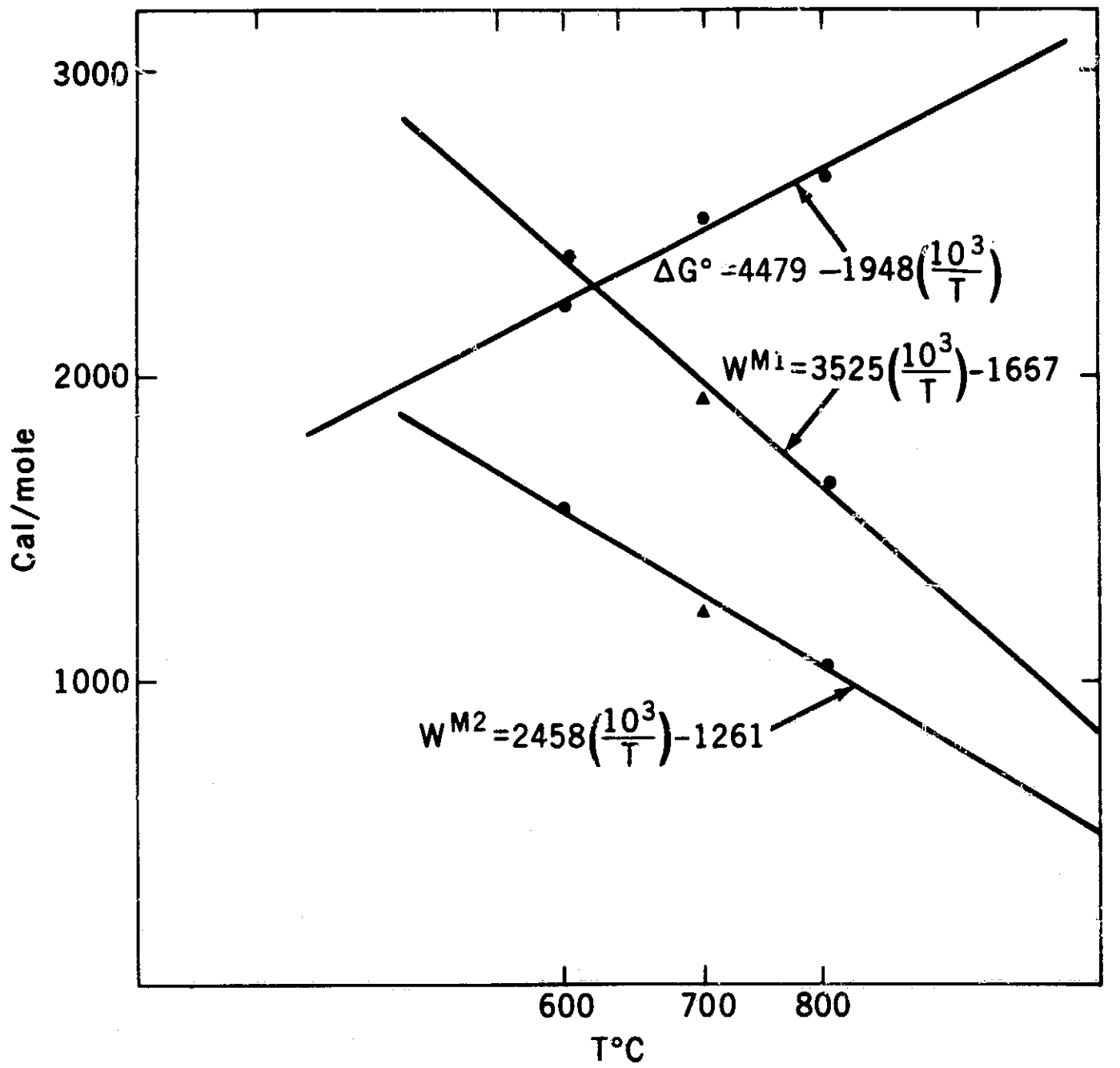

Figure 7-3. W^{M1}, W^{M2} and ΔG° plotted against $1/T$. W's are the energy constant of the 'simple mixture' model and ΔG^0 is the standard free energy of inter-site ion-exchange.

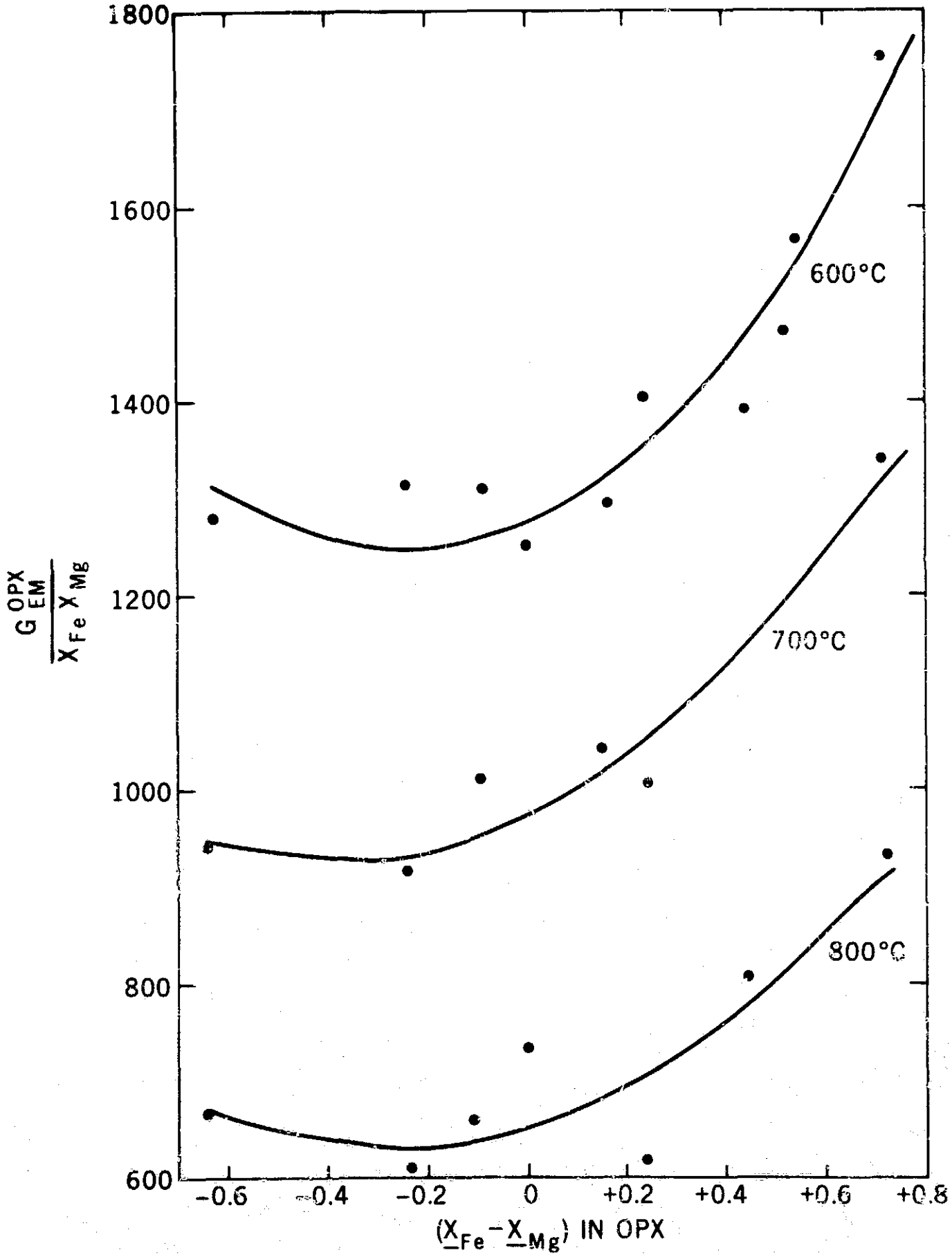

Figure 7-4 Reduced excess free energy of mixing plotted against $(x_{Fe} - x_{Mg})$ in orthopyroxene. The curves are leastsquares fit using the equation (7.8). This fit yields the constants A_0, A_1 and A_2.

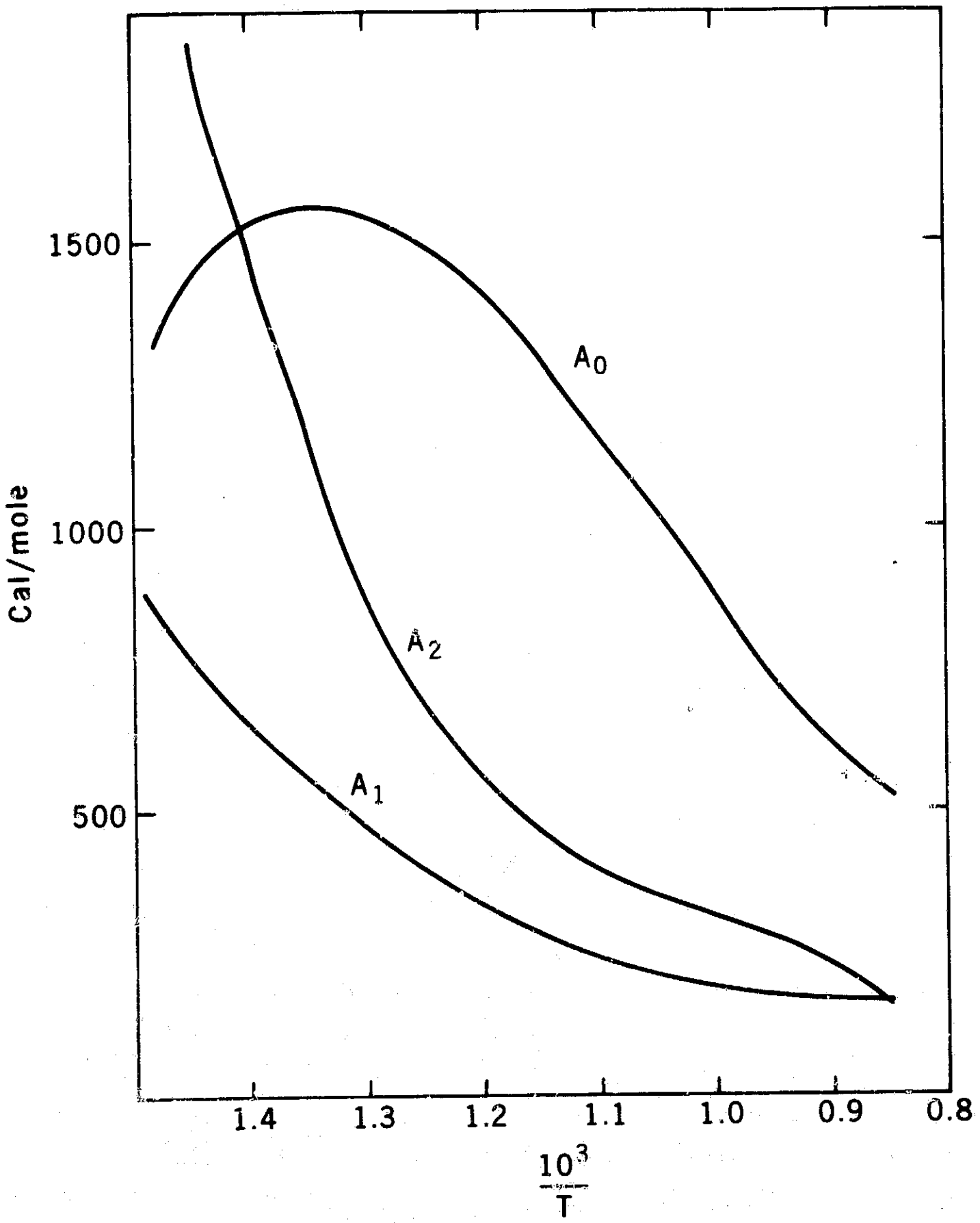

Figure 7-5. Leastsquares curves showing A_0, A_1 and A_2 as a function $1/T$. The equations to the curves are (7.9) (7.10) and (7.11).

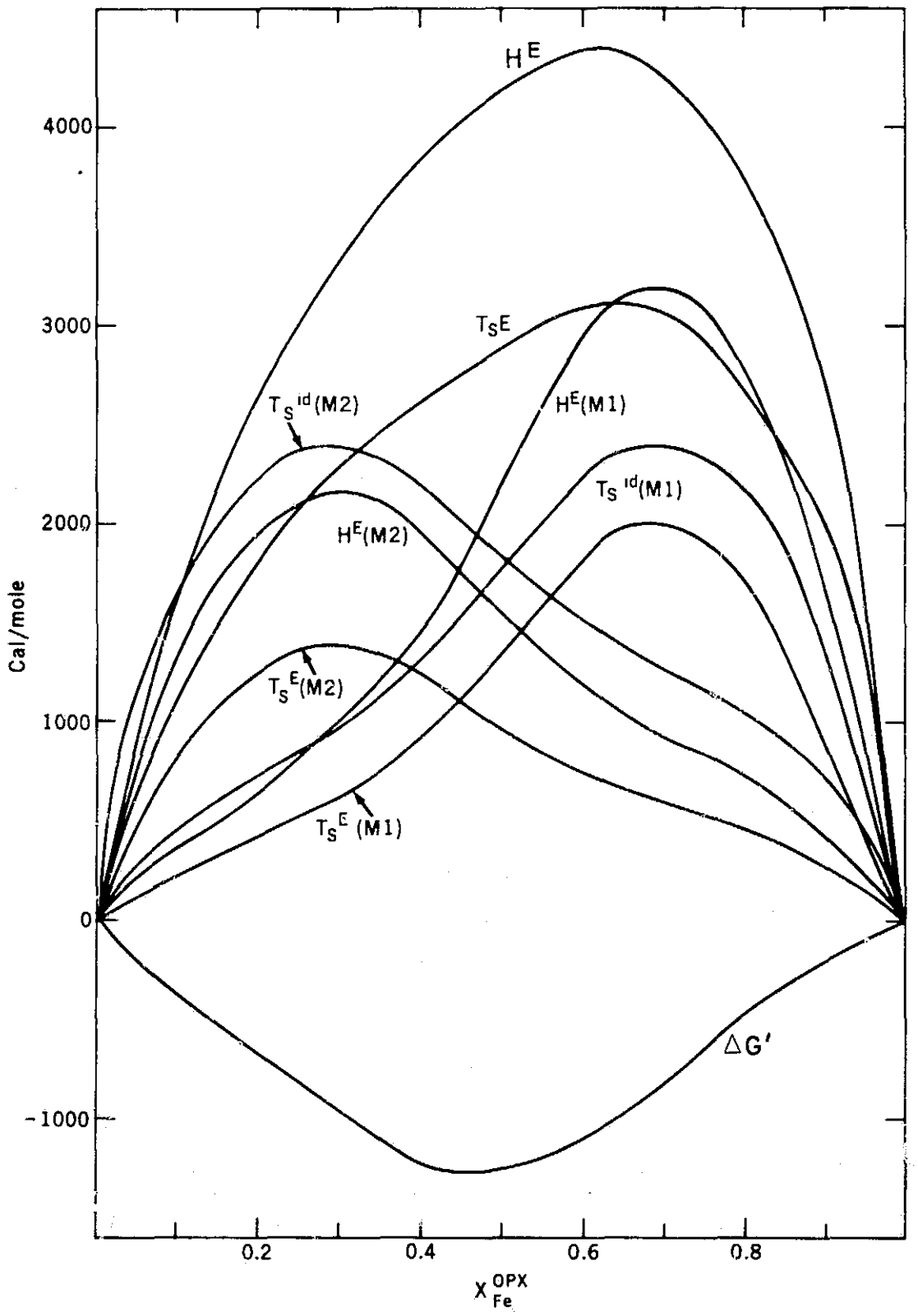

Figure 7-6. Thermodynamic functions of mixing in orthopyroxene at 600 °C, both at the sites and in the crystal as a whole plotted against x_{Fe}^{Opx}. The functions of mixing at the sites correspond to the atomic fractions at M1 and M2 which in turn correspond to an equilibrium distribution at 600 °C in the crystal with x_{Fe}^{Opx} as measured on the abscissa. $\Delta G'$ is

$$\{(x_{Fe}^{M1} - x_{Fe}^{M2})/2\}\,\Delta G_{7a}^{0}$$

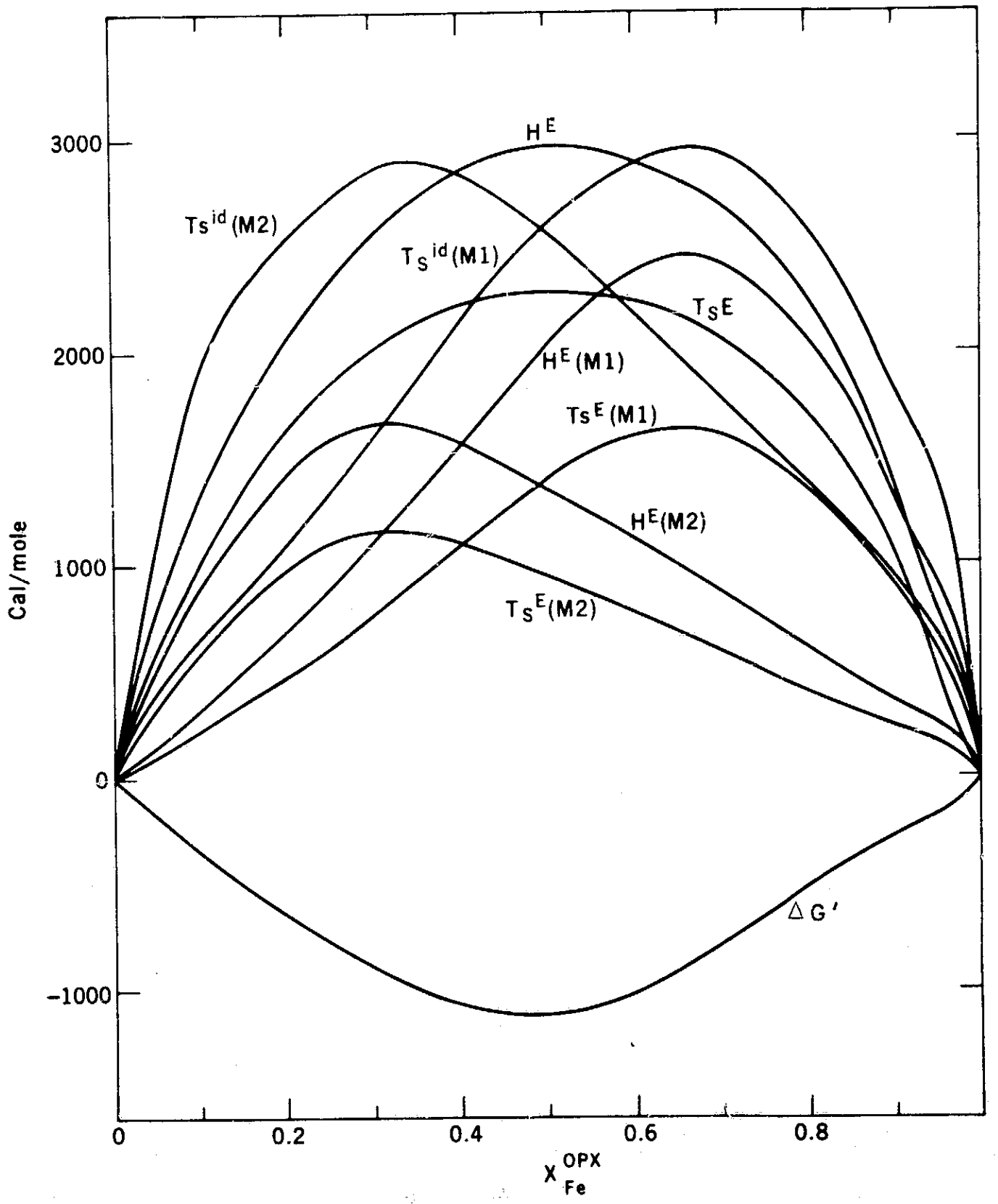

Figure 7-7. Thermodynamic functions of mixing in orthopyroxene at 800 °C plotted similarly as in Fig. 7-6.

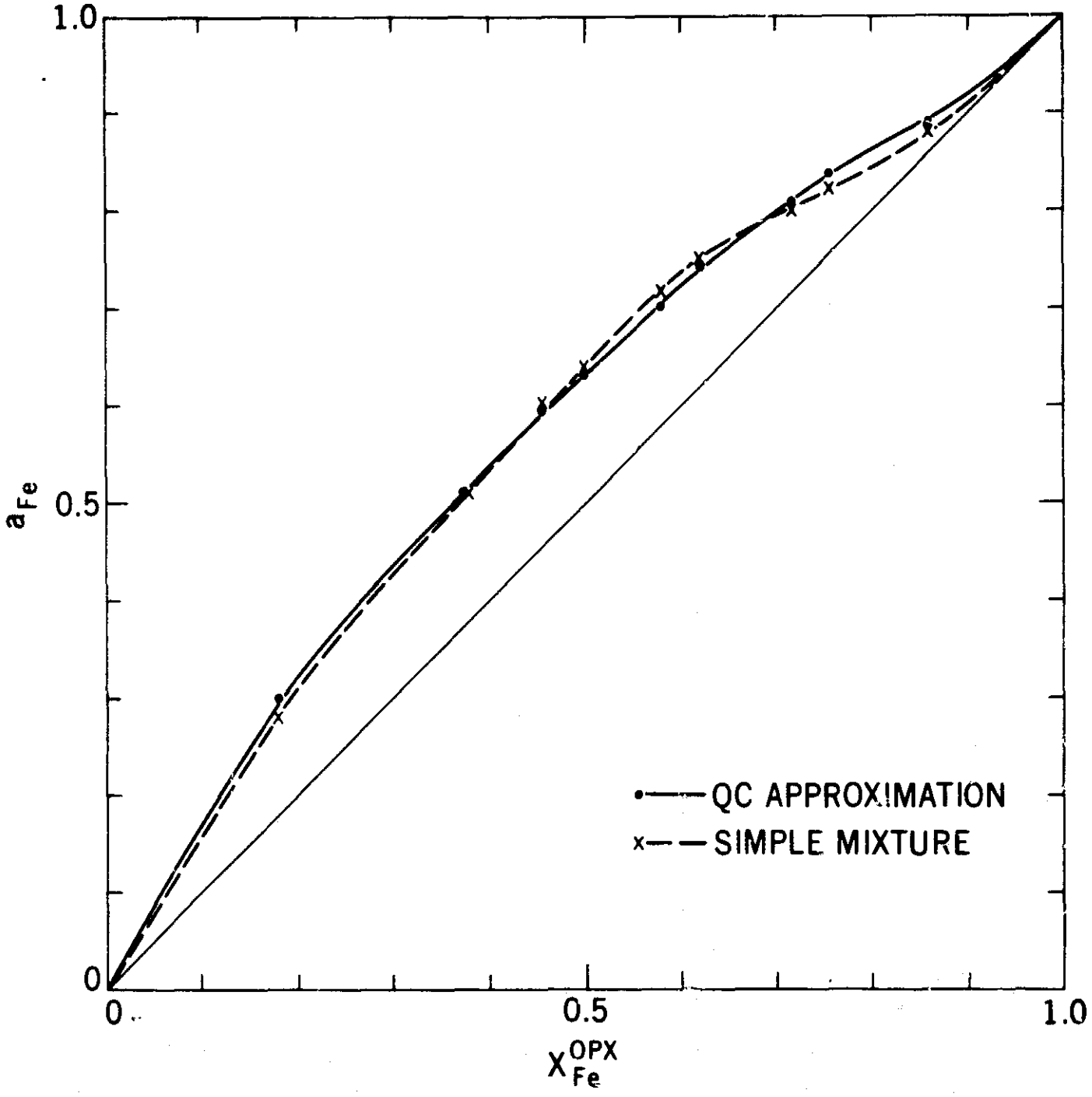

Figure 7-8. Activity composition relation for $FeSiO_3$ in orthopyroxene crystalline solution using 'simple mixture' and quasi-chemical models for the sites.

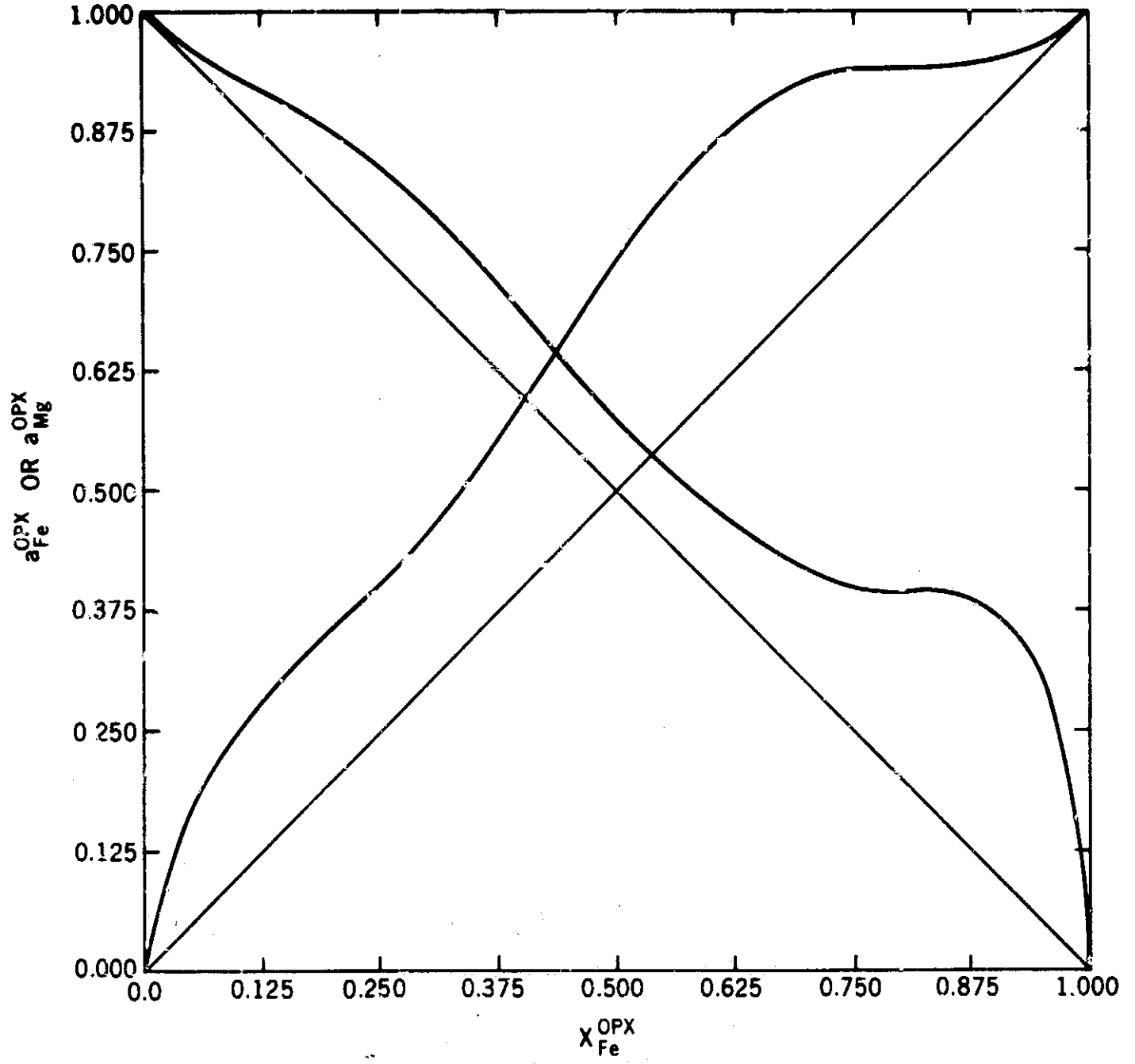

Figure 7-9. Activity-composition relation in orthopyroxene at 450 °C which is close to the temperature of unmixing the critical composition is estimated to be $x_{Fe} = 0.83$.

Section 8

CRYSTALLINE SOLUTIONS AND GEOTHERMOMETRY

The concept of metamorphic facies evolved through the attempts of the petrologists to distinguish the mineral assemblages formed at different P and T in the field. In several cases, the experimentalists have simulated the physical-chemical conditions of the formation of rocks in the laboratory. However, relevent thermodynamic data on the rock forming minerals is meagre and causes difficulties in making a meaningful interpretation and in checking the validity of most experiments. From our existing knowledge, it is only possible to obtain certain qualitative to semi-quantitative estimates of P and T of the formation of a mineral assemblage. Such methods are based on the knowledge of the chemical reactions which occur as a result of changing P and T within and in between the crystalline solutions.

This section is not a review of the methods of geothermometry. Ingerson (1965) has made an excellent review of such methods. We shall be mainly considered here with coexisting crystalline solutions and their thermodynamic properties of mixing as a function of P and T .

Inter-crystalline Equilibria

Distribution of a component between coexisting simple mixtures

Let us assume that we have data on the distribution of a component A between two binary phases (A, B) M and (A, B) N. The distribution data covers a large compositional range in both the phases. Let (A, B) M be a simple mixture whose activity-composition relations are known at several different temperatures but the activity-composition relation in (A, B) N is unknown. If the form of the

distribution isotherm, whose temperature is unknown, does not indicate (A, B) N to be too non-ideal, we may assume that the distribution follows the following equation:

$$\ln K = \ln K_D + \frac{W^{\alpha}}{R\,T}(1 - 2\,x^{\alpha}_{Fe}) - \frac{W^{\beta}}{R\,T}(1 - 2\,x^{\beta}_{Fe}) \qquad (8.1)$$

where K is the equilibrium constant, K_D the distribution coefficient and α and β represent (A, B) M and (A, B) N respectively.

To find the temperature of the distribution isotherm (considering that the effect of P is negligible on the equilibrium constant K), we may assume the temperature to be T_1 and solve equation (8.1) by a least squares method. We repeat this work by assuming various temperatures T_2, T_3 etc. In practice we could rely on geologic evidence to fix the limits T_1 and T_2 within which the actual temperature of the ion-exchange equilibrium might lie. These calculations yield a set of W^{α} and W^{β} values at temperatures T_1 and T_2. Such values of W^{α} at T_1 and T_2 differ from the experimental values of W^{α} at these temperatures because of the actual temperature of the isotherm being different from the assumed T_1 or T_2. We may, therefore, plot the calculated values of W^{α} and the experimental values of W^{α} against T as in Figure 8.1. The intersection of the two lines yields the temperature of the distribution isotherm.

This method was used by Saxena (1971) in estimating temperature of crystallization for coexisting pyroxenes in the metamorphic rocks. Unfortunately most minerals are not binary solutions and many of those which are quasi-binary may not be strictly symmetric simple mixtures.

Distribution of $NaAlSi_3O_8$ between coexisting plagioclase and alkali feldspar

Barth (1956, 1962) proposed that the ratio mole fraction of albite (Ab) in alkali feldspar: mole fraction of albite (Ab) in plagioclase varies linearly with inverse of absolute temperature. This is true if mixing of the end members Ab and Or (orthoclase, $KAlSi_3O_8$) and Ab and An (anorthrite, $Ca_2Al_2Si_2O_8$) is ideal or nearly ideal in the compositional range.

The properties of sanidine crystalline solution has been studies by Thompson and Waldbaum (1968, (1969) and by Thompson (1969a). Even in the high temperatu: range 700 to 1000°C, the solution deviates significantly from ideal mixture. Similarly it is expected that there will be significant deviation from ideality in the plagioclase feldspars.

Plagioclase and sanidine may be considered as two ternary solutions at a certain P and T, we have the following ion-exchange reactions

$$\underset{NaAlSi_3O_8}{\text{Plagioclase}} \rightleftharpoons \underset{NaAlSi_3O_8}{\text{Sanidine}} \tag{8.2}$$

$$K\ AlSi_3O_8 \rightleftharpoons K\ AlSi_3O_8 \tag{8.3}$$

$$CaAl_2Si_2O_8 \rightleftharpoons CaAl_2Si_2O_8 \tag{8.4}$$

The corresponding equilibrium constants are

$$K_2 = a^S_{Ab}/a^{Pl}_{Ab} = \frac{x^S_{Ab}}{x^{Pl}_{Ab}} \frac{f^S_{Ab}}{f^{Pl}_{Ab}}$$

$$K_3 = a^S_{Or}/a^{Pl}_{Or} = \frac{x^S_{Or}}{x^{Pl}_{Or}} \frac{f^S_{Or}}{f^{Pl}_{Or}}$$

$$K_4 = \frac{a^{S}_{An}}{a^{Pl}_{An}} = \frac{x^{S}_{An}}{x^{Pl}_{An}} \frac{f^{S}_{An}}{f^{Pl}_{An}}$$

where x = Ab/Ab + An + Or. The activity coefficients f are functions of P, T and the ratio of two of the other mole fractions.

In actual practice, we may simplify the situation somewhat by assuming that both sanidine and plagioclase are binary solutions. Therefore we write K_1 as

$$K_2 = \frac{x^{S}_{Ab}}{x^{Pl}_{Ab}} \cdot \frac{f^{S}_{Ab}}{f^{Pl}_{Ab}}$$

where x^{S}_{Ab} = Ab/Ab + Or in sanidine and x^{Pl}_{A6} = Ab/Ab + An. f^{S}_{Ab} is now a function of P, T and x^{S}_{Ab}, and similarly f^{Pl}_{Ab}. Even in the simplified case, we have to know the activity-composition relations in both sanidine and plagioclase solutions. The activity-composition data on sanidine crystalline solution is available (Thompson and Waldbaum 1968, 1969b) but we have yet to learn about the plagioclase crystalline solution. Only sanidine and high temperature plagioclase have been considered above. The temperature estimate at lower range of temperatures is further complicated by the structural changes in the feldspars as a function of T and composition.

Distribution of Fe and Mg in Coexisting Minerals

The use of the distribution coefficient involving two multicomponent minerals in problems of petrogenesis is severely limited. The distribution of Fe^{2+} and Mg^{2+} between coexisting garnet and biotite is one example. Such a distribution

is a function of P, T and the concentrations of Mn and Ca in garnet and of Al^{3+}, Fe^{3+} and Ti in biotite (Kretz, 1959, Albee, 1965, Sen and Chakraborty, 1968, Saxena 1968c).

Fortunately garnet-biotite pair is one of the most investigated pairs and several chemical analyses are available in literature. It is, therefore, possible to improve the usability of the K_D by analyzing its compositional dependence by a multivariate statistical analysis. Saxena (1969b) used the 'principal component analysis' and obtained the 'transformed distribution coefficient' as

$$\begin{aligned}\text{Transf. } K_D = {} & 0.5013\, K_D - 0.4420\, x^{gar}_{Fe} + 0.1506\, x^{bi}_{Fe} - 0.3474\, x^{gar}_{Mn} \\ & + 0.0865\, x^{gar}_{Ca} - 0.0333\, x^{bi}_{Al^{IV}} - 0.3165\, x^{bi}_{Al^{VI}} \\ & + 0.5488\, x^{bi}_{Ti}\end{aligned}$$

where x_{Fe} is $Fe^{2+}/(Fe^{2+} + Mg)$, K_D is $x^{bi}_{Fe}\, x^{gar}_{Mg} / x^{gar}_{Fe}\, x^{bi}_{Mg}$ and the other x's represent ions on 12 O basis in garnet and 22 O basis in biotite. The transformed K_D could be shown to vary systematically with temperature inferred on geologic evidence. Figure 8.2 shows the use of such a transformed K_D in estimating the temperature of crystallization of rocks containing garnet and biotite. Using this method of estimating temperature, Dennen, Blackburn and Quesada (1970) obtained an average temperature of 650°C for certain Grenville gneisses which agrees well with their independent estimate based on the concentration of Al^{3+} in quartz. Some of the garnet compositions particularly from low grade metamorphic rocks may represent zoning. Therefore, there is further possibility of improving the quality of the transformed K_D as a temperature indicator. It is assumed that P variation between 4 to 8 Kb does not change K_D and other substitutional relations significantly.

Concentration of Ca^{2+} in clinopyroxene

The concentration of Ca^{2+} in clinopyroxene coexisting in equilibrium with orthopyroxene may be used to estimate the P and T of crystallizstion of the rock. The solvus relations in the systems enstatite diopside (Davis and Boyd, 1966, Warner, 1971) and ferrosilite-hedenbergite (Lindsley and Munoz, 1969) may be used for this purpose. Change in P has only slight influence on this relationship (Davis and Boyd, 1966a, Warner, 1971). The main uncertainty in such estimates arise due to the fact that climopyroxene in natural assemblages are not binary solutions. Even if the concentrations of Al^{3+}, Fe^{3+} and Ti^{4+} are neglected, we still have to reckon with a ternary solution with Fe^{2+}, Ca^{2+} and Mg^{2+}.

Intra-crystalline Equilibria

Order-disorder

Chemical reactions within the crystal involve the order-disorder phenomena or the distribution of cations in the nonequivalent structural sites. The distribution isotherms for Fe^{2+}-Mg distribution between M1 and M2 sites in orthopyroxene shown in Figure 7.1 may be used to estimate the temperature of equilibrium for the intracrystalline ion-exchange reaction. Figure 8.3 shows a geothermometer for this purpose. A knowledge of the distribution coefficient K_D for the ion-exchange equilibrium

$$Fe^{2+}\ (M2) + Mg^{2+}\ (M1) \rightleftharpoons Fe^{2+}\ (M1) + Mg^{2+}\ (M2)$$

and x_{Fe}^{2+} in the orthopyroxene is enough for estimating the equilibrium temperature.

The intracrystalline ion-exchange is a rapid process. The ion-exchange, therefore, continues even after the crystallization has been completed and until the rock has cooled below a certain critical temperature. If the rock is quenched

as certain meteoritic bodies and some volcanic lavas, the intracrystalline equilibrium temperature would correspond to the temperature of the formation of the rock. In all other cases this temperature will be much lower than the actual temperature of crystallization. More information on the cooling rates of the rocks and the kinetics of ion-exchange process is necessary for estimating the temperature of crystallization of the mineral assemblage.

The peristerite solvus

Many crystalline solutions show unmixing below a certain critical temperature. This property may sometimes be used as an indicator of P and T. Plagioclases (An_2 to An_{18}) unmix into two phases with comppsitions in the range An_{0-1} and An_{25-28} below a certain critical temperature. This temperature has not been determined but it probably lies below 600°C which is the temperature of Al-Si ordering in the plagioclase (see Ribbe 1960, 1962, Brown, 1960, 1962). An experimental determination of peristerite solvus could be very useful for estimating temperature of crystallization. Crawford (1966) has made a useful study of the composition of plagioclases in rocks of varying metamorphic grade. Such petrologic studies should be useful to those who are attempting to fix the peristerite solvus experimentally.

In the system FeS-znS, the amount of FeS in sphalerite is a function of T of formation (Kullerud, 1953) when FeS coexists as a phase with sphalerite.

Sub-solidus compositional relationships between coexisting phases such as calcite-dolomite (Goldsmith and Newton, 1969) and forsterite-monticelite (Warner, 1971) may also be used for temperature estimates. It should be possible to

consider unmixing in some other crystalline solutions such as magnetic (see Rumble, 1970) as probable indicators of P and T in natural assemblages.

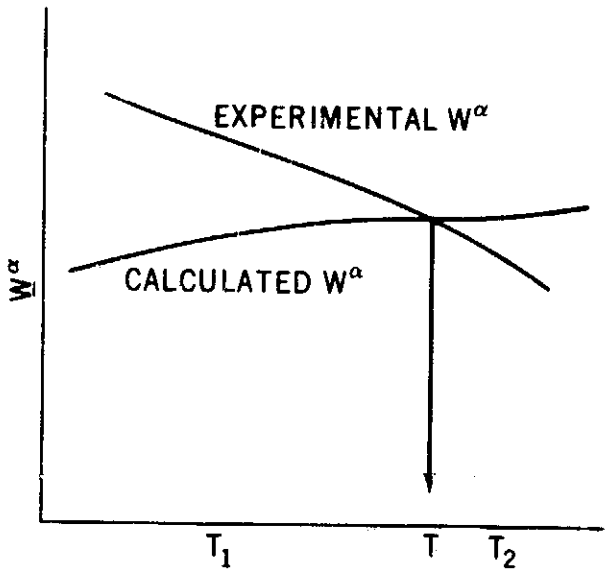

Figure 8-1. Estimation of temperature of crystallization. See text for explanation.

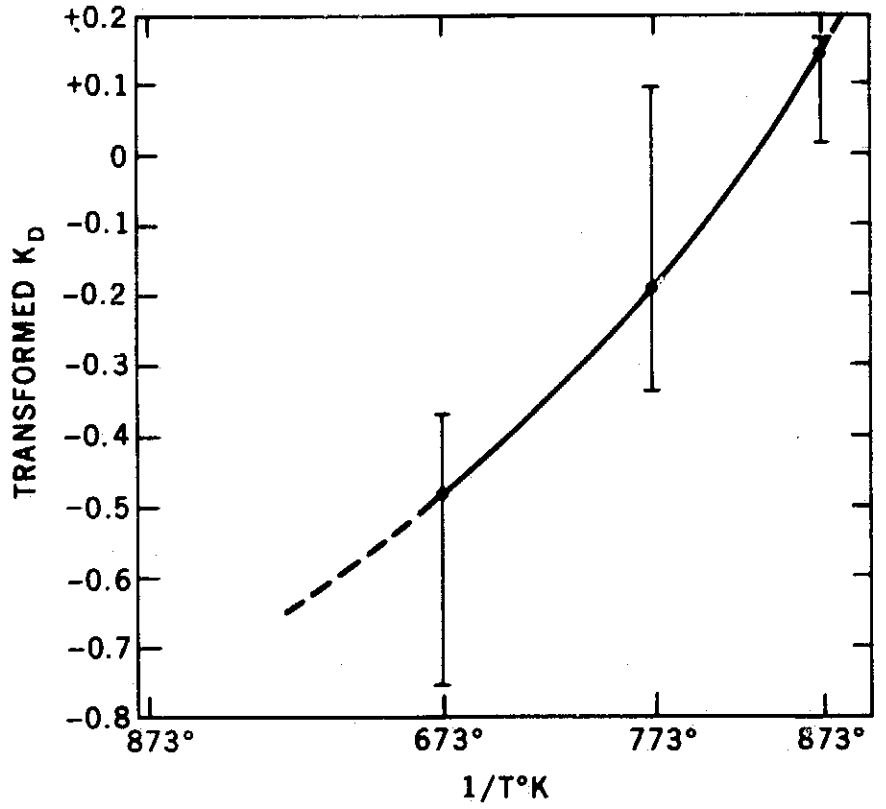

Figure 8-2. Estimation of approximate temperature of crystallization using the Mg-Fe^{2+} distribution between garnet and biotite. The bars represent the spread in the 'transformed K_D' values from rocks of the same metamosphic grade.

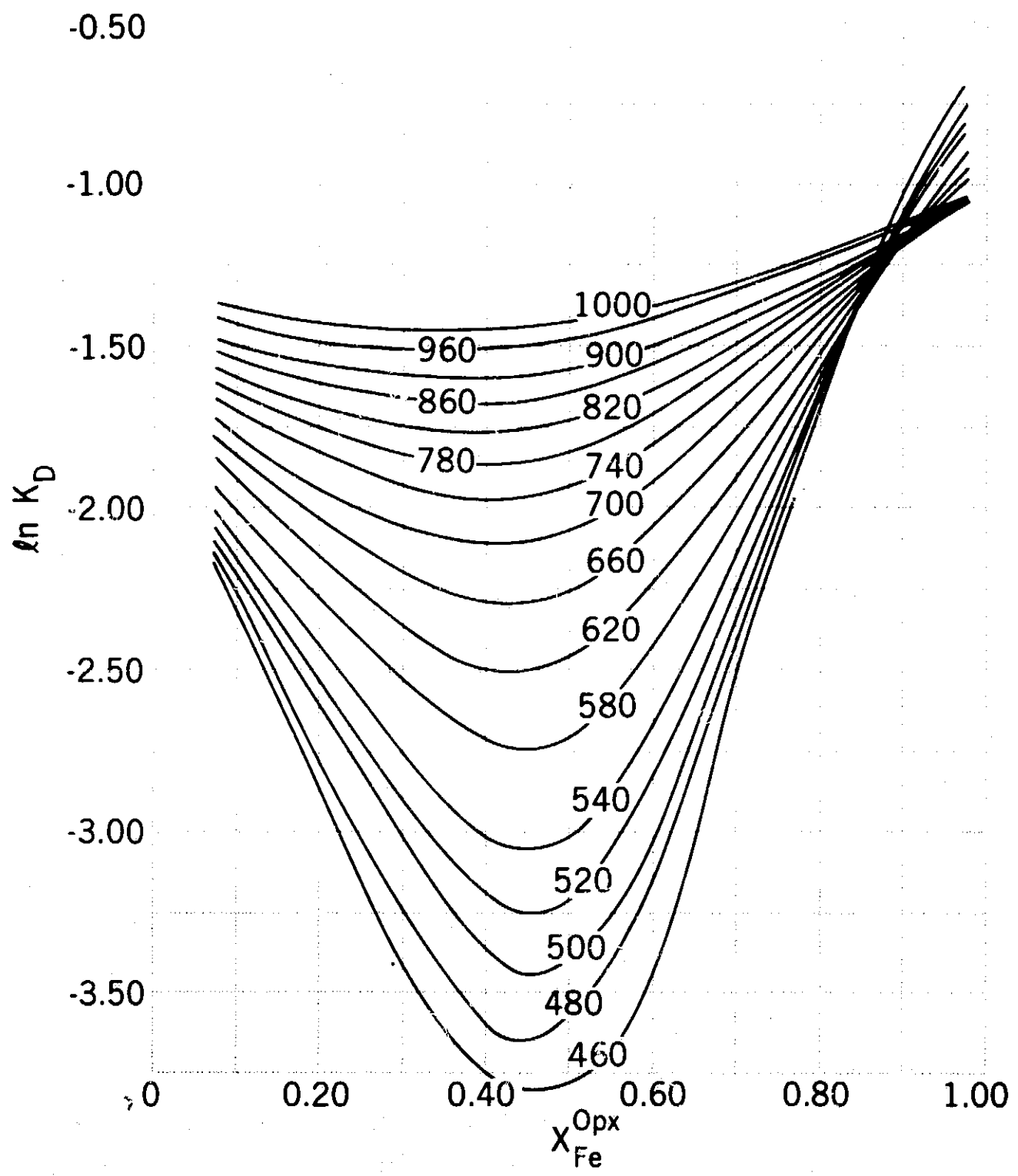

Figure 8-3. Estimation of temperature of intersite ion-exchange equilibrium in orthopyroxene. K_D is $x_{Fe}^{M1}\, x_{Mg}^{M2} / x_{Mg}^{M1}\, x_{Fe}^{M2}$. In certain rocks quenched quickly such as some meteorites and volcanics, the temperature estimated by this method is close to the temperature of rock formation.

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