

RETRIEVAL OF THERMODYNAMIC DATA FROM A STUDY OF INTER-CRYSTALLINE AND INTRA-CRYSTALLINE ION-EXCHANGE EQUILIBRIUM

S. K. SAXENA,

*Department of Geological Sciences, Virginia Polytechnic Institute
and State University, Blacksburg, Virginia 24061*

ABSTRACT

By studying the distribution of a component between two coexisting phases (inter-crystalline ion-exchange equilibrium) or between two nonequivalent sites in a crystalline solution (intra-crystalline ion-exchange equilibrium) at a certain P and T , we may obtain useful thermodynamic quantities which include the free energy, heat and entropy of mixing, and the activity-composition relation in the crystalline solutions involved. The determination of these quantities involves the use of suitable solution models for the phases or for the mixing on the individual structural sites. Examples of calculations are given for the coexisting olivine and chloride solutions and for the orthopyroxene crystalline solution. The thermodynamic properties calculated are the activity-composition relation and excess free energy of mixing in Fe^{2+} - Mg^{2+} olivine between 500 to 650°C, and the heat and entropy of mixing in orthopyroxene at 600 and 800°C.

INTRODUCTION

To understand the general principles which are the basis of our numerous petrologic phase diagrams and which can explain the chemistry and genesis of the natural mineral assemblages, we need the thermodynamic quantities for the phases involved. Kelley (1960) and Robie (1966), among others, have gathered thermodynamic data on several mineral phases. However, for most of the rock-forming crystals and crystalline solutions the data are still meager. It is, therefore, an attractive proposition to be able to obtain some useful thermodynamic information by the study of phase equilibria in either synthetic systems or in natural mineral assemblages. One such approach has been used by Thompson (1967), Thompson and Waldbaum (1969), and Green (1970). This method uses the data on coexisting minerals on the solvus bounding a two-phase region. The two phases form by unmixing of homogeneous crystalline solution at temperatures below the critical temperature of mixing. In order that we may be able to calculate the thermodynamic functions of mixing from the solvus data by using Thompson and Waldbaum's (1969) equations (5), both these phases must obey the same equation of state. In other words, the crystal structure must be the same in the two phases. Unfortunately most rock-forming solutions unmix into phases which do not have the same crystal structure. This limits

the use of the solvus data in calculating the thermodynamic quantities for such solutions if the data on the free energy of formation for the end members are not known.

The purpose of this paper is to discuss two other alternative methods. In the first method, the data on the distribution of a component between two coexisting phases at a certain P and T are used. In the second method, the data on the cation site occupancies in the crystal are used. We may term these two methods as inter-crystalline ion-exchange equilibrium method and the intra-crystalline ion-exchange equilibrium method respectively.

INTER-CRYSTALLINE ION-EXCHANGE EQUILIBRIUM METHOD

Thermodynamics

Let the excess free energy of mixing G_{EM} for a binary solution represented by the chemical formula $(A, B) M$ be given by a power series in the mole fraction $x_A (= A/A + B)$ (Guggenheim, 1937) as

$$G_{EM} = x_A x_B \{A_0 + A_1(x_A - x_B) + A_2(x_A - x_B)^2 + \dots\} \quad (1)$$

where A_0 , A_1 , and A_2 etc. are constants for a fixed P and T . The activity coefficients f are then given by

$$RT \ln f_A = x_B^2 [A_0 + A_1(3x_A - x_B) + A_2(x_A - x_B)(5x_A - x_B) + \dots] \quad (2)$$

$$RT \ln f_B = x_A^2 [A_0 - A_1(3x_B - x_A) + A_2(x_B - x_A)(5x_B - x_A) + \dots] \quad (3)$$

we may also write

$$RT \ln \frac{f_A}{f_B} = A_0(x_B - x_A) + A_1(6x_A x_B - 1) + A_2(x_B - x_A)(1 - 8x_A x_B) \quad (4)$$

An ion-exchange equilibrium at a certain P and T between two binary solutions α and β whose chemical formulae are $(A, B) M$ and $(A, B) N$ respectively may be expressed by the reaction



The equilibrium constant K_a is given by

$$K_a = \left(\frac{x_B^\alpha x_A^\beta}{x_A^\alpha x_B^\beta} \right) \left(\frac{f_B^\alpha f_A^\beta}{f_A^\alpha f_B^\beta} \right) \quad (5)$$

where α and β are used to denote phases containing M and N respectively. The term in the first bracket is the distribution coefficient

K_D . Transforming (5) into the logarithmic form, and rearranging we have

$$\ln K_D = \ln K_a - \ln \left(\frac{f_B^\alpha}{f_A^\alpha} \right) - \ln \left(\frac{f_A^\beta}{f_B^\beta} \right) \quad (6)$$

substituting relations such as (4) in (6), we have

$$\begin{aligned} \ln K_D = \ln K_a - \frac{A_0^\alpha}{RT} (x_A^\alpha - x_B^\alpha) - \frac{A_1^\alpha}{RT} (6x_A^\alpha x_B^\alpha - 1) \\ - \frac{A_0^\beta}{RT} (x_B^\beta - x_A^\beta) - \frac{A_1^\beta}{RT} (6x_A^\beta x_B^\beta - 1) \end{aligned} \quad (7)$$

It may be solved by a numeric least squares method yielding $\ln K_a$ and other constants.

If we put A_1 and A_2 equal to zero in equation (1), we have the 'simple mixture' symmetric solution model. In such a case, equation (7) may be used in the following familiar form:

$$\ln K_D = \ln K_a + \frac{W^\alpha}{RT} (1 - 2x_A^\alpha) - \frac{W^\beta}{RT} (1 - 2x_A^\beta) \quad (8)$$

where W 's are equivalent to A_0 's in equation (1).

We may also use the regular solution model with quasi-chemical approximation (Guggenheim, 1952). According to the quasi-chemical model, f_A is given by

$$f_A = \left[1 + \frac{\phi_B(\beta_1 - 1)}{\phi_A(\beta_1 + 1)} \right]^{zq_A/2} \quad (9)$$

where

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

$$\beta_1 = \{1 + 4\phi_A\phi_B(\exp 2W/zRT - 1)\}^{1/2}$$

zq may be regarded as an 'effective coordination number'. z is the coordination number and q 's are contact factors and may roughly correspond to the atomic radii ratio or the molar volume ratio (see Guggenheim, 1944, 1952; Green, 1970).

Substituting in (5) values of f_A and f_B from relations as (9), we have

$$K_D \frac{\left\{ 1 + \frac{\phi_A^\alpha(\beta_1^\alpha - 1)}{\phi_B^\alpha(\beta_1^\alpha + 1)} \right\}^{z^\alpha q_B^\alpha/2} \left\{ 1 + \frac{\phi_B^\beta(\beta_1^\beta - 1)}{\phi_A^\beta(\beta_1^\beta + 1)} \right\}^{z^\beta q_A^\beta/2}}{\left\{ 1 + \frac{\phi_B^\alpha(\beta_1^\alpha - 1)}{\phi_A^\alpha(\beta_1^\alpha + 1)} \right\}^{z^\alpha q_A^\alpha/2} \left\{ 1 + \frac{\phi_A^\beta(\beta_1^\beta - 1)}{\phi_B^\beta(\beta_1^\beta + 1)} \right\}^{z^\beta q_B^\beta/2}} = K_a \quad (10)$$

Given the quantities q_A^α , q_B^α , q_A^β , q_B^β , z^α , z^β the interchange energy W can be calculated by solving equation (6) using a numeric least squares method and substituting values of f 's from equation (9).

Example: Distribution of Fe^{2+} and Mg^{2+} between olivine and Fe-Mg chloride solution

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

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. We assume that the chloride solution is a homogeneous solution phase and present the ion-exchange equilibrium as done by Schulien *et al.* as



The equilibrium constant is given by

$$K_b = \frac{x_{Mg}^{sol}(x_{Fe}^{ol})^{1/2} f_{Mg}^{sol}(f_{Fe}^{ol})^{1/2}}{x_{Fe}^{sol}(x_{Mg}^{ol})^{1/2} f_{Fe}^{sol}(f_{Mg}^{ol})^{1/2}}$$

We may now use one of the three methods represented by equations (7), (8), and (10). 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 (7) or the quasi-chemical approximation (10).

W/RT values calculated by using the 'simple mixture' model are listed in Table 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 's, K_b , and $1/T$ (Figs. 1 and 2), we find that W^{ol}/RT at 450°C is 2.0, and W^{sol}/RT and K_b are 0.91 and 0.76 respectively.

Figure 3 shows the distribution isotherms calculated by using the data in Table 1 at 500, 550, and 650°C. The isotherm at 450°C is plotted using the linearly extrapolated values of K_b , W^{ol} , and W^{sol} . The model does not fit to this distribution isotherm at the Mg-rich end. Figure 4 shows the activity-composition relation in olivine (Fe_2SiO_4 - Mg_2SiO_4) at 500 and 550°C. At 650°C olivine is close to ideal solution.

TABLE 1. INTER-CHANGE ENERGY W AND THE STANDARD FREE ENERGY CHANGE ΔG^0 IN OLIVINE-CHLORIDE SOLUTION SYSTEM

T°C	$\frac{W^{so1}}{RT}$	$\frac{W^{o1}}{RT}$	$-RT \ln K$ = ΔG_{sb}^0 , 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

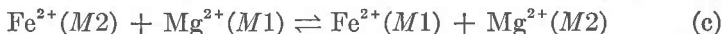
INTRACRYSTALLINE ION-EXCHANGE EQUILIBRIUM METHOD

If in a binary crystalline solution, we have two or more non-equivalent structural sites, the two components are distributed between the sites. This distribution may be a function of temperature and chemical composition. The equations (a) and (5) to (10) are equally applicable to such an ion-exchange equilibrium. We may then consider that α and β refer to the nonequivalent sites within a crystalline solution. The method of calculating the thermodynamic functions of mixing is explained by using the site occupancy data in orthopyroxenes.

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 non-equivalent 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.

Inter-site ion-exchange

$M1$ 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



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

$$K_c = \frac{x_{F_o}^{M1_f} x_{M_g}^{M2_f}}{x_{F_o}^{M2_f} x_{M_g}^{M1_f}}$$

K_c is mainly a function of T , P has little influence. The standard

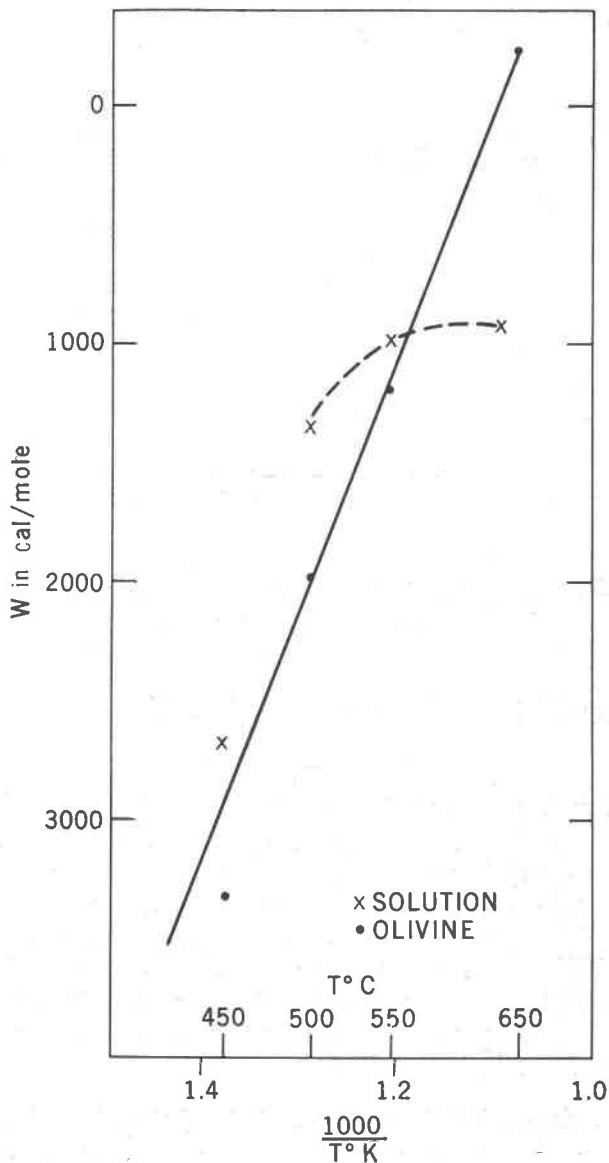


FIG. 1. W^{o1} and W^{s1} plotted against $1/T$.

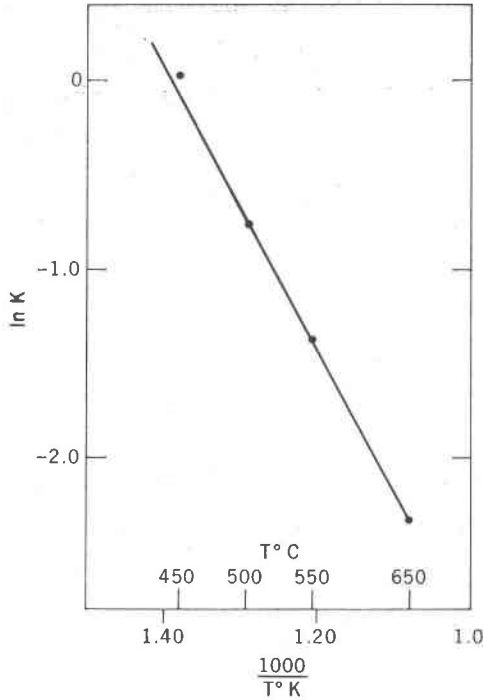


FIG. 2. $\ln K$, for the distribution of Mg^{2+} and Fe^{2+} between chloride solution and olivine, plotted against $1/T$.

free energy for ion-exchange at a certain T is

$$\Delta G_c^0 = -RT \ln K_c \quad (11)$$

This energy is a part of the total Gibbs free energy of the crystal and is, therefore, an important thermodynamic quantity. To determine ΔG_c^0 or K_c , we need first, the determination of the atomic fractions x_{Fe}^{M1} and x_{Fe}^{M2} 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 5 (Figs. 1 and 2, Ghose, 1965) shows a scheme of ordering in orthopyroxene crystals as a whole. In hypersthene ($\text{Fs}_{50} \text{En}_{50}$) 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 expect 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, thermodynamics of the ion-exchange below a certain transition temperature precludes the ordered structure shown in Figure 5, at all temperatures above absolute zero.

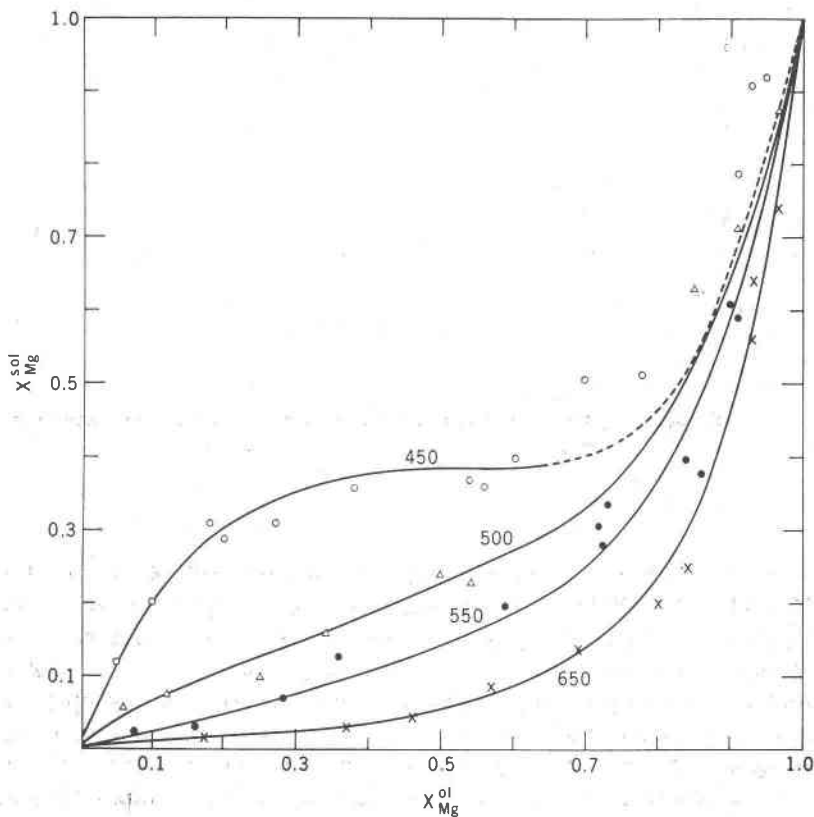


Fig. 3. Distribution of Mg^{2+} and Fe^{2+} between olivine and chloride solution. The data points are from Schullien *et al.* (1970). Crosses 650°C, solid circles 550°C, triangles 500°C, and open circles 450°C. The curves are least squares curves using 'simple mixture' model for both the solutions.

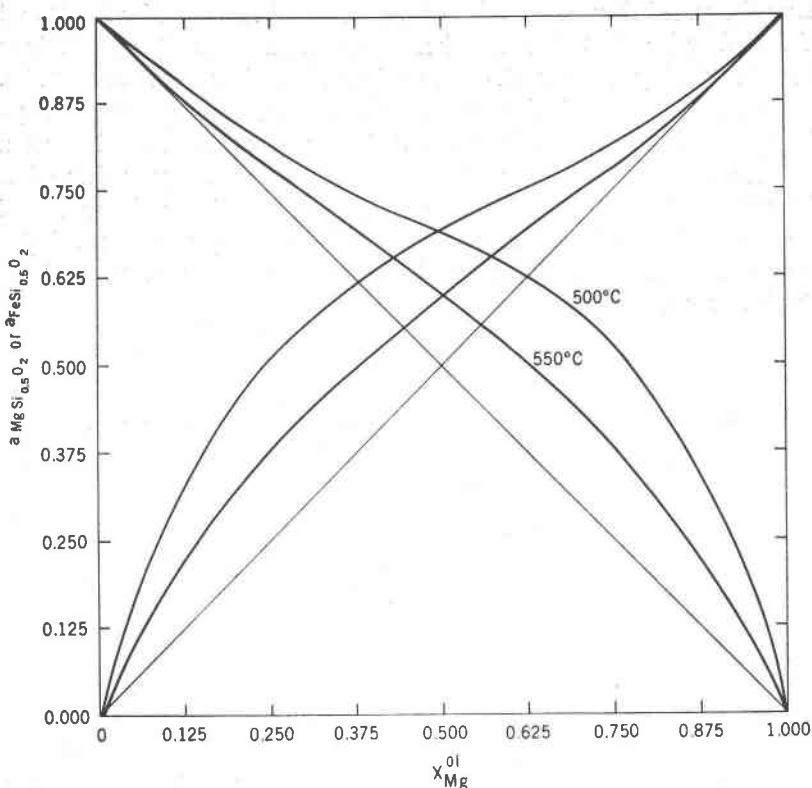


FIG. 4. Activity-composition relation in olivine $(\text{MgFe}) \text{Si}_{1.5}\text{O}_2$ at 500 and 550°C. At 650°C, olivine is found to be nearly ideal.

For considering the ion-exchange (c) we are required to consider $M1$ and $M2$ individually as sub-systems. Complete order in the crystal as a whole as shown in Figure 5 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 the 'simple mixture' model. The thermodynamic functions of mixing using this model have been calculated and discussed before by Saxena and Ghose (1971). The effect of ordering on the sites is considered here by using the quasi-chemical approximation.

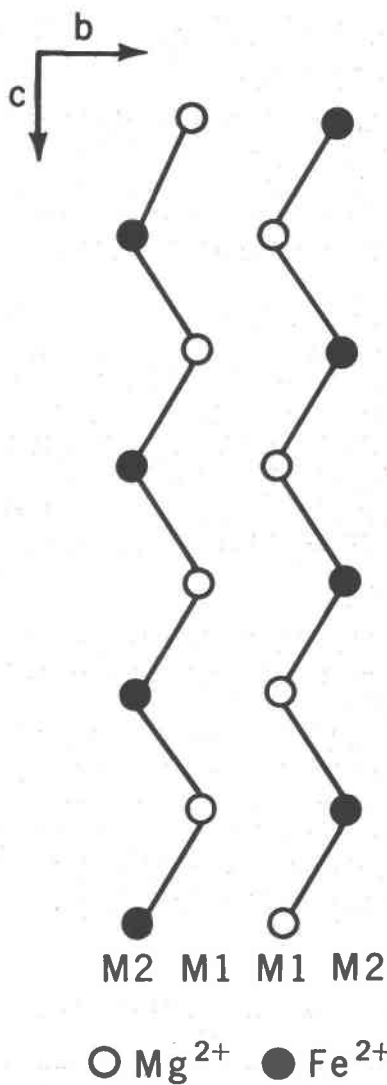


Fig. 5. Mg²⁺-Fe²⁺ ordering scheme in an orthopyroxene (Ghose, 1965).

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

If we substitute $M1$, $M2$, Mg²⁺ and Fe²⁺ for α , β , A and B in equations (9) and (10), we have the relation among K_α , β^{M1} and β^{M2} . β 's are given by the equations:

$$\beta^{M1} = \{1 + 4\phi_{M2}^{M1}\phi_{Fe}^{M1}(\exp 2W^{M1}/RTz^{M1} - 1)\}^{1/2} \quad (12)$$

$$\beta^{M2} = \{1 + 4\phi_{Mg}^{M2}\phi_{Fe}^{M2}(\exp 2W^{M2}/RTz^{M2} - 1)\}^{1/2} \quad (13)$$

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^{2+} 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 5 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 (10) $Z^{M1} = Z^{M2} = 2$ and all q 's as unity.

Results of calculations

The intracrystalline distribution data presented in Saxena and Ghose (1971) was used to determine the quasi-chemical parameters W^{M1} and W^{M2} and the equilibrium constant K_c by using least squares analysis as suggested in the previous section. The distribution data at 500°C was not used and the number of data points at 700°C was not found sufficient for a satisfactory convergence. The values of W^{M1} , W^{M2} , and K_c at 600 and 800°C are listed in Table 2. Chi square values for the simple mixture model and for the quasi-chemical approximation are not significantly different.

TABLE 2. QUASI-CHEMICAL PARAMETERS W^{M1} AND W^{M2} AND K_c AS CALCULATED BY (10).

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

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

Activity-composition relation at 600°C

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

$$f_{\text{Fe}}^{M1} = \left\{ 1 + \frac{\phi_{\text{Mg}}^{M1}(\beta - 1)}{\phi_{\text{Fe}}^{M1}(\beta + 1)} \right\}^{z_{\text{Fe}}^{M1/2}} \quad (14)$$

and similarly for f_{Fe}^{M1} and finally determine the activity-composition relation in the crystal as a whole by the equation:

$$a_{\text{Fe}}^{\text{Opx}} = (x_{\text{Fe}}^{M1} f_{\text{Fe}}^{M1})^{1/2} (x_{\text{Fe}}^{M2} f_{\text{Fe}}^{M2})^{1/2} \quad (15)$$

The results of such calculations are presented in Figure 6. The figure shows that there is very little difference between the activities calculated by assuming the sites as 'simple mixtures' or as solutions with quasi-chemical approximation.

Free energy, heat, and entropy of mixing in orthopyroxene

The free energy of mixing was calculated for the crystal as a whole by Saxena and Ghose (1971), using the following relation:

$$G_{\text{EM}}^{\text{Opx}} / x_{\text{Fe}}^{\text{Opx}} x_{\text{Mg}}^{\text{Opx}} = A_0 + A_1(x_{\text{Fe}}^{\text{Opx}} - x_{\text{Mg}}^{\text{Opx}}) + A_2(x_{\text{Fe}}^{\text{Opx}} - x_{\text{Mg}}^{\text{Opx}})^2 + \dots \quad (16)$$

which is of the form $Y = a_0 + a_1x_1 + a_2x_1^2 + \dots$ and may be solved by a least squares program. The values of excess free energy as calculated by Saxena and Ghose (1971) are used to calculate the three constants A_0 , A_1 , and A_2 shown in Table 3 by using a least squares program on equation (16). Figure 7 shows three curves at 600, 700, and 800°C fitted to the data on reduced excess free energy ($G_{\text{EM}}/x_{\text{Fe}} x_{\text{Mg}}$) versus $(x_{\text{Fe}} - x_{\text{Mg}})$. 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 $1/T$ are given by

$$A_0 = 10802 - 33862\left(\frac{10^3}{T}\right) + 35135\left(\frac{10^3}{T}\right)^2 - 11202\left(\frac{10^3}{T}\right)^3 \quad (17)$$

$$A_1 = 1789 - 3612\left(\frac{10^3}{T}\right) + 2008\left(\frac{10^3}{T}\right)^2 \quad (18)$$

$$A_2 = -13863 + 41051\left(\frac{10^3}{T}\right) - 40299\left(\frac{10^3}{T}\right)^2 + 13426\left(\frac{10^3}{T}\right)^3 \quad (19)$$

The heat of mixing and the entropy of mixing can now be readily

calculated using the following equations:

$$-S_{EM}^{OPx} = x_{Fe}^{OPx} x_{Mg}^{OPx} \left[\frac{\partial A_0}{\partial T} + \frac{\partial A_1}{\partial T} (x_{Fe}^{OPx} - x_{Mg}^{OPx}) + \frac{\partial A_2}{\partial T} (x_{Fe}^{OPx} - x_{Mg}^{OPx})^2 + \dots \right] \quad (20)$$

$$H_{EM}^{OPx} = x_{Fe}^{OPx} x_{Mg}^{OPx} \left[A_0 - T \left(\frac{\partial A_0}{\partial T} \right) + \left\{ A_1 - T \left(\frac{\partial A_1}{\partial T} \right) \right\} (x_{Fe}^{OPx} - x_{Mg}^{OPx}) + \left\{ A_2 - T \left(\frac{\partial A_2}{\partial T} \right) \right\} (x_{Fe}^{OPx} - x_{Mg}^{OPx})^2 + \dots \right] \quad (21)$$

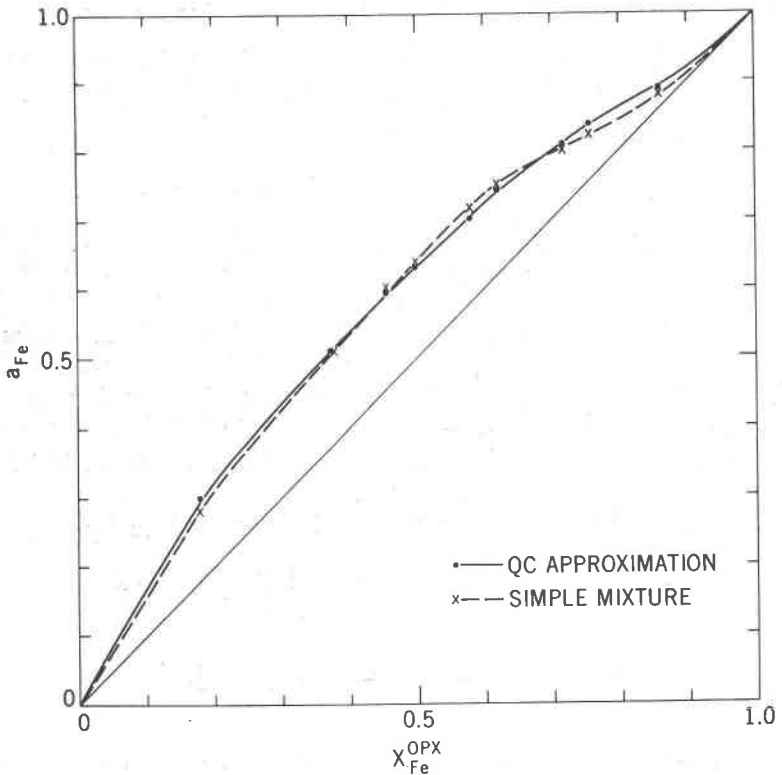


Fig. 6. Activity-composition relation for $FeSiO_3$ in orthopyroxene crystalline solution using 'simple mixture' and quasi-chemical models for the sites.

TABLE 3. THE THREE CONSTANTS A_0 , A_1 , AND A_2 OBTAINED BY A LEAST SQUARES FIT TO EQUATION (16). THE VALUES IN PARENTHESES WERE CALCULATED BY USING EQUATIONS (17) TO (19)

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)

Free energy of mixing and the M1 and M2 polyhedra

The free energy of mixing is given by

$$G_M^{\text{Opx}} = H_{EM}^{\text{Opx}} - TS_{EM}^{\text{Opx}} + RT(x_{Fe}^{\text{Opx}} \ln x_{Fe}^{\text{Opx}} + x_{Mg}^{\text{Opx}} \ln x_{Mg}^{\text{Opx}}) \quad (22)$$

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

$$G_M^{\text{Opx}} = \left(\frac{x_{Fe}^{M1} - x_{Fe}^{M2}}{2} \Delta G_c^0 \right) + (H_{EM}^{M1} + H_{EM}^{M2}) - T(S_I^{M1} + S_I^{M2} + S_{EM}^{M1} + S_{EM}^{M2}) \quad (23)$$

Equation (23) is similar to the equation derived by Grover and Orville (1969).

Note that $H_{EM}^{\text{Opx}} \neq (H_{EM}^{M1} + H_{EM}^{M2})$ and similarly $TS_{EM}^{\text{Opx}} \neq T(S_{EM}^{M1} + S_{EM}^{M2})$. The expression (23) divides the total free energy of mixing into three terms. The term in the first bracket is the potential due to the difference in the 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. Figures 8 and 9 show a comparison of the various functions of mixing at 600 and 800°C. The values of H_{EM} and TS_{EM} for the crystal as a whole are obtained by

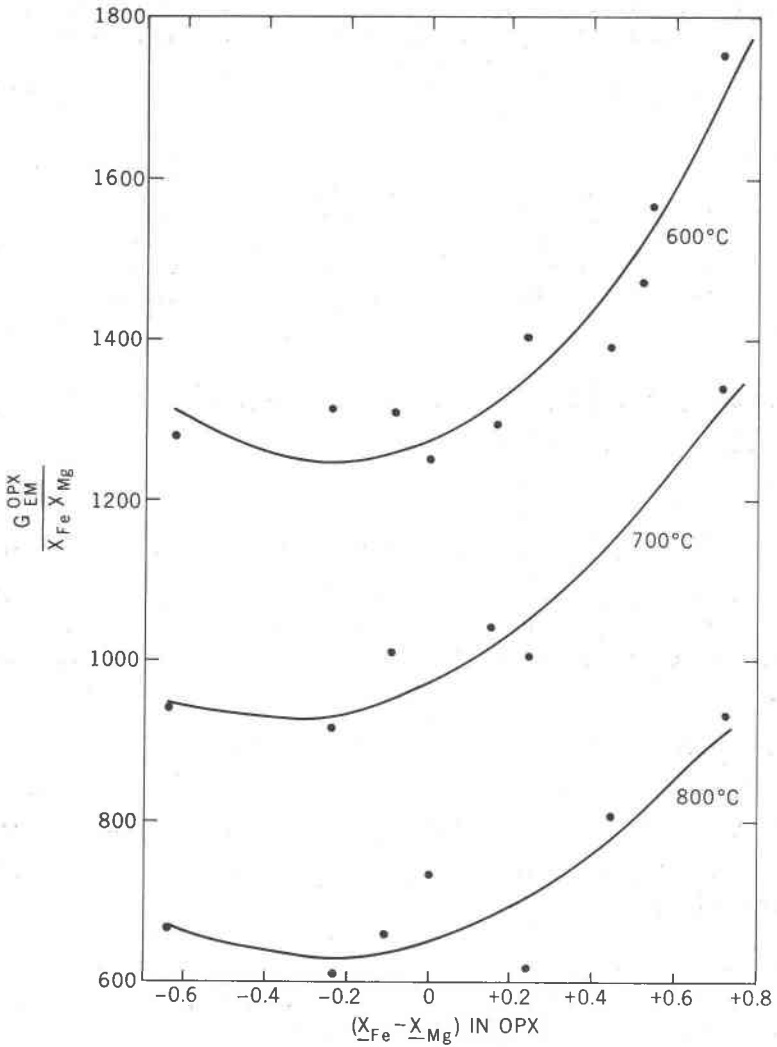


FIG. 7: Reduced excess free energy of mixing plotted against $(x_{Fe} - x_{Mg})$ in orthopyroxene. The curves are least squares fit using the equation (16).

using equations (20) and (21). It may be noted that the first energy term

$$\left(\frac{x_{Fe}^{M1} - x_{Fe}^{M2}}{2} \Delta G_c^0 \right)$$

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

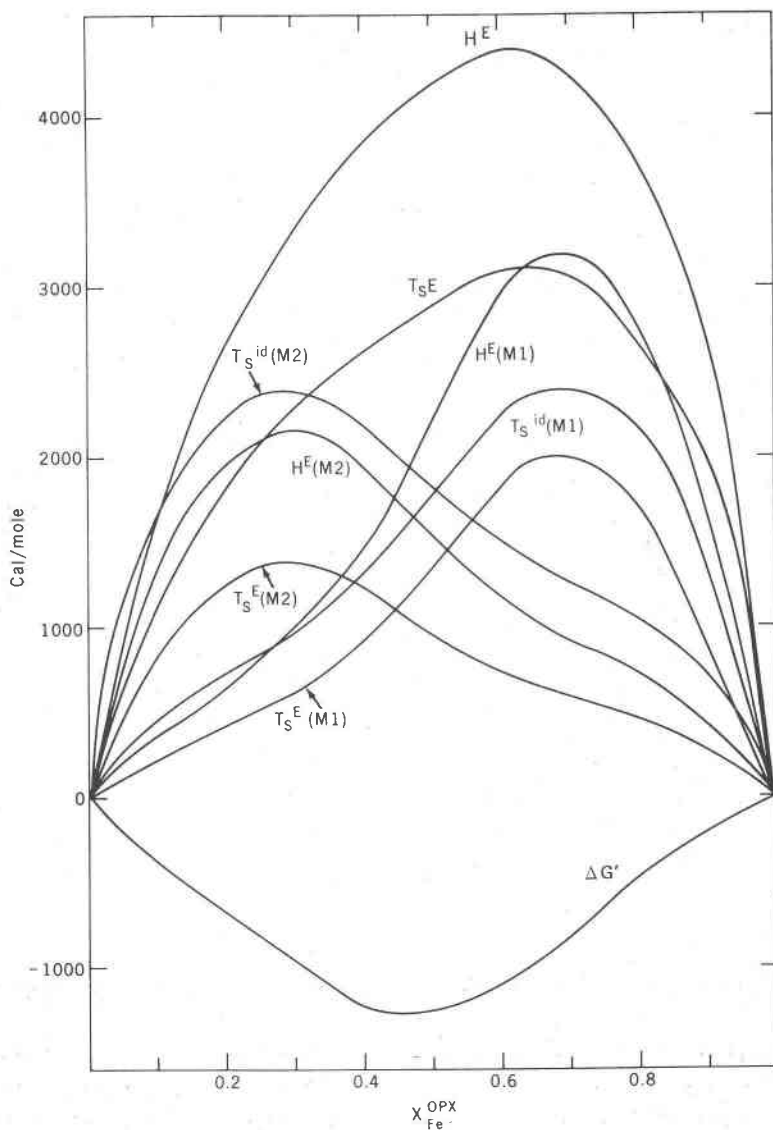


Fig. 8. Thermodynamic functions of mixing in orthopyroxene at 600°C, both at the sites and in the crystal as a whole plotted against x_{Fe}^{OPX} . The functions of mixing at the sites correspond to the atomic fractions at $M1$ and $M2$ which in turn correspond to an equilibrium distribution at 600°C in the crystal with x_{Fe}^{OPX} as measured on the abscissa. The symbols S^E , H^E , and S^{id} are excess entropy, excess enthalpy, and ideal entropy of mixing. $\Delta G'$ is $1/2(x_{Fe}^{M1} - x_{Fe}^{M2})\Delta G_c^0$.

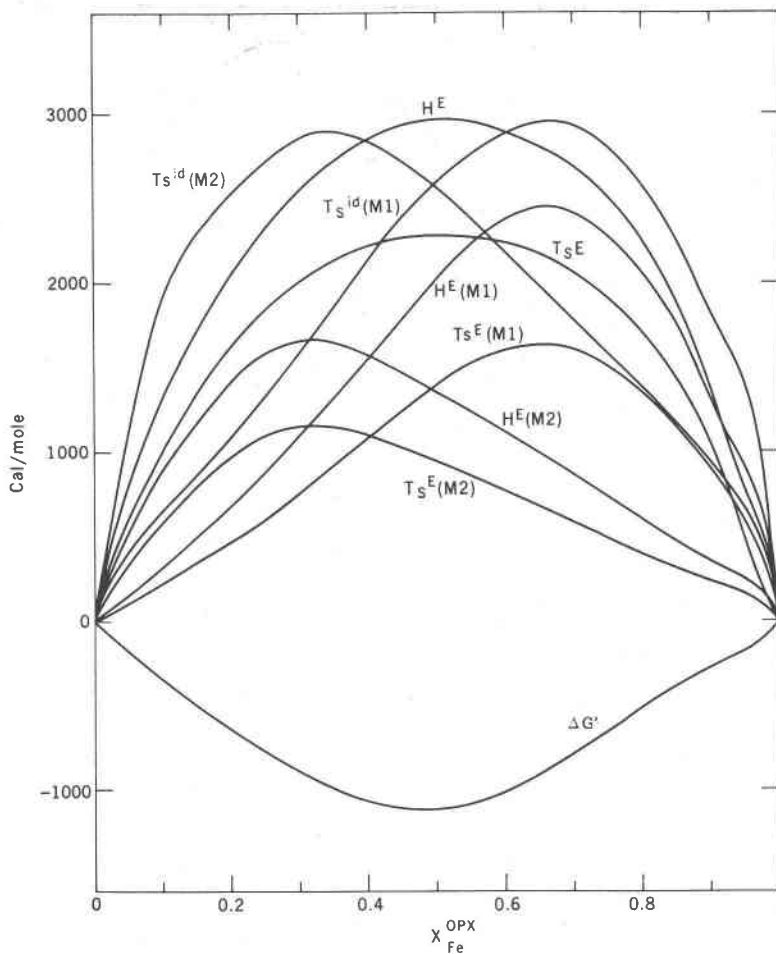


FIG. 9. Thermodynamic functions of mixing 800°C plotted similarly as in Figure 8.

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.

According to a preliminary observation by Virgo and Hafner (1969), the *M1* polyhedra is somewhat distorted at the enstatite end but becomes more and more regular with increasing $\text{Fe}^{2+}/\text{Mg}^{2+}$ ratio. The *M2* polyhedra is quite distorted at the enstatite end and the distortion increases with increasing Fe^{2+}/Mg ratio. These changes in the polyhedra are directly correlated with the entropy and enthalpy of mixing on the sites. As the regularity increases in *M1*, the energies of mixing increase. As the distortion increases in *M2*, the energies of mixing decrease. Thus we require more energy into the system to increase the regularity of *M1*. Energy requirements become less as distortion increases in *M2*.

These results indicate that it may be possible to predict the changes in the *M1* and *M2* polyhedral spaces as a function of temperature and composition by determining the thermodynamic functions of mixing at the sites. Since the geometry of the polyhedra is determined by the various bond lengths, such correlations between the functions of mixing and the geometry of the polyhedra may eventually lead to bridging the gap between crystal-chemistry and thermodynamics of silicate crystalline solutions.

ACKNOWLEDGMENTS

Thanks are due to Dr. R. F. Mueller for useful discussions. Collaboration with Dr. S. Ghose provided the basis for development of some of the ideas expressed here. Mrs. Patricia Comella gave her invaluable help in programming. A least squares program by Dr. L. Finger at the Geophysical Laboratory is thankfully acknowledged. Dr. L. S. Walter encouraged this approach and provided many excellent facilities for work at the Goddard Space Flight Center.

REFERENCES

- EVANS, B. J., S. GHOSE, AND S. HAFNER (1967) Hyperfine splitting of ^{57}Fe and Mg-Fe order-disorder in orthopyroxenes (MgSiO_3 - FeSiO_3) solid solution. *J. Geol.* **75**, 306-322.
- GHOSE, S. (1965) Mg^{2+} - Fe^{2+} order in an orthopyroxene, $\text{Mg}_{0.88}\text{Fe}_{1.07}\text{Si}_2\text{O}_6$. *Z. Kristallogr.* **122**, 81-99.
- GREEN, E. J. (1970) Predictive thermodynamic models for mineral systems. I. Quasi-chemical analysis of the halite-sylvite subsolidus. *Amer. Mineral.* **55**, 1692-1713.
- GROVER, J. E., AND P. M. ORVILLE (1969) The partitioning of cations between co-existing single- and multi-site phases with application to the assemblages: orthopyroxene-clinopyroxene and orthopyroxene-olivine. *Geochim. Cosmochim. Acta*, **33**, 205-226.
- GUGGENHEIM, E. A. (1937) Theoretical basis of Raoult's law. *Trans. Faraday Soc.* **33**, 151-159.
- (1944) Statistical thermodynamics of mixtures with non-zero energies of mixing. *Proc. Royal Soc. London A*, **183**, 213-227.

- (1952) *Mixtures*. Clarendon Press, Oxford.
- KELLEY, K. K. (1960) Contributions to the data on theoretical metallurgy. XIII. High-temperature heat-content, heat-capacity and entropy data for the elements and inorganic compounds. *U. S. Bur. Mines Bull.* 584.
- ROBIE, R. A. (1966) Thermodynamic properties of minerals. *Geol. Soc. Amer. Mem.* 97, 442-458.
- SAXENA, S. K., AND S. GHOSE (1971) Mg^{2+} - Fe^{3+} order-disorder and the thermodynamics of the orthopyroxene-crystalline solution. *Amer. Mineral.* 56, 532-559.
- SCHULIEN, S., H. FRIEDRICHSEN, AND E. HELLNER (1970), Das mischkristallverhalten des olivine zwischen 240° and 650°C bei 1 kb druck. *Neues. Jahrb. Mineral. Monatsh.* 4, 141-147.
- THOMPSON, J. B. JR. (1967) Thermodynamic properties of simple solutions. In P. H. Abelson, ed. *Researches in Geochemistry II*, John Wiley and Sons, New York, p. 340-361.
- , AND D. R. WALDBAUM (1969) Analysis of the two-phase region halite-sylvite in the system NaCl-KCl. *Geochim. Cosmochim. Acta*, 33, 671-690.
- VIRGO, D., AND S. HAFNER (1969) Fe^{2+} , Mg^{2+} order-disorder in heated orthopyroxenes. *Mineral. Soc. Amer. Spec. Pap.* 2, 67-81.

Manuscript received, November 27, 1971; accepted for publication, May 19, 1972.