APPLICATION OF THERMODYNAMICS TO SILICATE CRYSTALLINE SOLUTIONS

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The application of chemical thermodynamics to petrology and mineralogy requires a special discussion of thermodynamic parameters and concepts such as the definitions of crystalline solutions and chemical components and their potentials. A brief review of thermodynamic relations is presented, describing Guggenheim's regular solution models, the simple mixture, the zeroth approximation, and the quasi-chemical model. The possibilities of retrieving useful thermodynamic quantities from phase equilibrium studies are discussed. Such quantities include the activity-composition relations and the free energy of mixing in crystalline solutions. Theory and results of the study of partitioning of elements in coexisting minerals are briefly reviewed. A thermodynamic study of the intercrystalline and intracrystalline ion-exchange relations gives useful information on the thermodynamic behavior of the crystalline solutions involved. Such information is necessary for the solution of most petrogenic problems and for geothermometry. Thermodynamic quantities for tungstates (CaWO$_4$-SrWO$_4$) are calculated.
FOREWORD

Today petrologists, mineralogists, and crystallographers are the possessors of very-well-equipped laboratories. The laser probe, the electron microprobe, and the ion microprobe mass analyzer can produce results within minutes, results that used to take days and weeks to attain. Besides X-ray methods, there are several spectroscopic techniques, such as Mössbauer spectroscopy, that can be used to examine the distribution of cations over nonequivalent structural sites in a crystal. The experimental methods of synthesizing mineral assemblages in the laboratories have been greatly improved. Refined techniques exist for the control of gas fugacities and the creation of low to very high pressure and temperature conditions in petrological experiments. These technical capabilities are further enhanced by the use of computers, which can analyze numerical data and the consistency or inconsistency of experiments.

As a result of increased experimental capability, phase equilibria data have been gathered both from efforts to synthesize mineral assemblages in the laboratory and from chemical analysis of natural mineral assemblages. To make a meaningful analysis of both these types of data, thermodynamic data on rock-forming phases and crystalline solutions must be available. Unfortunately, obtaining these quantities by thermochemical and calorimetric methods has been a very slow process, and the possibility of obtaining such quantities by other methods must be considered.

In suitable cases, retrieving thermodynamic data from the phase diagrams themselves may be considered. These quantities 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 (1969a,b), and Green (1970). These methods, however, are of limited use for rock-forming silicates because many crystalline solutions do not show any solvus relationship. The second type of phase diagram is the Roozeboom-type figure in which the concentration of a component in one phase is plotted against the concentration of the same component in the coexisting phase. Such a distribution relationship, based on simple ion-exchange reactions, was discussed initially by Ramberg and DeVore (1951) and later by Kretz (1959) and Mueller (1960). It is possible to retrieve useful thermodynamic information from the distribution data in ion exchange 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 an interesting Fe$^{2+}$-Mg$^{2+}$ distribution in cummingtonite. Since then, Fe$^{2+}$-Mg$^{2+}$ order-disorder has been studied in several silicates by crystallographers. Theoretical framework for considering the homogeneous equilibria of intracrystalline...
cation distribution has been presented in papers by Mueller (1962), Matsui and Banno (1965), Perchuk and Ryabchikov (1968), Thompson (1969), and Grover and Orville (1969).

The purpose of this work is to discuss these methods of obtaining thermodynamic quantities and some aspects of partitioning elements in coexisting phases by considering the definition of crystalline solutions, the definition of components in a silicate mineral, and the definition of chemical potentials of these components. The solution models involved are also considered. An example of calculating thermodynamic functions of mixing in the CaWO$_4$-SrWO$_4$ system is given.

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

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

\[ d_A^a \] activity of component A in phase \(a\)

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

\( A, B, C \) 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

\( f \) activity coefficient

\( G \) molar Gibbs free energy

\( G_{EM} \) excess molar Gibbs free energy of mixing

\( G_{IM} \) ideal molar Gibbs free energy of mixing (= \( \sum RT \ln x_i \))

\( G_M \) total molar Gibbs free energy of mixing

\( H \) molar enthalpy

\( H_{EM} \) excess molar enthalpy of mixing

\( H_M \) molar enthalpy of mixing

\( K \) thermodynamic equilibrium constant

\( K_D \) distribution coefficient

\( M1, M2 \) structural sites in the crystal

\( \mathcal{N} \) Avogadro’s number

\( P \) pressure

\( q \) contact factor

\( R \) gas constant

\( S \) molar entropy

\( S_{EM} \) excess molar entropy of mixing
$S_{IM}$ ideal molar entropy of mixing

$S_M$ molar entropy of mixing

$T$ absolute temperature

$T_c$ critical temperature

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

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

$W'$ $\sim w$ where $w$ is independent of $P$ and $T$

$x_i^\alpha$ mole fraction of a component $i$ in phase $\alpha$

$z$ coordination number

$\mu_i^\alpha$ chemical potential of a component $i$ in phase $\alpha$

$\mu_i^{AM}$ chemical potential of a pure component AM

alm almandine: $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

bi biotite: $\text{K(Fe, Mg)}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$

en enstatite: $\text{MgSi}_3\text{O}_6$ or $\text{MgMgSi}_2\text{O}_6$

gar garnet: $(\text{Mg, Fe, Ca, Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$

ol olivine: $(\text{Fe, Mg})_2\text{SiO}_4$

opx orthopyroxene: $(\text{Mg, Fe})\text{SiO}_3$ or $(\text{Mg, Fe})_2\text{Si}_2\text{O}_6$
Chapter 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 (1966), Guggenheim (1952, 1967), and Prigogine and Defay (1954), among others. Recently Thompson (1967) also considered the properties of simple solutions. Besides a summary of thermodynamic relations in solutions, the difficulties encountered in their application to silicate minerals will be considered. 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

The crystalline solutions considered here are rock-forming silicates forming isomorphous series with one another. Such crystalline solutions have a definite structural framework 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.

Orthopyroxene (opx) (Mg, Fe)\textsubscript{2}Si\textsubscript{2}O\textsubscript{6} may be considered as an example. In the crystal structure there are single silicate chains parallel to the c-axis held together by the octahedrally coordinated Mg\textsuperscript{2+} and Fe\textsuperscript{2+}. There are two kinds of structurally nonequivalent sites M1 and M2 occupied by Mg\textsuperscript{2+} and Fe\textsuperscript{2+}. The M1 octahedral space is nearly regular polyhedral, but the M2 space is quite distorted. As a result of varying Mg\textsuperscript{2+} and Fe\textsuperscript{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\textsubscript{3} and FeSiO\textsubscript{3} or the molecules MgO, FeO, and SiO\textsubscript{2} or the ions Mg\textsuperscript{2+}, Fe\textsuperscript{2+}, Si\textsuperscript{4+}, and O\textsuperscript{2−}. In petrological studies, the choice of a component is determined by
known or postulated chemical reactions involving a mineral. In such studies, the use 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, when the thermodynamic properties of silicate crystalline solutions are being considered, 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 orthopyroxene does not produce 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

$$\mu_i = \mu^i + R T \ln x_i,$$

where $\mu_i$ is the chemical potential of $i$ in a solution and $\mu^i$ is the chemical potential of pure $i$. $\mu^i$ is a function of pressure ($P$) and temperature ($T$) only. In a binary solution $\alpha$ whose composition is $(A, B)M$, where $M$ represents the anion group or the silicate framework and $A$ and $B$, the cations that 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

$$x^\alpha_A = \frac{A}{A + B},$$

or

$$x^{\alpha AM}_A = \frac{AM}{AM + BM}.$$

These expressions could be considered equivalent to each other. For chemical potentials,

$$\mu^{\alpha}_A = \mu^{AM}_A + R T \ln x^{\alpha}_A,$$

or

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

where $\mu^{AM}_A$ and $\mu^{AM}$ 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 experimentally measurable, but the meaning of free energy of Mg$^{2+}$ in pure enstatite (en) is little understood and experimental methods remain to be developed for its measurement.

In theoretical discussions, however, in which the measured values of the potentials are not of concern, 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

$$\mu^{AM}_A + R T \ln x^{\alpha}_{AM},$$
\[ \mu_{\text{Mg}} = \left( \frac{\partial G}{\partial n_{\text{Mg}}} \right)_{P, T, n_{\text{Fe}}, n_{\text{Si}}, n_{0}} \]  

(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 (ol) \([\text{Fe}, \text{Mg})_2\text{SiO}_4]\) and garnet (gar) \([\text{Fe, Mg)}_3\text{Al}_2\text{Si}_3\text{O}_{12}\). The chemical potential of a component using the molecular model is expressed as

\[ \mu_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} = \mu_{\text{Fe}_2\text{SiO}_4} + RT \ln x_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} \]  

(1-5)

and

\[ \mu_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} = \mu_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}} + RT \ln x_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} \]  

(1-6)

where the first \( \mu \) in both equations is the chemical potential of the end member in the solution and the second \( \mu \) is the chemical potential of the pure end member. If the cation \( \text{Fe}^{2+} \) is considered as a component,

\[ \mu_{\text{Fe}}^{\text{ol}} = \frac{1}{2} \mu_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} + 2RT \ln x_{\text{Fe}}^{\text{ol}} \]  

(1-7)

and

\[ \mu_{\text{Fe}}^{\text{gar}} = \frac{1}{3} \mu_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} + 3RT \ln x_{\text{Fe}}^{\text{gar}} \]  

(1-8)

where the first \( \mu \) in both equations is the chemical potential of \( \text{Fe}^{2+} \) in the crystalline solution and the second \( \mu \) is the chemical potential of \( \text{Fe}^{2+} \) in the pure end member. The mole fractions \( x \) are the same quantities in both the molecular and ionic models. It may be desirable to consider the chemical formula on a one-cation basis; i.e., olivine is considered to be \((\text{Fe, Mg})_0.5\text{Si}_0.5\text{O}_2\) and garnet to be \((\text{Mg, Fe})_{2/3}\text{Si}_0.5\text{O}_4\). In this case,

\[ \mu_{\text{Fe}}^{\text{ol}} = \frac{1}{2} \mu_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} + RT \ln x_{\text{Fe}}^{\text{ol}} \]  

or

\[ \mu_{\text{FeSi}_{0.5}\text{O}_2}^{\text{ol}} = \frac{1}{2} \mu_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} + RT \ln x_{\text{FeSi}_{0.5}\text{O}_2}^{\text{ol}} \]  

(1-10)

and

\[ \mu_{\text{Fe}}^{\text{gar}} = \frac{1}{3} \mu_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} + RT \ln x_{\text{Fe}}^{\text{gar}} \]  

(1-11)

or

\[ \mu_{\text{FeAl}_{2/3}\text{Si}_0.5\text{O}_4}^{\text{gar}} = \frac{1}{3} \mu_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} + RT \ln x_{\text{FeAl}_{2/3}\text{Si}_0.5\text{O}_4}^{\text{gar}} \]  

(1-12)

The usefulness of these relations is mentioned later in connection with the composition of coexisting minerals.
The activities of the components will be the primary concern of this document. For a binary ideal solution, the activity is equal to its mole fraction. In olivine the activity of the fayalite (fa) molecule is

$$a_{fa} = x_{fa}^{01},$$

or for Fe$^{2+}$,

$$a_{Fe} = (x_{Fe}^{01})^2.$$  

(1-13)

(1-14)

Similarly for garnet and almandine (alm),

$$a_{alm} = x_{alm}^{gar},$$

and

$$a_{Fe} = (x_{Fe}^{gar})^3.$$  

(1-15)

(1-16)

It is desirable to consider many reactions, particularly the ion-exchange reaction, on a one-cation basis; i.e., to 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 $x_{Fe}$ [the mole fraction Fe$^{2+}$/ (Fe$^{2+}$ + Mg$^{2+}$)] is numerically the same as $x_{fa}$ (the percent of fayalite), the activities are different. $x_{Fe} = (a_{Fe})^{1/2}$ in the ionic model, but $x_{fa} = a_{fa}$ (the activity of fayalite) in the solution.

**NONIDEAL BINARY SOLUTIONS**

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

$$\mu_i = \mu^i_i + RT \ln a_i.$$  

(1-17)

The ideal solution is the limiting case when $a_i$ is equal to the mole fraction $x_i$. In all other cases, the relation between $a_i$ and $x_i$ may be expressed as

$$a_i = f_i x_i,$$  

(1-18)

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

$$G_M = x_A RT \ln a_A + x_B RT \ln a_B$$

$$= RT (x_A \ln x_A + x_B \ln x_B) + RT (x_A \ln f_A + x_B \ln f_B)$$

$$= G_{IM} + G_{EM}.$$  

(1-19)

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 that is due to the nonideal nature 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

The thermodynamic properties of crystalline solutions of mineral assemblages either obtained in experiments or occurring in rocks must often be calculated. In many situations the use of certain models for the activity composition relationship helps to assess such properties closely. The regular solution model of Guggenheim (1952) 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., the approximation of complete disorder, is given by

$$G_{EM} = x_A x_B W',$$

where $A$ and $B$ are components of a solution $(A, B)M$, $W'$ is equal to $\frac{1}{2} n w$, and $n$ is Avogadro's number. $W'$ is often referred to as the interchange energy. Regular solutions are very important in this work; therefore, the parameter $w$ will be briefly discussed. A simplified account of this parameter is presented by Denbigh (1966). It is assumed that the cations $A$ and $B$ are of roughly the same size and can be interchanged between lattice sites without change of lattice structure and without change in the lattice vibrations. There is interaction between $A$ and $B$, given by the energy $w$, which is given by

$$w = 2 w_{AB} - w_{AA} - w_{BB},$$

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. $w_{AB}$ and $w_{BB}$ are similarly defined. 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

$$G_{EM} = H_{EM} = x_A x_B W'$$

and

$$S_{EM} = 0.$$
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 A-A pair and a B-B pair are converted into two A-B 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

$$G_{EM} = x_A x_B W,$$  \hspace{1cm} (1-24)

$$-S_{EM} = x_A x_B \frac{\partial W}{\partial T},$$  \hspace{1cm} (1-25)

and

$$H_{EM} = x_A x_B \left( W - T \frac{\partial W}{\partial T} \right).$$  \hspace{1cm} (1-26)

The activity coefficient is related to the mole fraction by

$$\ln \gamma_A = \frac{W}{RT} x_B^2.$$  \hspace{1cm} (1-27)

### Quasi-Chemical Model

The main assumptions required for this model are similar to those of the regular solution model in the preceding sections. Only the configurational partition function of the solution contributes to the thermodynamic excess functions. The intermolecular forces are central and short range, 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 are the result of ordering considered in the latter.

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

$$f_A = \left[ \frac{\beta + 1 - 2 x_B}{x_A (\beta + 1)} \right]^{\frac{z}{2}}$$  \hspace{1cm} (1-28)

and

$$f_B = \left[ \frac{\beta - 1 + 2 x_B}{x_A (\beta + 1)} \right]^{\frac{z}{2}}$$  \hspace{1cm} (1-29)

where $z$ is the coordination number and $\beta$ is given by

$$\beta = \left[ 1 + 4 x_A x_B (e^{2W/RT} - 1) \right]^{1/2}.$$  \hspace{1cm} (1-30)
\( \beta = 1 \) for a perfectly random mixture. If \( \beta > 1 \), a tendency for clustering exists, and if \( \beta < 1 \), a trend for compound formation exists.

\[ G_{EM} \text{ and } H_{EM} \text{ are given by} \]

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

and

\[
H_{EM} = \frac{2}{\beta + 1} x_A x_B \left( \frac{W}{T} \frac{\partial W}{\partial T} \right).
\]

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

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

and

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

\( f_B \) may be obtained by replacing \( A \) by \( B \) in Equation 1-34.

For molecules that are not very similar in size, a contact factor must be included (Guggenheim, 1952, p. 216) in these equations to take the size differences into account. The contact factors may be found roughly proportional to the molar volumes or ionic radii. The activity coefficients are given by

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

and

\[
f_B = \left[ 1 + \frac{\phi_A (\beta - 1)}{\phi_B (\beta + 1)} \right]^{2q_B/2},
\]

where \( q_A \) and \( q_B \) are contact factors related to the contact fractions \( \phi_A \) and \( \phi_B \) and the mole fractions \( x_A \) and \( x_B \) by

\[
\phi_A = \frac{x_A q_A}{x_A q_A + x_B q_B}
\]

(1-37a)
For more details on the derivation and significance of the constants $q_A^\circ$ and $q_B^\circ$ and the fractions $\phi_A^\circ$ and $\phi_B^\circ$, reference may be made to Guggenheim (1952, p. 216) and King (1969, p. 488). $\beta$ in Equations 1-35 and 1-36 is obtained by replacing $x_A$ and $x_B$ by $\phi_A^\circ$ and $\phi_B^\circ$, respectively, in Equation 1-30.

The other excess functions are given by

$$C_{EM} = \frac{1}{2} \left\{ x_A q_A \ln \left[ 1 + \frac{\phi_B}{\phi_A} (\beta - 1) \right] + x_B q_B \ln \left[ 1 + \frac{\phi_A}{\phi_B} (\beta - 1) \right] \right\}$$

and

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

$S_{EM}$ 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 equation is

$$x_A \, d \ln f_A + x_B \, d \ln f_B = 0.$$ 

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

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

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

$$\ln f_A = a_A x_A + b_A x_A^2 + c_A x_A^3 + d_A x_A^4 + \ldots ,$$

and

$$\ln f_B = a_B x_B + b_B x_B^2 + c_B x_B^3 + d_B x_B^4 + \ldots .$$
When the series is terminated at $x^3$, the following relations exist between the coefficients:

\[
\begin{align*}
  a_A &= a_B = 0, \\
  b_B &= b_A + 3 \frac{c_A}{2} + 2 d_A + \ldots, \\
  c_B &= -(c_A + 8 \frac{d_A}{3} + \ldots).
\end{align*}
\]

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

\[
\log f_A = (2 B - A) (1 - x_A)^2 + 2 (A - B) (1 - x_A)^3
\]

and

\[
\log f_B = (2 A - B) x_A^2 + 2 (B - A) x_A^3.
\]

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

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

\[
\log f_A = \frac{A}{1 + \left[ \frac{A x_A}{B (1 - x_A)} \right]^2}.
\]

Similarly for the other component,

\[
\log f_B = \frac{B}{1 + \left[ \frac{B (1 - x_A)}{A x_A} \right]^2}.
\]

For many chemical systems, van Laar’s equation provides a better representation of the data than the Margules two-constant equation. The relative merits of these two equations were discussed by Carlson and Colburn (1942). Finally, it may be remarked that a power series expansion as (see Equation 1-49) for the $G_{EM}$ is now widely preferred. Therefore, only such expressions and not the equations mentioned in this section will be used. Expressing $G_{EM}$ as a power series is a means of giving empirical description to deviations from the ideal, 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 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 CRYSTALLINE SOLUTIONS

Excess functions in nonideal 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

$$G_{EM} = x_A x_B \left[ A_0 + A_1 (x_A - x_B) + A_2 (x_A - x_B)^2 + \cdots \right], \quad (1-49)$$

where $A_0$, $A_1$, and $A_2$ are constants. When odd terms in Equation 1-49 vanish, the solution becomes symmetric. If $A_2$ and other higher terms are also zero, the simple mixture model with $A_0$ as the energy constant $W$ in Equation 1-24 results. The expressions for the activity coefficients are obtained from

$$R T \ln f_A = G_{EM} + x_B \frac{\partial G_{EM}}{\partial x_A}$$

$$= x_B^2 \left[ A_0 + A_1 (3 x_A - x_B) + A_2 (x_A - x_B) (5 x_A - x_B) + \cdots \right]. \quad (1-50)$$

and

$$R T \ln f_B = G_{EM} - x_A \frac{\partial G_{EM}}{\partial x_B}$$

$$= x_A^2 \left[ A_0 - A_1 (3 x_B - x_A) + A_2 (x_B - x_A) (5 x_B - x_A) + \cdots \right]. \quad (1-51)$$

Equations for other excess functions of mixing may be derived from Equation 1-49:

$$-S_{EM} = x_A x_B \left[ \frac{\partial A_0}{\partial T} + \left( \frac{\partial A_1}{\partial T} \right) (x_A - x_B) + \left( \frac{\partial A_2}{\partial T} \right) (x_A - x_B)^2 + \cdots \right]. \quad (1-52)$$

and

$$H_{EM} = x_A x_B \left\{ A_0 - T \left( \frac{\partial A_0}{\partial T} \right) + \left[ A_1 - T \left( \frac{\partial A_1}{\partial T} \right) \right] (x_A - x_B) + \left[ A_2 - T \left( \frac{\partial A_2}{\partial T} \right) \right] (x_A - x_B)^2 + \cdots \right\}. \quad (1-53)$$
INTRINSIC AND EXTRINSIC STABILITY

A crystalline solution in an ideal state adds a certain amount of negative free energy of mixing to the free energy of the system. With increasing positive deviations from the ideal state, this contribution becomes less and less. Below a certain critical temperature of unmixing, the solution unmixes to form two or more solutions. These energy changes obviously affect the stability of the entire system of the mineral assemblage. This instability of a crystalline solution, which is the result of 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 unstable if the physical and chemical conditions change in such a way that certain reaction products form a lower free energy assemblage than the crystalline solution. This instability can be called extrinsic. A solution may be both intrinsically and extrinsically unstable. The division is essentially artificial; however, it helps in understanding and describing 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 temperatures (~1400 K). In spite of their ideal character, orthopyroxenes with more than 55 mole percent of ferrosilite were found unstable at liquid-state temperatures by Bowen and Schairer (1935). The iron-rich pyroxene is unstable because of the instability of ferrosilite relative to fayalite and quartz. This is extrinsic instability.

At low temperatures (~900 K) the situation is little different. Orthopyroxene is somewhat non-ideal, and high values of \(G_{FM}\) are associated with the high ferrosilite content of the solution. The extrinsic instability of the solution relative to olivine and quartz is less because iron-rich pyroxenes (about 86 percent FeSiO\(_3\)) are stable in metamorphic rocks. The instability of pyroxenes with higher ferrosilite in metamorphic rocks may be due to both 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

\[
\frac{\partial^2 G_M}{\partial x^2} = 0
\]  

(2-1)
and
\[ \frac{\partial^3 G_M}{\partial x^3} = 0. \]  

(2-2)

These may be expressed in terms of \( G_{EM} \) as
\[ \frac{\partial^2 G_{EM}}{\partial x^2} = - R T / x (1 - x) \]  

(2-3)

and
\[ \frac{\partial^3 G_{EM}}{\partial x^3} = - R T (2 x - 1) / x^2 (1 - x)^2. \]  

(2-4)

**Simple Mixture**

For a simple mixture,
\[ G_{EM} = x (1 - x) W, \]  

(2-5)

where

\[ W = W (T, P). \]

By successive differentiation of Equation 2-5,
\[ \frac{\partial^2 G_{EM}}{\partial x^2} = - 2 W \]  

(2-6)

and
\[ \frac{\partial^3 G_{EM}}{\partial x^3} = 0. \]  

(2-7)

By substituting Equations 2-3 and 2-4 into Equations 2-6 and 2-7, respectively,
\[ - 2 W = - R T / x (1 - x) \]  

(2-8)

and
\[ 0 = R T (2 x - 1) / x^2 (1 - x)^2. \]  

(2-9)

These give the critical composition when \( x = 0.5 \) and \( 2RT_c = W \).

**General Nonideal Solution**

For a binary solution that is not a symmetric solution,
\[ G_{EM} = x (1 - x) \left[ A_0 + A_1 (1 - 2 x) + A_2 (1 - 2 x)^2 + \ldots \right]. \]  

(2-10)

Successive differentiation of Equation 2-10 with respect to \( x \) gives
\[ \frac{\partial^2 G_{EM}}{\partial x^2} = - 2 A_0 - 6 A_1 (2 x - 1) - A_2 \left[ 10 - 48 x (1 - x) \right] \]  

(2-11)
and

\[ \frac{\partial}{\partial x^3} G_{EM} = -12 A_1 + 48 A_2 (1 - 2 x) . \]  

(2-12)

Substitution of Equations 2-3 and 2-4 into Equations 2-11 and 2-12, respectively, gives equations that are transcendental and cannot be solved without a computer program using an iteration method.

**Formation of Miscibility Gaps in a Ternary Simple Mixture**

Consider a ternary simple mixture with components 1, 2, and 3. \( W \) for the three binary systems are \( W_{12}, W_{13}, \) and \( W_{23} \). The chemical potentials of the components in the solution are given by

\[ \mu_1 = \mu_1^0 (T, P) + RT \ln \gamma_1 + RT \ln f_1 \ldots , \]  

(2-13)

where \( RT \ln f \) may be expanded in terms of \( x \) and \( W \) as follows:

\[ RT \ln f_1 = (x_2)^2 W_{12} + (x_3)^2 W_{13} + x_2 x_3 (W_{12} - W_{23} + W_{13}) , \]  

(2-14a)

\[ RT \ln f_2 = (x_3)^2 W_{23} + (x_1)^2 W_{12} + x_3 x_1 (W_{23} - W_{13} + W_{12}) , \]  

(2-14b)

and

\[ RT \ln f_3 = (x_1)^2 W_{13} + (x_2)^2 W_{23} + x_1 x_2 (W_{13} - W_{12} + W_{23}) . \]  

(2-14c)

At equilibrium in the two separated coexisting phases \( \alpha \) and \( \beta \),

\[ \mu_1^\alpha (x_2^\alpha, x_3^\alpha, T) - \mu_1^\beta (x_2^\beta, x_3^\beta, T) = 0 . \]  

(2-15)

\( \mu_2 \) and \( \mu_3 \) are similarly defined. Substituting Equations 2-13 and 2-14 into Equation 2-15 and rearranging (see Kaufman and Bernstein, 1970, p. 226),

\[ RT \ln (x_1^\beta / x_1^\alpha) + W_{12}[(x_2^\beta)^2 - (x_2^\alpha)^2] + W_{13}[(x_3^\beta)^2 - (x_3^\alpha)^2] + \Delta W (x_2^\beta x_3^\beta - x_2^\alpha x_3^\alpha) = 0 , \]  

(2-16a)

\[ RT \ln (x_2^\beta / x_2^\alpha) + W_{12}[(1 - x_2^\beta)^2 - (1 - x_2^\alpha)^2] + W_{13}[(x_3^\beta)^2 - (x_3^\alpha)^2] \]

\[ - \Delta W \left[ x_3^\beta (1 - x_2^\beta) - x_2^\alpha (1 - x_3^\alpha) \right] = 0 , \]  

(2-16b)

and

\[ RT \ln (x_3^\beta / x_3^\alpha) + W_{12}[(x_2^\beta)^2 - (x_2^\alpha)^2] + W_{13}[(1 - x_3^\beta)^2 - (1 - x_3^\alpha)^2] \]

\[ - \Delta W \left[ x_2^\beta (1 - x_3^\beta) - x_3^\alpha (1 - x_2^\alpha) \right] = 0 . \]  

(2-16c)

where \( \Delta W = W_{12} + W_{13} - W_{23} \).
With the help of Equations 2-16, compositions of coexisting phases may be calculated and the miscibility gap may be plotted on a ternary diagram. However, first the compositions of the coexisting phases on three binary edges must be calculated.

In a binary solution, the miscibility gap can be calculated by finding the composition of the coexisting phases that together represent the minimum free energy of the system. This may be done graphically by the tangent method, 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. Alternately, the relations

\[ \mu_1^\alpha = \mu_1^\beta \]

and

\[ \mu_2^\alpha = \mu_2^\beta \]

may be considered. For the binary regular solution, there is a symmetric miscibility gap and therefore

\[ x_1^\alpha + x_2^\alpha = 1 \]
\[ x_1^\beta + x_2^\beta = 1 \]
\[ x_1^\alpha = x_1^\beta \]

and

\[ x_2^\alpha = x_2^\beta \].

Therefore,

\[ R T \ln (1 - x_1) + x_1^2 \frac{W}{R T} = R T \ln (1 - x_2) + x_2^2 \frac{W}{R T} \] (2-17)
\[ R T \ln x_1 + (1 - x_1)^2 \frac{W}{R T} = R T \ln x_2 + (1 - x_2)^2 \frac{W}{R T} \] (2-18)

Substituting \( x_2 = 1 - x_1 \) into Equation 2-17,

\[ \frac{W}{R T} = \frac{1}{1 - 2 x_1} \ln \frac{1 - x_1}{x_1} \] (2-19)

Equation 2-19 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 Equations 2-16 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.
Chapter 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. Because Fe\(^{2+}\) and Mg\(^{2+}\) are similar in ionic charge and size, olivine and orthopyroxene may be assumed to be binary ideal solutions. This assumption will be reexamined later.

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

\[
\text{Mg Si O}_3 + \frac{1}{2} \text{Fe}_2 \text{Si O}_4 \rightleftharpoons \text{Fe Si O}_3 + \frac{1}{2} \text{Mg}_2 \text{Si O}_4 .
\] (3-1)

The equilibrium constant for this reaction at a certain \(P\) and \(T\) is

\[
K_{3-1} = \frac{x_{\text{Fe}}^{\text{opx}} (1 - x_{\text{Fe}}^{\text{ol}})}{(1 - x_{\text{Fe}}^{\text{opx}}) x_{\text{Fe}}^{\text{ol}}} .
\] (3-2)

The equilibrium constant \(K\) is a function of \(P\) and \(T\) only. In the present case, however, \(K_{3-1}\) is not found to be constant except at high temperatures. (See Olsen and Bunch, 1970.)

It may be noted that Equation 3-1 is written on a one-cation exchange basis. It may also be written as

\[
2 \text{Mg Si O}_3 + \text{Fe}_2 \text{Si O}_4 \rightleftharpoons 2 \text{Fe Si O}_3 + \text{Mg}_2 \text{Si O}_4 .
\] (3-3)

The equilibrium constant for this reaction is

\[
K_{3-3} = \frac{(x_{\text{Fe}}^{\text{opx}})^2 (1 - x_{\text{Fe}}^{\text{ol}})}{(1 - x_{\text{Fe}}^{\text{opx}})^2 x_{\text{Fe}}^{\text{ol}}} .
\]
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 $K_{33}$ are very cumbersome to handle and inconsistent with petrological observations. One may, therefore, prefer to use the distribution data on a one-cation exchange basis. It is obvious that in actual calculations of the energy values, it will be necessary to adjust for the activity-composition relations, such as Equations 1-7, 1-8, 1-14, and 1-16, as discussed before.

Generally olivine and pyroxene coexist with several other minerals of fixed or variable composition. If no significant change in the concentration of the minor components changes the binary character of the two minerals, $K_{31}$ 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 $T$ the stability of the olivine and pyroxene combination is a function of the presence or absence of quartz, but the value of $K_{31}$ itself is not affected.

Kretz (1959) used Roozeboom plots extensively to show the orderly distribution of cations 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. If at the same time both the solutions are ideal, it will be of the form shown in Figure 3-1.

![Figure 3-1—Distribution of a component A between two ideal crystalline solutions α and β. The numerical values are equilibrium constants.](image-url)
Coexisting Ternary Ideal Solutions

Consider two coexisting ternary phases $\alpha$ and $\beta$ with the formulae $(A, B, C)_M$ and $(A, B, C)_N$. The pure components are $AM$, $BM$, and $CM$ in $\alpha$ and $AN$, $BN$, and $CN$ in $\beta$. The chemical potentials of the components in $\alpha$ and $\beta$ are

$$\mu^\alpha_{AM} = \mu^{AM} + RT \ln x^\alpha_{AM} \quad (3-4)$$

and

$$\mu^\beta_{AN} = \mu^{AN} + RT \ln x^\beta_{AN} \quad (3-5)$$

The potentials of all the pure components $\mu$ are functions of $P$ and $T$ only. $x^\alpha_A$ and $x^\beta_A$ may be substituted for $x^\alpha_{AM}$ and $x^\beta_{AM}$, respectively, without altering the results. (See discussion before.)

The distribution of $A$ between $\alpha$ and $\beta$ may be represented by the ion exchanges

$$A \alpha + B \beta \overset{\leftarrow}{\rightarrow} B \alpha + A \beta \quad (3-6)$$

and

$$A \alpha + C \beta \overset{\leftarrow}{\rightarrow} C \alpha + A \beta \quad (3-7)$$

The equilibrium constants may be written as

$$K_{3-6} = \frac{x^\alpha_A x^\beta_B}{x^\alpha_B x^\beta_A}$$

and

$$K_{3-7} = \frac{x^\alpha_A x^\beta_C}{x^\alpha_C x^\beta_A}$$

where $x^\alpha_A = A/(A + B + C)$, and the other $x$'s are defined similarly. Both $K_{3-6}$ and $K_{3-7}$ will be constants for all ratios of $A$ to $B$ to $C$. A plot of $x^\alpha_A$ against $x^\beta_A$ will produce a symmetric ideal distribution curve.

NONIDEAL SOLUTIONS

Distribution of a Component Between Two Simple Mixtures

For the ion-exchange equation

$$A \alpha + B \beta \overset{\leftarrow}{\rightarrow} A \beta + B \alpha \quad (3-6)$$

at equilibrium,

$$\mu^\alpha_B + \mu^\beta_A = \mu^\beta_B + \mu^\alpha_A \quad (3-8)$$
If \((A, B)\alpha\) and \((A, B)\beta\) are simple mixtures,

\[
\mu_B^\alpha = \mu_B + R \ln (1 - x_A^\alpha) + \frac{W}{x_A^\alpha}^2,
\]

and the other \(\mu\)'s are similarly defined. Substituting the values found by Equation 3-9 into Equation 3-8 and rearranging,

\[
1 \ln \frac{x_A^\beta (1 - x_A^\alpha)}{(1 - x_A^\beta) x_A^\alpha} = \left[ \frac{W^\alpha}{R T} (1 - 2 x_A^\alpha) - \frac{W^\beta}{R T} (1 - 2 x_A^\beta) \right] = - \frac{\Delta G_a^\circ}{R T}
\]

where

\[
\Delta G_a^\circ = \mu_B^\alpha + \mu_A^\beta - \mu_B^\beta - \mu_A^\alpha.
\]

Or

\[
1 \ln K_{3-6} = 1 \ln K_D - \frac{W^\alpha}{R T} (1 - 2 x_A^\alpha) + \frac{W^\beta}{R T} (1 - 2 x_A^\beta)
\]

where \(K_{3-6} = \exp (-G_a^\circ / RT)\) and \(K_D\) is the distribution coefficient.

If a good least-square fit can be obtained for the distribution data by using Equation 3-11, it may be found that both minerals are close to being simple mixtures.

As one or both of the minerals becomes less ideal, the distribution isotherms may attain different forms. (See Mueller, 1964.) Figure 3-2 shows an example where one of the mineral's \(\alpha\) is ideal and \(\beta\) is nonideal. \(W^\beta\) is assumed to vary linearly with \(1/T\). The values of \(W^\beta / RT\) and \(K_a\) at 673 and 1673 K are 2.75, 1.603, 0.77, and 1.518, respectively (see Saxena, 1969). The forms of the distribution isotherms are very different from the symmetric ideal curves.

![Figure 3-2—Distribution of a component A between an ideal solution α and a regular solution β for the following data:](image)

<table>
<thead>
<tr>
<th>(T (K))</th>
<th>(\frac{W^\beta}{RT})</th>
<th>(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>2.75</td>
<td>1.60</td>
</tr>
<tr>
<td>1673</td>
<td>.77</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Coexisting Regular Ternary Solutions

The composition of two coexisting phases that 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. \( W'_{AB}, W'_{BC}, \) and \( W'_{AC} \) are assumed to be 6300, 29000, and 38000 J/mole (1500, 7000, and 9000 cal/mole), respectively, and the values of \( W' \) are assumed not to be functions 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 \( \alpha \) and the phase poor in C by \( \beta \). For the chemical potentials,

\[
\mu_A^{\alpha} = \mu_A^{AM} + RT \ln \chi_A^\alpha \\
\mu_A^{\beta} = \mu_A^{AM} + RT \ln \chi_A^\beta 
\]

and

\[
\mu_B^{\alpha} = \mu_B^{BM} + RT \ln \chi_B^\alpha \\
\mu_B^{\beta} = \mu_B^{BM} + RT \ln \chi_B^\beta
\]

Any one of the following ion exchanges between \( \alpha \) and \( \beta \) may be considered:

\[
\begin{align*}
A^\beta + B & \xrightleftharpoons{} A^\alpha + B^\beta, \\
B^\alpha + C^\beta & \xrightleftharpoons{} B^\beta + C^\alpha,
\end{align*}
\]

and

\[
A^\alpha + C^\beta \xrightleftharpoons{} C^\alpha + A^\beta.
\]
The equilibrium constant for Equations 3-14 is

\[ \frac{x_A^\alpha x_B^\beta}{x_A^\beta x_B^\alpha} \frac{f_A^{\alpha}}{f_B^{\beta}} = K_{3-14} \tag{3-15} \]

In this particular case because \( \alpha \) and \( \beta \) obey the same equation of state, \( \Delta G^0 = 0 \) and \( K_{3-14} = 1. \) In other cases where \( \alpha \) and \( \beta \) are minerals with different crystal structures, the equilibrium constant is not equal to 1. The \( f \) terms in Equation 3-15 are functions of \( P, T, \) and the ratio of \( A \) to \( B \) to \( C. \) Therefore \( K_D (x_B^\alpha x_B^\beta / x_A^\alpha x_B^\beta) \) also changes with \( P, T, \) and the ratios of \( A \) to \( B, \) \( B \) to \( C, \) and \( A \) to \( C. \)

Let the ratio of \( A \) to \( B \) to \( C \) change systematically as listed in Table 3-1. A plot of \( x_B^\alpha \) against \( x_B^\beta, \) 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

\[ R T \ln f_A = (x_B^\alpha)^2 w_{AB}' + (x_C^\alpha)^2 w_{AC}' + x_B x_C (w_{AB}' - w_{BC} + w_{AC}') \tag{3-16a} \]

\[ R T \ln f_B = (x_C^\alpha)^2 w_{BC}' + (x_A^\alpha)^2 w_{AB}' + x_A x_C (w_{BC}' - w_{AC} + w_{AB}') \tag{3-16b} \]

and

\[ R T \ln f_C = (x_A^\alpha)^2 w_{AC}' + (x_B^\alpha)^2 w_{BC}' + x_A x_B (w_{AC}' - w_{AB} + w_{BC}') \tag{3-16c} \]

where \( x_A = A/(A + B + C) \) and the other \( x \)'s are similarly defined. It may be checked that substitution of \( f \) values into Equation 3-15 gives the equilibrium constant as unity.

| Table 3-1—Composition of coexisting phases in ternary regular solutions. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( \alpha \)     | \( \beta \)     | \( x_B^\alpha \) | \( x_B^\beta \) | \( K_D \)       |
| \( B \) | \( A \) | \( C \) | \( B \) | \( A \) | \( C \) | \( B \) | \( A \) | \( C \) |
| 0.010 | 0.082 | 0.908 | 0.043 | 0.868 | 0.089 | 0.108 | 0.047 | 0.406 |
| 0.040 | 0.079 | 0.881 | 0.174 | 0.718 | 0.109 | 0.336 | 0.195 | 0.478 |
| 0.080 | 0.071 | 0.849 | 0.339 | 0.522 | 0.140 | 0.530 | 0.394 | 0.576 |
| 0.100 | 0.066 | 0.834 | 0.413 | 0.431 | 0.156 | 0.602 | 0.489 | 0.632 |
| 0.130 | 0.056 | 0.814 | 0.512 | 0.309 | 0.179 | 0.699 | 0.624 | 0.715 |
| 0.170 | 0.037 | 0.793 | 0.625 | 0.171 | 0.205 | 0.821 | 0.785 | 0.796 |
| 0.200 | 0.020 | 0.780 | 0.700 | 0.081 | 0.219 | 0.909 | 0.896 | 0.862 |

\( x_B = \frac{B}{B + A} \) and \( K_D = \frac{x_B^\beta}{x_B^\alpha}. \)
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 information. 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 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 octahedral coordination. Such differently coordinated ions may be regarded as forming submixtures. The distribution of Fe$^{2+}$ or Mg$^{2+}$ or any other octahedrally coordinated ion may be examined in two or more such submixtures 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 beforehand 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$^{2+}$ 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 that are quasi-binary solutions out of an entire assemblage of five or six minerals could not be useful. That is, the presence or absence of a third or fourth mineral in the assemblage ought to 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. For example, TiO$_2$ is only sparingly soluble in olivine and orthopyroxene. The chemical potential of TiO$_2$ may increase or decrease in the rock, and rutile may be added or removed from the assemblage, but $K_D$ for the distribution of Fe$^{2+}$ and Mg$^{2+}$ would not change. However, if the change in $\mu_{\text{TiO}_2}$ 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. 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 if 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). Such orderly distribution of Mn is common in other rocks as well. The distribution of Fe$^{2+}$ and Mg$^{2+}$ between coexisting olivine

![Figure 3-5—Distribution of Mn in coexisting minerals in charnockites of Varberg, Sweden (Saxena, 1968b).]
and orthopyroxene at 1073 and 1173 K 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 1073 and 1173 K show some scatter. The difficulties are related to the kinetics of the ion-exchange reaction as equilibrium is approached, particularly when the distribution approaches a 1 to 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 (Capx) in metamorphic rocks as studied by Kretz (1963) is remarkably orderly. Most distribution points fall on a smooth curve, and a distribution curve representing igneous rocks is clearly separated from a distribution curve for the metamorphic rocks.

Studies of partitioning of cations between coexisting minerals in natural rocks by petrologists (Albee, 1965; Annersten, 1968; Binns, 1962; Butler, 1969; Kretz, 1959; Gorbatschev, 1969; Hietnan, 1971; and Mueller, 1960, among many others) are attempts to rationalize the concept of metamorphic facies on a mineral and 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 equilibria are distribution problems, and a statistical approach to such problems may be made to avoid the consideration of the thermodynamic properties of solutions in individual minerals. Such approaches have been made principally by Greenwood (1967) and Perry$^1$ and should be applicable in solving the petrogenetic problem of incompatible assemblages and the recognition of chemical equilibrium in natural or experimental systems.

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$^1$K. Perry, Jr.: "Construction of a Single (m + 2) Dimensional Phase Diagram From Petrochemical Data." To be published.
Chapter 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 difficulties and the measured values are subject to large errors. Therefore, obtaining such activity-composition relations from phase diagrams would be very convenient.

However, there is no direct method of doing this without some kind of a solution model. The use of a solution model brings in 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. Assume that the solution \((A, B)M\) unmixes into two coexisting solutions, \(\alpha\), rich in \(AM\), and \(\beta\), rich in \(BM\). At equilibrium,

\[
\mu_A^\alpha + R T \ln x_A^\alpha + W (1 - x_A^\alpha)^2 = \mu_B^\beta + R T \ln x_B^\beta + W (1 - x_B^\beta)^2
\]

so that according to the simple mixture model,

\[
\mu_A^\alpha = \mu_B^\beta
\]

and

\[
\mu_B^\alpha = \mu_B^\beta \tag{4-1}
\]

where \(\alpha_0\) and \(\beta_0\) stand for the same pure end member structure \(AM\). Eliminating \(\mu_A^\alpha\) and \(\mu_B^\alpha\) and substituting \(x_B^\beta = 1 - x_A^\alpha\),

\[
R T \ln x_A^\alpha + W (1 - x_A^\alpha)^2 = R T \ln (1 - x_A^\alpha) + W (x_A^\alpha)^2 \tag{4-3}
\]
or

\[
\frac{\psi}{R \, T} = \frac{1 \ln \left[ \frac{(1 - x_A^a)/x_A^a}{1 - 2 \, x_A^a} \right]}{1 - 2 \, x_A^a}.
\] (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

\[
W = 2 \, R \, T_c
\]

into Equation 4-4:

\[
T = 2 \, T_c \frac{1 - 2 \, x_A^a}{1 \ln \left[ \frac{(1 - x_A^a)/x_A^a}{1 - 2 \, x_A^a} \right]}.
\] (4-5)

If there are 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 may require an expression with two or more constants to represent \(G_{EM}\):

\[
G_{EM} = x_A^a \left( 1 - x_A^a \right) \left[ A_0 + A_2 \left( 1 - 2 \, x_A^a \right)^2 \right].
\] (4-6)

For such a solution, Equation 4-3 is

\[
R \, T \, 1 \ln x_A^a + \left[ A_0 + A_2 \left( 1 - 2 \, x_A^a \right)^2 \right] \left( 1 - x_A^a \right)^2 + \left[ A_0 + A_2 \left( 1 - 2 \, x_A^a \right)^2 \right] \left( 1 - x_A^a \right)^2.
\] (4-7)

Using the relation \(\mu_B^a = \mu_B^b\), an equation similar to Equation 4-7 can be written, and the two equations can be solved simultaneously to obtain \(A_0, A_2\), and the activity-composition relation.

**ASYMMETRICAL SOLUTIONS**

**Subregular Model**

As mentioned before, \(G_{EM}\) 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:

\[
G_{EM} = x_A \, x_B \left[ A_0 + A_1 (x_A - x_B) + A_2 (x_A - x_B)^2 + \ldots \right].
\] (1-49)

If \(A_2 = 0\) is substituted into Equation 1-49, a two-constant equation for an asymmetrical solution is the result. Proceeding as in the previous sections,

\[
R \, T \, 1 \ln x_A^a + R \, T \, 1 \ln f_A^a = R \, T \, 1 \ln x_B^a + R \, T \, 1 \ln f_A^a
\] (4-8)
and

\[ RT \ln x_B^A + RT \ln f_B^A = RT \ln x_B^\beta + RT \ln f_B^\beta. \]  \hspace{1cm} (4-9)

Substituting values of \( RT \ln f \) from Equations 1-50 and 1-51,

\[ RT \ln x_A^a + (x_B^a)^2 \left[ A_0 + A_1 (3x_A^a - x_B^a) \right] = RT \ln x_A^\beta + (x_B^\beta)^2 \left[ A_0 + A_1 (3x_A^\beta - x_B^\beta) \right] \]  \hspace{1cm} (4-10)

and

\[ RT \ln x_B^a + (x_A^a)^2 \left[ A_0 - A_1 (3x_A^a - x_B^a) \right] = RT \ln x_B^\beta + (x_A^\beta)^2 \left[ A_0 - A_1 (3x_A^\beta - x_B^\beta) \right]. \]  \hspace{1cm} (4-11)

Equations 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 (1969a,b). Thompson’s (1967) equation for \( G_{EM} \) is

\[ G_{EM} = x_A G_2 + x_B G_1 \]  \hspace{1cm} (4-12)

where

\[ G_2 = x_A x_B W_{G_2} \]

and

\[ G_1 = x_A x_B W_{G_1}. \]

This is as if the crystalline solution is composed of \( x_A \) moles of a simple mixture with \( W_{G_2} \) and \( x_B \) moles of another simple mixture with \( W_{G_1} \). Then,

\[ G_{EM} = (W_{G_1} x_B + W_{G_2} x_A) x_A x_B \]

\[ = \left[ W_{G_1} (1 - x_A) + W_{G_2} (1 - x_B) \right] x_A x_B \]

\[ = W_{G_1} \frac{2 - 2x_A}{2} + W_{G_2} \frac{2 - 2x_B}{2} x_A x_B. \]  \hspace{1cm} (4-13)

Substituting \( 1 = x_A + x_B \) into Equation 4-13,

\[ G_{EM} = \left[ \frac{W_{G_1}}{2} (1 - x_A + x_B) + \frac{W_{G_2}}{2} (1 + x_A - x_B) \right] x_A x_B \]

\[ = \left[ \frac{W_{G_2}}{2} + \frac{W_{G_2} - W_{G_1}}{2} (x_A - x_B) \right] x_A x_B \]  \hspace{1cm} (4-14)

which is of the same form as Guggenheim’s equation with two constants \( A_0 \) and \( A_1 \).
Therefore,

\[ A_0 = \frac{W_{G_2} + W_{G_1}}{2} \]  

and

\[ A_1 = \frac{W_{G_2} - W_{G_1}}{2}. \]

\[ (4-15a) \]

\[ (4-15b) \]

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

For the activity coefficient,

\[ RT \ln f_A = (x_B)^2 [A_0 + A_1 (3x_A - x_B) + \ldots]. \]

\[ (1-50) \]

Substitution of Equations 4-15 into Equation 1-50 gives

\[ RT \ln f_A = (x_B)^2 \left[ \frac{W_{G_2} + W_{G_1}}{2} + \frac{W_{G_2} - W_{G_1}}{2} (x_A - x_B + 2x_A) \right] \]

\[ = x_B^2 \left[ \frac{W_{G_2} + W_{G_1}}{2} + \frac{W_{G_2} - W_{G_1}}{2} (x_A - x_B) \right] + (W_{G_2} - W_{G_1}) x_A \]

\[ = x_B^2 \left[ (W_{G_1} x_B + W_{G_2} x_A) + (W_{G_2} x_A - W_{G_1} x_A) \right] \]

\[ = x_B^2 \left[ W_{G_1} (x_B - x_A) + 2 W_{G_2} x_A \right] \]

\[ = x_B^2 \left[ W_{G_1} (1 - 2x_A) + 2 W_{G_2} x_A \right] \]

\[ = x_B^2 \left[ W_{G_1} + 2x_A (W_{G_2} - W_{G_1}) \right] \]

\[ (4-16) \]

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

Substituting the calculated values of \( A_0 \) and \( A_1 \) into Equation 1-49, \( G_{EM} \) can be estimated. The solvs bounding the two-phase region can then be determined by the graphical tangent method or by a suitable iteration numerical method. The calculated values of \( x_A^q, x_B^q, x_A^\theta, \) and \( x_B^\theta \) are then compared to the observed mole fractions to test the applicability of the model. Other excess functions of mixing may be calculated by Equations 1-52 and 1-53.

**Quasi-Chemical Approximation**

This model has been used by Green (1970) to study the halite-sylvite solvus. Consider two coexisting phases M and N with components A and B. At equilibrium at a certain \( P \) and \( T \),
and

\[ \mu^M_A = \mu^N_A, \]

or

\[ \mu^M_B = \mu^N_B \]

and

\[ \mu^A_M + RT \ln x^M_A + RT \ln f^M_A = \mu^A_N + RT \ln x^N_A + RT \ln f^N_A \quad (4-17) \]

Because 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 canceled.

Substituting values of \( f^A_A \) and \( f^B_B \) from Equations 1-35 and 1-36, respectively, into Equations 4-17,

\[ 1 \ln x^M_A + \frac{z q_1}{2} 1 \ln \left[ 1 + \frac{\phi^M_B (\beta - 1)}{\phi^M_A (\beta + 1)} \right] = 1 \ln x^N_A + \frac{z q_1}{2} 1 \ln \left[ 1 + \frac{\phi^N_B (\beta' - 1)}{\phi^N_A (\beta' + 1)} \right] \quad (4-18) \]

and

\[ 1 \ln x^M_B + \frac{z q_1}{2} 1 \ln \left[ 1 + \frac{\phi^M_A (\beta - 1)}{\phi^M_B (\beta + 1)} \right] = 1 \ln x^N_B + \frac{z q_1}{2} 1 \ln \left[ 1 + \frac{\phi^N_A (\beta' - 1)}{\phi^N_B (\beta' + 1)} \right], \quad (4-19) \]

where \( \beta \) and \( \beta' \), which correspond to phases M and N, respectively, and the \( \phi \)'s are defined by Equations 1-30 (using \( \phi_A \) instead of \( x_A \), etc.) and 1-37. \( q_1 \) and \( q_2 \) are the contact factors discussed before. They are not independent and should approach 1 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 \( T \). Substitution of \( q_1/q_2 \) back into 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 caused by the inadequacy of the solution model to fit to the experimental data.

The solvus bounding the two-phase region may 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 by Equations 1-38 and 1-39.

EXAMPLE OF CALCULATION OF FUNCTIONS OF MIXING: THE CaWO\(_4\)-SrWO\(_4\) SYSTEM

Chang (1967) presented the data on the two-phase regions with solvus in the binary tungstate R\(_{11}\)WO\(_4\) type of crystalline solution. Table 4-1 shows the data on the composition of the coexisting phases \( \alpha \) and \( \beta \) 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
Table 4-1—Chemical composition of unmixed phases in the system CaWO$_4$-SrWO$_4$.$^a$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$x_{Sr}^a$</th>
<th>$x_{Ca}^a$</th>
<th>$x_{Sr}^b$</th>
<th>$x_{Ca}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>0.005</td>
<td>0.995</td>
<td>0.995</td>
<td>0.005</td>
</tr>
<tr>
<td>873</td>
<td>0.010</td>
<td>0.990</td>
<td>0.980</td>
<td>0.020</td>
</tr>
<tr>
<td>923</td>
<td>0.025</td>
<td>0.975</td>
<td>0.955</td>
<td>0.045</td>
</tr>
<tr>
<td>973</td>
<td>0.035</td>
<td>0.965</td>
<td>0.905</td>
<td>0.095</td>
</tr>
<tr>
<td>1023</td>
<td>0.067</td>
<td>0.933</td>
<td>0.800</td>
<td>0.200</td>
</tr>
<tr>
<td>1073</td>
<td>0.120</td>
<td>0.880</td>
<td>0.630</td>
<td>0.370</td>
</tr>
</tbody>
</table>

$^a$$a$ and $b$ are coexisting phases rich in CaWO$_4$ and SrWO$_4$, respectively. The compositions are from Chang (1967, Figure 3).

Table 4-2—The calculated $A_0/RT$ and $A_1/RT$ in (Ca, Sr)WO$_4$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$A_0/RT$</th>
<th>$A_1/RT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>4.364</td>
<td>-0.327</td>
</tr>
<tr>
<td>650</td>
<td>3.524</td>
<td>-0.348</td>
</tr>
<tr>
<td>700</td>
<td>3.119</td>
<td>-0.455</td>
</tr>
<tr>
<td>750</td>
<td>2.537</td>
<td>-0.514</td>
</tr>
<tr>
<td>800</td>
<td>2.021</td>
<td>-0.607</td>
</tr>
<tr>
<td>900$^a$</td>
<td>0.839</td>
<td>-0.739</td>
</tr>
<tr>
<td>1000$^a$</td>
<td>-0.296</td>
<td>-0.884</td>
</tr>
</tbody>
</table>

$^a$From Equations 4-20 and 4-21.

Note: An error of ±5 percent in the mole fractions (Table 4-1) results in a ±800 J/mole (±200 cal/mole) error in determining $A_0$ and $A_1$.

Linear and is given by

$$\frac{A_0}{RT} = 14.1526 - 0.0115T$$

(4-20)

and

$$\frac{A_1}{RT} = 0.9616 - 0.00145T.$$  

(4-21)

$G_{EM}$ can then be calculated 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

$$RT \ln f_{SrWO_4} = x_{CaWO_4}^2 [A_0 + A_1 (3x_{SrWO_4} - x_{CaWO_4})].$$
and

\[ R T \ln f_{\text{CaWO}_4} = x_{\text{SrWO}_4}^2 [A_0 - A_1 (3 x_{\text{CaWO}_4} - x_{\text{SrWO}_4})] . \]

Figure 4-1 shows the activity-composition relation at 1073 and 1273 K. \( G_{EM} \) can also be plotted against composition, and the composition of the coexisting phases can be found by the tangent method. 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 \( \text{CaWO}_4-\text{SrWO}_4 \), calculation shows that the use of quasi-chemical approximation predicts the solvus with the same accuracy that the subregular model does. The use of quasi-chemical approximation requires the values of \( q_1, q_2 \), and the coordination number \( z \), the number of the nearest \( \text{Ca}^{2+} \) or \( \text{Sr}^{2+} \) ions surrounding each other. In \( \text{CaWO}_4 \) there are four \( \text{Ca}^{2+} \) ions surrounding each \( \text{Ca}^{2+} \) at a distance of approximately 0.39 nm. There are four more \( \text{Ca}^{2+} \) ions at a distance of 0.5 nm. \( z \) may be assumed equal to 4, and the two equations of the quasi-chemical approximation (Equations 4-18 and 4-19) can be solved simultaneously to find \( q_1 / q_2 \).

In this case, it may be assumed that either \( q_1 + q_2 = 2 \) or \( \sqrt{q_1 q_2} = 1 \). The differences in the calculations of \( W \) using either of the two assumptions are small. (See Green, 1970.) A computer program may be used to solve each of the two equations independently by using various values for \( q_1 \) and \( q_2 \) and to compare the \( W \) values so obtained until the best set of \( W \) values is found. The \( W \) values with \( z = 4 \) are listed in Table 4-3. \( q_1 \) and \( q_2 \) are 1.20 and 0.80, corresponding to \( \text{SrWO}_4 \) and \( \text{CaWO}_4 \), respectively. The atomic radii (R) for \( \text{Sr}^{2+} \) and \( \text{Ca}^{2+} \) are 1.12 and 0.99, respectively (Ahrens, 1952); therefore, the ratio of \( q_1 \) to \( q_2 \) is 1.50 and the ratio of the radii of \( \text{Sr}^{2+} \) to \( \text{Ca}^{2+} \) is 1.13; these values are not similar.

![Figure 4-1—Activity-composition relation in \( \text{CaWO}_4-\text{SrWO}_4 \) crystalline solution at 1073 and 1273 K.](image)
Table 4-3—$2W/zRT$ for the system CaWO$_4$-SrWO$_4$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Equation 4-18</th>
<th>Equation 4-19</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>5.883</td>
<td>5.361</td>
</tr>
<tr>
<td>923</td>
<td>5.173</td>
<td>4.821</td>
</tr>
<tr>
<td>973</td>
<td>4.919</td>
<td>4.460</td>
</tr>
<tr>
<td>1023</td>
<td>4.495</td>
<td>4.301</td>
</tr>
<tr>
<td>1073</td>
<td>4.183</td>
<td>4.386</td>
</tr>
</tbody>
</table>

$z = 4; q_1 = 1.20; q_2 = 0.80.$

The following equation describes the relation between the calculated $W$ (the average of the two values listed in Table 4-3) and $T$:

$$\frac{2W}{zRT} = 34.64 - 0.05506 T + 0.000025 T^2.$$ (4-22)

Figure 4-2 shows a comparison of $G_{EM}$ at 1073 K calculated according to both the subregular (SR) model and the quasi-chemical (QC) model. The value of $G_{EM}$ according to the latter is nearly twice that calculated according to the former. Differences between the other calculated functions of mixing, $H_{EM}$ and $S_{EM}$, are even more marked. Unfortunately there are no data on experimentally determined $H_{EM}$ and $S_{EM}$ for the CaWO$_4$-SrWO$_4$ system, and, therefore, there is no way to know which model predicts the thermodynamic functions better in this particular case.

For the system NaCl-KCl, Green (1970) compared the thermodynamic quantities calculated by the subregular model and the quasi-chemical model with those determined by experiments. The thermodynamic quantities predicted by the 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 from the quasi-chemical model is not satisfactory. This may be in part caused by the neglect of the nonconfigurational 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 mineralogists and petrologists. The fact that there is no unique analysis of a solvus and two or more solution models may be applicable to the same solvus data need not be a barrier to acquiring and interpreting more phase data 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 get physically meaningful results.

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Figure 4.2—Thermodynamic excess functions of mixing in (Ca, Sr)WO$_4$ according to the two-constant asymmetric model and the quasi-chemical approximation.
Chapter 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 precise P and T are not important, such data may be used 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 that do not obey the same equations of state may be used to find the activity-composition relations in each phase in suitable cases. Consider α and β with chemical formulas (A, B)M and (A, B)N, respectively, which are in ion-exchange equilibrium at a certain P and T. From Chapter 3,

\[ \text{A}_\alpha + \text{B}_\beta \rightleftharpoons \text{B}_\alpha + \text{A}_\beta. \] (3-6)

The equilibrium constant \( K_{3-6} \) is given by

\[ K_{3-6} = \left( \frac{x^A_B x^\beta_A}{x^\alpha_A x^\beta_B} \right)^{f^\alpha_B f^\beta_A / f^\alpha_A f^\beta_B}. \] (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

The simple mixture model, the two-constant asymmetric model, and the regular solution model with quasi-chemical approximation are the possible choices. According to simple mixture model,

\[ \ln K_{3-6} = \ln K_D - \frac{W^\alpha}{R T} (1 - 2 x^\alpha_A) + \frac{W^\beta}{R T} (1 - 2 x^\beta_A). \] (3-11)

A nonlinear least-square fit using the data on \( x^\alpha_A \) and \( x^\beta_A \) finally yields \( K_{3-6} \), \( W^\alpha \), and \( W^\beta \).
According to the Redlich and Kister equations (King, 1969, p. 326),

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

and

\[ RT \ln f_B = x_A^2 \left[ A_0 - A_1 (3x_B - x_A) + A_2 (x_B - x_A) (5x_B - x_A) + \cdots \right]. \quad (5-3) \]

Therefore,

\[ RT \ln \frac{f_A}{f_B} = A_0 (x_B - x_A) + A_1 (6x_A x_B - 1) + A_2 (x_B - x_A) (1 - 8x_A x_B). \quad (5-4) \]

Substituting the values of \( f_A^\alpha/f_A^\beta \) and \( f_B^\alpha/f_B^\beta \) by using Equation 5-4 in Equation 5-1, neglecting the constants \( A_2 \)'s, and rearranging in logarithmic form yields

\[ \ln K_{3-6} = \ln K_D + \frac{A_0^\alpha}{RT} (x_A^\alpha - x_B^\alpha) + \frac{A_1^\alpha}{RT} (6 x_A^\alpha x_B^\alpha - 1) + \frac{A_0^\beta}{RT} (x_B^\beta - x_A^\beta) + \frac{A_1^\beta}{RT} (6 x_A^\beta x_B^\beta - 1). \quad (5-5) \]

Equation 5-5 is of the form

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

where the \( N \) and the \( x \)'s are known quantities. It may be solved by a numeric least-square method yielding \( M = \ln K_{3-6} \) and other constants. There must be a minimum of five distribution points.

According to the quasi-chemical approximation,

\[ f_A = \left[ 1 + \frac{\phi_B (\beta - 1)}{\phi_A (\beta + 1)} \right]^{x_A/2} \quad (1-35) \]

and \( f_B \) is defined as in Equation 1-36. Substituting these values of \( f \) into Equation 5-1,

\[ K_D = \left[ \frac{1 + \frac{\phi_A (\beta - 1)}{\phi_A (\beta + 1)}}{x_A/2} \right]^{x_A/2} \left[ \frac{1 + \frac{\phi_B (\beta - 1)}{\phi_B (\beta + 1)}}{x_B/2} \right]^{x_B/2} = K_{3-6} \quad (5-6) \]

where \( \beta^\alpha \) and \( \beta^\beta \) are for phases \( \alpha \) and \( \beta \), respectively, and are given by Equation 1-30, with \( x_A \) replaced by \( \phi_A \), etc. \( q^\alpha \) and \( q^\beta \) are contact factors for phases \( \alpha \) and \( \beta \), respectively. A numerical least-square method may be used to solve Equation 5-6.
COMPOSITION DATA ON A COMPLETE DISTRIBUTION ISOTHERM AND THE ACTIVITY-COMPOSITION RELATION IN ONE OF THE TWO COEXISTING PHASES

Depending on the accuracy of the data, Equations 3-11, 5-5, and 5-6 may be used. If necessary, all three constants in Equation 5-4 may be used. Equation 5-4 may be written as

\[ \frac{f_A}{f_B} = x_B \left( 2A_0 + 6A_1 + 10A_2 \right) - x_B^2 \left( 6A_1 + 24A_2 \right) + x_B^3 \left( 16A_2 \right) - (A_0 + A_1 + A_2). \]  

(5-7)

Transforming Equation 5-1 into logarithmic form and substituting values from Equation 5-7 for \( f_A^B / f_B^A \),

\[ \ln K_D + \ln \frac{f_A^B}{f_A^B} = \left( \ln K_{3.6} + \frac{A_0 + A_1 + A_2}{RT} \right) - x_B \left( \frac{2A_0 + 6A_1 + 10A_2}{RT} \right) \]

\[ + x_B^2 \left( \frac{6A_1 + 24A_2}{RT} \right) - x_B^3 \left( \frac{16A_2}{RT} \right). \]

(5-8)

Equation 5-8 is of the form

\[ Y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots. \]

If the activity-composition relation in \( \alpha \) is known, Equation 5-8 may be solved by least-square analysis.

If sufficient number of distribution points are available, Equation 5-5 may be used with the third constant \( A_2 \) and the results compared with those obtained by using Equation 5-8.

The olivine-chloride solution system (Schulien et al., 1970) has been used by Saxena\(^1\) for calculating the activity-composition relation in binary solutions using the distribution data.

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\(^1\)S. K. Saxena: "Retrieval of Thermodynamic Data From a Study of Inter-Crystalline and Intra-Crystalline Ion Exchange Equilibria." To be published in *Amer. Mineral.*, 1972.
ORDER-DISORDER IN Fe$^{2+}$-Mg$^{2+}$ SILICATES

Long-range order-disorder phenomena in ferromagnesian silicates differ from those in alloys in several important respects. First, as opposed to alloys, the silicate framework remains more or less inert and only a certain number of cations take part in the site exchange. Second, a complete crystalline solution usually exists between the Mg and Fe end members. Third, because 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, and 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 $\alpha$ and $\beta$. M is the inert silicate framework. Following Dienes (1955) and Mueller (1960, 1962, 1969), the disordering process may be represented by the following exchange reaction:

$$A\alpha + B\beta \rightleftharpoons A\beta + B\alpha .$$

(3-6)

In terms of kinetic theory, the time rate of change of A in site $\beta$ is given by

$$-\frac{dx^\beta_A}{dt} = K^\beta_{\alpha} \phi^\beta_{\alpha} x^\beta_A x^\alpha_B - K^\alpha_{\beta} \phi^\alpha_{\beta} x^\alpha_B x^\beta_A ,$$

(6-1)

where $x$ refers to the mole fractions, $K^\beta_{\alpha}$ and $K^\alpha_{\beta}$ are rate constants and functions of $P$ and $T$ only, and are $\phi^\beta_{\alpha}$ and $\phi^\alpha_{\beta}$ analogous to activity coefficient products in a macroscopic chemical system and are functions of $P$, $T$, and $\phi$. At equilibrium,

$$\frac{dx^\beta_A}{dt} = 0$$

and

$$K_{3-6} = \frac{K^\beta_{\alpha}}{K^\alpha_{\beta}} = \frac{x^\beta_A x^\alpha_B}{x^\beta_B x^\alpha_A} = \frac{a^\beta_A a^\alpha_B}{a^\beta_B a^\alpha_A}$$

(6-2)
where $f$ is the partial activity coefficient and $a$ the partial activity. The product of the $f$'s appears as $\phi$ in Equation 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

$$K_D = \frac{x_A^\beta x_B^\alpha}{x_B^\beta x_A^\alpha}.$$  

$K_D$ 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. $S = 1$ corresponds to the highest possible order, and $S = 0$, to complete disorder. This is the opposite in the case of $K_D$. Further, $K_D$ will be used to describe order-disorder in nonstoichiometric 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 ratio of $A$ to $B$ in the crystal and, therefore, is of little thermodynamic significance.

The equilibrium constant $K_{3-6}$ is a function of $P$ and $T$ only. However, as the volume changes involved in the ion exchange are negligible, the dependence of $K_{3-6}$ on $P$ is ignored, and $K_{3-6}$ is considered to be only temperature dependent.

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

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

and

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

where the $\mu^0$'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,

$$\mu_A^\alpha = \mu_A^\beta,$$

and

$$\mu_A^{\alpha 0} = \mu_A^{\beta 0}.$$

To avoid this difficulty, Borghese (1967) regards $A$ in site $\alpha$ as a distinct species from $A$ in site $\beta$. 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, 1969) could also be considered.
The use of a site preference potential may be avoided in practice, particularly because its quantitative use in thermodynamics is rarely of importance.

The standard site preference energy or the intracrystalline ion-exchange energy $\Delta G^0$ for the exchange reaction (Equation 3-6) is given by

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

(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 phenomena is to investigate the thermodynamic properties of the crystalline solution as a whole. In case of an ideal macrophase, the activity-composition relation is given by

$$a_i = (x_i)^N,$$

(6-7)

where $N$ is the number of structural sites in the crystal. When there are two sites,

$$a_i = (x_i)^2,$$

and if these sites are different,

$$a_i = (x_i^\alpha + x_i^\beta),$$

(6-8)

or

$$a_i = (x_i)^\alpha (x_i)^\beta,$$

(6-9)

where $\alpha$ and $\beta$ are two nonequivalent structural sites. The latter method has been generally used (Mueller, 1962; Thompson, 1969). Extending the above method to the nonideal case,

$$a_i = (a_i^\alpha (a_i^\beta),$$

(6-10)

where $a_i^\alpha$ and $a_i^\beta$ are partial activities referring to the sites. In an orthopyroxene (MgMgSi$_2$O$_6$-FeFeSi$_2$O$_6$) where there are two sites, M1 and M2, the activity of Fe$^{2+}$ in the crystal may be expressed as

$$a_{Fe^{2+}}^{op} = \frac{a_{M1}^{M1}}{a_{Fe^{2+}}^{Fe^{2+}}} + \frac{a_{M2}^{M2}}{a_{Fe^{2+}}^{Fe^{2+}}}.$$

(6-11)

If the activity is considered on a one-cation basis, i.e., for the crystal (MgSiO$_3$-FeSiO$_3$),

$$a_{Fe^{2+}}^{op} = \left(\frac{a_{M1}^{M1}}{a_{Fe^{2+}}^{Fe^{2+}}} + \frac{a_{M2}^{M2}}{a_{Fe^{2+}}^{Fe^{2+}}}\right)^{1/2}.$$

(6-12)

The partial activity $a_i^\alpha$ is equal to $f_i^{\alpha} x_i^{\alpha}$ where $f_i$ is the partial activity coefficient. At a certain temperature the atomic ratio $x_i$ in the two sites $\alpha$ and $\beta$ 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 end members AM and BM may be
chosen and heated at a certain temperature for a time long enough to attain equilibrium for the intra-
crystalline ion exchange (Equation 3-6). Several such distribution isotherms may be obtained. A
model suitable for interrelating the partial activity coefficient with the atomic fraction at the site
must be found. The simple mixture or regular solution model may be found useful in cases where the
form of the distribution isotherms does not indicate too much of a nonideal state of mixing A and B
at $\alpha$ and $\beta$. Thus,

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

(6-13)

where $W$ is related to the partial activity coefficient by

$$
RT \ln f_A^a = W (1 - x_A^\alpha)^2.
$$

(1-27)

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

$$
G_M^a = x_A^\alpha R T \ln a_A^\alpha + x_B^\alpha R T \ln a_B^\alpha
$$

(6-14)

$$
G_M^\beta = x_A^\beta R T \ln f_A^a + x_B^\beta R T \ln f_B^a + T (x_A^\alpha R T \ln x_A^\alpha + x_B^\alpha R T \ln x_B^\alpha).
$$

(6-15)

Substituting $S_M^a = -R(x_A^\alpha \ln x_A^\alpha + x_B^\alpha \ln x_B^\alpha)$ and Equation 1-27 into Equation 6-15,

$$
G_M^a = W x_A^\alpha x_B^\alpha - T S_M^a.
$$

(6-16)

The term $W x_A^\alpha x_B^\alpha$ 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

$$
G_M = \frac{x_A^\alpha + x_B^\beta}{2} R T \ln a_A^\alpha \cdot a_B^\beta + \frac{x_B^\alpha + x_B^\beta}{2} R T \ln a_B^\alpha \cdot a_B^\beta
$$

(6-17)

which can be shown to be

$$
G_M = \frac{x_A^\alpha - x_A^\beta}{2} R T \ln K_{3-6} + G_M^a + G_M^\beta
$$

(6-18)

$$
G_M = \frac{x_A^\alpha - x_A^\beta}{2} R T \ln K_{3-6} - T (S_M^a + S_M^\beta) + W x_A^\alpha x_B^\alpha + W x_B^\alpha x_B^\beta.
$$

(6-19)

This expression is similar to the one derived by Grover and Orville (1969) for ideal mixing at the sites.
Note that in the above expression $K_{3-6}$ is the equilibrium constant and not the distribution coefficient,
as in the case of ideal mixing.

Substituting $\Delta G^a = -RT \ln K_{3-6}$ into Equation 6-19,

$$
G_M = \frac{x_B^\beta - x_A^\alpha}{2} \Delta G^a - T (S_M^a + S_M^\beta) + (G_{EM}^a + G_{EM}^\beta).
$$

(6-20)
Thus the free energy of mixing in the crystal as a whole is a result of the energy due to the distribution of the cation between \( \alpha \) and \( \beta \) sites, the entropy change due to the distribution of A and B within \( \alpha \) and \( \beta \) sites, and finally the excess energy of mixing that is the result of the nonideal state of the solution in \( \alpha \) and \( \beta \).

The partial excess free energies of mixing at the sites are

\[
G_{EM}^{\alpha} = H_{EM}^{\alpha} - T S_{EM}^{\alpha}
\]  \hspace{1cm} (6-21)

and

\[
G_{EM}^{\beta} = H_{EM}^{\beta} - T S_{EM}^{\beta}.
\]  \hspace{1cm} (6-22)

Substituting Equations 6-21 and 6-22 into Equation 6-20,

\[
G_M = \frac{x_A^\beta - x_A^\alpha}{2} \Delta G^o + H_{EM}^{\alpha} + H_{EM}^{\beta} - T (S_{IM}^{\alpha} + S_{EM}^{\alpha} + S_{IM}^{\beta} + S_{EM}^{\beta}).
\]  \hspace{1cm} (6-23)

The thermodynamic relations presented in this and earlier sections have been used in analyzing the data on site occupancies in orthopyroxene (Saxena;\(^1\) see also Saxena and Ghose, 1971).

**KINETICS OF ORDER-DISORDER**

Virgo and Hafner (1969) made the important observation that there is an apparent cutoff 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 750 K. Above this temperature the activation energy required for diffusion to start in the direction of disordering is of the order of 80 kJ (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 that 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 it may be noted that no orthopyroxene shows a degree of order representing temperatures lower than 723 K.

Mueller (1970) proposed a two-step mechanism for order-disorder kinetics 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 at any temperature because of slow cooling rate. The same applies to such equilibria in metamorphic rocks. However, in metamorphic rocks attainment of such equilibria is possible below the transition temperature if crystallization or recrystallization occurs at these temperatures. Because of rapid cooling in volcanic rocks, it is very possible that the intracrystalline equilibria are quenched and the temperature indicated by order-disorder is not very much lower than the original temperature of crystallization.

\(^1\)S. K. Saxena: "Retrieval of Thermodynamic Data From a Study of Inter-Crystalline and Intra-Crystalline Ion Exchange Equilibria." To be published in Amer. Mineral., 1972.
Figure 6-1—Temperature estimate of the ion-exchange equilibrium between sites in natural orthopyroxenes; 723 K appears to be the transition temperature below which no more ordering takes place because of a potential barrier.
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