

KINETICS AND THERMODYNAMICS OF INTRACRYSTALLINE DISTRIBUTIONS

ROBERT F. MUELLER

Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, Maryland 20771

ABSTRACT

A general kinetic and thermodynamic model is presented for the distribution of two or more particles between two or more lattice sites. Certain qualitative aspects of the general model are discussed in relation to complex ferromagnesian minerals and quantitative versions of the equation are developed for the quasibinary case with all sites behaving as ideal solutions.

Although the integrated form of the rate equation is obtained only for the ideal, two-site case of the quasibinary crystal, the forms of the rate equations and their implicit solutions are also discussed in some detail for three or more sites. It is shown that the quasibinary model yields a system of nonlinear, first-order differential equations. As a consequence the atomic fraction on any given site is a function only of the atomic fraction on one other site, and this is true for both the rate and equilibrium equations.

An attempt is also made to calculate the specific rate constant and free energy of activation for orthopyroxene, and applications to the study of the thermal history of rocks are suggested.

INTRODUCTION

In a sense all rate and equilibrium phenomena can be considered as distribution problems in which a certain assembly of atoms, ions, or other particles are distributed among a given number of lattice sites. In the limiting case of equilibrium these particles change "positions" only in a detailed microscopic sense but maintain statistically constant occupation numbers at each site. This results in the macroscopically static identity known as a "phase assemblage." But in the case of rate phenomena these distributions change with time so that the quantity, chemical character and detailed internal structure of each phase also change in a macroscopic sense. In this paper we shall be concerned with kinetic and equilibrium aspects of the internal or homogenous intracrystalline distributions of ferromagnesian silicates with particular emphasis on the pyroxenes and amphiboles.

Ordinary phase equilibria are not usually regarded as distribution problems because many of them involve transformations between nearly stoichiometric phases for which the distributions are relatively constant. However, such transformations are characteristic of simple systems. Much more common in nature are the complex solid solutions from which the distribution character of phase equilibria is readily apparent in the sympathetic variations of the compositions of coexisting minerals. The thermodynamic significance of these heterogeneous distributions were initially stressed by Ramberg (1944, 1952) and in recent years they have come to play an increasingly important role in the interpretation of mineral assemblages.

Interest in the intracrystalline distributions of the ferromagnesian silicates dates at least to the classic work of Goldschmidt (1927) who tried to correlate such parameters as the ionic radius and bonding and polarization characteristics of the ions with crystal structure. An analogous approach was also employed by Ramberg (1954) and by DeVore (1957).

Although the classical approach to the solution of crystal structures by X-ray diffraction involves the determination of stoichiometric distributions, some of the first evidence for nonstoichiometric distributions in a complex silicate was obtained by Whittaker (1949) in his study of the amphibole crocidolite. A more recent and petrologically important contribution of this type is the determination by Morimoto, Appleman and Evans (1960) of the structures of clinoenstatite and pigeonite. However, most of the present interest in this general subject was stimulated by the work of Ghose (1961) on the distribution of Mg^{2+} and Fe^{2+} in cummingtonite. Presently investigations of this type are being pursued by a number of workers using X-ray diffraction and such recently developed techniques as infrared, Mössbauer and electron spin resonance spectroscopy.

Study of the kinetics of intracrystalline distributions (order-disorder phenomena) has received its greatest impetus in metallurgy. A particularly important contribution to theoretical aspects of this problem was made by Dienes (1955) who adapted energetic analogues of the early equilibrium model of Bragg and Williams (1934).

When the relatively simple metallic alloys are ordered or disordered, all of the particles and lattice positions are directly involved and large energy and structural changes may occur. In such systems the degree of order is conveniently characterized by a parameter O which is limited by the values zero and unity, corresponding to completely disordered and ordered states respectively. In the disordered state all the lattice sites become energetically equivalent and there is no site preference, whereas in the ordered state the different atoms are almost completely segregated into the nonequivalent sites.

In the case of certain complex crystals such as the ferromagnesian silicates it appears that the intracrystalline distributions may be more conveniently treated by a modified form of the Dienes theory (Mueller, 1967a) and which is

closely analogous to the models employed for heterogeneous distributions. In these ferromagnesian crystals only a fraction of the lattice positions and particles may participate directly in the order-disorder phenomena. For example, in the pyroxenes and amphiboles Mg^{2+} and Fe^{2+} may change their site occupancy numbers as a function of compositional and temperature changes, while Si^{4+} and O^{2-} remain relatively fixed in their positions. Also the ionic characteristic such as radius and charge of such particles as Mg^{2+} and Fe^{2+} are quite similar so that mutual substitution readily occurs over a wide range of compositions and with minimum lattice distortion. Under these circumstances it might be expected that the exchange energies would be relatively independent of the composition at constant volume (or pressure) and temperature and that the identities of the sites would be maintained over the entire temperature range by the relatively rigid framework of nonparticipating particles. Such characteristics imply ideal or near-ideal mixing on each site with a separation of the sites by constant standard exchange energies.

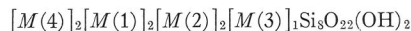
Although the postulate of near constant exchange energy simplifies the treatment of order-disorder phenomena in certain complex silicates where Mg^{2+} and Fe^{2+} are the dominant exchangeable cations, this is not likely where species such as Fe^{3+} , Al^{3+} , Ca^{2+} , Na^{+} of diverse charges and radii are concerned. Indeed it is likely that in such systems the exchange energies are even more compositionally dependent than in the metallic alloys. However, it is still possible to discuss these types of exchange phenomena qualitatively in terms of the most general type of rate equation which is here proposed. With these model resources available we shall concern ourselves with the following aspects of intracrystalline distributions:

1. The forms of the phenomenological rate equations in terms of various concentration units, the structurally dependent stoichiometric coefficients and the deduced relations between the concentration variables and the time
2. The temperature dependence of the rate and equilibrium constants
3. Mechanisms of exchange in terms of the theory of absolute reaction rates
4. Interpretation of existing experimental and observational data in light of the theory
5. Implications of the rate and equilibrium studies in the interpretation of the thermal histories of rocks.

PHENOMENOLOGICAL DEVELOPMENT

General model for two or more sites and particles. We may begin by imagining the most general case possible, that of a crystalline phase in which m different particles (atoms, ions, etc.) are distributed among n nonequivalent sites. Now, in principle, we might expect that there would be a finite probability for any given particle to occupy any of the available sites. However, we know that some of the site occupation numbers will be vanishingly small. This is especially true for the "ionic" crystals which are our major

concern here and in which certain sites are restricted to either anions or cations. Consequently n in our model will refer only to those sites which contain mutually exchangeable ions m in number. To illustrate this we may consider the following formula for an amphibole (Warren, 1930):



This formula expresses the observation that in the amphibole considered there are four major different kinds of metal or cationic sites in addition to those for Si, and these have been designated $M(1)$, $M(2)$, $M(3)$, and $M(4)$. Furthermore the different sites are present in the relative numbers indicated by the outer subscripts. These seven sites of exchangeable cations per formula unit are associated with a relatively constant framework of 8 Si, 22O and 2OH. Although in very complex amphiboles there is considerable substitution in the M positions by such species as Fe^{3+} and Al^{3+} , these positions are usually occupied by Mg^{2+} , Fe^{2+} and Ca^{2+} . Similarly the complex amphiboles usually show considerable Al^{3+} in the Si^{4+} position, but this is a topic beyond our present discussion.

If we now consider the distribution of Mg^{2+} , Fe^{2+} and Ca^{2+} among the $M(1)$, $M(2)$, $M(3)$ and $M(4)$ sites we note that there is very strong tendency for Ca^{2+} to enter the $M(4)$ site (Warren, 1930) while Mg^{2+} and Fe^{2+} are concentrated in the $M(1)$, $M(2)$ and $M(3)$ sites. This partitioning is so strong that the composition of the crystal may approach stoichiometric $Ca_2(Mg, Fe)_5 Si_8 O_{22} (OH)_2$ (actinolite). However in the absence of Ca^{2+} the $M(4)$ site shows a strong preference for Fe^{2+} while Mg^{2+} is heavily concentrated in the remaining sites (Ghose, 1961). Among the pyroxenes analogous behavior is shown by $Ca (Mg, Fe) Si_2 O_6$ and $(Mg, Fe) SiO_3$ (Warren and Bragg, 1928; Ghose, 1964).

The marked partitioning of Ca^{2+} and Fe^{2+} into the $M(4)$ site of cummingtonite is a consequence of the highly distorted polyhedron of oxygen ions which surround this site, while the relatively small degree of partitioning among the $M(1)$, $M(2)$ and $M(3)$ sites results from comparative similarity and regularity of these octahedra.

In the cases of species such as Al^{3+} , Mg^{2+} and Na^{+} which have different valence states there is a strong tendency for coupling such that ions of high charge are concentrated in positions near those of low charge. This was noted by Whittaker (1949) who found that in crocidolite Fe^{3+} tended to concentrate in the $M(2)$ site while Na^{+} concentrated in the adjacent $M(4)$ site so that Pauling's (1948) rule for local electroneutrality is satisfied. According to Papike and Clark (1968) the same relationships hold for the amphibole glaucophane.

On the phenomenological level we may represent the time rate of change of concentration of a species K on the i th lattice site of any crystal as follows:

$$\frac{dC_i^K}{dt} = \sum_{L=1}^{m-1} \sum_{j=1}^{n-1} K_i^K L_j^K L_i^K C_j^K C_i^L - \sum_{L=1}^{m-1} \sum_{j=1}^{n-1} K_j^L L_i^K L_i^K C_j^K C_i^L \quad (1)$$

$(i \neq j; K \neq L)$

TABLE 1. DIFFERENT TYPES OF CRYSTAL LATTICES TO WHICH EQ. (1) AND (2) APPLY

No. of sites	Types of participating particles	Example	Compositional effect	Thermal effect
I few	quite different	simple alloys	large variation in ϕ factors	$K_{ji}^{\circ} \phi_{ji}/\phi_{ij} \rightarrow 1$ at high temperature
II many	quite similar	complex silicates	small variation in ϕ factors	$K_{ji}^{\circ} \phi_{ji}/\phi_{ij} \neq 1$ at high temp.
III many	quite different	complex silicates	large variation in ϕ factors	$K_{ji}^{\circ} \phi_{ji}/\phi_{ij} \neq 1$ at high temp.

The C 's which enter into this expression are the molar or ionic concentrations (per cm^3). $K_i^{K_jL}$ and $K_j^{L_iK}$ represent the specific rate constants for the species and sites indicated by the super and subscripts respectively. For example $K_i^{K_jL}$ is the rate constant for the transport of the species K from the i site and L from the j site. These constants are by definition functions only of the temperature and the volume (or pressure). The ϕ 's are analogous to activity coefficient products in macrosystems and in general are functions of the total crystal composition as well as the volume and temperature.

Although Eq. (1) is quite general as written we shall find it necessary to confine our quantitative discussion to the more restricted forms for which all $\phi = 1$ and which correspond to ideal mixing on each site.

Equation (1) states that the time rate of change of concentration of a given particle on any site is the sum of the positive and negative exchange rates with every other particle on every other site. In elementary kinetic terms a K particle on an i site may be thought of as "reacting" with an L particle on a j site to produce a K particle on a j site and an L particle on an i site.

It may be shown, that when $(dC_i^K/dt) = 0$, corresponding to equilibrium, that each pair of terms must independently equal zero so that in general

$$K_{ji}^{\circ LK} = \frac{K_j^{L_iK}}{K_i^{K_jL}} = \frac{C_i^K C_j^L \phi_i^{K_jL}}{C_i^L C_j^K \phi_j^{L_iK}}, \quad (2)$$

where $K_{ji}^{\circ LK}$ is the equilibrium constant and, like $K_j^{L_iK}$ and $K_i^{K_jL}$, is a function only of the temperature and volume or pressure.

It should be noted that in this derivation there is no need to assign chemical potentials to individual particles on each site; all that enters into equations are the energy differences between the state of order or disorder and the activated state.

We can now recognize a spectrum of possible lattice types to which the general Eqs. (1) and (2) might be applied. However, it is useful to divide this spectrum into certain representative types for which different developments of the equations prove convenient. These types are described in Table 1.

Type I of Table 1, to which the Dienes' modification of the Bragg and Williams model is applicable, presents analytical difficulties because the ϕ factors are exponential

functions of the composition so that numerical solutions of Eq. (1) are required even for the simplest case of binary alloys. Type II on the other hand permits the simplest development possible when the ϕ factors all reduce to unity or are almost constant over certain compositional ranges. It is this type of behavior which is our primary interest here.

Type III on the other hand contains elements of both of the previous types. In the simple alloys of Type I the differences in the particles result largely from such factors as atomic size, but in Type III crystals gross differences of ionic charge may also occur as already discussed for the amphiboles crocidolite and glaucophane. It seems likely that the latter difference might result in even larger variations in the ϕ factors than occurs in the metallic alloys.

As in the case of Type II the $K_j^{\circ} \phi_{ji}/\phi_{ij}$ factors or distribution coefficients of Type III also do not reach unity at high temperatures. In both types this results directly from the maintenance of the nonequivalence of the lattice sites by the relatively inert framework structure.

Quasibinary crystals. A number of important applications of the model occur in systems of two exchangeable ions distributed over two or more sites. Among the amphiboles and pyroxenes the greatest interest is attached to the distribution of Mg^{2+} and Fe^{2+} since these species show a wide range of mutual substitution because of their similarity, lend themselves well to experiment by several techniques, and should provide a good test for the simplest version of the model.

Since only two ions are involved, the complexity of Eqs. (1) and (2) are considerably reduced by the conditions of the type:

$$X_i^K + X_i^L = 1, \quad (3)$$

where the X s refer to the atomic or ionic fraction of the K and L species on each site. It is in fact most convenient to transform Eqs. (1) and (2) into forms which incorporate these ionic fractions. However, if this is done it is also necessary to introduce the proper stoichiometric coefficients V_{ij} and V_{ji} which relate the concentrations on the individual sites to the total concentration C_0 and which are particularly important in crystals which possess nonequivalent sites in different numbers.

If now, as allowed by the condition (3), we omit refer-

ence to the species involved, Eq. (1) becomes:

$$-\frac{dX_i}{dt} = C_0 \sum_{j=1}^{n-1} V_{ij} K_{ij} \phi_{ij} X_i (1 - X_j) - C_0 \sum_{j=1}^{n-1} V_{ji} K_{ji} \phi_{ji} X_j (1 - X_i) \quad (j \neq i). \quad (4)$$

In this expression C_0 is the total concentration of all n sites per unit volume of the crystal and the X s are the atomic or ionic fractions of one of the two exchangeable species on the sites i and j . Furthermore it will be apparent that in each case $V_{ij} = V_{ji}$.

It should be mentioned that C_0 is not quite constant, although it is treated as such here. The reason for this is that C_0 will vary with the K/L ratio since the unit-cell dimensions of the crystals are functions of this ratio. However, in all cases under discussion the amount of this variation is much smaller than other uncertainties and will have no bearing on the result.

To illustrate Eq. (4) we shall first make use of the orthopyroxene type lattice since this type presents the simplest case of only two nonequivalent sites which occur in equal numbers. Consequently $V = 1/2$ and we obtain

$$-\frac{dX_1}{dt} = \frac{1}{2} C_0 [K_{12} \phi_{12} X_1 (1 - X_2) - K_{21} \phi_{21} X_2 (1 - X_1)]. \quad (5)$$

For any fixed bulk composition of the crystal the atomic fractions on the different lattice sites will be related as follows:

$$X_1 + X_2 = 2X, \quad (6)$$

where X is the total atomic fraction for each exchangeable species in the crystal.

If now we consider the case of ideal mixing¹ on both lattice sites $\phi_{12} = \phi_{21} = 1$, and substitution of (6) into (5) yields

$$-\frac{dX_1}{dt} = \frac{1}{2} C_0 K_{12} [(1 - K_{21}^\circ)(X_1)^2 + (2K_{21}^\circ X - 2X + K_{21}^\circ + 1)X_1 - 2K_{21}^\circ X], \quad (7)$$

where K_{21}° is the equilibrium constant and is equal to

$$K_{21}^\circ = \frac{K_{21}}{K_{12}}.$$

For the limiting case of equilibrium we also have

$$K_{21}^\circ = \frac{X_1(1 - 2X + X_1)}{(2X - X_1)(1 - X_1)}. \quad (8)$$

Equation (7) may be integrated directly for both the cases of ordering and disordering under isothermal-isobaric conditions since under these conditions K_{12} , K_{21} and K_{21}° remain constant (Mueller 1967a). Then for ordering we obtain:

¹ It is important to keep in mind that ideal mixing on individual lattice sites is in general equivalent to non-ideal mixing in the crystal as a whole (Mueller, 1962, Matsui and Banno, 1965).

$$-\frac{1}{2} C_0 K_{12} \Delta t = \frac{1}{2 \left(\frac{b^2}{4} - ca\right)^{1/2}} \ln \frac{cX_1 + \frac{b}{2} - \left(\frac{b^2}{4} - ca\right)^{1/2}}{cX_1 + \frac{b}{2} + \left(\frac{b^2}{4} - ca\right)^{1/2}} \Bigg|_{X_1'}^{X_1''}, \quad (9)$$

and for disordering:

$$\frac{1}{2} C_0 K_{12} \Delta t = \frac{1}{2 \left(\frac{b^2}{4} - ca\right)^{1/2}} \ln \frac{\left(\frac{b^2}{4} - ca\right)^{1/2} + \left(cX_1 + \frac{b}{2}\right)}{\left(\frac{b^2}{4} - ca\right)^{1/2} - \left(cX_1 + \frac{b}{2}\right)} \Bigg|_{X_1'}^{X_1''}, \quad (10)$$

where the constants are defined as follows:

$$\begin{aligned} c &= 1 - K_{21}^\circ \\ b &= 2K_{21}^\circ X - 2X + K_{21}^\circ + 1 \\ a &= -2K_{21}^\circ X \end{aligned}$$

These equations have an interesting and useful form in that a single rate constant occurs only on the left while the constants on the right contain only the bulk composition X and the equilibrium constant K_{21}° . Since both of the latter parameters are measurable independently of the rate data it is left merely to measure X_1 as a function of Δt the time interval. Although both Eqs. (9) and (10) yield curves of similar form, the case of disordering will be stressed here since it lends itself best to the laboratory time scale.

If we wish to disorder the crystal according to Eq. (10) it is necessary to begin with an ordered crystal with the corresponding low temperature values of K_{21}° , X_1 and X_2 . However, the value of K_{21}° , which enters into Eq. (10) through a , b and c and which determines the ultimate degree of equilibrium disorder is that which corresponds to the disordering temperature. The initial low temperature value of K_{21}° occurs only implicitly in (10) through its determination of the initial value $X_1 = X_1'$ of the lower limit of integration. In graphical terms this yields a plot of $1/2 C_0 K_{12} \Delta t$ as a function of X_1 .

For convenience in relating Eq. (10) to the experimental data on the pyroxenes we choose the following values of the equilibrium constants:

$$\begin{aligned} K_{21}^\circ \text{ (low temp.)} &= 51 \\ K_{21}^\circ \text{ (high temp.)} &= 3.24 \end{aligned}$$

Then for a crystal with $X = 0.5$, Eq. (8) yields

$$\begin{aligned} X_1 \text{ (initial)} &= 0.878 \\ X_1 \text{ (final)} &= 0.643 \end{aligned}$$

The isothermal-isobaric equilibrium distribution corresponding to the low-temperature ordered crystal with $K_{21}^\circ = 51$ is shown as curve (1) in Figure 1, while the high temperature disordered equilibrium distribution with $K_{21}^\circ = 3.24$ is shown as curve (3) in this figure. The curve (2) corresponding to $K_{21}^\circ = 10$, is for an intermediate tempera-

ture of disordering. Also shown for comparison is the 45° dashed line which represents complete disorder and which is excluded by the model except as a limiting case.

The arrows designated (a), (b) and (c) in Figure 1 indicate the displacement of points on the curve which occurs during disordering of two crystals of different bulk compositions, one with $X = 0.5$ and the other with $X = 0.6$. The corresponding rate curves are shown in Figure 2.

As an illustration of the next step in complexity involving a three-site quasibinary lattice we may utilize the structure of the amphibole actinolite. However, we shall not be concerned primarily at this point about the actual mineral actinolite or whether it indeed behaves as outlined here. We shall assume simply that all the $M(4)$ sites are unavailable because they are filled with Ca^{2+} and that Mg^{2+} and Fe^{2+} are distributed among the $M(1)$, $M(2)$ and $M(3)$ sites. Now there are two sites each of $M(1)$ and $M(2)$ but just one of $M(3)$ per formula unit since $M(3)$ occupies the crystallographic origin (Warren, 1930). Consequently the bulk atomic fraction X is related to these sites as:

$$5X = 2X_1 + 2X_2 + X_3, \quad (11)$$

where the X 's refer to one of the two mutually substituted ions so that

$$X = \text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+}).$$

There are then three simultaneous differential equations such as (4) which express the variation of X_1 , X_2 and X_3 with the time. However, because of (11) only two of these equations are independent. If we choose the equations for

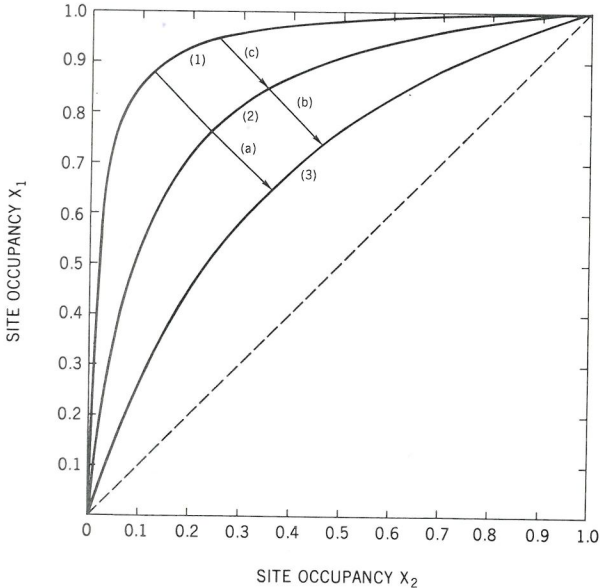


FIG. 1. Equilibrium isotherms (Curves 1, 2 and 3) for the distribution of two atoms among the nonequivalent sites 1 and 2. The lettered arrows indicate the movement of points on the curves with increasing temperature for two different values of the total atomic fraction.

X_1 and X_2 and at the same time assume ideal solutions at all three sites we obtain:

$$-\frac{dX_1}{dt} = C_0 \left[\frac{2}{5} K_{12} X_1 (1 - X_2) + \frac{1}{5} K_{13} X_1 (1 - X_3) - \frac{2}{5} K_{21} X_2 (1 - X_1) - \frac{1}{5} K_{31} X_3 (1 - X_1) \right], \quad (12)$$

$$-\frac{dX_2}{dt} = C_0 \left[\frac{2}{5} K_{21} X_2 (1 - X_1) + \frac{1}{5} K_{23} X_2 (1 - X_3) - \frac{2}{5} K_{12} X_1 (1 - X_2) - \frac{1}{5} K_{32} X_3 (1 - X_2) \right]. \quad (13)$$

If now (11) is substituted into (12) and (13) these become

$$\frac{dX_1}{dt} = A' + B'X_1 + C'X_2 + D'X_1X_2 + E'(X_1)^2, \quad (14)$$

$$\frac{dX_2}{dt} = A + BX_1 + CX_2 + DX_1X_2 + E(X_2)^2, \quad (15)$$

with the constants defined as follows:

$$A = C_0(K_{32}X)$$

$$B = C_0 \left(\frac{2}{5} K_{12} - \frac{2}{5} K_{32} \right)$$

$$C = C_0 \left(-\frac{2}{5} K_{21} - \frac{1}{5} K_{23} + K_{23}X - \frac{2}{5} K_{32} - K_{32}X \right)$$

$$D = C_0 \left(\frac{2}{5} K_{21} - \frac{2}{5} K_{23} - \frac{2}{5} K_{12} + \frac{2}{5} K_{32} \right)$$

$$E = C_0 \left(-\frac{2}{5} K_{23} + \frac{2}{5} K_{32} \right)$$

$$A' = C_0(K_{31}X)$$

$$B' = C_0 \left(-\frac{2}{5} K_{12} - \frac{1}{5} K_{13} + K_{13}X - \frac{2}{5} K_{31} - K_{31}X \right)$$

$$C' = C_0 \left(\frac{2}{5} K_{21} - \frac{2}{5} K_{31} \right)$$

$$D' = C_0 \left(\frac{2}{5} K_{12} - \frac{2}{5} K_{13} - \frac{2}{5} K_{21} + \frac{2}{5} K_{31} \right)$$

$$E' = C_0 \left(-\frac{2}{5} K_{13} + \frac{2}{5} K_{31} \right)$$

In order to obtain even an implicit solution for (14) and (15) it is desirable first to eliminate the time. These two equations then yield the following first order equation:

$$[A + BX_1 + CX_2 + DX_1X_2 + E(X_2)^2]dX_1 - [A' + B'X_1 + C'X_2 + D'X_1X_2 + E'(X_1)^2]dX_2 = 0. \quad (16)$$

This equation is not exact and although Boole (1859) discussed a solution to a more restricted version of this general form, the writer is unaware of a solution for this general form.

It would of course be possible to determine the nature of the function if reasonable values of the rate constants could be estimated, but so far this information seems unobtainable. In any case, the complexities of these equations increase rapidly with the number of nonequivalent sites.

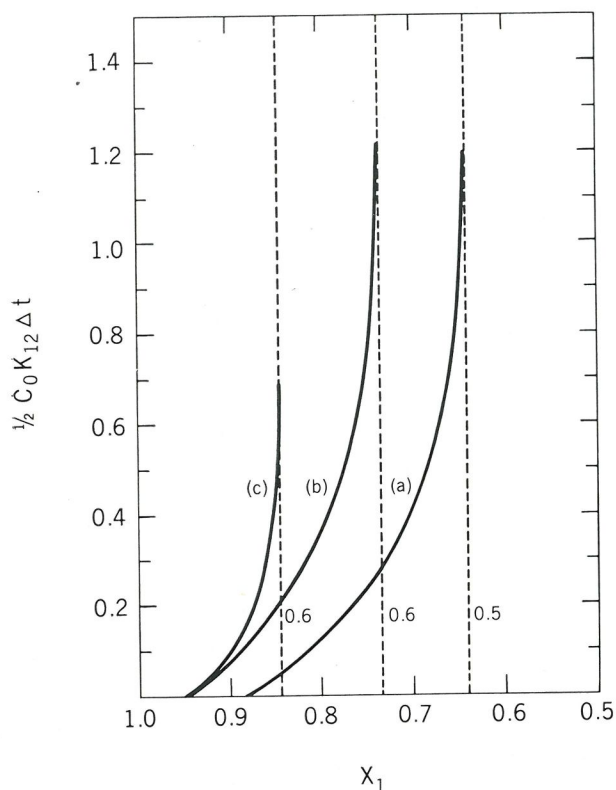


FIG. 2. Isothermal disordering curves for two different total atomic fractions $X = 0.5$ and $X = 0.6$ and two different temperatures. The letters are the same as appear in Fig. 1.

In the absence of explicit solutions for equations of the type (16) it is still possible to derive information from their general forms and from the implicit solutions. The system of rate equations of the form (4) will always lead to a system of nonlinear first order equations in the site occupancy factors. Thus in general for n sites we obtain the system:

$$\begin{aligned} \frac{dX_2}{dX_1} &= f_2(X_1, X_2, \dots, X_{n-1}) \\ \frac{dX_{n-1}}{dX_1} &= f_{n-1}(X_1, X_2, \dots, X_{n-1}), \end{aligned} \quad (17)$$

where X_1 is regarded as the independent variable. So that Eq. (16) for three sites yields the single equation

$$\frac{dX_2}{dX_1} = f_2(X_1, X_2).$$

The implicit solutions of the system (17) are

$$\begin{aligned} X_2 &= X_2(X_1, C_1, \dots, C_{n-2}) \\ &\dots \dots \dots \\ X_{n-1} &= X_{n-1}(X_1, C_1, \dots, C_{n-2}), \end{aligned} \quad (18)$$

where C_s are constants of integration. Also X_n may be obtained from relations of the type of (11). Thus the solution of (16) becomes

$$X_2 = X_2(X_1, C_1). \quad (19)$$

Once solutions of the form of (18) have been obtained they may be substituted back into the original rate equations of the form (4) involving the time. In this manner all the site occupancy factors except X_1 may be eliminated and the equation integrated as in the case of (7) to yield X_1 as a function of Δt .

As an interesting and important illustration of the rate equations one step beyond (14) and (15) we may choose the model for the cummingtonite type lattice in which the exchangeable cations are distributed over four nonequivalent sites of the amphibole structure. The equation analogous to (11) then is

$$7X = 2X_1 + 2X_2 + X_3 + 2X_4 \quad (20)$$

From this number of sites there will result three independent rate equations analogous to (12) and (13) which for brevity may be presented as in Table 2. In these equations X_4 has been regarded as eliminated through the relation (20) and if this is done these equations can be transformed into three equations analogous to (14) and (15), but with the three site occupancy factors, X_1 , X_2 , and X_3 appearing explicitly in each. If the time were now eliminated from the latter the existence of the following solutions would be implied:

$$\begin{aligned} X_2 &= X_2(X_1, C_1, C_2), \\ X_3 &= X_3(X_1, C_1, C_2). \end{aligned}$$

It is of some importance that the existence of these systems of ordinary first order equations implies that if any one of the compositional variables is chosen as independent all the others are functions only of this variable. Further-

TABLE 2. RATE CONSTANTS AND CORRESPONDING STOICHIOMETRIC COEFFICIENTS FOR THE CUMMINGTONITE TYPE LATTICE

Rate constant	Stoichiometric coefficient	
$\frac{dX_1}{dt}$	K_{12}	2/7
	K_{21}	2/7
	K_{13}	1/7
	K_{31}	1/7
	K_{14}	2/7
$\frac{dX_2}{dt}$	K_{21}	2/7
	K_{12}	2/7
	K_{23}	1/7
	K_{32}	1/7
	K_{24}	2/7
$\frac{dX_3}{dt}$	K_{42}	2/7
	K_{32}	2/7
	K_{23}	2/7
	K_{31}	2/7
	K_{13}	2/7
$\frac{dX_4}{dt}$	K_{34}	2/7
	K_{43}	2/7

more, although the equations have been derived under the assumptions that the ϕ factors were all equal to one, the same type of dependency would hold if these factors were functions of the same set of variables as appear in the rest of the rate equation. Of course the solutions would be even more complicated in this event.

However, if the ϕ factors were at the same time functions of other compositional variables other than those of the quasibinary system, the above stated simple dependency could no longer hold. Such a situation might arise in a real crystal when the framework structure shows compositional variation.

Effect of temperature. One of the central aspects of the study of intracrystalline exchange is the effect of temperature on the equilibrium and rate constants. The effect of temperature on the equilibrium constant is sometimes known from experiments. In the examples studied so far this change has been found to be in accord with simple thermodynamic considerations. Thus if K_{21}° is an ordering equilibrium constant and ΔE_{21}° is the standard internal energy change¹ in the exchange process then

$$\frac{\partial \ln K_{21}^\circ}{\partial T} = \frac{\Delta E_{21}^\circ}{RT^2}. \quad (21)$$

Now the internal energy is related to the Helmholtz free energy as follows:

$$\Delta F_{21}^\circ = \Delta E_{21}^\circ - T\Delta S_{21}^\circ. \quad (22)$$

The quantity ΔS_{21}° is the standard entropy change and would be expected to be small. Consequently if we write the exchange reaction for ordering so that $\Delta F_{21}^\circ < 0$ we should expect that $\Delta E_{21}^\circ < 0$ also. As a consequence of the negative value of ΔE_{21}° , K_{21}° decreases toward unity. We shall see that this accords with the examples studied so far.

Similarly we know that the experimental energy of activation E_{ex}^* is related to the rate constant K as follows:

$$\frac{\partial \ln K}{\partial T} = \frac{E_{\text{ex}}^*}{RT^2}. \quad (23)$$

We shall see that E_{ex}^* is always positive since it contains the potential energy change of the barrier between stable states. Consequently

$$\frac{\partial K_{21}^\circ}{\partial T} < 0, \quad \frac{\partial K_{21}}{\partial T} > 0, \quad \frac{\partial K_{12}}{\partial T} > 0, \quad (24)$$

while

$$K_{21}^\circ = \frac{K_{21}}{K_{12}} > 1. \quad (25)$$

If we differentiate (25) we obtain

$$\frac{\partial K_{21}^\circ}{\partial T} = \frac{1}{K_{12}} \left(\frac{\partial K_{21}}{\partial T} - K_{21}^\circ \frac{\partial K_{12}}{\partial T} \right). \quad (26)$$

¹ Internal energy is used here to be consistent with the concentration standard state, which is formally required in the kinetic treatment.

Then as a consequence of the relations (24) we find that

$$\frac{\partial \ln K_{12}}{\partial T} > \frac{\partial \ln K_{21}}{\partial T}, \quad (27)$$

so that

$$E_{\text{ex}12}^* > E_{\text{ex}21}^*.$$

Thus for each increase in the temperature the disordering rate constant increases more proportionately than that for ordering and this results in a decrease in K_{21}° .

To see how the changes in the rate and equilibrium constants with temperature affect the time scale of disordering we rewrite Eq. (10) as follows:

$$\frac{1}{2} C_0 K_{12} \Delta t = \frac{1}{2 \left(\frac{b^2}{4} - ca \right)} \ln Z \equiv Y. \quad (28)$$

Here $\ln Z$ refers to the difference of the log terms with the limiting composition X_1' and X_1'' . If we compare the values of Y corresponding to the same values of X_1 for both curves (b) and (c) of Figure 2 we see that $K_{12} \Delta t$ is greater the lower the temperature of disordering. Then since K_{12} has a smaller value at the lower temperature, Δt the time interval at which the same value of X_1 is attained must increase with decreasing temperature of disordering.

On the other hand if we now compare the fractional attainment of equilibrium disorder for the two curves, we obtain a somewhat different result. For example, in the case of curve (b), one half the equilibrium degree of disorder is attained when $X_1 = 0.840$ whereas in the case of (c) one half disorder is attained when $X_1 = 0.895$. In this case Y decreases almost $\frac{1}{2}$ with the temperature of disordering. As a result the time interval Δt for fractional disordering may in some cases remain essentially constant. These results are of considerable interest in the interpretation of experimental data.

MECHANISMS AND ABSOLUTE REACTION RATES

It is desirable to further elucidate the rate equations already presented by considering the exchange mechanism from the standpoint of the theory of absolute reaction rates (Glasstone, Laidler and Eyring, 1941). According to this theory if two particles A and B are concentrated in the lattice sites 1 and 2 respectively in the low temperature ordered state, then for disordering to occur they must first pass through an activated transitional state astride a potential energy barrier as shown in Figure 3. The change of potential energy ΔU^* is always positive because the stable ordered and disordered states lie in potential wells. Also since the potential energy changes make the largest contribution to E_{ex}^* the energy of activation, the magnitude of this quantity is directly related to the corresponding value of ΔU^* . However, we have already seen that $E_{\text{ex}12}^*$ is greater than $E_{\text{ex}21}^*$ and this is the reason Figure 3 has been constructed with $\Delta U_{12}^* > \Delta U_{21}^*$.

The transitional state is regarded as being in equilibrium

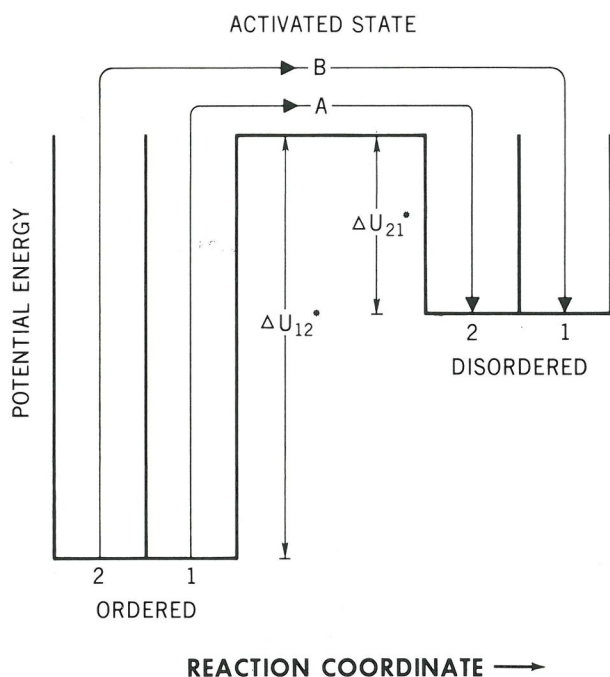


FIG. 3. Potential energy diagram for an intracrystalline exchange process involving particles A and B in sites 1 and 2. The potential energy differences of individual particles and sites are not distinguished and the shapes of the wells and barrier have no significance. Arrows indicate the disordering process.

with the reactant state and as possessing thermodynamic properties just as does this state. Similarly in the ordering process the particles of the disordered state are regarded as being in equilibrium with the same activated complex.

According to the theory the specific rate constant K may be expressed as

$$K = \kappa \frac{kT}{h} K^* \quad (29)$$

where k is Boltzmann's constant, h is Planck's constant, κ is the transmission coefficient and K^* is the equilibrium constant linking the particles in the reactant and activated states. But Eq. (29) takes this simple form only if all the particles are regarded as forming ideal solutions (Glasstone, *et al.*, 1941). Also, in conformity with common practice and because of lack of information on κ we set this parameter equal to one.

The equilibrium constant is defined as

$$K^* = \exp(-\Delta G^*/RT), \quad (30)$$

where ΔG^* is the change in Gibbs free energy in going from the reactant to the activated state.

Technically if the standard state is defined in concentration units as it is here Eq (29) should be differentiated at constant volume to obtain the temperature effect. If this is done we obtain the following alternative expression for Eq. (23):

$$\frac{E_{ex}^*}{RT^2} = \frac{1}{T} + \left(\frac{\partial \ln K^*}{\partial T} \right)_v, \quad (31)$$

so that

$$E_{ex}^* = RT + \Delta E^*, \quad (32)$$

where ΔE^* is the change in internal energy on activation. Also

$$\Delta H^* = \Delta E^* + P\Delta V^*, \quad (33)$$

where ΔH^* is the enthalpy change and ΔV^* the volume change of activation.

Although ΔV^* cannot be readily estimated it should not be large, and since P the pressure is low to moderate in most experimental situations, $\Delta E^* \sim \Delta H^*$ and $\Delta G^* \simeq \Delta F^*$ where ΔF^* is the Helmholtz free energy change.

Now Eq. (10) provides us with a method of calculating the rate constant of disordering K_{12} from the experimentally determined values of K_{21}° , X_1 and Δt . However, a crude value of K_{12} can also be estimated even though X_1 and Δt are only poorly known. To make this estimate we define a "characteristic time" of disordering for which X_1 has just virtually attained its equilibrium value and the quantity Y of Eq. (28) has some value Y_0 . If we examine Figure 2 we see that for curves (a) and (b) a convenient value is $Y_0 = 1$ so that if the characteristic time is Δt then

$$\frac{1}{2} C_0 K_{12} \Delta t = 1. \quad (34)$$

Once K_{12} is known it is possible to estimate ΔG^* through Eq. (30) and then if the corresponding entropy change ΔS^* can be estimated, the expression $\Delta G^* = \Delta H^* - T\Delta S^*$ can also be used to estimate ΔH^* or ΔE^* . However the estimation of ΔS^* is difficult. Now the exchange process requires the simultaneous activation of both A and B particles and the probability of this event is incorporated into the rate constant as a frequency factor. This probability will in turn be governed by the configuration of the activated complex and since this involves a somewhat ordered state for A and B it seems likely that $\Delta S^* < 0$. Since ΔG^* also is positive, we should expect that $\Delta H^* < \Delta G^*$ and that $\Delta E^* < \Delta F^*$.

APPLICATIONS TO THE PYROXENES AND AMPHIBOLES

We have already indicated that the derived model is applicable in various ways to the complex silicates. The qualitative aspects of the general model which distinguishes the different lattice types have been presented in Table 1. However, the development for the quasibinary solutions appears particularly suitable to the $Mg^{2+} - Fe^{2+}$ pyroxenes and amphiboles such as orthopyroxene, cummingtonite, anthophyllite and actinolite.

At the present time only very limited experimental data exist for the application of the rate equations, and the thermodynamic data, although somewhat more abundant, are also still in a preliminary stage. Thus the work of Ghose and Hafner (1967) on orthopyroxene has indicated

that continuous distribution curves analogous to those of Figure 1 are adhered to. These authors have also shown that when metamorphic pyroxenes are heated the curves move toward the 45° line. Similarly the distribution curves of rapidly quenched volcanic pyroxenes lie closer to the 45° line than do those of unheated metamorphic pyroxenes. Thus the existing data provide rather striking confirmation of the simple thermodynamic model represented by Eq. (2). However, there is some evidence that the distributions obtained for orthopyroxene are not quite as simple as those shown in Figure 1 for which ϕ factors are all equal to unity. If this is true the mixing on the lattice sites is not ideal and may take a form similar to that already proposed earlier (Mueller, 1962) for cummingtonite. However, for the present purposes it will be adequate to assume that if the ϕ factors which enter into Eq. (5) are not all unity that they may at least be regarded as small over the range of conditions discussed here.

Ghose and Hafner (1967) applied this simple ideal solution model to unheated metamorphic pyroxenes and obtained a value of approximately 48 for K_{21}° . Similarly for the volcanic orthopyroxene they obtained $K_{21}^\circ = 12$.

Recently also a preliminary report was given by Hafner and Virgo (1968) on the kinetics of disordering of orthopyroxene.¹ They found that at 1000°C virtually the maximum degree of disorder was attained in about a day for a crystal for which $X_1 = \text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+})$ on the $M1$ site was approximately 0.7 and for which the total atomic fraction $X = \text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+})$ was 0.6. If these data are substituted into Eq. (8) the equilibrium constant for the disordered state is $K_{21}^\circ = 2.33$. Both this high temperature value and the low temperature value of $K_{21}^\circ = 48$ may, within the limits of uncertainty, be represented by curves (1) and (3) of Figure 1 and curve (b) of Figure 2. Consequently we may employ these curves directly to estimate K_{12} by setting $\frac{1}{2}C_0K_{12}\Delta t = 1$. The characteristic time so defined may be inaccurate by a factor of 10 or 100, but this will have only a small influence on the value of ΔG^* thus determined. For example it may happen that the measured time actually corresponds to $\frac{1}{2}C_0K_{12}\Delta t = 100$, but this will change ΔG_{12}^* by only $RT \ln 100$, which is still quite small relative to the magnitude of ΔG_{12}^* .

If we now consult the unit-cell volume data (Robie, Bethke, Toulmin and Edwards, 1966) we find that $C_0 \simeq 0.032$ mole cm^{-3} , although this value will vary slightly with composition. Then since $\Delta t = 8.64 \times 10^4$ sec per day we find that K_{12} at 1000°C is approximately 7.33×10^{-4} cm^3 mole⁻¹ sec⁻¹. If we now solve Eq. (29) for ΔG_{12}^* we find this amounts to 232,800 calories at 1000°C.

Although the activation process involves the simultaneous breaking of 12 M -O bonds, this value of ΔG^* seems high. This is especially true in view of the 20,000 calories ob-

tained for E_{ex}^* by Virgo and Hafner (1969). Such a large difference between ΔG^* and E_{ex}^* can be explained either by large negative values of ΔS^* or by a small transmission coefficient. It is interesting that both of these effects are possible and in the right direction from a theoretical standpoint. Although there is no way to evaluate the transmission coefficient, we may estimate ΔS^* by ignoring the RT term in equation (32) and by setting E_{ex}^* equal to ΔE^* (or ΔH^*). This yields $\Delta S^* \simeq -167$ e.u. It is interesting that negative values of ΔS^* almost this large are encountered from electrostatic forces when ions with high charges of the same sign react in dilute aqueous solutions (Glasstone *et al.*, 1941). It is possible that a similar but somewhat magnified effect is involved here.

Although no kinetic data comparable to the foregoing yet exist for other pyroxenes and amphiboles, some data of thermodynamic significance exist for cummingtonite. An equilibrium model for the distribution of Mg^{2+} and Fe^{2+} in this mineral was originally proposed (Mueller, 1962) to correlate the intracrystalline and heterogeneous distributions of these ions for the coexisting minerals. This correlation was based on the single distribution point which has been measured by Ghose (1961) from X-ray data and which first disclosed the strong concentration of Fe^{2+} in the $M(4)$ site. In the equilibrium model an attempt was made to determine in a quantitative way the distribution between the $M(4)$ site (V sublattice) and the weighted average of the $M(1)$, $M(2)$ and $M(3)$ sites (W sublattice) over the entire range of composition. Two different equilibrium distributions were derived from the heterogeneous equilibria between cummingtonite and actinolite. One of these derived distributions is based on an ideal solution model for both the V and W sublattices while the other is equivalent to the assumption that all of the nonideality observed in cummingtonite is concentrated in the $M(4)$ site. The ideal solution model for the V and W sublattice was also applied by Matsui and Banno (1965) who showed that it results in a fairly good fit of the macroscopic distribution data for coexisting cummingtonite and actinolite.

Subsequent to Ghose's (1961) determination of the cummingtonite distribution by X-rays a number of studies were undertaken to determine the distribution over a wider range. In particular Bancroft, Burns and Maddock (1967) were the first to apply Mössbauer and infrared spectra to this end. Although their experimental data show considerable scatter, they are in strong qualitative agreement with the X-ray results. Unfortunately neither the X-ray nor other published data are precise or abundant enough to establish the detailed course of the distribution curve or to demonstrate the continuity predicted by the thermodynamic model. More recently, however, Ghose and Hafner (1968) examined ⁵⁷Fe hyperfine Mössbauer resonance absorption spectra of 14 cummingtonites for values of $X = \text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+})$ ranging from 0.02 to 0.62. These spectra consist of two doublets, one for the smaller nuclear quadrupole splitting attributable to ⁵⁷Fe at the $M(4)$ site

¹ The values quoted here are somewhat different from the final refined values (Virgo and Hafner, 1969), but this difference does not change the calculations significantly.

(V sublattice) and the other of ^{57}Fe at the $M(1)$, $M(2)$ and $M(3)$ sites (W sublattice) as previously determined by Bancroft, *et al.* (1967). However, the doublets distinguishing $M(1)$, $M(2)$ and $M(3)$ from each other could not be resolved. Furthermore it is concluded by Ghose and Hafner from the nearly identical temperature dependence of the splitting at these sites that a similar degree of distortion from the regular octahedron prevails at each of the three types of sites. Thus the latest data tend to justify the grouping of sites into the V and W sublattices.

Interpretation of the data of Ghose and Hafner (1968) also strongly supports the continuous distribution model. Their points fall close to the curve for which $K_{vw}^\circ = (1.8)^{7/2}$ and where 1.8 refers to the macroscopic distribution constant for coexisting cummingtonite and actinolite (Mueller, 1961). Indeed, it appears that the fitted distribution curve even exhibits the same type of curvature shown by the model which ascribes a small degree of non-ideality to the $M(4)$ site. If the latter situation holds true it will be necessary to retain small ϕ factors in Eq. (4) to adequately treat the energetic behavior of this mineral.

GENERAL PETROLOGIC APPLICATIONS

The intracrystalline exchange phenomena provide us with a means of studying the thermal history of rocks and meteorites which supplements those of the heterogeneous reactions between coexisting minerals. However, it is important to realize that these two classes of phenomena may frequently apply to quite different temperature ranges. This is readily apparent if we consider the heterogeneous exchange involving Ca-pyroxene and orthopyroxene.



This reaction is applicable to a variety of igneous and metamorphic rocks and meteorites, and it has been shown to reflect the temperature of crystallization rather well (Kretz, 1963). Among known igneous rocks perhaps the closest approach to equilibrium between coexisting minerals is exhibited by the Stillwater complex of Montana (Hess, 1960; McCallum, 1968). McCallum has found that in this complex macrocrystals of coexisting Ca-pyroxene and orthopyroxene have distribution coefficients of approximately 1.35, corresponding to magmatic or near magmatic temperatures. On the other hand these same macrocrystals also exhibit exsolution lamellae. Within the Ca-pyroxene macrocrystals, where these lamellae attain the greatest width, the

distribution coefficient for Fe^{2+} and Mg^{2+} between unmixed orthopyroxene and Ca-pyroxene host is about 1.8, which corresponds to an unmixing temperature in the range of 600–700°C. Since some of these lamellae are of the order of 50 microns in width it appears that Ca^{2+} , Mg^{2+} and Fe^{2+} were able to redistribute themselves over this distance within a single crystal during the slow cooling of this plutonic rock. However, the retention of the high temperature distributions by the macrocrystals indicates that redistribution on a scale of their dimensions did not occur.

If we know that exsolution has occurred in Ca-pyroxene it is predictable that intracrystalline ordering should have occurred even more readily since the reaction coordinate of exchange in the ordering process should be measured in angstrom units rather than the microns required for the diffusion path of unmixing. This follows because the activation energy per unit jump in exsolution should be of the same order as that involved in ordering. As a consequence we should expect overlapping ranges of temperatures in which the different processes occur: (1) Heterogeneous reactions such as (a) will occur only at high temperatures or when at lower temperatures a rock is subject to differential stresses (Mueller, 1967b); (2) Exsolution occurs during slow cooling under static conditions with a lower limit perhaps somewhere in the range of high grade metamorphism; and (3) Ordering of cations occurs throughout the range of (1) and (2) but probably continues to even somewhat lower temperatures than those for which exsolution is possible.

When cooling is rapid enough, as in certain volcanic rocks and meteorites, a considerably disordered state may be quenched in as is shown by the measurement of Ghose and Hafner (1966). However, it is likely that the value of 12 observed for K_{21}° represents a temperature somewhat lower than the highest attained. As has been pointed out (Mueller, 1967a) the suppression of the ordering process results from the decrease of the rate constants with temperature. However, once the temperature dependence of the rate constants has been experimentally determined it should be possible, at least in principle, to estimate the time scale of ordering over a broad temperature range and to determine cooling rates for many rocks.

ACKNOWLEDGMENTS

The writer appreciates the opportunity for numerous discussions with Drs. Subrata Ghose and Stefan Hafner on the problems of intracrystalline distributions. He also appreciates their generosity in allowing him to study their unpublished data.

REFERENCES

- BANCROFT, G. M., R. G. BURNS, AND A. G. MADDOCK (1967) Determination of cation distribution in the cummingtonite-grunerite series by Mössbauer spectra. *Amer. Mineral.* **52**, 1009–1026.
- BOOLE, GEORGE (1859) *Differential equations*. Chelsea, New York.
- BRAGG, W. L. AND E. J. WILLIAMS (1934) Effect of thermal agitation on atomic arrangement in alloys. *Proc. Roy. Soc. (London)* **145A**, 699–730.
- DE VORE, G. W. (1957) The association of strongly polarizing cations with weakly polarizing cations as a major influence in element distribution, mineral composition, and crystal growth. *J. Geol.* **65**, 178–195.
- DIENES, G. J. (1955) Kinetics of order-disorder transformations. *Acta Met.* **3**, 549–557.
- GHOSE, S. (1961) The crystal structure of a cummingtonite. *Acta Crystallogr.* **14**, 622–627.

- (1964) Mg^{2+} - Fe^{2+} order in orthopyroxene, $Mg_{0.93}Fe_{0.07}Si_2O_6$. *Z. Kristallogr.* **122**, 82-99.
- , AND S. HAFNER (1967) Mg^{2+} - Fe^{2+} distribution in metamorphic and volcanic orthopyroxenes. *Z. Kristallogr.* **125**, 157-162.
- AND — (1968) Mg-Fe distribution over (M_1 , M_2 , M_3) and M_4 in cummingtonite (abstr.). *Geol. Soc. Amer. Mexico City Meet.* [*Geol. Soc. Amer. Spec. Pap.* **121**, 110 (1969).]
- GLASSTONE, S., K. J. LAIDLER AND H. EYRING (1941) *The Theory of Rate Processes*. McGraw-Hill, New York.
- GOLDSCHMIDT, V. M. (1927) Geochemische Verteilungsgesetze der Elemente. VIII. *Skr. Norsk Vid. Akad. Oslo Mat. Kl.*, **1925**, No. 8.
- HAFNER, S., AND D. VIRGO (1968) An experimental investigation of the order-disorder kinetics in the orthopyroxene series. (abstr.) *Amer. Geophys. Un. Trans.* **49**, 340.
- HESS, H. H. (1960) Stillwater igneous complex, Montana. *Geol. Soc. Amer. Mem.* **80**.
- KRETZ, R. (1963) Distribution of magnesium and iron between orthopyroxene and calcic pyroxene in natural mineral assemblages. *J. Geol.* **71**, 773-785.
- MATSUI, Y., AND S. BANNO (1965) Intracrystalline exchange equilibrium in silicate solid solutions. *Proc. Jap. Acad.* **41**, 461-466.
- MCCALLUM, I. S. (1968) *Equilibrium Relationships Among the Coexisting Minerals in the Stillwater Complex, Montana*. PhD Thesis, Univ. Chicago, Chicago, Ill.
- MORIMOTO, N., D. E. APPLEMAN, AND H. T. EVANS (1960) The crystal structures of clinoenstatite and pigeonite. *Z. Kristallogr.* **114**, 120-147.
- MUELLER, R. F. (1961) Analysis of relations among Mg, Fe and Mn in certain metamorphic minerals. *Geochim. Cosmochim. Acta* **25**, 267-296.
- (1962) Energetics of certain silicate solid solutions. *Geochim. Cosmochim. Acta* **26**, 581-598.
- (1967a) Model for order-disorder kinetics in certain quasi-binary crystals of continuously variable composition. *J. Phys. Chem. Solids* **28**, 2239-2243.
- (1967b) Mobility of the elements in metamorphism. *J. Geol.* **75**, 565-582.
- PAPIKE, J. J., AND J. R. CLARK (1968) The crystal structure and cation distribution of glaucophane. *Amer. Mineral.* **53**, 1156-1173.
- PAULING, L. (1948) *The Nature of the Chemical Bond*. Cornell University Press, Ithaca.
- RAMBERG, H. (1944) Petrologic significance of sub-solidus phase transformations to mixed crystals. *Norsk Geol. Tidsskr.* **24**, 42-74.
- (1952) *The Origin of Metamorphic and Metasomatic Rocks*. Univ. Chicago Press, Chicago, Ill.
- (1954) Relative stabilities of some simple silicates as related to the polarization of the oxygen ions. *Amer. Mineral.* **39**, 250-271.
- ROBIE, R. A., P. M. BETHKE, M. S. TOULMIN, AND J. L. EDWARDS (1966) X-ray crystallographic data, densities and molar volumes of minerals. *Geol. Soc. Amer. Mem.* **97**.
- VIRGO, D., AND S. HAFNER (1969) Fe^{2+} , Mg order-disorder in heated orthopyroxenes. *Mineral. Soc. Amer. Spec. Paper* **2**, 67-81.
- WARREN, B. E. (1930) The structure of tremolite. *Z. Kristallogr.* **72**, 42-57.
- AND W. L. BRAGG (1928) The crystal structure of diopside, $CaMg(SiO_3)_2$. *Z. Kristallogr.* **69**, 168-193.
- WHITTAKER, E. J. W. (1949) The structure of Bolivian crocidolite. *Acta Crystallogr.* **2**, 312-317.