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CHEMICAL REACTIONS IN CRYSTALS¹

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INTRODUCTION

The Mineralogical Society of America, as stated in its constitution and implied in the construction of its seal, exists primarily to further the three related sciences of mineralogy, petrology, and crystallography. Mineralogy, the only one appearing in the name of the Society, clearly occupies a central role, and quite properly so, for there is much of crystallography and of petrology that is not mineralogic, and the Society has never attempted to cover the nonmineralogical aspects of these fields. There is, however, little in mineralogy that is not either petrologic or crystallographic in nature, and in this era of increasing specialization most of us tend to regard ourselves as either mineralogist-crystallographers or mineralogist-petrologists. We have thus begun to polarize into two groups that, though both are concerned with minerals, have tended to go their separate ways; one group, the introverted mineralogists, concentrating on phenomena within the boundaries of a mineral grain, and the other group, the extroverted mineralogists, looking outward to the interaction of the mineral with other minerals and various environmental stimuli. Though a petrologist, I hope in this paper to call attention to recent crystallographic researches that will surely prove to be of great petrologic significance.

Specifically petrologists have regarded the individual mineral phase as a more or less static entity, capable of being heated, cooled, or varied in composition, but otherwise uncomplicated. We must now abandon this misconception for it is overwhelmingly clear, from the evidence that has been amassed over the past forty years by crystallographers, that interesting things actually happen *inside* minerals. We should not be surprised by this for we have long been aware of processes taking place inside liquids and gases, namely that molecules and ions can and do

¹ Presidential address, Mineralogical Society of America. Delivered at the 49th Annual Meeting of the Society, November 12, 1968.

react with each other to form new molecules and ions, the properties of the phase varying accordingly. In fact much of classical physical chemistry is primarily concerned with the understanding of just these homogeneous reactions and homogeneous equilibria, in fluids, whereas petrologists have focused their attention on heterogeneous, or polyphase, reactions and equilibria.

Recognition of the fact that the things that happen in crystals are closely analogous to homogeneous reactions in fluids, has, however, been surprisingly slow in coming. This is partly because most of the key discoveries have been made by crystallographers or physicists rather than by chemists, and partly because terms such as "order", "disorder", "defects", and "vacancies" have little apparent kinship to the words by which we describe homogeneous reactions in fluids. Further confusion has arisen because differences in theoretical approach have led to differences in notation so that results that may be in fact almost identical can look very different on paper.

There has even been, in the past fifteen or twenty years, a note of despair that chemical thermodynamics is somehow inadequate to deal with the phenomena observed in crystalline phases, and this, despite the fact that early analyses of order-disorder phenomena by Bragg and Williams (1934, 1935) and by others were thermodynamic to a large degree. The fact that physical properties of crystals were in part dependent on past history and hence not uniquely defined by pressure, temperature, and bulk composition was taken as negating the very concept of an equation of state for such substances. That similar statements could be made about gases and liquids for which the homogeneous reactions are sluggish, and do not always proceed to completion, was unfortunately overlooked by these pessimists.

In the past five to ten years the quantity and quality of information relating to the processes taking place inside crystals have grown enormously. Detailed distribution of atomic, molecular, or ionic species among the various crystallographic sites of a crystal can now be obtained for many substances of interest including some of the major rock-forming minerals. Al-Si distribution among the tetrahedral sites in feldspars and other minerals may now be deduced by the method of mean interatomic distances as developed by Smith and Bailey (1963), and also by the method of direct site population refinements as developed by Burnham (Burnham and Radoslovich, 1964) and Fischer (1966). Fe-Mg distributions in pyroxenes and amphiboles have also been investigated by Ghose and Hellner (1959), and Ghose (1961, 1962, 1965) through trial and error refinements and also by direct site population refinements. These distributions have more recently been investigated by the use of Mössbauer

spectra as in the work of Ghose and Hafner (1967; also Evans, Ghose and Hafner, 1967), and of Bancroft and Burns (1967; also Bancroft, Burns and Maddock, 1967a, 1967b; Bancroft, Burns, and Howie, 1967; and Bancroft, Burns, Maddock, and Strens, 1966). Important information bearing on proton distribution associated with hydroxyl groups may be obtained from infrared spectra as in the work of Bassett (1960), and the bearing of this on the distribution of other species in some hydrous silicates has been studied successfully by Wilkins (1967), and by Wilkins and Ito (1967). There are also strong indications that neutron diffraction studies and investigations of such phenomena as nuclear magnetic resonance and electron spin resonance may produce further information of this kind in the near future.

Spurred in part by these developments several papers have appeared in the last few years that have made encouraging progress in applying the methods of thermodynamic analysis that have long been successful in dealing with homogeneous equilibria in fluids, to the related problem of homogeneous equilibria in mineral crystals. Notable in this regard are recent papers by Mueller (1962); Matsui and Banno (1965); Banno and Matsui (1966 and 1967); Perchuk and Ryabchikov (1968); and by Grover and Orville (1969).

The purpose of this paper is to derive, in generalized form, the conditions that must be met for equilibrium in a crystal where several homogeneous reactions of various kinds may take place simultaneously, and, at the same time, to demonstrate a method by which departures from ideality may be taken into account with respect to the substitutions taking place in real rather than hypothetical crystals. Finally, we shall examine one or two specific problems concerning homogeneous equilibria in rock-forming minerals, and make some tentative and preliminary calculations on the basis of data now at hand.

CONDITIONS FOR HOMOGENEOUS EQUILIBRIUM IN CRYSTALS

Thermodynamic considerations. Although the classic work of Gibbs is best known for its thorough exposition of heterogeneous equilibria, it also contains a consideration of homogeneous equilibria that is essentially complete, at least as far as simple molecular fluids are concerned. Although homogeneous reactions in crystals were not specifically considered by Gibbs—they scarcely could have been at that time—the essential features of his approach should be applicable to any homogeneous phase whatsoever and will be followed here. There are, however, several options that may be taken as to specific procedure. For example we might consider a wholly isolated crystal and seek the conditions that maximize its entropy, or we might consider a crystal of fixed chemical content (a

closed crystal) and seek the conditions that minimize its Gibbs function at some specified temperature and pressure. Because these, and other methods, are mathematically consistent the final results will be unaffected, hence we shall choose the minimizing of the Gibbs function at constant pressure and temperature because of its familiarity and simplicity.

We shall suppose further that the numbers, kinds and distributions of the various atomic, ionic, or molecular species that make up a crystal uniquely determine the magnitude of any extensive thermodynamic functions such as G , the Gibbs function. Thus our first problem is how to relate variations in the numbers, kinds, and distributions of these species to variations in various thermodynamic functions, and in particular to G .

The possible variations of a crystal. Let us consider a complex crystal and denote a given species by the subscript s and a given site by the subscript q . The quantities n_{sq} are then to be understood as indicating the number of species of a given kind upon a given site. Let us define q as the number of sites of a given kind, q , in a unit quantity of crystal, and let us define the quantity of crystal n as equal to the number of unit cells multiplied by the number that is the greatest common divisor of the ranks of the equipoints of the space group to which the crystal belongs (see Buerger, 1956, Chapter 18). The number of sites q in the crystal as a whole is then qn , and q must be an integer such that $1 \leq q \leq 48$.¹ In certain instances the numbers q may be identified as the subscripts in the standard chemical formula of a crystal or as simple multiples of them. We shall regard the vacancy as one of the species that may occupy a site, and when we wish to distinguish it, shall do so by an open square such that the number of vacancies on a given site would be $n_{\square q}$. Our assumption that variations in the Gibbs function for a crystal at a given pressure and temperature are determined by variations in the kinds and distributions of the various species in the crystal may then be written formally as

$$\delta G = f \left(\sum_s \sum_q \delta n_{sq} \right) \quad (1)$$

where the summation must be over all species and all sites. Equation (1) as it stands, however, raises some problems. The number of terms δn_{sq} , in particular, is infinite simply because the number of different kinds of sites is not finite. Further difficulties arise in that the number of sites of

¹ The only permissible values of q , as defined, are, in fact: 1, 2, 4, 8, 16, and 3, 6, 12, 24, and 48. Its maximum value is 2 in triclinic crystals, 4 in monoclinic crystals, 8 in orthorhombic crystals, 16 in tetragonal crystals, 24 in hexagonal crystals, and 48 in cubic crystals.

two kinds are always in the same ratio neglecting possible minor imbalances that may arise at the outer boundary of the crystal. Thus for two sites, a and b ,

$$\frac{an}{bn} = \frac{a}{b} = \text{constant}$$

and we must have a relationship, one for *each* site, q , of the form

$$qn = \sum_s n_{sq} \quad (2)$$

hence

$$q\delta n = \sum_s \delta n_{sq} \quad (2a)$$

We shall refer to equations (2) or (2a) as the *site constraints* on the variations of the quantities n_{sq} . An additional constraint on the variations of the n_{sq} is that in most substances there is a valence balance of some sort that must be considered as well. In an ionic crystal, as in an electrolyte fluid, this would be a condition of *electroneutrality*, but we shall not restrict it to this particular case inasmuch as a valence balance may be operative under other circumstances. If we denote the valence, whatever its nature, of a given species as Z_s we may write the valence condition as

$$0 = \sum_s \sum_q Z_s n_{sq} \quad (3)$$

hence

$$0 = \sum_s \sum_q Z_s \delta n_{sq} \quad (3a)$$

and shall refer to (3) or (3a) as the *valence constraint* on the variations of the n_{sq} . We shall take the valence of a vacancy, Z_{\square} , to be zero.

Let us now arbitrarily select one species on each site and indicate that species by the subscript, Q . The quantities n_{qQ} for each site q may now be eliminated from (1) using the site constraints (2a). In so doing, however, it should be observed that we introduce into (1) the quantity δn . It is also convenient to take the site constraints into account in the valence constraint (3a). To do this we multiply each site constraint (2a) by the appropriate Z_q and subtract the result from (3a) obtaining

$$0 = \sum_s \sum_q (Z_s - Z_q) \delta n_{sq} + \left(\sum_q q Z_q \right) \delta n \quad (4)$$

hence it is apparent from (4) that the valence constraint can eliminate an additional n_{sq} only if there are sites that contain species of more than one valence. If not, the quantities in parentheses in (4) must all vanish.

It is also evident that, at the small price of introducing the quantity n , the site restrictions make it possible to eliminate from further consideration the quantities n_{sq} for sites that contain only one species. Now the number of sites occupied by species other than vacancies must be finite even though the total number of sites is not. Each of the quantities $n_{\square q}$ for a site occupied only by vacancies, however, is eliminated by its *corresponding* site restriction, hence we need consider in what follows only a finite number of sites (only those occupied by species other than the vacancy), and only a finite number of quantities n_{sq} plus the quantity, n . The number of such quantities may, in fact, be evaluated in terms of the following general formula

$$\tau = \sum_q (\sigma - 1) + 1 - \pi \quad (5)$$

where τ is the number of ^{quantities} varieties, n_{sq} or n , that may be varied independently; σ is the number of different kinds of species occupying a given site, q ; and π a number that is unity if (4) has nonzero terms and zero if it does not. Now the number of independent ways, τ , in which the crystal can be varied must *include* the number of independent ways in which its bulk chemical content may be varied. This latter number, γ , is in fact the number of independently variable components of the crystal, and is a quantity that is often known in advance. τ must be equal to or greater than γ and the difference, ρ , must then be the number of *independent internal variations* or *internal reactions* that can occur in a crystal of fixed chemical content (a closed crystal). We may then write

$$\rho = \tau - \gamma = \sum_q (\sigma - 1) + 1 - \pi - \gamma \quad (6)$$

There are thus γ constraints of closure. Though their number (γ) may be known in advance, and though a set of independently variable components may be already identified, it is not always evident what form these constraints must have, particularly if the components have complex chemical formulas. We shall therefore outline a systematic procedure by which a sufficient set of constraints of closure, γ in number, may be obtained. For each chemical element, e , in the crystal there is a relation of the form

$$n_e = \sum_s \sum_q \nu_{es} n_{sq} \quad (7)$$

where n_e is the number of atoms of element e in the crystal, and ν_{es} is to be

read as the number of atoms of element e required to make species s . For a closed crystal each δn_e must be zero hence

$$0 = \delta n_e = \sum_s \sum_q \nu_{es} \delta n_{sq} \quad (7a)$$

Equations (7) or equations (7a) are not independent in most crystals because of the fact that the site and valence constraints commonly prevent independent variations of the contents of the various elements. The number of elements, ϵ , is thus typically greater than the number of components, γ , although equal to it in some crystals. To obtain a set of independent equations from (7) we may take the site and valence constraints into account as follows:

Let us again select a species, Q , for each site and, using (2), remove all terms of the form n_{Qq} from each equation (7) and from (3). Taking these results we obtain the following system of equations

$$\left. \begin{aligned} n_e &= \sum_s \sum_q (\nu_{es} - \nu_{eQ}) n_{sq} + \left(\sum_q q \nu_{eQ} \right) n \\ 0 &= \sum_s \sum_q (Z_s - Z_Q) n_{sq} + \left(\sum_q q Z_Q \right) n \end{aligned} \right\} \quad (8)$$

The site constraints have all been taken into account in (8). The number of equations (8) is then $\epsilon + \pi$ (π is again either zero or unity), and the number of quantities n_{sq} and n on the right-hand side of the system (7) is $\sum_q (\sigma - 1) + 1$. The number of *independent* equations in the system (8) must be $\gamma + \pi$, hence the rank of the matrix of the quantities in parentheses in (8) must also be $\gamma + \pi$. The row-nullity (Aitken, 1958, Chapter III) of this matrix is then $\epsilon - \gamma$, the number by which the number of elements exceeds the number of components, and the column-nullity is then $\sum (\sigma - 1) + 1 - (\gamma + \pi)$, hence equal to ρ , the number of independent internal reactions. It is thus clear that we may proceed with our problem if we know the rank of the above matrix and can obtain a set of independent constraints from (8). Fortunately, both of these ends may be accomplished by the simple procedure of employing each suitable equation in (8), successively, to eliminate one n_{sq} (or n) from all of the others. The process may be continued either until all equations (8) have been so employed, or until all coefficients on the right-hand side of each remaining equation have vanished. In the first case the number of elements, ϵ , is equal to the number of components, γ , and all of the equations (8) are independent. In the second case the row-nullity of the above matrix is equal to the number of remaining equations, and these remaining equations are a sufficient set to define the constraints preventing independent

variation of the quantities n_s . The other equations are all independent and are the desired relations among the quantities n_{sq} and \mathbf{n} . There are $(\gamma + \pi)$ independent equations, and for a *crystal* of fixed chemical content the variation in the left-hand side of each must vanish. Some actual examples have been worked out in the Appendix in order to clarify the procedure.¹

We have now developed a formal procedure for determining how many of the quantities n_{sq} and \mathbf{n} in a given crystal may be varied independently in either an open or a closed crystal, and a specific means for identifying a set of quantities having the form n_{sq} or \mathbf{n} that is sufficient to describe these variations in either case. The actual set obtained, however, is not necessarily a unique one and alternate sets may be obtained with different choices of species Q , and a different sequence of operations in the reduction of the matrix in (8). The quantities ρ and γ , however, are independent of the specific procedure followed. We shall refer below to the set of equations (8), in one of the forms obtainable through reduction by the procedure outlined above, as the *site population equations*. Examples of these for three major types of mineral crystal are given in the Appendix.

Conversion to intensive parameters. The quantities n_{sq} and \mathbf{n} are all extensive properties of a homogeneous crystal, hence are quantities such that the value of each for the whole is the sum of the values for its parts. We shall now define *site occupancy fractions*, N_{sq} , according to the convention

$$N_{sq} \equiv \frac{n_{sq}}{qn} \quad (9)$$

The ratio of any two extensive properties is necessarily an intensive property hence is a property such that the value for the homogeneous whole is equal to the value for each of its parts. The introduction of the quantities N_{sq} could have come earlier in the above discussion but has been delayed in the interest of clarity. It should be noted, however, that the key equations (1), (2), (3), and (7) then take the following forms, respectively, remembering $\mathbf{n} \neq 0$

$$\delta G = f\left(\mathbf{n}, \sum_s \sum_q \delta N_{sq}\right) \quad (10)$$

$$1 = \sum_s N_{sq} \quad (11)$$

$$0 = \sum_s \sum_q q Z_s N_{sq} \quad (12)$$

¹ See Note added in proof on page 373.

and

$$n_c \mathbf{n}^{-1} = \sum_s \sum_q q v_{es} N_{sq} \quad (13)$$

We may also introduce the N_{sq} by substituting directly, using (9), into the site population equations already obtained. With (9) we have only one surviving extensive property, namely \mathbf{n} , our measure of quantity. For present purposes it is convenient to define the *mole* of a crystal as a quantity of crystal such that \mathbf{n} is equal to Avogadro's number, N . This will correspond either to the conventional formula unit or to some simple multiple of it. Any extensive property may then be converted to the corresponding *molar* property if we multiply it by $N\mathbf{n}^{-1}$. The number of atoms of an element per mole of crystal is thus $n_c N\mathbf{n}^{-1}$, and the number of *gram-atoms* per mole of crystal is $n_c \mathbf{n}^{-1}$, as on the left-hand side of (13).

Equilibrium in a closed crystal. We may now, from the site population equations, select a set of quantities, N_{sq} , and possibly \mathbf{n} , that may be varied independently in a closed crystal. Indicating a set that may be so varied by primes we have, from (10)

$$\delta G = \sum_s \sum_q \left(\frac{\partial G}{\partial N'_{sq}} \right) \delta N'_{sq} + \left(\frac{\partial G}{\partial \mathbf{n}'} \right) \delta \mathbf{n}' \quad (14)$$

Variations of \mathbf{n} in a closed crystal of fixed chemical content may arise only through creation or destruction of vacancies and must be taken into account when this possibility exists. (For the examples in the Appendix, however, and the possibilities of site occupancy there indicated, \mathbf{n} cannot be varied in a closed crystal, inasmuch as the site population equations relate it directly to the contents of certain elements, and in particular to the content of elements such as oxygen and fluorine that form species of negative valence. Should evidence for significant populations of vacancies on "anion" sites arise, on the other hand, it might be necessary to consider the possibility that $\delta \mathbf{n} \neq 0$ in such crystals.)

In actual application it is often convenient to introduce new variables, X_r , for each reaction r , such that they are simple linear functions of the quantities N_{sq}' (and if necessary \mathbf{n}') and equal to the latter in number. We may then write for our closed phase

$$\delta G = \sum_r \left(\frac{\partial G}{\partial X_r} \right)_{P, T, \text{ all other } X_r} \delta X_r \quad (14a)$$

When $\delta \mathbf{n}$ for a closed phase is zero, as in each of the applications below,

the number of moles of the closed crystal cannot vary and we may simply write, for one mole

$$\delta\bar{G} = \sum_r \left(\frac{\partial\bar{G}}{\partial X_r} \right)_{P,T, \text{ all other } X_r} \delta X_r \quad (14b)$$

where the bars indicate a molar property.

At a stable (or metastable) internal equilibrium in a closed crystal, at a given temperature and pressure, the Gibbs function must be at a minimum with respect to variations of the independent parameters X_r . We must then have for each r a condition of the form

$$\left(\frac{\partial G}{\partial X_r} \right)_{P,T, \text{ all other } X_r} = 0 \quad (15)$$

If any one of the conditions (15) were not satisfied, a mechanism would then exist where, by appropriate variations of the corresponding X_r , the value of G could be lowered. If so, however, G is clearly not at a minimum and the crystal is not in stable or metastable equilibrium. (Equation 15 must also be satisfied when G is at a maximum, but this is an unstable equilibrium and need not concern us here.)

The number of reactions, r , is equal to ρ as in (6). For a crystal for which ρ is zero the variance or number of independent variations in the sense of Gibbs (1928, p. 96) is $\gamma+1$. For a crystal that is not necessarily in internal equilibrium the variance is $(\gamma+\rho)+1$ or $\tau+1$, but the variance, under circumstances where conditions (15) are always met, returns again to $\gamma+1$. The quantities γ and τ thus correspond to the numbers of "ultimate" and "proximate" components, respectively, as in the treatment by Gibbs (1928, p. 138) of homogeneous equilibria in fluids. Inasmuch as conditions (15) are most likely to be met during very slow processes we may regard τ as effectively the number of *short-term* components and γ as the number of *long-term* components of a given crystal, the latter being the usual sense of the word "component" unless otherwise specified.

FORMULATION OF THE THERMODYNAMIC PROPERTIES OF A CRYSTAL

Ideal configurational entropy. The distribution of a given species, s , on a given site, q , can almost certainly be regarded as a random distribution under the special circumstances of extreme dilution ($N_{sq} \rightarrow 0$) or of complete occupancy ($N_{sq} \rightarrow 1$). Under other circumstances ($0 < N_{sq} < 1$) we may anticipate some degree of "short-range ordering" or departure from random distribution of the species. In limiting cases where the species

distribution is random, however, it gives rise to singularities in the variations of the entropy, S , as related to the N_{sq} , that must be taken into account in order to understand the behavior of the entropy and of the Gibbs function in these limits.

Let us therefore define S_{iq} as the contribution that would be made to the total entropy, S , if the distribution of species on site q were truly random. This may be evaluated from simple statistical considerations. The number of ways of arranging the various species s on site q is $(qn)! / \prod_s n_{sq}!$ hence

$$S_{iq} = k \ln \frac{(qn)!}{\prod_s n_{sq}!} \quad (16)$$

where k is the Boltzmann constant. For any appreciable quantity of crystal we may assume $\ln n!$ is very nearly equal to $n \ln n - n$, hence (16) becomes

$$S_{iq} = -qk \sum_s N_{sq} \ln N_{sq} \quad (16a)$$

and

$$S_i \equiv \sum_q S_{iq} = -nk \sum_s \sum_q q N_{sq} \ln N_{sq} \quad (17)$$

or, for one mole of crystal

$$\bar{S}_i = S_i N n^{-1} = -R \sum_s \sum_q q N_{sq} \ln N_{sq} \quad (18)$$

where R is the gas or molar entropy constant.

Other thermodynamic properties. We may now define the quantities S^* and G^* by the relations

$$\begin{aligned} S^* &\equiv S - S_i \\ G^* &\equiv G + TS_i = H - TS^* = E + PV - TS^* \end{aligned} \quad (19)$$

where H , E , and V are enthalpy, internal energy, and volume, respectively. We have then

$$\bar{G} = \bar{G}^* - T\bar{S}_i = \bar{G}^* + RT \sum_s \sum_q q N_{sq} \ln N_{sq} \quad (20)$$

or

$$\frac{\bar{G}}{RT} = \frac{\bar{G}^*}{RT} + \sum_s \sum_q q N_{sq} \ln N_{sq} \quad (20a)$$

We shall assume that at any given pressure and temperature the function \bar{E} , \bar{V} , and \bar{S}^* show no singularities in the limits where $N_{sq} \rightarrow 0$ or where $N_{sq} \rightarrow 1$, and that they may be expressed as Taylor expansions about any given reference state in terms of the composition variables and the reaction parameters X_r that have been selected. If so \bar{G}^*/RT may also be so expanded and the corresponding expansions for the functions \bar{H}/R , \bar{E}/R , \bar{V}/R , and \bar{S}^*/R may be obtained from the temperature and pressure dependence of the coefficients in the expression for \bar{G}^*/RT . This formulation is entirely consistent with Henry's Law and Raoult's Law for crystalline solutions in which there are no internal reactions (see Thompson, 1967). For the circumstance where only the first degree terms of the expansion are necessary it describes an *ideal* solution, nonideality being accounted for by terms of higher degree. We shall therefore proceed on the assumption that such a formulation is valid, until proven otherwise, and investigate some problems relating to homogeneous reactions in some common rock-forming minerals. The processes considered will all be related to the exchange of pairs of real (nonvacancy) species between pairs of sites (long-range ordering). Other types of internal reaction, however, are equally amenable to the treatment outlined above. These would include oxidation-reduction equilibria among species, as well as generalized problems involving vacancies and interstitial species.

HOMOGENEOUS EQUILIBRIA IN FELDSPARS

Monoclinic alkali feldspar. From the site population equations (A2) in the Appendix and (9) we may obtain the following independent equations

$$\left. \begin{aligned} n_{Na} &= 2nN_{Na(M)} \\ (n_{Na} + n_K) &= 4nN_{A1(T1)} + 4nN_{A1(T2)} \\ (n_{Na} + n_K) &= 2n \end{aligned} \right\} \quad (21)$$

We may eliminate all extensive quantities from the right-hand sides of the first two if we divide each by the third, obtaining thereby

$$\left. \begin{aligned} \frac{n_{Na}}{n_{Na} + n_K} &= N_{Na(M)} \equiv N_{Ab} \\ 1 &= 2N_{A1(T1)} + 2N_{A1(T2)} \\ (n_{Na} + n_K) &= 2n \end{aligned} \right\} \quad (22)$$

The identity in the first equation of (22) indicates that the standard alkali feldspar components *Or* and *Ab*, are here identifiable with the site occupancy fractions for the M-site. For a closed crystal

$$0 = \delta N_{Ab} \equiv \delta n = \delta N_{A1(T1)} + \delta N_{A1(T2)} \quad (23)$$

We might therefore choose either of the $N_{A1(q)}$ or, with (11) either of the corresponding $N_{Si(q)}$ as our measure of internal reaction. Algebraic symmetry is gained, however, by defining a new quantity, Z , a *long-range ordering* parameter, by the relation

$$Z \equiv 2(N_{A1(T1)} - N_{A1(T2)}) \tag{24}$$

From (24), (11), and the second equation of (22) we may write

$$\left. \begin{aligned} N_{A1(T1)} &= \frac{1+Z}{4}; & N_{A1(T2)} &= \frac{1-Z}{4} \\ N_{Si(T1)} &= \frac{3-Z}{4}; & N_{Si(T2)} &= \frac{3+Z}{4} \end{aligned} \right\} \tag{25}$$

We also have then

$$\begin{aligned} \frac{\bar{G}}{RT} - \frac{\bar{G}^*}{RT} &= -\frac{\bar{S}_i}{R} = \sum_s \sum_q q N_{sq} \ln N_{sq} = 2Z \operatorname{artanh} Z + 2Z \operatorname{artanh} \frac{Z}{3} \\ &+ \ln(1-Z^2)(9-Z^2)^3 - 16 \ln 2 \\ &+ 2N_{Ab} \ln N_{Ab} + 2(1-N_{Ab}) \ln(1-N_{Ab}) \end{aligned} \tag{26}$$

and

$$\frac{\bar{G}^*}{RT} = g_0 + g_N N_{Ab} + g_Z Z + g_{NN} N_{Ab}^2 + g_{NZ} N_{Ab} Z + g_{ZZ} Z^2 \dots \tag{27}$$

where the quantities g are dimensionless Taylor expansion coefficients as indicated. Terms of higher than the second degree are probably needed, at least in N_{Ab} (see Thompson and Waldbaum, 1968), but the form of the continued expansion is clear from (27). With (26), (27) and (15) we may now obtain our equilibrium condition:

$$\begin{aligned} \left[\frac{\partial}{\partial Z} \left(\frac{\bar{G}}{RT} \right) \right]_{P,T,N_{Ab}} &= 2 \operatorname{artanh} \left(\frac{4Z}{3+Z^2} \right) + g_Z + g_{NZ} N_{Ab} \\ &+ 2g_{ZZ} Z \dots \\ &= 0 \text{ (at equilibrium)} \end{aligned} \tag{28}$$

The resemblance of (28) to certain conditions for homogeneous equilibria in fluids is not apparent but may readily be made so. Let us define a quantity $K_{Z'}$ such that

$$K_{Z'} \equiv \frac{N_{A1(T1)} N_{Si(T2)}}{N_{Si(T1)} N_{A1(T2)}} \tag{29}$$

K_Z' thus has the form of an apparent equilibrium constant. With (25) we may write

$$\ln K_Z' = 2 \operatorname{artanh} Z + 2 \operatorname{artanh} \left(\frac{Z}{3} \right) = 2 \operatorname{artanh} \left(\frac{4Z}{3 + Z^2} \right) \quad (30)$$

If, for a feldspar of fixed composition, we define \bar{G}_i° as \bar{G} when $Z=1$, and define \bar{G}_i° as \bar{G} when $Z=-1$ we find that

$$\begin{aligned} \frac{\bar{G}_1^\circ}{RT} &= 2N_{Ab} \ln N_{Ab} + 2(1 - N_{Ab}) \ln (1 - N_{Ab}) - 4 \ln 2 \\ &\quad + g_0 + g_N N_{Ab} + g_Z + g_{NN} N_{Ab}^2 + g_{NZ} N_{Ab} + g_{ZZ} \dots \quad (31) \end{aligned}$$

and

$$\begin{aligned} \frac{\bar{G}_1^\circ}{RT} &= 2N_{Ab} \ln N_{Ab} + 2(1 - N_{Ab}) \ln (1 - N_{Ab}) - 4 \ln 2 \\ &\quad + g_0 + g_N N_{Ab} - g_Z + g_{NN} N_{Ab}^2 - g_{NZ} N_{Ab} + g_{ZZ} \dots \quad (32) \end{aligned}$$

hence

$$\frac{\Delta \bar{G}^\circ}{RT} \equiv \frac{\bar{G}_1^\circ - \bar{G}_1^\circ}{RT} = 2g_Z + 2g_{NZ} N_{Ab} \dots \quad (33)$$

and therefore

$$\ln K_Z' = - \frac{(\bar{G}_1^\circ - \bar{G}_1^\circ)}{2RT} - 2g_{ZZ} Z \dots \quad (34)$$

The analogy to a simple reciprocal equilibrium among four species in a fluid, or to a simple exchange equilibrium between two phases is thus complete. It is also clear that where only first degree terms are required for the expansion of \bar{G}^*/RT the situation is analogous to equilibrium in an ideal or ideally dilute fluid, or to exchange equilibrium between two simple ideal solutions, and that nonideality must be taken care of by higher order terms in the expansion (27). It should be emphasized, however, that in obtaining (34) we have not, as have some authors, appealed to inherently unmeasurable quantities such as the chemical potential or the activity coefficient of a single species on a given site.

Some tentative calculations. Preliminary site occupancies have been obtained by Colville and Ribbe (1968) for an adularia (Spencer B) and for an orthoclase (Spencer C). The calculated value of Z for the adularia is 0.56 and that for the orthoclase is 0.40, giving values of $\ln K_Z'$ of 1.643 and 1.116, respectively. Ribbe (1963) has refined the structure of a sani-

dine prepared by heating Spencer C at 1075°C. Site populations calculated by Waldbaum (1966) from Ribbe's data yield a value of 0.08 for Z and a value of 0.214 for $\ln K_{z'}$. If we assume that the first-degree terms in (27) are sufficient, in the absence of evidence to the contrary, and also assume that the Spencer C sanidine actually equilibrated at 1075°C, we may make some tentative calculations. For this idealized case we may write

$$-\ln K_{z'} = \frac{\bar{G}_1^\circ - \bar{G}_1^\circ}{2RT} = \frac{(\bar{H}_1^\circ - \bar{H}_1^\circ)}{2R} \left(\frac{1}{T} \right) - \frac{(\bar{S}_1^\circ - \bar{S}_1^\circ)}{2R} \quad (35)$$

We shall also neglect any possible temperature dependence of $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$, and shall neglect the fact that Spencer B (the adularia) does not have the same composition as Spencer C. A further assumption that might be made is that $\Delta\bar{S}^\circ$ is zero. This is consistent with the suggestion that $\ln K_{z'}$ and Z will approach zero (complete Al-Si disorder) at very high temperatures. If so, we may calculate tentative temperatures of equilibration for the orthoclase and the adularia using (35). The results so obtained, however, are unreasonable (-15°C for the orthoclase and -98°C for the adularia!) hence it appears that this assumption is not good. Another approach is to estimate a temperature of equilibration for the orthoclase, calculate $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$, and then test the results on the adularia. Orthoclase Spencer C, unfortunately, is a stream cobble from Burma, but its chemical analysis is such that from comparison with the alkali feldspar solvus as determined by Orville (1963) and by Luth and Tuttle (1966; see also Thompson and Waldbaum, 1969), we may assume fairly safely that its temperature of crystallization was at least 500°C . Assuming equilibration at 500°C we obtain -3.97 cal/deg for $\Delta\bar{S}^\circ$ and -6.49 kcal for $\Delta\bar{H}^\circ$. The temperature of equilibration for the adularia would then be 340°C which is not unreasonable. The negative value of $\Delta\bar{S}^\circ$ would suggest that $\ln K_{z'}$ and Z itself may become negative at higher temperature. There are, however, so many assumptions involved in these calculations that they must be regarded as highly speculative.

Figure 1 shows the form that the curve showing \bar{G} as a function of Z would have in the ideal case. The equilibrium value of Z indicated is about that of Spencer B adularia. For the nonideal case the form of this curve may be more complicated as shown in Figure 2, indicating that there might, in the nonideal case, be an actual discontinuity in the equilibrium value of Z at some particular temperature. Because intensive physical properties (such as the optic angle, for example) are almost certainly continuous functions of Z , a discontinuity should also appear in molar volume and molar enthalpy if there is one in Z . A discontinuity in Z would thus correspond, thermodynamically, to a first order transition

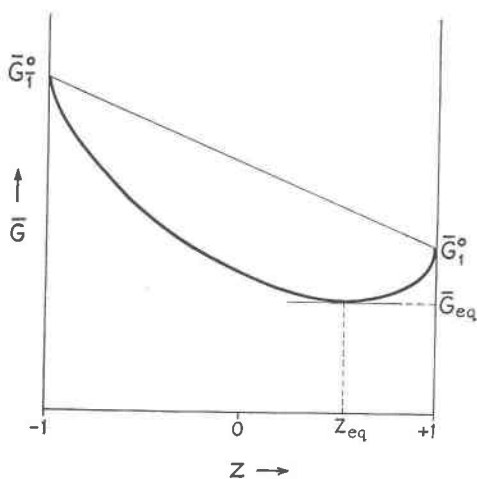


FIG. 1. General form of curve showing molar Gibbs function, \bar{G} , as a function of an ordering parameter, Z , for a crystal of fixed chemical content at some arbitrary temperature and pressure. The curve shown is for the ideal case (first-degree terms only in the Taylor expansion of \bar{G}^*/RT), and the value shown for the equilibrium value of Z (Z_{eq}) is approximately that for the adularia (Spencer B) discussed in the text. The ordering here is non-convergent ($\bar{G}_1^0 \neq \bar{G}_{\bar{1}}^0$), hence \bar{G} as plotted, is *not* symmetric about $Z=0$. Values of \bar{G}^* are given by the line joining $\bar{G}_{\bar{1}}^0$ and \bar{G}_1^0 in this ideal (linear) case.

(Fig. 3b). Even further possibilities may arise. Specifically, it is quite conceivable that the magnitude of ΔZ could decrease along the ^{invariant} curve for the transition, and that such a curve could actually terminate at a critical point as in Figure 3c. These speculations, however, are only a part of the problem of phase transitions in alkali feldspars, for we have not yet considered feldspars having structures of the microcline or low albite type.

Triclinic alkali feldspar. From equations (A4) in the Appendix we may write, allowing for a calcium component, An

$$\left. \begin{aligned}
 \frac{n_K}{n_K + n_{Na} + n_{Ca}} &= N_{K(M)} \equiv N_{Or} \\
 \frac{n_{Ca}}{n_K + n_{Na} + n_{Ca}} &= N_{Ca(M)} \equiv N_{An} \\
 n_K + n_{Na} + n_{Ca} &= 2n \\
 \frac{n_{A1}}{n_K + n_{Na} + n_{Ca}} &= \frac{n_K + n_{Na} + 2n_{Ca}}{n_K + n_{Na} + n_{Ca}} \\
 &= N_{A1(T10)} + N_{A1(T1m)} + N_{A1(T20)} + N_{A1(T2m)}
 \end{aligned} \right\} (36)$$

From the second and the last equation of (36) we obtain further

$$1 + N_{An} = N_{Al(T10)} + N_{Al(T1m)} + N_{Al(T20)} + N_{Al(T2m)} \quad (37)$$

Here, for a closed crystal, any three of the four $N_{Al(q)}$ may be varied independently. It is more convenient, however, to define three new long-range ordering parameters, X , Y , and Z according to the relations

$$\left. \begin{aligned} X &\equiv N_{Al(T20)} - N_{Al(T2m)} \\ Y &\equiv N_{Al(T20)} - N_{Al(T1m)} \\ Z &\equiv N_{Al(T10)} + N_{Al(T1m)} - (N_{Al(T20)} + N_{Al(T2m)}) \end{aligned} \right\} \quad (38)$$

From these, (37) above, and (11) we obtain

$$\left. \begin{aligned} N_{Al(T10)} &= \frac{1 + N_{An} + Z + 2Y}{4}; & N_{Al(T1m)} &= \frac{1 + N_{An} + Z - 2Y}{4} \\ N_{Al(T20)} &= \frac{1 + N_{An} - Z + 2X}{4}; & N_{Al(T2m)} &= \frac{1 + N_{An} - Z - 2X}{4} \\ N_{Si(T10)} &= \frac{3 - N_{An} - Z - 2Y}{4}; & N_{Si(T1m)} &= \frac{3 - N_{An} - Z + 2Y}{4} \\ N_{Si(T20)} &= \frac{3 - N_{An} + Z - 2X}{4}; & N_{Si(T2m)} &= \frac{3 - N_{An} + Z + 2X}{4} \end{aligned} \right\} \quad (39)$$

from which the terms N_{sq} in N_{sq} may be evaluated. The expansion of \bar{G}^*/RT here takes the form

$$\begin{aligned} \frac{\bar{G}^*}{RT} &= g_{\text{O}} + g_{K}N_{Or} + g_{C}N_{An} + g_{Z}Z + g_{KK}N_{Or}^2 + g_{KC}N_{Or}N_{An} \\ &+ g_{KZ}N_{Or}Z + g_{CC}N_{An}^2 \\ &+ g_{CZ}N_{An}Z + g_{XX}X^2 + g_{XY}XY + g_{YY}Y^2 + g_{ZZ}Z^2 \dots \quad (40) \end{aligned}$$

The omission of all terms for which the sum of the powers of X and Y is odd from the expansion (40) may be surprising but is necessary because \bar{G} and like properties should be symmetrical about the Z -axis ($X=0, Y=0$). The reason for this may be appreciated by consideration of Figure 4, a sketch of the feldspar structure projected onto $(\bar{2}01)$ that shows the essential features of the tetrahedral framework. Neglecting site occupancy (itself a form of labeling) the sites labeled T_{10} and T_{1m} are topologically identical even though they are crystallographically distinct in a triclinic feldspar. Rotation of the crystal about its b -axis, in fact, reverses the labeling. An alkali feldspar with all of its Al in T_{10} would ob-

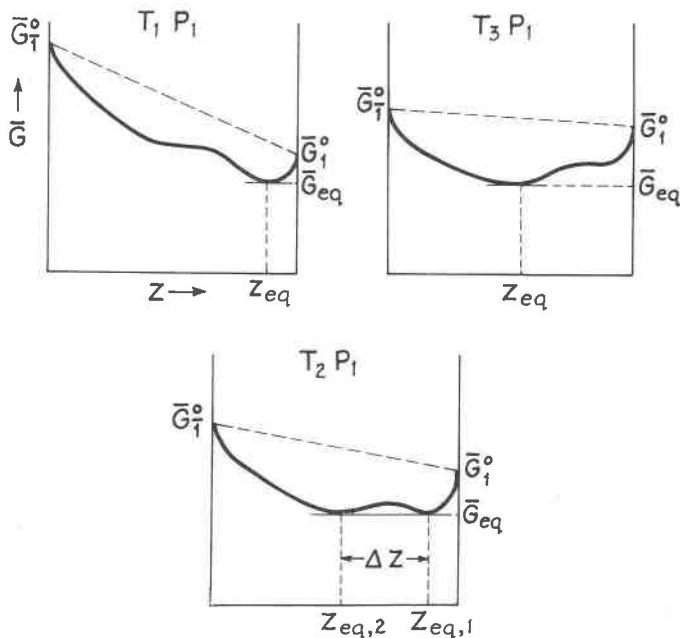


FIG. 2. Possible behavior of \bar{G} as a function of Z in the nonideal case. Diagrams show possible relationships at three successive temperatures, T_1 , T_2 , T_3 , at a constant pressure, P_1 . The discontinuity in Z_{eq} at T_2 , implies similar discontinuities in properties such as density and molar enthalpy that are also continuous functions of Z . Such a transition is thus a *first order* transition, in the thermodynamic sense, and is possible only in the nonideal case. Here \bar{G}^* must be a nonlinear function of Z , hence the lines joining \bar{G}_1° and \bar{G}_1° are dashed.

viously distort oppositely in all ways to one with all of its Al in T_{1m} . Because of certain conventions in crystallographic orientation, however, it would immediately be "turned over" and described as a T_{1m} -ordered feldspar. It is therefore evident that any feldspar, for which either X or Y is not zero, may be assigned two sets of values of X and Y : the conventional one and an unconventional one with the signs of X and Y reversed. Because of this thermodynamic functions such as \bar{V} , \bar{S} , \bar{H} , or \bar{G} should be symmetrical about the Z -axis which is thus an axis of two-fold symmetry for these functions. If the origin for the Taylor expansion is about any point on the Z -axis, symmetry then requires that all coefficients must vanish for terms containing $X^n Y^m$ where $n+m$ is odd. This is in fact our principal reason for using the coordinates X , Y , and Z rather than the $N_{A1(q)}$ directly.

A second reason for the choice of coordinates is that feldspars for which X and Y are both zero have met a necessary condition for monoclinic symmetry. In this sense the monoclinic alkali feldspars may be regarded

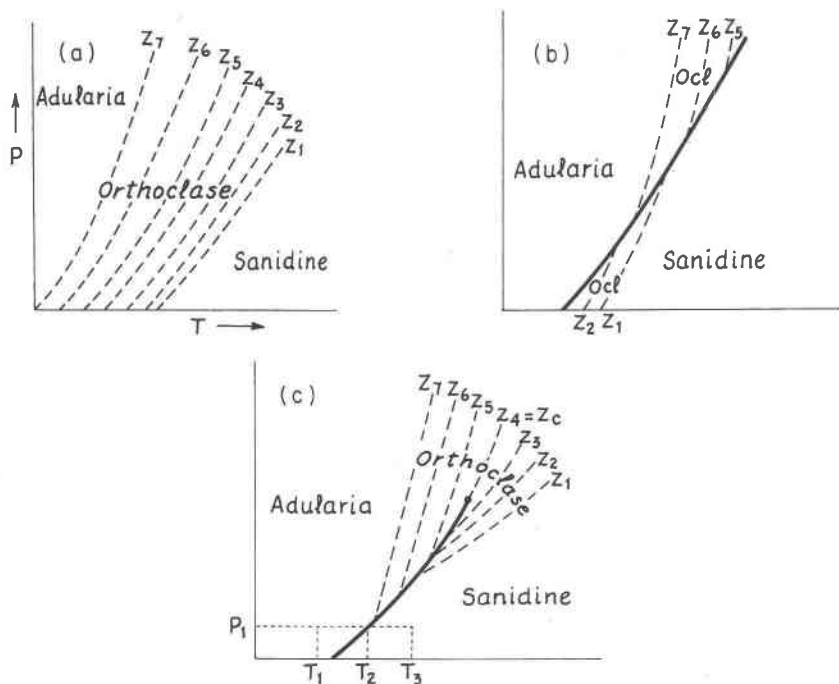


FIG. 3. Possible pressure-temperature diagrams for monoclinic K-feldspar: (a) shows a continuous change in phase possible in either the ideal or the non-ideal case; (b) shows a first-order phase discontinuity, possible only in the non-ideal case; and (c) shows a first order discontinuity terminating at a critical point. T_1 , T_2 , and T_3 in (c) are consistent with the diagrams in Figure 2. The possible appearance of a triclinic form such as microcline or a "triclinic adularia" has, for simplicity, not been included.

as a special case of the triclinic ones inasmuch as the triclinic crystals may differ from monoclinic ones in ways that are, quantitatively, vanishingly small. It should be made clear, however, that though the vanishing of X and Y is a necessary condition for monoclinic symmetry it is not a sufficient one. Specifically, certain feldspars studied by MacKenzie (1952) show a readily reversible symmetry change that is almost certainly not related to redistribution of Al and Si, hence not related to changes in X , Y , or Z . Such feldspars, even when triclinic, must therefore have zero values of X and Y . If, however, a feldspar grew or equilibrated as a triclinic crystal, it is likely that with a real, though perhaps small, difference between a pair of sites there should also be a real, though perhaps small, difference in their Al-Si occupancy. We shall therefore assume, until there is evidence to the contrary, that feldspars for which X and Y are both zero either grew or at some time equilibrated as monoclinic crystals.

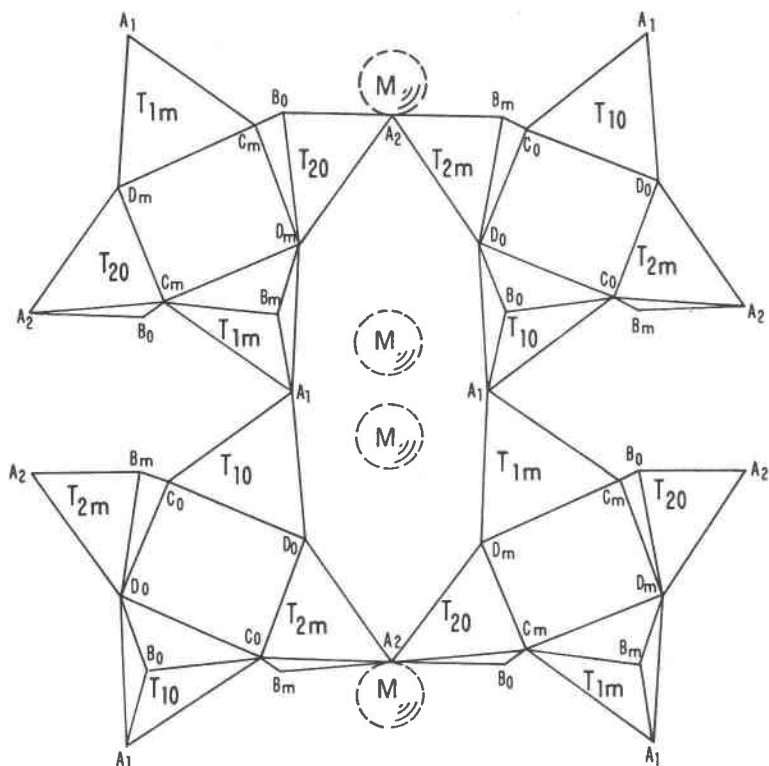


FIG. 4. Schematic view of the feldspar structure as sectioned on $(\bar{2}01)$. The notation for the sites is modified after that of Megaw (1956).

The physically accessible region in X - Y - Z space is bounded by planes for which the equations may be obtained by setting the various N_{sq} at zero in equations (39). These define a polyhedron that for pure alkali ($N_{An}=0$) feldspars is the tetrahedron shown in Figure 5. The existence of this tetrahedron was also deduced by Barth (1965), but was represented by him in terms of the barycentric coordinates $N_{Al(q)}$ rather than the coordinates X , Y , and Z as presented here. With increasing N_{An} this tetrahedron (or tetragonal disphenoid), bounded by the planes $N_{Al(q)}=0$, expands and is truncated at the corners by another tetrahedron bounded by the planes $N_{Si(q)}=0$. For a pure Ca-feldspar ($N_{An}=1$), though none is known that has this structure, the polyhedron would be an octahedron (or tetragonal dipyramid) bounded by the planes $2 \pm Z \pm 2X=0$ and $2 \pm Z \pm 2Y=0$, and having vertices at the coordinates $(0, 0, \pm 2)$ and $(\pm 1, \pm 1, 0)$. The vertices of these polyhedra can correspond to perfectly ordered crystals only when $N_{An}=0$ or $N_{An}=1$. No perfectly ordered

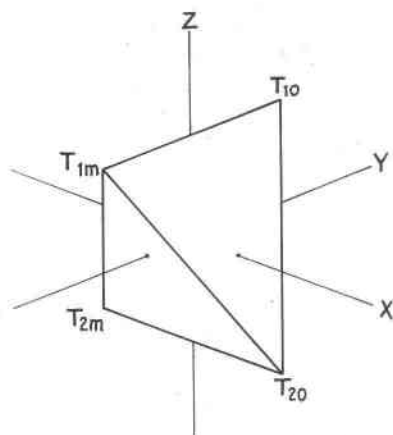


FIG. 5. Physically accessible regions for an alkali feldspar in terms of the ordering parameters X , Y , and Z as defined in the text. The corners of the tetrahedron correspond to perfectly ordered crystals having all their aluminum in the sites indicated. Monoclinic crystals must have $X = Y = 0$. If a calcium (An) component is present, the tetrahedron is expanded to larger values of $\pm X$, $\pm Y$, $\pm Z$, but truncated at its corners as explained in the text.

Al-Si distributions other than these ten (of which only six are physically distinct) are possible for feldspars of this structure type unless one can occur with a 3- or 4-valent atom in the M-site.

The site occupancies for seven triclinic feldspars as calculated, tentatively, by the method of Smith and Bailey (1963) and normalized to one Al per four tetrahedra, are given in Table 1 with the values of X , Y , and Z calculated therefrom. These results are also shown in X - Y projection

TABLE 1. OCCUPANCY OF TETRAHEDRAL SITES IN MICROCLINES AND ALBITES

Feldspar	$N_{Al(T10)}$	$N_{Al(T1m)}$	$N_{Al(T20)}$	$N_{Al(T2m)}$	X	Y	Z	\bar{s}_i (cal/deg)
Low albite, Ramona, Calif. ^a	0.86	0.03	0.06	0.05	0.01	0.83	0.77	1.43
Low albite, Ramona, Calif. ^b	.78	.065	.09	.065	.02	.71	.69	2.57
High albite, hydrothermal ^b	.37	.15	.19	.29	-.10	.22	.04	4.32
High albite, Amelia, Va. (1065°C) ^c	.29	.22	.23	.26	-.03	.07	.02	4.45
Microcline, Pellotsalo, Finland ^d	0.88	0.05	0.03	0.04	-0.01	0.83	0.86	1.72
Microcline, Pontiskalk, Switz. ^e	.89	.05	.09	.02	.07	.79	.78	2.05
Microcline, Spencer U ^f	.65	.27	.05	.03	.02	.38	.84	3.13

Values of $N_{Al(q)}$ (here normalized to $\sum N_{Al(q)} = 1$) were calculated by D. R. Waldbaum (1966) from data of:

^a Ribbe *et al.*, (1962); ^b Williams and Megaw (1964); ^c Ferguson *et al.*, (1958); ^d Brown and Bailey (1964); ^e Finney and Bailey (1964); and ^f Bailey and Taylor (1955).

in Figure 6, and in $Y-Z$ projection in Figure 7, together with the data for the three monoclinic feldspars discussed above. The distinction between K-rich and Na-rich specimens is most marked in Figure 7. It is also clear from Figure 6 that values of X are consistently small and may well be zero, considering the uncertainties in the calculations.

Convergent and nonconvergent ordering. When X and Y are both near zero the distinction, not only in occupancy but in other ways as well between the T_{10} -sites and the corresponding T_{1m} -sites may become vanishingly small. This convergent effect, coupled with the symmetry in \bar{C} about the line $X=0, Y=0$, leads to singular behavior in this region. The approach to this critical region (in our case the Z -axis) is typically precipitous and, if equilibration is rapid enough, is commonly associated with a "lambda" anomaly in the heat capacity of such crystals. Most long-range ordering phenomena observed in metallic crystals are in fact of this *convergent* type. In silicates, on the other hand, both convergent

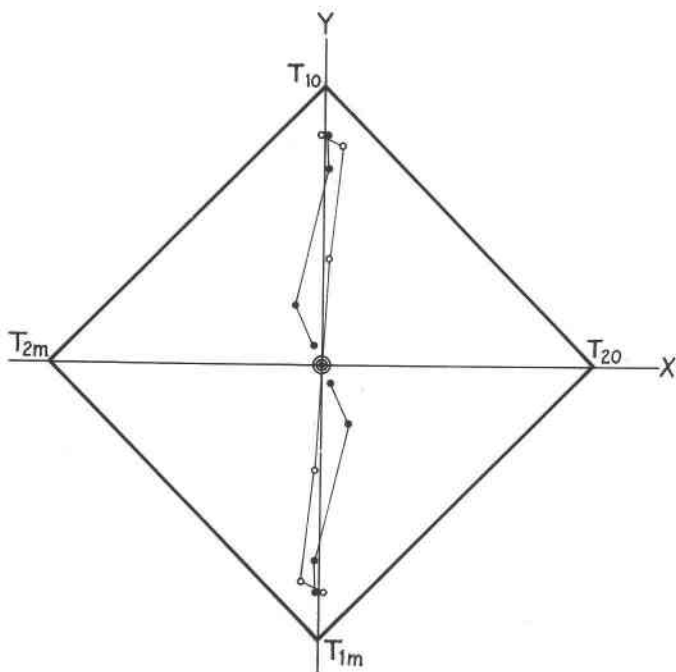


FIG. 6. Tetrahedron of Figure 5 as seen in projection onto $X-Y$ plane. The solid circles show the $X-Y$ coordinates of Na-rich feldspars, and the open circles show those of K-rich feldspars. The values plotted are those listed in Table 1. The three monoclinic feldspars discussed in the text all plot at the origin.

and *nonconvergent* ordering are of common occurrence. The *Z* ordering in monoclinic alkali feldspars is a good example of the nonconvergent type. The T_1 -sites and T_2 -sites are topologically distinct as well as crystallographically distinct and must remain distinct even when their occupancies may be identical. The condition $Z=0$ is only unique numerically and does not imply singular behavior of any sort. Lambda points and their associated "superlattices" and symmetry changes are associated only with ordering of the convergent type.

In summary, then, the intensive properties of an alkali feldspar or sodic plagioclase are, in general, functions of P , T , N_{Or} , N_{An} , and of the ordering parameters X , Y , and Z . If in special circumstances, we are dealing only with fully equilibrated feldspars, then the feldspars are subject to the equilibrium conditions

$$\left. \begin{aligned} \left(\frac{\partial \bar{G}}{\partial X} \right)_{P, T, N_{Or}, N_{An}, Y, Z} &= 0 \\ \left(\frac{\partial \bar{G}}{\partial Y} \right)_{P, T, N_{Or}, N_{An}, X, Z} &= 0 \\ \left(\frac{\partial \bar{G}}{\partial Z} \right)_{P, T, N_{Or}, N_{An}, X, Y} &= 0 \end{aligned} \right\} \quad (41)$$

and the intensive properties of *these* feldspars may be regarded as functions of P , T , N_{Or} and N_{An} . The first two equilibria in (41) are convergent in nature and the last is nonconvergent.

HOMOGENEOUS EQUILIBRIUM IN HYPERSTHENE

General formulation. We may proceed from the site population equations given in the Appendix by substantially the same route as that followed in our analysis of the corresponding phenomena in feldspars. We shall therefore omit here the intermediate steps and proceed directly to the choice of compositional and ordering parameters. We have now two components, hence only one composition parameter is necessary, and there is but one internal reaction. The familiar composition parameter for a simple hypersthene, N_{Fs} , may now be defined by the relation

$$N_{Fs} \equiv \frac{n_{Fe}}{n_{Fe} + n_{Mg}} = \frac{N_{Fe(M1)} + N_{Fe(M2)}}{2} \quad (42)$$

We shall find it convenient, however, to center our coordinate system by defining a composition parameter, r , such that

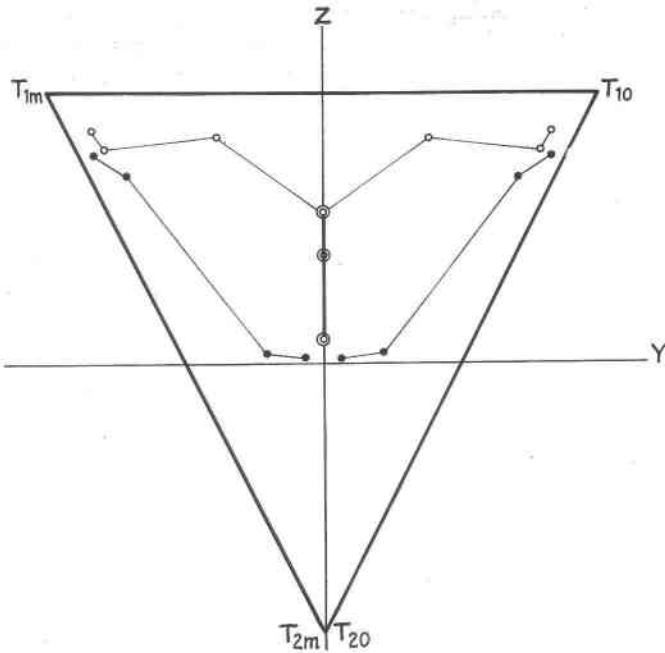


FIG. 7. Tetrahedron of Figure 5 as seen in $Y-Z$ projection. The $Y-Z$ coordinates for the triclinic feldspars are given in Table 1, and the Z coordinates of the monoclinic feldspars are given in the text. Legend same as Fig. 6. Circles have same significance as in Fig. 6.

$$r \equiv N_{\text{Fe}(M2)} + N_{\text{Fe}(M1)} - 1 = 2N_{\text{Fs}} - 1 \quad (43)$$

and an ordering parameter, s , such that

$$s \equiv N_{\text{Fe}(M2)} - N_{\text{Fe}(M1)} \quad (44)$$

The physically accessible region in terms of r and s is then a square with vertices at $(0, \pm 1)$ and $(\pm 1, 0)$. We have also, from (43) and (44)

$$\left. \begin{aligned} N_{\text{Fe}(M1)} &= \frac{1+r-s}{2}; & N_{\text{Mg}(M1)} &= \frac{1-r+s}{2} \\ N_{\text{Fe}(M2)} &= \frac{1+r+s}{2}; & N_{\text{Mg}(M2)} &= \frac{1-r-s}{2} \end{aligned} \right\} \quad (45)$$

from which the $N_{\text{sq}} \ln N_{\text{sq}}$ terms may be recast in terms of r and s . The expansion for \bar{G}^*/RT here takes the form

$$\frac{\bar{G}^*}{RT} = g_0 + g_r r + g_s s + g_{rr} r^2 + g_{rs} r s + g_{ss} s^2 \dots \quad (46)$$

because the ordering is nonconvergent symmetry of the thermodynamic functions is not required about the line $s=0$. The condition for internal equilibrium is then

$$\left[\frac{\partial}{\partial s} \left(\frac{\bar{G}}{RT} \right) \right]_{P,T,r} = 2 \operatorname{artanh} \left(\frac{2s}{1 - r^2 + s^2} \right) + g_s + g_{rs} r + g_{ss} s \dots$$

$$= 0 \text{ (at internal equilibrium)} \quad (47)$$

If we define K'_s by

$$K'_s \equiv \frac{N_{Fe(M2)} N_{Mg(M1)}}{N_{Mg(M2)} N_{Fe(M1)}} \quad (48)$$

We then, with (45), have

$$\ln K'_s = 2 \operatorname{artanh} \left(\frac{2s}{1 - r^2 + s^2} \right)$$

$$= -g_s - g_{rs} r - g_{ss} s \dots \quad (49)$$

The vertices of the square bounding the physically accessible region correspond to ordered crystals. By successively setting r and s at the coordinates of each of these vertices, and by using (45), (46), and (20a), we obtain

$$\left. \begin{aligned} g_r &= \frac{1}{2RT} (\bar{G}_{10}^\circ - \bar{G}_{\bar{1}0}^\circ) \\ g_s &= \frac{1}{2RT} (\bar{G}_{01}^\circ - \bar{G}_{0\bar{1}}^\circ) \end{aligned} \right\} \quad (50)$$

where the subscripts indicate values of r and s in that order. Let us now assume that the second degree terms in (46) are sufficient and insert the N_{sq} , from (45), into (46). If we then set any one of the N_{sq} at zero (its complementary N_{sq} is then unity) we find that (20) has a form like that of the expression giving \bar{G} for a simple symmetrical solution (Thompson, 1967), and that we may then identify two nonideality parameters analogous to those for symmetrical solutions. One of them, W_{M1} , applies to nonideality in the substitution of species on the M(1) site and the other, W_{M2} , applies to nonideality in the substitution of species on the M(2) site. With these we may express the remaining coefficients for the second degree expansion for \bar{G}^*/RT in the form

$$\left. \begin{aligned}
 g_0 &= \frac{1}{4RT} (\bar{G}_{10}^\circ + \bar{G}_{10}^\circ + \bar{G}_{01}^\circ + \bar{G}_{01}^\circ + W_{M1} + W_{M2}) \\
 g_{rr} &= \frac{1}{4RT} (\bar{G}_{10}^\circ + \bar{G}_{10}^\circ - \bar{G}_{01}^\circ - \bar{G}_{01}^\circ - W_{M1} - W_{M2}) \\
 g_{rs} &= \frac{1}{2RT} (W_{M1} - W_{M2}) \\
 g_{ss} &= \frac{1}{4RT} (-\bar{G}_{10}^\circ - \bar{G}_{10}^\circ + \bar{G}_{01}^\circ + \bar{G}_{01}^\circ - W_{M1} - W_{M2})
 \end{aligned} \right\} \quad (51)$$

We shall denote the mean value of W_{M1} and W_{M2} as W_M and assume that their difference is negligible by comparison. It is also perhaps not unreasonable to assume that $\bar{G}_{10}^\circ + \bar{G}_{10}^\circ \approx \bar{G}_{01}^\circ + \bar{G}_{01}^\circ$. With these somewhat arbitrary assumptions (49) takes the form

$$-\ln K_s' = \frac{(\bar{G}_{01}^\circ - \bar{G}_{01}^\circ)}{2RT} - \frac{W_M}{2RT} \quad (52)$$

Quantities such as W_M are positive for most if not all silicate crystalline solutions. No Fe^{2+} -Mg solutions are known to have miscibility gaps, however, even at room temperature. Critical unmixing at 25°C would require that W be about 1.2 kcal (Thompson, 1967, Eq. 62), hence it is probable that $0 < W_M < 1$ kcal. We may now tentatively make some simple calculations.

A hypersthene from Greenland. Ghose and Hafner (1967) have investigated the ordering in some natural and heat-treated hypersthene by analysis of their Mössbauer spectra. These results for one such specimen yield the following values:

Specimen 37218	r	s	$\ln K_s'$
Original sample	0.064	0.75	3.97
Heated at 1000°C	.064	.49	2.16
Heated at 1100°C	.064	.45	1.95

from these values we may calculate the following using (52) and assuming that the heat treatment produced equilibration

If $W_M = 0$	If $W_M = 1$ kcal
$(\bar{S}_{01}^\circ - \bar{S}_{01}^\circ) - 1.38$ cal/deg	-0.98 cal/deg
$(\bar{H}_{01}^\circ - \bar{H}_{01}^\circ) - 7.23$ kcal	-6.23 kcal

The calculated temperature of formation or equilibration of the original sample (a metamorphic hypersthene from the pyroxene granulite facies) would then be 500°C with the ideal assumption ($W_M=0$) and 513°C assuming maximum probable departure from ideality ($W_M=1$ kcal). The negative $\Delta\bar{S}^\circ$ would also imply that at higher temperatures (above 6000°C!) this hypersthene might become anti-ordered (negative s). This last inference cannot be confirmed, however, because it would assuredly melt first.

Of more significance is the strong ordering found in these pyroxenes, even at high temperatures, and the magnitude of the energy effect ($\Delta\bar{G}^\circ$) that this implies. It is clear that Fe²⁺-Mg fractionation between the M(1) and M(2) sites in hypersthene is as strong as that between separate ferromagnesian minerals. The effects of such ordering on heterogeneous Fe²⁺-Mg exchange equilibria may be considerable as has been emphasized by Grover and Orville (1969).

Comparison with ordering in dolomite. The similarity between the chemical formula of an ordered hypersthene which may be written FeMg(SiO₃)₂, and that of an ordered dolomite, CaMg(CO₃)₂ suggests that the same general analysis may be applied to the Ca-Mg carbonates. It can in fact, up to a point, but there are some important differences. In particular, the distinction between ordered ($s=1$) and anti-ordered ($s=-1$) dolomite is an accident of labeling and the two are actually physically identical. Ordered and anti-ordered hypersthene, on the other hand, are distinctly different and the M1 and M2 sites are always distinct even where their occupancies might be identical. The ordering in dolomite is thus convergent in contrast to that in hypersthene which is nonconvergent. This means that the Gibbs function for dolomite must be symmetrical about the line $s=0$, and that all coefficients g for terms containing odd powers of s in the expansion of \bar{G}^*/RT must vanish. The value of q for both of the metal sites in dolomite is 2, as in hypersthene, hence, if we let Ca take the role played by Fe²⁺ in hypersthene, we have the following equilibrium condition

$$\begin{aligned}
 -\ln K_s' &= -2 \operatorname{artanh} \left(\frac{2s}{1-r^2+s^2} \right) \\
 &= g_{ss}s \dots \dots \dots
 \end{aligned}
 \tag{53}$$

The simpler form obtained here, however, is due to the vanishing of g_s , g_{rs} , g_{rrs} , and other coefficients with an odd index in s . It is of interest to consider the idealized one-to-one composition CaMg(CO₃)₂. For this composition r is zero and, with second degree terms only, (53) may be

written

$$\frac{1}{2s} \operatorname{artanh} \left(\frac{2s}{1+s^2} \right) = \frac{\operatorname{artanh} s}{s} = -\frac{g_{ss}}{4} \quad (54)$$

This last equation has the same form as one derived by Bragg and Williams (1934, 1935) for the convergent ordering equilibrium in β -brass. From symmetry we must here have

$$\left. \begin{aligned} \bar{G}_{01}^{\circ} &= \bar{G}_{0\bar{1}}^{\circ} \equiv \bar{G}_s^{\circ} \\ W_{M1} &= W_{M2} \equiv W_M \end{aligned} \right\} \quad (55)$$

hence

$$g_{ss} = \frac{(2\bar{G}_s^{\circ} - \bar{G}_{10}^{\circ} - \bar{G}_{\bar{1}0}^{\circ}) - 2W_M}{4RT} \quad (56)$$

The treatment of Bragg and Williams here differs from ours in that they deal only with the quantity in parentheses in (56) thereby assuming tacitly that W_M is zero. If so, however, there could not be a two-phase region calcite-dolomite. For such a two-phase region to exist there must be a positive W_M . Third or higher degree terms in the series expansion for \bar{G}^*/RT must also be necessary to account for the observed asymmetry about $r=0$ in the phase diagram of Goldsmith and Heard (1961, Fig. 4) for the system $\text{CaCO}_3\text{-MgCO}_3$. Similarly, for hypersthene, there can be no miscibility gap unless W_M is positive. A positive W_M in (52) would imply, at low temperatures, two binodal curves symmetrically disposed about the one-to-one composition ($r=0$).

CORRELATION OF PHYSICAL PROPERTIES WITH ORDERING PARAMETERS

As we observed in the discussion of monoclinic alkali feldspars certain easily measurable physical properties such as, in that case, the optic angle, appear to be sensitive to variations in the ordering parameters. Colville and Ribbe (1968) and Stewart and Ribbe (in press) have investigated optic properties and X-ray diffraction data with respect to site populations (hence to ordering parameters) in the alkali feldspars with some success, and Winchell (1963) has considered the dependence of various physical properties on ordering in pyroxenes.

Equation (47) for hypersthene, in the ideal case (first-degree terms only), is symmetrical about $r=0$, though it should not be expected to be so when higher degree terms are included in the expansion of \bar{G}^*/RT . The equation for the equilibrium path defined by (47) in the ideal case, at a

given pressure and temperature, may then be written

$$\begin{aligned}
 2s &= (1 - r^2 + s^2) \tanh\left(-\frac{g_s}{2}\right) \\
 &= (1 - r^2 + s^2) \tanh\left(\frac{\bar{G}_{01}^{\circ} - \bar{G}_{01}^{\circ}}{4RT}\right) \quad (57)
 \end{aligned}$$

In the square of physical accessibility this defines a hyperbolic segment that is symmetrical about $s=0$ and passes through the points $(-1, 0)$ and $(1, 0)$. If an intensive physical property exists that is sensitive to s and relatively insensitive to r (such that the contoured values are indicated by lines roughly parallel to the r -axis), then the values of that property, for a series of isothermally (and isobarically) equilibrated pyroxenes, should, when plotted against N_{Fs} or r show a departure from linearity that is more marked for low temperature occurrences than for high temperature ones. Precisely this relationship was in fact demonstrated by Hess (1952, Fig. 2) for the optic angle ($2V$) of plutonic orthopyroxenes as contrasted with those of volcanic origin. These observations have been interpreted as due to variations in the content of other components but it now appears likely that there may be a more direct correlation with variations in s .

Although the data now available on site populations and on the values of ordering parameters has been obtained by refinements of X-ray crystallographic data and by spectral methods, it seems likely that in time these may be correlated with more easily measurable physical properties, and these in turn with the essential thermodynamic properties \bar{H} , \bar{V} , and \bar{S}^* . When this can be done, the investigation of homogeneous equilibria in crystals will almost certainly be of great value in dealing with problems of petrogenesis.

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APPENDIX

SITE OCCUPANCY CONSTRAINTS IN SOME MINERAL CRYSTALS

Feldspar. Let us consider first a monoclinic alkali feldspar with the space group $C2/m$. The conventional unit cell contains four formula units, $(K,Na)AlSi_3O_8$, but the unit of quantity we are using here contains only

TABLE A1. SITE OCCUPANCY FOR A MONOCLINIC ALKALI FELDSPAR

Site	M	T ₁	T ₂	A ₁	A ₂	B	C	D
<i>q</i>	2	4	4	2	2	4	4	4
Species <i>Q</i>	K	Si	Si	O	O	O	O	O
Other Species	Na	Al	Al					
($\sigma-1$)	1	1	1	0	0	0	0	0

two. The site occupancy (notation modified from Megaw, 1956) is shown in Table A1. There are five elements and there is at least one site that has species of more than one valence, hence (4) has nonzero terms ($\pi=1$). We therefore have six equations (8) as follows

$$\left. \begin{aligned}
 n_{\text{Na}} &= n_{\text{Na(M)}} \\
 n_{\text{Al}} &= n_{\text{Al(T1)}} + n_{\text{Al(T2)}} \\
 n_{\text{K}} &= -n_{\text{Na(M)}} + 2n \\
 n_{\text{Si}} &= -n_{\text{Al(T1)}} - n_{\text{Al(T2)}} + 8n \\
 n_0 &= 16n \\
 0 &= -n_{\text{Al(T1)}} - n_{\text{Al(T2)}} + 2n
 \end{aligned} \right\} \quad (\text{A1})$$

All terms of the form n_{Qq} are absent and the simplicity of the coefficients arises from the fact that $(v_{\text{es}}-v_{\text{eQ}})$ and $(z_{\text{s}}-z_{\text{Q}})$ are in practice usually either -1 , or 1 , if not zero. Reduction of system (A1) by the procedure outlined in the text leads immediately to

$$\left. \begin{aligned}
 n_{\text{Na}} &= n_{\text{Na(M)}} \\
 n_{\text{Al}} &= n_{\text{Al(T1)}} + n_{\text{Al(T2)}} \\
 (n_{\text{Na}} + n_{\text{K}}) &= 2n \\
 (n_{\text{Al}} + n_{\text{Si}}) - 4(n_{\text{Na}} + n_{\text{K}}) &= 0 \\
 n_{\text{O}} - 8(n_{\text{Na}} + n_{\text{K}}) &= 0 \\
 n_{\text{Al}} - (n_{\text{Na}} + n_{\text{K}}) &= 0
 \end{aligned} \right\} \quad (\text{A2})$$

Most mineralogists will have anticipated results (A2) in this simple example but it serves well enough to illustrate the method. The row-nullity of the coefficient matrix is 3, hence, with 5 elements, there are 2 components. The column-nullity is 1, hence there is 1 internal reaction. Because the n_{Qq} have already been eliminated, the first three equations of (A2) constitute the valence and closure constraints on the quantities

TABLE A3. SITE OCCUPANCY OF A HORNBLENDE

Site	A	M ₁	M ₂	M ₃	M ₄	T ₁	T ₂	P	O ₁	O ₂	O ₃	O ₄	O ₅	O ₆	O ₇
<i>q</i>	1	2	2	1	2	4	4	2	4	4	2	4	4	4	2
Species <i>Q</i>	K	Mg	Mg	Mg	Mg	Si	Si	H	O	O	O	O	O	O	O
Other Species	Na □	Fe ²⁺ Fe ³⁺ Al	Fe ²⁺ Fe ³⁺ Al	Fe ²⁺ Fe ³⁺ Al	Fe ²⁺ Ca Na	Al	Al	□	F						
(<i>σ</i> -1)	2	3	3	3	3	1	1	1	0	0	1	0	0	0	0

(notations modified from Burnham *et al.* 1967, and Ghose and Hellner, 1959). For the hypersthene, as given in Table A2, there are no sites containing species of more than one valence. The valence equation (9) then has no nonzero terms ($\pi=0$) and we may obtain as our final result

$$\left. \begin{aligned}
 n_{\text{Fe}} &= n_{\text{Fe}^{2+}(\text{M1})} + n_{\text{Fe}^{2+}(\text{M2})} \\
 (n_{\text{Fe}} + n_{\text{Mg}}) &= 4n \\
 n_{\text{Si}} - (n_{\text{Fe}} + n_{\text{Mg}}) &= 0 \\
 n_{\text{O}} - 3(n_{\text{Fe}} + n_{\text{Mg}}) &= 0
 \end{aligned} \right\} \quad (\text{A5})$$

This hypersthene thus has two components and one internal reaction. The final result for the hornblende takes the form

$$\left. \begin{aligned}
 (n_{\text{O}} + n_{\text{F}}) &= 24n \\
 \frac{1}{3}(n_{\text{O}} + n_{\text{F}}) - n_{\text{Si}} &= n_{\text{A1}(\text{T1})} + n_{\text{A1}(\text{T2})} \\
 (n_{\text{A1}} + n_{\text{Si}}) - \frac{1}{3}(n_{\text{O}} + n_{\text{F}}) &= n_{\text{A1}(\text{M1})} + n_{\text{A1}(\text{M2})} + n_{\text{A1}(\text{M3})} \\
 (n_{\text{H}} + n_{\text{K}} + n_{\text{Na}}) + 2(n_{\text{Ca}} + n_{\text{Mg}}) + 3(n_{\text{A1}} + n_{\text{Fe}}) + 4n_{\text{Si}} - 2n_{\text{O}} - n_{\text{F}} \\
 &= n_{\text{Fe}^{2+}(\text{M1})} + n_{\text{Fe}^{2+}(\text{M2})} + n_{\text{Fe}^{2+}(\text{M3})} + n_{\text{Fe}^{2+}(\text{M4})} \\
 2n_{\text{O}} + n_{\text{F}} - (n_{\text{H}} + n_{\text{K}} + n_{\text{Na}}) - 2(n_{\text{Ca}} + n_{\text{Mg}} + n_{\text{Fe}}) - 3n_{\text{A1}} - 4n_{\text{Si}} \\
 &= n_{\text{Fe}^{3+}(\text{M1})} + n_{\text{Fe}^{3+}(\text{M2})} + n_{\text{Fe}^{3+}(\text{M3})} \\
 n_{\text{Ca}} &= n_{\text{Ca}(\text{M4})} \\
 \frac{5}{8}(n_{\text{O}} + n_{\text{F}}) - (n_{\text{Ca}} + n_{\text{Mg}} + n_{\text{Fe}} + n_{\text{A1}} + n_{\text{Si}}) &= n_{\text{Na}(\text{M4})} \\
 (n_{\text{Na}} + n_{\text{Ca}} + n_{\text{Mg}} + n_{\text{Fe}} + n_{\text{A1}} + n_{\text{Si}}) - \frac{5}{8}(n_{\text{O}} + n_{\text{F}}) &= n_{\text{Na}(\text{A})} \\
 n_{\text{F}} &= n_{\text{F}(\text{O3})} \\
 \frac{1}{12}(n_{\text{O}} + n_{\text{F}}) - n_{\text{H}} &= n_{\square(\text{P})} \\
 \frac{2}{3}(n_{\text{O}} + n_{\text{F}}) - (n_{\text{K}} + n_{\text{Na}} + n_{\text{Ca}} + n_{\text{Mg}} + n_{\text{Fe}} + n_{\text{A1}} + n_{\text{Si}}) &= n_{\square(\text{A})}
 \end{aligned} \right\} \quad (\text{A6})$$

No further reduction of system (A6) is possible, hence the row-nullity of the coefficient matrix is zero and the number of components is equal to the number of elements. This means that the content of each of the ten elements listed in Table A3 may be varied independently in such an amphibole, an unusual circumstance in silicates, but one that has been essentially verified experimentally by Yoder and Tilley (1962) who obtained virtually complete crystallization to amphibole from melts of basaltic composition. This flexibility is in part due to the vacancies on the A and P sites. It is evident, in fact, from (A6) that the absence of vacancies on either of these sites must reduce the number of components by one. The column-nullity of the coefficient matrix of (A6) is 8, hence there are eight independent internal reactions.

It is of interest that the value of n in each of the examples given here is directly related to either n_o or $n_o + n_F$. This is true, as far as we know, of most silicates, oxides, and oxy-salts. One known exception is mullite which has vacancies on certain oxygen sites.

Note added in proof: In certain applications it may be necessary to select as species Q , for one or more sites, a species that is identical in chemical content and valence to one or more other species, Q' , occupying the same site, but differing from the species Q in some other way as, for example, in the *orientation* of an atom or ion that is asymmetric. When this occurs the above procedure will result in the elimination of the terms $n_{Q'q}$ as well as n_{Qq} from the right-hand sides of the equations in (8), and unless corrected will result in too small a value of ρ . To correct for this we may simply add to the system (8), for each such site, the corresponding equation (2) rearranged so that all non-zero terms are on the right-hand side. If there are η such sites containing species Q' , we will then have $\epsilon + \pi + \eta$ equations in system (8). The number of variables on the right-hand side of (8) will be $\sum_q(\sigma - 1) + 1 + \eta$, and the number of independent equations in (8) will be $\gamma + \pi + \eta$, the rank of the matrix of the coefficients on the right-hand side. The row-nullity is then $\epsilon - \gamma$ and the column-nullity is then $\sum_q(\sigma - 1) + 1 - \pi - \gamma$, or ρ , as in the special case above when $\eta = 0$.

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