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MIXING PROPERTIES OF SANIDINE CRYSTALLINE SOLUTIONS: I. CALCULATIONS BASED ON ION-EXCHANGE DATA[1]

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ABSTRACT

A statistical analysis of the ion-exchange data of Orville (1963) for highly disordered alkali feldspars shows that the Gibbs energy of mixing of these feldspars can be represented satisfactorily by an asymmetric Margules equation containing only two empirical parameters at a given temperature and pressure.

The data indicate that at 650°C and 2 kbar the excess Gibbs energy of mixing for monoclinic alkali feldspar is very nearly:

$$\overline{G}_{ex} = 4.20\, N_{Or} N^2_{Ab} + 2.95\, N_{Ab} N^2_{Or} \text{ kcal mole}^{-1}$$

The temperature range of the data is too limited to permit satisfactory determination of the temperature dependence of the mixing parameters.

The isothermal-isobaric exchange curves appear to have a break in slope in the high-Na region suggesting a second or higher order transition in the feldspars. The positions of these breaks correspond closely to the rapidly reversible (displacive) monoclinic-triclinic symmetry change observed by MacKenzie (1952).

INTRODUCTION

A knowledge of the thermodynamic mixing properties of alkali feldspar crystalline solutions is essential to a thorough understanding of the phase equilibria in many common rocks. The system $Na(AlSi_3O_8)$-$K(AlSi_3O_8)$ forms an essential part of certain model systems of considerable interest in theoretical petrology such as the "granite system" of Tuttle and Bowen (1958), as well as model systems useful in the consideration of metamorphic facies (Thompson, 1961), or of weathering, wall rock alteration, and related phenomena (Garrels and Howard, 1959).

For many such purposes it is desirable that the thermodynamic mixing properties be expressed in analytic form, both as an aid in smoothing, evaluating, and comparing the data, and for the extrapolation of existing data to phase equilibria under conditions that are difficult of access or for other reasons not yet explored. Such calculations may be made on data from a wide variety of sources. Volumes of mixing may be obtained either from direct density determinations or by careful measurement of unit cell parameters (Donnay and Donnay, 1952; Orville, 1967). En-

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thalpies of mixing may be measured by solution calorimetry (Kracek and Neuvonen, 1952; Waldbaum, 1966; Waldbaum and Robie, 1967), and entropies of mixing, at least in part, by heat capacity measurements. All of the above mixing properties and also the total Gibbs energy of mixing may be calculated from data such as that of Bowen and Tuttle (1950), Yoder, Stewart, and Smith (1957), Orville (1963), and Luth and Tuttle (1966) on the compositions of alkali feldspars coexisting at a variety of temperatures and pressures. Calculations on all of the available two-phase data have in fact been made by us, and will be presented in Part III of this series.

The calculations below are based on Orville's ion-exchange experiments between an aqueous Na-K chloride solution and alkali feldspars of the sanidine-high albite series, and do not take into account his two-feldspar assemblages as such. From the exchange data it is possible to calculate the Gibbs energy of mixing of sanidine at several temperatures; and from the temperature dependence of $\overline{G}_{mix}$ the enthalpy and entropy of mixing of these feldspars at two kilobars can be derived. This coupled with Orville's (1967) cell-volume measurements (Part II, Waldbaum and Thompson, 1968) makes possible a preliminary estimate of the internal energy of mixing and leads to a tentative polythermal-polybaric equation of state from which phase diagrams may be calculated.

Allmann and Hellner (1962) gave a brief preliminary analysis of Orville's data based, as is ours, on the condition for exchange equilibrium, but gave no numerical values for the mixing properties other than those implied graphically in their Figures 2 and 3. Perchuk (1965) also presented a brief analysis making some use of Orville's data and assuming a Margules-type formula, but again gave no numerical values for the mixing properties of alkali feldspar other than those implied graphically by his Figure 1a. A later paper by Perchuk and Ryabchikov (1968) presents a more extended treatment (p. 126–130) based on Orville's data. Here a different approach is used, not dependent on a Margules expansion for the excess functions as in Perchuk's earlier paper, but based on graphical methods and also making use in part of coexisting feldspar compositions. Here again, no analytic expression is given for the mixing properties, although these may be inferred from their Figures 1 and 3. Because our aim in this and subsequent papers of this series is to obtain the thermodynamic mixing properties of the alkali feldspars in analytic form, we shall be concerned below with problems in the selection and statistical analysis of the data. Such matters as the possibility of partial or incomplete equilibrium between pairs of feldspars occurring in Orville's experiments, and of Al-Si ordering and related symmetry changes, must also be considered insofar as possible in order to separate their effects from those of K-Na mixing.

Thermodynamic Relations

In each of Orville's (1963) experiments an Na-K feldspar was permitted to react with an aqueous Na-K chloride solution. The aqueous chloride solution has three independently variable components: NaCl, KCl, and H_2O; and the feldspar has two: $NaAlSi_3O_8$ or "*Ab*", and $KAlSi_3O_8$ or "*Or*". With but one fluid phase present, however, the ratio of H_2O to NaCl+KCl in the fluid is constant in any given experiment inasmuch as the only possible variations in the composition of the fluid are by alkali *exchange* with the feldspar crystals present. For equilibrium at a given temperature and pressure between a feldspar and such a solution in a sealed capsule, the Gibbs function must be at a minimum for the contents of the capsule, or[1]

$$\begin{aligned} 0 = dG &= dG_{\text{fsp}} + dG_{\text{fluid}} \\ &= \mu_{\text{Or,fsp}} dn_{\text{Or,fsp}} + \mu_{\text{Ab,fsp}} dn_{\text{Ab,fsp}} \\ &\quad + \mu_{\text{KCl,fluid}} dn_{\text{KCl,fluid}} + \mu_{\text{NaCl,fluid}} dn_{\text{NaCl,fluid}} \\ &\quad + \mu_{\text{H}_2\text{O,fluid}} dn_{\text{H}_2\text{O,fluid}} \end{aligned} \tag{1}$$

Under the experimental conditions, however, the quantities dn are not independent, but are constrained as follows:

$$\left.\begin{aligned} dn_{\text{H}_2\text{O,fluid}} &= 0 \\ dn_{\text{Or,fsp}} + dn_{\text{Ab,fsp}} &= 0 \\ dn_{\text{KCl,fluid}} + dn_{\text{NaCl,fluid}} &= 0 \end{aligned}\right\} \tag{2}$$

and either

$$dn_{\text{KCl,fluid}} + dn_{\text{Or,fsp}} = 0 \tag{3}$$

or

$$dn_{\text{NaCl,fluid}} + dn_{\text{Ab,fsp}} = 0 \tag{4}$$

since (3) and (4) are not independent. With (2) we may rewrite (1)

$$\begin{aligned} 0 = dG = &(\mu_{\text{Or,fsp}} - \mu_{\text{Ab,fsp}}) dn_{\text{Or,fsp}} \\ &+ (\mu_{\text{KCl,fluid}} - \mu_{\text{NaCl,fluid}}) dn_{\text{KCl,fluid}} \end{aligned} \tag{1a}$$

and, again, with (3) it becomes

$$0 = dG = [(\mu_{\text{Or,fsp}} - \mu_{\text{Ab,fsp}}) - (\mu_{\text{KCl,fluid}} - \mu_{\text{NaCl,fluid}})] dn_{\text{Or,fsp}} \tag{1b}$$

emphasizing that under the experimental conditions only one of the quantities dn may be taken as independent. At equilibrium then, so

[1] The notation used in this paper is summarized in Appendix D.

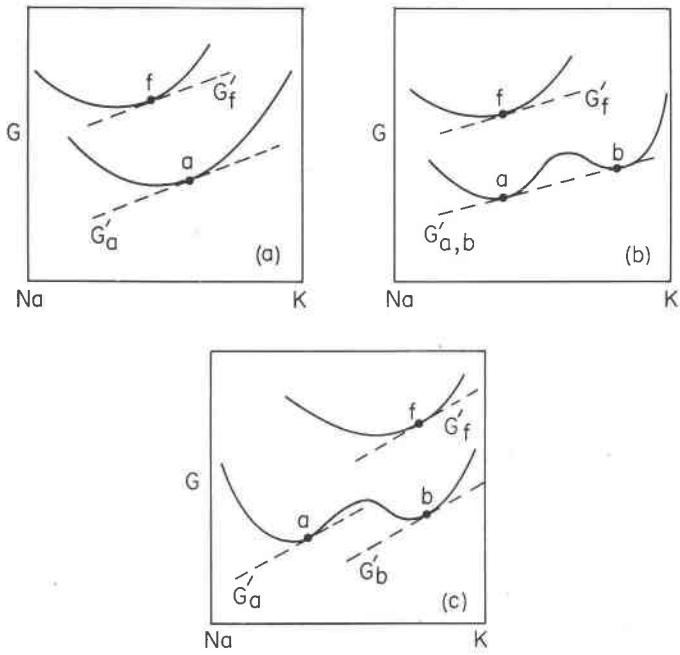

FIG. 1. Isothermal, isobaric equilibrium conditions for ion-exchange between fluid (f) and feldspar (a,b) phases. Lines G_a', G_b', and G_f' denote the slopes of the tangents to the Gibbs surfaces for the feldspar and fluid phases, respectively; these correspond to the left- and right-hand sides of Eq. (5). a) equilibrium between (supercritical) fluid and supercritical feldspar ($G_f'=G_a'$). b) complete equilibrium between fluid and two subcritical feldspars ($G_{a,b}'=G_f'$). c) exchange equilibrium only (partial equilibrium) between two feldspars ($G_a'=G_b'=G_f'$).

that $dG=0$ for minor variations in $dn_{\mathrm{Or,fsp}}$, the bracketed quantity on the right hand side of (1b) must be zero or

$$(\mu_{\mathrm{Or,fsp}} - \mu_{\mathrm{Ab,fsp}}) = (\mu_{\mathrm{KCl,fluid}} - \mu_{\mathrm{NaCl,fluid}}) \tag{5}$$

Condition (5) may also be written in a rearranged form that is conventional in the treatment of ternary reciprocal equilibria

$$\mu_{\mathrm{Or,fsp}} + \mu_{\mathrm{NaCl,fluid}} = \mu_{\mathrm{Ab,fsp}} + \mu_{\mathrm{KCl,fluid}} \tag{5a}$$

but there are advantages in keeping it in the form of (5) rather than that of (5a). The quantities enclosed in parentheses in (5) are properties of but one phase only, and we may note that

$$\left(\frac{\partial \overline{G}_{\mathrm{fsp}}}{\partial N_{\mathrm{Or,fsp}}}\right)_{P,T} = (\mu_{\mathrm{Or,fsp}} - \mu_{\mathrm{Ab,fsp}}) \tag{6}$$

Similarly if we define the quantities M_{KCl} and M_{NaCl} in the fluid by

$$(1 - M_{\mathrm{NaCl}}) = M_{\mathrm{KCl}} \equiv \frac{n_{\mathrm{KCl}}}{n_{\mathrm{sf}}} = 1 - \frac{n_{\mathrm{NaCl}}}{n_{\mathrm{sf}}}$$

where $n_{\mathrm{sf}} \equiv n_{\mathrm{KCl}} + n_{\mathrm{NaCl}}$, we may write (see Appendix A)

$$\left(\frac{\partial \tilde{G}_{\mathrm{fluid}}}{\partial M_{\mathrm{KCl,fluid}}}\right)_{P,T,n_{\mathrm{sf}},n_{\mathrm{H_2O}}} = (\mu_{\mathrm{KCl,fluid}} - \mu_{\mathrm{NaCl,fluid}}) \tag{7}$$

and the equilibrium condition (5) may be written in yet another form

$$\left(\frac{\partial \overline{G}_{\mathrm{fsp}}}{\partial N_{\mathrm{Or,fsp}}}\right)_{P,T} = \left(\frac{\partial \tilde{G}_{\mathrm{fluid}}}{\partial M_{\mathrm{KCl,fluid}}}\right)_{P,T,n_{\mathrm{sf}},n_{\mathrm{H_2O}}}. \tag{5b}$$

This last form of the equilibrium conditions is shown graphically in Figure 1a. We have then from (5b) for exchange curves such as in Figures 4–8 of Orville (1963)

$$\left(\frac{\partial^2 \overline{G}_{\mathrm{fsp}}}{\partial N^2_{\mathrm{Or,fsp}}}\right)_{P,T} dN_{\mathrm{Or,fsp}} = \left(\frac{\partial^2 \tilde{G}_{\mathrm{fluid}}}{\partial M^2_{\mathrm{KCl,fluid}}}\right)_{P,T,n_{\mathrm{sf}},n_{\mathrm{H_2O}}} dM_{\mathrm{KCl,fluid}} \tag{8}$$

where $M_{\mathrm{KCl,fluid}}$ and $N_{\mathrm{Or,fsp}}$ are the ordinate and abscissa, respectively, and the experiments from which the curve has been constructed were carried out at constant P, T, and total salt molality. Hence

$$\left(\frac{dM_{\mathrm{KCl,fluid}}}{dN_{\mathrm{Or,fsp}}}\right) = \frac{\left(\dfrac{\partial^2 \overline{G}_{\mathrm{fsp}}}{\partial N^2_{\mathrm{Or,fsp}}}\right)_{P,T}}{\left(\dfrac{\partial^2 \tilde{G}_{\mathrm{fluid}}}{\partial M^2_{\mathrm{KCl,fluid}}}\right)_{P,T,n_{\mathrm{sf}},n_{\mathrm{H_2O}}}} \tag{9}$$

The second derivatives in (8) and (9) are positive quantities for phases stable with respect to unmixing and zero in the limiting case of a phase of critical mixing. Thus for equilibrium between a noncritical liquid and a critical feldspar we have

$$\left(\frac{\partial^2 \overline{G}_{\mathrm{fsp}}}{\partial N^2_{\mathrm{Or,fsp}}}\right)_{P,T} = 0 \tag{10}$$

$$\left(\frac{dM_{\mathrm{KCl,fluid}}}{dN_{\mathrm{Or,fsp}}}\right) = 0 \tag{10a}$$

It is therefore evident from Orville (1963, Figs. 7 and 8) that for alkali feldspars at 2 kilobars the critical temperature is not far from 675°C and the critical composition not far from 0.35 mol fraction Or.

Because of the immiscibility in feldspar at low temperatures, many of Orville's experiments involved the presence of two feldspars rather than one. This raises some interesting possibilities for metastable equilibria such that both feldspars are in exchange equilibrium with the fluid but not in full equilibrium with each other. This may be clarified by an extension of the procedure followed above. We now have

$$\begin{aligned} dG &= dG_f + dG_a + dG_b \\ &= \mu_{H_2O,f}dn_{H_2O,f} + \mu_{NaCl,f}dn_{NaCl,f} + \mu_{KCl,f}dn_{KCl,f} \\ &\quad + \mu_{Or,a}dn_{Or,a} + \mu_{Or,b}dn_{Or,b} + \mu_{Ab,a}dn_{Ab,a} + \mu_{Ab,b}dn_{Ab,b} \end{aligned}$$

subject to the constraints

$$\left.\begin{aligned} dn_{H_2O,f} &= 0 \\ dn_{NaCl,f} + dn_{KCl,f} &= 0 \\ dn_{Or,a} + dn_{Ab,a} + dn_{Or,b} + dn_{Ab,b} &= 0 \\ dn_{Or,a} + dn_{Or,b} + dn_{KCl,f} &= 0 \end{aligned}\right\} \tag{12}$$

Proceeding as before we obtain the following result upon eliminating the interdependence of the dn's

$$\begin{aligned} dG = {} & (\mu_{Or,a} - \mu_{Or,b})dn_{Or,a} + (\mu_{Ab,a} - \mu_{Ab,b})dn_{Ab,a} \\ & + [(\mu_{KCl,f} - \mu_{NaCl,f}) - (\mu_{Or,b} - \mu_{Ab,b})]dn_{KCl,f} \end{aligned} \tag{11a}$$

Hence, at equilibrium

$$(\mu_{Or,b} - \mu_{Ab,b}) = (\mu_{Or,a} - \mu_{Ab,a}) = (\mu_{KCl,f} - \mu_{NaCl,f}) \tag{13}$$

and also

$$\left.\begin{aligned} \mu_{Or,b} &= \mu_{Or,a} \\ \mu_{Ab,b} &= \mu_{Ab,a} \end{aligned}\right\} \tag{14}$$

These equilibrium conditions are shown graphically in Figure 1b. The metastable or *partial* equilibrium may arise when the feldspar grains are not in direct contact and equilibrate only through the fluid. We may explore the consequences by introducing either the constraint

$$dn_{Ab,a} + dn_{Or,a} = 0 \tag{15}$$

or the corresponding one for b (which is not independent). We then obtain only conditions (13) and not conditions (14). This type of metastable or partial equilibrium is shown in Figure 1c. It can be shown (Appendix B) that it is indeed *not* an unstable equilibrium, though one's intuition may at first suggest otherwise. It is, however, metastable with respect to some more stable state (having a lower value of G) of either

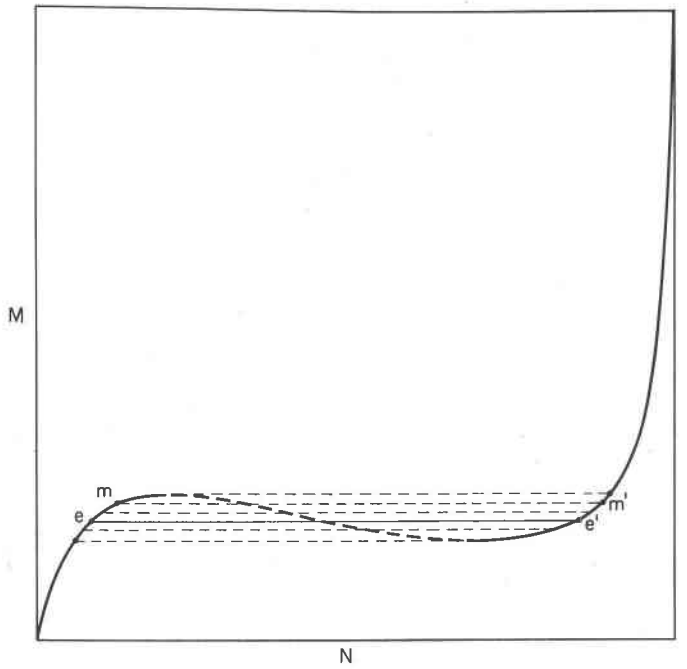

FIG. 2. Idealized ion-exchange isotherm illustrating possible compositions of two feldspars in exchange equilibrium with fluid. The feldspars at m and m' are only in exchange equilibrium with each other, but those at e and e' are in complete equilibrium with each other. When plotted in reciprocal ternary coordinates, the tie lines corresponding to m and m' cross the tie lines corresponding to e and e'. Dashed portion of curve denotes feldspars unstable with respect to diffusion.

the type shown in Figure 1a or that of Figure 1b. For the more stable states to be realized, however, either a center of phase b must nucleate in a grain of a, or there must be direct a-b interfaces. In either of these cases the constraint (15) is inoperative and the reaction may proceed toward the full set of conditions (13) and (14). Figure 2 shows an idealized exchange isotherm illustrating the various possibilities.

Inasmuch as the following analysis requires only that exchange equilibrium be achieved between each feldspar and the fluid, it has been possible to include certain runs that clearly must correspond to partial equilibria such as shown by Figures 1c and 2 ($m-m'$), and in Figure 9 of Orville (1963).

THE FLUID PHASE

For the fluid phase we may write formally (see Denbigh, 1955, Chaps. 9–10 and especially Eq. 10.35)

$$\mu_{KCl} = \mu_{K^+} + \mu_{Cl^-}$$
$$= \mu^{\square}_{K^+} + \mu^{\square}_{Cl^-} + RT \ln(m_{K^+} m_{Cl^-} \gamma_{KCl}^{\pm}) \quad (16a)$$

$$\mu_{NaCl} = \mu_{Na^+} + \mu_{Cl^-}$$
$$= \mu^{\square}_{Na^+} + \mu^{\square}_{Cl^-} + RT \ln(m_{Na^+} m_{Cl^-} \gamma_{NaCl}^{\pm}) \quad (16b)$$

Hence

$$(\mu_{KCl} - \mu_{NaCl}) = (\mu^{\square}_{K^+} - \mu^{\square}_{Na^+}) + RT \ln\left(\frac{m_{K^+}}{m_{Na^+}} \cdot \frac{\gamma_{KCl}^{\pm}}{\gamma_{NaCl}^{\pm}}\right) \quad (17)$$

But

$$\frac{m_{K^+}}{m_{Na^+}} \approx \frac{n_{KCl}}{n_{NaCl}} = \frac{M_{KCl}}{M_{NaCl}} \quad (18)$$

so

$$(\mu_{KCl} - \mu_{NaCl}) = \left[(\mu^{\square}_{K^+} - \mu^{\square}_{Na^+}) + RT \ln \frac{\gamma_{KCl}^{\pm}}{\gamma_{NaCl}^{\pm}}\right] + RT \ln \frac{M_{KCl}}{M_{NaCl}} \quad (19)$$

If 2 molal KCl and 2 molal NaCl aqueous solutions mix ideally or very nearly so (as seems reasonable) then the bracketed quantity in (19) above is constant, or very nearly so, at any given P and T (Appendix C). If so, the ratio $\gamma_{KCl}^{\pm}/\gamma_{NaCl}^{\pm}$ for 2 molar K-Na chloride solutions should be very nearly constant for such solutions at any given P and T.[1] There is sufficient data on the values of these coefficients for such solutions (Robinson, 1961; Stern and Anderson, 1964) to indicate that the assumption of constant γ-ratio is not far off at low temperatures and one atmosphere. At the conditions of Orville's experiments the fluid phase is considerably less dense than one of comparable composition at 25°C and one atmosphere, hence should mix more ideally owing to less interaction between K^+ and Na^+ ions. The recent results of Gammon, Borcsik, and Holland (1967) provide more direct confirmation of this assumption, and the conditions of their hydrothermal experiments are more nearly those of Orville's. We shall therefore assume, until proven otherwise, that the bracketed quantity in (19) may be regarded as constant at any given P, T, and at the total salt molality of Orville's experiments.

[1] As the total salt molality approaches zero, the ratio $\gamma_{KCl}^{\pm}/\gamma_{NaCl}^{\pm}$ must also approach unity.

The Feldspar Phase

Both hydrothermal syntheses (Orville, 1963; Luth and Tuttle, 1966) and natural occurrences (Barth, 1951) of coexisting alkali feldspars show that the miscibility gap is decidedly asymmetric in any given series and such that the compositions of critical mixing must be at approximately $N_{Or}=1/3$. This alone shows that a symmetrical formula (Thompson, 1967, p. 348) based on a Margules expansion, can not give an adequate representation of the excess Gibbs function. We must therefore include at least the third order terms in the formulas for the excess Gibbs function. If the third order terms are sufficient, we may write (Thompson, 1967, Eq. 70a)

$$\overline{G}_{ex,fsp} = N_{Or}N_{Ab}(W_{GOr}N_{Ab} + W_{GAb}N_{Or}) \tag{20}$$

From this we may derive the relation (see Thompson, 1967, Eq. 75)

$$(\mu_{Or} - \mu_{Ab}) = (\mu^{\circ}_{Or} - \mu^{\circ}_{Ab}) + RT \ln \frac{N_{Or}}{N_{Ab}} + W_{GOr}N_{Ab}(1 - 3N_{Or}) - W_{GAb}N_{Or}(1 - 3N_{Ab}) \tag{21}$$

for Na-K substitutions in only one crystallographic site ($\alpha=1$). Equation (21) can be rearranged in a power series in N_{Or}

$$(\mu_{Or} - \mu_{Ab}) = [(\mu^{\circ}_{Or} - \mu^{\circ}_{Ab}) + W_{GOr}] + RT \ln \frac{N_{Or}}{N_{Ab}} + 2(W_{GAb} - 2W_{GOr})N_{Or} + 3(W_{GOr} - W_{GAb})N^2_{Or} \tag{22}$$

Should terms of higher than third order be necessary to describe the excess function adequately, the resulting formulas for G_{ex} would be similar in form to (22) but with extra terms added in higher powers of N_{Or}. The bracketed quantity in (22) is constant at any given P and T.

Before proceeding, however, we must discuss briefly some problems in dealing with high-temperature alkali feldspars that complicate the interpretation of the mixing properties. These have to do with the ordering of Al and Si among the tetrahedral sites, and with the monoclinic-triclinic symmetry change that takes place in Na-rich alkali feldspars.

No alkali feldspars are yet known that do not have at least a center of symmetry. The conventional C-centered cell contains 4 alkali sites and sixteen tetrahedral sites, but the primitive cell or repeat unit contains only half these. In the primitive repeat unit, however, all sites occur in pairs related by the center of symmetry, hence we need consider only the formula $(Na,K)_1Al_1Si_1Si_1Si_1O_8$ to represent all possible limiting

configurations of centrosymmetric alkali feldspars. In a centrosymmetric triclinic feldspar the four tetrahedral sites are crystallographically distinct, hence may have different Al-Si occupancies, but in a centrosymmetric monoclinic feldspar such as sanidine, $T_1(0)$ must be identical to $T_1(m)$, and $T_2(0)$ must be identical to $T_2(m)$. To be crystallographically identical a pair of sites must have identical occupancy, hence we shall speak of monoclinic alkali feldspars [or triclinic feldspars that can invert to monoclinic by means of a rapid hence presumably displacive (Buerger, 1948) symmetry change] as "*m*-disordered" feldspars. The T_2 and T_1 sites on the other hand are topologically distinct in the feldspar framework hence can never be crystallographically identical. Because of this it is unlikely that their Al-Si populations would ever be exactly identical, although the observed departures therefrom in some sanidines and high albites are known to be very small (Ferguson, Traill, and Taylor, 1958; Ribbe, 1963). By the same reasoning it is unlikely that any feldspar that formed originally or thoroughly recrystallized as a triclinic feldspar would ever be *completely* *m*-disordered. This is supported by the structure refinement data of Williams and Megaw (1964) for a hydrothermally grown high albite. We shall assume, therefore, that any feldspar that is known to be *m*-disordered or that can invert displacively to a monoclinic form, either grew or achieved its present Al-Si distribution as a monoclinic feldspar.

The feldspars used as starting materials in Orville's experiments were synthesized hydrothermally at 700°C and 2 kilobars, ground, then annealed dry for several hours at 1050°C. These were presumably *m*-disordered, or if originally triclinic, very nearly *m*-disordered, and all presumably also had a high degree of disorder between the T_1 and T_2 sites, although more data would clearly be desirable. There is some evidence (O'Neil and Taylor, 1967; Martin, 1967) that Al-Si ordering should have proceeded to equilibrium fairly rapidly under the hydrothermal conditions of Orville's experiments, but it is by no means conclusive and there is evidence that indicates otherwise (MacKenzie, 1957; Chagnon and Saull, 1966). Because of this there is some uncertainty in interpreting the exchange data. Some of Orville's starting feldspars were grown as monoclinic crystals, others as triclinic crystals, and they were grown at different compositions hence there was probably some initial variation in Al-Si distribution. In addition, we are not sure of the extent of re-equilibration with respect to Al-Si distribution during the course of the runs. Either initial variations, if frozen in, or erratic and incomplete equilibration during the runs will produce scatter in the results derived using the above equations. Furthermore until the Al-Si distribution in such feldspars is fully known it is not possible in the

analysis below to separate entirely the effects of simple Na-K substitution from possibly related variations in Al-Si ordering. We can only suppose, until we find otherwise, that effects in Orville's experiments related to variations in Al-Si distribution are minor and may be neglected.

A monoclinic-triclinic transformation, however, should be considered more carefully (Waldbaum and Thompson, 1968, Appendix). Whether the symmetry change is an equilibrium one (hence related to the onset of ordering between the T(0) and T(m) sites) or the displacive transformation (probably metastable) found in Na-rich, m-disordered feldspars, it must be accompanied by a change in the configuration of the oxygen atoms about the alkali site and should thereby have some effect on the Na-K mixing properties. There is no clear evidence such as an observed two-phase region that demands a first-order transition associated with this symmetry change, and it seems likely from the results of Donnay and Donnay (1952) that the transition is of second or higher order. If it is in fact second-order, a plot of volume, $\overline{V}$, against composition at constant P and T (Waldbaum and Thompson, 1968) or of $(\partial \overline{G}/\partial N_{\mathrm{Or}})_{P,T}$ or of $(\partial \overline{G}_{\mathrm{ex}}/\partial N_{\mathrm{Or}})_{P,T}$ against composition at constant P and T, should show a break in slope at the symmetry change. If such a break is well-marked, a fitted curve that neglected it could lead to serious error on both sides of the transition. The two sides would then better be fitted separately. The interpretation of the data when a problem such as this exists is beset with statistical hazards but must nonetheless be considered in what follows.

Method of Analysis of the Exchange Data

Considering equations (13), (19), and (22) we obtain

$$RT \ln K' \equiv RT \ln \frac{N_{\mathrm{Or}} M_{\mathrm{NaCl}}}{N_{\mathrm{Ab}} M_{\mathrm{KCl}}}$$

$$= -\left[(\mu^{\circ}_{\mathrm{Or}} - \mu^{\circ}_{\mathrm{Ab}}) - (\mu^{\square}_{\mathrm{K}^+} - \mu^{\square}_{\mathrm{Na}^+}) + RT \ln \frac{\gamma_{\mathrm{NaCl}^{\pm}}}{\gamma_{\mathrm{KCl}^{\pm}}} + W_{G\mathrm{Or}} \right] \qquad (23)$$

$$- 2(W_{G_{\mathrm{Ab}}} - 2W_{G_{\mathrm{Or}}}) N_{\mathrm{Or}} - 3(W_{G_{\mathrm{Or}}} - W_G) N^2_{\mathrm{Or}}$$

If we assume a constant γ-ratio as discussed above, the bracketed quantity in (23) is again a constant in any set of Orville's (1963) experiments at a given P, T, and total salt molality. The quantities in parentheses in (23) are also constant at any given P and T, hence for such a set of experiments (23) may be put in the form

$$RT \ln K' = a_0 + a_1 N_{\mathrm{Or}} + a_2 N^2_{\mathrm{Or}} \qquad (24)$$

such that a_1 and a_2 depend on P and T, and a_0 depends on P, T, and total salt molality. The quantity $RT \ln K'$ for each of Orville's runs has been calculated and the results are given in Table 1.[1] Plots of $RT \ln K'$ versus N_{Or} for Orville's data at 2 kb and with 2.0 molal salt solutions are given in Figures 3–8 for temperatures of 700°, 680°, 670°, 650°, 600°, and 500°C, respectively. The method of obtaining the fitted curves will be discussed below. For the moment we need note only two conspicuous features inherent in the data: namely that any adequately fitted curve must have negative slope and must have positive curvature.

The positive curvature means that $W_{G_{Or}} > W_{G_{Ab}}$ which indicates that the feldspar solution is *asymmetric* and such that the composition of critical mixing must be at $N_{Or} < 1/2$ (see Thompson, 1967, Eq. 73). A straight line of negative slope would imply a *symmetric* solution with $W_G > 0$, and a straight horizontal line would imply an *ideal* solution. It is clear then that the exchange data require at least a simply asymmetric model for the feldspar phase.

It will be noted that

$$RT \ln K' = (\text{const.})_{P,T,n_{sf},n_{H_2O}} + \left(\frac{\partial \overline{G}_{ex,fsp}}{\partial N_{Or}}\right)_{P,T} \tag{25}$$

and thus Figures 3–8 may be regarded, except for a scale factor on the ordinate, as plots of $RT \ln K'$ versus N_{Or} at the pressure and temperature in question. Such plots have been used extensively by other investigators in the study of binary solutions (for example, Herington, 1947; Ames, 1964). These plots have several interesting properties:

For *any* binary solution where we have a plot of $(\partial \overline{G}_{ex}/\partial N_2)_{P,T}$ versus N_2, the area, Z, between the curve and the abscissa is

$$Z = \int_{N_2'}^{N_2''} \left(\frac{\partial \overline{G}_{ex}}{\partial N_2}\right)_{P,T} dN_2 \tag{26}$$

but we also have the situation

$$dG_{ex}\Big|_{P,T} = \left(\frac{\partial \overline{G}_{ex}}{\partial N_2}\right)_{P,T} dN_2\Big|_{P,T} \tag{27}$$

and from Henry's law:

[1] Table 1, containing detailed calculations of all of Orville's runs, may be ordered as NAPS Document 00101 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001; remitting in advance $1.00 for microfiche or $3.00 for photocopies.

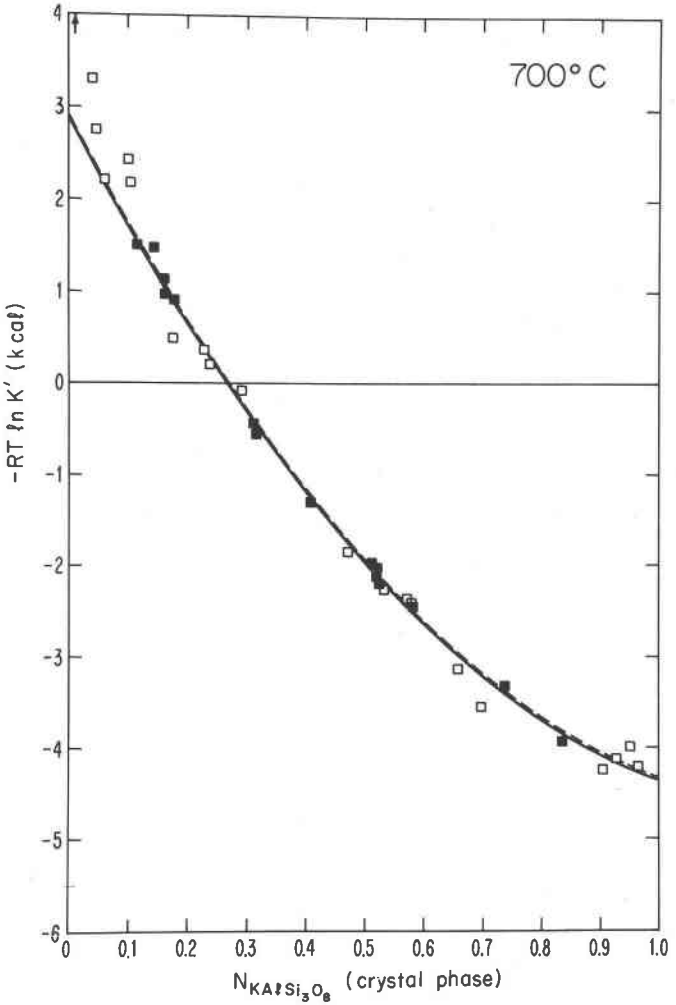

FIG. 3. $RT\ln K'$ *vs.* N_{Or} ion-exchange curve at 2 kbar and 700°C (data of Orville, 1963, Table 1). Solid line corresponds to isothermal least squares result (33), and dashed line corresponds to polythermal equation (39). Solid squares are the data points used to obtain (39). Arrow indicates run 551 which plots off scale at +6.9 kcal.

$$\overline{G}_{ex} \to 0 \begin{cases} \text{as} & N_2 \to 0 \\ \text{as} & N_2 \to 1 \end{cases} \tag{28}$$

Hence

$$Z = (\overline{G}''_{ex} - \overline{G}'_{ex}) \tag{29}$$

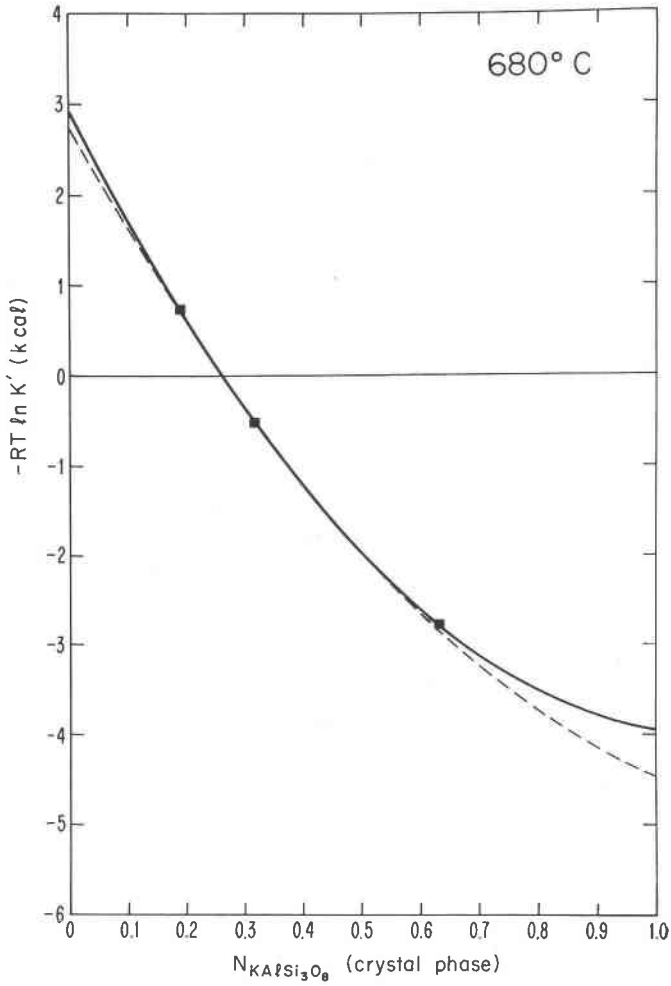

FIG. 4. $RT\ln K'$ *vs.* N_{Or} ion-exchange curve at 2 kbar and 680°C (data of Orville, 1963, Table 1). Solid squares are the data points used to obtain equation (39).

and when $N_2'' \equiv 1$ and $N_2' \equiv 0$ we must have

$$Z = \overline{G}_{ex}'' = \overline{G}_{ex}' = 0 \tag{30}$$

From this it is evident (see Herington, 1947, p. 610) that the two shaded areas in Figure 9a must be equal. For a plot of $(\partial \overline{G}_{ex}/\partial N_2)_{P,T}$ that obeys an equation having the form of (24) there are further interesting properties as shown in Table 2 and Figure 9b. Such a curve is, of course, a parabola with its axis parallel to the ordinate.

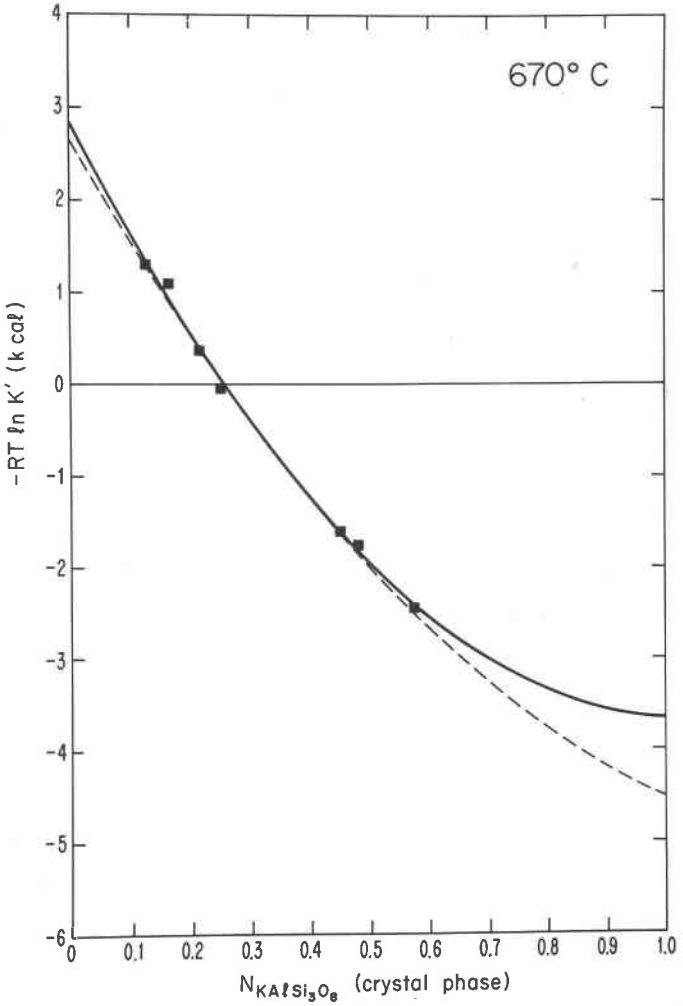

FIG. 5. $RT\ln K'$ *vs.* N_{Or} ion-exchange curve at 2 kbar and 670°C (data of Orville, 1963, Table 1). Solid squares are the data points used to obtain equation (39).

The form of Eq. (24), or its extension to include higher degree terms in N_{Or}, is such that the data may be smoothed by a polynomial least-squares fit. Such a fit provides values for a_0, a_1, a_2, etc., and when a second degree (parabolic) fit is adequate we have

$$\left.\begin{aligned} W_{G_{Ab}} &= W_{G_1} = -\tfrac{1}{2}a_1 - \tfrac{2}{3}a_2 \\ W_{G_{Or}} &= W_{G_2} = -\tfrac{1}{2}a_1 - \tfrac{1}{3}a_2 \end{aligned}\right\} \tag{31}$$

$$\left[(\mu^{\circ}_{\mathrm{Or}} - \mu^{\circ}_{\mathrm{Ab}}) - (\mu^{\square}_{\mathrm{K}^+} - \mu^{\square}_{\mathrm{Na}^+}) - RT \ln \frac{\gamma_{\mathrm{NaCl}^{\pm}}}{\gamma_{\mathrm{KCl}^{\pm}}} + W_{G_{\mathrm{Or}}}\right] = a_0 \quad (32)$$

Selection of Data

In what follows we shall suppose that second degree expansions for the exchange curves are adequate even though strict application of the Gauss criterion (Worthing and Geffner, 1943) suggests that forms of higher degree are justifiable in some instances. There are several reasons for this supposition:

(a) A second degree expression for the exchange curve (a first derivative property)

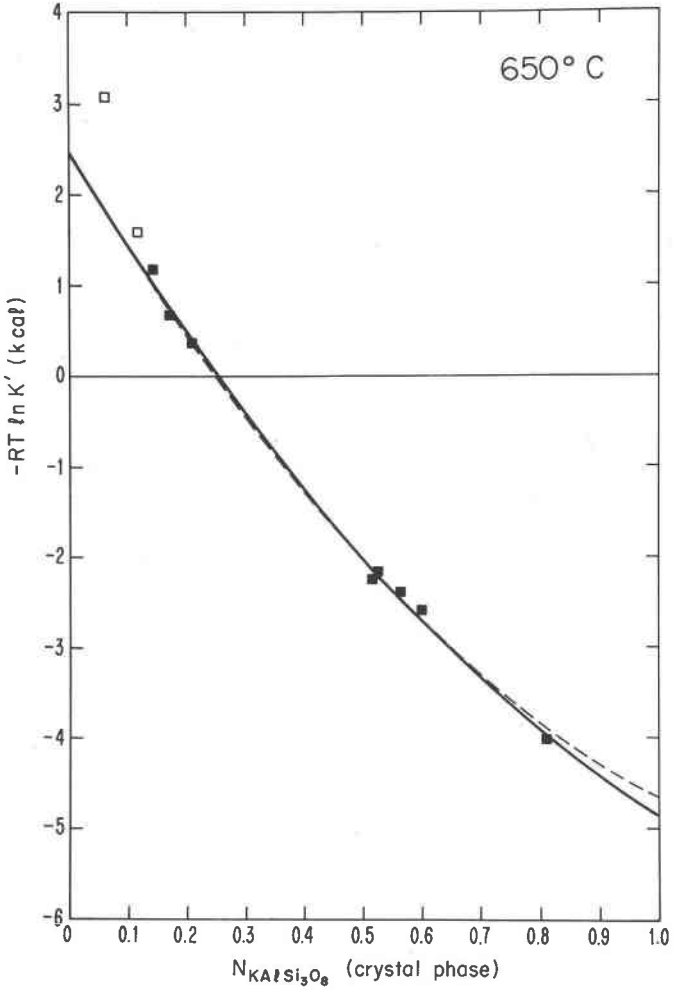

FIG. 6. $RT\ln K'$ *vs.* N_{Or} ion-exchange curve at 2 kbar and 650°C (data of Orville, 1963, Table 1). Solid squares are the data points used to obtain equation (39).

corresponds to a third degree expression for the excess functions as in a simple asymmetric Margules solution (Thompson, 1967). Waldbaum (1966) has shown that a third degree fit for his enthalpy data on a low albite-microcline exchange series is all that the data warrants, and Waldbaum and Thompson (1968) show that much of the volume data on alkali feldspar can be expressed adequately by a second degree fit and that no feldspar volume data yet warrants a fit of higher degree than the third.

(b) Each of Orville's exchange curves represents a series of feldspars in which there must be a monoclinic–triclinic symmetry change. Use of a more complicated expression for

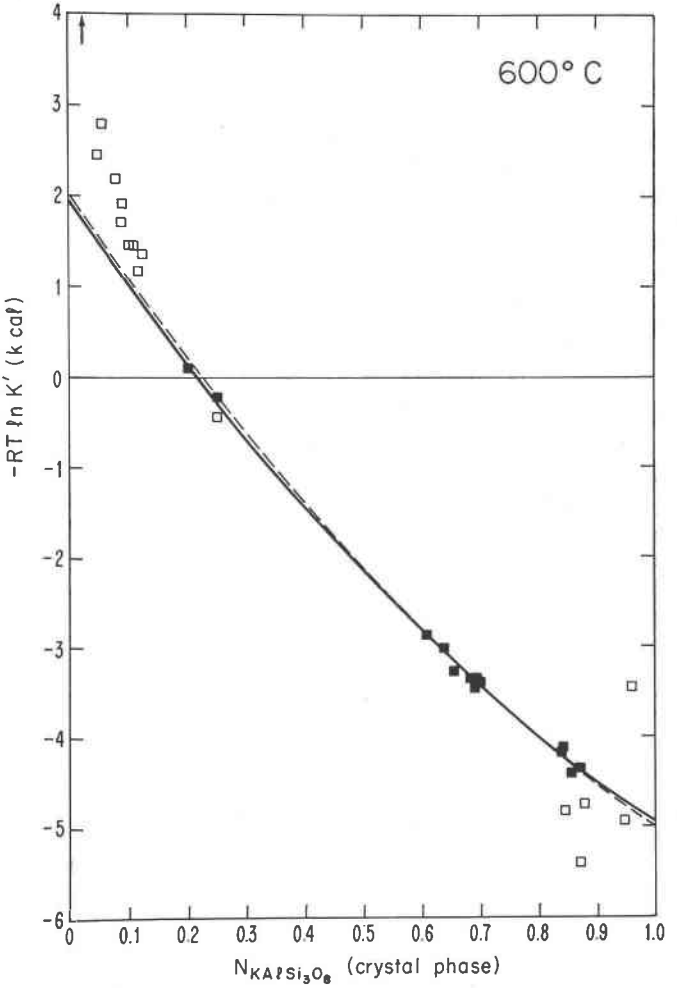

FIG. 7. $RT\ln K'$ *vs.* N_{Or} ion-exchange curve at 2 kbar and 600°C (data of Orville, 1963, Table 1). Solid squares are the data points used to obtain equation (39). Arrow indicates runs 259, 432, and 445 which plot off scale at +7.3, 7.1, and 4.7 kcal respectively.

what may in fact be two curves separated by a first or higher order discontinuity would thus be fictitious.

(c) There are probably systematic errors in Orville's determinative curves, related in part at least, to the symmetry problem.

(d) The simpler formula, with but two empirical parameters for each excess function at a given pressure and temperature, is much easier to manipulate and can be readily modified should convincing evidence show that it is insufficient.

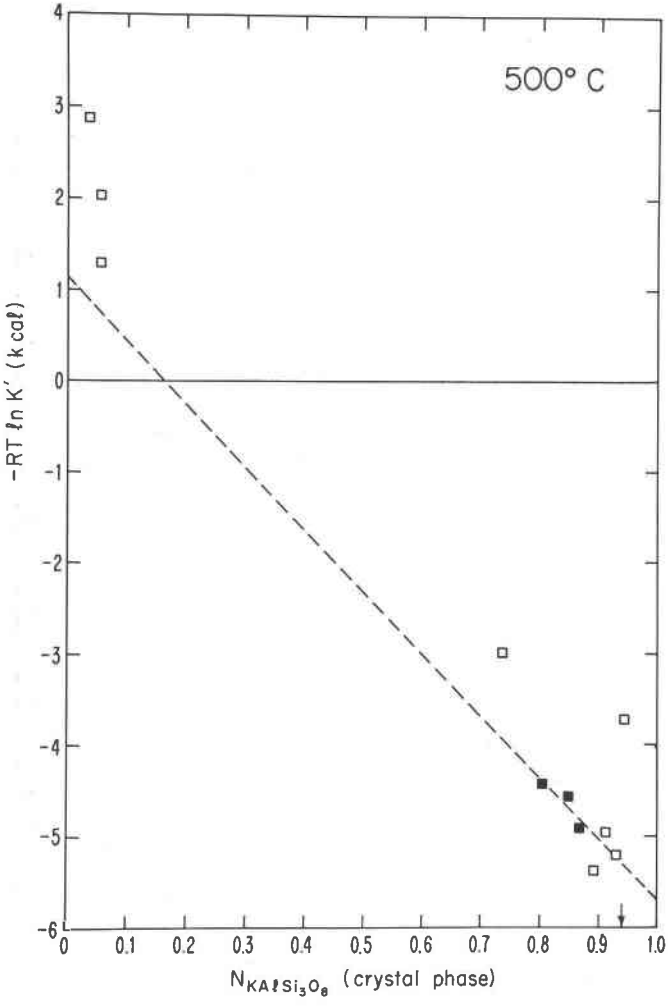

FIG. 8. $RT\ln K'$ *vs.* N_{Or} ion-exchange curve at 2 kbar and 500°C (data of Orville, 1963, Table 1). Solid squares are the data points used to obtain equation (39). Arrow indicates run 258 which plots off scale at −6.2 kcal.

The data in Table 1 and the plots of $RT\ln K'$ versus N_{Or} show that the short-term runs have the greatest scatter. To test this we made a series of least-squares fits with short term runs successively eliminated (Table 3a), and compared their standard deviations, finding a minimum when runs of less than 48 hours were eliminated. This application of the Gauss criterion (Wensel and Tuckerman, 1938) suggests that equilibration was reliably achieved only for runs at 700°C and 2 kbar that were of 48 hours or more duration. This agrees with Orville's estimate (Orville, 1963, p. 217) of the time required for equilibration on the K-rich side but is less conservative than his estimate of 144 hours as the time required on the Na-rich side. We believe, however, that his difficulties on the Na-rich side may be related at least in part to other causes to be discussed more fully below.

There is also a relatively large scatter in points near the K-rich and Na-rich ends, even when only the longest term runs are considered. This shows up in Table 3b where a series

TABLE 2. PROPERTIES OF RT ln K' ION-EXCHANGE CURVE AS SHOWN IN FIGURE 9b

N_1	N_2	$RT\ ln\ K'$	$d(RT\ ln\ K')/dN_2$
1	0	const.$+W_2$	$2W_1-4W_2$
2/3	1/3	const.$+\frac{W_1}{3}$	$-2W_2$
1/2	1/2	const.$-\frac{W_2-W_1}{4}$	$-(W_1+W_2)$
1/3	2/3	const.$-\frac{W_2}{3}$	$-2W_1$
0	1	const.$-W_1$	$2W_2-4W_1$

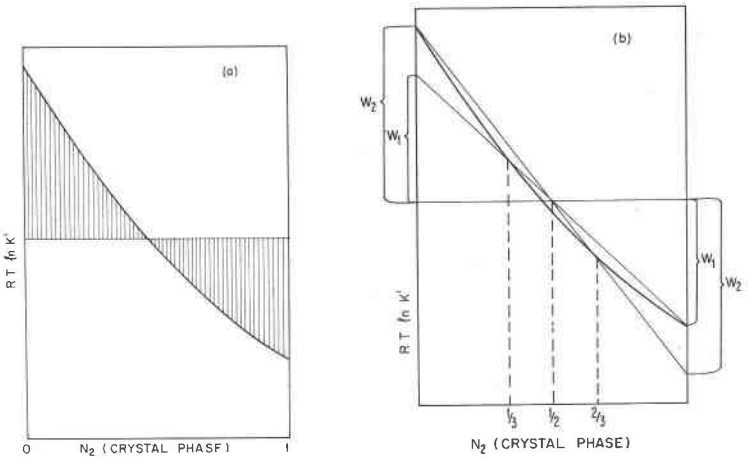

FIG. 9. Geometrical properties of $RT\ln K'$ ion-exchange curve: a) equal-area relation; b) properties summarized in Table 2.

TABLE 3. EFFECT ON EQUATIONS 31–32 OF REMOVING 700°C ION-EXCHANGE DATA POINTS FROM SUCCESSIVE LEAST-SQUARES FITS[a]

Duration of shortest run (hours)	N_{Or} of most Na-rich point retained	No. of data points	$W_{G_{Ab}}$ (kcal)	$W_{G_{Or}}$ (kcal)	Least-squares standard deviation (kcal)	$-a_0$ kcal
Table 3a. Removal of Short-term Runs from All Data						
1.5	0.010	35	2.49	5.39	0.65	3.93
24	.040	31	2.70	4.78	.23	3.28
32	.040	24	2.68	4.76	.24	3.23
48	.040	23	2.71	4.79	.21	3.28
49	.040	18	2.72	4.83	.22	3.35
96	.040	17	2.70	4.82	.23	3.35
144	.040	16	2.70	4.82	.24	3.35
168	.160	4	0.84	4.41	.03	3.40
Table 3b. Removal of Short-term Runs After First Removing Compositions $\geq 90\%$ Or and $\leq 10\%$ Or						
1.5	0.100	27	2.71	4.68	0.22	3.15
24	.100	24	2.63	4.66	.22	3.17
32	.102	17	2.70	4.53	.20	3.00
48	.102	16	2.72	4.60	.15	3.09
49	.102	13	2.82	4.57	.17	3.06
96	.102	12	2.40	4.58	.16	3.16
144	.102	11	2.41	4.57	.17	3.16
Table 3c. Elimination of Data Corresponding to the Most Na-rich Feldspars[b]						
48	0.059	17	2.75	4.57	0.15	3.05
48	.102	16	2.72	4.60	.15	3.09
48	.113	15	2.81	4.45	.10[c]	2.91
48	.142	14	2.79	4.49	.10	2.95
48	.160	13	2.83	4.38	.08	2.82
48	.175	11	2.84	4.32	.08	2.74
48	.309	10	2.91	4.02	.07	2.36
48	.314	9	2.92	3.86	.07	2.16
48	.405	8	2.93	3.49	.07	1.68
48	.490	7	2.92	2.75	.08	0.74
48	.518	6	2.87	2.29	.07	0.14

[a] Equation defining standard deviation will be given in Thompson and Waldbaum, (in press, Appendix B). All values weighted equally in least-squares computations.

[b] Runs held at 700°C for ≥ 48 hours (with runs ≥ 90 percent Or omitted).

[c] Isothermal fit given in Eq. (33).

of fits similar to those of Table 3a is shown, but with all runs where $N_{Or} \geq 0.9$ or ≤ 0.1 eliminated. The reason for this is that a given small error in either N_{Or} or M_{KCl} makes a much greater difference in $\ln K'$ near the limiting compositions than it does elsewhere. This could be handled in principle by an elaborate weighting scheme to favor the runs in the central portion, but simply eliminating runs outside the limits 0.1 to 0.9 N_{Or} cuts the standard deviation drastically without undue sacrifice of data.

Although a pruning of the data by the relatively straightforward methods outlined above brings about a marked improvement in the standard deviation, numerous experimental fits were made to see whether any further improvement could be obtained. Several of Orville's final feldspar compositions as given in his Table 1 are enclosed in parentheses with the notation that their ($\bar{2}01$) peaks were broad or indistinct. This implies either the presence of zoned grains or that some grains had not fully reacted with the fluid. Most of these runs are short term and thus already eliminated. The four survivors are runs 564, 756b, 837a, and 905. (It is interesting that run 564 is the inconsistent one in Orville's Figure 2 and accompanying discussion.) Two of these, 564 and 837a, were eventually eliminated for other reasons given below, but elimination of the other two, 756b and 905, brought no further improvement and they were therefore retained in the data finally selected. Certain of Orville's high-Na starting samples (including run 564) appear to have reacted sluggishly but most of these were eliminated on a time or extreme-composition basis and the rest are taken care of in what follows.

The most fruitful approach in a final trimming of the data was to eliminate *successively* the more Na-rich runs until no significant improvement in standard deviation could be obtained by continuing the procedure. The results for the 700° data are given in Table 3c and for other temperatures in Table 4. The standard deviation can thereby be cut to about ± 100 cal, while still retaining some 50 runs for the least-squares analyses for all temperatures. This procedure was adopted when it was observed that the high-Na runs plotted consistently on the high side of the best fit curves (Figs. 3, 6, and 7). This one-sided deviation is, in fact, precisely what would be expected if the true exchange curve had a break (or rapid change) in slope related to a second- (or higher-) order transition in the high-Na region. It was on this basis that the final selection of data was made. That this selection is indeed related to the monoclinic-triclinic transformation is strongly suggested by the results shown in Figure 10. The solid line is a least-squares fit to MacKenzie's (1952) data (circles) on the location of a displacive symmetry change, and it also closely approximates the results obtained by Laves (1952) on natural feldspars. The dashed isothermal segments are bounded, where appropriate, by two vertical marks: that on the right is at the composition of the most sodic feldspar retained by the above procedure, and that on the left is the most potassic one discarded. The numbers by each are the standard deviations for the corresponding least-squares fits. If the breaks in the data are related to an equilibrium symmetry change as we have suggested, then the equilibrium phase boundary and the displacive symmetry change are virtually coincident at these temperatures as suggested by Laves (1961, p. 65).

Mixing Properties of Sanidine at 2 kbar

The data after selection as outlined above yields the following results for those isotherms with sufficient data to warrant a least-squares fit:

$$\left.\begin{aligned}
\overline{G}_{ex,700°C} &= 4.45N_{Or}N_{Ab}^2 + 2.81\ N_{Ab}N_{Or}^2 \\
\overline{G}_{ex,680°C} &= 4.40N_{Or}N_{Ab}^2 + 2.455N_{Ab}N_{Or}^2 \\
\overline{G}_{ex,670°C} &= 4.29N_{Or}N_{Ab}^2 + 2.21\ N_{Ab}N_{Or}^2 \\
\overline{G}_{ex,650°C} &= 4.21N_{Or}N_{Ab}^2 + 3.14\ N_{Ab}N_{Or}^2 \\
\overline{G}_{ex,600°C} &= 3.90N_{Or}N_{Ab}^2 + 3.02\ N_{Ab}N_{Or}^2
\end{aligned}\right\} \quad (33)$$

where $\overline{G}_{ex}$ is in kcal mole^{-1}. The number of data points used for each temperature is given in Tables 3 and 4, the equations are plotted as solid lines in Figures 3 through 7, and the least-squares standard deviations are given in Table 5.

The temperature dependence of W_{G1} or W_{G2} may be obtained by formulas (Thompson, 1967) of the type

$$\left(\frac{\partial W_{G_1}}{\partial T}\right)_P = -W_{S_1} \quad (34)$$

TABLE 4. EFFECT ON LEAST SQUARE FITS OF SUCCESSIVELY REMOVING THE MOST Na-RICH DATA POINT FROM THE EXCHANGE DATA (EQUIVALENT TO 700°C RESULTS IN TABLE 3c)

Temperature	Duration of shortest run (hours)	N_{Or} of most Na-rich point retained	No. of data points	W_{Ab} (kcal)	W_{Or} (kcal)	Least-squares standard deviation (kcal)	$-a_0$
670°C	288	0.125	7	2.21	4.29	0.10[a]	2.85
	288	.163	6	1.80	4.38	.11	3.06
	288	.214	5	2.86	4.05	.06	2.42
	288	.249	4	3.21	3.85	.04	2.09
650°C	288	.060	10	2.60	4.83	.34	3.26
	288	.115	9	3.06	4.36	.14	2.67
	288	.142	8	3.14	4.21	.12[a]	2.49
	288	.170	7	3.18	4.06	.09	2.30
	288	.208	6	3.18	4.09	.11	2.33
600°C	96	.055	21	2.78	4.71	.23	2.94
	96	.079	20	2.88	4.57	.17	2.78
	96	.088	19	2.92	4.48	.15	2.68
	96	.089	18	2.93	4.46	.15	2.65
	96	.099	17	2.96	4.37	.13	2.54
	96	.110	16	2.96	4.35	.13	2.52
	96	.117	15	2.98	4.28	.13	2.43
	96	.124	14	2.98	4.28	.14	2.43
	96	.200	13	3.02	3.90	.08[a]	1.96
	96	.250	12	3.03	4.00	.08	2.09

[a] Isothermal fit given in Eq. (33).

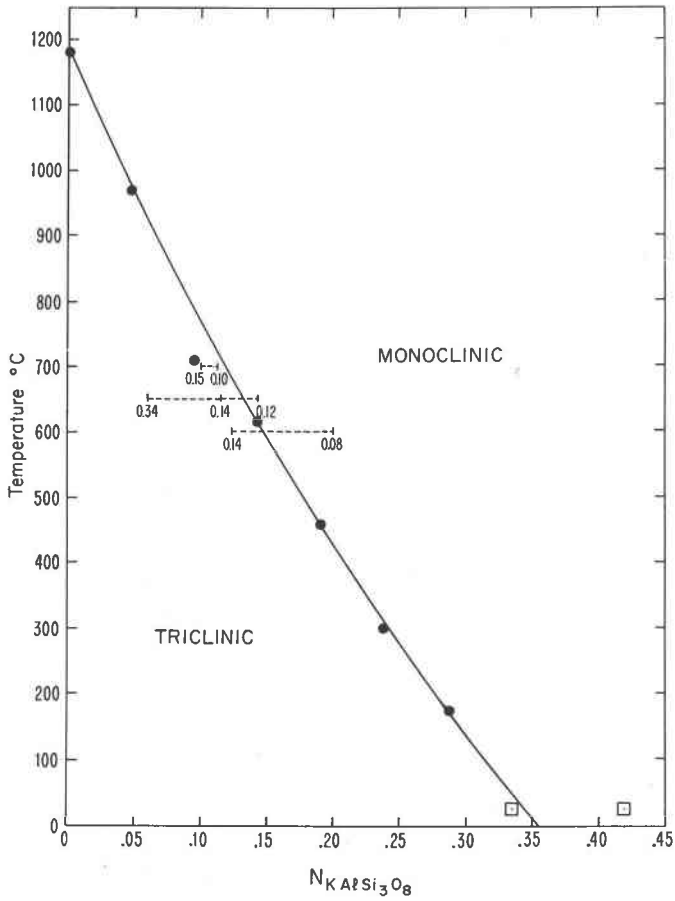

FIG. 10. Monoclinic-triclinic transformation in Na-rich feldspars as determined at 1 atm by MacKenzie (1952) (circles) compared with results of statistical analysis of Orville's (1963) ion-exchange data (see text). MacKenzie's feldspars were synthesized hydrothermally at 800°C and 981 bars. Squares denote compositions at which the symmetry change was placed by Donnay and Donnay (1952, low-*Or* point) and by Orville (1967) from analysis of X-ray diffraction data for sanidine—high albite solutions.

or

$$\left(\frac{\partial(W_{G_1}/T)}{\partial(1/T)}\right)_P = W_{H_1} \tag{35}$$

but, noting that $W_{G_1}=W_{H_1}-TW_{S_1}$ or $W_{G_1}/T=(W_{H_1}/T)-W_{S_1}$, the procedure finally adopted was to obtain a multiple least-squares fit to the data for the relation

TABLE 5. MARGULES PARAMETERS FOR SANIDINE CRYSTALLINE SOLUTIONS OBTAINED FROM 49 SELECTED DATA POINTS OF ORVILLE (1963).[a] ENTHALPY AND GIBBS ENERGY PARAMETERS IN KCAL MOLE^{-1}; ENTROPY PARAMETERS IN CAL DEG^{-1} MOLE^{-1}.

Margules parameter	Polythermal $R\ln K'$ $(1/T, N)$			Isothermal $RT\ln K'$ (N)	
	6 constants Eq. (39)	$b_2=0$ Eq. (40)	$c_2=0$ Eq. (41)	3 constants Eq. (33)	s_y (kcal)
$W_{H_{Or}}$	-0.46 ±0.41	3.51 ±0.21	4.31 ±0.22	—	—
$W_{H_{Ab}}$	5.68 ±0.27	3.51 ±0.20	3.00 ±0.20	—	—
$W_{S_{Or}}$	-5.05 ±0.44	-0.81 ±0.21	$+0.04$ ±0.22	—	—
$W_{S_{Ab}}$	$+2.96$ ±0.30	$+0.61$ ±0.22	$+0.04$ ±0.22	—	—
700°C $W_{G_{Or}}$	4.45	4.31	4.27	4.45 ±0.05	0.10
700°C $W_{G_{Ab}}$	2.80	2.92	2.96	2.81 ±0.08	
680°C $W_{G_{Or}}$	4.35	4.29	4.27	4.40	0.0
680°C $W_{G_{Ab}}$	2.86	2.93	2.96	2.455	
670°C $W_{G_{Or}}$	4.30	4.28	4.27	4.29 ±0.12	0.10
670°C $W_{G_{Ab}}$	2.89	2.94	2.96	2.21 ±0.78	
650°C $W_{G_{Or}}$	4.20	4.26	4.27	4.21 ±0.12	0.12
650°C $W_{G_{Ab}}$	2.95	2.95	2.97	3.14 ±0.21	
600°C $W_{G_{Or}}$	3.95	4.22	4.27	3.90 ±0.08	0.08
600°C $W_{G_{Ab}}$	3.10	2.98	2.97	3.02 ±0.06	
500°C $W_{G_{Or}}$	3.44	4.14	4.27	—	—
500°C $W_{G_{Ab}}$	3.40	3.04	2.97	—	—

[a] These supercede values given by Waldbaum (1966).

$$R \ln K' = -\left[(\overline{H}^{\circ}_{Or} - \overline{H}^{\circ}_{Ab}) - (\tilde{H}^{\square}_{K+} - \tilde{H}^{\square}_{Na+}) + W_{H_{Or}}\right]\frac{1}{T}$$
$$- 2(W_{H_{Ab}} - 2W_{H_{Or}})\frac{N_{Or}}{T} - 3(W_{H_{Or}} - W_{H_{Ab}})\frac{N_{Or}^2}{T}$$
$$+\left[(\overline{S}^{\circ}_{Or} - \overline{S}^{\circ}_{Ab}) - (\tilde{S}^{\square}_{K+} - \tilde{S}^{\square}_{Na+}) - R \ln \frac{\gamma_{NaCl\pm}}{\gamma_{KCl\pm}} + W_{S_{Or}}\right]$$
$$+ 2(W_{S_{Ab}} - 2W_{S_{Or}})N_{Or} + 3(W_{S_{Or}} - W_{S_{Ab}})N_{Or}^2 \qquad (36)$$

or

$$R \ln K' = b_0\left(\frac{1}{T}\right) + b_1\left(\frac{N_{Or}}{T}\right) + b_2\left(\frac{N_{Or}^2}{T}\right) + c_0$$
$$+ c_1 N_{Or} + c_2 N_{Or}^2 \qquad (36a)$$

The desired quantities may then be calculated from the relations

$$\left.\begin{aligned} W_{H_{Ab}} &= -\tfrac{1}{2}b_1 - \tfrac{2}{3}b_2 \\ W_{H_{Or}} &= -\tfrac{1}{2}b_1 - \tfrac{1}{3}b_2 \end{aligned}\right\} \qquad (37)$$

$$\left.\begin{aligned} W_{S_{Ab}} &= \tfrac{1}{2}c_1 + \tfrac{2}{3}c_2 \\ W_{S_{Or}} &= \tfrac{1}{2}c_1 + \tfrac{1}{3}c_2 \end{aligned}\right\} \qquad (38)$$

From the selected data we thus obtain

$$\overline{G}_{ex} = (-463 + 5.052\,T)N_{Or}N_{Ab}^2$$
$$+ (5679 - 2.954\,T)N_{Ab}N_{Or}^2 \text{ cal mole}^{-1} \qquad (39)$$

The standard deviation in $R \ln K'$ for this result is ± 0.10 cal deg^{-1} which compares with the mean standard deviation of ± 0.11 in $R \ln K'$ (not $RT \ln K'$) for the above selected *isothermal* fits. The exchange curves corresponding to Eq. (39) are those shown as dashed lines in Figures 3 through 8.

In using Eq. (36a) as the basis for a least-squares approximation to determine 6 parameters we are possibly pressing the data beyond its capabilities. We therefore obtained least-squares equations for the same data, first with the b_2 term eliminated and then with the c_2 term eliminated. The first must yield a symmetric enthalpy of mixing ($W_{H1} = W_{H2}$) and the second a symmetric entropy of mixing ($W_{S1} = W_{S2}$). The results for these simplified forms of (36) are:

$$\overline{G}_{ex} = 3514\, N_{Or}N_{Ab} - T(-0.813\, N_{Or}N_{Ab}^2 + 0.611\, N_{Ab}N_{Or}^2)\ \text{cal mole}^{-1} \quad (40)$$

with b_2 eliminated, and

$$\overline{G}_{ex} = 4306\, N_{Or}N_{Ab}^2 + 3002\, N_{Ab}N_{Or}^2 - T(0.041\, N_{Ab}N_{Or})\ \text{cal mole}^{-1} \quad (41)$$

with c_2 eliminated. To eliminate both the b_2 and c_2 terms however, would yield a wholly symmetrical solution at 2 kbar, and this is not consistent with known facts. These results are compared in Table 5 along with individual values of W_G calculated from Eqs. (39), (40), and (41) for 500°, 600°, 650°, 670°, 680°, and 700°C. The standard deviations of (40) and (41) are ± 0.11 and ± 0.12 cal deg^{-1} respectively, and are not significantly different from the standard deviation of (39). We have no reason to believe that either the entropy or enthalpy of mixing is symmetrical, hence we consider (39) to be the best fitting approximation to Orville's ion-exchange data.

In comparing these results with other studies, the uncertainties in the W's are of greater interest than the values of s_y, but they cannot be readily computed from a least-squares solution to (36a). Equation (36) may be written in a form which combines (19) and (21)

$$R \ln K' = \left[(\overline{S}^\circ_{Or} - \overline{S}^\circ_{Ab}) - (\tilde{S}^\square_{K+} - \tilde{S}^\square_{Na+}) + R \ln \frac{\gamma_{NaCl}^{\pm}}{\gamma_{KCl}^{\pm}}\right] - \left[(\overline{H}^\circ_{Or} - \overline{H}^\circ_{Ab}) - (\tilde{H}^\square_{K+} - \tilde{H}^\square_{Na+})\right]\frac{1}{T} + W_{S_{Ab}}x + W_{S_{Or}}z - W_{H_{Ab}}\frac{x}{T} - W_{H_{Or}}\frac{z}{T} \quad (36b)$$

where the variables used in this least-squares solution are

$$x \equiv 2N_{Or} - 3N_{Or}^2$$
$$z \equiv 1 - 4N_{Or} - 3N_{Or}^2$$

and $(1/T)$, (x/T), and (z/T), from which the Margules parameters of (39) are obtained directly. Similar expressions can be written to obtain the Margules parameters of (40) and (41) directly. The precision index used by the present authors (Thompson and Waldbaum, in press, Appendix A) for equation of state parameters is the standard *thermochemical uncertainty* of Rossini and Deming (1939), and was calculated for each Margules parameter in Table 5 in the usual way from the diagonal terms of the inverse normal equations matrix.

Conclusions

The results of this analysis show that equation of state parameters for sanidine solutions can be derived from ion-exchange experimental data, but it is evident from the results in Table 5 that neither the sign nor the magnitude of W_{H_j} or W_{S_j} can be obtained with any certainty from the data now at hand. Because of this a solvus calculated on the basis of (39) should be accepted as reliable only in the central portion of the temperature range of Orville's experiments. Values of W_{G_j} in this temperature range are known with much less uncertainty (± 0.2 kcal) and are clearly positive.

Waldbaum (1966) showed that calorimetric determination of W_{H_j} for microcline—low albite solutions yields values on the order of $+7$ kcal at 2 kbar with an uncertainty of ± 0.2 kcal. Similarly, the calorimetric data of Kracek and Neuvonen (1952) indicate that W_{H_j} for sanidine solutions must have positive values on the order of several kilocalories. It is essential to know both the sign and magnitude of W_{H_j} and W_{S_j}, and to know the values with an accuracy of 1 percent, if these parameters are to be used in phase equilibrium calculations pertaining to the full range of crustal temperatures and pressures.

The present treatment of Orville's (1963) data illustrates the manner in which a thermodynamic equation of state can be applied to the analysis of experimental data. This analysis shows that the ion-exchange experimental method provides considerably more data on a system than determination of pressure-temperature-composition phase diagrams. It seems clear, however, that still more experimental work of this kind is needed on the alkali feldspars—especially in view of the recent work of Luth and Tuttle (1966) and Martin (1967) and the discontinuities in the exchange curves suggested by the present interpretation of Orville's data. The following suggestions are presented as a guide to future work of this type:

1. Isothermal ion-exchange curves obtained above the two-phase region will provide data over a greater range of temperatures and thus reduce the uncertainties in the W_{H_j} and W_{S_j} parameters. Obtaining data above 700°C also reduces possible complications introduced by the equilibrium monoclinic-triclinic symmetry change inasmuch as a larger range of compositions will have monoclinic symmetry at the time of growth. The study of a supercritical ion-exchange curve tends to favor more reliable results because of the shorter time required for equilibrium, and the necessity to determine the composition of only a single feldspar. The appearance of two feldspars under conditions known to be supercritical (for the feldspar) provides an unambiguous indication of disequilibrium or of difficulties in quenching the run.

2. As will be shown in Part III, data obtained at different pressures can be utilized to obtain a polythermal, polybaric equation of state. Complete isotherms or isobars are not necessary, and data may be obtained anywhere in P-T-N space, provided the number of runs in each pressure, temperature, and composition range yields a good statistical distribution of data points. Isothermal, isobaric ion-exchange curves are more useful, however, in studying the monoclinic-triclinic inversion.

3. In using an aqueous alkali halide fluid phase, the validity of assuming ideal K-Na mixing requires further study. It is necessary that such a fluid phase be maintained at constant total *molality* in a given set of experiments. Other exchange media such as fused alkali halides can be utilized to maintain a fixed Al-Si distribution in the crystals (Wyart and Sabatier, 1956), and to work at atmospheric pressure, hence at higher temperatures.

4. Complications caused by Al-Si ordering in the feldspar framework in the presence of alkali chloride hydrothermal solutions require that more than one X-ray parameter be utilized to characterize the feldspars. It is also essential that the feldspar compositions be determined independently of the fluid phase as done by Orville (1963), and not by difference (Iiyama, 1965), in order to make use of the theoretical treatment of ion-exchange data presented here.[1]

Orville reported "negative" compositions for some Na-rich feldspars crystallized between 250°–500°C using his ($\bar{2}01$) determinative curve. He re-investigated the sanidine-high albite curve (Orville, 1967) used in his 1963 paper and found no reason to modify it. However, the "negative" compositions could be readily explained (Part II) if the Al-Si distribution in the crystals were more ordered. It would seem desirable therefore to determine all the lattice parameters of the synthetic feldspars by least-squares analysis of X-ray data (Luth and Tuttle, 1966), and also to determine the compositions independently of determinative curves based on physical property measurements.

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[1] Iiyama, Wyart, and Sabatier (1963) and Iiyama (1965) reported having obtained data similar to those of Orville (1963) in the range 500 to 800°C at 1000 bars. Iiyama (1967, personal comm.) indicated that the compositions of the feldspar phases in each run were later determined independently of the fluid phase, but that these experimental data are as yet unpublished.

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APPENDIX A. FORMULATION FOR THE FLUID PHASE

The Gibbs-Duhem equation for the fluid may be written

$$n_{H_2O}d\mu_{H_2O} + n_{NaCl}d\mu_{NaCl} + n_{KCl}d\mu_{KCl} = V_f dP - S_f dT \tag{A-1}$$

$$\left(\frac{n_{H_2O}}{n_{sf}}\right) d\mu_{H_2O} + M_{NaCl}d\mu_{NaCl} + M_{KCl}d\mu_{KCl} = \left(\frac{V_f}{n_{sf}}\right)dP - \left(\frac{S_f}{n_{sf}}\right)dT. \tag{A-2}$$

Similarly

$$G_f \equiv \frac{G_f}{n_{sf}} = \left(\frac{n_{H_2O}}{n_{sf}}\right)\mu_{H_2O} + \mu_{NaCl}M_{NaCl} + \mu_{KCl}M_{KCl} \tag{A-3}$$

Differentiating (A-3) and combining with (A-2) we obtain, for processes at constant P, T, n_{H2O}, and n_{sf}

$$\begin{aligned} d\bar{G}_f &= \mu_{NaCl}dM_{NaCl} + \mu_{KCl}dM_{KCl} \\ &= (\mu_{KCl} - \mu_{NaCl})dM_{KCl} \end{aligned} \tag{A-4}$$

or

$$\left(\frac{\partial \bar{G}_f}{\partial M_{KCl}}\right)_{P,T,n_{sf},n_{H_2O}} = (\mu_{KCl} - \mu_{NaCl}) \tag{A-5}$$

APPENDIX B. REQUIREMENTS FOR STABILITY IN EXCHANGE EQUILIBRIA

Let us denote the feldspars by a, b, and the fluid by f. We shall consider fully only the 3-phase equilibrium which includes the 2-phase equilibrium (Fig. 1a) as a special case. We have

$$\left.\begin{aligned} (\mu_{K,f} - \mu_{Na,f}) &= \left(\frac{\partial \bar{G}_f}{\partial M_{K,f}}\right)_{P,T} \equiv L_K \\ (\mu_{K,b} - \mu_{Na,b}) &= \left(\frac{\partial \bar{G}_b}{\partial N_{K,b}}\right)_{P,T} \equiv B_K \\ (\mu_{K,a} - \mu_{Na,a}) &= \left(\frac{\partial \bar{G}_a}{\partial N_{K,a}}\right)_{P,T} \equiv A_K \end{aligned}\right| \tag{B-1}$$

where the subscript K denotes the components Or or KCl, and Na denotes Ab or NaCl. Let

$$n_a \equiv n_{K,a} + n_{Na,a}; \qquad n_b \equiv n_{K,b} + n_{Na,b}; \quad \text{and} \quad n_{sf} \equiv n_{KCl,f} + n_{NaCl,f}$$

Where the *only* process is alkali exchange:

$$0 = dn_a = dn_b = dn_{sf} \tag{B-2}$$

also

$$\left.\begin{aligned} dn_{\mathrm{K},a} &= n_a dN_{\mathrm{K},a} \\ dn_{\mathrm{K},b} &= n_b dN_{\mathrm{K},b} \\ dn_{\mathrm{K},f} &= -dn_{\mathrm{K},a} - dn_{\mathrm{K},b} \end{aligned}\right\} \tag{B-3}$$

hence we may rewrite Eq. (11) in the text as follows

$$dG = (n_b \boldsymbol{B}_{\mathrm{K}} - n_b \boldsymbol{L}_{\mathrm{K}}) dN_{\mathrm{K},b} + (n_a \boldsymbol{A}_{\mathrm{K}} - n_a \boldsymbol{L}_{\mathrm{K}}) dN_{\mathrm{K},a} \tag{B-4}$$

This emphasizes that under the specified conditions $G = \mathrm{f}(N_{\mathrm{K},a}, N_{\mathrm{K},b})$, hence

$$\left.\begin{aligned} \left(\frac{\partial G}{\partial N_{\mathrm{K},b}}\right) &= (n_b \boldsymbol{B}_{\mathrm{K}} - n_b \boldsymbol{L}_{\mathrm{K}}) \\ \left(\frac{\partial G}{\partial N_{\mathrm{K},a}}\right) &= (n_a \boldsymbol{A}_{\mathrm{K}} - n_a \boldsymbol{L}_{\mathrm{K}}) \end{aligned}\right\} \tag{B-5}$$

and if

$$\boldsymbol{B}_{\mathrm{KK}} \equiv \left(\frac{\partial^2 \overline{G}_b}{\partial N^2_{\mathrm{K},b}}\right)_{P,T}; \qquad \boldsymbol{A}_{\mathrm{KK}} \equiv \left(\frac{\partial^2 \overline{G}_a}{\partial N^2_{\mathrm{K},a}}\right)_{P,T}; \quad \text{and} \quad \boldsymbol{L}_{\mathrm{KK}} \equiv \left(\frac{\partial^2 \tilde{G}_f}{\partial M^2_{,\mathrm{K}f}}\right)_{P,T}$$

we have

$$\left.\begin{aligned} \left(\frac{\partial^2 G}{\partial N^2_{\mathrm{K},b}}\right) &= n_b \boldsymbol{B}_{\mathrm{KK}} - n_b \boldsymbol{L}_{\mathrm{KK}} \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},b}}\right)_{N_{\mathrm{K},a}} \\ \left(\frac{\partial^2 G}{\partial N_{\mathrm{K},b} \partial N_{\mathrm{K},a}}\right) &= n_b \boldsymbol{B}_{\mathrm{KK}} \left(\frac{\partial N_{\mathrm{K},b}}{\partial N_{\mathrm{K},a}}\right)_{N_{\mathrm{K},b}} - n_b \boldsymbol{L}_{\mathrm{KK}} \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},a}}\right)_{N_{\mathrm{K},b}} \\ &= -n_b \boldsymbol{L}_{\mathrm{KK}} \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},a}}\right)_{N_{\mathrm{K},b}} \\ \left(\frac{\partial^2 G}{\partial N_{\mathrm{K},a} \partial N_{\mathrm{K},b}}\right) &= n_a \boldsymbol{A}_{\mathrm{KK}} \left(\frac{\partial N_{\mathrm{K},a}}{\partial N_{\mathrm{K},b}}\right)_{N_{\mathrm{K},a}} - n_a \boldsymbol{L}_{\mathrm{KK}} \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},b}}\right)_{N_{\mathrm{K},a}} \\ &= -n_a \boldsymbol{L}_{\mathrm{KK}} \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},b}}\right)_{N_{\mathrm{K},a}} \\ \left(\frac{\partial^2 G}{\partial N^2_{\mathrm{K},a}}\right) &= n_a \boldsymbol{A}_{\mathrm{KK}} - n_a \boldsymbol{L}_{\mathrm{KK}} \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},a}}\right)_{N_{\mathrm{K},b}} \end{aligned}\right\} \tag{B-6}$$

Relations (B-6) may be further simplified. We may write

$$dn_{\mathrm{K},f} = n_{\mathrm{sf}} dM_{\mathrm{K},f}$$

hence, using (B-3), we have

$$0 = n_a dN_{\mathrm{K},a} + n_b dN_{\mathrm{K},b} + n_{\mathrm{sf}} dM_{\mathrm{K},f} \tag{B-7}$$

hence

$$\left.\begin{aligned} \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},b}}\right)_{N_{\mathrm{K},a}} &= -\frac{n_b}{n_{\mathrm{sf}}} \\ \left(\frac{\partial M_{\mathrm{K},f}}{\partial N_{\mathrm{K},a}}\right)_{N_{\mathrm{K},b}} &= -\frac{n_a}{n_{\mathrm{sf}}} \end{aligned}\right\} \tag{B-8}$$

and equations (B-6) become

$$\left.\begin{aligned}\left(\frac{\partial^2 G}{\partial N^2_{\mathrm{K},b}}\right) &= \frac{n_b}{n_{\mathrm{sf}}}\left(n_{\mathrm{sf}}\boldsymbol{B}_{\mathrm{KK}} + n_b\boldsymbol{L}_{\mathrm{KK}}\right)\\ \left(\frac{\partial^2 G}{\partial N_{\mathrm{K},b}\partial N_{\mathrm{K},a}}\right) &= \left(\frac{\partial^2 G}{\partial N_{\mathrm{K},a}\partial N_{\mathrm{K},b}}\right) = \frac{n_a n_b}{n_{\mathrm{sf}}}\boldsymbol{L}_{\mathrm{KK}}\\ \left(\frac{\partial^2 G}{\partial N^2_{\mathrm{K},a}}\right) &= \frac{n_a}{n_{\mathrm{sf}}}\left(n_{\mathrm{sf}}\boldsymbol{A}_{\mathrm{KK}} + n_a\boldsymbol{L}_{\mathrm{KK}}\right)\end{aligned}\right\} \tag{B-9}$$

Now for an equilibrium to be stable or metastable (as opposed to unstable or conditional) the matrix of the second derivatives of G must be positive definite (Gibbs, 1876; 1928, p. 112; Prigogine and Defay, 1954, p. 224), hence

$$\left(\frac{\partial^2 G}{\partial N^2_{\mathrm{K},b}}\right) = \frac{n_b}{n_{\mathrm{sf}}}\left(n_{\mathrm{sf}}\boldsymbol{B}_{\mathrm{KK}} + n_b\boldsymbol{L}_{\mathrm{KK}}\right) > 0 \tag{B-10}$$

$$\begin{vmatrix}\left(\frac{\partial^2 G}{\partial N^2_{\mathrm{K},b}}\right) & \left(\frac{\partial^2 G}{\partial N_{\mathrm{K},b}\partial N_{\mathrm{K},a}}\right)\\ \left(\frac{\partial^2 G}{\partial N_{\mathrm{K},a}\partial N_{\mathrm{K},b}}\right) & \left(\frac{\partial^2 G}{\partial N^2_{\mathrm{K},a}}\right)\end{vmatrix} = \frac{n_a n_b}{n_{\mathrm{sf}}}\left(n_{sf}\boldsymbol{B}_{\mathrm{KK}}\boldsymbol{A}_{\mathrm{KK}} + \boldsymbol{L}_{\mathrm{KK}}n_b\boldsymbol{A}_{\mathrm{KK}} + \boldsymbol{L}_{\mathrm{KK}}\boldsymbol{B}_{\mathrm{KK}}n_a\right) > 0 \tag{B-11}$$

But we know that $\boldsymbol{A}_{KK}$, $\boldsymbol{B}_{KK}$, $\boldsymbol{L}_{KK}$ are all greater than zero if the phases are internally stable with respect to diffusion, hence the equilibrium is either stable or metastable, the left hand sides of (B-10) and (B-11) being positive unless critical or internally unstable phases are present. To obtain the corresponding relations with only one feldspar present, say b, we may repeat the process with all terms involving $\boldsymbol{a}$ eliminated. We then obtain only condition (B-10) which is sufficient.

These conclusions may also be justified graphically using Figure 1 by making use of the lever law and remembering that the quantitative proportions of the two kinds of feldspar remain unaltered in the simple exchange process considered.

Appendix C. Mixing of n-Molal KCl and NaCl Solutions

Let us consider a quantity of solution such that the total number of moles of salt is unity (i.e.: $n_{\mathrm{KCl}}+n_{\mathrm{NaCl}}=1=n_{\mathrm{sf}}$; $n_{\mathrm{H_2O}}=\text{const.}$; $n_{\mathrm{KCl}}=M_{\mathrm{KCl}}$; $n_{\mathrm{NaCl}}=M_{\mathrm{NaCl}}$). We then have (see Appendix A, Eq. A-3)

$$\tilde{G}_f = n_{\mathrm{H2O}}\mu_{\mathrm{H2O}} + \mu_{\mathrm{KCl}}M_{\mathrm{KCl}} + \mu_{\mathrm{NaCl}}M_{\mathrm{NaCl}} \tag{C-1}$$

and

$$\mu_{\mathrm{H_2O}} = \overset{\circ}{\mu}_{\mathrm{H}\,0} + RT\ln N_{\mathrm{H_2O}}\gamma_{\mathrm{H_2O}} \tag{C-2}$$

$$\left.\begin{aligned}\mu_{\mathrm{NaCl}} &= \overset{\square}{\mu}_{\mathrm{Na+}} + \overset{\square}{\mu}_{\mathrm{Cl-}} + RT\ln m_{\mathrm{Na+}}m_{\mathrm{Cl-}}\gamma_{\mathrm{NaCl}\pm}\\ \mu_{\mathrm{KCl}} &= \overset{\square}{\mu}_{\mathrm{K+}} + \overset{\square}{\mu}_{\mathrm{Cl-}} + RT\ln m_{\mathrm{K+}}m_{\mathrm{Cl-}}\gamma_{\mathrm{KCl}\pm}\end{aligned}\right\} \tag{C-3}$$

Combining, we obtain

$$\begin{aligned}\tilde{G}_f = {} & M_{\mathrm{KCl}}\left[n_{\mathrm{H_2O}}\overset{\circ}{\mu}_{\mathrm{H_2O}} + \overset{\square}{\mu}_{\mathrm{Cl-}} + \overset{\square}{\mu}_{\mathrm{K+}} + RT(n_{\mathrm{H_2O}}\ln N_{\mathrm{H_2O}} + \ln m_{\mathrm{Cl-}})\right]\\ & + M_{\mathrm{NaCl}}\left[n_{\mathrm{H_2O}}\overset{\circ}{\mu}_{\mathrm{H_2O}} + \overset{\square}{\mu}_{\mathrm{Cl-}} + \overset{\square}{\mu}_{\mathrm{Na+}} + RT(n_{\mathrm{H_2O}}\ln N_{\mathrm{H_2O}} + \ln m_{\mathrm{Cl-}})\right]\\ & + RT(M_{\mathrm{KCl}}\ln M_{\mathrm{KCl}} + M_{\mathrm{NaCl}}\ln M_{\mathrm{NaCl}})\\ & + RT(n\mathrm{H_{2O}}\ln\gamma_{\mathrm{H_2O}} + M_{\mathrm{KCl}}\ln\gamma\mathrm{K_{Cl}}^{\circ} + M_{\mathrm{NaCl}}\ln\gamma_{\mathrm{NaCl}}{}^{\circ})\end{aligned} \tag{C-4}$$

The bracketed quantities in the first two terms of (C-4) are constant for the mixing process here considered. Now if the liquids are to be said to mix ideally, the last term of (C-4) must either be zero *or* a *linear* function of M_{KCl} at a given P and T. If a linear function of M_{KCl} this last term may be written in the form

$$M_{KCl}q_K + M_{NaCl}q_{Na} \tag{C-5}$$

where q_K and q_{Na} are constants at any given P and T, and added to the first two terms, thus preserving the form of the equation of an ideal binary solution. This is possible if $\ln \gamma_{H_2O}$ and $\ln \gamma_{NaCl}^{\pm}$ vary linearly with M_{KCl} and if $\ln(\gamma_{KCl}^{\pm}/\gamma_{NaCl}^{\pm})$ is constant. This becomes apparent if we write the last term of (C-4) in the form

$$RT\left[n_{H_2O}(\ln \gamma_{H_2O}) + (\ln \gamma_{NaCl}^{\pm}) + \left(M_{KCl} \ln \frac{\gamma_{KCl}^{\pm}}{\gamma_{NaCl}^{\pm}}\right)\right] \tag{C-6}$$

and bear in mind that the terms in parentheses can contain no powers of M_{KCl} higher than the first.

Appendix D. Notation

Special symbols used to denote variables, functions, constants, and abbreviations will be defined as they are introduced in the text. However, the following symbols are generally valid in Parts I and II of this series:

a	Subscript denoting a phase rich in component 1.
b	Subscript denoting a phase rich in component 2.
a_i, b_i, c_i	Polynomial coefficients.
C_P	Heat capacity.
cal	Calorie (4.1840 absolute joules).
$\overline{E}$	Molar internal energy.
ex	Subscript denoting excess mixing property.
fsp	Subscript denoting feldspar phase.
$\overline{G}$	Molar Gibbs energy.
$\overline{H}$	Molar enthalpy.
ln	Logarithm to the base e = 2.71828 . . .
M_j	See text following Eq. (6).
m_j	Molality of j-th species.
mix	Subscript denoting mixing property.
n_j	Number of moles of j-th component.
N_j	Mole fraction of j-th component.
N_{Or}	Mole fraction $KAlSi_3O_8$.
P	Total pressure on system.
R	Molar gas constant (1.98726 ± 0.00008 cal deg^{-1} mol^{-1}).
$\overline{S}$	Molar entropy.
s_y	Standard deviation of least-squares fit.
T	Absolute temperature.
$\overline{V}$	Molar volume.
W_j, W_{Ej}, W_{Vj}, W_{Sj}, W_{Hj}	Excess function parameters.
γ_j	Activity coefficient of j-th component.
μ_j	Chemical potential of j-th component.

μ_j^0 Molar Gibbs energy of pure substance at the same pressure and temperature as that of the solution under discussion.

$\mu_j^\square$ Chemical potential of j-th species in a hypothetical solution of specified molality at the same pressure and temperature as the solution under discussion.