

MIXING PROPERTIES OF SANIDINE CRYSTALLINE SOLUTIONS:

II. CALCULATIONS BASED ON VOLUME DATA¹

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ABSTRACT

Statistical analysis of the molar volume data for high-temperature alkali feldspars of Donnay and Donnay (1952) and of Orville (1967) shows that the volume data in the monoclinic range may be fitted satisfactorily by a second degree curve. The excess molar volume of mixing may be represented by

$$\bar{V}_{\text{ex}} = 0.090 N_{\text{Or}} N_{\text{Ab}} \text{ cal bar}^{-1}$$

Analyses of standard deviations of data having restricted ranges of compositions indicates a discontinuity in the volume-composition curves between 33.7 and 38.6 mole percent KAlSi_3O_8 for Orville's volume data. This discontinuity in volume is in the same composition range as a monoclinic-triclinic symmetry change at 25°C which Orville established from plots of 2θ -values and lattice angles versus composition. A similar analysis of Donnay and Donnay's data led to inconclusive results because the data points are too few and unevenly spaced. Another apparent break in Orville's data between 5 and 10 percent KAlSi_3O_8 may be related to a "fossil" symmetry change inherited from the temperature of synthesis.

INTRODUCTION

In obtaining the thermodynamic mixing properties of crystalline solutions one can make use of many types of phase equilibrium or physical property measurements. In Part I of this investigation (Thompson and Waldbaum, 1968) we illustrated the use of phase equilibrium data for crystalline feldspars and coexisting aqueous alkali chloride solutions. In the present paper we have made use of X-ray crystallographic data to derive parameters related to the dependence of the Gibbs energy of mixing on pressure. The methods outlined here are also applicable to any measurements of properties such as compressibility, thermal expansion (Vergano, Hill, and Uhlmann, 1967), and heats of solution (Waldbaum, 1966).

THERMODYNAMIC RELATIONS

It is convenient to define a quantity \bar{G}_{ex} which is the excess molar Gibbs energy of mixing of a nonideal binary solution (Scatchard and Hamer, 1935; Thompson, 1967).²

¹ Published under the auspices of the Committee on Experimental Geology and Geophysics of Harvard University. Preliminary results reported by Waldbaum (1966) and Thompson and Waldbaum (1967).

² See Appendix D of Part I for notation used in this paper.

$$\bar{G}_{ex} \equiv \bar{G} - \mu_1^{\circ}N_1 - \mu_2^{\circ}N_2 - RT(N_1 \ln N_1 + N_2 \ln N_2)$$

Similarly, for the excess volume of mixing:

$$\bar{V}_{ex} \equiv \bar{V} - \bar{V}_1^{\circ}N_1 - \bar{V}_2^{\circ}N_2$$

The results of Donnay and Donnay (1952) and Orville (1967) indicate that the variation in molar volume with composition is not that of an ideal solution and raise the possibility, furthermore, that \bar{V}_{ex} is not symmetrical about $N=1/2$. To account for asymmetric terms in \bar{V}_{ex} it is necessary to include at least third order terms in any analytic representation of the data based on a Margules expansion. This is shown by the derivation given below.

Let \bar{V} (or molar properties such as \bar{E} and \bar{H}) be expressed as a polynomial in N_2 :

$$\bar{V} = A + BN_2 + CN_2^2 + DN_2^3 \tag{1}$$

which is a form that can be used in most computer programs written for curve-fitting. When $N_2=0$,

$$\bar{V} = A = \bar{V}_1^{\circ} \tag{2}$$

and

$$\left(\frac{\partial \bar{V}}{\partial N_2}\right)_{P,T,N_2=0} = B \tag{3}$$

and when $N_2=1$,

$$\bar{V} = A + B + C + D = \bar{V}_2^{\circ} \tag{4}$$

and

$$\left(\frac{\partial \bar{V}}{\partial N_2}\right)_{P,T,N_2=1} = B + 2C + 3D \tag{5}$$

Let

$$\left. \begin{aligned} \bar{V}_1^* &\equiv \bar{V}_2^{\circ} - 1 \times \left(\frac{\partial \bar{V}}{\partial N_2}\right)_{P,T,N_2=1} \\ \bar{V}_2^* &\equiv \bar{V}_1^{\circ} + 1 \times \left(\frac{\partial \bar{V}}{\partial N_2}\right)_{P,T,N_2=0} \end{aligned} \right\} \tag{6}$$

Solving equations (2), (3), (4), and (5) for the polynomial coefficients, we obtain:

$$\begin{aligned} \bar{V} = & \bar{V}_1^{\circ} + (\bar{V}_2^* - \bar{V}_1^{\circ})N_2 + [(\bar{V}_1^* - \bar{V}_1^{\circ}) - 2(\bar{V}_2^* - \bar{V}_2^{\circ})]N_2^2 \\ & + [(\bar{V}_2^* - \bar{V}_2^{\circ}) - (\bar{V}_1^* - \bar{V}_1^{\circ})]N_2^3 \end{aligned} \quad (7)$$

which has the following properties:

a. when $C=D=0$,

$$\bar{V}_2^{\circ} = \bar{V}_2^* \quad \text{and} \quad \bar{V}_1^{\circ} = \bar{V}_1^*$$

hence, the solution is ideal:

$$\begin{aligned} \bar{V} = & \bar{V}_1^{\circ} + (\bar{V}_2^* - \bar{V}_1^{\circ})N_2 \\ = & N_1\bar{V}_1^{\circ} + N_2\bar{V}_2^{\circ} \end{aligned} \quad (8)$$

b. when $D=0$,

$$(\bar{V}_2^{\circ} - \bar{V}_2^*) = (\bar{V}_1^{\circ} - \bar{V}_1^*)$$

hence, the solution is of the strictly regular or *symmetric* form (Thompson, 1967, p. 348):

$$\bar{V} = \bar{V}_1^{\circ}N_1 + \bar{V}_2^{\circ}N_2 + (\bar{V}_2^* - \bar{V}_2^{\circ})N_1N_2 \quad (9)$$

c. when $C \neq 0$ and $D \neq 0$, Eq. (7) may be rearranged to give an asymmetric regular solution (Thompson, 1967, p. 352):

$$\bar{V} = \bar{V}_1^{\circ}N_1 + \bar{V}_2^{\circ}N_2 + (\bar{V}_2^* - \bar{V}_2^{\circ})N_1^2N_2 + (\bar{V}_1^* - \bar{V}_1^{\circ})N_1N_2^2 \quad (10)$$

Equations (8), (9), and (10) can be obtained from Eqs. (18), (27), (47) and (69) of Thompson (1967) when

$$\left. \begin{aligned} W_{V_1} & \equiv (\bar{V}_1^* - \bar{V}_1^{\circ}) \\ W_{V_2} & \equiv (\bar{V}_2^* - \bar{V}_2^{\circ}) \end{aligned} \right\} \quad (11)$$

These relations are shown graphically in Figure 1.

Combining Eqs. (6), (7), and (11) we have for the Margules parameters

$$\left. \begin{aligned} W_{V_1} & = -(C + 2D) \\ W_{V_2} & = -(C + D) \end{aligned} \right\} \quad (11a)$$

which may be derived directly from total, or *integral*, molar property experimental data expressed as a polynomial in N_2 , and the excess volume of mixing may be expressed as:

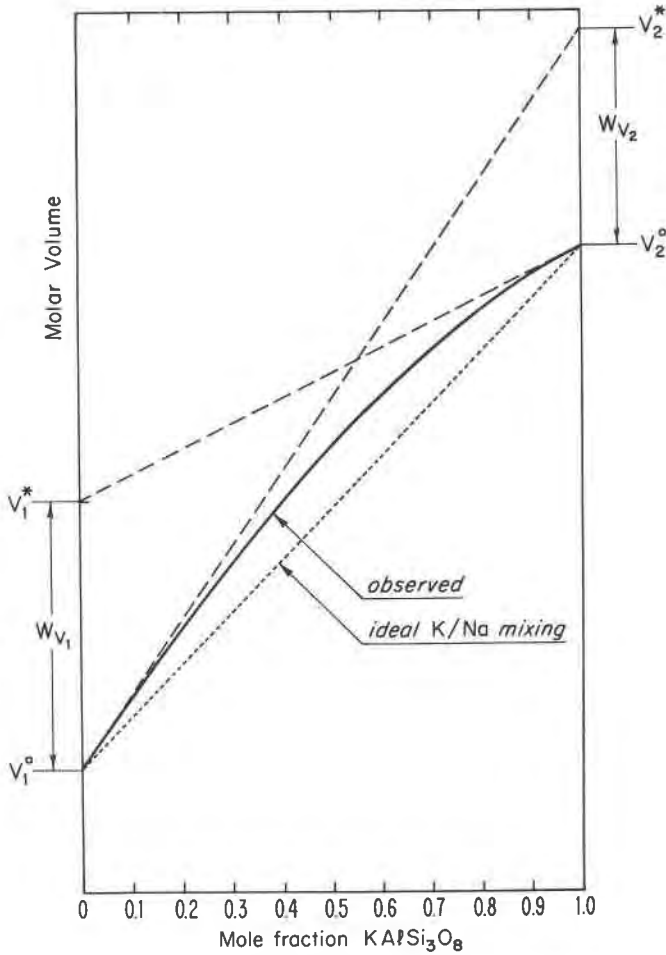


FIG. 1. Molar volumes of nonideal (K-Na) crystalline solutions. Hypothetical observed values shown as solid curve. Short dashed line indicates theoretical values for ideal solution. Light dashed lines denote limiting slopes of $\bar{V}=f(N_2)$ polynomial (partial molar volumes at infinite dilution).

$$\bar{V}_{ex} = -(C + 2D)N_1N_2^2 - (C + D)N_2N_1^2 \quad (12)$$

The expansion of \bar{V} as a polynomial could be carried to quartic and higher-order terms, but this is not warranted by the precision and number of points in most sets of data. A least-squares solution to Eq. (1) will not yield individual standard errors for \bar{V}_2° or the Margules parameters. However, if a least-squares approximation is obtained for

TABLE 1. MOLAR VOLUME DATA FOR SANIDINE-HIGH ALBITE CRYSTALLINE SOLUTIONS AFTER DONNAY AND DONNAY (1952) AND ORVILLE (1967)
(1 cal bar⁻¹ = 41.840 cm³)

Donnay and Donnay (1952)		Orville (1967)	
N_{Or}	\bar{V} (cal bar ⁻¹)	N_{Or}	\bar{V} (cal bar ⁻¹)
0.0000	2.40180	0.0000	2.39737
.0948	2.42692	.0472	2.40568
.1906	2.45272	.0948	2.42119 _s
.2876	2.47281	.1426	2.43394
.3268	2.48555	.1906	2.44610
.3366	2.48882	.2390	2.45758
.3858	2.49994	.2876	2.47313
.4851	2.52319	.3366	2.47954
.5856	2.54486	.3858	2.49616
.7903	2.58157	.4353	2.50851
1.0000	2.60687	.4851	2.51823
1.0000	2.60464	.5352	2.52733
		.5856	2.53687
		.6363	2.54914
		.6873	2.55587
		.7387	2.56516
		.8422	2.58214 _s
		.8945	2.58686
		.9471	2.59687
		1.0000	2.60057

either equations (9) or (10), then \bar{V}_1° , \bar{V}_2° , the W 's, and their standard errors are obtained directly without the need for the intermediate steps (4) and (11a). For a given set of data the least-squares approximation, \bar{V} (calculated), and standard deviation of fit to (1) and (10) will be identical.

ANALYSIS OF DATA

Margules parameters. Molar volumes calculated from the lattice parameters of Donnay and Donnay (1952),¹ and Orville (1967) are given in Table 1 and Figure 2. Donnay and Donnay's data refer to feldspars synthesized at 700°C for some compositions and 800°C for others at

¹Wright and Stewart (1968) have recently recomputed lattice parameters from Donnay and Donnay's data, but their results appeared after this manuscript was completed. With the exception of the volume of high albite, which was published earlier by Stewart and von Limbach (1967) and included in Table 1, there is no significant difference between the 1952 and the 1968 molar volumes. The 1968 refinements yield $W_V = 0.086 \pm 0.006$ cal bar⁻¹.

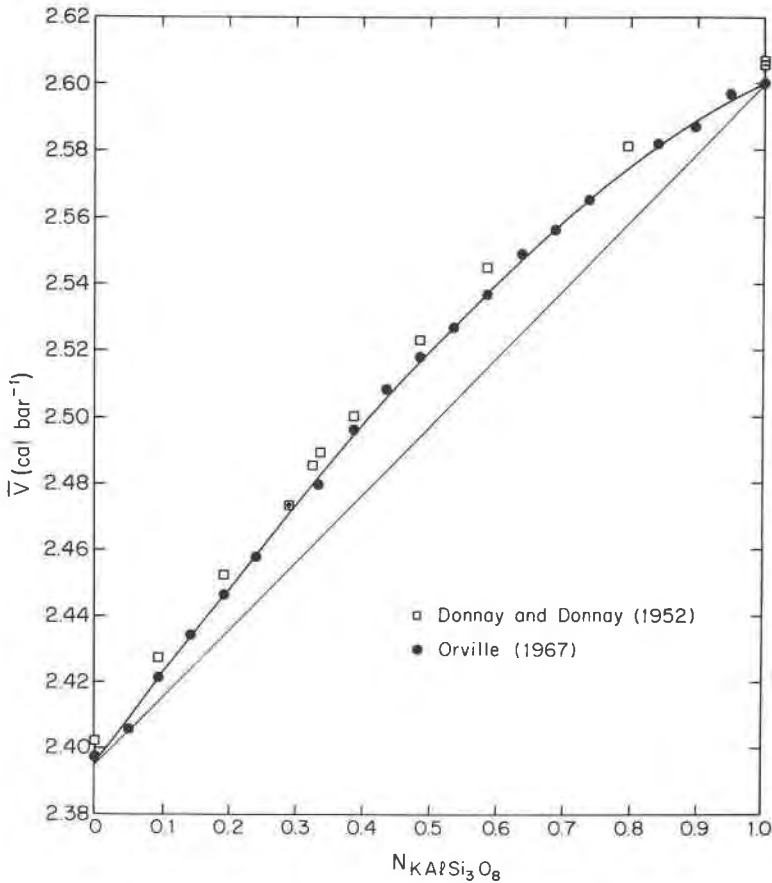


FIG. 2. Molar volumes of sanidine—high albite crystalline solutions measured at room temperature. The ideal mixing line refers to the volumes of the end-members given by Eq. (16).

981 bars water pressure, with crystallization times ranging from 1 to 9 days. Orville's feldspars were synthesized hydrothermally at 800°C and 1000 bars over periods of 5 to 7 days.

Both sets of data were fitted separately to quadratic and cubic polynomials (Eq. 1) by the method of least-squares using a program written in CAL (Conversational Algebraic Language) for a Scientific Data Systems model 940 time-shared computer which enabled 12 significant figures to be carried through all computations. The results obtained for Donnay and Donnay's data are:

$$\begin{aligned} \bar{V} &= 2.39954 + 0.29581 N_2 - 0.08832 N_2^2 \\ &\pm 0.0024 \text{ cal bar}^{-1} \end{aligned} \quad (13)$$

$$\begin{aligned} \bar{V} &= 2.40222 + 0.25450 N_2 - 0.02594 N_2^2 - 0.07689 N_2^3 \\ &\pm 0.0014 \text{ cal bar}^{-1} \end{aligned} \quad (14)$$

and for Orville's data:

$$\begin{aligned} \bar{V} &= 2.39369 + 0.29778 N_2 - 0.08938 N_2^2 \\ &\pm 0.0019 \text{ cal bar}^{-1} \end{aligned} \quad (15)$$

$$\begin{aligned} \bar{V} &= 2.39515 + 0.27742 N_2 - 0.03655 N_2^2 - 0.03535 N_2^3 \\ &\pm 0.0019 \text{ cal bar}^{-1} \end{aligned} \quad (16)$$

where component 1 is $\text{NaAlSi}_3\text{O}_8$ (*Ab*) and component 2 is KAlSi_3O_8 (*Or*) as in Part I. Equation (16) is plotted in Figure 2. The uncertainties above are the least-squares standard deviations, s_y (Thompson and Waldbaum, in press). The standard deviations of (13) and (14) indicate that an asymmetric equation is the best representation of \bar{V}_{ex} for *all* of Donnay and Donnay's data, but the standard deviations of (15) and (16) are essentially the same, suggesting that equations of higher than second order cannot be justified for Orville's data. The W_V 's calculated from (14) and (15) are given in Table 2 and compared with data for two other K-Na crystalline solution series: microcline—low albite and sylvite—halite. Where excess parameters for the feldspars indicate asymmetry in \bar{V}_{ex} it is toward KAlSi_3O_8 , that is, $W_{V_{\text{Ab}}} > W_{V_{\text{Or}}}$.

Barth (1967) presented a discussion and analysis of Donnay and Donnay's (1952) data in which his Figure 1 suggests that $W_{V_{\text{Or}}}$ should be negative. Smith (1956) and Stewart and von Limbach (1967) have shown, however, that the 1952 results for pure $\text{NaAlSi}_3\text{O}_8$ were in error. These later results are also consistent with Orville's (1967) data and other recent lattice parameter determinations for high albite (Waldbaum, 1966, Table 2-8; Stewart and von Limbach, 1967, Table 4), therefore, there is no conclusive evidence as yet to support negative volumes of mixing in alkali feldspars or other K-Na crystalline solutions.

Monoclinic-triclinic symmetry change. Both Donnay and Donnay and Orville have shown the existence of a symmetry change in the sanidine—high albite series at 33 (Donnay and Donnay) and 42 (Orville) mol percent KAlSi_3O_8 (Fig. 10, Part I). The composition of the symmetry change was determined by noting an abrupt change in the variation of α^* , γ^* , and other X-ray parameters with composition. However, no

such break (or rapid change) in slope is apparent in the data points in Figure 2.

If the symmetry change were first order, a discontinuity in the volume would be expected; but if the symmetry change were second or n th-order, discontinuities in the first or $(n-1)$ th derivatives, respectively, of volume with respect to composition are to be expected. If there were a break in slope (2nd-order transition) at the symmetry change, one could locate the symmetry change by successively elim-

TABLE 2. EXCESS MOLAR VOLUME PARAMETERS OF Na-K CRYSTALLINE SOLUTIONS. Na-COMPONENTS ARE $\text{NaAlSi}_3\text{O}_8$ AND NaCl , K-COMPONENTS ARE KAlSi_3O_8 AND KCl

	$W_{V_{\text{Na}}}$ cal bar ⁻¹	$W_{V_{\text{K}}}$ cal bar ⁻¹
Sanidine solutions preferred values (Eq. 18)	0.090 $\pm 0.007^a$	0.090 ± 0.007
Sanidine-high albite (Eq. 14, Donnay and Donnay)	0.128 ± 0.007	0.051 ± 0.007
Sanidine-high albite (Eq. 15, Orville)	0.089 ± 0.002	0.089 ± 0.002
Microcline-low albite (Table 2-12, Waldbaum, 1966)	0.110 ± 0.003	0.110 ± 0.003
Microcline-low albite (Table 2A, Orville, 1967)	0.123 ± 0.009	0.123 ± 0.009
Sylvite-halite (Waldbaum, 1964)	0.0125	0.0125

^a The uncertainties given are *thermochemical uncertainties* (two times the standard errors of the coefficients). For both sets of microcline-low albite data the Gauss criterion indicates that only a quadratic fit is justified.

inating the more *Na-rich* feldspars from the quadratic and cubic least-squares analyses until a significant improvement (decrease) in the standard deviation or any other index of dispersion were obtained (Gauss criterion, see Wensel and Tuckerman, 1938). The results obtained using the standard deviation as the dispersion index are given in Tables 3a and 4a.

The results for the data of Donnay and Donnay in Table 4 are inconclusive as far as determining a break in the volume-composition curve because the data points are too few and unevenly spaced. Barth (1967, Fig. 1) placed a break in their volume data at the same composition that Donnay and Donnay give for the change in symmetry (based

TABLE 3. EFFECT OF SUCCESSIVE REMOVAL OF MOLAR VOLUMES FROM LEAST-SQUARES ANALYSES. DATA OF ORVILLE (1967). UNITS ARE cal bar^{-1}

Table 3a. Removal of Most Na-rich Sanidine-high Albite Solutions

No. Data Points	N_{Or} of most Na-rich data point	Quadratic			Cubic			
		$\bar{V}_{\text{Ab}}^{\circ}$	W_{T}	s_{y}	$\bar{V}_{\text{Ab}}^{\circ}$	W_{VAb}	W_{Vor}	s_{y}
20	0.0000	2.3937	.0894	.0019	2.3951	0.1072	0.0719	0.0018
19	.0472	2.3917	.0956	.0016	2.3926	.1017	.0873	.0016
18	.0948	2.3919	.0951	.0017	2.3939	.1035	.0806	.0017
17	.1426	2.3908	.0980	.0017	2.3925	.1023	.0879	.0017
16	.1906	2.3896	.1011	.0017	2.3896	.1012	.1011	.0018
15	.2390	2.3887	.1031	.0017	2.3862	.1009	.1155	.0018
14	.2876	2.3900	.1003	.0018	2.3899	.1003	.1008	.0019
13	.3366	2.3852	.1100	.0017	2.3654	.1093	.1914	.0017
12	.3858	2.3956	.0903	.0012	2.4069	.0877	.0475	.0013
11	.4353	2.3972	.0875	.0013	2.4279	.0742	-.0211	.0013
10	.4851	2.3912	.0977	.0013	2.4156	.0833	.0170	.0014
9	.5352	2.3836	.1096	.0014	2.3799	.1123	.1213	.0015
8	.5856	2.3836	.1097	.0015	2.3742	.1173	.1372	.0017
7	.6363	2.4028	.0823	.0015	2.6303	-.1158	-.5423	.0016
6	.6873	2.3673	.1301	.0015	2.4022	.0980	.0393	.0018
5	.7387	2.3711	.1253	.0018	2.6681	-.1560	-.6146	.0026

Table 3b. Removal of Most K-rich Sanidine-high Albite Solutions

No. data points	N_{Or} of most K-rich data point	Quadratic			Cubic			
		$\bar{V}_{\text{Ab}}^{\circ}$	W_{T}	s_{y}	$\bar{V}_{\text{Ab}}^{\circ}$	W_{VAb}	W_{Vor}	s_{y}
20	1.0000	2.3937	0.0894	0.0019	2.3951	0.1072	0.0719	0.0018
19	.9471	2.3939	.0866	.0019	2.3951	.1065	.0721	.0018
18	.8945	2.3938	.0879	.0020	2.3955	.1245	.0688	.0018
17	.8422	2.3942	.0816	.0019	2.3954	.1187	.0693	.0018
16	.7387	2.3943	.0791	.0020	2.3958	.1612	.0693	.0018
15	.6873	2.3945	.0747	.0020	2.3960	.1851	.0714	.0019
14	.6363	2.3949	.0652	.0020	2.3960	.1760	.0702	.0020
13	.5856	2.3948	.0669	.0021	2.3964	.2916	.0915	.0019
12	.5352	2.3952	.0519	.0021	2.3964	.2917	.0915	.0020
11	.4851	2.3957	.0295	.0020	2.3962	.1704	.0597	.0021
10	.4353	2.3960	.0119	.0021	2.3959	-.0144	.0051	.0022
9	.3858	2.3958	.0238	.0022	2.3961	.2379	.0873	.0024
8	.3366	2.3954	.0667	.0023	2.3968	1.8718	.6645	.0019
7	.2866	2.3963	-.0611	.0017	2.3965	.3250	.0789	.0019
6	.2390	2.3960	-.0022	.0018	2.3970	4.5318	1.7696	.0015

on plots of lattice angles against composition). Although expected for the reasons cited above, Barth's conclusion (1967, p. 123) is not borne out by application of the Gauss criterion.

The results for Orville's cell volumes, however, clearly indicate a

break in the standard deviations of both quadratic and cubic equations between 33.7 and 38.6 mol percent *Or*. This suggests that the Na-rich (<35%) and K-rich (>35%) data would be better represented by separate equations.

Successive removal of the most *K-rich* feldspars (Tables 3b and 4b) yielded similar but somewhat less reliable results owing to the smaller

TABLE 4. EFFECT OF SUCCESSIVE REMOVAL OF MOLAR VOLUMES FROM LEAST-SQUARES ANALYSES. DATA OF DONNAY AND DONNAY (1952)

Table 4a. Removal of Most Na-rich Sanidine-high Albite Solutions								
No. Data Points	N_{Or} of most Na-rich data point	Quadratic			Cubic			
		\bar{V}_{Ab}	W_V	s_y	\bar{V}_{Ab}	$W_{V_{Ab}}$	$W_{V_{Or}}$	s_y
12	0.0000	2.3995	0.0883	0.0024	2.4022	0.1279	0.0510	0.0014
11	.0948	2.3965	.0974	.0022	2.4036	.1300	.0427	.0014
10	.1906	2.3920	.1097	.0020	2.4058	.1310	.0322	.0015
9	.2876	2.3834	.1305	.0012	2.3866	.1317	.1157	.0013
8	.3268	2.3863	.1244	.0010	2.4037	.1264	.0477	.0009
7	.3366	2.3860	.1249	.0011	2.4072	.1247	.0352	.0009
6	.3858	2.3810	.1342	.0011	2.3999	.1288	.0607	.0011
5	.4851	2.3747	.1449	.0012	2.4005	.1284	.0590	.0016

Table 4b. Removal of Most K-rich Sanidine-high Albite Solutions								
No. data points	N_{Or} of most K-rich data point	Quadratic			Cubic			
		\bar{V}_{Ab}	W_V	s_y	\bar{V}_{Ab}	$W_{V_{Ab}}$	$W_{V_{Or}}$	s_y
12	1.0000	2.3995	0.0883	0.0024	2.4022	0.1279	0.0510	0.0014
10	.7953	2.4010	.0643	.0017	2.4022	.1256	.0512	.0014
9	.5856	2.4018	.0410	.0014	2.4020	.0754	.0444	.0015
8	.4851	2.4020	.0305	.0015	2.4019	-.0297	.0186	.0017
7	.3858	2.4021	.0260	.0017	2.4017	-.4278	-.1087	.0018
6	.3366	2.4020	.0336	.0019	2.4015	-1.0775	-.0336	.0020

number of data points used in the least-squares analyses in the vicinity of the symmetry change.

In Part I, a similar approach was utilized in analyzing Orville's (1963) ion-exchange data. These results suggested a break in slope in the exchange data corresponding to a monoclinic-triclinic symmetry change at the temperature of the runs (Figs. 3, 6, and 7; Thompson and Waldbaum, 1968). We emphasize, however, that this interpretation pushes the existing data to their limit. Higher precision data spaced at smaller composition intervals are needed if these discontinuities are to be accurately resolved.

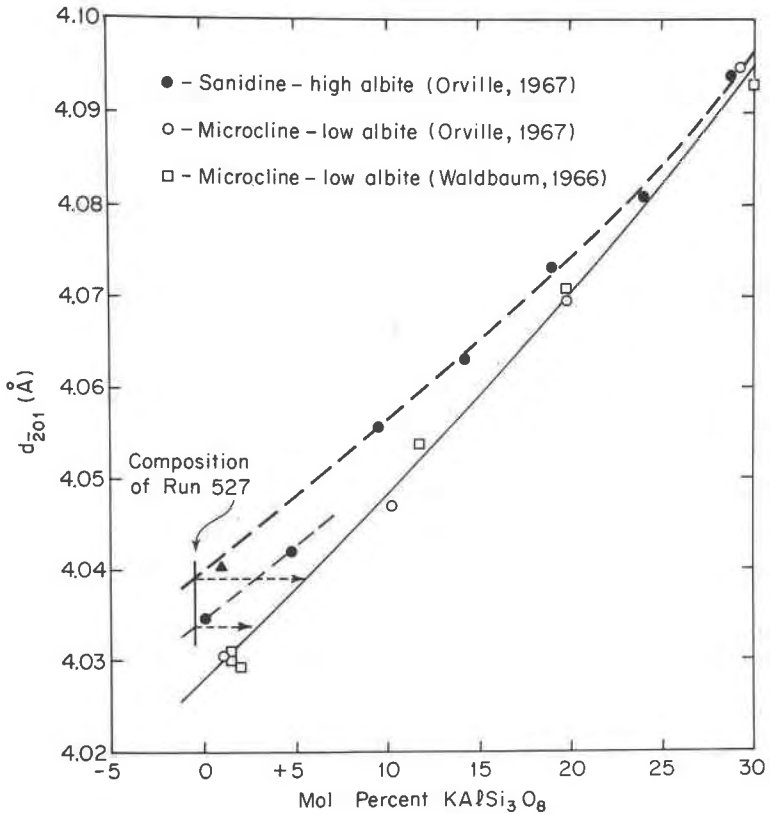


FIG. 3. Values of $d(201)$ calculated from least-squares refined lattice parameters. Triangle denotes Amelia albite heated (dry) for 668 hours at 1060°C (sample 6406-C1, Table 2-8, Waldbaum, 1966; also Waldbaum, 1968, Table 7).

Fossil symmetry change. Orville's (1967) feldspars were synthesized at a temperature of 800°C , hydrothermally. From results obtained in Part I (Fig. 10) it is likely (see Appendix) that those containing less than 9 percent *Or* were triclinic at temperature of synthesis, hence were not restricted to being *m*-disordered;¹ and that the more K-rich feldspars grew as *m*-disordered monoclinic phases. This suggests that there may be yet another break in the curves relating volume (measured at room temperature) to composition at about 9 percent *Or*. There are not sufficient data to rigorously locate this "fossil" symmetry change in-

¹ The term *m-disordered* is used here to indicate that the $T_1(0)$ and $T_1(m)$ sites have equal Al-populations and that the $T_2(0)$ and $T_2(m)$ sites have equal Al populations, which is an Al-Si distribution that is consistent with monoclinic symmetry but does not demand it. In general, the T_1 and T_2 sites may be expected to have different Al-occupancies.

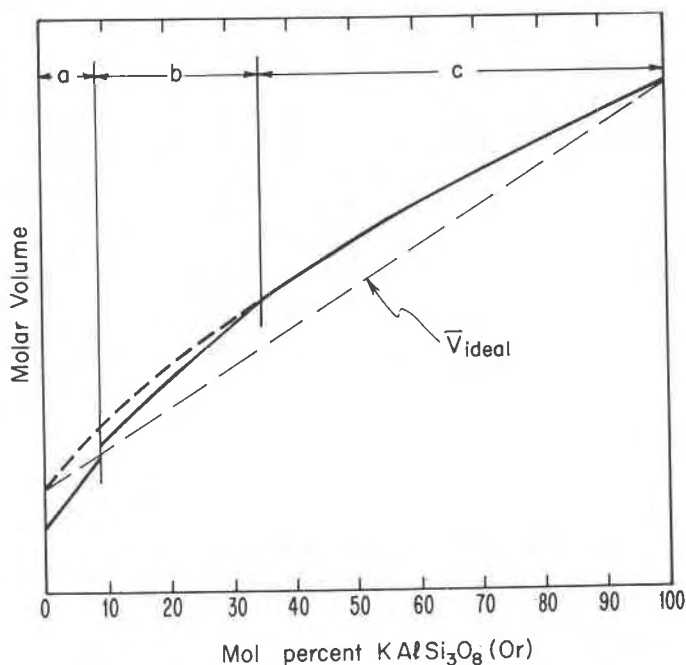


FIG. 4. Schematic representation of transitions in sanidine—high albite data. Solid curves denote volumes observed at 25°C for samples synthesized at 800°C. Dashed curve is continuation of group *c* monoclinic data, representing \bar{V} of Na-rich sanidine solutions.

herited from the temperature of synthesis, but such a discontinuity between 5 and 10 percent *Or* is suggested by Orville's (1967) calculated $(\bar{2}01)$ *d*-values shown by solid circles in Figure 3. It would thus appear that both Orville's 1963 and 1967 synthetic feldspars should be separated into the three groups shown in Figure 4:

a. Crystals that nucleated and grew as triclinic phases, hence their Al atoms must be ordered to some extent between the T(0) and T(*m*) sites. These crystals should remain triclinic below the temperature of synthesis.

b. Crystals that nucleated and grew as monoclinic phases (*m-disordered*), but are triclinic phases at 25°C owing to a displacive symmetry change in cooling from 800° to 25°C.

c. Crystals that nucleated and grew as monoclinic phases (*m-disordered*) and remain monoclinic at 25°C. The more Na-rich of these should convert to triclinic symmetry as did *b*, if cooled to still lower temperatures (MacKenzie, 1952, Table 1).

The break between groups *b* and *c* will be characterized by a discontinuity in first or higher derivatives of volume, entropy, enthalpy, or

free energy with respect to composition. Group *a* feldspars, being triclinic at the time of synthesis, are likely to be partially ordered with respect to the T(0) and T(*m*) sites, but the monoclinic crystals whose Al-Si distributions are constrained by the mirror plane in the structure cannot be. Breaks between *a* and *b* observed at room temperature should, therefore, have the properties of a first-order transition as shown in Figure 4. Specifically, if the transition is second-order at the temperature of synthesis, there should be a discontinuity in thermal expansion, hence, even though there were no discontinuity in the volume-composition diagram at the temperature of synthesis, there would be one at room temperature. Related discontinuities can also be expected in X-ray determinative curves.

The distinct probability of discontinuities in the ($\bar{2}01$) determinative curves suggests that the compositions of Orville's 1963 ion-exchanged feldspars should be redetermined by some means independent of physical property measurements. The errors in the determined compositions are probably greatest in group *a* for which Orville actually reported *negative Or*-contents. For example, the feldspar from run 527 (Orville, 1963, Table 1) has a $d(\bar{2}01)$ -value of 4.037 ± 0.002 Å according to Orville's (1967) sanidine—high albite determinative data; but using Orville's (1967) microcline—low albite ($\bar{2}01$) data, this range of d -values gives an *Or*-content of 4.5 ± 1.5 percent as shown in Figure 3. The true composition of feldspar 527 probably lies between 0 and 5 percent. Similarly, all of Orville's (1963) Na-rich feldspars that are in group *a* probably contain more potassium than indicated by the determinative curve. Both Orville's 1963 and 1967 determinative curves will give the most accurate results for feldspars crystallized hydrothermally at 800°C and 1000 bars.

CONCLUSIONS

It will be noted in Table 3a that on both sides of the symmetry change the standard deviation is lower for the quadratic equation. We have thus adopted for the monoclinic portion (group *c*):

$$\bar{V} = 2.39563 + 0.29620 N_{Or} - 0.09031 N_{Or}^2 \pm 0.0012 \text{ cal bar}^{-1} \quad (17)$$

$$\bar{V}_{cx} = 0.0903 N_{Or} N_{Ab} \text{ cal bar}^{-1} \quad (18)$$

The volumes calculated from Eq. (17) are compared with the observed data in Figure 5. The quadratic fit to the remaining triclinic data in Table 3b is:

$$\bar{V} = 2.39543 + 0.27834 N_{Or} - 0.06669 N_{Or}^2 \quad (19)$$

but it is based on very limited data and does not take into account the suspected break between groups *a* and *b* as discussed above.

The least-squares standard deviations indicate that an asymmetric excess volume of mixing is not now warranted for sanidine solutions. The data in Table 3 show that removing only one data point may have considerable effect on the numerical values of the Margules parameter,

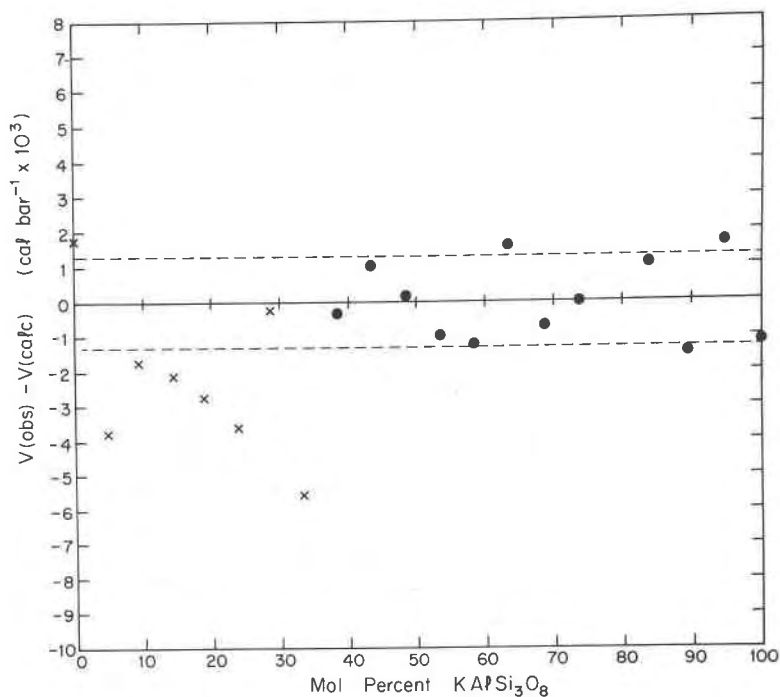


FIG. 5. Residual plot of Orville's (1967) sanidine—high albite molar volumes compared with Eq. (17). Circles denote data used in obtaining (17); crosses denote Na-rich phases not included in least-squares fit (groups *a* and *b* of Figure 4). Dashed lines denote least-squares standard deviation.

thus, only the sign and order of magnitude of the W_V 's are actually known with any certainty. Because \bar{V}_{ex} of the alkali feldspars is a maximum of 1 percent of the total volume measured, \bar{V} must be determined with a precision and accuracy of 1 part in 10 if the asymmetry is to be known with any certainty. For thermodynamic purposes, the most useful data on sanidine solutions would be cell volumes determined at the temperature of synthesis—800°C for Orville's (1967) feldspars. The monoclinic range is greater at high temperatures, and it is furthermore in this temperature range that the volume of mixing of

sanidine solutions is of greatest geological and thermodynamic significance.

We have made a simplifying assumption in presenting the results of Eq. (17) that each of Orville's initially monoclinic feldspars (groups *b* and *c*) crystallized with identical Al-Si distributions, implying that the excess parameter of Eq. (18) refers only to volumes of K-Na mixing. However, if the Al-Si distributions of these feldspars equilibrated completely under the conditions of synthesis, it is very likely that each bulk composition in groups *b* and *c* will have different degrees of order between the T_1 and T_2 sites (Appendix), but the crystallographic methods used to determine Al-occupancies are not as yet sufficiently precise to detect what are probably small differences within groups *b* and *c* for a series of feldspars synthesized at a given temperature and pressure.

Even if the Na-rich monoclinic phases were more ordered, the effect on the values of W_V would be negligible as is evident from the results shown in Table 2. The effect of ordering on W_V would also be thermodynamically insignificant—at least for pressures less than 20 kbar. The effects of thermal expansion or the substitution of hydronium for alkali ion (Luth and Tuttle, 1966) on the volume excess parameters can be expected to far outweigh any effects of monoclinic ordering.

The foregoing discussion indicates that more alkali feldspar volume data would be desirable to achieve a better understanding of the higher-order transformations and the effects of Al-Si ordering, but there seems little doubt that the sign and order of magnitude of the excess molar volume of alkali feldspars at 25°C is well established. The results of the four independent crystallographic investigations summarized in Table 2 and the phase diagrams calculated by Waldbaum (1966), Barth (1967), and Thompson and Waldbaum (1967) further indicate that the volumes of mixing of alkali feldspars cannot be neglected in thermodynamic analyses involving feldspar crystalline solutions—as suggested by Perchuk and Ryabchikov (1968, p. 137 and Fig. 10). This fact is also evident from the strong pressure dependence of the critical temperature in the system observed by Yoder, Stewart, and Smith (1957) and Luth and Tuttle (1966), and is further supported, as will be shown in Part III of this series, by the results of Orville (1963) and Luth and Tuttle (1966) whose data for co-existing feldspars yield Margules volume parameters on the order of $+0.1 \text{ cal bar}^{-1}$.

ACKNOWLEDGMENTS

We are indebted to P. M. Orville, Yale University, for providing us with his experimental data in advance of publication. We also thank J. F. Hays and G. L. Hovis, Harvard University, and P. M. Orville for their helpful comments on the manuscript. This research

was carried out under a Guggenheim Senior Postdoctoral Fellowship (JBT), a joint postdoctoral fellowship of the Committee on Experimental Geology and Geophysics and the Harvard Computing Center under a grant from the International Business Machines Corporation (DRW), and the Higgins Fund of Harvard University.

REFERENCES

- BARTH, T. F. W. (1967) Structure and volume relations of the alkali feldspar mixed crystals. *Schweiz. Mineral. Petrog. Mitt.*, **47**, 121–128.
- DONNAY, G., AND J. D. H. DONNAY (1952) The symmetry change in the high-temperature alkali-feldspar series. *Amer. J. Sci.*, **Bowen Vol.** 115–132.
- LAVES, F. (1960) Al/Si-Verteilungen, Phasen-Transformationen und Namen der Alkali-feldspate. *Z. Kristallogr.*, **113**, 265–296.
- LAVES, F. (1961) Discussion of paper by W. S. Mackenzie and J. V. Smith: Experimental and geological evidence for the stability of alkali feldspars. *Cursillos Conf. Inst. Lucas Mallada*, **8**, 64–69.
- LUTH, W. C., AND O. F. TUTTLE (1966) The alkali feldspar solvus in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. *Amer. Mineral.*, **51**, 1359–1373.
- MACKENZIE, W. S. (1952) The effect of temperature on the symmetry of high-temperature soda-rich feldspars. *Amer. J. Sci.*, **Bowen Vol.** 319–342.
- ORVILLE, P. M. (1963) Alkali ion exchange between vapor and feldspar phases. *Amer. J. Sci.*, **261**, 201–237.
- (1967) Unit-cell parameters of the microcline-low albite and the sanidine-high albite solid solution series. *Amer. Mineral.*, **52**, 55–86.
- PERCHUK, L. L., AND I. D. RYABCHIKOV (1968) Mineral equilibria in the system nepheline—alkali feldspar—plagioclase and their petrological significance. *J. Petrology*, **9**, 123–167.
- SCATCHARD, G., AND W. J. HAMER (1935) The application of equations for the chemical potentials to partially miscible solutions. *J. Amer. Chem. Soc.*, **57**, 1805–1809.
- SMITH J. (1956) The powder patterns and lattice parameters of plagioclase feldspars. I. The soda-rich plagioclases. *Mineral. Mag.*, **31**, 47–68.
- STEWART, D. B., AND D. VON LIMBACH (1967) Thermal expansion of low and high albite. *Amer. Mineral.*, **52**, 389–413.
- THOMPSON J. B., JR. (1967) Thermodynamic properties of simple solutions. In P. H. Abelson, ed. *Researches in Geochemistry II*, John Wiley and Sons, New York, 340–361.
- , AND D. R. WALDBAUM (1967) Thermodynamic mixing properties of sanidine/high-albite crystalline solutions (abstr.). *Trans. Amer. Geophys. Union*, **48**, 230.
- , AND ——— (1968) Mixing properties of sanidine crystalline solutions. I. Calculations based on ion-exchange data. *Amer. Mineral.*, **53**, 0000–0000.
- , AND ——— (in press) Analysis of the two-phase region halite-sylvite in the system $\text{NaCl}-\text{KCl}$. *Geochim. Cosmochim. Acta*.
- VERGANO, P. J., D. C. HILL AND D. R. UHLMANN (1967) Thermal expansion of feldspar glasses. *J. Amer. Ceram. Soc.*, **50**, 59–60.
- WALDBAUM, D. R. (1964) Unsymmetrical binary solution as a thermodynamic model for sylvite-halite solid solutions. (abstr.) *Geol. Soc. Amer. Spec. Pap.*, **82**, 215–216.
- (1966) *Calorimetric investigation of alkali feldspars*. Ph. D. Thesis, Harvard University, 247 pp.
- (1968) High-temperature thermodynamic properties of alkali feldspars. *Beitr. Mineral. Petrology*, **17**, 71–77.
- WENSEL, H. T., AND L. B. TUCKERMAN (1938) Note on the method of least squares and the thermoelectric power of rhodium. *Rev. Sci. Instr.*, **9**, 237–241.

- WRIGHT, T. L., AND D. B. STEWART (1968) X-ray and optical study of alkali feldspar. I. Determination of composition and structural state from refined unit-cell parameters and 2V. *Amer. Mineral.*, **53**, 38-87.
- YODER, H. S., D. B. STEWART AND J. R. SMITH (1957) Ternary feldspars. *Carnegie Inst. Wash. Year Book*, **56**, 207-214.

Manuscript received, November 8, 1968; accepted for publication, August 8, 1968.

APPENDIX. DISPLACIVE AND EQUILIBRIUM SYMMETRY CHANGES

A possible relationship between the different types of symmetry change in alkali feldspar is sketched in Figure 6, appropriate to some fixed pressure. Let line E represent

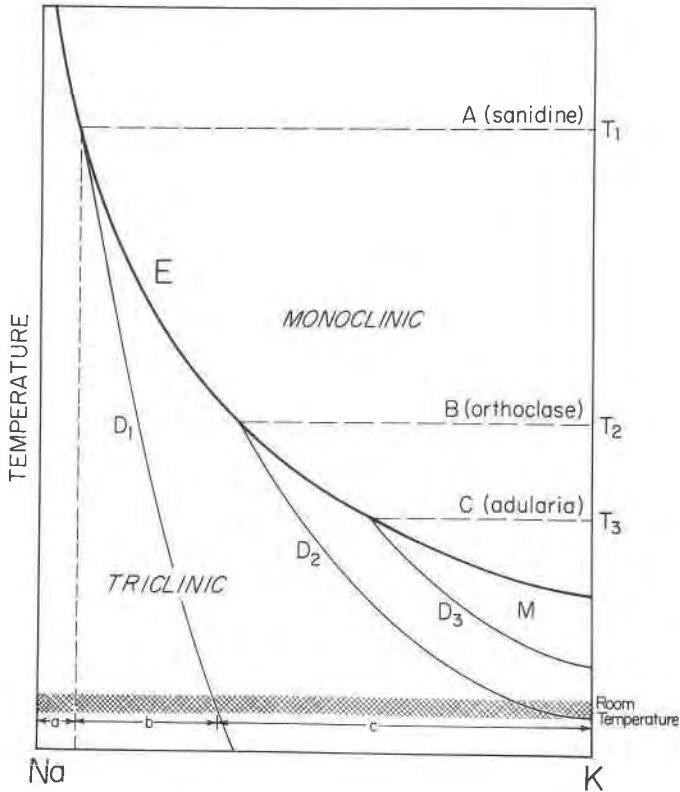


FIG. 6. Schematic representation of stable (long-term) equilibrium and metastable (displacive) symmetry changes in the alkali feldspar phase diagram at a fixed pressure. Two-phase region has been omitted. The heavy line E denotes the symmetry change for complete internal Al-Si equilibrium (approximately the "diffusive" symmetry change of Laves, 1961, p. 65). Lines D_1 , D_2 , and D_3 illustrate displacive symmetry change curves corresponding to feldspars equilibrated at T_1 , T_2 , and T_3 , respectively. The labels "monoclinic" and "triclinic" refer to curve E.

the equilibrium symmetry change appropriate to that pressure, realizing of course that the central portion of it is probably metastable relative to two-phase pairs. Line E would then be the limit for *m*-disorder in feldspars that have reached a final long-term Al-Si distribution appropriate to the pressure and temperature in question. Many monoclinic feldspars, however, undergo a displacive symmetry change on cooling that does not appear to affect the Al-Si distribution which presumably remains *m*-disordered. The temperature at which this occurs must depend on pressure, composition, and degree of order between the T_1 and T_2 sites, (whatever the equilibrium degree of order may be at a given *P*, *T*, and *N*).

Curves D_1 , D_2 and D_3 are possible curves for the displacive change for isothermal (and isobaric) series of equilibrium monoclinic feldspars¹ formed at temperatures T_1 , T_2 , and T_3 respectively. Figure 6 is qualitative and tentative in form, but is consistent with much of the known behavior of alkali feldspars: (1) If A were a K-rich sanidine it would remain monoclinic at room temperature; (2) If B were an ordinary "orthoclase" or adularia it would be monoclinic, triclinic, or ambiguous at room temperature, depending on the temperature and composition at which it formed; (3) C, on the other hand, might be a clearly triclinic, yet *m*-disordered feldspar such as a triclinic adularia; and (4) A twinned microcline that does not show a displacive symmetry change might be a feldspar that has experienced some ordering between the $T(0)$ and $T(m)$ sites after change of symmetry, whereas an untwinned microcline M may have formed initially in the triclinic field.

If T_1 is the temperature of synthesis and equilibration of Orville's (1967) feldspars, then *a*, *b*, and *c* in Figure 6 would correspond to *a*, *b*, and *c* of Figure 4 (provided both diagrams refer to the same pressure).

¹ Not a fused-salt exchange series in the sense of Wright and Stewart's (1968) "orthoclase-equivalent" series.