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Calorimetric investigation of Na-K mixing and polymorphism in the alkali feldspars[*]

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Auszug

Im System $Na(AlSi_3O_8)$—$K(AlSi_3O_8)$ wurden die Enthalpien für die Na-K-Mischung, für die Al-Si-Ordnung und für das Schmelzen sowohl der Endglieder wie auch der Mischkristalle kalorimetrisch bestimmt. Dazu diente ein isoperibolisches, vakuumisoliertes Kalorimeter mit dem die Lösungswärmen in 20,1-%iger Flußsäure im Bereich von 40—60 °C gemessen wurden. Bei 49,7 °C können die Lösungswärmen von synthetisch hergestelltem Mikroklin(Tiefalbit)-Mischkristallen durch folgende Gleichung ausgedrückt werden,

$$\bar{H}_{\mathrm{sol}} = -149{,}408 + 5{,}230\,N_2 - 5{,}928\,N_2N_2^2 - 8{,}457\,N_2N_1^2\ \mathrm{kcal/mol},$$

wobei N_1 und N_2 den Molanteilen von $NaAlSi_3O_8$ bzw. $KAlSi_3O_8$ entsprechen. Die Fehlergrenze bei dieser aus 39 Einzelmessungen ermittelten Least-squares-Formel beträgt $\pm$ 0,032 kcal/mol.

Die mit Least-squares-Verfeinerung aus den Röntgendaten erhaltenen Gitterkonstanten zeigen, daß die Überschußvolumina der Na-K-Mischung in diesen Mischkristallen über den ganzen Zusammensetzungsbereich positiv sind. Die Kombination der kalorimetrischen und der kristallographischen Daten führt zu folgendem Ausdruck für die Änderung der molaren Mischungsenthalpie mit dem Druck:

$$\bar{H}_{\mathrm{ex}} = (5928 + 0{,}110\,P)\,N_1N_2^2 + (8457 + 0{,}110\,P)\,N_2N_1^2\ \mathrm{cal/mol}.$$

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Das Vorzeichen und die Größenordnung von $\bar{H}_{ex}$, aus kalorimetrischen Messungen ermittelt, stimmt sehr gut mit dem aus einer Margules-Formel dritter Ordnung berechneten $\bar{H}_{ex}$ überein, entsprechend der Formulierung von Hochtemperatur-Zweiphasen-Gleichgewichtsdaten für den kritischen Bereich.

Abstract

Heat of solution measurements of the enthalpies of Na-K mixing, Al-Si ordering, and fusion for crystalline solutions and end-member phases in the system $Na(AlSi_3O_8)$—$K(AlSi_3O_8)$ were obtained with a vacuum-jacketed, isoperibolic calorimeter using 20.1 percent hydrofluoric acid at temperatures ranging from 40 to 60°C. Heat of solution data for artificially prepared microcline (—low-albite) crystalline solutions at 49.7°C are represented by

$$\bar{H}_{sol} = -149.408 + 5.230\,N_2 - 5.928\,N_1N_2^2 - 8.457\,N_2N_1^2 \text{ kcal/mole}$$

based on 39 measurements of 14 different bulk compositions, where N_1 and N_2 denote the mole fractions of $NaAlSi_3O_8$ and $KAlSi_3O_8$ respectively. The thermochemical uncertainty of the above least-squares formulation is $\pm$ 0.032 kcal/mole.

Unit-cell parameters determined by least-squares refinement of diffraction data indicate that the excess volumes of Na-K mixing of these microcline solutions are positive over the entire composition range. Combining the calorimetric and crystallographic data leads to the following expression for the variation of molar enthalpy of mixing with pressure:

$$\bar{H}_{ex} = (5928 + 0.110\,P)\,N_1N_2^2 + (8457 + 0.110\,P)\,N_2N_1^2 \text{ cal/mole}\,.$$

The sign and magnitude of $\bar{H}_{ex}$ determined by calorimetry agree closely with $\bar{H}_{ex}$ calculated from a third-order Margules formulation of high-temperature two-phase equilibrium data in the critical region.

Introduction

The thermodynamic properties and phase relations of alkali feldspars are similar in many respects to those of other Na-K crystalline solutions having very different crystal structures (THOMPSON and WALDBAUM, 1969a, 1969b; EUGSTER *et al.*, 1972). The $AlSi_3O_8$ framework of the feldspars, however, is more complex than the frameworks of other Na-K crystalline solutions such as the micas and chlorides. There are at least two and possibly four non-equivalent tetrahedral cation sites in the alkali-feldspar structure (TAYLOR, 1934; LAVES and HAFNER, 1962; THOMPSON, 1969, Fig. 4 and references cited therein). With four distinct tetrahedral sites, one must specify three sets of homogeneous equilibrium parameters in addition to Na-K mixing parameters in order to completely describe the equilibrium properties of an alkali feldspar (HAFNER and LAVES, 1957; BARTH, 1965).

In many natural alkali feldspars, microclines and low albites, the ordering parameters Y and Z defined by THOMPSON (1969, 1970) are very nearly $+1$ and the X parameter is close to zero, where:

$$\begin{aligned} X &\equiv N_{\mathrm{Al(T20)}} - N_{\mathrm{Al(T2}m\mathrm{)}} \\ Y &\equiv N_{\mathrm{Al(T10)}} - N_{\mathrm{Al(T1}m\mathrm{)}} \\ Z &\equiv N_{\mathrm{Al(T10)}} + N_{\mathrm{Al(T1}m\mathrm{)}} - N_{\mathrm{Al(T20)}} - N_{\mathrm{Al(T2}m\mathrm{)}} \end{aligned}$$

and N_{Al} is the average atomic fraction Al/(Al+Si) in the tetrahedral sites $\mathrm{T_1}(0)$, $\mathrm{T_1}(m)$, $\mathrm{T_2}(0)$, and $\mathrm{T_2}(m)$.

Structure data for synthetic sanidines and high albites, which are representative of the most highly disordered feldspars known, indicate that all three X, Y, and Z parameters are near zero (THOMPSON, 1969, Table 1, Figs. 6 and 7). Anti-ordered Al-Si distributions (negative Z) are theoretically possible structures, but have not as yet been discovered among natural or synthetic feldspars.

The effects of temperature, pressure, and composition on equilibrium values of X, Y, and Z are known only qualitatively from experimental studies such as those of TUTTLE and BOWEN (1950), DONNAY and DONNAY (1952), GOLDSMITH and LAVES (1954), MACKENZIE (1957), ORVILLE (1963, 1967), LINDSLEY (1966), LUTH and TUTTLE (1966), PARSONS (1968), MARTIN (1969), and MORSE (1970), mainly because direct structure determinations have not been carried out on the synthetic feldspars (one exception being the high albite studied by WILLIAMS and MEGAW, 1964). The difficulties encountered in interpreting such data are well-illustrated in discussions by LAVES (1960) and MACKENZIE and SMITH (1961). It is unlikely that homogeneous and heterogeneous phase relations in natural or synthetic feldspars can be interpreted accurately, or at least unambiguously, without the additional crystallographic, phase equilibrium, and calorimetric data needed to formulate a complete thermodynamic equation of state for the alkali feldspars.

In the present investigation we have obtained calorimetric and crystallographic data on the enthalpies and volumes of Al-Si disordering and the enthalpies of fusion of the sodium and potassium end-members, and data on the enthalpies and volumes of Na-K mixing for highly ordered low-albite—microcline crystalline solutions. For practical experimental reasons, we initially selected alkali feldspars with highly-ordered ($X \cong 0$, $Y \cong Z \cong 1$) and highly-disordered ($X \cong Y \cong Z \cong 0$) frameworks. Well-defined, highly-ordered feldspars are abundant in nature and highly-disordered ones can be reproducibly prepared in large quantities. As in previous thermodynamic and synthesis studies, the tetrahedral-site populations of these feldspars were not determined from single-crystal structure data. Hence, the terms "highly-ordered" and "highly-disordered" are qualitative and based only on a comparison of unit-cell parameters with those of previously determined feldspar structures.

Hydrofluoric acid solution calorimetry was used to obtain the enthalpy data. KRACEK and NEUVONEN (1952) also used this method successfully to obtain similar data on natural feldspars; however, the samples used by KRACEK and NEUVONEN contained varying amounts of other feldspar components, and the descriptions indicate substantial differences in Al-Si distributions and homogenity among the samples (detailed x-ray crystallographic data were not obtained). Recent development of a vacuum-jacketed solution calorimeter for use with hydrofluoric acid (ROBIE, 1965) and improved methods for purifying and controlling the synthesis of alkali feldspars (WYART and SABATIER, 1956; HAFNER and LAVES, 1957; ORVILLE, 1967) suggested that data of considerably higher precision could be obtained on more accurately characterized samples.

Synthesis, composition, and unit-cell data

The kinetics of both Na-K phase separation and Al-Si ordering in feldspars are slow enough to permit phases that may be thermodynamically metastable at room temperature and pressure to be quenched and preserved indefinitely (for all practical purposes) without the special precautions usually needed for alloys and alkali halides. It is therefore possible to obtain calorimetric data on the Na-K mixing properties of alkali feldspars for a framework of given constant Al-Si distribution for all bulk compositions, even though that distribution may be metastable with respect to some other distribution for the conditions of synthesis or the conditions of the calorimetric experiments. It is emphasized that the Al-Si distributions in the feldspars described below were not necessarily the most stable internal equilibrium values at either the annealing temperatures or the conditions under which the calorimetric and crystallographic data were obtained.

(a) End-member feldspars

Calorimetric samples of the end-member polymorphs were obtained from a single starting material—a natural low albite from the Rutherford Mine in Amelia County, Virginia (SINKANKAS, 1968). "Amelia albite" (var. cleavelandite) is well known for its high chemical and phase purity, and it was also used in calorimetric studies by KRACEK and NEUVONEN (1952) and HOLM and KLEPPA (1968). The present material was selected from a group of water-clear cleavage fragments about 1 cm across. All cloudy white crystals or fragments having a blue iridescence (peristerite) were excluded. Unit-cell parameters of this material are given in Table 1.

Quantitative emission-spectrographic analysis indicates that this albite has a low strontium content compared with other feldspars (HEIER, 1962), but that other minor elements are present in the ranges found in most other albites. The analytical data are given in Tables 2 and 3. The gravimetric analysis yielded a CaO content of 0.02 weight percent. All materials were crushed and ground in a 4-cm-diameter tungsten-carbide ball mill, and sized with Nylon sieves. No contamination by tungsten carbide was detected in any of the spectrographic analyses.

High albite (sample 6406-Cl) was prepared by heating some of the low albite in a platinum crucible in a silicon-carbide furnace for 668 hours at 1060 °C. This temperature was probably high enough for the albite to acquire dimensional monoclinic symmetry (GRUNDY *et al.*, 1967), and the material is thus likely to have a monoclinic Al-Si distribution despite its triclinic symmetry at room temperature. The monoclinic Al-Si distribution appears to be confirmed by the fact that a monoclinic sanidine was produced when the high albite was exchanged in fused KCl (see below).

Low albite (6454) with a lower K content was prepared by heating the original Amelia albite in fused NaCl at 900 °C. The slight decrease in the *a* cell dimension (Table 1) is consistent with a loss of K due to ion exchange. The unit-cell parameters of the albites given in Table 1 are also compared in Table 2 of KASTNER and WALDBAUM (1968) with previous determinations on high and low albites prepared in a similar way and by hydrothermal synthesis (see also ORVILLE, 1967; WRIGHT and STEWART, 1968), and with albites whose Al-Si distributions have been determined by complete structure refinements. This comparison indicates that the fused-salt ion-exchange treatment had no detectable effect on the original Al-Si distribution.

Potassium feldspars having corresponding Al-Si distributions were prepared by converting portions of the above-described albite polymorphs to microcline (6452) and sanidine (6457), respectively, by ion-exchange in fused KCl for 24 hours at 900 °C (platinum crucible).

Table 1. *Unit-cell parameters of end-member alkali feldspars*

Least-squares standard errors as defined by BURNHAM (1962) are given below each parameter. Refinements numbered in italics were obtained by D. B. STEWART (1965, written comm.) with fluorite as an internal standard; refinement MK from KASTNER (1969), silicon standard; LQS from LUTH and QUEROL-SUÑE' (1970), spinel standard

Sample/ Refinement No./ No. lines	Synthesis history*	*a* (Å)	*b* (Å)	*c* (Å)	α	β	γ	*V* (cal/bar)
6306 R292 30	Low albite, Nc (Amelia, Virginia)	8.1414 ±.0016	12.7836 .0020	7.1571 .0011	94.233° .016	116.592° .012	87.680° .015	2.3907 .0009
6454 R191 19	Low albite EDNc: 910°C, 24hr, NaCl	8.1359 .0031	12.7844 .0049	7.1573 .0014	94.245 .022	116.568 .014	87.689 .027	2.3897 .0014
6601H R315 51	Low albite, Nch	8.1425 .0016	12.7912 .0022	7.1617 .0011	94.221 .019	116.639 .013	87.749 .018	2.3931 .0010
6406A1 R298 27	Albite ANc: 1060, 173	8.1529 .0051	12.8043 .0038	7.1423 .0035	94.067 .039	116.546 .032	88.371 .041	2.3945 .0027
6406B1 R211 34	High albite ANc: 1060, 508	8.1574 .0021	12.8704 .0015	7.1132 .0012	93.541 .017	116.461 .012	90.121 .020	2.3895 .0010
6413 R260 23	High albite EDED(6409): 915,24, NaCl	8.1559 .0024	12.8645 .0020	7.1148 .0018	93.573 .021	116.478 .016	90.182 .024	2.3987 .0014
6406C1 R247 34	High albite ANc: 1060, 668	8.1627 .0020	12.8729 .0016	7.1141 .0010	93.545 .019	116.460 .011	90.131 .023	2.4026 .0009
6609H R331 43	High albite ANch: 1045, 840	8.1586 .0017	12.8738 .0009	7.1126 .0010	93.462 .010	116.431 .009	90.240 .013	2.4018 .0008
6301 R144 26	Microcline EDNc: 860, 24, KCl	8.5840 .0017	12.9714 .0020	7.2234 .0010	90.653 .014	115.919 .012	87.619 .016	2.6012 .0009
6452 R300 52	Microcline EDNc: 910, 25, KCl	8.5836 .0016	12.9723 .0015	7.2238 .0009	90.619 .013	115.924 .010	87.650 .012	2.6014 .0009
6452 R*739* 28	Microcline (see above)	8.5801 .0021	12.9646 .0011	7.2218 .0026	90.611 .014	115.938 .012	87.642 .014	2.5977 .0010
6452 LQS 62	Microcline (see above)	8.5830 .0010	12.9647 .0011	7.2226 .0009	90.617 .010	115.920 .010	87.658 .010	2.5994 .0003
6804 MK 23	Microcline EDNc: 816,29, KCl	8.5764 .0026	12.9621 .0017	7.2221 .0019	90.612 .023	115.918 .015	87.686 .020	2.5967 .0015
6442KX R*704* 19	Microcline EDAMED(6442): (?), KCl	8.6018 .0036	12.9650 .0027	7.2206 .0011	90.522 .023	115.876 .018	87.852 .027	2.6057 .0010
6407 R232 28	Microcline ED(6406A1): 882, 19, KCl	8.5939 .0034	12.9809 .0025	7.2040 .0021	90.315 .028	115.913 .018	88.428 .032	2.6005 .0018
6409 R256 44	Sanidine ED(6406B1): 881, 22, KCl	8.6061 .0016	13.0283 .0014	7.1828 .0014	90.0	115.999 .012	90.0	2.6052 .0011
6457 R254 64	Sanidine ED(6406C1): 910, 24, KCl	8.6079 .0012	13.0354 .0011	7.1817 .0009	90.0	116.012 .008	90.0	2.6065 .0007

* Symbols denoting synthesis history are as follows: *A*, heated (annealed) in air; *ED*, fused-salt-exchange derivative; *F*, fused in air; *M*, mechanical mixture; *Nc*, (natural) Amelia albite (this study); *Nch*, Amelia albite (HOLM and KLEPPA, 1968); *Nz*, (natural) Amelia microcline. Numbers in parentheses give sample number of starting material. Data following colon are: temperature (°C), time (hours), and reagent composition. Additional details in Table 2–5 of WALDBAUM (1966).

Table 2. *Spectrographic analyses of minor elements*

Symbols are: *, natural starting material; SQ, semiquantitative; Q, quantitative; *nd*, looked for but not detected; —, not looked for. The following elements were also looked for but not detected: Fe, Mg, Ti, P, Mn, Ag, As, Au, Bi, Cd, Ce, Co, Cr, Ge, Hf, Hg, In, La, Li, Mo, Nb, Ni, Pd, Pt, Re, Sb, Sc, Sn, Ta, Te, Th, U, V, W, Y, Yb, Zn, and Zr. Semiquantitative results are reported in weight-% to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.15, 0.1, etc., which represent approximate midpoints of group data on a geometric scale. The assigned group will include the quantitative value 30% of the time (analysts, J. L. HARRIS and J. D. FLETCHER, U. S. Geological Survey)

Sample**		Tl	Cu	Be	Ca	Sr	Ba	Pb	B	Ga
Amelia albite and ion-exchange derivatives:										
6306*	SQ	nd	.0001	.0007	.07	.0007	.0003	.01	.003	.007
6306*	Q	—	—	—	.019	.0022	<.002	.017	<.002	.005
6314*	SQ	nd	.0020	.0007	.07	.001	nd	.01	.003	.007
6454	SQ	nd	.0003	.0007	.05	.001	.0003	.01	.003	.007
6452	SQ	nd	.0007	.0005	.05	.001	.0003	.007	.003	.005
6457	Q	—	—	—	.0019	—	—	—	—	—
Amelia microcline and ion-exchange derivatives:										
6308*	SQ	nd	.0003	.0005	.007	.003	.002	.07	.003	.003
6308*	Q	—	—	—	.002	.0023	<.002	.14	<.002	.0023
6427	SQ	.007	.0015	.0005	.0005	.0015	nd	.05	.003	.002
6438	SQ	.007	.0002	.0003	.001	.0015	.001	.07	.003	.003
6453A	SQ	nd	.0005	.0005	.007	.0015	.0015	.05	.003	.003
6444	SQ	nd	.0007	.0005	.005	.0015	.0015	.07	.003	.005
6443	SQ	nd	.0007	.0003	.003	.0015	.001	.05	.003	.003
6440	SQ	nd	.0007	.0005	.002	.0015	.0015	.07	.003	.005
6426	SQ	.001	.001	.0007	.0015	.002	nd	.05	.003	.003
6429	SQ	nd	.0003	.0007	.0015	.0015	.0015	.05	.003	.005

** Synthesis history given in Tables 1 and 3.

Here again no significant change in Al-Si distribution during ion exchange is indicated. No petrographic, diffraction, or electron microprobe evidence was found to suggest that phases other than a single homogeneous alkali feldspar resulted from fused-salt ion exchange. Partial chemical analyses of the ion-exchanged derivatives are given in Tables 2 and 3.

The physical properties of these feldspars should, in a strict sense, only be compared with synthetic feldspars annealed by simple dry heating, or those heated in a fused salt, or crystallized in a peralkaline hydrothermal fluid, inasmuch as feldspars crystallized in pure water

Table 3. *Partial chemical analyses for major elements (wt-$^0/_0$)*
Methods of analysis: Na_2O, K_2O-I, and Rb_2O, flame photometry (J. J. WARR, JR., U.S.G.S., and H. W. KREUGER, analysts); K_2O-II, x-ray fluorescence (ROBENA BROWN and H. J. ROSE, U.S.G.S.); italics denote atomic absorption analyses (J. ITO, Harvard); SiO_2 and Al_2O_3, gravimetric (J. J. FAHEY, U.S.G.S.). Each value represents replicate (2 to 6) analyses on separate splits. Analyses for Cs_2O and Li_2O (flame) indicated less than 0.05 and 0.005 wt-$^0/_0$ respectively for all samples. Values in parentheses are estimates based on electron microprobe analyses

Sample	Synthesis history*	Na_2O	K_2O-I	K_2O-II	Rb_2O	SiO_2	Al_2O_3
6308	Amelia microcline (Nz)	1.74 *1.73* 1.70 1.83	13.56 *13.6* 13.52 13.33	13.7	0.83 *0.83*	65.34	18.74
6446	EDNz: 925 °C, 145 hr, KCl	<0.10	16.58	16.7	0.77	—	—
6438	EDNz: 910, 24, KCl	<0.10	16.21	16.3	0.81	—	—
6427	EDNz: 910, 24, KCl	<0.10	15.91	16.1	0.60	—	—
6439	AMED (6429 + 6436): 925,145	1.17	14.48	14.6	0.57	63.36	18.86
6442	AMED (6426 + 6436): 925,148	2.20	12.98	13.3	0.70	65.10	19.08
6449	AMED (6440 + 6438): 945,169	3.73	11.55	11.5	0.48	—	—
6434	AMED (6426 + 6427): 925,144	4.23	10.50	10.4	0.55	66.00	18.98
6453A	MED (6437 + 6445)	—	—	8.70	(0.20)	—	—
6453F	AMED (6453A): 940, 363	—	—	8.80	(0.20)	—	—
6441	AMED (6429 + 6436): 926,152	5.82 *5.90*	8.15 *8.16*	8.25	0.50 *0.64*	66.24	19.62
6448	AMED (6440 + 6438): 945,169	6.60	6.61	6.70	0.24	—	—
6447	AMED (6440 + 6436): 935,146	8.08	5.31	5.10	0.46	67.00	19.62
6451	AMED (6443,6444 + 6438): 945, 159	8.78	3.48	3.55	0.38	—	—
6450	AMED (6443 + 6438): 935,154	10.64	1.95	2.05	0.34	67.44	19.88
6426	EDNz: 910, 24, NaCl	—	—	0.26	(0.15)	—	—
6440	EDNz: 915, 48, NaCl	—	—	0.20	(0.15)	—	—
6443	EDNz: 907, 25, NaCl	—	—	0.17	(0.20)	—	—
6444	EDNz: 910, 26, NaCl	11.33	0.22	0.18	0.15	—	—
6429	EDED (6426): 905, 18, NaCl	—	—	0.02	(0.02)	—	—
6306	Amelia albite (Nc)	—	—	0.16	—	68.68	20.26
6452	EDNc: 910, 25, KCl	0.10	16.80	16.8	<0.05	64.54	19.06
6460	EDFNc: 910, 24, KCl	0.36 0.43	15.34 15.55	15.1	<0.05	64.10	18.68
6461	EDFNc: 909, 23, NaCl	11.80 11.78	0.07 0.03	—	<0.05	—	—

* See note in Table 1.

may contain significant amounts of hydronium in the alkali site (THOMPSON and WALDBAUM, 1969a, p. 826—828). Electrolytic determinations of the water content of Amelia albite exchanged in fused NaCl and KCl gave 0.0034 ± 0.0008 and 0.0009 ± 0.0004 weight percent H_2O, respectively, between 200 and 1000 °C (KASTNER, 1969, p. 172).

Glasses of the end-member compositions were prepared by fusing crystal fragments of the natural albite at 1325 °C (6411) and by exchanging the resulting Na glass in fused KCl (6460). Partial analyses of these glasses are given in Table 3, and their preparation and properties are discussed further by WALDBAUM (1969).

(b) Extent of disorder in high albite and sanidine

The b and c cell parameters of Amelia albite and its derivatives (Table 1) are compared in Fig. 1 with the cell parameters of alkali feldspars whose Al-Si distributions are known from structure-refinement data. For the monoclinic K feldspars 6409 and 6457, the ordering parameter Z is estimated to be 0.17 and 0.14 (± 0.02), respectively, from the tentative empirical relation given by HOVIS *et al.* (1970):

$$Z = -16.823 + 8.620\,(c - 0.400\,b)$$

where the uncertainty is based on those of the cell parameters and not on the uncertainties in the site populations used to derive the equation.

It appears from Fig. 1 (and bearing in mind the uncertainties in the cell parameters) that 6409 and 6457 are not as disordered as the preferred " high sanidine" of STEWART and RIBBE (1969) which yields a value of Z equal to 0.11 from the above relation. Subsequent annealing of sample 6457 at 1052 ± 10 °C for 448 hours showed that apparent further disordering was possible. The b and c parameters of this "sanidinized sanidine" (7025E) are 13.0317 ± 0.0014 Å and 7.1705 ± 0.0013 Å, respectively, with Z estimated to be 0.05 ± 0.02. The calorimetric data for 6457 should not, therefore, be considered as applying to "highest" sanidine (whatever value of Z that may be).

Microcline 6452 has also been annealed at 1052 °C for successive periods of time. In the first stage of 707 hours (7026A) the x-ray pattern indicated that the material was a mixture of monoclinic and triclinic crystals. The second stage of annealing lasted an additional 240 hours (7026B) and the x-ray data still showed signs of heterogeneity in the powder. After an additional 530 hours at 1052 °C (7075),

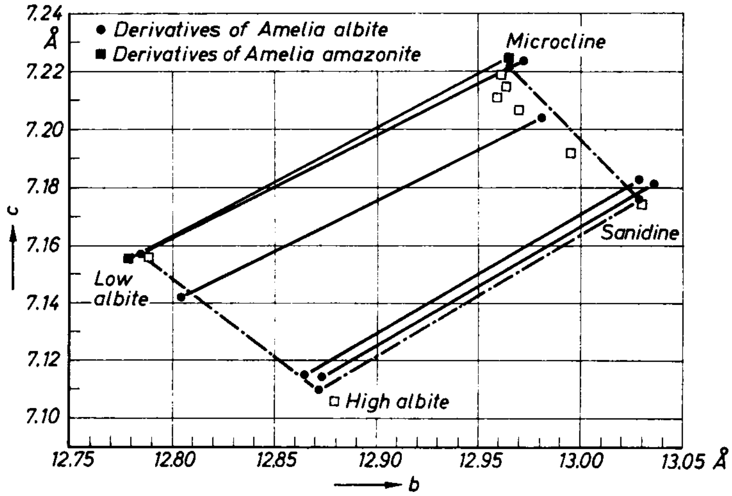

Fig. 1. b and c cell dimensions of end-member alkali feldspars. Solid lines connect exchange pairs derived from Amelia albite and from Amelia microcline (Table 1). Dot-dash lines connect preferred limiting reference values of Stewart and Ribbe (1969, p. 450). Open squares indicate feldspars used in structure refinements (references in Thompson, 1969)

the diffraction pattern showed sharp, well-defined peaks of a typical high sanidine with $b = 13.0295 \pm 0.0030$, $c = 7.1771 \pm 0.0019$ Å, and a value of Z of 0.12 ± 0.02 estimated as above.

(c) Microcline solutions

Microcline—low-albite crystalline solutions were prepared from natural microcline (var. amazonite, Rutherford mine, Amelia, Va.) because of its greater resistance to Al-Si disordering under prolonged heating (Spencer, 1937, p. 480; Rao, 1959). Sodium and potassium derivatives of this material (150 g each, −100 to +400 mesh) were first prepared by ion exchange in fused reagent NaCl and KCl in platinum crucibles[1]. The crystalline solutions were then prepared by

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[1] The bright green color of the Amelia amazonite is lost during fused-salt exchange, which is consistent with the experimental data of Oftedal (1957). Kastner (1969) observed that the K-rich phase of the amazonite emits a bright blue cathodoluminescence (see Smith and Stenstrom, 1965) at 20 kV both before and after ion exchange. It was also noted that the intensity of the luminescence varies directly with the K and Rb content of the end members and homogenized solutions (Table 3) and can be used to detect (K + Rb) and (Na)

"homogenizing" the alkali atoms of mechanical mixtures of these end-members (HAFNER and LAVES, 1957). The mixtures were heated in 4 to 15 g quantities in platinum crucibles for approximately 150 hours at 935 ± 15 °C in ceramic-lined furnaces which had not been used previously for fused salt studies (to minimize the possibility of external alkali contamination). Every 48 hours during homogenization each crucible was removed from the furnace and cooled. The powders were then remixed vigorously to promote uniform alkali distribution throughout the sample, and were replaced in the crucibles and returned to the furnaces for further heat treatment. The course of the homogenization process was monitored by diffraction patterns after each successive heat treatment.

Partial chemical analyses of the parent microcline, several Na and K derivatives, and the homogenized mixtures are given in Tables 2 and 3 (compare HEIER, 1962; PLYUSNIN, 1969, Table 4). The natural material (6308) has the bulk composition $K_{0.82}Na_{0.16}Rb_{0.02}AlSi_3O_8$. Calcium was not detected by gravimetric analysis (see also Table 2)[2]. The material is slightly perthitic, which accounts for most of the Na content, and it is assumed that the albite phase is at least as highly ordered as the microcline (MACKENZIE and SMITH, 1962). The albite-pericline grid twinning in the K phase of the parent material was not affected by the above exchange procedures.

The unit-cell parameters of these samples are summarized in Table 4 and compared with several independent determinations on the same materials kindly obtained by D. B. STEWART (open circles in Fig. 2) and with those of ORVILLE (1967) for homogenized derivatives of microcline from the Hugo, South Dakota pegmatite. Figure 2 emphasizes the major differences rather than the similarities in the

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zoning in individual grains (M. KASTNER, pers. comm., 1970). Similar luminescence is not observed in natural Amelia albite or its exchange products (both of which contain less than 0.05% Rb_2O).

[2] Infrared spectra and thermal-analysis data for amazonite and ordinary microcline (PLYUSNIN, 1969, Figs. 6 and 8) suggest that amazonite may contain hydronium, most likely in the alkali site. Raman spectra obtained on the Amelia amazonite used in this study (6308) and an NaCl-exchanged derivative (6443) showed no unequivocal evidence for hydronium in either, although Raman lines are present in the principal hydronium bending and stretching frequency ranges in both materials (Raman spectra were obtained between 2.5 and 50 μm on powdered material at room temperature using a Spectra-Physics-Model-700 instrument with an argon laser source, 300 mW at 5145 Å; details will be reported elsewhere).

Table 4. *Unit-cell parameters of microcline crystalline solutions*

Least-squares standard errors as defined by BURNHAM (1962) are given below each parameter. Refinements numbered in italics were obtained by D. B. STEWART (1965, written comm.) with fluorite as an internal standard ($a = 5.4620$ Å)

Sample	Refinement No.	Number of lines	Composition K/(K + Na)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (cal/bar)
6426	R222	21	0.0016	8.1413	12.7743	7.1551	94.105	116.606	87.741	2.3883
				±.0052	.0072	.0035	.053	.033	.048	.0026
6455	R192	8	0.0194	8.1336	12.7790	7.1561	94.152	116.640	87.732	2.3864
				.0058	.0099	.0041	.093	.037	.100	.0028
6440	R194	8	0.0148	8.1418	12.7759	7.1552	93.983	116.602	87.912	2.3893
				.0040	.0088	.0030	.057	.027	.059	.0019
6444	R271	32	0.0150	8.1515	12.7842	7.1575	94.133	116.633	87.729	2.3933
				.0042	.0065	.0025	.038	.025	.037	.0021
6450	R171	18	0.1078	8.1964	12.7982	7.1719	93.737	116.493	87.813	2.4181
				.0059	.0065	.0038	.051	.035	.051	.0031
6451	R177	27	0.1977	8.2346	12.8314	7.1838	93.003	116.279	87.925	2.4459
				.0058	.0066	.0040	.042	.034	.045	.0032
6447	R176	14	0.3014	8.2908	12.8515	7.1876	92.569	116.010	87.708	2.4740
				.0036	.0037	.0027	.032	.022	.028	.0020
6448	R167	17	0.3958	8.3350	12.8775	7.2017	92.049	116.098	87.862	2.4961
				.0036	.0090	.0023	.037	.020	.067	.0015
6441	R178	30	0.4741	8.3680	12.9055	7.2043	91.534	115.922	87.831	2.1564
				.0050	.0051	.0041	.042	.033	.039	.0032
6453E	R165	23	0.4998	8.3893	12.9204	7.2071	91.535	115.954	87.684	2.5258
				.0062	.0062	.0043	.055	.038	.046	.0034
6434	R164	38	0.6240	8.4380	12.9493	7.2123	91.068	115.954	87.709	2.5482
				.0024	.0024	.0017	.029	.016	.025	.0013
6434	R*755*	22	0.6240	8.4316	12.9478	7.2080	91.071	115.970	87.640	2.5440
				.0038	.0046	.0018	.052	.025	.039	.0024
6449	R163	30	0.6868	8.4698	12.9651	7.2078	90.850	115.910	87.777	2.5586
				.0022	.0017	.0018	.027	.015	.025	.0013
6449	R*754*	16	0.6868	8.4937	12.9514	7.2032	90.863	115.946	87.791	2.5625
				.0074	.0055	.0029	.062	.038	.062	.0041
6442	R162	27	0.7953	8.5138	12.9653	7.2119	90.774	115.921	87.708	2.5748
				.0031	.0030	.0019	.034	.021	.028	.0015
6442	R*705*	18	0.7953	8.5341	12.9676	7.2157	90.790	115.881	87.718	2.5837
				.0045	.0043	.0018	.033	.029	.035	.0025
6439	R161	36	0.8986	8.5553	12.9674	7.2191	90.629	115.957	87.751	2.5896
				.0022	.0013	.0015	.018	.014	.018	.0012
6439	R*753*	27	0.8986	8.5576	12.9600	7.2183	90.656	115.952	87.732	2.5886
				.0021	.0033	.0014	.029	.016	.028	.0016
6427	R137	15	0.9954	8.5999	12.9652	7.2246	90.671	115.911	87.699	2.6056
				.0045	.0027	.0035	.043	.029	.040	.0020

three sets of data, and illustrates the uncertainty with which the *b*-*c* composition relations are presently known for the highly ordered low-albite—microcline series. In other respects, Orville's results and the present data are in good agreement [see, for example, ($\bar{2}01$) *d* values in Fig. 3 of Waldbaum and Thompson, 1968]. It is not likely that the differences can be attributed to the rubidium in the present samples (see Martin and Lagache, 1970).

The cell parameters in Tables 1 and 4 were determined by least-squares refinement of x-ray diffraction data using the digital computer program LCLSQ of Burnham (1962); the uncertainties reported in the cell parameters are least-squares standard errors as defined by Burnham. The data were obtained with a Philips x-ray goniometer (model 42201) with Ni-filtered copper radiation, and only lines that could be indexed unambiguously were refined. Each sample was mixed with semiconductor-grade silicon as an internal standard and then deposited on a glass slide with collodion as a binder to give a permanent powder mount. The cell dimension (5.43054 ± 0.00017 Å at 25 °C) assigned to the silicon (analysis: 99.999% Si, less than 0.003 ppm B; from United Mineral and Chemical Corporation, New York), and the x-ray wave-

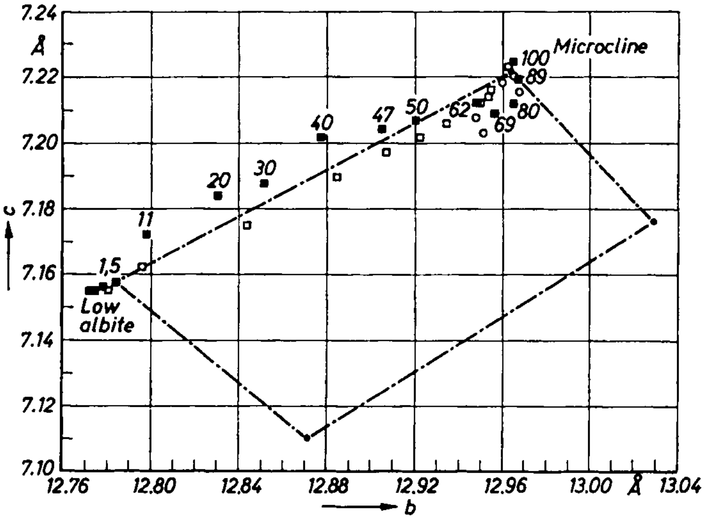

Fig. 2. *b* and *c* cell dimensions of microcline solutions. Filled squares are from this study (Table 4); numbers denote mole-% K/(K + Na). Open squares are from Table 2A of Orville (1967). Dot-dash lines are the same as in Fig. 1

lengths used are from PARRISH (1960). Two forward and reverse scans were made at ¼° 2θ per minute in the range 20 to 60 degrees 2θ at a chart speed of one inch per minute. The diffractometer was operated with a Geiger sensing element, 1° scatter and divergence slits, 0.003-inch receiving slit, and usually with a time constant of 8 seconds, a scale factor of 1, and multiplier of 4.

A least-squares formulation of the molar volumes in Table 4 gave:

$$\bar{V} = 2.38505(\pm .0006) + 0.21878(\pm .0010)N_2 + 0.1101(\pm .0036)N_1N_2 \tag{1}$$

in cal/bar-mole[3] (STEWART's refinements R 704, R 705, R 753, R 754, and R 755 not included), where N_1 and N_2 are mole fraction $NaAlSi_3O_8$ and $KAlSi_3O_8$, respectively. Inclusion of STEWART's five refinements gave:

$$\bar{V} = 2.38497(\pm .0006) + 0.21962(\pm .0009)N_2 + 0.1096(\pm .0033)\ N_1N_2\ .$$

These results are in good agreement with ORVILLE's (1967, Table 2A) data from which we obtained:

$$\bar{V} = 2.38116(\pm .0020) + 0.21794(\pm .0025)N_2 + 0.1226(\pm .0090)\ N_1N_2\ .$$

Strict application of the Gauss criterion (WORTHING and GEFFNER, 1943, p. 260) to the standard deviations of fit of higher-order formulations suggest that cubic or higher-order fits are not justified by the data.

(d) Further observations on alkali homogenization

The K and Na derivatives of Amelia microcline were also subjected to the above homogenization procedures as control samples to check for possible Al-Si disordering or alkali contamination. Cell parameters in Table 4 for "homogenized" (6455) and "unhomogenized" (6426) albites, both Na derivatives, indicate no significant differences in the two materials. The cleavelandite variety of Amelia albite, on the other hand, shows fairly significant structural changes when subjected to similar heat treatment for 150 hours (McKIE and McCONNELL, 1963).

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[3] The uncertainties (precision) given for all least-squares coefficients in this paper are "thermochemical uncertainties" (ROSSINI and DEMING, 1939; THOMPSON and WALDBAUM, 1969b, Appendix A). Enough significant figures have been given here to avoid serious round-off errors in calculations based on the coefficients. The number of figures should not be interpreted as an indication of the precision or accuracy of the results. One cal/bar = 41.840 cm^3.

The K derivatives 6427 (a single-exchange derivative) and 6442KX (prepared first as a K-Na solution by homogenization and later re-exchanged in KCl) also show no x-ray evidence for disordering. The K/(K + Na) ratios calculated from the alkali analyses in Table 3 agree within ± 1 mole-$^0/_0$ with those calculated from the weights of the end members in the initial mixtures.

The sharpness of individual x-ray peaks and the smooth relationships of the refined cell parameters with composition suggests that a high percentage of each of the grains must be near the bulk composition of a given mixture. However, electron-microprobe analyses obtained on 15 to 30 grains of each sample indicate that a few percent of the grains in some samples range in composition as much as two to three times that shown for 6453F in Fig. 3. This is equivalent to a range as large as ± 10 mole-$^0/_0$ in each sample, and is by far the greatest single source of uncertainty in the experimental data for 6434, 6441, 6442, 6447, 6448, and 6449.

The difficulties in obtaining complete homogenization were not as serious as those noted by RAO (1959), probably because the same initial natural material was used to prepare both end-member constituents of the mechanical mixtures (see also ORVILLE, 1967; and WRIGHT and STEWART, 1968). However, the microprobe data clearly demonstrate that the presence of a single sharp, narrow x-ray line such as ($\bar{2}01$) is not a sufficient criterion for complete homogeneity. This was noted for the samples referred to above and in particular for an equimolar mechanical mixture (6453A) which was heated for 24, 49, 93, 191, and 363 hours as above at 940 ± 10 °C. The ($\bar{2}01$) peaks obtained under identical instrumental conditions for samples 6453C (49 hours) through 6453F (363 hours) are virtually indistinguishable in position, width, and sharpness, yet the electron-microprobe analyses for Na and K shown in Fig. 3 suggest that complete alkali homogenization required considerably more than 49 hours.

The coarse grain size and large quantities of the materials homogenized in this study did not permit the use of pressed pellets of the mechanical mixtures; the powders were simply poured into the crucibles. This is most likely the main reason for the lack of uniform homogenization. There is no evidence in the electron-microprobe results (such as texture or a bimodal distribution of analyses) to suggest that 920 °C is subcritical for this feldspar series, or that the phases unmixed after removal from the furnace as suggested by BARTH (1965, p. 24). Heterogeneity appears to be principally confined to the larger grains, and usually takes the form of concentric zoning. New x-ray diffraction patterns obtained five years after synthesis confirm that phase separation has not taken place, although the microprobe data which were obtained both in 1968 and 1970 are more reliable in this respect.

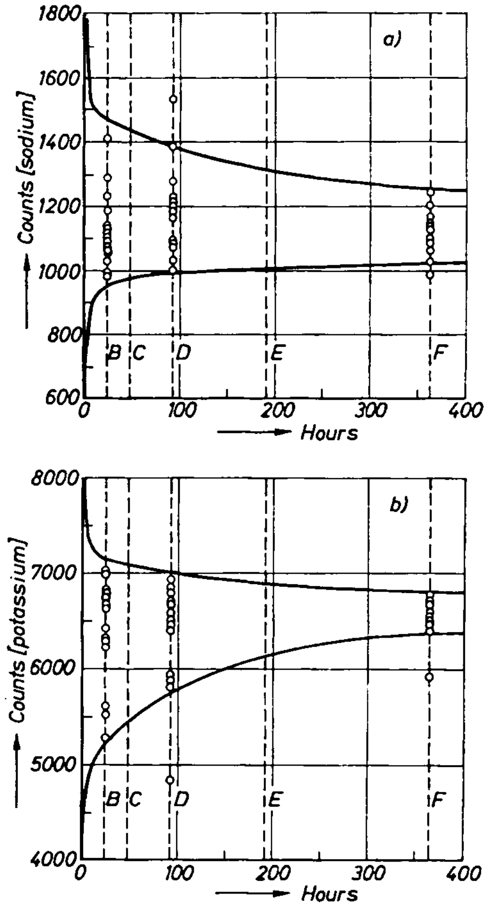

Fig. 3. Electron-microprobe analytical data showing the effect of time of homogenization (at 940 ± 10 °C) on the distribution of Na and K in sample 6453 [50 mole-% K/(K + Na)]. The range of counts for 6453F is comparable to the Na and K end-member derivatives of the amazonite which yielded a Na range of ± 180 counts (at 2400 counts) and a range for K of ± 500 counts (at 11900) under the same instrumental conditions on the same day. Data were obtained using an Applied Research Laboratories, Inc., Model EMX microprobe operated at 20 kV with a 20 nA sample current. Counts refer to a time interval of constant electron flux (10000 counts). Grain size ranged from 20 to 100 μm; beam diameter about 4 μm; 16 individual grains of each sample analyzed

Calorimetry

The solution calorimeter used in this investigation was described in detail by ROBIE (1965) and WALDBAUM (1966). Certain experimental and numerical procedures not previously published are summarized below.

(a) Procedures

In each heat-of-solution run the calorimeter vessel was loaded with a new charge of 940.10 ± 0.01 g reagent-grade hydrofluoric acid (J. T. Baker and Fisher), so that the vessel was always filled to the same level. To maintain a basis for interlaboratory comparison, the amount and concentration (20.1 %) of the acid used here were the same as those used by other laboratories previously engaged in HF solution calorimetry (KING, 1951; KRACEK and NEUVONEN, 1952).

Each feldspar sample is contained inside the calorimeter in a hollow teflon stirring impeller, so that the sample is initially isolated from the acid (WALDBAUM and ROBIE, 1970). In previous studies on silicates, the samples were introduced into the acid by enclosing them in gelatin capsules and dropping them down a tube into the calorimeter at the appropriate time. In this study, the samples were introduced by pushing on a spring-loaded plunger which forced out two protective gold-foil disks and the sample into the acid. With the internal sample container, silicate powders mix freely with the acid within five seconds after release. The reaction time of feldspar particles was usually on the order of 15 to 60 minutes for the size fractions used in this study.

KRACEK and NEUVONEN (1952) reported the formation of both crystalline and gelatinous precipitates in some of their calorimetric runs on plagioclase feldspars. Therefore, at the end of each solution run the acid, sample container, and calorimeter were examined carefully for unreacted material or precipitates formed in the reaction. We found no evidence to suggest that any undissolved feldspar or precipitates were in the calorimeter at the end of the experiments. The final solutions were water-clear and no deposits were noted on the inner surfaces of the calorimeter vessel. KRACEK and NEUVONEN's results are partly explained by the fact that their feldspar samples contained substantial amounts of calcium, resulting in a CaF_2 precipitate. The other substances noted in their experiments, although apparently not crystalline feldspar, may have been incompletely-reacted acid-leached feldspar. The use of water-elutriated fines as samples and the use of gelatin capsules to contain the samples are recognized as sources of error in HF solution calorimetry (COUGHLIN, 1962), in that part of the sample may become armored by gelatin or a precipitate. The present use of an internal sample container constructed of inert materials, and the use of relatively coarse-grained samples appears to promote complete reaction.

(b) Thermometry

The temperature sensor of the calorimeter is a copper resistance thermometer having a sensitivity of 1100 microvolts per degree, and the heater used for electrical calibration of the calorimeter is a manganin coil. The heater and thermometer are both wound as bifilar coils directly on the outer surface of the calorimeter (Fig. 4), and are thus protected from corrosion by the acid—a problem frequently encountered in earlier solution calorimeters. This design also ensures that the thermometer integrates the temperature over the *outer* surface of the calorimeter vessel, and that the superheating effects on the surface due to the heater are smaller in magnitude and more uniformly distributed (see for example GUNN, 1964) and therefore can be conveniently measured. This arrangement of heater and thermometer provides considerable improvement in the accuracy of evaluating the heat-exchange corrections.

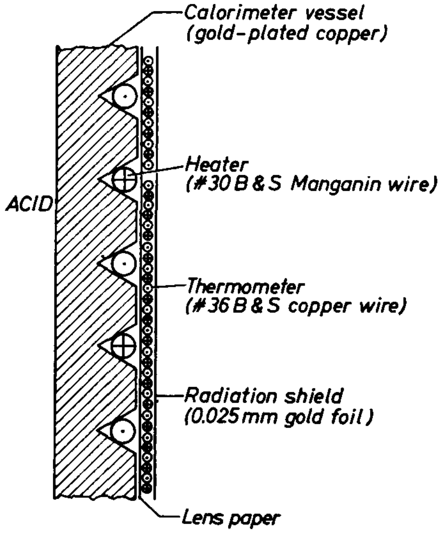

Fig. 4. Heater and thermometer configuration

The copper thermometer was calibrated in November, 1963 at the ice point (0.00 °C) and against a platinum resistance thermometer (MEYERS, 1932, Serial No. 231) which had been calibrated at fixed points of the International Practical Temperature Scale of 1948 (IPTS-48; STIMSON, 1961) by the National Bureau of Standards. For calibration of the copper thermometer, the plunger rod of the calorimeter (ROBIE, 1965, Fig. 1) was removed and the platinum thermometer was inserted directly into the calorimeter vessel which contained distilled water. The copper-platinum calibration points were obtained near 16, 30, 37, 55, and 69 °C. A least-squares fit to the original calibration data gave the following new formulation:

$$R_\theta = R_0\,[1 + 4.25122\,(10^{-3})\,\theta + 13.0159\,(10^{-7})\,\theta^2 - 1.32596\,(10^{-8})\,\theta^3] \tag{2}$$

for the copper thermometer, where θ denotes temperature on IPTS-48. The coefficients in (2) were obtained by fitting the quantity $[(R_\theta/R_0) - 1]/\theta$ as a simple power series in θ. This numerical procedure has the effect of forcing all copper resistance values to be based on the measured resistance at the ice point ($R_0 = 262.59910 \pm 0.00025$ ohms). A formulation of higher than third order is not warranted by the data. Equation (2) reproduces IPTS-48 accurately within ± 0.01% from 0 to 70 °C, and supercedes that in WALDBAUM (1966, p. 79) which was obtained by graphical methods.

(c) Reduction of data

The appropriate heat-exchange correction equations for an isoperibolic (temperature of surroundings held constant) calorimeter were derived from the relations given by COOPS, JESSUP, and VAN NES (1956) and are summarized in WALDBAUM (in prep.). The equations take advantage of the fact that our heat-exchange modulus, k, is considerably less than that of air-jacketed calorimeters of similar size (COUGHLIN, 1962), so that the temperature-time curves are linear over periods of 100 to 200 minutes (five times longer than the actual rating periods). In other hydrofluoric-acid solution calorimeters (TORGESON and SAHAMA, 1948; HUMMEL and SCHWIETE, 1959; FITZSIMMONS and KIRKBRIDE, 1970) the value of k is so large that the temperature-time curves show noticeable curvature even within one-half degree of the adiabatic temperature of the system. As a result, such experimental data must be converted to a logarithmic form and re-plotted (COUGH-

LIN, 1962) which makes 'real-time' evaluation of the temperature-time curves difficult and is an additional source of error in final reduction of the data. The present calorimeter represents a significant improvement over the air-jacketed calorimeter because the data needed for computing the uncorrected temperature rise and heat-exchange corrections can be obtained directly from the recorder charts.

In correcting the observed temperature rise for heat exchange, the heat capacity and k of the calorimeter were not assumed to be constant from one experiment to the next (as is often the procedure), but were computed from new calibration data obtained in each run. An additional small correction was added to the usual heat-exchange correction (NEWTON's cooling law) to account for superheating of the outer surface of the calorimeter (COLE *et al.*, 1960; WALDBAUM, 1966; STOUT, 1968) during electrical calibration. Superheating occurs because the heater is located between the thermometer and the wall of the calorimeter vessel (Fig. 4), so that the thermometer and radiation shields, as well as the copper vessel and its contents, are heated. Since the electrical heating is not transferred instantaneously to the fluid inside the vessel, the outer surface of the calorimeter tends to superheat by about 0.04 °C above the temperature of the fluid. The need to correct for this effect arises from the fact that it is the temperature of the *outer* surface that is referred to in the NEWTON's law corrections. This correction amounted to $+0.02$ percent of the total temperature rise compared with an average of ± 0.4 percent contributed by the simple NEWTON's law correction alone.

The heat-exchange correction for dissolution was computed directly by trapezoidal integration of data recorded at 30-second intervals over periods of $^1/_2$ to 3 hours. The magnitudes of the corrections are listed in Tables 5 through 8 as percentage of the corrected temperature rise.

The heat capacity of the acid and solid parts of the calorimeter vary with temperature during a run, and this variation must be taken into account when assigning the heat of solution to a specific temperature. The temperature coefficient of the heat capacity of the calorimeter was determined in several separate experiments, and appears to be the same for the system *before* release of the sample as that of the system *after* sample release, although a difference might be expected due to a slight change in the level of the fluid and due to the change in state of the sample from crystal to ionic species. The value of 0.436 cal deg^{-2} obtained here compares favorably with (and is expectedly somewhat larger due to gold, teflon, copper, and other materials

Table 5. *Heat of solution data for Amelia albite and Na derivatives*

Sample number	Description*	$\frac{K}{K+Na}$	Run	Mass**	Temp. on IPTS-68	% Correction due to heat exchange	$-H_{sol}$ at T_i, T_f	$-\bar{H}_{sol}$ (kcal/mole) at mean T
6314	Low albite, Nc – 400 mesh	0.0	153	1.08490 g	39.13558 °C 39.81303	0.39	2391.30 j/g 2390.67	149.883** 149.819
6314	(as above)	0.0	154	1.08328	39.03041 39.70847	0.13	2389.49 2390.05	149.769 149.780
6306	– 200/+ 325 mesh Nc	0.0	123	1.08171	49.04939 49.73331	– 1.23	2390.10 2397.55	149.808 150.250
6321	– 325/+ 400 mesh Nc	0.0	124	1.08197	49.19687 49.87126	– 0.13	2390.47 2390.54	149.830 149.811
6314	(as above)	0.0	125	1.08312	49.19022 49.86551	– 0.01	2392.34 2393.75	149.947 150.012
6314	(as above)	0.0	152	1.08104	48.79961 49.48100	– 0.98	2394.38 2393.83	150.076 150.017
6314	(as above)	0.0	127	1.08453	59.26687 59.93919	0.44	2397.46 2398.04	150.268 150.281
6321	(as above)	0.0	128	1.07949	59.21878 59.88977	– 0.06	2391.60 2392.10	149.901 149.909
6454	Low albite EDNc: 910, 24, NaCl – 160/+ 200 mesh	0.0	122	1.08226	48.93366 49.62938 48.93366 49.62938	– 2.92 – 3.00	2394.58 2394.34 2392.48 2394.87	150.088 150.048 149.956 150.082
6406 C1	High albite ANc: 1060, 668	0.0	141	0.39905	49.58145 49.83327	0.78	2439.05 2440.14	152.868 152.927
6406 C1	(as above)	0.0	145	0.50252	49.56458 49.87914	1.19	2430.29 2426.53	152.320 152.073
6411	$NaAlSi_3O_8$ glass FNc: 1325, 1	0.0	143	0.49919	49.64375 49.98236	0.59	2617.50 2616.49	164.054 163.977
6411	(as above)	0.0	146	0.47455	49.42226 49.74723 49.74723	– 0.17	2624.96 2621.39 2620.94	164.521 164.284 164.256

* Symbols in parentheses indicate synthesis history. See footnote and details in Tables 1 and 3. Minus 400-mesh fraction here does not include particles remaining suspended in *n*-propyl alcohol after 5 minutes settling-time.

** Masses corrected to vacuum: density of feldspar 2.59; density of weights 7.8 g/cm^3. Formula weights are based on 1966 atomic weights and atomic fractions in col. 3, assuming that the phases consist of only $NaAlSi_3O_8$ (262.2245 g/mole) and $KAlSi_3O_8$ (278.3367 g/mole).

in the calorimeter) 0.31 cal deg^{-2} for the 940 g of 20.1% hydrofluoric acid alone (ROTH and TROITZSCH, 1932).

All electrical measurements were recorded to 8 figures, utilizing 6 digits from the potentiometer dials and 3 digits from the null-detector (chart) with one digit overlap between the two instruments. A minimum of 9 significant figures were carried through the computations

Table 6. *Heat of solution data for K derivatives of Amelia albite*

Sample number	Description	$\frac{K}{K + Na}$	Run	Mass*	Temp. on IPTS-68	% Correction due to heat exchange	$-H_{sol}$ at T_i, T_f	$-\overline{H}_{sol}$ (kcal/mole) at mean T
6452	Microcline	1.0	132	1.14683g	49.20659 °C 49.85753	− 0.05	2176.30 J/g 2178.90	144.756 144.906
6452	(as above)	1.0	134	0.30197	49.44567 49.61758	− 0.43	2173.89 2175.79	144.587 144.707
6452	(as above)	1.0	129	1.02354	59.29832 59.87820	0.15	2182.98 2183.17	145.199 145.191
6452	(as above)	1.0	130	1.14285	59.29376 59.94062	0.09	2180.59 2182.58	145.041 145.151
6457	Sanidine EDANc: 910,24, KCl	1.0	138	0.29937	49.63172 49.80394	0.21	2211.61 2211.31	147.096 147.070
6457	(as above)	1.0	144	0.25751	49.62931 49.77686	0.01	2200.34 2199.44	146.346 146.281
6460	$KAlSi_3O_8$ glass ED(6411): 910,24, KCl	0.967	140	1.22916	49.82345 50.57193	1.25	2369.88 2367.16	157.371 157.162
6460	(as above)	0.967	142	1.14000	49.34448 50.04541	0.51	2373.22 2371.92	157.591 157.479

* See notes in Table 5.

using a digital computer source program written in double-precision arithmetic (IBM 7094, 16 significant figures). Temperatures were computed from (2) by Newton-Raphson iteration: the residual of iteration was set at 0.1 μdeg. With the chart record and the use of double-precision arithmetic, we are reasonably certain of a precision of 7 significant figures in the computed temperatures and an accuracy of 0.00005 °C in the computed temperature differences.

The temperatures reported in this paper have been corrected to IPTS-68 (BARBER, 1969) using the following formulation:

$$\theta\,[0.101816595 - 1.498414\,(10^{-5})\,\theta]$$

$$= T'\,[0.101821571 - 1.503389\,(10^{-5})\,T'] - 6\,(10^{-8}) \qquad (3)$$

where T' is in °C and refers to a hypothetical platinum resistance thermometer calibrated on IPTS-68 (t' of BARBER, 1969). Equation (3) is given in a form equivalent to combining (62) and (63a) of DOUGLAS (1969), and can be used with θ's obtained from any IPTS-48 platinum thermometer from the ice point to the antimony point (derivation of the coefficients in the above equation will be discussed in a subsequent paper). Equation (9) of BARBER (1969) was used in the final step of correcting the data to IPTS-68.

(d) Results

The calorimetric data obtained in this study summarized in Tables 5 through 8 represent the results of 64 heat-of-solution experiments having two or more heat-capacity determinations (electrical calibrations) in each experiment. From each heat capacity, a value of H_{sol} was calculated from the corrected temperature rise of dissolution. These quantities, given in j/g in the tables, are assigned to the initial and final temperatures of dissolution in accord with ROSSINI (1956). These are the basic calorimetric results and are independent of the choice of atomic weights or the chemical analyses. The values in the last column of the tables are expressed as the defined calorie, equal to exactly 4.1840 joules, and were calculated with the assumption that the compositions of these samples are precisely on the $(Na,K)AlSi_3O_8$ join. No corrections were made for phase impurities (none were detected) or for minor element content. All sample weights are corrected to true mass. The values in kcal/mole are assigned to the mean temperature of dissolution (in run 153 of Table 5, for example, 39.4743 °C). The data were obtained at 1 atm (1.013 bar) pressure.

Temperature dependence and grain-size effects

The data in Table 5 provide a tentative estimate of the dependence of the heats of solution of low albite and microcline on the mean temperature of dissolution. Least-squares formulations of the data gave

$$\overline{H}_{sol} = -149.263\,(\pm .13) - 0.0137\,(\pm .0025)\,T \text{ kcal/mole} \qquad (4)$$

for low albite (samples 6306, 6314, and 6321), and

$$\overline{H}_{sol} = -142.688\,(\pm .12) - 0.0414\,(\pm .0022)\,T \text{ kcal/mole} \qquad (5)$$

for microcline (sample 6452), where T is in °C. The temperature coefficients in (4) and (5) enable us to compare the present results with those of KRACEK and NEUVONEN (1952) obtained at 74.7 °C.

Equations (4) and (5) refer to heats of solution where the initial temperature of the sample is the same as the acid. Previous heat of solution measurements on quartz (summarized by HUMMEL and SCHWIETE, 1959) have given some indication of the variation of the

Table 7. *Heat of solution data for Amelia microcline Na and K derivatives and homogenized mixtures**

Sample number	$\frac{\text{K}}{\text{K}+\text{Na}}$	Run	Mass	T_i, T_f on IPTS-68	% Correction due to heat exchange	$-H_{sol}$ at T_i, T_f	$-\bar{H}_{sol}$ (kcal/mole) at mean T
6444	.0150	82	1.01844g	49.37341°C 50.00360	0.42	2379.73j/g 2381.98	149.294 149.412
	.0150	83	1.00369	49.40396 50.02353	0.74	2382.37 2383.10	149.459 149.483
	.0150	84	0.92218	49.36777 49.93981	0.20	2381.67 2380.83	149.415 149.341
6450	.1084	103	0.90958	49.66249 50.22085	0.63	2368.67 2368.80	149.451 149.439
	.1084	104	0.91270	49.35605 49.92012	0.16	2373.63 2372.62	149.764 149.680
	.1084	115	0.99991	49.46246 50.07846	0.55	2373.77 2375.91	149.774 149.887
6451	.1977	101	1.01085	49.38780 50.00523	0.81	2359.72 2359.10	149.699 149.637
	.1977	102	1.00986	49.27074 49.89208	0.04	2359.20 2360.09	149.666 149.700
	.1977	111	1.01068	49.22938 49.85113	−0.07	2357.80 2357.73	149.577 149.550
	.1977	112	1.01307	49.31198 49.93466	0.27	2362.29 2361.94	149.862 149.818
6447	.3014	95	0.90319	49.56344 50.11103	0.74	2341.11 2339.97	149.452 149.360
	.3014	96	0.90226	49.36948 49.91860	0.31	2338.36 2338.97	149.276 149.296
	.3014	110	1.02422	49.33836 49.96110	0.51	2341.59 2343.39	149.484 149.576

* See notes in Table 5.

Table 7. *(Continued)*

Sample number	$\frac{K}{K+Na}$	Run	Mass	T_i, T_f on IPTS-68	% Correction due to heat exchange	$-H_{sol}$ at T_i, T_f	$-\bar{H}_{sol}$ (kcal/mole) at mean T
6448	.3958	97	1.00274g	49.48725 °C 50.08645	1.45	2323.56 j/g 2324.21	149.177 149.198
	.3958	98	1.00382	49.43971 50.04357	0.61	2319.00 2320.18	148.884 148.938
	.3958	113	1.05249	49.30887 49.94567	0.20	2322.95 2326.27	149.138 149.329
6441	.4741	91	1.00986	49.40316 50.00769	0.42	2306.08 2305.76	148.751 148.708
	.4741	92	1.01262	49.39019 49.99353	0.87	2302.57 2303.40	148.524 148.556
	.4741	119	0.99671	49.31217 49.91003	0.17	2300.70 2304.61	148.404 148.634
6453E	.4998	57	0.70490	49.21070 49.63733	−0.77	2300.04 2300.12	148.586 148.575
	.4998	58	0.70568	49.49792 49.91885	0.71	2300.16 2301.25	148.622 148.649
6434	.6240	88	1.00315	49.62456 50.21154	1.44	2273.63 2275.38	147.970 148.063
	.6240	89	1.00271	49.53406 50.12077	1.16	2269.42 2267.03	147.696 147.519
	.6240	90	1.00359	49.40199 49.99293	0.63	2270.93 2272.35	147.794 147.865
	.6240	108	1.00020	49.40564 49.99519	0.49	2272.28 2271.42	147.881 147.805
6449	.6868	99	1.00395	49.52233 50.10766	0.98	2255.42 2256.42	147.330 147.375
	.6868	100	1.00427	49.41577 50.00420	0.33	2252.60 2254.31	147.146 147.237

Table 7. *(Continued)*

Sample number	$\frac{K}{K+Na}$	Run	Mass	T_i, T_f on IPTS-68	% Correction due to heat exchange	$-H_{sol}$ at T_i, T_f	$-\overline{H}_{sol}$ (kcal/mole) at mean T
6449	.6868	116	1.02239g	49.21872 °C 49.82120	−0.27	2253.70 j/g 2255.96	147.218 147.345
6442	.7953	93	1.00561	49.41826 49.99945	0.54	2226.70 2227.64	146.384 146.426
	.7953	94	1.00826	49.43884 50.02193	0.42	2224.97 2224.88	146.270 146.244
	.7953	114	1.00885	50.41597 50.97645	4.37	2220.34 2220.90	145.966 145.983
6439	.8945	105	1.00219	49.60126 50.16784	1.50	2200.15 2198.83	145.479 145.372
	.8945	106	1.02059	49.29704 49.88166	−0.03	2193.61 2194.66	145.046 145.096
	.8945	107	1.01388	49.40139 49.97892	0.61	2195.36 2200.56	145.162 145.486
	.8945	120	1.00109	49.27591 49.85035	0.02	2202.10 2201.30	145.608 145.535
6427	.9954	80	1.00469	48.89646 49.47958	−2.48	2167.39 2167.41	144.155 144.136
6438	.9955	86	1.01182	49.36587 49.93677	0.04	2163.14 2161.49	143.873 143.744
	.9955	87	1.00573	49.33469 49.90302	−0.02	2164.94 2167.97	143.992 144.175
	.9955	121	1.00479	49.24444 49.81431	−0.19	2168.84 2171.54	144.252 144.412
6446	.9987	117	1.01105	49.33454 49.90551	0.11	2167.81 2165.44	144.211 144.033
	.9987	118	1.02557	49.32321 49.90290	0.15	2170.86 2169.13	144.414 144.279

Table 8. *Heat of solution data for a mechanical mixture of Na and K derivatives**

Sample number	$\frac{K}{K+Na}$	Run	Mass	T_i, T_f on IPTS-68	% Correction due to heat exchange	$-H_{sol}$ at T_i, T_f	$-\bar{H}_{sol}$ (kcal/mole) at mean T
6453 A	.4998	55	1.12270g	49.35378 °C	0.86	2273.70j/g	146.888
				50.01447		2275.34	146.971
	.4998	56	0.70092	49.42266	0.82	2276.11	147.040
				49.83559		2277.10	147.089
	.4998	71	0.71008	49.51411	0.60	2269.80	146.632
				49.93188		2270.07	146.634

* See notes in Table 5.

heats of solution of silicates with temperature, but the principal effect that was observed in these studies resulted from the fact that the sample and acid were initially at different temperatures. The present results give a more accurate indication of the effect of temperature on the heat of solution alone, inasmuch as the small differences in heats of solution are not masked by the "sensible heat" correction (COUGHLIN, 1962) and other uncertainties introduced by the use of gelatin capsules.

The present data also indicate that feldspar samples having particle sizes up to 100 microns can be used in hydrofluoric acid solution calorimetry provided the calorimeter has low heat-exchange characteristics and good thermal stability lasting for several hours. Although the use of different size fractions affected the reaction times by a factor of three (50 minutes in runs 124 and 125; 160 minutes in run 122) and the heat-exchange corrections differ by as much as two orders of magnitude (Table 5, column VII), the heats of solution are in excellent agreement, showing no systematic variation within the limits of experimental error (compare FITZSIMMONS and KIRKBRIDE, 1970, on silica glass). These results are important in eliminating several possible sources of systematic error which can result from surface effects such as adsorption of water, surface hydrolysis, and surface energy of the crystals when water-elutriated fines are used as samples (KRACEK and NEUVONEN, 1952; COUGHLIN, 1962).

Enthalpy and internal energy of Al-Si disordering

The difference in molar *enthalpy* between highly-ordered and highly-disordered polymorphs of $NaAlSi_3O_8$ and $KAlSi_3O_8$ are obtained from the differences in their respective heats of solution (Table 9). Kracek and Neuvonen (1952) obtained hydrofluoric acid calorimetric data at 74.7 °C on natural Amelia low albite, natural low albite from Varuträsk, Sweden, and on these same materials annealed for 2040 hours at 1050 °C (F. C. Kracek, unpublished notes, v. 9, p. 32). They obtained 2.20 ± 0.16 kcal/mole for the difference between the high and low Amelia albite, and 2.43 ± 0.30 kcal/mole for the Varuträsk samples, compared with 2.60 ± 0.30 kcal/mole obtained in this study.

Holm and Kleppa (1968) measured the heats of solution at 698 °C of Amelia low albite and the same material heated 840 hours at 1045 ± 5 °C using a lead-cadmium-borate melt as the solvent. They also obtained high-temperature heat-capacity data on their low albite and on sample 6406-Cl of this study. Combining the two sets of measurements, Holm and Kleppa obtained 2.6 ± 0.35 kcal/mole at 25 °C. No comparable data for microcline and sanidine have been obtained previously. More recent studies with the same calorimeter and some of the same samples (Hovis *et al.*, 1970) reproduced the differences between high and low albite, and between sanidine and microcline within 50 cal/mole.

Table 9. *Summary of heats of solution of Na and K derivatives (cal/mole at 49.7 °C)*

$NaAlSi_3O_8$	$\bar{H}_{sol}$	$\Delta\bar{H}$	$\Delta\bar{E}$	$KAlSi_3O_8$	$\bar{H}_{sol}$	$\Delta\bar{H}$	$\Delta\bar{E}$
Amelia albite and derivatives							
Low albite	−149,944 ± 70			Microcline	−144,746 ± 50		
		2,603 ± 300	2,603 ± 300			1,952 ± 320	1,952 ± 320
High albite	−152,547 ± 290			Sanidine	−146,698 ± 310		
		11,658 ± 340	11,658 ± 340			10,703 ± 340	10,703 ± 340
Glass	−164,205 ± 160			Glass	−157,401 ± 170		
Derivatives of Amelia microcline (amazonite)							
Low albite (Eq. 7, $N_2 = 0$)	−149,408 ± 32	—	—	Microcline ($N_2 = 1$)	−144,178 ± 32	—	—

The differences in molar *internal energy* of the highly ordered and disordered polymorphs in Table 9 were calculated from the relation

$$\bar{E} = \bar{H} - P\bar{V}$$

using the volume data in Table 1. From these values of $\Delta\bar{E}$ and $\Delta\bar{V}$, the values of $\Delta\bar{H}$ calculated for 10 kbar and 25 °C are 2.72 kcal for high—low albite and 2.00 kcal/mole for sanidine—microcline, neglecting the differences in compressibilities of the polymorphs (which have not as yet been determined).

The effect of temperature on the enthalpy difference of high and low albite is much larger than the effect of pressure. HOLM and KLEPPA (1968) measured 3.4 ± 0.25 kcal at 698 °C and when extrapolated to higher temperatures (WALDBAUM, 1968) yield 3.9 kcal/mole at 1127 °C, or an increase of 50% from 25 °C to the melting point of high albite. These results and the thermal expansion data of STEWART and VON LIMBACH (1967) indicate that the vibrational properties of high and low albite must differ considerably at high temperatures as well as at room temperature (compare spectral data of LAVES and HAFNER, 1956, 1962).

Enthalpy and internal energy of the glass phases

The heats of solution of the glasses of $NaAlSi_3O_8$ and $KAlSi_3O_8$ composition are summarized in Table 9. KRACEK and NEUVONEN (1952) obtained similar data at 74.7 °C on glass prepared from Amelia albite and Varuträsk albite. The differences in the glasses and the respective *low* albites (corrected to 49.7 °C) are 11.65 and 12.53 kcal/mole compared with 14.26 ± 0.20 kcal/mole for Amelia albite and its glass determined in this study. HLABSE and KLEPPA (1968) measured 15.08 ± 0.38 kcal for Amelia (low) albite and its glass, each dissolved in a lead borate melt at 691 °C. Their results yield 14.07 ± 0.40 kcal/mole when corrected to 49.7 °C.

The only comparable data for $KAlSi_3O_8$ are the hydrofluoric acid calorimetric results of TAMMANN (1903), who obtained a difference of 23 ± 5 kcal/mole between a "microcline" and its glass, and by MÜLERT (1912) who measured a difference of 28 ± 5 kcal/mole between an "adularia" and its glass. The reasons for the large discrepancies with the present results are not known.

Differences in the internal energies of glass and crystal (Table 9) are again nearly identical to the enthalpy differences at 1 bar. The available data suggest, however, that effects of temperature and pressure on $\Delta \bar{H}$ are considerably greater than noted above for the crystals (White, 1919; Vergano *et al.*, 1967; Chao and Bell, 1969; Bell and Roseboom, 1969, p. 159), but much experimental work is still needed to determine the effects of annealing and densification on the enthalpies, heat capacities, compressibilities, and thermal expansions of liquids in this system.

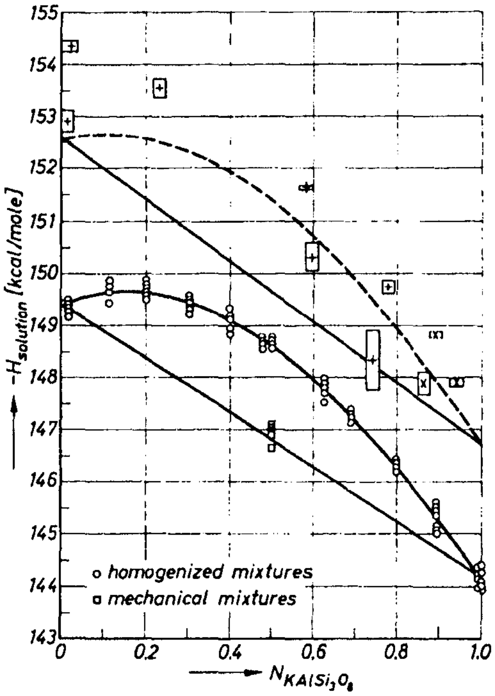

Fig. 5. Heats of solution of natural and synthetic alkali feldspar crystalline solutions in 20.1% hydrofluoric acid referred to 49.7 °C. Solid curve represents equation (7). Dashed curve refers to sanidine solutions, calculated from data for end members in Table 9 and enthalpy of mixing parameters at 1 bar obtained from (2a) and (2b) of Waldbaum and Thompson (1969). Straight lines refer to mechanical mixtures of the end members calculated from (7) by setting the last two coefficients equal to zero, and from the high albite and sanidine values. Rectangles represent data of Kracek and Neuvonen (1952) corrected to 49.7 °C (width of bars corresponds to ±1.5 mole-%); × denotes samples containing low-albite lamellae, and are therefore not strictly comparable to sanidine solutions

Low-albite—microcline crystalline solutions

Calorimetric data for the microcline crystalline solutions (Table 7) are plotted as open circles in Fig. 5. It is clear that the magnitude of the heat of solution does not vary linearly with the K/(K + Na) ratio of the crystal, as KRACEK and NEUVONEN's data in Fig. 5 might be interpreted. Least-squares fits to the data in Table 7 yield the following quadratic and cubic formulations (in kcal/mole):

$$\bar{H}_{\text{sol}} = -149.527(\pm.011) + 5.414(\pm.012)N_2 - 7.075(\pm.044)N_1N_2 \quad (6)$$

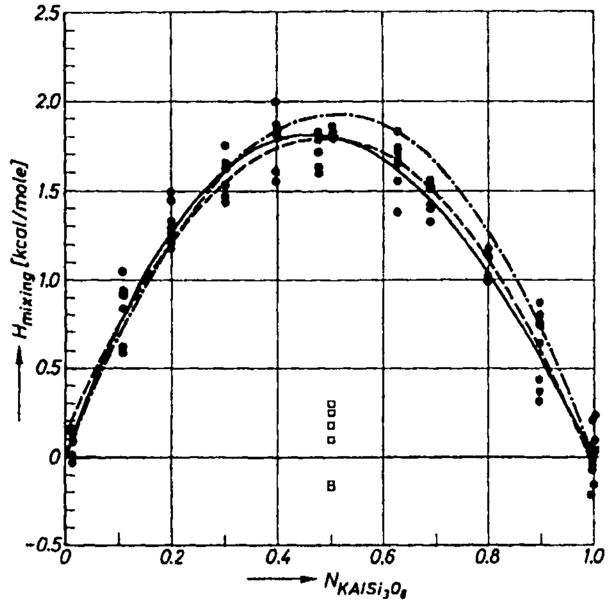

Fig. 6. Enthalpies of mixing of microcline crystalline solutions at 1 bar. Solid curve represents (7) or (8) as in Fig. 5. Circles (solutions) and squares (mixture) represent difference between observed values in Tables 7 and 8 and the line of mechanical mixtures for microclines in Fig. 5. Dashed curve refers to the difference between quadratic equation (5) and the same line of mechanical mixtures. Dot-dash curve is calculated from enthalpy parameters based on 2-phase data (11)

and

$$\bar{H}_{\text{sol}} = -149.408\ (\pm\ .013) + 5.230\ (\pm\ .017)\ N_2$$
$$-\ 5.928\ (\pm\ .085)\ N_1N_2^2 - 8.457\ (\pm\ .099)\ N_2N_1^2 \quad (7)$$

The standard deviation of (6) is ± 0.15 kcal, and is ± 0.13 kcal for (7). The residuals were not improved by going to higher-order fits, although more closely spaced data might eventually warrant it. Equation (7) is plotted in Fig. 5.

The heat of solution of an equimolar mechanical mixture of K and Na exchange derivatives of Amelia microcline was also determined in this study (Table 8). The data fall close to the hypothetical line representing the heats of solution of mechanical mixtures as calculated from (7) and shown in Figs. 5 and 6.

The heats of solution of the pure K and Na derivatives of Amelia *microcline* (amazonite) calculated from (7) are less negative than the results for Amelia *albite* and its K derivative (6452) in Table 9 by about 550 cal/mole. It is possible that some of this difference can be attributed to the rubidium or lead content of 6427 or 6444 (Tables 2 and 3). Judging from the poorer overall quality of the x-ray patterns of the microcline derivatives (WALDBAUM, 1966, Figs. 2—5), the differences in heats of solution may also be due to structural defects at grain boundaries within the perthite or, less likely, due to twinning.

Excess mixing properties of microcline and other simple Na-K crystalline solutions

The heat of solution data of the microcline crystalline solutions yield from (7) a simple two-parameter Margules formulation (THOMPSON, 1967) for the excess enthalpy of mixing, $\bar{H}_{ex}$, at 1 atm:

$$\bar{H}_{ex[1\,atm]} = 5928\ N_1N_2^2 + 8457\ N_2N_1^2\ \text{cal/mole}\ . \qquad (8)$$

Equation (8) is plotted as a solid curve in Fig. 6. The dashed curve in Fig. 6 is the difference between the quadratic formulation (6) and the line of mechanical mixtures computed from (7). The observed data shown in Fig. 6 are also referred to the same line of mixtures, and it is evident that the cubic equation (7) is a more precise fit to the data, particularly for Na-rich compositions.

The volume data obtained at 25 °C and 1 atm yield, from (1):

$$\bar{V}_{ex} = 0.1101\ N_1N_2^2 + 0.1101\ N_2N_1^2\ \text{cal/bar-mole} \qquad (9)$$

indicating positive volumes of mixing over the entire composition range. The values of the Margules parameters are similar in magnitude to those of sanidine crystalline solutions (WALDBAUM and THOMPSON, 1968).

Subtracting $P\bar{V}_{ex}$ from (8) as above gives the following relation for the excess internal energy of K-Na mixing (at zero pressure):

$$\bar{E}_{ex} = 5928\ N_1N_2^2 + 8457\ N_2N_1^2\ \text{cal/mole}\ . \qquad (10)$$

The Margules parameters W_{E1} and W_{E2} are identical with the enthalpy parameters in (8) to the nearest calorie owing to the small $P\bar{V}_{ex}$ ($= P\bar{V}_{mix}$) contribution between 1 atm and zero pressure. It will be noted that the excess enthalpy, volume, and internal energy parameters obtained here are from direct physical measurements on bulk

Table 10

Internal energies of Na—K mixing of some crystalline silicates and halides

System	Source	W_{E1}	W_{E2}	$\bar{E}_{mix}/50:50$	T_c	N_{2c}
		(kcal/mole)		(kcal/mole)	(°C) (at 1 bar)	
$(Na,K)AlSi_3O_8$: *low albite, microcline* [highly ordered Al–Si distribution, $Z \simeq 0.9$]	calorimetry[a]	5.93	8.46	1.80	—	—
	2-phase data[b]	7.97	7.49	1.93	885	0.27
$(Na,K)AlSi_3O_8$: *adularia* [$Z \simeq 0.6$]	calorimetry[h]	8.02	8.02	2.01	—	—
$(Na,K)AlSi_3O_8$: *sanidine* [highly disordered Al–Si distribution, $Z \simeq 0.1$]	2-phase data[c]	6.33	7.67	1.75	648	0.33
	calorimetry[h]	6.0	6.0	1.5	—	—
$(Na,K)Al_2AlSi_3O_{10}(OH)_2$: *paragonite, muscovite*	2-phase data[d]	3.08	4.16	0.91	769	0.39
(Na,K)Cl: *halite, sylvite*	calorimetry[e]	3.68	4.66	1.04	—	—
	2-phase data[f]	5.76	8.18	1.74	499	0.35
(Na,K)Br	2-phase data[g]	5.64	4.83	1.31	399	0.38
(Na,K)I	2-phase data[g]	3.88	3.53	0.93	240	0.40

[a] This study.

[b] BACHINSKI and MÜLLER (1971, Table 9).

[c] THOMPSON and WALDBAUM (1969a).

[d] EUGSTER, ALBEE, BENCE, THOMPSON and WALDBAUM (1972).

[e] Calculations based on data of TICHELAAR (1956).

[f] THOMPSON and WALDBAUM (1969b), calculations based on data of BARRETT and WALLACE (1954).

[g] Calculations based on data of CHANH (1964).

[h] Based on preliminary results (WALDBAUM, unpublished data).

phases, and hence it is not possible to separate the effects of long-range and short-range ordering of the alkali atoms or of tetrahedral cations on these properties.

The internal energy of mixing of an equimolar microcline solution calculated from (10) is given in Table 10. For the same composition, $P\bar{V}_{ex}$ at 10 kbar is 1101/4 = 225 cal/mole. Although 225 cal is relatively small compared with $\bar{H}_{ex}$ (and almost within the uncertainty in the data), it will have a substantial effect on the calculated phase relations at 10 kbar (compare Figs. 1 and 2 of Waldbaum and Thompson, 1969).

Since the work of Eastman and Milner (1933), it has generally been accepted that the excess entropy of mixing of crystalline solutions is near zero, and if not zero, more likely negative (due to short-range ordering). If the excess entropy of Na-K mixing of microcline solutions is assumed to be zero, we calculate from (8) a critical temperature, T_c, of 1649 °C and a critical composition of 39 mole-% $KAlSi_3O_8$ ($N_{2c} = 0.39$) at 1 atm. However, this is not in agreement with the critical temperatures suggested by the alkali homogenization results of Orville (1967), the two independent studies of Bachinski and Müller (1971), and this study, all of which indicate that T_c for microcline solutions is less than 950 °C at 1 atm. (A critical temperature *higher* than 1649 °C results if the excess entropy is assumed to be negative.) To obtain a critical temperature that agrees with the direct observations on the two-phase region, it is necessary to assume relatively large, positive excess-entropy parameters.

A simple polythermal Margules formulation of Bachinski's two-phase data (method I of Thompson and Waldbaum, 1969a) does in fact yield positive values of W_{S1} and W_{S2} on the order of +4 cal/deg-mole, and an excess entropy of +1 cal/deg-mole at the 1:1 composition. The sign of this result implies that the excess entropy of homogeneous microcline crystalline solutions is predominantly vibrational (Thompson and Waldbaum, 1969b, p. 685). Phase-equilibrium data alone, however, do not permit one to determine how the total excess entropy is partitioned between short-range ordering (clustering) and excess vibrational entropy. Heat capacity data for the crystalline solutions are needed to separate these effects.

The excess enthalpy of mixing also obtained from the two-phase data is given by

$$\bar{H}_{ex} = 7973\ (\pm\ 990)\ N_1 N_2^2 + 7491\ (\pm\ 380)\ N_2 N_1^2\ \text{cal/mole} \qquad (11)$$

which is in good agreement with that obtained by solution calorimetry (see Table 10 and dot-dash curve in Fig. 6).

Table 10 also compares mixing properties of some other Na-K crystalline solutions: sanidines, micas, and halides. The similarities in the mixing properties and critical compositions would seem to be unusual for phases having such widely different structures, chemical compositions, and other physical properties. Although any conclusions based on Table 10 must be regarded as tentative, it appears that atoms or structural groups other than K and Na exert relatively little influence on the mixing properties of simple (one alkali site) K-Na crystalline solutions.

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