Calorimetric investigation of the excess entropy of mixing in analbite-sanidine solid solutions: lack of evidence for Na,K short-range order and implications for two-feldspar thermometry

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Abstract

Heat capacities (5–380 K) have been measured by adiabatic calorimetry for five highly disordered alkali feldspars ($Ab_{99}Or_1$, $Ab_{85}Or_{15}$, $Ab_{55}Or_{45}$, $Ab_{25}Or_{75}$, and Ab_1Or_{99}). Positive heat capacity deviations from a linear combination of the end-member heat capacities, which are present mostly at very low temperatures, result in an excess entropy for intermediate compositions. The excess entropy at 298.15 K is well described by the symmetric expression $S^{xs}_{298} = X_{Ab}X_{Or}(10.3\pm0.3 \text{ J/mol·K})$. For practical calculations, the entropy and enthalpy of mixing can be regarded as temperature-independent above room temperature.

The excess entropy and volume of mixing have been combined with solvus determinations to obtain a calculated enthalpy of mixing. Because the measured enthalpies of mixing are essentially coincident with those calculated from the solvus determinations, no short-range order for the alkali site could be inferred.

The new data for the alkali feldspars have been combined with recent data for plagioclase feldspars to derive an expression for the two-feldspar thermometer that is consistent with present knowledge of the thermodynamics of these solid solutions.

$$T_K = \frac{(X_{Or}^{AF})^2(18810 + 17030 X_{Ab}^{AF} + 0.364P) - (X_{An}^{Pl})^2(28230 - 39520 X_{Ab}^{Pl})}{10.3 (X_{Or}^{AF})^2 + 8.3143\ln\left\{\dfrac{(X_{Ab}^{Pl})^2(2 - X_{Ab}^{Pl})}{X_{Ab}^{AF}}\right\}}$$

where the mole fractions refer to the ternary system and P is in bars. Temperatures calculated from this expression tend to be higher than those calculated from previous formulations.

Introduction

In most discussions of the mixing properties of mineralogic solid solutions, the heat capacity is implicitly assumed to vary linearly with composition. As a result, the mixing properties at constant pressure are defined entirely by entropy and enthalpy terms that are temperature independent. For many solutions of geologic interest, the inclusion of temperature-dependent terms is not required for the representation of available data; however, the necessity for such terms has been demonstrated conclusively, through calculations based on phase-equilibrium, data for pyrope-grossular garnets (Hensen *et al.*, 1975) and for alkali feldspar (*e.g.*, Thompson and Waldbaum, 1968; Thompson and Hovis, 1979).

Haselton and Westrum (1979) showed that the heat capacities of pyrope-grossular garnets are nonlinear with respect to composition at temperatures below about 120 K. These heat-capacity deviations from a linear combination of the end-member heat capacities result in an excess

entropy of mixing. For this garnet join, the excess entropy and enthalpy of mixing can be assumed to be constant at higher temperatures, because there the heat-capacity deviations are most probably negligible. When volume terms were added to the temperature-dependent activity expressions derived from calorimetry, the results of Hensen et al. (1975) were easily reproduced in calculations.

Recently, Thompson and Hovis (1979) refined the earlier calculations (Thompson and Waldbaum, 1968) of excess entropy parameters for high structural state alkali feldspars by combining measured enthalpies (Hovis and Waldbaum, 1977) and volumes of mixing (Hovis, 1977) with phase-equilibrium data (Orville, 1963; Iiyama, 1965, 1966; Delbove, 1971; and Traetteberg and Flood, 1972). Their calculations indicate that an excess entropy of mixing, which is greatest for potassic compositions, is necessary to make the available thermodynamic data self-consistent. The maximum magnitude of the predicted excess entropy is approximately half of the expected configurational entropy of mixing; clearly, it cannot be neglected in phase-equilibrium calculations.

Thompson and Waldbaum (1969a) noted that, although short-range order (SRO) could be an important source of deviations from the ideal configurational entropy of mixing, the principal source of an excess entropy is probably vibrational. If the vibrational contributions are significant, as they appear to be in the alkali feldspars, they can be measured quite readily and precisely by modern low-temperature adiabatic calorimetry. The contributions can be positive or negative; they are expected, if present, only at low temperatures, because the effects of structure on the heat capacities generally diminish as temperature increases.

With regard to SRO in the alkali distribution, Thompson and Hovis (1979) noted that this effect could only decrease the entropy of mixing because of the non-random configuration. They suggested that short-range ordering might be identified through phase-equilibrium calculations once the excess entropy attributable to vibrational contributions had been quantified. In practice, however, because of the slope of the function relating configurational entropy to order, the energy effect associated with small amounts of ordering from a disordered configuration will be very difficult to detect unambiguously.

The environment of the Na ion in highly disordered alkali feldspars has features that affect interpretations relating heat capacities to structure. In analbite, the Al/Si feldspar framework collapses about the alkali site, producing triclinic symmetry, because the Na ion is apparently too small to maintain a more symmetric site. At 35 to 40 mole percent $KAlSi_3O_8$, the structure becomes monoclinic (Hovis, 1980; Kroll et al., 1980). In a rigorous thermodynamic description of high structural state alkali feldspar solid solutions, terms describing the symmetry change should be included. At present, however, phase equilibrium data are not sufficiently precise to permit a meaningful quantitative formulation. At very high temperatures, topochemically monoclinic albite becomes symmetrically monoclinic (Okamura and Ghose, 1975; Kroll et al., 1980), but most applications to geological problems and the most useful phase-equilibrium data are for triclinic albite.

The mode of residence of Na on the alkali site may also affect the entropy. The results of several X-ray diffraction studies (Ribbe et al., 1969; Prewitt et al., 1976) indicate that the Na ion in analbite may vibrate about two or more nodes, which are probably determined by the occupancy of the adjacent tetrahedral sites (Brown and Fenn, 1979). Alternatively, the X-ray data could result from an unexpectedly large vibrational amplitude about a single node. From structural refinements at a variety of temperatures, Prewitt et al. (1976) have provided good evidence for the space average, but whether the number of nodes present is 2 or 4 is still unknown (Brown and Fenn, 1979; Prewitt et al., 1976). An X-ray structure refinement of $Ab_{42}Or_{58}$ (Fenn and Brown, 1977) provides some evidence for the existence of multiple nodes for the Na ion in Or-rich (Ab = $NaAlSi_3O_8$, Or = $KAlSi_3O_8$) solid solutions. Unlike the Na ion, the K ion apparently is centrally located in the alkali site; no indication of multiple nodes has been found. Both the change of symmetry and the probable existence of multiple nodes suggest that the vibrations related to the Na ion may result in unexpectedly large contributions to the heat capacity at temperatures less than 298 K.

A prodigious amount of work has been published on the solvus relations of high-structural-state alkali feldspar solid solutions since the initial study by Tuttle and Bowen (1958). Luth (1974) and Parsons (1978) have discussed the attempts by Orville (1963), Luth and Tuttle (1966), Seck (1972), Goldsmith and Newton (1974), Smith and Parsons (1974), and others to locate the binodal solvus directly at a variety of pressures up to 15 kbar. Many determinations of the distribution coefficients of Na and K between alkali feldspars and aqueous alkali halide solutions or fused alkali chlorides are available (Orville, 1963; Iiyama, 1965, 1966; Delbove, 1971; Traetteberg and Flood, 1972; Lagache and Weisbrod, 1977; and Merkel and Blencoe, 1980). Volumes of mixing for high alkali feldspar, prepared by alkali ion exchange from natural starting materials and from glasses and gels, have been measured by Donnay and Donnay (1952), Orville (1967), Luth and Querol-Suñé (1970), and Hovis (1977). Hovis and Waldbaum (1977) measured enthalpies of mixing for an alkali exchange series prepared from Al/Si disordered Amelia albite. Low-temperature (15–375 K) heat capacities for analbite and sanidine prepared from Amelia albite have been measured (Openshaw et al., 1976). Heat capacities from 320 to 1000 K have been measured by differential scanning calorimetry on the same samples (Hemingway et al., 1981). The heat capacities of analbite and sanidine are the same within analytical error (0.2 percent to 380 K, 1 percent from 380 to 1000 K) at temperatures above ~220 K.

X-ray evidence of Al/Si ordering is cited in some of the

phase equilibrium studies mentioned above. Knowledge of the mixing properties of low structural state alkali feldspars is necessary for assessing this additional variable. The low feldspar solvus has been located independently by Bachinski and Müller (1971) and Delbove (1975) using ion exchange in fused alkali halides and homogenization-unmixing techniques. Enthalpies of mixing were measured for a low alkali feldspar series by Waldbaum and Robie (1971). Volumes of mixing have been given by Orville (1967), Waldbaum and Robie (1971), and Hovis and Peckins (1978).

In the present work, low-temperature heat capacities (5–380 K) have been measured for a series of five high structural state alkali feldspars. The excess entropy arising from excess heat capacities has been quantified and has been combined with phase-equilibrium data to examine the possibility of short-range order in the alkali site. The evaluation leads to mixing expressions for high alkali feldspars that, together with recent measurements for plagioclase feldspars (Newton et al., 1980), permit a reformulation of the two-feldspar thermometer.

Experimental

Samples

Two of the samples, $Ab_{99}Or_1$ and Ab_1Or_{99}, are identical to samples used for low-temperature heat-capacity measurements by Openshaw et al. (1976). These samples were derived from clear cleavage fragments of low albite from the Rutherford Mine, Amelia County, Virginia. The analbite was prepared by heating the low albite at 1325 K for 755 hours. The sanidine was obtained by ion-exchanging a second analbite sample in fused KCl at 1138 K for 31–40 hours. The measurements on these samples were repeated to improve the internal consistency of this study. Also, Openshaw et al. (1976) had encountered difficulties at the lowest temperatures with the particular calorimeter and adiabatic shield combination used for their set of measurements.
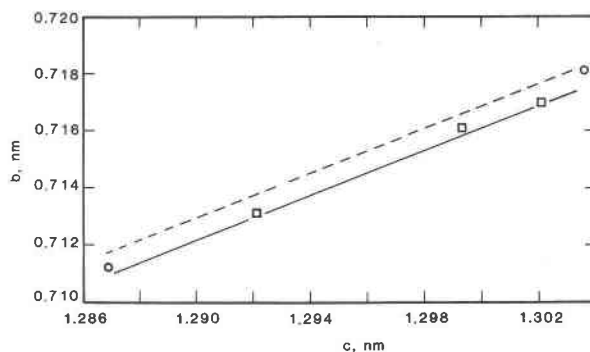

Fig. 1. b vs. c cell parameters. The three intermediate compositions are represented by squares. The parameters measured by Openshaw et al. (1976) for analbite and sanidine are indicated by circles. The solid line connects the preferred parameters for disordered analbite and sanidine as chosen by Stewart and Wright (1974), the dashed line indicates approximately 90% disorder.

The $Ab_{85}Or_{15}$ was prepared by homogenizing appropriate amounts of analbite and sanidine at one atmosphere according to methods described by Hovis (1977). Briefly, the mixed powders were pressed into platinum crucibles and heated in air for approximately 420 hours at 920°C. After low-temperature measurements were completed on this sample, additional sanidine was added to a portion of the $Ab_{85}Or_{15}$ to yield a bulk composition of $Ab_{55}Or_{45}$. Again after homogenization and measurements, $Ab_{25}Or_{75}$ was prepared similarly from the $Ab_{55}Or_{45}$. Because of the large quantity of material needed at each composition (~35 g), the feldspar powders were remixed every 2 days in order to promote chemical homogeneity.

Cell parameters for the three intermediate compositions (Table 1) were refined from powder-diffraction data by using the least-squares program LCLSQ (Burnham, 1962) as modified by Blasi (1979). The diffraction data were collected with a powder diffractometer at a scan speed of $0.25° 2\theta$ min^{-1} with $CuK\alpha$ radiation. Silicon of $a = 0.543054$ nm (Parrish, 1960) was used as an internal standard. Also listed are the cell parameters for analbite (7001) and sanidine (71105-71108) as determined by Openshaw et al. (1976). The four sets of parameters that were presented for sanidine by Openshaw et al. have been averaged, and the standard deviations listed for sanidine reflect this averaging. The cell parameters are in good agreement with previous determinations (e.g., Hovis, 1977). All these samples are highly disordered in the tetrahedral sites as demonstrated by a plot of b against c. (Figure 1). The solid line connects the limiting values for high structural state alkali feldspars chosen by Stewart and Wright (1974); the dashed line for $t_10 + t_1m = 0.55$ indicates approximately 90% Al/Si disorder. Despite the multiple homogenizations, the distribution of the ions on the tetrahedral sites of the solid solutions is essentially identical to the ion distributions in the analbite and sanidine.

Table 1. Cell parameters of calorimetric samples

Sample # X_{Or}	7001 0.01	8001 0.15	8008 0.45	8034 0.75	71105-8 0.99
a (nm)	0.8177(5)	0.8232(3)	0.8367(1)	0.8499(1)	0.8606(1)
b (nm)	1.2869(3)	1.2921(2)	1.2993(1)	1.3021(1)	1.3026(3)
c (nm)	0.7112(3)	0.7131(1)	0.7161(1)	0.7170(1)	0.7181(1)
α (°)	93.46(3)	92.55(2)	90.00	90.00	90.00
β (°)	116.51(2)	116.36(2)	116.13(1)	116.00(1)	116.01(1)
γ (°)	90.26(4)	90.09(3)	90.00	90.00	90.00
$V(nm^3)$	0.6681(3)	0.6787(2)	0.6989(1)	0.7132(1)	0.7235(3)

Number in parentheses is one standard deviation in terms of the least significant figure.

Table 2. Analyses of $Ab_{85}Or_{15}$, $Ab_{55}Or_{45}$, and $Ab_{25}Or_{75}$*

Sample	Analyzed bulk composition**	Number of analyses	Mean	Standard deviation	Range
$Ab_{85}Or_{15}$	84.9	27	90.8	3.3	98.1 – 82.3
$Ab_{55}Or_{45}$	56.0	22	57.8	8.4	84.5 – 50.3
$Ab_{25}Or_{75}$	26.7	25	26.8	2.0	33.5 – 24.5

* Compositions are expressed in terms of the molecular percentage of $NaAlSi_3O_8$.
**Analyses performed by N. Suhr of The Pennsylvania State University.

The bulk chemical compositions for the analbite and sanidine, listed by Openshaw et al. (1976, Table 1), are $Ab_{98.4}Or_{1.2}An_{0.4}$ and $Ab_{0.6}Or_{99.2}An_{0.2}$. Analyses performed by N. Suhr of The Pennsylvania State University of the intermediate compositions are listed in Table 2. To check the homogeneity of the three intermediate compositions, we analyzed 22 to 27 grains from each sample by electron microprobe. The analyses (Table 2) indicate some heterogeneity, and the means deviate from the nominal compositions. These results are not unexpected despite the relatively sharp X-ray diffraction peaks. Deviations of the means from the stated compositions probably reflect the method by which these samples were synthesized. When samples are very fine-grained, analysis of the rims is difficult; hence, the analyses are more representative of the core compositions. Additionally, the sanidine starting material is finer grained than is the analbite from which it was produced. This size reduction results from the alkali exchange process. Because of the sequence of sample preparation, subsequent samples are richer in potassium, and we would therefore expect that the smallest grains and the rims of the larger grains would be potassium-rich relative to the cores of the larger grains. Compositional heterogeneity decreases the observed excess heat capacities, but the observed heat capacities suggest that range of heterogeneity in these samples is not an important source of error. For investigations in which only a very limited amount of heterogeneity can be tolerated, sintering of alkali feldspar powders at 1 atmosphere may not produce sufficiently homogeneous samples.

Due to the method of synthesis, the concentrations of additional components in the intermediate compositions should be similar to the concentrations found in the analbite and sanidine. Our electron probe analyses show approximately the same $CaAl_2Si_2O_8$ (An) concentration as in the end-members. Waldbaum and Robie (1971) obtained emission spectrographic analyses for other elements on another sample of Amelia albite. Their results indicate that concentrations of additional elements are too small to be a significant source of error.

Calorimetry

The adiabatically shielded, low-temperature calorimeter and data-aquisition system have been described in detail (Robie and Hemingway, 1972; Robie et al., 1976). This calorimetric system was used for the measurements on analbite, sanidine, and $Ab_{85}Or_{15}$ and for some of the measurements on $Ab_{55}Or_{45}$. Additional measurements were made on the $Ab_{55}Or_{45}$ with the control and data-acquisition system modified for automatic operation. Although no changes were made to the cryostat and calorimeter, several electronic components were replaced, therefore, measurements were completed on the $Ab_{55}Or_{45}$ with both systems before the sample was removed from the calorimeter. The two data sets are identical within the precision of measurement, demonstrating that internal consistency was maintained despite the changes in the measurement system. After automation, the measurement precision was essentially unchanged at the lowest temperatures but decreased slightly above 55 K. All heat capacity data for the $Ab_{25}Or_{75}$ sample were collected with the automated system.

The sample weights in vacuo were 43.5737 g analbite, 29.0809 g sanidine, 33.0201 g $Ab_{85}Or_{15}$, 32.9870 g

Table 3. Experimental heat capacities for analbite

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
Series	1	Series	4	Series	7
299.90	205.3	26.72	10.17	170.11	136.2
302.59	206.5	29.79	12.84	175.43	139.8
307.33	208.6	32.93	15.76	180.72	143.3
313.15	211.0	36.50	19.20	186.08	146.7
		40.01	22.65	191.53	150.2
Series	2	43.34	26.02	196.91	153.5
		46.67	29.32	202.25	156.7
5.77	0.0774	50.89	33.79	207.69	159.8
6.53	0.1207			213.22	163.0
7.31	0.1836	Series	5	218.74	166.1
8.22	0.2747			224.23	169.2
9.23	0.4290	58.91	42.03	229.68	172.1
10.28	0.6276	65.10	48.08		
11.39	0.8988	71.61	54.48	Series	8
12.61	1.255	77.67	60.42		
13.93	1.738	83.18	65.76	234.50	174.7
15.33	2.349	88.75	71.04	239.73	177.5
16.84	3.102	95.05	76.87	244.99	180.2
18.53	4.081	101.58	82.76	250.33	182.9
20.14	5.135	107.71	88.14	255.77	185.5
21.95	6.397	113.53	93.18	261.29	188.2
24.49	8.346	119.10	97.88	267.18	191.0
27.43	10.77	123.86	101.8	273.91	194.2
		128.00	105.2	281.04	197.3
Series	3	132.66	108.9	288.25	200.6
				295.74	203.8
53.21	36.24	Series	6	303.44	206.9
58.76	41.82			311.05	210.0
65.29	48.19	137.83	113.0		
73.04	55.82	143.21	117.0	Series	9
		148.62	121.1		
		154.07	125.1	296.38	204.0
		159.52	128.9	303.67	207.1
		164.92	132.7	311.08	210.1
				318.58	213.0
				326.09	216.0
				333.64	218.9
				341.16	221.6
				348.66	224.2
				356.23	226.8
				363.78	229.3
				371.32	231.8

Table 4. Experimental heat capacities for analbite$_{85}$sanidine$_{15}$

Temp. (K)	Heat capacity (J/(mol·K))	Temp. (K)	Heat capacity (J/(mol·K))	Temp. (K)	Heat capacity (J/(mol·K))
Series 1		Series 4		Series 7	
307.23	209.5	57.91	42.01	208.98	161.3
314.17	212.3	61.46	45.56	214.81	164.7
321.13	215.1	65.71	49.76	220.80	168.0
Series 2		70.14	54.11	226.95	171.3
		Series 5		233.19	174.7
5.47	0.0042				
5.81	0.0162	56.49	40.58	Series 8	
6.30	0.0439	61.73	45.83	239.26	177.9
6.92	0.1071	66.94	50.97	245.18	181.0
7.73	0.1705	71.96	55.54	251.08	184.0
8.59	0.2973	76.72	60.60	257.05	186.9
9.39	0.4389	81.54	65.27	263.04	189.7
10.20	0.6043	86.61	70.13	269.01	192.6
11.15	0.8487	91.65	74.80		
12.16	1.152	96.59	79.30	Series 9	
13.33	1.559	101.48	83.65	275.38	195.5
14.66	2.124	106.43	88.00	282.30	198.7
16.17	2.850	111.40	92.30	289.28	201.9
Series 3		116.38	96.53	296.31	204.9
15.79	2.651	121.42	100.7	303.39	207.7
17.70	3.686	126.54	104.9	310.54	210.7
19.62	4.929	Series 6		317.67	213.5
21.31	6.135	131.87	109.2	324.76	216.4
23.22	7.599	137.46	113.5	331.80	219.1
25.67	9.622	143.10	117.8	339.01	221.7
28.37	12.01	148.82	122.1	346.42	224.4
31.34	14.79	154.55	126.2	353.86	227.0
34.57	17.98	160.25	130.3	Series 10	
38.20	21.65	165.88	134.2	361.33	229.5
42.31	25.83	171.44	138.0	368.84	232.1
46.85	30.45	177.02	141.7		
51.22	35.02	182.54	145.2		
55.91	39.89	187.67	148.5		
		192.77	151.7		
		198.19	155.0		
		203.70	158.3		

but it was not observed in this study. The monoclinic structure may be quenched at low temperatures or the transition may have no obvious heat-capacity signature.

Table 5. Experimental heat capacities for analbite$_{55}$sanidine$_{45}$

Temp. (K)	Heat capacity (J/(mol·K))	Temp. (K)	Heat capacity (J/(mol·K))	Temp. (K)	Heat capacity (J/(mol·K))
Series 1		Series 7		Series 12	
300.72	206.3	220.16	167.9	5.25	0.0436
307.82	209.3	225.14	170.7	5.72	0.0535
Series 2		230.08	173.4	6.12	0.0510
107.63	90.76			6.41	0.0942
111.44	93.99	Series 8		6.64	0.1240
115.46	97.33	220.82	168.4	6.94	0.1231
120.01	101.1	225.77	170.7	7.29	0.1652
Series 3		230.69	173.6	7.71	0.2163
51.81	38.14	235.62	176.1	8.33	0.2542
55.79	41.99	240.54	178.7	8.92	0.3401
60.56	46.92	245.44	181.4	9.64	0.4882
65.27	51.60	250.32	183.8	10.53	0.6866
70.38	56.76	255.19	185.8	11.58	0.9856
75.57	61.72	260.04	188.1	12.78	1.335
80.70	66.53	264.92	190.7	14.15	1.890
85.52	71.10	269.83	192.9	15.70	2.631
90.08	75.35	274.73	194.8	17.43	3.638
94.62	79.37	279.62	197.2	19.37	4.971
99.09	83.48	284.50	199.5	21.55	6.649
103.50	88.12	289.35	202.1	23.99	8.743
Series 4		294.19	203.9	26.72	11.28
109.92	92.73	299.02	205.7	29.75	14.30
114.24	96.22	303.85	207.7	33.15	17.78
118.66	99.86	308.66	209.6	37.23	22.27
122.89	103.4	313.45	211.6	40.91	26.22
127.00	106.7	318.24	213.8	44.00	29.58
131.11	109.8	323.02	215.2	47.88	33.45
135.18	113.2	Series 9		53.04	39.12
139.23	116.0	300.72	206.3	58.57	44.80
143.25	119.3	307.82	209.3	Series 13	
147.90	122.5	Series 10		311.77	210.7
153.02	126.1	119.54	100.6	316.40	212.2
157.79	129.5	126.19	106.0	321.56	214.6
162.66	132.7	107.63	90.76	327.14	216.6
167.83	136.2	111.44	93.99	332.57	218.8
Series 5		115.46	97.33	337.99	220.6
79.20	65.24	120.01	101.1	343.41	222.9
83.49	69.40	Series 11		348.87	224.9
87.61	72.98	5.67	0.0480	Series 14	
91.72	76.96	6.27	0.0663	337.39	220.7
96.82	81.51	6.94	0.1220	343.36	223.0
102.06	85.93	7.72	0.2001	Series 15	
107.74	90.96	8.60	0.3029	79.78	65.63
113.40	95.65	9.60	0.4324	84.59	70.27
119.03	100.3	10.63	0.7041	89.40	74.72
124.63	104.6	11.79	1.022	94.35	79.19
130.18	109.0	13.10	1.472	Series 16	
135.69	113.6	14.57	2.089	145.63	120.9
141.17	117.7	16.19	2.905	151.65	125.2
146.62	121.7	17.99	3.995	Series 17	
152.04	125.7	19.96	5.408	216.24	165.7
157.43	129.5	22.05	7.065	222.21	169.0
162.79	133.0	24.32	9.045	228.20	172.3
168.12	136.4	26.85	11.41	234.22	175.5
173.40	139.9	29.69	14.23	Series 18	
178.69	143.3	32.86	17.56	263.09	189.7
183.95	146.6	36.43	21.41	269.11	192.7
Series 6		40.43	25.71	275.15	195.2
189.51	150.3	44.81	30.38	281.15	198.0
194.67	153.6	49.63	35.50	Series 19	
199.74	156.5			347.65	224.5
204.85	159.3			354.72	226.9
209.99	162.2			361.75	229.4
215.12	165.1			368.76	231.5
				375.73	233.9

Ab$_{55}$Or$_{45}$, and 30.3261 g Ab$_{25}$Or$_{75}$. Approximately 4×10^{-5} moles of dry He gas were added after evacuating the calorimeter to aid thermal equilibration. At temperatures greater than 10 K, the fraction of the total heat capacity attributable to the sample was between 40% and 60%. The formula weights of 262.225 g/mol for NaAlSi$_3$O$_8$ and 278.333 g/mol for KAlSi$_3$O$_8$ are based on the 1975 values for the atomic weights (Commission on Atomic Weights, 1976). Temperatures are referred to the International Practical Temperature Scale of 1968 (IPTS-68).

Results

The heat-capacity measurements for the five alkali-feldspar compositions are listed in chronological order in Tables 3–7. These measurements have been corrected for curvature but not for the compositional deviation from the alkali feldspar binary caused by the small amount of An component. No anomalous heat capacity behavior was observed for any of the samples. The temperature of the monoclinic-to-triclinic transition for topochemically monoclinic alkali feldspars decreases with increasing Or content. The transition is projected to occur at approximately 200 K in the Ab$_{55}$Or$_{45}$ sample (Kroll et al., 1980),

Table 6. Experimental heat capacities for analbite₂₅sanidine₇₅

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
Series 1		Series 2		Series 4	
5.95	0.0976	131.24	111.4	324.59	215.8
6.10	0.1101	136.78	115.7	329.42	217.8
6.35	0.1053	142.29	119.4	334.23	219.5
6.93	0.1474	147.77	123.4	339.05	221.7
7.34	0.1603	153.21	127.4	343.91	223.3
7.87	0.1936	158.62	131.0	348.78	225.6
8.49	0.2525	164.01	134.9	358.52	229.0
9.17	0.3406	180.02	145.6	363.38	229.8
10.00	0.4796			368.22	231.7
11.00	0.6986	Series 3		373.04	232.4
13.38	1.396			377.85	234.4
14.82	1.984	185.33	148.7		
16.42	2.771	195.87	155.0	Series 5	
18.21	3.846	200.88	157.1		
20.22	5.269	210.91	163.2	169.32	138.1
22.47	7.057	215.90	166.2	174.70	141.9
24.99	9.309	220.93	169.3	179.89	145.1
27.83	12.06	225.96	172.2	185.06	148.5
31.01	15.40	230.99	174.3	190.33	151.3
34.57	19.35	236.01	177.1	200.82	157.6
38.54	24.15	241.02	179.4	206.04	160.6
42.97	28.94	246.01	182.1	211.25	163.2
		251.00	185.0	216.44	166.1
Series 2		255.97	187.2	221.61	169.3
		260.92	189.4	226.77	172.2
46.56	32.72	265.91	191.8	231.93	174.8
51.59	38.20	270.91	193.9	237.08	177.8
55.79	42.60	275.90	196.0	242.22	180.2
60.89	48.05	280.88	198.5		
67.01	54.38	285.84	200.0	Series 6	
73.00	60.28	290.78	202.4		
79.07	66.34	295.72	204.5	335.04	220.4
85.11	72.07	300.64	206.9	339.81	221.7
91.08	77.46	305.55	208.9	344.64	223.4
97.01	82.68	310.45	210.9	349.49	225.3
102.85	87.30	315.34	212.5	354.35	226.9
108.63	92.67	320.22	214.7	359.21	229.0
114.35	97.45			364.06	230.8
120.02	102.0			368.91	231.8
125.65	106.7			373.75	233.6
				378.56	235.7

framework. If this linkage is energetically unfavorable, Al/Si short-range order may reduce this assumed configurational contribution to the zero-point entropy. The ideal zero point entropy attributable to the alkali ions is $-R(X_{Ab}\ln X_{Ab} + X_{Or}\ln X_{Or})$ where X_{Ab} and X_{Or} are the mole fractions of $NaAlSi_3O_8$ and $KAlSi_3O_8$.

Calculations based on phase-equilibrium studies of the reaction albite = jadeite + quartz (Holland, 1980; and Hemingway et al., 1981) indicate no evidence that existence of multiple nodes for the Na ion requires the inclusion of still another zero-point configurational entropy term. By extension, configurational entropy contributions associated with Na nodes in high alkali-feldspar solid solutions (Fenn and Brown, 1977) are not expected. Further, the activation energy for the movement of the Na ion between nodes on a given alkali site must be relatively small. If the activation energy is small, this disordering would result in a measurable heat capacity. Either the heat capacity due to the disordering of alkali ions on the nodes is spread over a large temperature range, or the occupation of a specific node must be

Table 7. Experimental heat capacities for sanidine

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
Series 1		Series 4		Series 9	
300.10	206.0	233.03	175.0	331.41	218.3
305.82	208.4			338.95	221.0
312.66	211.1	Series 4		346.48	223.6
320.09	214.1			354.03	226.3
		177.02	142.8		
Series 2		182.44	146.3	Series 10	
		187.91	149.7		
51.90	39.33	193.42	153.0	361.51	228.8
56.12	43.88	198.95	156.3	369.00	231.2
60.64	48.50	205.21	159.9	376.35	233.6
65.13	52.95	212.18	163.8		
69.95	57.67	219.12	167.6	Series 11	
74.94	62.53	226.07	171.3		
79.96	67.36			6.68	0.0708
85.03	72.09	Series 5		7.71	0.1501
90.10	76.75			8.47	0.2209
95.21	81.27	239.08	178.2	9.20	0.3334
100.31	85.71	246.01	181.7	9.98	0.4449
105.37	89.98			10.87	0.6034
110.42	94.22	Series 6		11.89	0.8027
115.50	98.42			13.00	1.098
120.60	102.6	253.03	185.1	14.25	1.528
125.70	106.6	260.05	188.4	15.66	2.132
122.16	103.8	267.05	191.7	17.20	2.958
127.44	108.0			18.90	4.082
132.91	112.2	Series 7		20.83	5.584
138.54	116.5			22.98	7.427
144.12	120.5	273.95	194.8	25.31	9.664
149.64	124.5	280.89	197.9		
155.20	128.3	287.88	201.0	Series 12	
		294.91	204.0		
Series 3				27.63	12.05
		Series 8		30.44	15.09
160.76	132.0			33.55	18.64
166.32	135.8	301.66	206.7	37.06	22.69
171.85	139.6	308.91	209.6	41.00	27.18
		316.40	212.6	45.40	32.08
		323.89	215.5	50.30	37.48
				55.39	43.05

For the measurements on sanidine, Ab₅₅Or₄₅, and Ab₂₅Or₇₅, the scatter in the C_p data is larger than expected below ~12 K. Because of the fine grain size of the samples other than analbite, the scatter may be related to helium adsorption. Though the scatter affects the accuracy of the heat-capacity values at the lowest temperatures, the error in $S_{298}-S_0$ is <0.01%, which is too small to influence our conclusions.

The heat-capacity data were extended smoothly to 0 K by means of a plot of C_p/T vs. T^2. Smoothed values of C_p, $(S_T - S_0)$, $(H_T - H_0)/T$ and $-(G_T - H_0)/T$ at selected temperatures are given in Tables 8–12. Their estimated accuracy is 0.2%. The tabulated entropies do not include zero-point contributions arising from the "frozen-in" disorder of the Al and Si in the tetrahedral sites and the disorder of Na and K in the alkali site. If a totally disordered Al,Si tetrahedral distribution is assumed, then the zero-point entropy attributable to Al/Si disorder is $S_0 = -4R(0.75\ln 0.75 + 0.25\ln 0.25) = 18.70$ J/mol·K for each of the five compositions. We should note that total Al,Si disorder requires that Al–O–Al linkages be present in the

Table 8. Smoothed thermodynamic functions for analbite

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_P°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN			J/(mol·K)	
5	0.050	0.015	0.011	0.004
10	0.579	0.159	0.123	0.036
15	2.195	0.654	0.506	0.148
20	5.042	1.647	1.259	0.388
25	8.752	3.157	2.374	0.783
30	13.03	5.124	3.787	1.337
35	17.75	7.483	5.441	2.042
40	22.65	10.17	7.283	2.887
45	27.65	13.13	9.270	3.859
50	32.83	16.31	11.36	4.943
60	43.07	23.21	15.81	7.404
70	52.87	30.59	20.40	10.18
80	62.69	38.29	25.08	13.21
90	72.21	46.23	29.79	16.44
100	81.35	54.31	34.49	19.82
110	90.14	62.48	39.15	23.33
120	98.63	70.69	43.76	26.93
130	106.8	78.91	48.29	30.61
140	114.6	87.11	52.76	34.36
150	122.1	95.28	57.13	38.15
160	129.3	103.4	61.42	41.97
170	136.2	111.4	65.61	45.82
180	142.8	119.4	69.72	49.69
190	149.2	127.3	73.74	53.56
200	155.3	135.1	77.66	57.45
210	161.2	142.8	81.50	61.33
220	166.8	150.5	85.25	65.21
230	172.3	158.0	88.92	69.08
240	177.6	165.4	92.50	72.94
250	182.7	172.8	96.01	76.79
260	187.6	180.1	99.44	80.62
270	192.3	187.2	102.8	84.44
280	196.9	194.3	106.1	88.23
290	201.3	201.3	109.3	92.01
300	205.4	208.2	112.4	95.77
310	209.7	215.0	115.5	99.51
320	213.7	221.7	118.5	103.2
330	217.5	228.3	121.4	106.9
340	221.2	234.9	124.3	110.6
350	224.7	241.4	127.1	114.2
360	228.0	247.7	129.9	117.8
370	231.4	254.0	132.6	121.4
380	234.7	260.2	135.2	125.0
273.15	194.1	189.5	103.8	85.63
298.15	204.9	206.9	111.8	95.08

sanidine and analbite are the higher precision of the present measurements, especially at very low temperatures, and the overall consistency of measurements for the series of five compositions. When the values are corrected to end-member composition and the zero-point entropy of 18.70 J/mol·K is included, $S_{298} = 225.7 \pm 0.4$ J/mol·K for analbite and 232.8 ± 0.4 J/mol·K for sanidine. The values of S_{298} for analbite and sanidine from Openshaw et al. (1976) are 226.4 ± 0.4 and 232.9 ± 0.4 J/mol·K respectively. Our values for the analbite and sanidine entropies do not differ significantly from those of Openshaw et al., because the C_p deviations of opposite sign largely cancel.

The smoothed heat-capacity deviations of the three intermediate compositions, $Ab_{85}Or_{15}$, $Ab_{55}Or_{45}$, and $Ab_{25}Or_{75}$, compared with linear combinations of the

Table 9. Smoothed thermodynamic functions for analbite$_{85}$sanidine$_{15}$

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_P°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN			J/(mol·K)	
5	0.037	0.011	0.008	0.003
10	0.580	0.139	0.110	0.029
15	2.283	0.652	0.514	0.138
20	5.204	1.678	1.294	0.384
25	9.063	3.240	2.449	0.791
30	13.52	5.279	3.916	1.363
35	18.42	7.727	5.634	2.093
40	23.49	10.52	7.548	2.969
45	28.56	13.58	9.601	3.975
50	33.75	16.85	11.76	5.098
60	44.18	23.93	16.29	7.638
70	54.00	31.47	20.97	10.50
80	63.79	39.33	25.72	13.61
90	73.30	47.39	30.48	16.91
100	82.35	55.59	35.22	20.37
110	91.10	63.85	39.90	23.95
120	99.58	72.14	44.52	27.62
130	107.7	80.43	49.07	31.36
140	115.5	88.70	53.54	35.16
150	122.9	96.93	57.92	39.01
160	130.1	105.1	62.21	42.88
170	137.0	113.2	66.41	46.78
180	143.6	121.2	70.51	50.69
190	149.9	129.1	74.53	54.61
200	156.1	137.0	78.45	58.54
210	161.9	144.7	82.29	62.46
220	167.5	152.4	86.04	66.37
230	173.0	160.0	89.70	70.28
240	178.3	167.5	93.28	74.17
250	183.4	174.8	96.79	78.05
260	188.3	182.1	100.2	81.91
270	193.0	189.3	103.6	85.76
280	197.6	196.4	106.8	89.58
290	202.2	203.4	110.1	93.39
300	206.4	210.4	113.2	97.17
310	210.5	217.2	116.3	100.9
320	214.6	224.0	119.3	104.7
330	218.4	230.6	122.2	108.4
340	222.1	237.2	125.1	112.1
350	225.6	243.7	127.9	115.7
360	229.1	250.1	130.7	119.4
370	232.5	256.4	133.4	123.0
380	235.9	262.6	136.0	126.6
273.15	194.8	191.6	104.6	86.96
298.15	205.9	209.1	112.6	96.47

coupled to other local features of the structure, as suggested by Brown and Fenn (1979).

The heat capacity measurements presented here for analbite and sanidine differ significantly from those given previously by Openshaw et al. (1976) on the same samples. The accuracy claimed in both the earlier study and the present one for values above 50 K is 0.2 percent. The differences between the smoothed values of the two data sets for analbite and sanidine have been plotted in Figure 2. Unlike the entries in Table 8 and 12, the plotted values were corrected to end member compositions. Above 125 K, the analbite measurements agree. The deviations below 125 K are disconcerting but not unreasonable in view of the differences in equipment used in the two studies. Above 250 K the sanidine measurements of Openshaw et al. (1976) are much lower (0.3–0.6%) than the present ones. We are unable to explain the difference. Our principal reasons for preferring the present data for

analbite and sanidine heat capacities, are shown in Figure 3. Any deviation from zero indicates an excess heat capacity (C_p^{xs}) and contributes to the excess entropy. Because the curves are the heat capacities divided by absolute temperature, the excess entropy is the integrated area beneath the curves. It is clear, especially for the $Ab_{55}Or_{45}$, that the largest contributions to the excess entropy of mixing are at low temperatures. Above 298 K, the deviations are within the experimental precision of 0.1% except the curve for $Ab_{85}Or_{15}$. If $(C_p/T)^{xs}$ decreases to zero at temperatures above 298 K, then the enthalpy and entropy of mixing can be regarded as temperature independent functions of composition in calculations of geologic interest. As discussed below, the assumption of $C_p^{xs} = 0$ at $T > 298$ K is quite reasonable. If C_p^{xs} is not negligible at high temperatures, then the quantity of heat

Table 10. Smoothed thermodynamic functions for analbite$_{55}$sanidine$_{45}$

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN		J/(mol·K)		
5	0.045	0.015	0.010	0.005
10	0.565	0.148	0.114	0.034
15	2.291	0.656	0.513	0.144
20	5.440	1.711	1.319	0.391
25	9.669	3.362	2.551	0.811
30	14.55	5.549	4.136	1.412
35	19.87	8.188	6.001	2.187
40	25.25	11.19	8.070	3.121
45	30.57	14.48	10.28	4.199
50	35.98	17.96	12.56	5.399
60	46.33	25.45	17.34	8.110
70	56.38	33.34	22.20	11.15
80	65.82	41.50	27.07	14.43
90	75.28	49.81	31.91	17.90
100	84.07	58.21	36.70	21.51
110	92.79	66.67	41.44	25.23
120	101.1	75.10	46.06	29.03
130	108.9	83.50	50.60	32.90
140	116.7	91.86	55.05	36.81
150	123.9	100.2	59.41	40.76
160	130.6	108.4	63.67	44.73
170	137.7	116.5	67.82	48.72
180	144.1	124.6	71.89	52.71
190	150.6	132.6	75.86	56.70
200	156.7	140.4	79.75	60.69
210	162.2	148.2	83.54	64.68
220	167.8	155.9	87.25	68.65
230	173.3	163.5	90.87	72.61
240	178.3	171.0	94.41	76.55
250	183.6	178.3	97.87	80.47
260	188.1	185.6	101.3	84.38
270	193.0	192.8	104.6	88.26
280	197.4	199.9	107.8	92.12
290	202.4	206.9	111.0	95.96
300	206.0	213.9	114.1	99.78
310	210.1	220.7	117.1	103.6
320	214.4	227.4	120.1	107.3
330	217.7	234.1	123.0	111.1
340	221.3	240.6	125.8	114.8
350	225.2	247.1	128.6	118.5
360	228.9	253.5	131.4	122.1
370	231.9	259.8	134.0	125.8
380	235.4	266.0	136.7	129.4
273.15	194.4	195.1	105.6	89.48
298.15	205.7	212.6	113.5	99.07

Table 11. Smoothed thermodynamic functions for analbite$_{25}$sanidine$_{75}$

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN		J/(mol·K)		
5	0.045	0.013	0.010	0.003
10	0.485	0.130	0.101	0.029
15	2.064	0.595	0.463	0.133
20	5.103	1.570	1.211	0.358
25	9.311	3.143	2.394	0.749
30	14.31	5.272	3.954	1.318
35	19.82	7.888	5.823	2.065
40	25.49	10.90	7.925	2.978
45	31.09	14.23	10.19	4.041
50	36.48	17.79	12.55	5.236
60	47.08	25.38	17.43	7.953
70	57.35	33.41	22.40	11.01
80	67.21	41.72	27.39	14.33
90	76.49	50.18	32.34	17.84
100	85.12	58.69	37.19	21.50
110	93.72	67.20	41.94	25.27
120	102.1	75.72	46.60	29.12
130	110.3	84.22	51.19	33.03
140	117.9	92.67	55.68	36.99
150	125.0	101.0	60.07	40.98
160	132.0	109.3	64.35	44.99
170	138.8	117.5	68.53	49.02
180	145.3	125.7	72.61	53.05
190	151.4	133.7	76.60	57.09
200	157.2	141.6	80.49	61.12
210	162.7	149.4	84.27	65.14
220	168.5	157.1	87.97	69.14
230	173.9	164.7	91.59	73.13
240	179.1	172.2	95.13	77.10
250	184.2	179.6	98.59	81.06
260	189.0	187.0	102.0	84.99
270	193.5	194.2	105.3	88.90
280	197.9	201.3	108.5	92.79
290	202.1	208.3	111.7	96.65
300	206.4	215.2	114.8	100.5
310	210.6	222.1	117.8	104.3
320	214.4	228.8	120.7	108.1
330	218.1	235.5	123.6	111.8
340	221.9	242.1	126.5	115.6
350	225.6	248.5	129.3	119.3
360	229.1	254.9	132.0	123.0
370	232.3	261.3	134.6	126.6
380	235.6	267.5	137.3	130.2
273.15	195.2	196.4	106.3	90.13
298.15	206.0	214.0	114.2	99.78

capacity data required for phase equilibrium calculations would increase greatly.

Discussion

Most considerations of nonideality in mineral solutions, especially feldspars, have involved quadratic and cubic series expansions whose properties have been discussed by Thompson (1967). To date, the data for alkali feldspars do not require more complicated expressions. A quadratic polynominal was fitted to the five (S_{298}–S_0) values by least squares. The resulting symmetrical representation for the excess entropy of mixing, plotted in Figure 4, is $S_{298}^{xs} = X_{Ab} X_{Or} (10.3\pm0.3$ J/mol·K); a higher order fit is unwarranted. The compositional heterogeneity of our samples (Table 2), which is greatest for $Ab_{55}Or_{45}$, could diminish the observed excess entropy of that sample by about 0.1 J/mol·K. The error would be

Table 12. Smoothed thermodynamic functions for sanidine

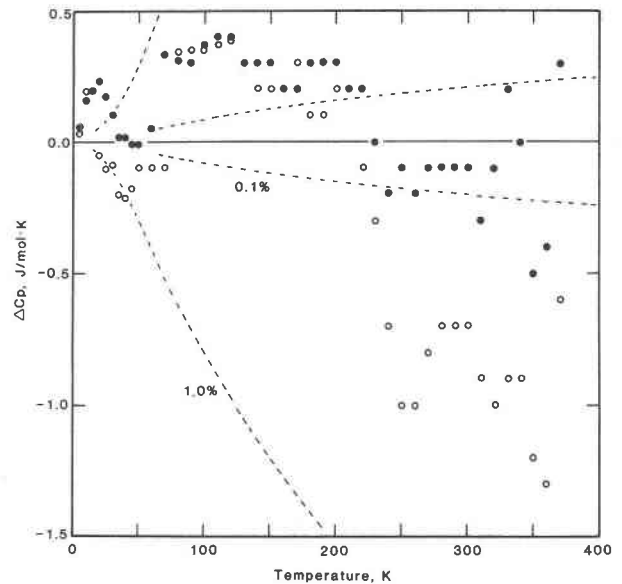| TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_P°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN		J/(mol·K)		
5	0.039	0.012	0.009	0.003
10	0.412	0.115	0.088	0.027
15	1.854	0.502	0.392	0.109
20	4.916	1.407	1.099	0.309
25	9.357	2.961	2.288	0.673
30	14.61	5.123	3.896	1.227
35	20.31	7.800	5.830	1.970
40	26.05	10.89	8.000	2.888
45	31.64	14.28	10.32	3.963
50	37.14	17.90	12.72	5.174
60	47.87	25.64	17.71	7.932
70	57.72	33.76	22.72	11.04
80	67.40	42.10	27.70	14.40
90	76.65	50.58	32.63	17.95
100	85.45	59.11	37.48	21.64
110	93.87	67.65	42.22	25.43
120	102.1	76.18	46.87	29.31
130	110.0	84.66	51.42	33.24
140	117.5	93.09	55.88	37.21
150	124.7	101.4	60.23	41.22
160	131.5	109.7	64.47	45.24
170	138.3	117.9	68.62	49.27
180	144.7	126.0	72.67	53.31
190	151.0	134.0	76.63	57.35
200	156.9	141.9	80.49	61.37
210	162.6	149.7	84.27	65.39
220	168.1	157.4	87.95	69.40
230	173.4	164.9	91.55	73.39
240	178.7	172.4	95.07	77.36
250	183.7	179.8	98.52	81.31
260	188.4	187.1	101.9	85.24
270	193.0	194.3	105.2	89.15
280	197.5	201.4	108.4	93.03
290	201.9	208.4	111.5	96.89
300	206.0	215.3	114.6	100.7
310	210.1	222.2	117.6	104.5
320	214.0	228.9	120.6	108.3
330	217.8	235.5	123.5	112.1
340	221.4	242.1	126.3	115.8
350	224.9	248.6	129.1	119.5
360	228.3	255.0	131.8	123.2
370	231.5	261.3	134.4	126.8
380	234.7	267.5	137.0	130.4
273.15	194.8	196.6	106.2	90.37
298.15	205.6	214.1	114.1	100.0

Fig. 2. Deviation plot comparing the smoothed heat capacities of Openshaw *et al.* (1976) and the present measurements for analbite (●) and sanidine (○). The present measurements are the reference values, and the dashed lines indicate relative deviations of 0.1% and 1.0%. Where the points for analbite and sanidine overlap, only the analbite points have been plotted.

the enthalpy of mixing data of Hovis and Waldbaum (1977) and Hovis (unpublished data).

Short-Range Order (SRO)

If SRO in the alkali site of high alkali feldspars is significant for practical calculations, its presence should be reflected in the phase-equilibrium studies. The movement of alkali ions is relatively fast, unlike ordering of Al and Si in the tetrahedral sites; indeed, the solvus determinations depend on a reasonable alkali ion exchange rate. Because the entropy of mixing arising from vibrational
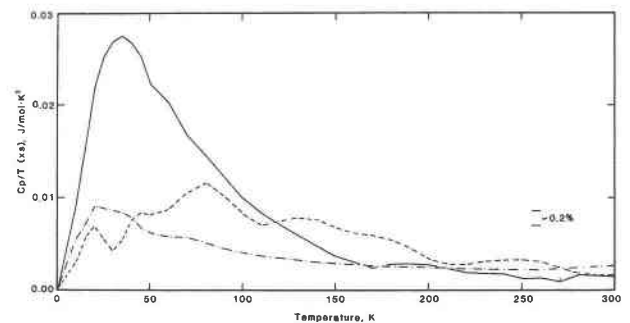

Fig. 3. Excess heat capacities divided by absolute temperature as a function of temperature for the three intermediate compositions: $Ab_{85}Or_{15}$ - · · · -, $Ab_{55}Or_{45}$ ———, and $Ab_{25}Or_{75}$ -------.

less for the other samples. The calculated excess entropies of mixing, deduced by Thompson and Hovis (1979) from the phase-equilibrium work of Orville (1963) and measured enthalpies of mixing (Hovis and Waldbaum, 1977), have been recalculated to reflect adjustments for a systematic calorimetric measurement error of ~1 percent (Hovis, 1982) and for new chemical analyses of the felspars used by Hovis and Waldbaum (1977) (Hovis, unpublished data). The magnitudes of the calculated entropy of mixing curves using a symmetric representation of the measured *enthalpy* of mixing data (W^H = 20.07 kJ/mol) and an asymmetric representation (W_{Ab}^H = 22.95 kJ/mol, W_{Or}^H = 17.71 kJ/mol) are somewhat less than the measured entropy values. If the excess entropy is symmetric, then the enthalpy of mixing, as calculated from the phase-equilibrium data, must be slightly asymmetric and have a maximum at Ab-rich compositions, rather than at sanidine-rich compositions as indicated by

contributions is now known quite precisely, we have combined this information with known volumes of mixing to obtain enthalpies of mixing from a number of solvus determinations. Systematic deviations of the calculated enthalpies from the measured enthalpies could suggest the presence of alkali SRO. No attempt has been made to assign uncertainties to the calculated enthalpies of mixing. Because most of the solvus data are not in the form of reversal brackets and because kinetic problems have been significant in these studies, the errors cannot be presumed to be normally distributed.

Thompson and Waldbaum (1969a, b) have presented a relatively simple process by which an asymmetric enthalpy of mixing can be deduced from the solvus data. Because similar calculations based on the alkali feldspar solvus determinations have been presented previously (*e.g.*, Thompson and Waldbaum, 1969b; Luth, 1974), the following discussion is rather brief.

At each temperature below the critical point, the compositions of the coexisting feldspar phases yield the values of two free-energy parameters B_G and C_G which are given in terms of W_{Ab}^G and W_{Or}^G in a Margules notation (Thompson, 1967).

$$B_G = \frac{W_{Or}^G + W_{Ab}^G}{2R} \tag{1a}$$

$$C_G = \frac{W_{Or}^G - W_{Ab}^G}{2R} \tag{1b}$$

The parameters for the enthalpy, volume, and, entropy are related to a Margules notation for enthalpy, volume, and entropy by expressions of identical form. The free-energy parameters B_G and C_G are related to enthalpy, volume, and entropy parameters by equations 2a and 2b:

$$B_G = \frac{B_H}{T} + \frac{PB_V}{T} - B_S \tag{2a}$$

$$C_G = \frac{C_H}{T} + \frac{PC_V}{T} - C_S \tag{2b}$$

We assume that the total excess entropy of mixing is given by the low temperature measurements presented here; therefore, $B_S = (10.3 \text{ J/mol·K})/R$ and $C_S = 0$ because S^{xs} is symmetric.

The excess volume of mixing at ambient conditions has been studied several times, most recently by Hovis (1977). He summarized the volume measurements and concluded that asymmetry in the volume of mixing had not been demonstrated conclusively. With the exception of the study of Luth and Querol-Suñé (1970), agreement on the magnitude of the symmetric W^V is excellent. We assume that W^V is the mean of the values from Donnay and Donnay (1952) as refined by Wright and Stewart (1968), Orville (1963), and Hovis (1977); thus $B_V = (0.364$
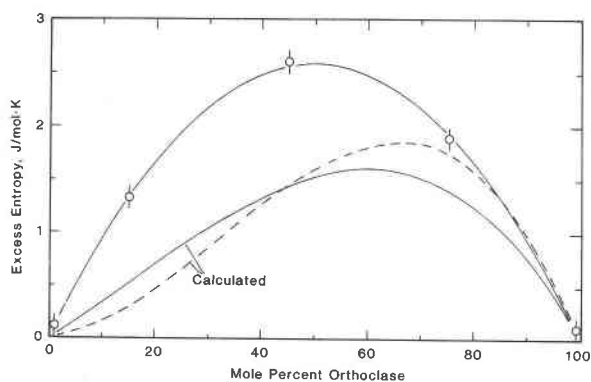

Fig. 4. Excess entropy of mixing at 298.15 K. The circles and solid curve represent the present measurements. The calculated entropy curves, similar to those of Thompson and Hovis (1979), are based on the phase equilibrium data of Orville (1963) and the symmetric (solid curve) and asymmetric (dashed curve) representations of the enthalpy of mixing data (Hovis and Waldbaum, 1977; Hovis, unpublished data).

J/bar)/R and $C_V = 0$. With the entropy and volume substitutions into equations 1a and 1b much of the freedom of the fitting process has been removed.

Values of B_G, C_G, W_{Ab}^H, and W_{Or}^H at 1 bar have been calculated for coexisting pairs from a number of solvus determinations. These values are listed in Table 13. There are no apparent systematic differences that can be attributed to the experimental method or the pressure of the experiments. Also, there is no consistent temperature variation in the enthalpy parameters. Solvi, all at 1 bar, have been calculated using the mean W^H parameters in Table 13. These solvi are superimposed in Figure 5. Parsons (1978) has cited some of the experimental errors in the determinations which account for at least some of the scatter among solvi. Importantly, equilibrium has not been demonstrated in most studies, and long times are required for apparent equilibration at low pressures (Smith and Parsons, 1974). Accordingly, the first-order break in slope of the Or-rich limb (Luth, 1974, and Martin, 1974), which is based on statistical arguments and has not been confirmed by reversed experiments, has been omitted from consideration. An additional source of variation is the differences in X-ray determinative curves from which feldspar compositions are obtained.

The mean enthalpy parameters for each experimental study listed in Table 13 were used to calculate a family of enthalpy of mixing curves, which are represented by the band in Figure 6. The experimentally determined enthalpies of mixing (Hovis and Waldbaum, 1977) are also plotted. Note that adjustments have been made to the heat of solution data of Hovis and Waldbaum (1977) (Hovis, unpublished data). The exact position of the experimental points in Figure 6 depends on the order of the least-squares fit to the heat of solution data, because the endpoints are not fixed. The point placements are

Table 13. Values of the free energy of mixing parameters, B_G and C_G, and the enthalpy of mixing parameters, W^H_{Ab} and W^H_{Or}, from experimental determinations of the analbite-sanidine solvus

T	P	x^1_{Or}	x^2_{Or}	r	s	B_G	C_G	W^H_{Ab}	W^H_{Or}
K	kbar							kJ	kJ
a) Orville (1963)									
773.2	2.0	0.034	0.803	-0.163	0.769	2.6609	0.8768	18.71	29.98
873.2	2.0	0.124	0.637	-0.239	0.513	2.0451	0.5698	18.98	27.25
923.2	2.0	0.208	0.525	-0.267	0.317	1.8782	0.4851	19.48	26.92
943.2	2.0	0.249	0.450	-0.301	0.201	1.7789	0.5184	18.87	27.00
873.2	5.0	0.066	0.688	-0.246	0.622	2.1505	0.8338	16.73	28.83
							Mean	18.54	28.00
b) Seck (1972)									
723.2	1.3	0.038	0.795	-0.167	0.757	2.6087	0.8400	17.63	27.73
723.2	1.3	0.024	0.811	-0.165	0.787	2.7581	1.0532	17.25	29.91
723.2	1.3	0.033	0.822	-0.145	0.789	2.7508	0.8258	18.57	28.50
773.2	1.3	0.047	0.703	-0.250	0.656	2.1913	1.0123	15.09	28.11
773.2	1.3	0.047	0.723	-0.230	0.676	2.2824	0.9466	16.10	28.27
773.2	1.3	0.047	0.744	-0.209	0.697	2.3729	0.8793	17.11	28.42
773.2	1.3	0.057	0.770	-0.173	0.713	2.4587	0.6868	18.90	27.73
773.2	1.3	0.052	0.780	-0.168	0.728	2.5059	0.7088	19.06	28.18
773.2	1.3	0.047	0.785	-0.168	0.738	2.5380	0.7506	19.00	28.65
823.2	1.3	0.095	0.636	-0.269	0.541	2.0025	0.7392	16.67	26.79
823.2	1.3	0.104	0.662	-0.234	0.558	2.0982	0.6180	18.16	26.62
823.2	1.3	0.100	0.708	-0.192	0.608	2.2281	0.5333	19.63	26.93
823.2	1.3	0.114	0.723	-0.163	0.609	2.2613	0.4292	20.57	26.44
823.2	1.3	0.109	0.723	-0.168	0.614	2.2640	0.4527	20.42	26.62
873.2	1.3	0.191	0.576	-0.233	0.385	1.9661	0.4385	19.63	26.00
673.2	2.5	0.009	0.837	-0.154	0.828	3.1142	1.5429	14.82	32.09*
673.2	2.5	0.009	0.853	-0.138	0.844	3.2238	1.4569	15.91	32.22*
723.2	2.5	0.038	0.806	-0.156	0.768	2.6554	0.8025	17.68	27.33
723.2	2.5	0.038	0.816	-0.146	0.778	2.6975	0.7682	18.14	27.38
723.2	2.5	0.038	0.847	-0.115	0.809	2.8277	0.6583	19.58	27.50
723.2	2.5	0.052	0.858	-0.090	0.806	2.7926	0.4599	20.56	26.09
773.2	2.5	0.071	0.810	-0.119	0.739	2.5578	0.4568	20.56	26.43
773.2	2.5	0.066	0.801	-0.133	0.735	2.5427	0.5193	20.06	26.74
773.2	2.5	0.057	0.775	-0.168	0.718	2.4765	0.6722	18.65	27.30
773.2	2.5	0.062	0.775	-0.163	0.713	2.4663	0.6258	18.89	26.93
773.2	2.5	0.066	0.775	-0.159	0.709	2.4586	0.5918	19.05	26.66
823.2	2.5	0.090	0.678	-0.232	0.588	2.1368	0.6664	17.63	26.75
823.2	2.5	0.081	0.667	-0.252	0.586	2.0901	0.7605	16.67	27.08
823.2	2.5	0.100	0.723	-0.177	0.623	2.2686	0.4986	19.68	26.51
823.2	2.5	0.104	0.749	-0.147	0.645	2.3324	0.4185	20.67	26.40
823.2	2.5	0.104	0.754	-0.142	0.650	2.3448	0.4070	20.83	26.40
873.2	2.5	0.157	0.596	-0.247	0.439	1.9750	0.5157	18.68	26.17
873.2	2.5	0.152	0.601	-0.247	0.449	1.9815	0.5249	18.66	26.28
873.2	2.5	0.162	0.631	-0.207	0.469	2.0584	0.4277	19.92	26.13
873.2	2.5	0.167	0.662	-0.171	0.495	2.1214	0.3526	20.93	26.05
773.2	5.0	0.057	0.863	-0.080	0.806	2.7869	0.3978	21.50	26.61
823.2	5.0	0.081	0.770	-0.149	0.689	2.4175	0.4965	19.80	26.60
823.2	5.0	0.081	0.785	-0.134	0.704	2.4607	0.4580	20.36	26.63
873.2	5.0	0.081	0.832	-0.087	0.751	2.5961	0.3300	22.16	26.68
873.2	5.0	0.095	0.698	-0.207	0.603	2.2000	0.5857	18.89	27.39
873.2	5.0	0.104	0.723	-0.173	0.619	2.2666	0.4776	20.16	27.09
873.2	5.0	0.100	0.739	-0.161	0.639	2.3106	0.4617	20.59	27.29
873.2	5.0	0.100	0.744	-0.156	0.644	2.3236	0.4501	20.77	27.30
923.2	5.0	0.147	0.586	-0.267	0.439	1.9357	0.5777	18.11	26.97
923.2	5.0	0.152	0.616	-0.232	0.464	2.0179	0.4939	19.38	26.96
773.2	10.0	0.024	0.868	-0.108	0.844	3.0458	0.8183	18.62	29.14
773.2	10.0	0.033	0.863	-0.104	0.830	2.9342	0.6707	18.85	27.48
773.2	10.0	0.043	0.895	-0.062	0.852	3.0031	0.4047	21.01	26.21
773.2	10.0	0.043	0.895	-0.062	0.852	3.0031	0.4047	21.01	26.21
773.2	10.0	0.033	0.889	-0.078	0.856	3.0571	0.5605	20.35	27.56
823.2	10.0	0.052	0.832	-0.116	0.780	2.6959	0.5477	19.52	27.02
823.2	10.0	0.052	0.853	-0.095	0.801	2.7737	0.4775	20.54	27.07
823.2	10.0	0.043	0.848	-0.109	0.805	2.8017	0.5906	19.95	28.04
823.2	10.0	0.047	0.863	-0.090	0.816	2.8390	0.4915	20.89	27.61
823.2	10.0	0.043	0.863	-0.094	0.820	2.8630	0.5357	20.75	28.08
873.2	10.0	0.066	0.759	-0.175	0.693	2.4058	0.6358	18.18	27.42
873.2	10.0	0.076	0.795	-0.129	0.719	2.5001	0.4639	20.12	26.85
873.2	10.0	0.071	0.810	-0.119	0.739	2.5578	0.4568	20.59	27.22
873.2	10.0	0.071	0.790	-0.139	0.719	2.4960	0.5122	19.74	27.17
873.2	10.0	0.071	0.801	-0.128	0.730	2.5300	0.4820	20.20	27.20
873.2	10.0	0.071	0.806	-0.123	0.735	2.5454	0.4680	20.42	27.21
973.2	10.0	0.090	0.626	-0.284	0.536	1.9555	0.8020	15.70	28.68
973.2	10.0	0.085	0.606	-0.309	0.521	1.8600	0.8993	14.14	28.81
973.2	10.0	0.090	0.586	-0.324	0.496	1.7914	0.9168	13.44	28.28
973.2	10.0	0.090	0.606	-0.304	0.516	1.8766	0.8580	14.61	28.49
1023.2	10.0	0.152	0.596	-0.252	0.444	1.9689	0.5354	19.08	28.19
1023.2	10.0	0.182	0.455	-0.363	0.273	1.6139	0.7420	14.30	26.92
973.2	10.0	0.090	0.606	-0.304	0.516	1.8766	0.8580	14.61	28.49
							Mean	18.92	27.27

Table 13. (continued)

T	P	x^1_{Or}	x^2_{Or}	r	s	B_G	C_G	W^H_{Ab}	W^H_{Or}
K	kbar							kJ	kJ
c) Luth and Tuttle (1966)									
823.2	2.0	0.083	0.795	-0.122	0.713	2.4866	0.4207	21.89	27.65
848.2	2.0	0.085	0.696	-0.219	0.612	2.1923	0.6584	18.83	28.11
850.2	2.0	0.057	0.724	-0.219	0.668	2.2885	0.8255	18.37	30.04
873.2	2.0	0.085	0.702	-0.213	0.617	2.2112	0.6373	19.69	28.95
898.2	2.0	0.195	0.575	-0.230	0.380	1.9673	0.4291	20.01	26.42
900.2	2.0	0.159	0.593	-0.248	0.435	1.9703	0.5152	19.44	27.15
908.2	2.0	0.132	0.622	-0.246	0.491	2.0134	0.5667	19.55	28.11
915.2	2.0	0.203	0.543	-0.254	0.340	1.9099	0.4657	19.69	26.78
923.2	2.0	0.226	0.526	-0.247	0.300	1.9054	0.4296	20.11	26.71
931.2	2.0	0.284	0.496	-0.220	0.212	1.9157	0.3447	21.03	26.37
938.2	2.0	0.285	0.526	-0.189	0.241	1.9582	0.2930	21.93	26.50
923.2	5.0	0.109	0.674	-0.217	0.565	2.1356	0.5633	19.75	28.40
923.2	10.0	0.050	0.758	-0.191	0.708	2.4272	0.7947	18.38	30.58
							Mean	19.90	27.83
d) Goldsmith and Newton (1974)									
873.2	9.0	0.035	0.775	-0.190	0.740	2.5307	0.9579	17.12	31.03
873.2	9.0	0.080	0.760	-0.160	0.680	2.3897	0.5285	19.21	26.89
823.2	9.0	0.025	0.850	-0.125	0.825	2.9444	0.8724	19.37	31.31
823.2	9.0	0.050	0.800	-0.150	0.750	2.5859	0.6694	18.30	27.47
873.2	14.0	0.035	0.845	-0.120	0.810	2.8390	0.7092	19.33	29.63
873.2	14.0	0.060	0.820	-0.120	0.760	2.6233	0.5124	19.19	26.63
823.2	14.0	0.025	0.895	-0.080	0.870	3.1758	0.6719	20.49	29.69
823.2	14.0	0.060	0.855	-0.085	0.795	2.7442	0.4009	19.39	24.88
773.2	14.0	0.025	0.920	-0.055	0.895	3.3226	0.5365	20.75	27.64
773.2	14.0	0.035	0.900	-0.065	0.865	3.0936	0.4803	19.64	25.81
723.2	15.0	0.010	0.970	-0.020	0.960	4.1727	0.5181	23.93	30.16
723.2	15.0	0.035	0.915	-0.050	0.880	3.1742	0.4031	18.62	23.64
673.2	15.0	0.020	0.985	0.005	0.965	4.1826	-0.1348	25.60	24.10
673.2	15.0	0.010	0.930	-0.060	0.920	3.7353	0.9326	17.13	27.57
623.2	15.0	0.001	0.999	0.000	0.998	6.9206	0.0000	36.78	36.78*
623.2	15.0	0.010	0.965	-0.025	0.955	4.0980	0.5909	19.10	25.22
							Mean	19.81	27.43
e) Smith and Parsons (1974)									
673.2	1.0	0.009	0.813	-0.178	0.804	2.9452	1.6715	13.70	32.41
673.2	1.0	0.017	0.803	-0.180	0.786	2.7718	1.3020	14.80	29.37
723.2	1.0	0.070	0.784	-0.146	0.714	2.4794	0.5359	18.77	25.22
723.2	1.0	0.042	0.767	-0.191	0.725	2.4775	0.8740	16.73	27.24
673.2	1.0	0.034	0.816	-0.150	0.782	2.7185	0.8306	17.14	26.44
723.2	1.0	0.062	0.790	-0.148	0.728	2.5168	0.5833	18.71	25.73
773.2	1.0	0.069	0.746	-0.185	0.677	2.3589	0.6461	18.61	26.92
823.2	1.0	0.082	0.654	-0.264	0.572	2.0440	0.7878	16.72	27.50
848.2	1.0	0.123	0.606	-0.271	0.483	1.9541	0.6458	17.60	26.71
873.2	1.0	0.224	0.563	-0.213	0.339	1.9701	0.3696	20.25	25.62
773.2	1.0	0.058	0.751	-0.191	0.693	2.3884	0.7318	18.25	27.66
823.2	1.0	0.096	0.671	-0.233	0.575	2.1192	0.6446	18.21	27.03
823.2	1.0	0.109	0.653	-0.238	0.544	2.0760	0.6109	18.15	26.51
848.2	1.0	0.148	0.550	-0.302	0.402	1.8329	0.6554	16.68	25.92
							Mean	17.45	27.16
f) Lagache and Weisbrod (1977)									
573.2	1.0	0.015	0.860	-0.125	0.845	3.1313	1.1170	15.14	25.79
623.2	1.0	0.025	0.840	-0.135	0.815	2.8950	0.9133	16.33	25.79
648.2	1.0	0.030	0.845	-0.125	0.815	2.8759	0.7923	17.54	26.08
673.2	1.0	0.035	0.810	-0.155	0.775	2.6869	0.8354	16.94	26.29
723.2	1.0	0.050	0.775	-0.175	0.725	2.4918	0.7463	17.58	26.56
773.2	1.0	0.075	0.730	-0.195	0.655	2.3020	0.6411	18.28	26.52
823.2	1.0	0.115	0.665	-0.220	0.550	2.1143	0.5518	18.81	26.37
833.2	1.0	0.145	0.640	-0.215	0.495	2.0689	0.4722	19.28	25.83
873.2	1.0	0.190	0.580	-0.230	0.390	1.9734	0.4340	19.81	26.11
898.2	1.0	0.220	0.520	-0.260	0.300	1.8845	0.4594	19.53	26.40
913.2	1.0	0.245	0.480	-0.275	0.235	1.8381	0.4681	19.45	26.56
918.2	1.0	0.270	0.465	-0.265	0.195	1.8464	0.4331	19.89	26.50
							Mean	18.22	26.23

Compositions are the mole fraction of sanidine in coexisting analbite-rich and sanidine-rich phases. The compositions of Luth and Tuttle (1966) have been corrected using the two equations in Table 4, Luth and Querol-Sune (1970) for the data of Orville (1967) as suggested by Luth (oral communication, 1982). The compositions of Goldsmith and Newton (1974), i.e., four points at a given pressure and temperature, have been used to avoid a systematic shift in derived mixing parameters. Lagache and Weisbrod (1977) did not specify the exact pressures of their runs; 1 kbar was assumed. Enthalpy parameters marked with an asterisk differ from the means by greater than 3 standard deviations and were omitted.

appropriate for the symmetrical or quadratic fit for which $\Delta H_{mix} = X_{Ab}X_{Or}$ (20.07 kJ/mol). The calculated enthalpies of mixing tend to be greater in magnitude than the measured values especially for Ab-rich compositions. The calculated curves are asymmetric toward Ab-rich solutions, as required by the symmetry of the entropy of mixing and the Ab-rich maximum in the solvus. A cubic fit to the measured enthalpy data deviates slightly further from the calculated enthalpy curves.

In the above calculations, we have assumed the absence of SRO in the alkali site and have hence calculated the maximum enthalpy of mixing allowed by the solvus data. Because the free energy of mixing is fixed by the solvus data, the inclusion of SRO in the calculations, which decreases the entropy of mixing, will only decrease the calculated enthalpy of mixing. Except for the measurements at $Or_{35.1}$, the calculated and measured enthalpies overlap. The difference between the dashed and solid curves representing the measured enthalpy data is almost entirely due to differences in the chemical analyses of the samples. The compositional uncertainty together with the
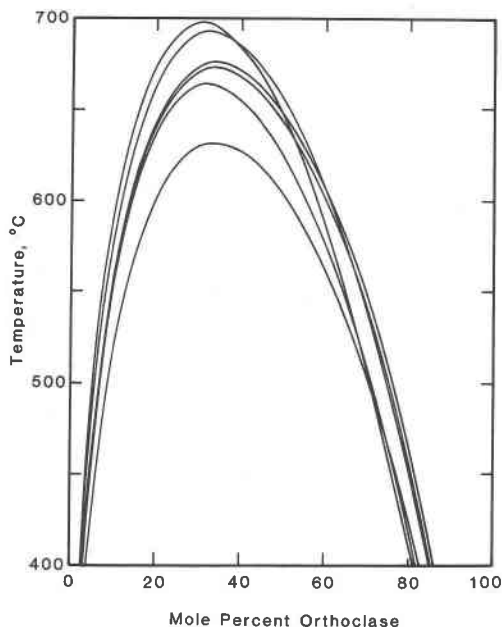
Fig. 5. Calculated solvi at 1 bar based on the phase-equilibrium studies (in order of decreasing critical temperature) of Orville (1963), Luth and Tuttle (1966), Seck (1972), Smith and Parsons (1974), Goldsmith and Newton (1974), and Lagache and Weisbrod (1977).

uncertainties in solvus and entropy measurements make small differences between the measured and calculated enthalpies meaningless. The essential coincidence of these values indicates that SRO is not a sigificant factor in synthetic, disordered alkali feldspars and, by extension, in natural alkali feldspars.

In the above calculations, we have assumed that the excess heat capacity is neglible above 298 K, but a small residual ΔC_p^{xs}, which should diminish at higher temperatures, is suggested in Figure 3. If ΔC_p^{xs} does not diminish, but continues at a value of $\Delta C_p^{xs} = 0.5$ J/mol·K at $X_{Or} = 0.5$, the resulting enthalpy and entropy differences between 298 and 1000 K are (0.5 J/mol·K)(1000 − 298) = 351 J/mol and (0.5 J/mol·K)ln(1000/298) = 0.65 J/mol·K. At 1000 K, the additional stabilization in ΔG_{mix} is −254 J/mol. If symmetrical, temperature-dependent terms of the above magnitude are incorporated into a solvus calculation, the critical temperature decreases by approximately 30°C. This decrease is considerably less than the range of critical temperatures resulting from the experimental determinations.

Temperature-dependent Al/Si ordering would tend to yield larger apparent W^H values at lower temperatures. Inspection of the entries in Table 13 generally shows the opposite result; hence, we conclude that the available solvus data are not sufficiently precise to detect the Al/Si ordering that has been observed by X-ray examination of the run products.

Two-feldspar thermometry

The two-feldspar geothermometer, initially suggested by Barth (1951), is based on the distribution of the Ab component between coexisting plagioclase and alkali feldspars. Because of the apparent near-ideality of mixing in high structural state plagioclases at high temperatures (Orville, 1972; Seil and Blencoe, 1979) and the pronounced nonideality in high alkali feldspars, the Ab component tends to concentrate in the plagioclase. As temperature decreases, the tie-line for a given bulk composition rotates, decreasing the $NaAlSi_3O_8$ in the alkali feldspar relative to plagioclase. General usage of the thermometer relies on the formulations by Stormer (1975) and Whitney and Stormer (1977). The earlier formulation of Stormer (1975) is applicable to high structural state feldspars. He assumed the very convenient standard state of pure albite at 1 bar and assumed that the mixing properties of plagioclase could be described by an ideal, single-site model. The alkali feldspar mixing was described by the parameters deduced by Thompson and Waldbaum (1969a) from the equilibrium data of Orville (1963). Whitney and Stormer (1977) incorporated the experimental data of Bachinski and Müller (1971) to make a correction for low structural state in the alkali feldspar while retaining the ideal 1-site formulation for plagioclase. Both formulations presume that the plagioclase and alkali feldspar are strictly binary. Powell and Powell (1977) modified Stormer's (1975) expression to account
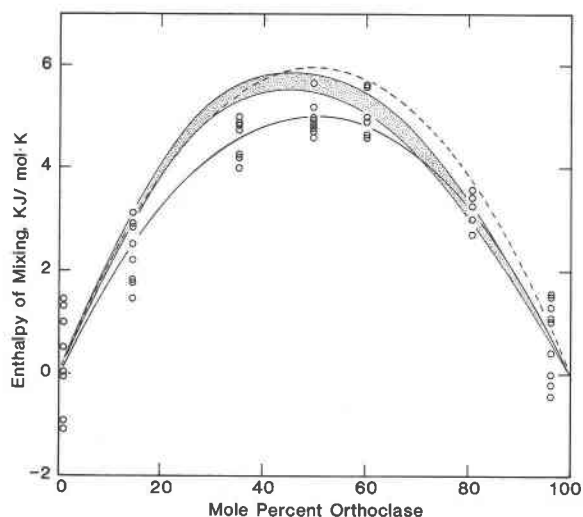
Fig. 6. Measured and calculated enthalpies of mixing at 1 bar. The circles are the values deduced from the measured data of Hovis and Waldbaum (1977) and Hovis (unpublished data). The symmetric fit to their data is given by the heavy solid curve. The data have been corrected with a ~1% calorimetric correction (Hovis, 1982), and with new chemical analyses. The dashed curve is the symmetric fit to the uncorrected data (Hovis and Waldbaum, Equation 3, 1977). The stippled band contains enthalpies of mixing calculated from the values in Table 13.

approximately for the solution of An component in alkali feldspars. At relatively high An contents, Powell and Powell showed that the calculated temperature may be decreased by 200°C or more, depending on the specific bulk composition and tie-line orientation. They retained the 1-site ideal mixing approximation for the plagioclase.

The assumption of an ideal, 1-site model for plagioclase was suggested initially by the general shape of the liquidus and solidus curves. The equilibration experiments of plagioclases in chloride solutions at 700°C by Orville (1972) and at 600–800°C by Seil and Blencoe (1979) show, however, that the free energies of mixing are slightly more positive than those predicted by the ideal 1-site model. For low structural state plagioclases, the assumption of the ideal 1-site model could induce significant error, because the presence of a variety of intergrowths (see Smith, 1974 for a review) evidences significant nonideality.

We have combined the recent calorimetric results of Newton et al. (1980) for high plagioclases and the present work on alkali feldspars to yield a new expression for the two-feldspar thermometer that partially accounts for ternary solution of each feldspar (Powell and Powell, 1977) and that yields higher temperatures than do formulations based on previous thermodynamic descriptions of alkali and plagioclase feldspars.

The activity of $NaAlSi_3O_8$ in the alkali feldspar (α_{Ab}^{AF}) is formulated from the mean of the enthalpy parameters from Table 13 ($W_{Ab}^H = 18.81$ kJ/mol, $W_{Or}^H = 27.32$ kJ/mol) and the entropy ($W^S = 10.3$ J/mol·K) and volume ($W^V = 0.364$ J/bar) parameters from above.

$$\alpha_{Ab}^{AF} = X_{Ab}^{AF}$$
$$\cdot \exp\left\{\frac{(X_{Or}^{AF})^2(18810 + 17030\,X_{Ab}^{AF} - 10.3T + 0.364P)}{8.314T}\right\}$$
$$(3)$$

where T is in kelvins and P is in bars.

The high-temperature solution calorimetry (Newton et al., 1980) makes the assumption of ideal activities in high plagioclases unnecessary and provides insight into the plagioclase solution properties. The measured enthalpy of mixing in plagioclases at 970 K is quite positive; ΔH_{mix} (kJ/mol) = $X_{Ab}^{Pl}\,X_{An}^{Pl}\,(28.23\,X_{An}^{Pl} + 8.47\,X_{Ab}^{Pl})$. When Newton et al. (1980) combined their enthalpy of mixing data with the Al-avoidance model of Kerrick and Darken (1975), the calculated free energy of mixing curve at 700°C, which is the temperature of Orville's (1972) exchange experiments, is very similar to that given by the ideal 1-site model and is almost identical with free energy of mixing calculated by Orville (1972) from his equilibrium experiments. In a preliminary report, Seil and Blencoe (1979) stated that their results are similar to those of Orville.

According to Newton et al. (1980),

$$\alpha_{Ab}^{Pl} = (X_{Ab}^{Pl})^2(2 - X_{Ab}^{Pl})$$
$$\cdot \exp\left\{\frac{(X_{An}^{Pl})^2\,(28230 - 39520\,X_{Ab}^{Pl})}{8.3143T}\right\} \quad (4)$$

The α_{Ab}^{Pl} expression contains no excess entropy or volume of mixing terms. No data are available from which the excess entropy, if significant, can be evaluated. Newton et al. (1980) demonstrated that the volume of mixing is negligible for a carefully controlled series of synthetic plagioclases. Results of experiments by Mark D. Barton of the Geophysical Laboratory, involving silica solubilities in H_2O buffered, in part, by plagioclases at 475°C, agree closely with the activities predicted by Newton et al.'s expressions but not with ideal 1-site mixing (M. D. Barton, personal communication, 1981). Hence, phase-equilibrium studies in the temperature range of 475–800°C support the combination of the Al-avoidance model and the enthalpy of mixing data. The activities from equation (4) are plotted at several temperatures in Figure 7. The ideal Al-avoidance curve results from assuming that $\Delta H_{mix} = 0$. Most natural plagioclases coexisting with alkali feldspar have compositions for which Ab activities are less than those predicted by the assumption of ideal 1-site mixing.

Substituting the activity expressions into the condition for equilibrium, $\alpha_{Ab}^{Pl} = \alpha_{Ab}^{AF}$, and solving for T
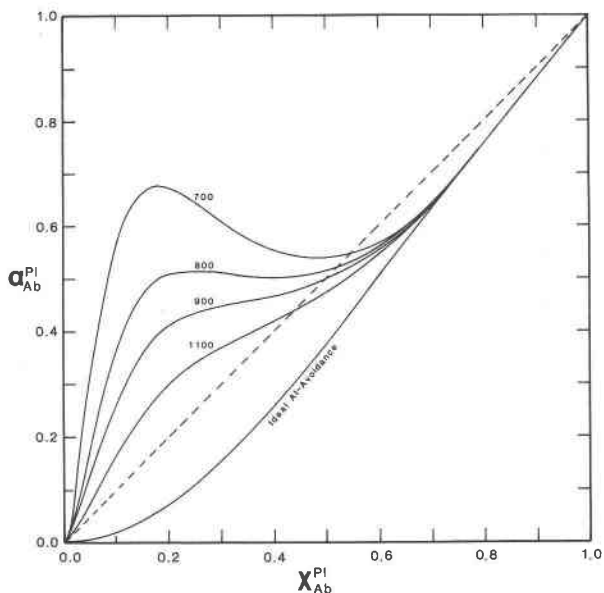

Fig. 7. Activities of $NaAlSi_3O_8$ in plagioclase, calculated from equation 4, at a range of temperatures. The 800 K isotherm is below the critical temperature in the plagioclase binary. Activities predicted by an ideal 1-site, mixing model are indicated by the dashed line.
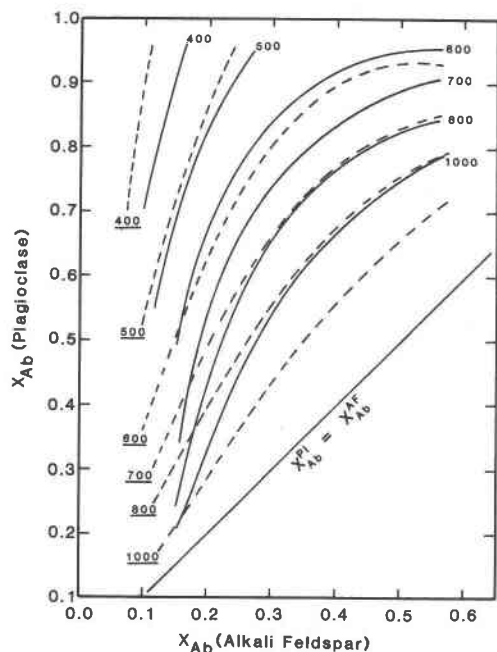
Fig. 8. The distribution of $NaAlSi_3O_8$ component between alkali feldspar and plagioclase at 1 bar and in the range 400°–1000°C. The present formulation given by equation 5 is represented by solid curves and that of Stormer (1975, Equation 18) by dashed curves. The temperatures of the isotherms for Stormer are underlined. The distribution of isotherms in the present formulation is complicated at low temperatures (<560°C) by the presence of a solvus in the plagioclase binary.

$$T_K = [(X_{Or}^{AF})^2(18810 + 17030\, X_{Ab}^{AF} + 0.364P)$$

$$- (X_{An}^{Pl})^2(28230 - 39520\, X_{Ab}^{Pl})] \Big/$$

$$\left[10.3\,(X_{Or}^{AF})^2 + 8.3143\, \ln\left\{\frac{(X_{Ab}^{Pl})^2(2 - X_{Ab}^{Pl})}{X_{Ab}^{AF}}\right\}\right] \quad (5)$$

The mole fractions refer to the ternary system and P is in bars. Although this expression includes nonideality in the plagioclase, it is not appreciably more complicated than the earlier formulation of Stormer (1975), because the entropy and volume of mixing are symmetrical. Isotherms from equation (5) are plotted as solid lines in Figure 8. Isotherms from Stormer (1975, Equation 18) are plotted as dashed lines to indicate where significant differences arise from the two formulations. The present formulation yields much higher temperatures for most feldspar pairs. At the highest temperatures, the two formulations differ by hundreds of degrees. The difference is caused principally by the plagioclase mixing models. At temperatures below 560°C, the configuration of the isotherms near the plagioclase axis is complicated by the solvus predicted from the plagioclase mixing model. This diagram is not appropriate for feldspars having significant ternary solution or those thought to

have equilibrated at high pressures. Temperatures for these pairs should be calculated directly from Equation (5). This formulation does involve a projection to the binary axes and hence should be used with caution for plagioclases with very large amounts of Or component.

Phase equilibrium data from which the thermometer can be calibrated are very limited. In a careful study Johannes (1979) has demonstrated an approach to equilibrium for coexisting plagioclase and alkali feldspar for one bulk composition at 2 kbar and 800°C. When Equation (5) is used, the bracketing pairs yield 783 and 862°C; according to Stormer (1975, Equation 18), the pairs yield 690 and 730°C. At present, equilibrium has not been demonstrated in experiments at lower temperatures; hence, the accuracy at lower temperatures, e.g., 500°C, cannot be assessed. Most of Seck's (1972) results involved the direct crystallization of gels; therefore, except for some preliminary experiments, equilibrium was inferred but not demonstrated. Also, the compositions of the plagioclases were inferred by projection rather than actually measured. In general, Seck's results are not in serious conflict with the present version of the thermometer. Because of the insensitivity of the thermometer for very high temperature pairs, calculated temperatures above 850°–900°C are likely to be grossly in error.

Acknowledgments

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