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 (Ab30Or70, Ab35Or65, Ab53Or47, Ab75Or25, and Ab90Or10). 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 $S_{\text{ex}} = X_{\text{Ab}}X_{\text{Or}}(10.3\pm0.3 \text{ J/mol.K})$. 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.

$$T_K = \frac{(X_{\text{Or}}^A)^2(18810 + 17030X_{\text{Ab}}^A + 0.364P) - (X_{\text{Or}}^P)^2(28230 - 39520X_{\text{Ab}}^P)}{10.3(X_{\text{Or}}^A)^2 + 8.31431n\left\{ \frac{(X_{\text{Or}}^P)^2(2 - X_{\text{Ab}}^P)}{X_{\text{Ab}}^A} \right\}}$$

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. The Na ion in analbite is expected, if present, only at low temperatures, because the effects of structure on the heat capacities generally diminish as temperature increases.

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; L. gache and Weisbrod, 1977; and Merkel and Blencoe, 1980). Volumes of mixing for high alkali feldspars, 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 albite. Low-temperature (15–375 K) heat capacities for analbite and sanidine prepared from Albite 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, Ab₉₉Or₁ and Ab₁Or₉₉, 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 feldspar samples used for low-temperature heat-capacity measurements by Openshaw et al. (1976). These samples were collected with a powder diffractometer at a scan speed of 0.25° 2θ min⁻¹ with CuKa radiation. Silicon of a = 0.543054 nm (Parrish, 1960) was used as an internal standard. Also listed are the cell parameters for disordered analbite and sanidine as chosen by Stewart and Wright (1974), the dashed line indicates approximately 90% disorder.

The Ab₉₅Or₁₅ 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 Ab₂₅Or₇₅ to yield a bulk composition of Ab₅₀Or₅₀. Again after homogenization and measurements, Ab₂₅Or₇₅ was prepared similarly from the Ab₅₀Or₅₀. 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° 2θ min⁻¹ with CuKα 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 t₁0 + t₁m = 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

<table>
<thead>
<tr>
<th>Sample #</th>
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<th>Or₅₀</th>
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</thead>
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<td>0.45</td>
</tr>
<tr>
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<td>0.45</td>
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<td>0.99</td>
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Number in parentheses is one standard deviation in terms of the least significant figure.
The bulk chemical compositions for the analbite and sanidine, listed by Otvos et al. (1976, Table 1), are $\text{Ab}_{98.4}\text{Or}_{1.2}\text{An}_{0.4}$ and $\text{Ab}_{0.6}\text{Or}_{99.2}\text{An}_{0.1}$. 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 $\text{CaAl}_2\text{Si}_2\text{O}_8$ (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-acquisition 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 $\text{Ab}_{98.4}\text{Or}_{1.2}\text{An}_{0.4}$ and for some of the measurements on $\text{Ab}_{0.6}\text{Or}_{99.2}\text{An}_{0.1}$. Additional measurements were made on the $\text{Ab}_{0.6}\text{Or}_{99.2}$ 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 $\text{Ab}_{0.6}\text{Or}_{99.2}$ 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 $\text{Ab}_{25}\text{Or}_{75}$ sample were collected with the automated system.

The sample weights in vacuo were 43.5737 g analbite, 33.0201 g $\text{Ab}_{55}\text{Or}_{45}$, and 32.9870 g $\text{Ab}_{25}\text{Or}_{75}$.
Ab$_5$Or$_{45}$, and 30.3261 g Ab$_{25}$Or$_{75}$. Approximately 4 x 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 topochromically monoclinic alkali feldspars decreases with increasing Or content. The transition is projected to occur at approximately 200 K in the Ab$_{5}$Or$_{45}$ sample (Kroll et al., 1980), 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.
For the measurements on sanidine, \( \text{Ab}_{55}\text{Or}_{45} \), and \( \text{Ab}_{25}\text{Or}_{75} \), 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 \( -(G_T - G_0)/T \) 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 \( S_0 = -4R(0.75\ln 0.75 + 0.25\ln 0.25) = 18.70 \text{ J/mol} \cdot \text{K} \) for each of the five compositions. We should note that total Al, Si disorder requires that Al–O–Al linkages be present in the 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 \(-R \ln X_{\text{Na}} + X_{\text{K}} \ln X_{\text{K}} \) where \( X_{\text{Na}} \) and \( X_{\text{K}} \) are the mole fractions of NaAlSi\(_3\)O\(_8\) and KAlSi\(_3\)O\(_8\).

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 new other 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 contribution 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...
sandine 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. For 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, \( \text{Ab}_{85}\text{Or}_{15}, \text{Ab}_{85}\text{Or}_{45}, \) and \( \text{Ab}_{25}\text{Or}_{75}, \) compared with linear combinations of the

**Table 9. Smoothed thermodynamic functions for analbite_{85}sanidine_{15}**

<table>
<thead>
<tr>
<th>TEMP.</th>
<th>( C_p^0 )</th>
<th>( (S^0 - S_{298})^0 )</th>
<th>( (H^0 - H_{298})^0 / T )</th>
<th>( -G^0 - G_{298}^0 / T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KELVIN</td>
<td>J/(mol·K)</td>
<td>J/(mol·K)</td>
<td>J/(mol·K)</td>
<td>J/(mol·K)</td>
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<td>20.37</td>
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</table>

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.
analbite and sanidine heat capacities, are shown in Figure 3. Any deviation from zero indicates an excess heat capacity ($C_p^{ex}$) 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$_{55}$Or$_{45}$. If ($C_p^o$/T)$_K$ 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 $C_p^o = 0$ at $T > 298$ K is quite reasonable. If $C_p^o$ is not negligible at high temperatures, then the quantity of heat capacity data required for phase equilibrium calculations would increase greatly.

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

<table>
<thead>
<tr>
<th>TEMP. (K)</th>
<th>$C_p^o$</th>
<th>$S_p^o$</th>
<th>$H_p^o$</th>
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<tr>
<td>302.95</td>
<td>0.047</td>
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<td>0.005</td>
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### 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 polynomial 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 $S_{298} = X_{AB} X_{Cr} (10.3 \pm 0.3 \text{ J/mol-K})$; 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
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 ($W_{H}^{M} = 20.07$ kJ/mol) and an asymmetric representation ($W_{H}^{A} = 22.95$ kJ/mol, $W_{H}^{B} = 17.71$ 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 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$_{75}$Or$_{45}$, and Ab$_{55}$Or$_{25}$. 

Table 12. Smoothed thermodynamic functions for sanidine

<table>
<thead>
<tr>
<th>TEMP. (K)</th>
<th>$C_p$</th>
<th>$(E^<em>_H - S^</em>_0)/T$</th>
<th>$(H^<em>_H - H^</em>_0)/T$</th>
<th>$(-G^<em>_H - G^</em>_0)/T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.039</td>
<td>0.012</td>
<td>0.009</td>
<td>0.003</td>
</tr>
<tr>
<td>10</td>
<td>0.412</td>
<td>0.115</td>
<td>0.088</td>
<td>0.027</td>
</tr>
<tr>
<td>15</td>
<td>1.854</td>
<td>0.502</td>
<td>0.392</td>
<td>0.109</td>
</tr>
<tr>
<td>20</td>
<td>4.916</td>
<td>1.407</td>
<td>1.099</td>
<td>0.309</td>
</tr>
<tr>
<td>25</td>
<td>9.357</td>
<td>2.961</td>
<td>2.888</td>
<td>0.673</td>
</tr>
<tr>
<td>30</td>
<td>14.61</td>
<td>5.123</td>
<td>3.896</td>
<td>1.227</td>
</tr>
<tr>
<td>35</td>
<td>20.31</td>
<td>7.800</td>
<td>5.830</td>
<td>1.970</td>
</tr>
<tr>
<td>40</td>
<td>26.05</td>
<td>10.89</td>
<td>8.000</td>
<td>2.888</td>
</tr>
<tr>
<td>45</td>
<td>31.64</td>
<td>14.28</td>
<td>10.32</td>
<td>3.963</td>
</tr>
<tr>
<td>50</td>
<td>37.14</td>
<td>17.90</td>
<td>12.72</td>
<td>5.174</td>
</tr>
<tr>
<td>55</td>
<td>42.87</td>
<td>21.64</td>
<td>17.71</td>
<td>7.932</td>
</tr>
<tr>
<td>60</td>
<td>47.72</td>
<td>25.44</td>
<td>22.72</td>
<td>11.04</td>
</tr>
<tr>
<td>65</td>
<td>52.60</td>
<td>30.10</td>
<td>27.70</td>
<td>14.40</td>
</tr>
<tr>
<td>70</td>
<td>57.72</td>
<td>35.89</td>
<td>32.63</td>
<td>17.25</td>
</tr>
<tr>
<td>75</td>
<td>62.90</td>
<td>41.58</td>
<td>33.11</td>
<td>19.18</td>
</tr>
<tr>
<td>80</td>
<td>68.15</td>
<td>47.27</td>
<td>33.63</td>
<td>20.79</td>
</tr>
<tr>
<td>85</td>
<td>73.54</td>
<td>52.95</td>
<td>34.15</td>
<td>22.23</td>
</tr>
<tr>
<td>90</td>
<td>78.94</td>
<td>58.63</td>
<td>34.6 vertical line</td>
<td></td>
</tr>
</tbody>
</table>

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.
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).

$$B_G = \frac{W_{Or}^G + W_{Ab}^G}{2R}$$ \hspace{1cm} (1a)

$$C_G = \frac{W_{Or}^G - W_{Ab}^G}{2R}$$ \hspace{1cm} (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:

$$B_G = \frac{B_H}{T} + \frac{P B_V}{T} - B_S$$ \hspace{1cm} (2a)

$$C_G = \frac{C_H}{T} + \frac{P C_V}{T} - C_S$$ \hspace{1cm} (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 $S^{\infty}$ 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 $B_V = (0.364 \text{ J/bar}/R$ 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 $B_G$, $C_G$, $W^H_{Ab}$, and $W^H_{Or}$ 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. Solvus, 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...
appropriate for the symmetrical or quadratic fit for which \( \Delta H_{\text{mix}} = X_{\text{Ab}}X_{\text{Or}} \) (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 \( T = 938.2 \) K, 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

Table 13. Values of the free energy of mixing parameters, \( B_0 \) and \( C_0 \), and the enthalpy of mixing parameters, \( W_{\text{AB}}^0 \) and \( W_{\text{Or}}^0 \), from experimental determinations of the analbite-sanidine solvus

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( T_P )</th>
<th>( X_{\text{Ab}}^0 )</th>
<th>( X_{\text{Or}}^0 )</th>
<th>( a )</th>
<th>( b )</th>
<th>( C_0 )</th>
<th>( W_{\text{AB}}^0 )</th>
<th>( W_{\text{Or}}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>773.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
<tr>
<td>823.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
<tr>
<td>873.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
<tr>
<td>923.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
</tbody>
</table>

Table 13. (continued)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( T_P )</th>
<th>( X_{\text{Ab}}^0 )</th>
<th>( X_{\text{Or}}^0 )</th>
<th>( a )</th>
<th>( b )</th>
<th>( C_0 )</th>
<th>( W_{\text{AB}}^0 )</th>
<th>( W_{\text{Or}}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>773.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
<tr>
<td>823.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
<tr>
<td>873.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
<tr>
<td>923.2 K</td>
<td>1.0</td>
<td>0.038</td>
<td>0.017</td>
<td>0.799</td>
<td>0.912</td>
<td>0.769</td>
<td>0.740</td>
<td>0.737</td>
</tr>
</tbody>
</table>

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 \( T = 938.2 \) K, 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
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$_3$O$_8$ 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 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 significant 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 negligible above 298 K, but a small residual $\Delta C_p^{ex}$, which should diminish at higher temperatures, is suggested in Figure 3. If $\Delta C_p^{ex}$ does not diminish, but continues at a value of $\Delta C_p^{ex} = 0.5 \text{ J/mol K}$ at $X_{Or} = 0.5$, the resulting enthalpy and entropy differences between 298 and 1000 K are

$$(0.5 \text{ J/mol K})(1000 - 298) = 351 \text{ J/mol}$$

and

$$(0.5 \text{ J/mol K}) \ln(1000/298) = 0.65 \text{ J/mol K}.$$  

At 1000 K, the additional stabilization in $\Delta G_{mix}$ is $-254 \text{ J/mol}$. 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.

Fig. 5. Calculated solvus 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).

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 70°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 NaAlSi3O8 in the alkali feldspar (α_{AF}^{pl}) is formulated from the mean of the enthalpy parameters from Table 13 (W_{Al}^{pl} = 18.81 kJ/mol, W_{Na}^{pl} = 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.

\[
α_{AF}^{pl} = \frac{(X_{AF}^{pl})^2(18810 + 17030 X_{AF}^{pl} - 10.3T + 0.364P)}{8.314T}
\]

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_{Al}^{pl} X_{An}^{pl} (28.23 X_{Al}^{pl} + 8.47 X_{An}^{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),

\[
α_{AB}^{pl} = (X_{Al}^{pl})^2(2 - X_{An}^{pl}) \cdot \exp \left\{ \frac{(X_{Al}^{pl})^2 (28230 - 39520 X_{Al}^{pl})}{8.314T} \right\}
\]

The ΔH_{mix} 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 H2O 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 ΔH_{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, \(α_{AB} = α_{AF}^{pl} \), and solving for T

\[
\text{Fig. 7. Activities of NaAlSi3O8 in plagioclase, calculated from equation 4, at a range of temperatures. The 800 K isotherm is below the critical temperature in the plagioclase binary. Activities predicted by an ideal 1-site, mixing model are indicated by the dashed line.}
\]
Fig. 8. The distribution of NaAlSi$_3$O$_8$ 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.

\[ T_K = \frac{10.3 (X_{AF}^p)^2 + 8.3143 \ln \left( \frac{(X_{AF}^p)^2 - X_{AF}^p}{X_{AF}^p} \right)}{(X_{AF}^p) (18810 + 17030 X_{AF}^p + 0.364 P) - (X_{AF}^p) (28230 - 39520 (X_{AF}^p) / (1)} \]

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

We wish to thank our U.S. Geological Survey colleagues, Priestley Toulmin, III and David B. Stewart, for their many helpful suggestions. We also much appreciate the critical reviews of Alexandra Navrotsky and James B. Thompson, Jr.

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