

Enthalpies of mixing for disordered alkali feldspars at high temperature: A test of regular solution thermodynamic models and a comparison of hydrofluoric acid and lead borate solution calorimetric techniques

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ABSTRACT

Enthalpies of solution have been measured for an 11-member analbite-sanidine series at 704 °C in molten lead borate. Enthalpies of K-Na mixing determined from the data are statistically equivalent to those determined by HF solution calorimetry at 50 °C (Hovis, 1988). This indicates that regular solution thermodynamic models, which assume enthalpies of mixing to be independent of temperature, are valid for the disordered alkali feldspars. The experiments also demonstrate the consistency of the HF and lead borate solution calorimetric techniques. Volumes of K-Na mixing at room temperature also are reported.

INTRODUCTION

It is a common practice in geology to apply certain kinds of thermodynamic data collected at one temperature and pressure, such as internal energies and volumes of mixing (E_{ex} and V_{ex} , respectively, using the terminology of Thompson, 1967), to a wide range of temperatures and pressures. Indeed so-called regular thermodynamic solution models assume that E_{ex} (essentially equivalent to H_{ex} , enthalpy of mixing, at low pressure) and V_{ex} are constant with both temperature and pressure, reflected in such models (for example, those utilizing Margules parameters) by the absence of both T and P terms in expressing E_{ex} and V_{ex} data (see Thompson, 1967, Eqs. 47, 49, and 69; also Eq. 3 of this paper). The assumption that enthalpies of mixing are independent of temperature implies that there are neither energetically significant phase transitions nor changes in the state of order over the temperature range considered, and also that excess vibrational heat capacities are negligible. This last assumption requires validation by calorimetry, either by heat-capacity measurements or by direct measurement of the enthalpies of mixing at two temperatures. Such calorimetric data are generally sparse for solid solutions of mineralogical importance.

Two calorimetric methods are commonly used to determine enthalpies of mixing in silicate solid solutions, hydrofluoric acid solution calorimetry near 50 °C (Hovis and Roux, 1993) and oxide melt solution calorimetry near 700 °C (Navrotsky, 1977). These methods never have been compared directly for the same solid solution series. Thus, the motivations for this study were twofold: to check the validity of the common assumption of temperature

independence of H_{ex} and to compare the results of calorimetry in aqueous HF and in molten $2PbO \cdot B_2O_3$.

The thermodynamic mixing properties of disordered alkali feldspars have been well studied (Hovis, 1986, 1988; Hovis et al., 1991). Highly precise enthalpies of K-Na mixing have been determined at 50 °C by Hovis (1988) using HF solution calorimetric techniques. Although a monoclinic to triclinic transformation does occur across the series, the energy effect of the transition is so low as to be undetectable with current techniques (Hovis, 1988). These minerals, therefore, constitute excellent solid solutions both for testing regular solution models and for comparing calorimetric techniques.

SAMPLE PREPARATION

An 11-member ion-exchange series from analbite to sanidine was prepared for the current study using techniques similar to those described by Hovis (1986, 1988). Analbite (sample 7001) was prepared by annealing pure hand-picked pieces of Amelia low albite at 1052 °C for 752 h. A corresponding sanidine (sample 7201) was produced by ion-exchange of the analbite powder (–325 mesh) in molten KCl at 815 °C for 24 h. Compositionally intermediate samples were made by combining powders of analbite and sanidine in the desired proportions, mixing and then compressing these powders in cylindrical Pt crucibles, and annealing them for various lengths of time (normally about 5 d) at 900–930 °C. Each sample was removed from the furnace approximately every 24 h, re-mixed in acetone (to randomize grains of various compositions), then repacked and reloaded for further annealing. Several intermediate compositions produced in

TABLE 1. Unit-cell dimensions and volumes

Feldspar	N_{or}	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Unit-cell V (Å ³)	Molar V (cm ³ /mol)	Molar V (J/bar·mol)
7001	0.010	8.1624(22)	12.8655(28)	7.1139(12)	93.496(27)	116.386(24)	90.129(26)	667.62(21)	100.516(32)	10.0518(32)
9101	0.075	8.2018(18)	12.8920(29)	7.1241(12)	93.088(23)	116.384(18)	90.074(29)	673.57(20)	101.412(30)	10.1414(30)
8001	0.140	8.2315(29)	12.9208(23)	7.1312(11)	92.555(22)	116.358(17)	90.093(29)	678.74(23)	102.190(35)	10.2192(35)
9102	0.215	8.2736(47)	12.9448(30)	7.1456(14)	91.911(39)	116.323(31)	90.021(41)	685.46(33)	103.202(50)	10.3204(50)
9103	0.290	8.2972(26)	12.9696(35)	7.1567(14)	91.035(54)	116.250(17)	90.029(42)	690.58(28)	103.973(42)	10.3975(42)
9104	0.365	8.3370(21)	12.9895(29)	7.1615(29)	90	116.185(24)	90	695.95(24)	104.781(36)	10.4783(36)
8008	0.440	8.3669(9)	12.9927(12)	7.1609(8)	90	116.130(8)	90	698.89(9)	105.224(14)	10.5226(14)
9105	0.589	8.4365(11)	13.0164(18)	7.1709(9)	90	116.068(11)	90	707.35(12)	106.497(18)	10.6499(18)
8034	0.738	8.4991(10)	13.0209(14)	7.1703(8)	90	116.004(8)	90	713.17(10)	107.374(15)	10.7376(15)
9106	0.862	8.5543(9)	13.0290(14)	7.1764(7)	90	115.988(9)	90	718.96(10)	108.245(15)	10.8248(15)
7201	0.986	8.6059(9)	13.0315(14)	7.1815(8)	90	116.004(10)	90	723.85(11)	108.982(17)	10.8984(17)

Note: uncertainties in the last decimal places given in parentheses. Data for 8001, 8008, and 8034 are from Haselton et al. (1983). For consistency with other feldspars studied during this investigation, compositions stated for these feldspars are based on compositions and weights of feldspars used for the syntheses and not from directly measured K and Na contents.

later stages of the investigation were made from preexisting intermediate compositions, rather than from end-member powders. All samples were elutriated to remove the finest grains prior to the calorimetric experiments. The ion-exchange procedures had no detectable effect on the Al-Si distributions of the various samples, owing to the sluggish kinetics of Al-Si reordering and the low temperatures of the ion-exchange procedures relative to the disordering temperature (see discussion in Hovis, 1986, p. 871).

The K and Na contents of end-member feldspars were measured by atomic absorption spectroscopy. The chemical compositions of intermediate members were in turn calculated from the chemical compositions and weighed amounts of the parent feldspars from which they were synthesized. As a check on the calculated compositions, we also measured the a unit-cell dimensions of all feldspars and confirmed that they were consistent with a - N_{or} relations reflected by Equation 2 of Hovis (1986). Compositions of all feldspars are included in Table 1.

EXPERIMENTAL TECHNIQUES

All feldspars were characterized by X-ray techniques utilizing a Scintag Pad V powder diffraction system. Unit-cell dimensions were computed using Burnham's (1962) lattice refinement program LCLSQ. The resulting unit-cell dimensions and volumes (Table 1) agree well with previously collected data on a similar disordered series, also made from Amelia analbite (Hovis, 1986). They reflect a high degree of sample homogeneity and a highly disordered Al-Si distribution (Fig. 1). Using techniques developed by Hovis (1988, 1989), we estimate that the mole fraction of Al in the T1 tetrahedral sites ($N_{\text{Al,T1}}$) of all series members is 0.28.

Calorimetric measurements were made at Princeton University with a twin Calvet-type microcalorimeter (Navrotsky, 1977). Pt sample containers were utilized with foil bottoms containing pinholes for good solvent access. Data reported are for experiments in which the Pt foil had been newly changed, which assured contamination-free experiments. Enthalpies of solution were made at

704 °C in molten lead borate (2PbO-B₂O₃), in most cases utilizing 20–30 mg of sample per experiment. At least three experiments were performed for each composition. Samples were allowed to equilibrate at 704 °C for at least 6 h (for most experiments, 16 h) before dissolution. Dissolutions were rapid, with completion after only a few minutes. Calibrations of the calorimeter was by the Pt-drop method (Navrotsky, 1977). In view of the short experimental durations and a dissolution temperature that was lower than the disordering temperature of the feldspars, there is virtually no chance that the Al-Si distributions of the samples changed during the course of the calorimetric experiments.

RESULTS

Volumes of K-Na mixing for analbite-sanidine at room temperature

Although the primary aim of this research was to determine enthalpies of mixing at elevated T , the room-

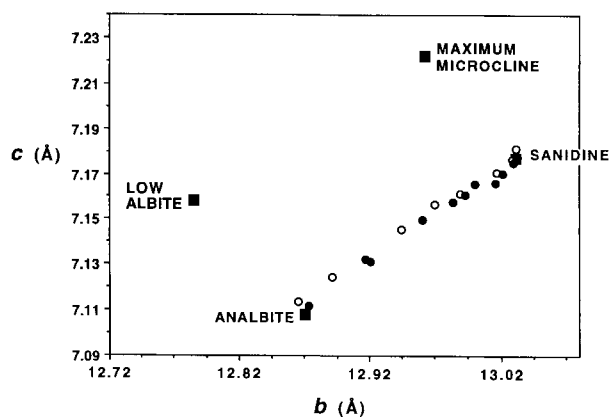


Fig. 1. Plot of b vs. c unit-cell dimensions for analbite-sanidine feldspars of the present investigation (open circles) along with those of Hovis (1986 and 1988; solid circles). Feldspars 8001, 8008, and 8034 are common to both investigations and are plotted as solid circles. The data indicate the disordered state of these solid solutions.

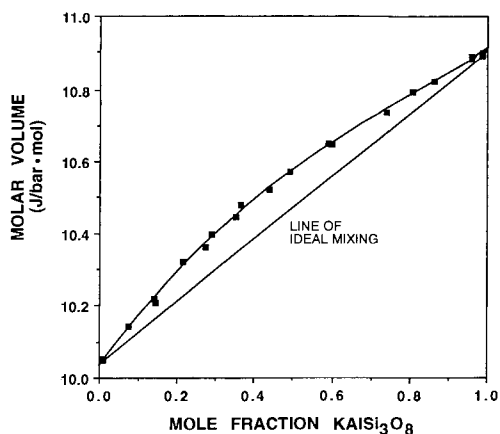


Fig. 2. Molar volumes for members of the present analbite-sanidine series, and those of Hovis (1986). The fitted curve to the data is given by Eq. 1.

temperature volumes determined for the newly synthesized feldspars added to a base of existing data for analbite-sanidine (Hovis, 1988). We have converted the new unit-cell volume data to molar volumes, combined these with the previous data, and fitted all 19 data points by least-squares methods as a function of composition (Fig. 2) to arrive at the following:

$$V(\text{J/bar}\cdot\text{mol}) = 10.0332(\pm 61) + 0.8766(\pm 99) N_{\text{Or}} \\ + 0.588(\pm 51) N_{\text{Or}} N_{\text{Ab}}^2 \\ + 0.257(\pm 60) N_{\text{Ab}} N_{\text{Or}}^2 \quad (1)$$

(uncertainties in the last two decimal places of each coefficient given in parentheses), where N_{Or} and N_{Ab} are the mole fractions of KAlSi_3O_8 and $\text{NaAlSi}_3\text{O}_8$, respectively. (These volumes can be converted to cubic ångströms per unit cell or to cubic centimeters per mole by multiplying all coefficients on the right side of Eq. 1 by 66.418 or

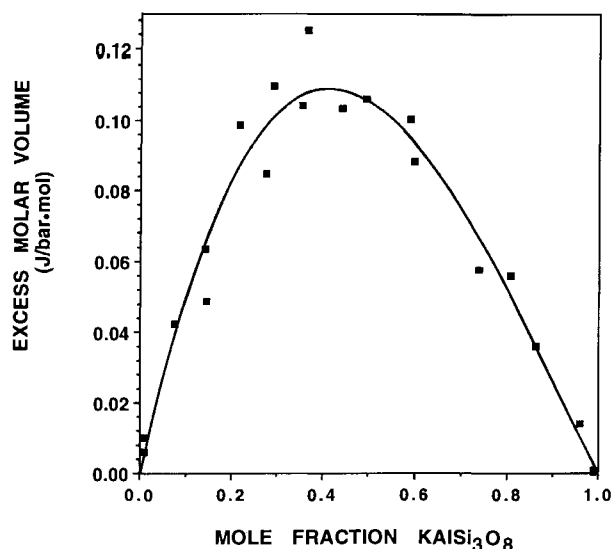


Fig. 3. Volumes of K-Na mixing determined from the data of Fig. 2. The fitted curve for volumes of mixing is expressed by the last two terms of Eq. 1.

9.9998, respectively.) The resulting standard error of the fit is ± 0.0092 J/bar·mol, and the correlation coefficient is 0.999. The resulting Margules parameters for volume, $W_{V,\text{Or}}$ and $W_{V,\text{Ab}}$ (0.588 and 0.257 J/bar·mol, respectively), have similar magnitudes and reflect the same asymmetry for V_{ex} (Fig. 3) as the general equation for topochemically monoclinic feldspars given by Hovis (1988, Eq. 1; also compare with his Table 2). Our results ignore any ΔV associated with the monoclinic to triclinic transformation, which at room temperature occurs near $N_{\text{Or}} = 0.35$. There is no obvious discontinuity in the volume data near the latter composition, despite the numerous data points in the vicinity.

Enthalpies of K-Na mixing at 704 °C

Results from our calorimetric investigation are presented in Table 2 and Figure 4. The data range constitutes 2–3% of the values for the enthalpies of solution at most compositions.

At 704 °C one can estimate that the monoclinic to triclinic transformation should occur at a composition near $N_{\text{Or}} = 0.10$, assuming a linear relation between transformation temperature and composition, and using the room-temperature transformation composition for the series (Hovis, 1980; Kroll et al., 1980) and the temperature for the analbite to monalbite transition (978 °C: Kroll et al., 1980; also Winter et al., 1979). As with Hovis's (1988) results at 50 °C, no discontinuity is evident in the lead borate calorimetric data near the estimated transformation composition. We shall therefore represent the data with a single enthalpy curve.

We have fitted the calorimetric data in Table 2 to equations having both a quadratic and a cubic form. Even though the latter fit yields a lower standard error (± 5.23

TABLE 2. Solution calorimetric data

Feldspar	N_{Or}	Mass (mg)	$-H_{\text{soln}}$ (kJ/mol)	Feldspar	N_{Or}	Mass (mg)	$-H_{\text{soln}}$ (kJ/mol)
7001	0.010	24.45	-72.340	9104	0.365	26.59	-78.250
	0.010	22.28	-72.950		0.365	22.48	-80.540
	0.010	21.05	-72.920		0.365	22.77	-79.880
	0.010	44.39	-72.220		0.365	24.31	-79.100
9101	0.075	23.48	-74.630	8008	0.440	20.63	-79.050
	0.075	28.75	-72.990		0.440	33.14	-80.790
	0.075	33.13	-71.460		0.440	28.06	-81.050
	0.075	21.54	-74.550		9105	0.589	27.00
8001	0.140	21.68	-75.010	8034	0.589	25.35	-86.460
	0.140	23.21	-72.170		0.589	24.55	-85.970
	0.140	23.26	-73.340		0.738	24.26	-89.820
	9102	0.215	27.05		-78.360	0.738	19.06
9102	0.215	21.70	-76.650	0.738	29.22	-90.350	
	0.215	32.06	-77.670	9106	0.862	22.84	-93.970
	0.215	25.28	-74.470	0.862	23.24	-94.900	
	0.215	26.02	-75.340	0.862	23.17	-92.200	
	9103	0.290	25.99	-78.400	7201	0.986	20.23
9103	0.290	21.53	-79.930	0.986	23.83	-100.490	
	0.290	27.81	-76.040	0.986	23.39	-102.240	
	0.290	21.78	-78.770	0.986	24.61	-101.420	
				0.986	27.62	-101.050	

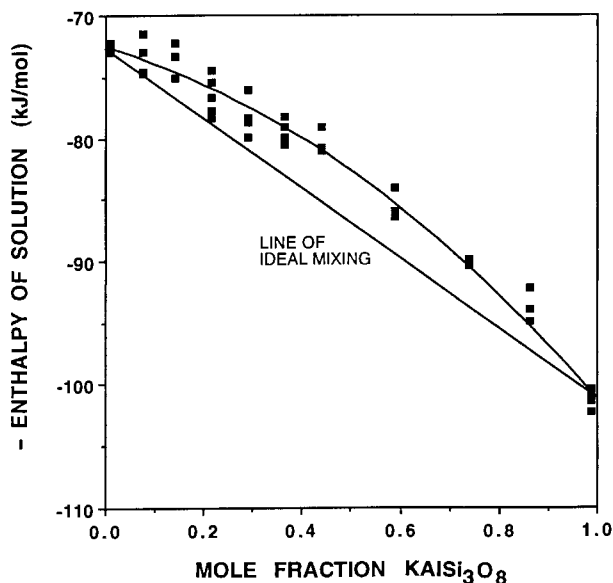


Fig. 4. Enthalpies of solution at 704 °C in molten lead borate. The fitted curve through the data is expressed by Eq. 2.

vs. ± 5.44 kJ/mol) and a better correlation coefficient (0.984 vs. 0.982), its use cannot be justified by the marginal degree of improvement over the second-degree equation. We accept the quadratic form, then, as the most reasonable fit to the data:

$$-H_{\text{soln}}(\text{kJ/mol}) = -72.61(\pm 48) - 28.60(\pm 63)N_{\text{Or}} + 17.0(\pm 2.4)N_{\text{Or}}N_{\text{Ab}} \quad (2)$$

(uncertainties in the last two figures of each coefficient given in parentheses).

The quadratic fit to the calorimetric data results in enthalpies of K-Na mixing that are symmetric about the composition $N_{\text{Or}} = 0.5$. A symmetric H_{ex} curve also resulted from the sanidine-analbite study at 50 °C of Hovis (1988). However, Hovis et al. (1991; see their Fig. 11) have noted the significant difficulty of calorimetrically detecting the small asymmetry that could exist in H_{ex} for this mineral series. Enthalpies of mixing are quite likely to be asymmetric with respect to composition, since along with entropies of mixing they are one of the two major contributors (at low P) to the Gibbs free energies of mixing (G_{ex}), which for this mineral series are required by the asymmetry of the alkali feldspar solvus to be asymmetric.

Enthalpies of K-Na mixing for our sanidine-analbite series (Fig. 5) may be expressed as a function of composition using the Margules parameter for enthalpy (W_H) derived from the last term of Equation 2:

$$H_{\text{ex}}(\text{kJ/mol}) = W_H N_{\text{Or}} N_{\text{Ab}} = 17.0(\pm 2.4) N_{\text{Or}} N_{\text{Ab}}. \quad (3)$$

DISCUSSION

The enthalpies of K-Na mixing for sanidine-analbite measured at 704 °C during the present study are statistically the same as those measured at 50 °C by Hovis

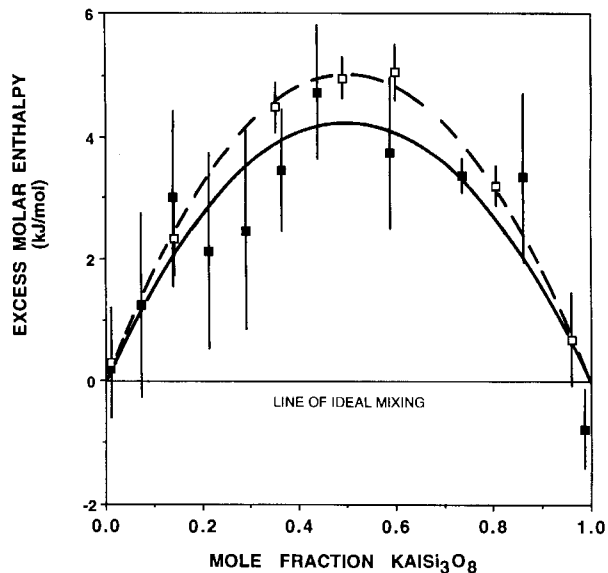


Fig. 5. Mean values (\pm standard deviations) of enthalpies of K-Na mixing for individual feldspars determined from the data at 704 °C from the present investigation (solid squares), given in Table 2 and Fig. 4, compared with the same for the HF data at 50 °C of Hovis (1988; open squares). Solid (Eq. 3) and dashed (Hovis, 1988, Table 7) curves, respectively, give fits to the data.

(1988). The W_H value of 20.1 ± 0.9 kJ/mol from the latter study compares with a value of 17.0 ± 2.4 kJ/mol from the present work. The combined uncertainties in the data from the two studies slightly exceed the 3.1 kJ/mol difference between these numbers. To illustrate this point further, we present in Figure 5 the mean values of H_{ex} for individual feldspars from this investigation and from Hovis (1988), along with heat of mixing curves for each. Note the substantial overlap of data from the present work with those based on HF measurements. These data also attest to the consistency of HF and lead borate calorimetric results. Although HF calorimetry produces less scatter in the data, lead borate calorimetry utilizes about one fifth the sample weight at each composition.

These results extend to substantially higher temperatures the conclusions drawn by Haselton et al. (1983). These workers directly measured the low-temperature heat capacities of five sanidine-analbite samples, including three samples of the present study (8001, 8008, and 8034). From their data it appeared that the change in the excess heat capacities of these minerals would be near zero above about -100 °C. However, their measurements were conducted only to a temperature of about $+100$ °C. In the present study we have confirmed that H_{ex} data collected by HF solution calorimetry at 50 °C can be applied to at least 700 °C and probably up to the melting temperatures of these minerals.

The results of this study also have a bearing on entropies of mixing calculated from the data of Hovis et al. (1991). These authors used H_{ex} values at 50 °C from Hov-

is (1988) in combination with G_{ex} values calculated from phase-equilibrium data determined at 800 °C to calculate total S_{ex} values for the present mineral series. They compared these with vibrational contributions to excess entropy determined from the data of Haselton et al. (1983) to conclude that short-range order could account for the differences between the two. Another explanation for the difference, however, could have been that H_{ex} values at 50 °C were not applicable at 800 °C, the temperature of the phase-equilibrium experiments. It now is evident that the latter is not the case, and that short-range order is indeed an important phenomenon in accounting for the thermodynamic behavior of these minerals. In fact, if the slightly lower Margules parameter for enthalpy at 704 °C (Eq. 2) were used, calculated total entropies of mixing would be even lower than those given by Hovis et al. (1991).

In conclusion, although thermodynamic mixing parameters such as H_{ex} and S_{ex} cannot be constant for non-ideal systems from 0 K to high temperatures, it is fruitful to ask whether there is a temperature above which they become constant. Regular solution thermodynamic models, which are normally applied at room temperature and above, indeed assume this to be the case. Within the precision of our data, the enthalpies of K-Na mixing in disordered alkali feldspars are indeed constant from 50 to 704 °C and most likely up to the melting temperatures of these minerals. This indicates that regular solution thermodynamic models for enthalpy are valid for the sanidine-analbite series. Such models may indeed be valid for all mineral series in which there are no complications due to phase transitions from room to high temperature nor structural reasons for suspecting significant excess vibrational heat capacities above room temperature. In such cases, enthalpies of mixing determined at one temperature may be applied over a very wide temperature range.

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