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Gibbs energies and entropies of K-Na mixing for alkali feldspars from phase equilibrium data: Implications for feldspar solvi and short-range order

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ABSTRACT

Reversed brackets have been achieved at T = 800 °C and P near 1 bar for K-Na partitioning between (K,Na)Br molten salts and members of two topochemically monoclinic alkali feldspar series that differ substantially in Al-Si distribution. The Gibbs energies of K-Na mixing derived from the phase equilibria for the two series are similar, but significantly less positive than those of a highly ordered topochemically triclinic series. These contrasting relations are consistent with higher critical temperatures for low microcline–low albite (Bachinski and Müller, 1971) and adularia-based feldspars, relative to highly disordered series.

Calculated entropies of mixing for highly disordered alkali feldspars, based both on this work and on solvus data, are somewhat uncertain; however, they are asymmetric with respect to composition and lower in magnitude than those from direct low-temperature heat capacity measurements. This, in turn, implies short-range order in such feldspars, consistent with recent observations in a more ordered low microcline–low albite series.

Recommended Margules parameters for internal energy, entropy, and volume for disordered alkali feldspars are $W_{E,\mathrm{Or}}$ = 5450 and $W_{E,\mathrm{Ab}}$ = 4670 cal/mol, $W_{S,\mathrm{Or}}$ = 1.5 and $W_{S,\mathrm{Ab}}$ = 2.5 cal/K·mol, $W_{V,\mathrm{Or}}$ = 0.110 and $W_{V,\mathrm{Ab}}$ = 0.078 cal/bar·mol. These parameters reproduce reversed low- and high-pressure solvi based on direct measurements by other investigators and are consistent with enthalpies of mixing from HF solution calorimetry as well as excess Gibbs energies from the present investigation.

INTRODUCTION

Enthalpies and volumes of K-Na mixing have recently been reported by Hovis (1988) for low microcline–low albite and for several alkali feldspar ion-exchange series that are topochemically monoclinic (i.e., they have monoclinic Al-Si distributions) and that represent a wide range of Al-Si distributions. To complete the thermodynamic characterization of the mixing properties of these minerals, data are needed on Gibbs energies ($\bar{G}_{\mathrm{ex}}$) and on entropies ($\bar{S}_{\mathrm{ex}}$; bars indicate molar quantities) of K-Na mixing.

Neither $\bar{G}_{\mathrm{ex}}$ nor total $\bar{S}_{\mathrm{ex}}$ can be measured directly. $\bar{G}_{\mathrm{ex}}$, however, can be calculated from phase equilibrium data. In the present study, K-Na exchange experiments were conducted between molten (K,Na)Br salts and two series of topochemically monoclinic feldspars differing substantially in degree of order. One was based on analbite parent material, henceforth referred to as the sanidine series (mole fractions of Al in the T1 and T2 tetrahedral sites of 0.28 and 0.22; Hovis, 1988), the other on a natural adularia specimen (mole fractions of Al in T1 and T2 of 0.43 and 0.07; Phillips and Ribbe, 1973; Hovis, 1988). Excess Gibbs energies of the feldspars were determined by entering the thermodynamic properties of the molten salts, as known. Entropies of K-Na mixing were in turn calculated using excess enthalpies and volumes reported for the same feldspars by Hovis (1988). Results from this study also were compared with similarly obtained data from a previous investigation of highly ordered topochemically triclinic low microcline–low albite feldspars (Delbove, 1975).

It is important to distinguish the excess entropies calculated for sanidine-analbite in this study from those measured directly by Haselton et al. (1983). The latter values, based on heat capacity data obtained from 5 to 380 K at five compositions, measured the vibrational component ($\bar{S}_{\mathrm{ex,vib}}$) of the excess entropies. Values based on the phase equilibrium data of the present investiga-

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Table 1. Beginning compositions and final feldspar-salt pairs used in thermodynamic calculations

Experiment number	N_{Or} of starting feldspar	M_{KBr} of starting salt	*a* unit-cell dimension of resulting feldspar (Å)	Calculated N_{Or} of resulting feldspar*	M_{KBr} of resulting salt	Experiment number	N_{Or} of starting feldspar	M_{KBr} of starting salt	*a* unit-cell dimension of resulting feldspar (Å)	Calculated N_{Or} of resulting feldspar*	M_{KBr} of resulting salt
		High sanidine series						**Adularia series**			
V-1	0.010	0.088	8.1616	0.004	0.092	I-2	0.537	0.351	8.4088	0.562[0.548]	0.330
V-2	0.010	0.213	8.1759	0.039	0.187	I-3	0.259	0.000	8.1560	0.038[0.039]	0.072
V-4	0.995	0.302	8.4745	0.679[0.681]	0.398	I-4	0.492	0.045	8.1847	0.095	0.164
V-5	0.995	0.390	8.5130	0.763	0.443	I-5	0.075	0.301	8.2158	0.160	0.252
V-6	0.995	0.578	8.5603	0.868	0.593	I-6	0.678	0.402	8.4768	0.700[0.682]	0.384
V-7	0.995	0.701	8.5767	0.904	0.700	I-7	0.860	0.449	8.5240	0.799	0.455
V-8	0.995	0.836	8.5926	0.940	0.830	I-8	0.678	0.813	8.5753	0.922	0.715
VI-1	0.522	0.242	8.3116	0.326	0.301	II-1	0.492	0.234	8.2887	0.314	0.278
VI-2	0.522	0.294	8.3627	0.436[0.408]	0.317	II-2	0.860	0.627	8.5617	0.887	0.635
VI-3	0.768	0.286	8.4211	0.562	0.344	II-3	0.678	0.942	8.5866	0.954[0.967]	0.845
VI-4	0.995	0.495	8.5465	0.837	0.526	II-4	0.075	0.188	8.1745	0.075	0.181
VI-5	0.264	0.248	8.2433	0.181	0.275	II-5**	0.188	0.464	8.3996	0.544	0.330
VI-7	0.522	0.363	8.4188	0.557	0.342	II-6	0.259	0.638	8.5128	0.775	0.447
VII-1	0.264	0.020	8.1647	0.015	0.094	II-7	0.075	0.377	8.2829	0.302	0.286
VII-2	0.264	0.133	8.1977	0.085[0.085]	0.203	III-1**	0.010	0.106	8.1560	0.038	0.097
VII-3	0.522	0.464	8.4799	0.691	0.417	III-2	0.492	0.164	8.2264	0.182	0.248
VII-4	0.522	0.564	8.5274	0.795	0.487	III-3**	0.188	0.393	8.3412	0.424	0.312
VII-5	0.768	0.670	8.5588	0.864	0.625	III-4**	0.259	0.538	8.4637	0.673	0.387
VII-6	0.768	0.771	8.5828	0.918	0.714	III-5	0.537	0.734	8.5588	0.880	0.592
VII-7	0.768	0.573	8.5537	0.853	0.558	III-6	0.860	0.737	8.5761	0.924	0.704
VII-8	0.768	0.912	8.5908	0.936[0.970]	0.844	III-7**	0.968	0.820	8.5842	0.947	0.816
VIII-2	0.010	0.153	8.1711	0.029[0.037]	0.158	III-8	0.860	0.532	8.5416	0.839	0.527
VIII-4**	0.505	0.266	8.3423	0.392	0.317	IV-1	0.860	0.332	8.4743	0.695	0.365
VIII-6	0.760	0.341	8.4576	0.642	0.381	IV-2**	0.995	0.571	8.5610	0.885	0.588
VIII-7**	0.505	0.505	8.5009	0.737	0.433	IV-3**	0.995	0.763	8.5829	0.943	0.765
VIII-8	0.760	0.835	8.5854	0.924	0.768	IV-5	0.678	0.298	8.4131	0.571	0.315
IX-4**	0.244	0.248	8.2431	0.180	0.298	IV-6	0.492	0.403	8.4343	0.614	0.356
IX-5**	0.010	0.309	8.2206	0.133	0.275	IV-7	0.075	0.335	8.2387	0.209[0.227]	0.271
IX-6**	0.522	0.244	8.3256	0.356	0.308	IV-8	0.678	0.592	8.5360	0.826	0.518
IX-7**	0.264	0.322	8.3317	0.369	0.307	IX-1**	0.259	0.241	8.2214	0.171	0.277
IX-8**	0.244	0.384	8.3798	0.473	0.333	IX-2	0.188	0.266	8.2230	0.175	0.262
X-2	0.010	0.216	8.1846	0.057	0.199						
X-3	0.264	0.015	8.1625	0.011	0.095						

* Compositions in brackets determined directly from atomic absorption analyses for K and Na.

** Total weight feldspar 0.0800 ± 0.0035 g and total weight salt 0.0955 ± 0.0085 g for all experiments except those designated by a double asterisk, where weights of feldspar and salt were generally 0.0625 ± 0.0035 and 0.0765 ± 0.0050 g, respectively. Mole fraction of [salt/(salt + feldspar)] was between 0.74 and 0.76 for all experiments.

tion, however, represent total excess entropies ($\bar{S}_{ex}$). The two are related as

$$\bar{S}_{ex} = \bar{S}_{ex,vib} + \bar{S}_{ex,config} + \bar{S}_{ex,other}. \quad (1)$$

Because the values calculated here are based on phase equilibria, they include all contributions to $\bar{S}_{ex}$, whereas the data of Haselton et al. (1983) do not. Note also that a solid solution series with constant structure and true long-range order in all crystallographic sites will have an excess configurational entropy ($\bar{S}_{ex,config}$) of zero, even though the configurational entropy itself ($\bar{S}_{config}$) will be nonzero. If short-range order is present, $\bar{S}_{ex,config}$ is negative and the absolute values of $\bar{S}_{ex}$ are thereby decreased.

Experimental methods

Feldspars and reagent-grade KBr and NaBr were loaded in Pt tubes, which were welded at both ends. Charges were held in furnaces at 800 °C for times ranging from 590 to 2870 h. Starting compositions and furnace conditions for all experiments are given in Tables 1 and 2. Experiments were conducted at 1 atm, but actual pressures inside the tubes were slightly higher because of air expansion and bromide vapor.

The feldspars used as starting materials originated from ion-exchanged adularia no. 7007 and analbite no. 7001 (equivalent to no. 7015) specimens, having been synthesized by previously described techniques (see Hovis, 1986, for details). Compositionally intermediate members of the adularia series used in this investigation are the same as those reported in Hovis (1986). However, a new suite of specimens was synthesized for sanidine-analbite at mole fractions $KAlSi_3O_8$ (N_{Or}) of 0.244, 0.264, 0.505, 0.522, 0.760, 0.768, and 0.995; these analytical data are from atomic absorption measurements for K and Na. All starting materials were finer than 325-mesh grain size and were elutriated to remove the finest grains.

At the conclusion of each experiment: the tubes were opened and both feldspar and bromide removed using deionized H_2O. The tubes and feldspars were thoroughly rinsed, and the resulting aqueous solutions were analyzed for K and Na using flame emission techniques. The separated feldspars were analyzed by X-ray powder diffraction; unit-cell dimensions were determined using the program LCLSQ of Burnham (1962) as modified by Blasi (1979). N_{Or} values were calculated using the a unit-cell dimensions of the feldspars and appropriate equations for the adularia and sanidine series (Table 7 of Hovis, 1986). Compositions of the resulting feldspars and salts are reported in Table 1.

As a check on the calculated compositions of the reactant feldspars, direct analyses were performed on ten of the feldspars using atomic absorption spectroscopy. Results are given in Table 1 and generally compare favorably with the indirectly determined N_{Or} values. Because differences between direct and indirect analyses are small and not consistently in the same direction, direct analyses would have little or no effect on the calculations that follow. For internal consistency, therefore, the thermodynamic calculations made here utilize only the compositions based on values of a.

DATA ANALYSIS

In analyzing our data, we have utilized Equation 23 of Thompson and Waldbaum (1968):

$$RT \ln \frac{N_{\mathrm{Or}} M_{\mathrm{NaBr}} \gamma_{\mathrm{NaBr}}}{N_{\mathrm{Ab}} M_{\mathrm{KBr}} \gamma_{\mathrm{KBr}}} = -[(\mu^0_{\mathrm{Or}} - \mu^0_{\mathrm{Ab}}) - (\mu^0_{\mathrm{KBr}} - \mu^0_{\mathrm{NaBr}}) + W_{G,\mathrm{Or}}] - 2(W_{G,\mathrm{Ab}} - 2W_{G,\mathrm{Or}})N_{\mathrm{Or}} - 3(W_{G,\mathrm{Or}} - W_{G,\mathrm{Ab}})N^2_{\mathrm{Or}} \quad (2)$$

in which the first term on the right side of the equation is the difference in the molar Gibbs energies of the pure end-member feldspars (at T, P), the second is the difference in the chemical potentials of the respective salt components (at T, P), the Ws are Margules parameters for the feldspar components, and N_{Or} is the mole fraction of $KAlSi_3O_8$ in the feldspar. In utilizing this equation, we have kept the nonideal term for the molten salt on the left side of the equation. Since

$$RT \ln \frac{\gamma_{\mathrm{NaBr}}}{\gamma_{\mathrm{KBr}}} = -(G_{\mathrm{ex,salt}}/M_{\mathrm{K,salt}}) \quad (3)$$

and since the right side (RS) for the KBr-NaBr system in turn can be expressed as

$$G_{\mathrm{ex,salt}}/M_{\mathrm{K,salt}}(\mathrm{cal/mol}) = -570 + 1260M_{\mathrm{KBr}} - 180M^2_{\mathrm{KBr}} \quad (4)$$

(see Delbove, 1975) based on the 770 °C data of Hersh and Kleppa (1965), Equation 2 was transformed to

$$RT \ln \frac{N_{\mathrm{Or}} M_{\mathrm{NaBr}}}{N_{\mathrm{Ab}} M_{\mathrm{KBr}}} + 570 - 1260M_{\mathrm{KBr}} + 180M^2_{\mathrm{KBr}} = -[(\mu^0_{\mathrm{Or}} - \mu^0_{\mathrm{Ab}}) - (\mu^0_{\mathrm{KBr}} - \mu^0_{\mathrm{NaBr}}) + W_{G,\mathrm{Or}}] - 2(W_{G,\mathrm{Ab}} - 2W_{G,\mathrm{Or}})N_{\mathrm{Or}} - 3(W_{G,\mathrm{Or}} - W_{G,\mathrm{Ab}})N^2_{\mathrm{Or}}. \quad (5)$$

TABLE 2. Furnace experiment conditions

Feldspar series	Temperature (°C)	Time at temperature (h)
I	800 ± 3	590
II	800 ± 3	998
III	803 ± 3	789
IV	800 ± 1	762
V	800 ± 1	650
VI	802 ± 2	664
VII	799 ± 1	669
VIII	800 ± 1	983
IX	799 ± 2	2314
X	800 ± 2	2870

This adjustment to the terms on the left side of the equation corrects for the enthalpy of K-Na mixing of the molten salt. Since there were no data on the entropies of mixing in the salt, they were necessarily assumed to be zero. Because enthalpies of mixing for the salt were quite small and because we were dealing with material in its molten state, the latter assumption seemed reasonable.

The right side of Equation 5 has the form

$$\mathrm{RS} = a_0 + a_1 N_{\mathrm{Or}} + a_2 N^2_{\mathrm{Or}}. \quad (6)$$

Thus, values of the left side of Equation 5 were calculated for exchange pairs in Table 1 and fit to second-order least-squares equations as Taylor expansion series in powers of N_{Or}. Margules parameters for Gibbs energy ($W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$) were determined from the resulting coefficients a_1 and a_2 as

$$W_{G,\mathrm{Or}} = (1/2)a_1 + (1/3)a_2 \quad (7)$$

and

$$W_{G,\mathrm{Ab}} = (1/2)a_1 + (2/3)a_2. \quad (8)$$

[Note that the signs of similar equations given by Thompson and Waldbaum (1968, p. 1979) are incorrect.]

Entropy parameters were calculated using the relationships

$$W_{G,\mathrm{Or}} = W_{E,\mathrm{Or}} + PW_{V,\mathrm{Or}} - TW_{S,\mathrm{Or}} \quad (9)$$

and

$$W_{G,\mathrm{Ab}} = W_{E,\mathrm{Ab}} + PW_{V,\mathrm{Ab}} - TW_{S,\mathrm{Ab}} \quad (10)$$

where Ws for E, V, and S are Margules parameters for internal energy, volume, and entropy, and P and T are pressure and temperature. Since Margules parameters for internal energy are essentially equal to corresponding parameters for enthalpy ($W_{H,\mathrm{Or}}$ and $W_{H,\mathrm{Ab}}$) when $P = 1$ bar, values of the latter based on solution calorimetric experiments conducted at atmospheric pressure (Hovis, 1988) were substituted for the former. Using $W_{V,\mathrm{Or}}$ and $W_{V,\mathrm{Ab}}$ data from Hovis (1988) and a temperature of 1073.15 K (that of the ion-exchange experiments), values of $W_{S,\mathrm{Or}}$ and $W_{S,\mathrm{Ab}}$ were obtained from the Margules parameters for Gibbs energy.

Note that for the sanidine and adularia series we have used Margules parameters for volume given in Equation 1 of Hovis (1988). For calculations involving Delbove's

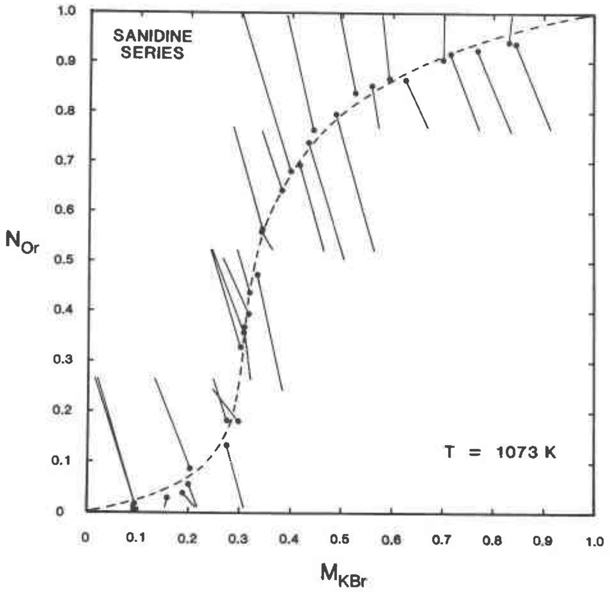


Fig. 1. Ion-exchange data for the sanidine series. Points give final compositions of coexisting salt (M_{KBr} is mole fraction KBr) and feldspar (N_{Or} is mole fraction $KAlSi_3O_8$). Ends of lines give starting salt-feldspar compositions. Dashed curve corresponds to least-squares fit of $-RT \ln K$ (corrected for nonideality of the salt) against N_{Or} for this series shown in Figure 3.

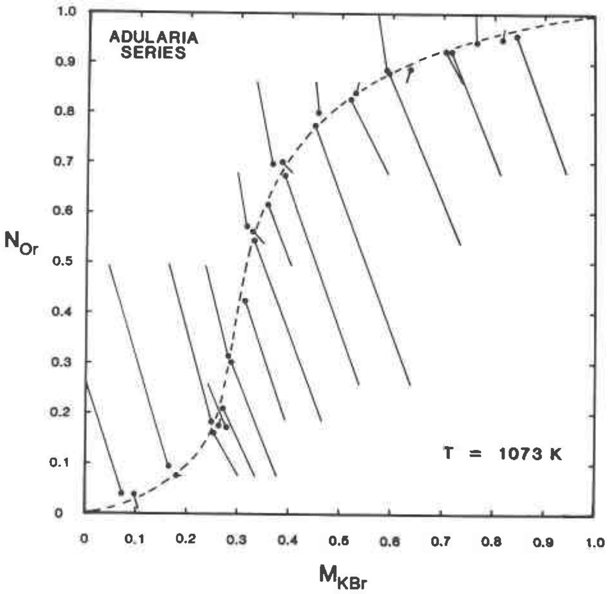


Fig. 2. Ion-exchange data for the adularia series. Dashed curve corresponds to least-squares fit of $-RT \ln K$ (corrected for nonideality of the salt) against N_{Or} for this series shown in Figure 3.

(1975) low microcline–low albite series, we have assumed that the closely spaced data of Kroll et al. (1986) best represent volume relations, even though their molar volumes are somewhat lower in the range 0.2–0.5 of N_{Or} than those of other workers (see discussion in Hovis, 1988). Furthermore, for consistency with other thermodynamic mixing parameters, we have used a third-order least-squares fit to the low microcline–low albite volume data ($W_{V,Or} = 0.040$ and $W_{V,Ab} = 0.134$ cal/bar·mol), despite the fact that relations are better represented by a fourth-order equation. This makes little difference in the calculated phase equilibria for pressures up to several kilobars, since the bulk of the nonideality for topochemically triclinic feldspars occurs in the enthalpy and entropy terms. For example, the calculated solvus for these feldspars based on symmetric vs. asymmetric volumes of mixing are within 0.01 N_{Or} of each other along both limbs of the solvus for a pressure of 2 kbar.

In the calculation of the left-side values above, care must be taken in data selection. A small change in N_{Or} or M_{KBr} for compositions near 0.0 and 1.0 changes the value of the equilibrium constant significantly because of the large effect on its denominator (discussed by Thompson and Waldbaum, 1968, p. 1985). Thus, small analytical errors are much more significant when they are made for near end-member compositions than in the middle of the compositional range. From mathematical tests made with the data (independently changing the N_{Or} and M_{KBr} values of coexisting feldspar-salt pairs in increments of 0.01), we have determined for the sanidine and adularia series that left-side values for feldspar-salt pairs where N_{Or} values are less than 0.07 or greater than 0.91 would be too sensitive to analytical error for our calculations. These were therefore excluded from the least-squares fits, although the data are shown in various figures.

Both the sanidine and adularia series undergo triclinic-monoclinic displacive transformations at room temperature as a function of composition at N_{Or} values of 0.353 and 0.309, respectively (Hovis, 1980). As discussed by Hovis (1988), no discontinuities can be seen either in the volume or enthalpy data near the transformation composition for either series, nor can discontinuities be seen in the left side of Equation 5 (although at 800 °C the transformation compositions would be near the sodic end-member); thus, we cannot rigorously account for the effects of the displacive transformation in the calculations below. The high precision of the calorimetric data indicates that such effects must be small.

It also is important to note that the enthalpies of mixing used in our calculations technically apply only at 50 °C, and that volumes of mixing apply only at room temperature. Low-temperature heat capacities measured for five members of the sanidine-analbite series (Haselton et al., 1983), however, indicate that excess heat capacities for disordered feldspars do not change (or at least do not change substantially) above about 200 K; thus, application of our enthalpy data at 323 K to elevated temperatures for such feldspars should be reasonable. There are, however, no similar data for adularia or microcline series, nor are volumes of mixing available for any feldspar series at high temperatures. By necessity, therefore, we have assumed that the lower temperature data can be

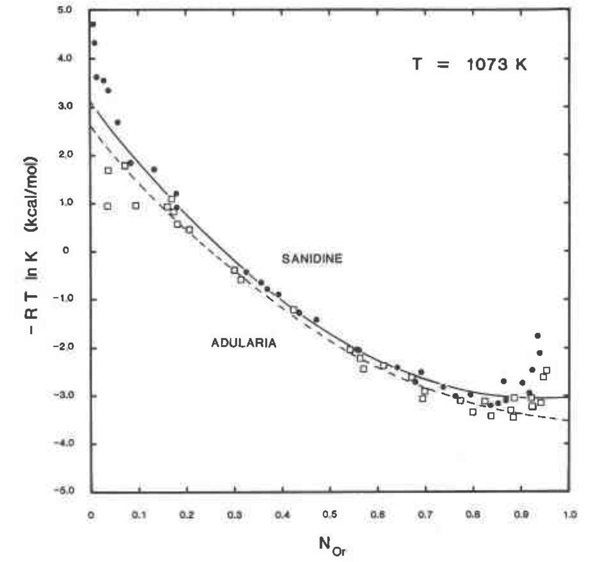


Fig. 3. Plot of $-RT \ln K$ (corrected for nonideality of the salt as given by the left-hand side of Eq. 5) vs. N_{Or} for adularia (open squares) and sanidine (closed circles) series based on feldspar-salt pairs given in Table 1. Curves represent second-order least-squares fits to the data for experiments in which the ending feldspars had N_{Or} values between 0.07 and 0.91.

applied to the higher temperature of the ion-exchange experiments.

To compare our data with those for Delbove's (1975) low microcline–low albite series, we have recalculated his feldspar compositions based on 2θ values for the $\bar{2}01$ interplanar spacing (for Cu$K\alpha$ radiation) developed from our own microcline–low albite series (Hovis, 1986):

$$N_{\mathrm{Or}} = 117.633 - 9.956\ 2\theta_{\bar{2}01} + 0.210\ (2\theta_{\bar{2}01})^2. \quad (11)$$

Use of this equation makes Delbove's feldspar compositions internally consistent with those from which enthalpies of mixing were determined (Hovis, 1988), although it should be noted that he did not use Amelia low albite as his starting material. We also have used a slightly wider data range at sodic compositions for these feldspars, relative to the sanidine and adularia series, because of the limited amount of data in the middle of the compositional range resulting from molten salt exchange equilibria conducted under conditions that were within the relatively high-temperature solvus of low microcline–low albite (see Fig. 4 of Delbove, 1975).

RESULTS

Thermodynamic data

Results of our ion-exchange experiments are given in Table 1 and can be seen in Figures 1 and 2. Note that, by starting with various feldspar-salt combinations, we have been able to obtain reversed equilibria and that the equilibrium curves are tightly constrained by the closely spaced data. What appear to be slight overlaps in the equilibria are the result of small uncertainties in feldspar and salt compositions (both estimated to be less than ±0.02). Data on the disordered series agree well with the earlier work of Delbove (1971) on similar (but synthetic) feldspars.

TABLE 3. Margules parameters for entropy derived from Hovis (1988) and present data

Feldspar series	Data range used (N_{Or})	Resulting $W_{G,\mathrm{Or}}$*, $W_{G,\mathrm{Ab}}$ (cal/mol)	Assumed $W_{H,\mathrm{Or}}$**, $W_{H,\mathrm{Ab}}$ (cal/mol)	Resulting $W_{S,\mathrm{Or}}$, $W_{S,\mathrm{Ab}}$ (cal/Kmol)	Critical T (°C) and N_{Or} for $P = 1$ and 2000 bars†
Sanidine	0–1	4993	4800	−0.180	869.2, 0.286
		1339	4800	3.225	923.7, 0.284
Sanidine	0.07–0.91	4262	4800	0.502	692.1, 0.336
		1923	4800	2.681	736.3, 0.333
Adularia	0–1	3715	6640	2.725	651.5, 0.357
		1779	6640	4.529	681.5, 0.353
Adularia	0–1	3715	10680	6.490	701.2, 0.319
		1779	2850	0.998	721.0, 0.323
Adularia	0.07–0.91	3959	6640	2.499	682.4, 0.362
		2113	6640	4.218	713.3, 0.358
Adularia	0.07–0.91	3959	10680	6.263	721.3, 0.330
		2113	2850	0.687	741.8, 0.335
Microcline‡	0–1	4413	6990	2.401	754.4, 0.387
		2993	6990	3.725	771.2, 0.400
Microcline‡	0–1	4413	11150	6.278	767.3, 0.372
		2993	2970	−0.021	778.5, 0.389
Microcline‡	0.06–0.91	4995	6990	1.859	835.5, 0.307
		1954	6990	4.693	846.1, 0.314
Microcline‡	0.06–0.91	4995	11150	5.735	820.2, 0.313
		1954	2970	0.947	827.0, 0.322

* Values of $W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ are calculated for 1073.15 K (and $P = 1$ bar), the temperature of the ion-exchange experiments, and not for the critical temperature of the solvus.

** From Table 6 of Hovis (1988).

† $W_{V,\mathrm{Or}}$ and $W_{V,\mathrm{Ab}}$ values used in solvus calculations are 0.110 and 0.078 cal/bar mol, respectively, for the sanidine and adularia series, and 0.040 and 0.134 cal/bar mol for the microcline series.

‡ W_G values derived from data of Delbove (1975); original N_{Or} values of his feldspars adjusted as described in the text.

Second-order least-squares fits of the left side (Eq. 5) are shown for the sanidine and adularia series in Figure 3. The resulting thermodynamic mixing parameters for Gibbs energies and for entropies based on Equations 9 and 10 are given in Table 3; they are compared with parameters calculated from feldspar–molten bromide results for Delbove's (1975) microcline series. To show the effect of data selection (discussed above), we give in Table 3 values of $W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ for our sanidine and adularia series resulting from use of all data vs. those resulting from use only of feldspar-salt pairs where feldspars have compositions in the range $0.07 < N_{\mathrm{Or}} < 0.91$ or, in the case of Delbove's microcline series, $0.06 < N_{\mathrm{Or}} < 0.91$.

Hovis (1988) has discussed the justification for the adoption of asymmetric vs. symmetric enthalpies of mixing ($\bar{H}_{\mathrm{ex}}$) for various alkali feldspar series. For the adularia and microcline series, the use of an asymmetric model seems statistically justified, based on least-squares analysis of the heat-of-solution data. For sanidine-analbite, however, there is essentially no statistical difference between quadratic and cubic fits to the calorimetric data.

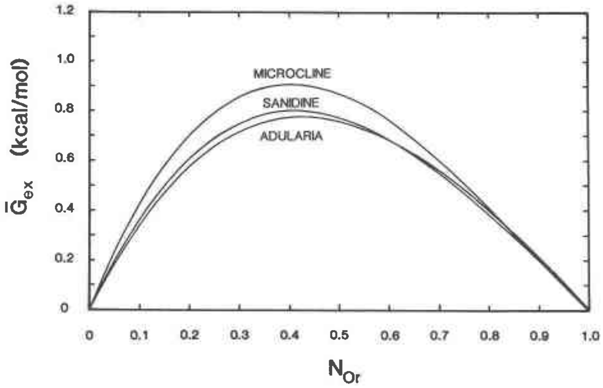


Fig. 4. Gibbs energies of mixing for the sanidine and adularia series derived from the ion-exchange data of this investigation and for microcline from the ion-exchange data of Delbove (1975). Margules parameters on which curves are based are given in Table 3.

The question is whether the sanidine series actually has symmetric $\bar{H}_{ex}$ values, or whether the asymmetry is simply less for this series and, therefore, more difficult to detect. Choice of the correct model for enthalpies of mixing is important because of its profound effect on calculated entropies of mixing. We have illustrated this in Table 3 by giving $W_{S,Or}$ and $W_{S,Ab}$ values for the adularia and microcline series based on both symmetric and asymmetric $\bar{H}_{ex}$ models; see the W_H column to distinguish the various calculations.

Note from Table 3 and Figures 1–3 that there are indeed detectable differences in the ion-exchange data for the two Al-Si distributions studied during this investigation, and also between these and the low microcline–low albite series of Delbove (1975). This is reflected first by a small difference in the resulting Gibbs energies of mixing for sanidine vs. adularia and then by a distinct increase from the topochemically monoclinic series to low microcline–low albite (Fig. 4). These differences in ion-exchange data correlate well with increases observed in enthalpies of mixing with increased order (Hovis, 1988), and with the higher critical temperature of the low microcline–low albite solvus (Bachinski and Müller, 1971) relative to the solvi determined for sanidine-analbite (references given below).

Solvus calculations

Effects of structural state on alkali feldspar solvi. From the thermodynamic data given in Table 3, it is possible to calculate alkali feldspar solvi for various temperatures and pressures. Solvi calculated for sanidine, adularia, and microcline all are metastable relative to an equilibrium solvus in that Al-Si distribution for each is constant for all temperatures and pressures. However, comparison of the various solvi gives an indication of the effect of structural state on critical temperatures and compositions, and thus gives a good qualitative feeling for the appearance of an actual equilibrium solvus. Note that along an equilibrium solvus not only would Al-Si distribution change as temperature decreases, but coexisting feldspars at a particular temperature and pressure would generally not have the same Al-Si distribution. Our calculations also ignore the triclinic-monoclinic displacive transformation, the thermodynamic effect of which cannot be estimated with present data.

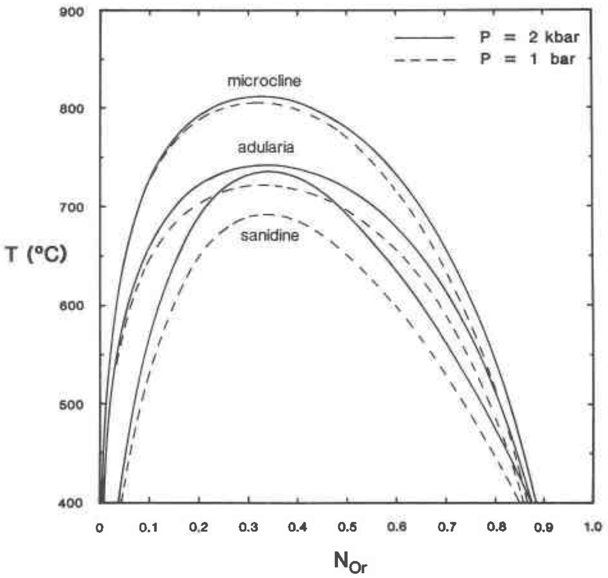


Fig. 5. Alkali feldspar solvi calculated for sanidine (bottom), adularia (middle), and microcline (top) series for pressures of 2 kbar (solid curves) and 1 bar (dashed curves). Calculations for sanidine and adularia are based on Gibbs energies of mixing from the ion-exchange equilibria of this investigation. Calculations for microcline are based on similar data from Delbove (1975). Enthalpies and volumes of mixing for all series are from Hovis (1988). Pertinent Margules parameters are given in Table 3.

Figure 5 shows solvi calculated for $P = 1$ and 2000 bars for the sanidine and adularia series from present data and for microcline based on data from Delbove (1975). At either pressure, as Al-Si distribution becomes increasingly ordered, critical temperatures (T_c) increase both within topochemically monoclinic series and from sanidine and adularia series to low microcline–low albite. Critical compositions of alkali feldspar solvi, however, appear to change very little with structural state, e.g., at $P = 1$ bar from N_{Or} of 0.336 to 0.330 to 0.313 from sanidine to adularia to microcline.

The sanidine solvus has a more pointed crest and limbs which are somewhat different in shape from those of the other series. This results from the use of symmetric enthalpies of mixing for this series. If indeed $\bar{H}_{ex}$ is slightly asymmetric for the sanidine-analbite, with $W_{H,Or} > W_{H,Ab}$ (as for other alkali feldspar series), the actual crest of the solvus would be somewhat flatter and the limbs more similar in shape to those of adularia and microcline.

From the solvi for individual Al-Si distributions, one can deduce that an equilibrium solvus would have a critical temperature and composition similar to that of sanidine but a relatively wider crest and limbs that are slightly less steep at lower temperatures than any of those shown in Figure 5, the result of increased Al-Si order with decreasing temperature. Additionally, monoclinic-triclinic inversions would take place along both limbs of the solvus, but at a higher temperature along the sodic than along the potassic side (see Thompson and Hovis, 1979). Feldspars along the sodic limb of the solvus would generally be more ordered than coexisting potassic feldspars.

Effect of pressure on alkali feldspar solvi. The effect of pressure on an alkali feldspar solvus relates to the Gibbs energy of mixing and its dependence on volumes of mixing. Data in the last column of Table 3 illustrate how feldspar series of different structural states can be affected to different degrees by pressure. The critical temperature for the sanidine series increases by 44 °C over a 2 kbar range, relative to an increase of 21 °C for the adularia series, even though the same Margules parameters for volume were used in the two calculations. Low microcline–low albite volumes of mixing, with a much different asymmetry than those of topochemically monoclinic series (based on the data of Kroll et al., 1986; discussion in Hovis, 1988), result in a mere 7 °C increase in T_c over a 2 kbar range. Note also from Figure 5 that, contrary to the assumption made by a number of previous workers, the effect of pressure on critical temperature, especially for microcline and adularia, does not translate into a constant-temperature effect along solvus limbs.

Whether structural state has as large an effect on volumes of mixing as reflected by the data of Kroll et al. (1986) is arguable. Nevertheless, the calculations here show the potential of the effect that structural state has on $\bar{V}_{ex}$ and the related pressure sensitivity of the solvus. One should not extend pressure corrections based on one ion-exchange series to other Al-Si distributions.

COMPARISON OF CALCULATED AND DIRECTLY DETERMINED ALKALI FELDSPAR SOLVI

Preliminary statement

One check on the thermodynamic parameters calculated from our exchange equilibria comes from solvus data. Solvi can be calculated from our data and compared with those determined directly by various investigators. Conversely, thermodynamic parameters can be obtained from solvus data and used to check, or amplify, data in the present paper. In what follows, we shall explore both of these avenues.

Solvus data are available from numerous investigators, mostly for low pressures but some for high pressures as well. Data are especially numerous for solvi based on specimens with highly disordered Al-Si distributions. Some of these are from hydrothermal or ion-exchange experiments on coexisting feldspar phases produced from gels, glasses, or precrystallized feldspars (see Bowen and Tuttle, 1950; Orville, 1963; Luth and Tuttle, 1966; Morse, 1970; Seck, 1972; Luth et al., 1974; Martin, 1974; Smith and Parsons, 1974; Lagache and Weisbrod, 1977; Parsons, 1978). Others are based on ion-exchange equilibria between single feldspars and either an aqueous solution or molten salt (see Orville, 1963, as discussed by Thompson and Waldbaum, 1968; Delbove, 1971). The high-pressure data are from piston-cylinder experiments that utilized both gels and crystalline feldspars as starting materials (Goldsmith and Newton, 1974). Direct and indirect solvus determinations also exist for highly ordered low microcline–low albite alkali feldspars (Bachinski and Müller, 1971; also at one temperature by Delbove, 1975). It is important for present purposes to note that we employed data only from those studies in which reversed equilibria were achieved and in which other experimental problems were avoided.

Sanidine-analbite low-pressure solvus

Some of the solvi determined at low pressures (mostly 1–2 kbar) for disordered feldspars are of limited value. It is now known, for directly determined solvi, that the compositions of the gels and solutions used as starting materials in these experiments affect the initial compositions of crystallizing feldspars and, furthermore, that equilibrium between pairs of feldspars is approached only after experiments of very long duration. Different curves have been used by various investigators to determine feldspar compositions from X-ray data. These and other factors have led to considerable disagreement among workers as to which solvus is *the* solvus for disordered feldspars. Parsons (1978) discussed these effects and reviewed in detail all previous solvus studies.

In his review, Parsons (1978) concluded that there was good agreement for a 1 kbar solvus between his data and those of Orville (1963), Smith and Parsons (1974), Goldsmith and Newton (1974), and Lagache and Weisbrod (1977). Pressure corrections made by Parsons to the Goldsmith and Newton data, however, employed W_V values (particularly $W_{V,\mathrm{Or}}$) that are not supported by numerous available direct determinations (see Table 2 of Hovis, 1988). In later papers, Brown and Parsons (1981, Appendix) and Parsons and Brown (1984) continued to utilize a $W_{V,\mathrm{Or}}$ value (0.168 cal/bar·mol) that is 50% higher than directly measured values of approximately 0.110 (±0.007) cal/bar·mol (Hovis, 1988). Although it can be argued that all existing volume data for alkali feldspars are based on room temperature and pressure measurements and, therefore are not strictly applicable to high pressures, volumes of mixing derived from such data are a valuable guide to the sensitivity of feldspar solvi to pressure. We would, therefore, question the use of such a high $W_{V,\mathrm{Or}}$ value and the claim that there is good agreement between the low-pressure data of Smith and Parsons (1974; also Parsons, 1978) and the high-pressure results of Goldsmith and Newton (1974). There also is little justification for the conclusion by Brown and Parsons (1981) and Parsons and Brown (1984) that the data of Goldsmith and Newton (1974) indicate a slightly more pointed feldspar solvus at high than at low pressure, given

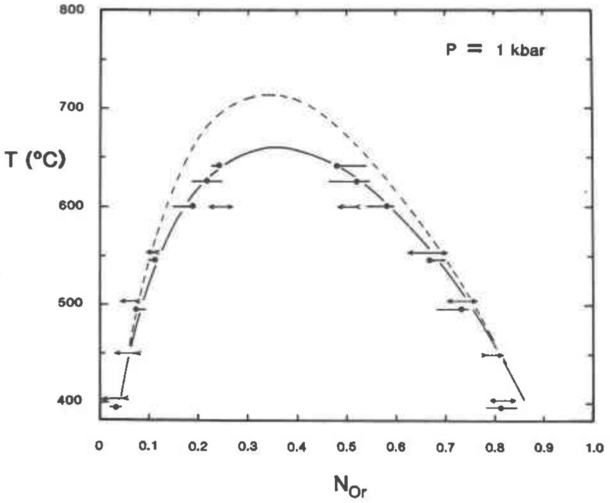


Fig. 6. Solvus data for sanidine-analbite at a pressure of 1 kbar. Broken curve calculated from the second data set for sanidine-analbite given in Table 3, solid curve from Equations 12–14 (see Summary and Conclusions). Other data are based on direct determinations. Bars without dots are from the data of Smith and Parsons (1974) and Parsons (1978). For the latter, arrows indicate direction of the change in feldspar compositions with time. If pointing toward or away from each other they indicate bracketed equilibria. If pointing in the same direction they indicate a range of results from different experiments and are unreversed. Bars with dots are from Lagache and Weisbrod (1977); dots indicate their preferred data for coexisting pairs. Bars represent uncertainties based on the raw data sent by Lagache; thus, preferred data points do not always fall in the middle of the various brackets. Multiple data points at individual temperatures have in some cases been slightly displaced in temperature for purposes of clarity.

the rather wide reversal brackets of both the low- and high-pressure work, and the fact that the high-pressure data were collected far from the vicinity of the critical temperature and composition.

The work of Smith and Parsons (1974) and Parsons (1978), nevertheless, was important in establishing initial crystallization products as a function of gel composition, in monitoring changes of initial feldspar composition with time over very long periods (so-called time and motion studies, Goldsmith and Newton, 1974), and in achieving apparent reversals at a number of temperatures. This research confirmed that the solvi of Morse (1970, 5 kbar), Luth et al. (1974), and Martin (1974) were indeed composition dependent. The results also called into question the assumed directions of compositional change, as well as sufficiency of experiment duration, in the 1.25 and 2.5 kbar experiments of Seck (1972). Although Seck utilized feldspars as well as gels and glasses as starting materials, the failure to differentiate among the various kinds of experiments in his table of data makes it difficult to evaluate his results.

There also seems to be justification for Parsons' (1978) claim of agreement with the results of Lagache and Weisbrod (1977). Although the latter authors did not report time and motion studies nor give uncertainties for their coexisting compositions based on duplicate experiments, raw data recently sent to us by Lagache for temperatures of 400, 500, 550, 625, and 640 °C (and for pressures from 600 to 2000 bars) seem to indicate that equilibria were indeed reversed and that there is substantial overlap between data of Smith and Parsons (1974) and Parsons (1978; hereafter referred to as SPP) and those of Lagache and Weisbrod (1977; hereafter referred to as LW), at least between 400 and 550 °C.

We summarize in Figure 6 our interpretation of SPP data for 1 kbar at temperatures for which there is a substantial amount of data; we also include interpretation of LW data based on the information sent to us by Lagache. We indicate for all studies those equilibria that appear to have been reversed. Note for SPP that the widths of bars drawn for most temperatures along the sodic limb of the solvus represent uncertainties based on duplicate experiments (at least in part from uncertainties in composition determination), and that they do not represent bracketed equilibria. As acknowledged by Parsons (1978), in contrast with the LW data, SPP equilibria were generally not reversed along the Na-rich limb of the solvus.

In drawing Figure 6, we have considered the time and motion studies of SPP based on various gel compositions; these were also helpful in interpreting LW data, although (unlike SPP) the latter authors equilibrated their feldspars with Na,K-bearing solutions. Even so, crystallization behavior is somewhat baffling. A good example is the SPP $Ab_{60}Or_{40}$ gel, which at 500 °C apparently began crystallization at a relatively potassic composition, then became more sodic, then migrated toward more K-rich compositions that were between the former and the latter. There are also the SPP data at 450 °C on the potassic limb of the solvus, where feldspars apparently continued to move toward more potassic compositions in even the longest experiments. The latter seem to be out of alignment with the potassic ends of the bracketed equilibria at temperatures 50 °C above and below. In general, inconsistencies among the results of various experiments (even for long-term experiments) produce rather wide brackets for both SPP and LW data. There also are clear differences between SPP and LW equilibria at 600 °C and above.

The 1 kbar solvus in Figure 6 calculated from our own data (hereafter referred to as HDR) is in excellent agreement, generally within 0.01–0.015 N_{Or}, with the sodic limb of the LW solvus between 400 and 550 °C. Both HDR and LW disagree somewhat with the relatively sodic compositions of SPP, which become even more sodic in the longest experiments. HDR and LW also have a steeper sodic limb than does SPP, especially evident at temperatures of 600 °C and above. The HDR calculated solvus lies significantly outside that of SPP at 600 °C, as does that of LW to a lesser degree.

Along the potassic limb of the solvus between 400 and 550 °C HDR compositions generally lie at, or within 0.01–0.02 N_{Or} of, the potassic ends of the SPP and LW brackets. LW data generally agree with those of SPP in this temperature range, but both LW and HDR indicate a steeper limb than SPP, as was also true on the sodic side of the solvus. At 600 °C and above, no overlap exists among the three data sets; unreversed SPP data continued to move to more sodic compositions even for the longest experiments.

Smith and Parsons (1974, p. 761–764) calculated a critical temperature of 657 °C for their alkali feldspar solvus at 1 kbar. Such a solvus requires limbs more like those of Lagache and Weisbrod (1977), which seems in conflict with their own data for 600 °C. However, the stated SPP T_c and critical composition ($N_{Or} = 0.36$) are in good agreement with the corresponding values of LW (661 °C, 0.363). The HDR solvus has a higher T_c (714 °C) than the other studies but a critical composition ($N_{Or} = 0.335$) near those of both SPP and LW.

In conclusion, the HDR solvus for disordered alkali feldspars calculated from thermodynamic parameters derived earlier in this paper is at slight odds with directly determined low-pressure solvi, particularly along the K-rich limb of the solvus. Although HDR, SPP, and LW all disagree in the vicinity of the critical temperature, where directly determined equilibria would be most difficult to achieve, it nevertheless seems significant that both SPP and LW reflect a lower critical temperature than that of HDR. We shall investigate the thermodynamic implications of this later.

Sanidine-analbite high-pressure solvi

Goldsmith and Newton (1974, hereafter referred to as GN) determined reversal brackets at a number of temperatures along both limbs of the sanidine-analbite solvus at pressures of 9, 11, 14, and 15 kbar, although there were fewer reversals along the sodic limb (in fact, none at 11 kbar). These investigators used both crystalline feldspars and gels or glasses as starting materials and in a number of instances monitored feldspar composition with time. Thus, unlike many of the low-pressure studies, their work is not open to question relative to the initial crystallization products of gels or glasses, or the direction of change in feldspar composition with time. Furthermore, their results do not suffer from the overlapping equilibria or inconsistencies in crystallization histories that confuse interpretation of gel-based studies. As such, the GN work constitutes the most internally consistent set of solvus results published to date. The only question arising from their data was the effect on their results of the state of ordering in the products from their lower temperature experiments (see their Fig. 8); it is evident from the present study, however, that the effect would have been negligible even for their most ordered feldspar, which roughly corresponds in Al-Si distribution to a slightly ordered sanidine. Results of GN are plotted in Figure 7, along with calculated solvi based on our preferred data for the sanidine series given in Table 3, and using $W_{V,Or}$ and $W_{V,Ab}$ values of 0.110 and 0.078 cal/bar·mol (Hovis, 1988), respectively, to correct our data to higher pressures.

Agreement between HDR and GN is excellent. Although a number of the GN brackets are rather wide (about the same as those of the SPP and LW solvi), with the exception of their reversal along the potassic limb of the solvus at 500 °C and 14 kbar (narrowly missed by our solvus), our data fall within even their narrowest brackets. Examples are those occurring along the K-rich limb at 600 °C for pressures of 9 and 15 kbar and those along the Na-rich limb for 500 °C at 14 kbar and 400–450 °C at 15 kbar.

Comparison of our calculated low- and high-pressure solvi shows how pressure, using directly measured room T,P values of $W_{V,Or}$ and $W_{V,Ab}$, affects the limbs of the alkali feldspar solvus. The same W_V values applied to SPP and LW data result in solvus shifts that are slightly less than those needed to make the latter data agree with the high pressure brackets of GN.

Low microcline–low albite low-pressure solvus

Bachinski and Müller (1971) have studied the low microcline–low albite solvus at pressures near 1 bar using three independent methods: (1) attempted equilibration of alkali feldspars coexisting in molten (K,Na)I salts, (2) attempted equilibration of coexisting feldspars in dry homogenization experiments starting with end-member compositions, and (3) unmixing experiments on homogeneous feldspars from within the solvus. We show in Figure 8 only their reversed equilibria, which in the case of fused salt experiments (B) occur at temperatures of 700 and 750 °C. Another fused salt reversal occurs along the potassic limb of the solvus at 800 °C, but conflicting results make that bracket quite wide. Results of experiments at 850 °C, which Bachinski and Müller (1971) believed to be within the solvus, are unidirectional and inconclusive. Our experiments with fused salts, although above the solvi of the feldspars we studied, suggest that most of the Bachinski and Müller experiments were of relatively short duration for full equilibration among the salt and two feldspars; this is particularly true for experiments near the solvus where equilibration between the feldspars is likely to take months, if not years. It is also possible that the brackets of Bachinski and Müller are only apparent reversals; refer to the discussion on p. 339–342 of their paper.

The homogenization-unmixing experiments (M) of Bachinski and Müller (1971) produced reversed equilibria only at 700 and 800 °C. Data for the potassic limb at 800 and for the sodic limb at 700 °C are in agreement with their fused salt results. However, the reversal for the potassic limb at 700 °C lies at a considerably more potassic composition than that based on the fused salt experiments. Unmixing experiments at high temperatures that would imply a T_c above 900 °C are unidirectional and almost certainly too short to have produced equilibrated assemblages. Data at temperatures below 700 °C suggest a wider solvus than does the fused salt work, but changes of feldspar composition with time here too are unidirectional. The authors admit that the latter experi-

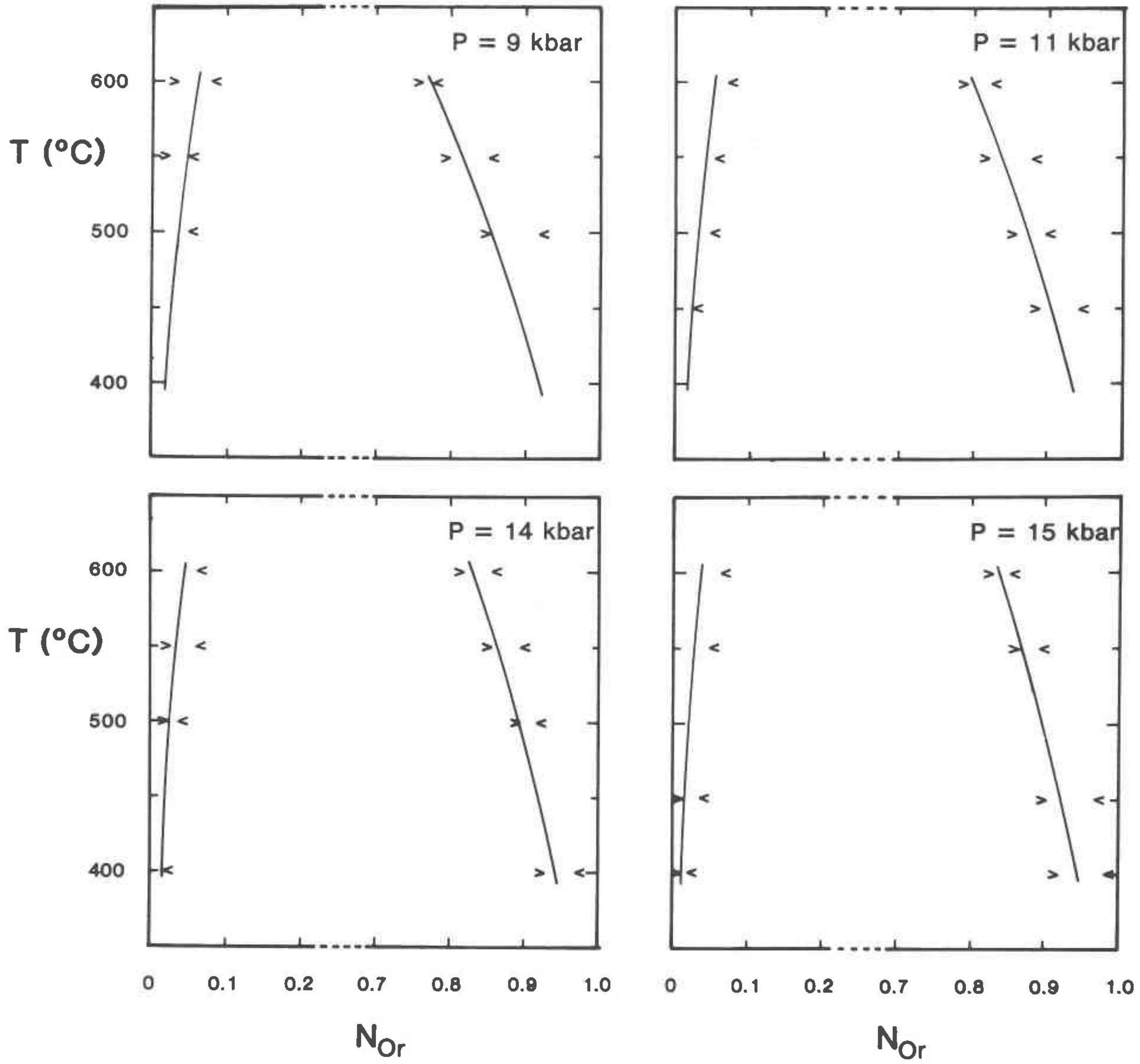


Fig. 7. High-pressure solvus data for sanidine-analbite from the piston-cylinder experiments of Goldsmith and Newton (1974); brackets are based on their time and motion studies. Solid curves are calculated from the preferred thermodynamic data of the present investigation given in Table 3 and on $W_{V,\mathrm{Or}}$ and $W_{V,\mathrm{Ab}}$ values of 0.110 and 0.078 cal/bar·mol (Hovis, 1988), respectively.

ments are likely to have been too limited in duration for full equilibration.

The low microcline–low albite system also has been studied by Delbove (1975) using ion-exchange equilibria in molten salts at 800 °C (P near 1 bar) and techniques similar to those of the present investigation. His experiments employed microcline as starting material; thus, equilibria were not reversed. Although he used potassium sodium bromide instead of iodide salts, Delbove's work produced feldspar pairs at 800 °C that may be compared with those of Bachinski and Müller (1971). Data in Figure 8 show that Delbove's (1975) results (D) compare favorably with the fused salt experiments of Bachinski and Müller (1971) on the potassic limb and with their homogenization-unmixing results on the sodic limb.

As noted above, Delbove's (1975) feldspar-salt pairs also have been utilized in the present study to calculate $\bar{G}_{ex}$ and (using calorimetric $\bar{H}_{ex}$ values from Hovis, 1988) $\bar{S}_{ex}$ data for low microcline–low albite. A feldspar solvus calculated from these parameters for 1 bar (since this is the pressure at which all experimental data on these minerals were obtained) is also shown in Figure 8. The latter is in good agreement with that of Bachinski and Müller (1971) for reversals at temperatures of 700 and 750 °C, but substantially inside their bracket for the sodic limb at 800 °C. The calculated composition along the potassic limb at 800 °C agrees with fused salt work of Bachinski and Müller and is inside their second bracket based on homogenization-unmixing reversals. The HDR 800 °C data are also inside those based on Delbove's (1975) fused salt work, particularly for the sodic limb. In general, the work of Bachinski and Müller (1971) would suggest a higher critical temperature than would our own calculation, especially considering their data for Na-rich feldspars, which imply a relatively steeper limb. However, the Bachinski and Müller (1971) data are themselves not internally consistent. The unidirectional fused salt experiments suggest a considerably more K-rich sodic limb at 800 °C, one that would agree better with our calculated solvus, than the apparent reversals based on homogenization-unmixing experiments. (Note movement of arrows on their Fig. 3 and compare to data at 800 °C on their Fig. 4).

THERMODYNAMIC IMPLICATIONS OF DIRECTLY DETERMINED SOLVUS DATA AND COMPARISON WITH PRESENT DATA

Just as it is possible to calculate solvi from thermodynamic data, it also is possible to derive thermodynamic parameters from solvus data. To understand the thermodynamic implications of differences in solvus data among various investigators, we have employed the technique described in the Appendix of Thompson and Waldbaum (1969) for handling two-phase data, and calculated Margules parameters for Gibbs energies based on the reversal brackets of Smith and Parsons (1974), Parsons (1978), Lagache and Weisbrod (1977), Goldsmith and Newton (1974), and Bachinski and Müller (1971). Haselton et al. (1983) completed a similar analysis of solvus data for sanidine-analbite, but did not differentiate between reversed and unreversed data nor between studies that employed time and motion techniques and those that did not. Furthermore, their objective was to calculate excess enthalpy data from their directly determined vibrational entropies of mixing, assuming the latter to be equal to the total excess entropy (see Eq. 1). Instead, we have made the calculation to check the internal consistency of the solvus data and to compare the excess Gibbs energies derived from the latter with those derived from ion-exchange data of the present investigation.

Since Margules parameters based on solvus data represent equilibria established over a range of temperatures that are generally lower than that of our ion-exchange study, it is necessary to plot the values of $W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ calculated for various solvus brackets against temperature and to extrapolate trends to 800 °C. Moreover, it is evident from Equations 9 and 10 that linear variations of $W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ with temperature are equivalent to the negatives of $W_{S,\mathrm{Or}}$ and $W_{S,\mathrm{Ab}}$. This constitutes a second means of calculating total $\bar{S}_{\mathrm{ex}}$, one that not only takes into account both solvus and ion-exchange equilibria but also is independent of $\bar{H}_{\mathrm{ex}}$ modeling.

Sanidine-analbite

Unlike Haselton et al. (1983), we have not calculated $W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ from individual pairs of feldspars but rather from the brackets shown in Figure 6, taking the inside vs. the outside compositions of each bracket to determine the range of $W_{G,\mathrm{Or}}$ values implied by the data for that temperature. Even larger uncertainties for $W_{G,\mathrm{Ab}}$ were obtained by taking inside-inside vs. outside-outside compositions for each bracket. We have corrected the high-pressure data of Goldsmith and Newton (1974), as well as our own 1-bar data, to a pressure of 1 kbar using the $W_{V,\mathrm{Or}}$ and $W_{V,\mathrm{Ab}}$ values stated earlier.

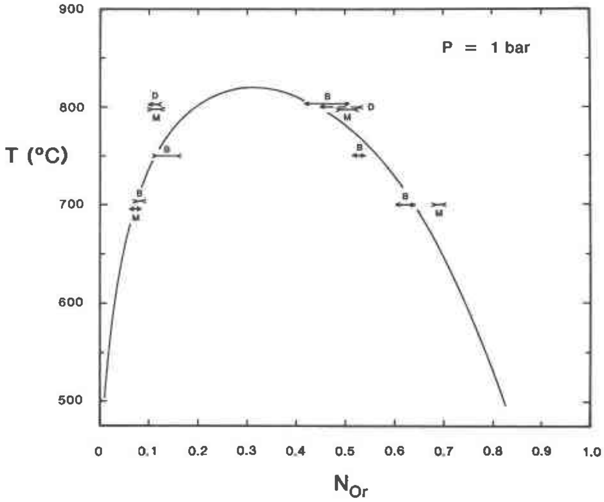
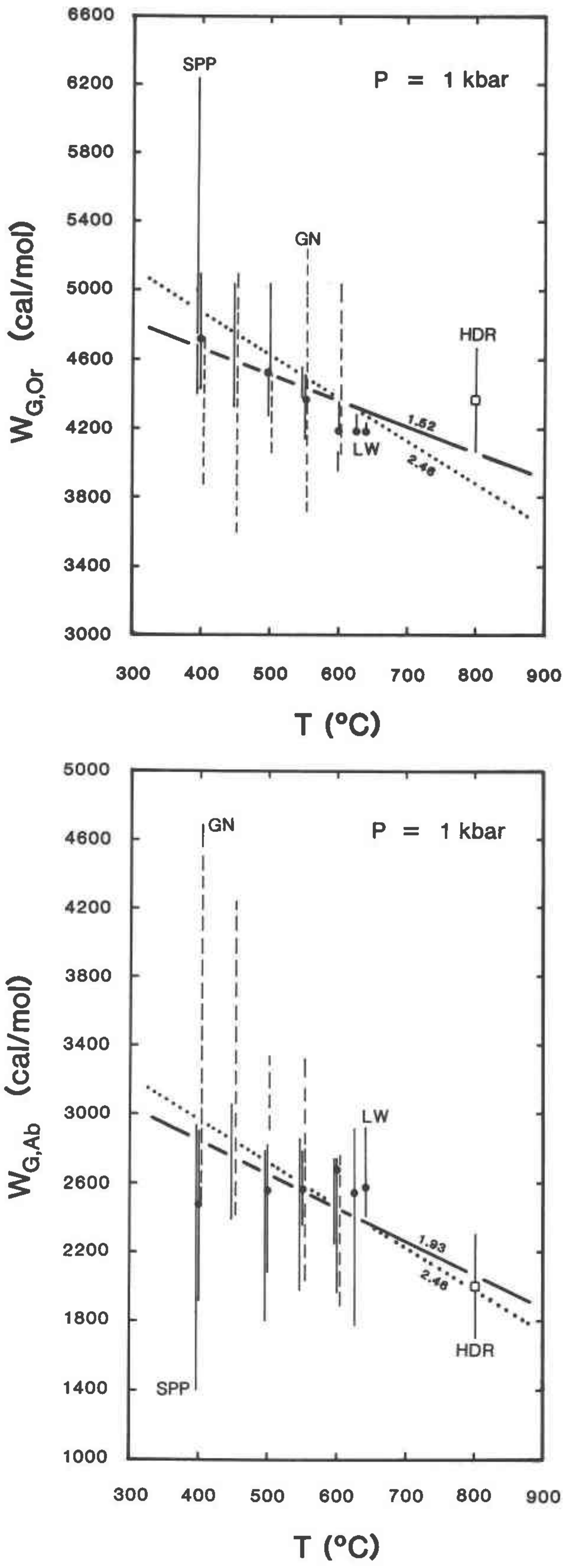


Fig. 8. Microcline–low albite solvus data at a pressure of 1 bar. The solid curve was calculated from the preferred thermodynamic data given in Table 3 based on the ion-exchange equilibria of Delbove (1975) and the asymmetric enthalpies of mixing of Hovis (1988). Bars are mostly from the direct determinations of Bachinski and Müller (1971), B from ion-exchange equilibria, and M representing homogenization-unmixing experiments. Data labeled D are from Delbove (1975). Arrows pointing toward each other represent reversed, or bracketed, equilibria. Arrows pointing in the same direction represent unreversed equilibria and a range of results based on different experiments.

All Margules parameters calculated for Gibbs energy are shown in Figure 9 along with data from the present investigation. $W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ values for Lagache and Weisbrod (1977) are based on the preferred coexisting feldspar compositions given in their Table 1. Since these are not always in the middle of brackets determined from the raw data sent to us by Lagache, their preferred W_G values are not always centered within the brackets shown. Uncertainties for our data (±300 cal/mol) are based on differences of least-squares fits which employed either more or less data than experiments for which resulting feldspars had compositions for N_{Or} between 0.07 and 0.91. Actual uncertainties are slightly larger, however, since entropies of mixing for the (K,Na)Br molten salts were not available for our calculations.

It is evident from Figure 9 that even a small uncertainty in a solvus bracket produces a substantial uncertainty (hundreds of calories) in the implied thermodynamic values. Because of these large error bars, it is difficult to conclude that any one data set is in substantial disagreement (or agreement) with any other, with the possible exception of the GN data for $W_{G,\mathrm{Ab}}$, which at lower temperatures seems to be slightly displaced from those of



SPP and LW; however, this disagreement could, in part, result from the pressure correction that we have applied. Although, not surprisingly, all studies agree that $W_{G,\mathrm{Or}} > W_{G,\mathrm{Ab}}$, data of Figure 9 cannot be used to obtain precise Gibbs energy parameters at any one temperature.

Because of the large uncertainties, it is also difficult to derive precise $W_{S,\mathrm{Or}}$ and $W_{S,\mathrm{Ab}}$ values from the variation of $W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ with temperature. Nevertheless, the data do limit the possibilities for entropies of mixing. In Figure 9 (top), a variety of slopes corresponding to $W_{S,\mathrm{Or}}$ values ranging from approximately +1.5 to −0.5 cal/K·mol could satisfy most of the data shown. A linear least-squares fit to all data produces a $W_{S,\mathrm{Or}}$ value of +1.52 (±0.85) cal/K·mol. Note that the value of +2.46 cal/K·mol determined from heat capacity measurements (Haselton et al., 1983), although satisfying much of the solvus data from 400 to 640 °C, misses data at 800 °C from the present investigation even with the rather wide error bar for the latter.

As for $W_{G,\mathrm{Ab}}$ (Fig. 9 bottom), the data of both SPP and LW suggest a slightly positive variation with temperature and, thus, negative $W_{S,\mathrm{Ab}}$. However, GN data suggest a strongly positive value for the same. Although the latter could imply that excess entropies are themselves functions of pressure, uncertainties in the data are much too great for the authors to be confident of such a conclusion. Overall, the only way that solvus data can be reconciled with data at 800 °C from the present investigation is with a negative slope. Thus, a linear least-squares fit to all data produces a value for $W_{S,\mathrm{Ab}}$ of +1.93 (±1.11) cal/K·mol. As shown in Figure 9 (bottom), this is not much different from the value of +2.46 cal/K·mol measured by Haselton et al. (1983) for the vibrational component of $W_{S,\mathrm{Ab}}$, nor from that of +2.68 ca/K·mol derived from our own data (Table 3). In fact, both these slopes pass through most of the solvus data as well as the data at 800 °C of the present investigation.

Whatever variations with temperature are obtained for

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Fig. 9. **(top)** Values of $W_{G,\mathrm{Or}}$ derived from solvus data (see text) and at 800 °C from present ion-exchange data (HDR, open square). Solid bars with dots (LW) are the preferred data of Lagache and Weisbrod (1977); uncertainties are based on the raw data sent by Lagache. Solid bars without dots (SPP) are from Smith and Parsons (1974) and Parsons (1978). Broken bars (GN) are based on the data of Goldsmith and Newton (1974). The data have been corrected to a pressure of 1 kbar, where necessary, using a value for $W_{V,\mathrm{Or}}$ of 0.110 cal/bar·mol from Hovis (1988). The heavy solid line is a least-squares fit to all data; the dotted line is from the work of Haselton et al. (1983). The two lines are labeled with corresponding values of $W_{S,\mathrm{Or}}$ in cal/K·mol. **(bottom)** Values of $W_{G,\mathrm{Ab}}$ derived from solvus data and, at 800 °C, from present ion-exchange data. Labeling is as in **top**. The data have been corrected to a pressure of 1 kbar, where necessary, using a $W_{V,\mathrm{Ab}}$ value of 0.078 cal/bar·mol from Hovis (1988). The heavy solid line is a least-squares fit to all data; the dotted line is based on work of Haselton et al. (1983). The two lines are labeled with corresponding values of $W_{S,\mathrm{Ab}}$ in cal/K·mol.

$W_{G,\mathrm{Or}}$ and $W_{G,\mathrm{Ab}}$ from Figure 9, it seems likely that the resulting value of $W_{S,\mathrm{Or}}$ is considerably less than the +2.46 cal/K·mol determined using heat capacity measurements (Haselton et al., 1983) and, further, that its value is less than that of $W_{S,\mathrm{Ab}}$. This, in turn, implies that total excess entropies for sanidine-analbite (Fig. 10) are asymmetric with regard to composition, maximized at potassic compositions, and generally less in magnitude than the values measured for the vibrational component of excess entropy alone (Eq. 1).

Low microcline-low albite

An analysis of low microcline–low albite solvus data, similar to that for sanidine-analbite (but at $P = 1$ bar), was also attempted. However, the reversal brackets of Bachinski and Müller (1971) and the ion-exchange data of Delbove (1975) cover only the temperature range of 700–800 °C. Analysis of $W_{G,\mathrm{Or}}$ data would imply a $W_{S,\mathrm{Or}}$ value between 0.0 and +5.0 cal/K·mol, but the limited data and large uncertainties make even this range questionable. Data for $W_{S,\mathrm{Ab}}$ are much worse, with large inconsistencies at 800 °C; no conclusions can be drawn as to slope. Overall, analysis of solvus data for low albite–low microcline does not lead to meaningful $W_{S,\mathrm{Or}}$ and $W_{S,\mathrm{Ab}}$ values that can be compared with those in Table 3.

Summary and conclusions

Relation of thermodynamic mixing parameters to Al-Si order

The reversed ion-exchange equilibria determined during the present investigation have produced Gibbs energies of K-Na mixing (Fig. 4) for two series of topochemically monoclinic alkali feldspars, one with a highly disordered Al-Si distribution, the other relatively ordered. Small but significant differences exist between exchange pairs for the two series (Figs. 1 and 2); these, in turn, imply real differences in the thermodynamic mixing properties as a function of structural state, emphasized further by contrast with data for a highly ordered topochemically triclinic series (Delbove, 1975). The higher critical temperature calculated for the adularia-based series, relative to disordered sanidine-analbite, seems to reflect this and fits well with a continued trend to an even higher T_c value for low microcline–low albite.

The factoring of Gibbs energies of K-Na mixing into enthalpies and entropies of mixing for the two relatively ordered series is problematic. Mixing parameters calculated for the adularia and microcline series (Table 3) rest mostly on the ion-exchange data of the present investigation and enthalpies of mixing derived from solution calorimetric data at 50 °C (Hovis, 1988). Even though the latter are highly precise, the combined errors in $\bar{H}_{\mathrm{ex}}$ and $\bar{G}_{\mathrm{ex}}$ make calculated values of $\bar{S}_{\mathrm{ex}}$ highly uncertain. This is shown clearly by Margules parameters for entropy in Table 3, which vary from $W_{S,\mathrm{Ab}} > W_{S,\mathrm{Or}}$ to $W_{S,\mathrm{Or}} \gg W_{S,\mathrm{Ab}}$, depending on the model employed for $\bar{H}_{\mathrm{ex}}$.

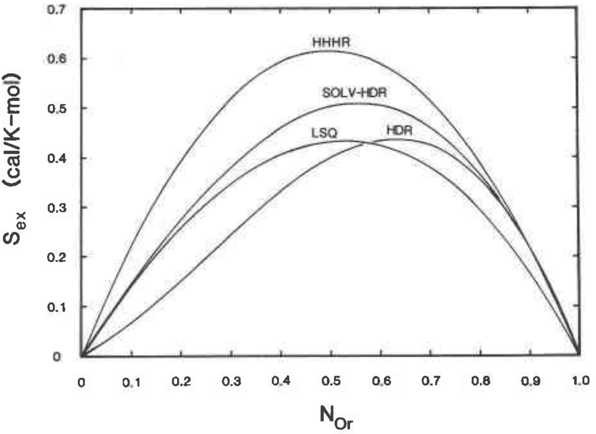

Fig. 10. Entropy of K-Na mixing curves for sanidine-analbite: HHHR from the heat capacity measurements of Haselton et al. (1983), LSQ from the solid line least-squares fits to data in Figure 9, SOLV-HDR from linear programming analysis (D.H. Lindsley, personal communication) of solvus and ion-exchange data as described in the text, and HDR from ion-exchange data of this investigation and enthalpies of mixing of Hovis (1988; Table 3 of the present paper). $W_{S,\mathrm{Or}}$ and $W_{S,\mathrm{Ab}}$ values, respectively, for the four curves are 2.46 and 2.46, 1.52 and 1.93, 1.50 and 2.50, and 0.50 and 2.68 cal/K·mol.

Clearly, more information is needed to limit further the factoring of Gibbs energies of mixing into enthalpy and entropy parameters for ordered alkali feldspar series. This might include the detection and quantification of short-range order in alkali feldspars of various structural states, low-temperature heat capacity measurements to determine $\bar{S}_{\mathrm{ex,vib}}$ as a function of structural state, quantification of the thermodynamic effect of the monoclinic-triclinic inversion in topochemically monoclinic feldspars, and assessment of the extent to which the modulated structure of the adularia series (see "Note added in proof" in Hovis, 1988) affects its thermodynamic properties.

Thermodynamic mixing parameters for disordered alkali feldspars

Thermodynamic mixing properties for disordered alkali feldspars are expressed by the ion-exchange data of the present investigation, the solution calorimetric and molar volume data of Hovis (1988), and the reversed solvus brackets of Smith and Parsons (1974), Parsons (1978), Lagache and Weisbrod (1977), and Goldsmith and Newton (1974). These data collectively limit the possibilities for the thermodynamic mixing parameters of these minerals. D. H. Lindsley (personal communication) has kindly assisted us in utilizing linear programming techniques to find which set of Margules parameters for enthalpy and entropy best fit both solvus data and the Gibbs energies of mixing derived from ion-exchange equilibria reported in this paper.

Linear programming analyses were especially effective in tightly constraining two of the four Margules parameters, $W_{H,\mathrm{Or}}$ (at 1 kbar) to values between 5340 and 5730 cal/mol (or $W_{E,\mathrm{Or}}$ to 5230–5620 cal/mol) and $W_{S,\mathrm{Or}}$ to

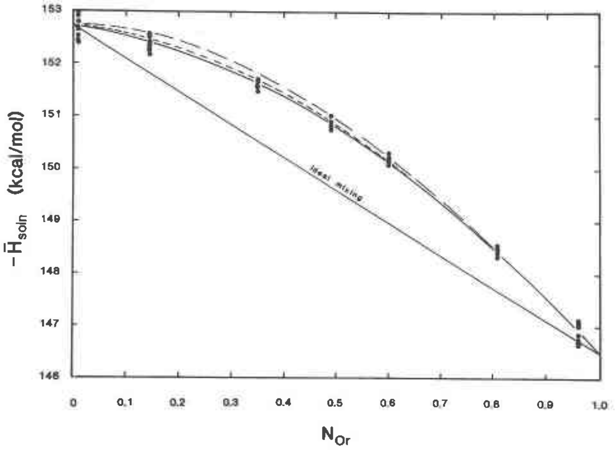

Fig. 11. Directly measured enthalpies of solution for the sanidine-analbite series from Hovis (1988). The solid (lower) curve represents a second-order least-squares fit ($W_{H,\text{Or}} = W_{H,\text{Ab}} = 4800$ cal/mol) through the data. The middle curve (short dashes; $W_{H,\text{Or}} = 5450$ cal/mol, $W_{H,\text{Ab}} = 4670$ cal/mol) is derived from linear programming analysis of data in Figure 9. The upper curve (long dashes; $W_{H,\text{Or}} = 6440$ cal/mol, $W_{H,\text{Ab}} = 4420$ cal/mol) is based on data from Table 13 of Haselton et al. (1983) as described in the text. The last two curves are superimposed on the line of ideal mixing connecting end-member heats of solution.

values between 1.11 and 1.55 cal/K·mol. By adding assumptions that $W_{E,\text{Ab}} = 4800$ cal/mol (Hovis, 1988) or $W_{S,\text{Ab}} = 2.46$ cal/K·mol (Haselton et al., 1983), we were able also to constrain narrowly the values for the other mixing parameters: $W_{E,\text{Ab}} = 4600\text{–}4720$ cal/mol and $W_{S,\text{Ab}} = 2.46\text{–}2.63$ cal/K·mol. Based on all analyses, we recommend use of the following Margules parameters for highly disordered alkali feldspars:

$$W_{E,\text{Or}} = 5450 \quad \text{and} \quad W_{E,\text{Ab}} = 4670 \text{ cal/mol} \tag{12}$$

$$W_{S,\text{Or}} = 1.5 \quad \text{and} \quad W_{S,\text{Ab}} = 2.5 \text{ cal/K·mol} \tag{13}$$

$$W_{V,\text{Or}} = 0.110 \quad \text{and} \quad W_{V,\text{Ab}} = 0.078 \text{ cal/bar·mol.} \tag{14}$$

Enthalpy parameters can be calculated for any pressure using

$$W_{H,\text{Or}} \text{ (cal/mol)} = 5450 + 0.110\, P \tag{15}$$

and

$$W_{H,\text{Ab}} \text{ (cal/mol)} = 4670 + 0.078\, P \tag{16}$$

and Margules parameters for Gibbs energy can be calculated for any P and T from Equations 9 and 10.

The solvus calculated from the above parameters (solid curve shown in Fig. 6) is in excellent agreement with the reversed solvus brackets of Lagache and Weisbrod (1977) and Smith and Parsons (1974; except at 600 °C). The calculated critical temperature of 660 °C at 1 kbar is virtually identical to those of both the SPP and LW studies. These parameters also produce high-pressure solvi that are in remarkable agreement with the data of Goldsmith and Newton (1974), differing only slightly from the curves shown in Figure 7 and fitting within virtually all bracketed equilibria.

Enthalpies of K-Na mixing implied by the above parameters are asymmetric with respect to composition and slightly greater in magnitude than the symmetric values reported by Hovis (1988; also Table 3). However, theoretical enthalpies of solution calculated by superimposing $\bar{H}_{\text{ex}}$ values (determined for 1 bar from the Margules parameters above) onto the line of ideal mixing given by Hovis (1988) are well within the uncertainties of his data (Fig. 11). It is clear that such a small degree of asymmetry would not have been calorimetrically detectable.

Haselton et al. (1983) took a different approach. They assumed that their directly measured $\bar{S}_{\text{ex,vib}}$ values for sanidine-analbite were equal to the total entropies of mixing ($W_{S,\text{Or}} = W_{S,\text{Ab}} = 2.46$ cal/K·mol) and, in turn, calculated enthalpies of mixing from W_G values derived from solvus data (some of them unreversed). They concluded that $\bar{H}_{\text{ex}}$ must be slightly asymmetric and maximized at sodic compositions ($W_{H,\text{Or}} > W_{H,\text{Ab}}$), which is qualitatively consistent with the values we have given above.

We have computed the mean Margules parameters for enthalpy and internal energy based on values in Table 13 of Haselton et al. (1983), but only for investigations that achieved reversed solvus brackets. The resulting $W_{E,\text{Or}}$ and $W_{E,\text{Ab}}$ values of 6440 and 4420 cal/mol, when combined with a W_S of 2.46 cal/K·mol based on heat capacity measurements, produce low-pressure solvi that are close to those calculated from the preferred data above ($T_c = 672$ °C at 1 kbar). However, the heats of solution derived from these enthalpy parameters are at the high end of those observed by Hovis (1988) over much of the sodic part of the compositional range (Fig. 11). Additionally, the sodic limbs of high-pressure solvi are inside a number of the higher temperature Goldsmith and Newton (1974) brackets. This implies Gibbs energies of mixing that are too small and, thus, entropies of mixing that are too large.

We believe the data of Figure 9 (including new $W_{G,\text{Or}}$ and $W_{G,\text{Ab}}$ values at 800 °C from the present study) are significant. Even with large uncertainties, these Gibbs energy parameters, which are independent of $\bar{H}_{\text{ex}}$ modeling, limit the possible values for $W_{S,\text{Or}}$ and $W_{S,\text{Ab}}$. Both the least-squares fits to data in Figure 9 and the linear programming analyses, which constrain both enthalpy and entropy parameters, suggest asymmetric entropies of mixing maximized at potassic compositions ($W_{S,\text{Ab}} > W_{S,\text{Or}}$) with magnitudes that are lower (Fig. 10) than entropies of mixing calculated from heat capacity data (Haselton et al., 1983).

If $\bar{S}_{\text{ex}} < \bar{S}_{\text{ex,vib}}$ for sanidine-analbite, the $\bar{S}_{\text{ex,config}}$ term in Equation 1 must be negative. This implies short-range order in disordered alkali feldspars. Such a conclusion fits well with the recent observations of Phillips et al. (1988), who on the basis of NMR data have reported the presence of Na clustering in ordered low microcline–low albite feldspars. The clustering, which is apparently more prevalent at sodic than at potassic compositions, would result in maximum deviations from ideal configurational entropy and, in turn, maximum negative $\bar{S}_{ex,config}$ contributions at sodic compositions. This too agrees qualitatively with the calculated values of $\bar{S}_{ex}$ based on present data.

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