Entropy of mixing in sanidine

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Abstract

The entropy of mixing in high-temperature alkali feldspars has been re-evaluated using recently-published heat-of-solution data in conjunction with the results of earlier equilibrium experiments. We find that the excess entropy of mixing is distinctly positive over most of the K–Na composition range and most strongly so for the more potassic compositions. The excess entropies at the sodic end of the series are much smaller and may even be slightly negative for compositions near the Na end. The asymmetry in the excess entropy appears to be the principal reason for the asymmetry of the alkali feldspar solvus.

Short-range K–Na ordering can only cause a negative excess entropy, hence is either negligible or overwhelmed by other effects of opposite sign. A likely explanation is that there is a positive excess (probably best seen at very low temperatures) in the vibrational heat capacity, and that this effect is greatest for the more K-rich compositions. This asymmetry is what would be expected if it is assumed that a small atom on a large-atom site would have greater vibrational freedom than a large atom on a small-atom site.

Introduction

Recently published measurements (Hovis and Waldbaum, 1977) of heats of solution for a sanidine–analbite exchange series permit the enthalpy terms relevant to equilibrium experiments on these feldspars to be entered as knowns. Each experiment resulting in equilibration then provides data on the entropies of the phases involved. Earlier attempts to obtain both enthalpies and entropies from equilibration experiments, though sound in principle, have often been unsatisfactory in practice, owing partly to the limited range of temperature investigated, and partly to the need to extract both enthalpy and entropy coefficients from a limited body of data. If the enthalpies are known well enough from independent sources, the need for a wide range of temperature is eliminated and less demand is placed on the experimental data in that only entropy coefficients are required as output.

Equilibrium investigations on high-temperature alkali feldspars include alkali-exchange experiments such as those of Orville (1963), Iiyama (1965, 1966),

Delbove (1971), Traetteberg and Flood (1972), and Volfinger (1976), and experiments to locate the two-phase region such as those of Orville (1963), Luth and Tuttle (1966), Luth (1974), Luth *et al.* (1974), and Goldsmith and Newton (1974). Of these, the more informative are the exchange studies, in that equilibration of the feldspars with an Na–K solution (dilute aqueous fluid or molten salt) of known mixing properties permits determination of the quantity $(\partial \bar{G}_{ex}/\partial N_{Or})_{P,T}$ over wide ranges of composition. This in turn permits evaluation of $\bar{G}_{ex}$ as a function of N_{Or} ($\bar{G}_{ex}$ must vanish when $N_{Or} = 0$ or $N_{Or} = 1$) at each temperature and pressure for which such experiments are available (Thompson and Waldbaum, 1968; Delbove, 1971).

If a sufficient range of temperatures and pressures has been investigated, it is also possible in principle to obtain formulations for $\bar{H}_{ex}$, $\bar{S}_{ex}$, $\bar{E}_{ex}$, and $\bar{V}_{ex}$ as well. In practice, however, this last has proved difficult owing to the limited range of temperatures and pressures that can be investigated successfully, and because of the large number of coefficients that must be extracted from a limited body of data. A better proce-

dure is to use direct volume measurements to formulate $\bar{V}_{\text{ex}}$, and heat-of-solution measurements to formulate $\bar{H}_{\text{ex}}$. With $\bar{V}_{\text{ex}}$, $\bar{H}_{\text{ex}}$ and therefore $\bar{E}_{\text{ex}}$ known, the exchange experiments now permit determination of $(\partial \bar{S}_{\text{ex}}/\partial N_{\text{Or}})_{P,T}$, hence $\bar{S}_{\text{ex}}$ as a function of N_{Or}.

Calculations of $\bar{G}_{\text{ex}}$ from two-phase data are less satisfactory, in that different results may be obtained with different assumptions as to the algebraic form of the expressions for the excess functions (see Thompson and Waldbaum, 1969, p. 824; also Delbove and Sabatier, 1974). With this limitation in mind, however, we may also make estimates from two-phase data of the implied values of $\bar{S}_{\text{ex}}$ where volumes and enthalpies are available.

Enthalpy and volume data

Heats of solution on a sanidine–analbite exchange series have recently been presented by Hovis and Waldbaum (1977). With the volume data of Hovis (1977) on the same feldspars, we obtain the coefficients for $\bar{E}_{\text{ex}}$ and $\bar{V}_{\text{ex}}$ that are given in Table 1. We shall assume that the coefficients in Table 1 are essentially constant in the range of temperatures and pressures of concern. The enthalpy coefficients are related to other coefficients in Table 1 by relations of the form $W_H = W_E + PW_V$ or $B_H = B_E + PB_V$ or $C_H = C_E + PC_V$; hence we may calculate $\bar{H}_{\text{ex}}$ at any P,T, or N_{Or} of interest. Two sets of coefficients are given, one assuming that $\bar{H}_{\text{ex}}$ is symmetric about $N_{\text{Or}} = \frac{1}{2}$, and one allowing it to be asymmetric. $\bar{V}_{\text{ex}}$ in each case is assumed to be symmetric, inasmuch as even the sense of any asymmetry here is questionable and because the effects are negligible in comparison with the uncertainties in the enthalpy data.

Alkali exchange data: feldspar–aqueous fluid

We have reexamined the data of Orville (1963) with the enthalpy terms now entered as known. We have done this in two ways: one uses the symmetric formulation for $\bar{H}_{\text{ex}}$ and the other the asymmetric formulation. For comparison with the results of

Thompson and Waldbaum (1968), we have here used the same selection from Orville's data for curve-fitting, retaining the unused runs for comparison. The fitted function is thus based on equation (36) of Thompson and Waldbaum (1968), with all terms containing $W_{H,\text{Ab}}$ or $W_{H,\text{Or}}$ transferred to the left-hand side. Otherwise, the procedure followed is essentially the one outlined in Thompson and Waldbaum (1968, p. 1987–1990), assuming the Na–K mixing in the fluid to be essentially ideal. The fitted function, Ψ, may then be defined as

$$\begin{aligned}\Psi \equiv\ & -R\ln K' - (\partial \bar{H}_{\text{ex,Fsp}}/\partial N_{\text{Or}})_{P,T}(1/T) \\ =\ & +(\bar{H}_{\text{Or}}^0 - \bar{H}_{\text{Ab}}^0 - \tilde{H}_{\text{K}_+}^{\square} + \tilde{H}_{\text{Na}_+}^{\square})(1/T) \\ & - (\bar{S}_{\text{Or}}^0 - \bar{S}_{\text{Ab}}^0 - \tilde{S}_{\text{K}_+}^{\square} + \tilde{S}_{\text{Na}_+}^{\square}) \\ & - (\partial \bar{S}_{\text{ex,Fsp}}/\partial N_{\text{Or}})_{P,T} \end{aligned} \qquad (1)$$

A Margules-type formulation assumes that $(\partial \bar{S}_{\text{ex,Fsp}}/\partial N_{\text{Or}})_{P,T}$ may be approximated well enough by a series of the type

$$(\partial \bar{S}_{\text{ex,Fsp}}/\partial N_{\text{Or}})_{P,T} = a_0 + a_1 N_{\text{Or}} + a_2 N_{\text{Or}}^2 + \cdots \qquad (2)$$

If only second-degree terms are needed, the coefficients a_i may be recast into parameters (Carlson and Colburn, 1942) of the form

$$\begin{aligned} W_{S,\text{Ab}} &= -(\tfrac{1}{2} a_1 + \tfrac{2}{3} a_2) = R(B_S - C_S) \\ W_{S,\text{Or}} &= -(\tfrac{1}{2} a_1 + \tfrac{1}{3} a_2) = R(B_S + \text{ct13}C_S) \end{aligned} \qquad (3)$$

or into parameters (Thompson and Waldbaum, 1969) of the form

$$\begin{aligned} B_S &= -(a_1 + a_2)/2R = (W_{S,\text{Or}} + W_{S,\text{Ab}})/2R \\ C_S &= a_2/6R \qquad\quad\ = (W_{S,\text{Or}} - W_{S,\text{Ab}})/2R \end{aligned} \qquad (4)$$

Equation (1) may then be recast for least-squares fitting as either

$$\begin{aligned}\Psi =\ & (\bar{H}_{\text{Or}}^0 - \bar{H}_{\text{Ab}}^0 - \tilde{H}_{\text{K}_+}^{\square} + \tilde{H}_{\text{Na}_+}^{\square})(1/T) \\ & - (\bar{S}_{\text{Or}}^0 - \bar{S}_{\text{Ab}}^0 - \tilde{S}_{\text{K}_+}^{\square} + \tilde{S}_{\text{Na}_+}^{\square}) \\ & - W_{S,\text{Ab}}X - W_{s,\text{Or}}Z \end{aligned} \qquad (1a)$$

Table 1. Internal energy, volume, and enthalpy coefficients for sanidine crystalline solutions

*$W_{E,\text{Ab}}$ (cal/mol)	*$W_{E,\text{Or}}$ (cal/mol)	*W_V (cal/bar-mol)	$W_{H,\text{Ab}}$ & $W_{H,\text{Or}}$ (cal/mol)			B_H & C_H		
			1 bar	1 kbar	2 kbar	1 bar	1 kbar	2 kbar
7474	4117	0.0862	7474,4117	7560,4203	7646,4289	2916,844.6	2960,844.6	3003,844.6
5691	5691	0.0862	5691,5691	5777,5777	5863,5863	2864, 0	2907, 0	2950, 0

*Data from Hovis (1977) and Hovis and Waldbaum (1977).

Table 2. Parameters calculated from data of Orville (1963)

	$W_{S,Ab}$ (cal/deg-mol)	$W_{S,Or}$ (cal/deg-mol)	B_S	C_S	$\Delta\bar{H}^O$ (cal/mol)	$\Delta\bar{S}^O$ (cal/deg-mol)
Calculations using						
asymmetric W_H's	5.192	−0.037	1.297	−1.316	4225	2.776
	±.014	±.010	±.004	±.005	±50	±.055
Calculations using						
symmetric W_H's	3.240	1.652	1.231	−0.399	4264	2.809
	±.014	±.010	±.004	±.005	±50	±.055

$$\Delta\bar{X}^O \equiv (\bar{X}^O_{Or} - \bar{X}^O_{Ab} - \tilde{X}^{\square}_{K+} + \tilde{X}^{\square}_{Na+})$$

where $x = 2N_{Or} - 3N_{Or}^2$ and $Z = 1 - 4N_{Or} + N_{Or}^2$ (note error in sign in Thompson and Waldbaum, 1968, p. 1990), or as

$$\Psi = (\bar{H}^0_{Or} - \bar{H}^0_{Ab} - \tilde{H}^{\square}_{K+} + \tilde{H}^{\square}_{Na+})(1/T)$$
$$- (\bar{S}^0_{Or} - \bar{S}^0_{Ab} - \tilde{S}^{\square}_{K+} + \tilde{S}^{\square}_{Na+}) - RB_S X' - RC_S Z' \tag{1b}$$

where $X' = (1 - 2N_{Or})$ and $Z' = (1 - 6N_{Or} + 6N_{Or}^2)$. (1a) and (1b) yield nearly identical results, but it is evident that B_S is a much better known quantity than C_S or either W_S taken separately. B_S is also simply related to the magnitude of $\bar{S}_{ex}$ when $N_{Or} = ½$ (we then have $\bar{S}_{ex} = RB_S/4$), and is relatively insensitive to whether the enthalpy data is formulated as symmetric or asymmetric about $N_{Or} = ½$, as can be seen from the results in Table 2. Figures 1 through 6 show Orville's data points and curves plotted using the coefficients in Table 2. The results are clearly more satisfactory than those of the earlier polythermal fit of Thompson and Waldbaum, in which both entropy and enthalpy coefficients were taken as unknown. This is true no matter which formulation for $\bar{H}_{ex}$ is employed. (Note especially the Na-rich region on the 500°C isotherm.)

The later experimental results of Iiyama (1965, 1966), in which alkali feldspars were equilibrated with aqueous Na–K solutions at 1000 bars, permit analysis by the same procedure. In our least-squares analysis of Iiyama's data we used only runs in which the values of N_{Or} in the feldspar were between 0.1 and 0.8. Elimination of the runs with highly sodic feldspars is consistent with our treatment of Orville's data and may be defended by the fact that many or all of these feldspars are triclinic, and by the sensitivity of $\ln K'$ to small errors in feldspar compositions if the feldspar is near an end-member. Iiyama (personal communication, 1977) also indicated reservations concerning his results with values of N_{Or} in feldspar greater than 0.8. Later experiments in his laboratory (Iiyama and Volfinger, 1976; Volfinger, 1976) give results closer to our fitted curve than do Iiyama's earlier data.

The results of the least-squares fits are given in Table 3 and in Figures 7 through 9. The entropy coefficient calculated from Iiyama's data agree well with those based on Orville's data. Note again that $W_{S,Or}$ is near zero when asymmetric W_H's are used in the calculation. The values of $\bar{S}_{ex}$ implied by our treatments or Orville's and Iiyama's data are given in Figure 10.

Also given in Tables 2 and 3 are the coefficients $\Delta\bar{H}^0$ and $\Delta\bar{S}^0$ corresponding to the terms $(\bar{H}^0_{Or} - \bar{H}^0_{Ab} - \tilde{H}^{\square}_{K+} + \tilde{H}^{\square}_{Na+})$ and $(\bar{S}^0_{Or} - \bar{S}^0_{Ab} - \tilde{S}^{\square}_{K+} + \tilde{S}^{\square}_{Na+})$, respectively, in equations (1). Although the coefficients based on Iiyama's data (at one kbar) are quite different from those based on Orville's data (at two kbar), the values of $\Delta\bar{G}^0(=\Delta\bar{H}^0 - T\Delta\bar{S}^0)$ in the temperature range of the experiments are more closely comparable. Here again we may have a good estimate of $\Delta\bar{G}^0$ in the range of the experiments, but an unreliable factoring of it into enthalpy and entropy terms.
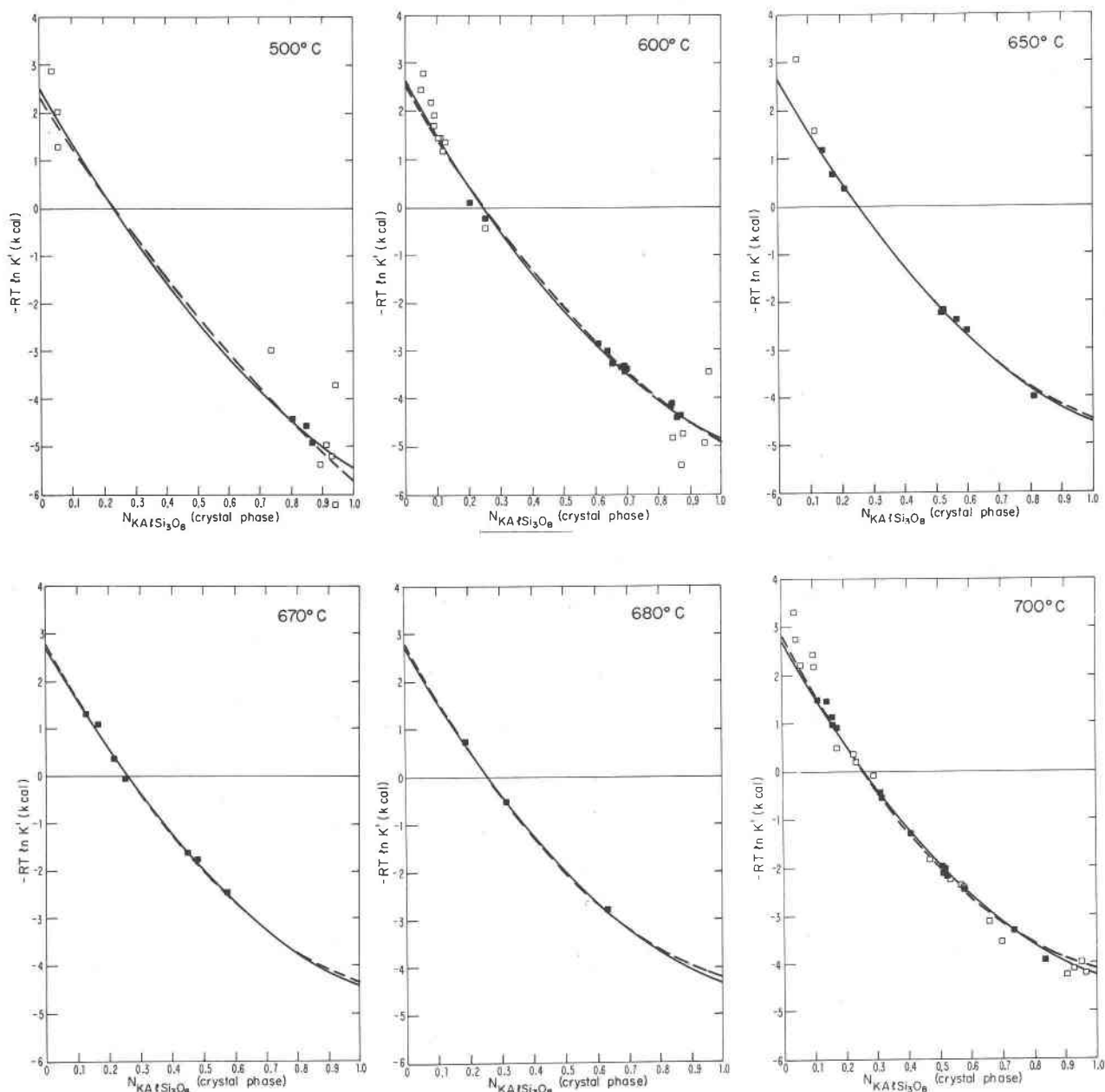
Figs. 1 through 6. $-RT \ln K'$ vs. N_{Or} isothermal ion-exchange curves at 2 kbar and the stated temperatures (data of Orville, 1963, Table 1). Solid curves represent calculations assuming symmetric W_H's, dashed curves assume asymmetric W_H's (see our Tables 1 and 2). Solid squares are data points used in the polythermal fit to Orville's data.

Alkali exchange data: feldspar–molten salt

Exchange data for equilibria between high-temperature alkali feldspars and fused Na–K halides at one atmosphere have been presented by Delbove (1971) and by Traetteberg and Flood (1972). Delbove presented three isotherms at 800°C, one for chloride melts, one for bromide melts, and one for iodide melts. Traetteberg and Flood presented isotherms at 850°C, 900°C, and 950°C, each with chloride melts. All authors corrected for non-ideality in the melt and formulated for results in expressions for $\bar{G}_{ex}$.

Delbove calculated $\bar{G}_{ex}$ by integration of the exchange data, presenting $\bar{G}_{ex}$ for each set, and the mean of the three, in tabular form (Delbove, 1971, p. 463). Delbove's curves (in his Figs. 2 and 5) show

Table 3. Parameters calculated from data of Iiyama (1965)

	$W_{S,Ab}$ (cal/deg-mol)	$W_{S,Or}$ (cal/deg-mol)	B_S	C_S	$\Delta\bar{H}^O$ (cal/mol)	$\Delta\bar{S}^O$ (cal/deg-mol)
Calculations using						
asymmetric W_H's	5.303	0.011	1.337	-1.331	2458	0.418
	±.042	±.023	±.009	±.014	±75	±.080
Calculations using						
symmetric W_H's	3.428	1.672	1.283	-0.442	2163	0.105
	±.043	±.024	±.010	±.015	±80	±.080

$$\Delta\bar{X}^O \equiv (\bar{X}^O_{Or} - \bar{X}^O_{Ab} - \tilde{X}^\square_{K+} + \tilde{X}^\square_{Na+})$$

anomalous behavior near the K-rich end which may or may not be real, in view of the magnified effect on $\ln K'$ of analytical error when the compositions are near the limiting end members. (See discussions by Thompson and Waldbaum, 1968, p. 1980–1985; and by Traetteberg and Flood, 1972, p. 613.) Nevertheless, Delbove's tabulated values of $\bar{G}_{ex}$ (combined with our formulation for $\bar{H}_{ex}$) lead to values of $\bar{S}_{ex}$ (Fig. 11) that are comparable to those obtained by our fits to Orville's and Iiyama's data.

The treatment by Traetteberg and Flood is closely analogous to that of Thompson and Waldbaum's polythermal results. Traetteberg and Flood give what is essentially an asymmetric Margules formulation with two temperature-dependent parameters.[1] The temperature-dependence of their parameters implies formulations for $\bar{H}_{ex}$ and $\bar{S}_{ex}$ which can be written as

$$\bar{H}_{ex} \text{ (cal/mol)} = 1115\, N_{Ab}N_{Or}^2 + 2965\, N_{Or}N_{Ab}^2 \quad (5)$$

$$\bar{S}_{ex} \text{ (cal/deg mol)} = -1.528\, N_{Ab}N_{Or}^2$$
$$- 1.245\, N_{Or}N_{Ab}^2 \quad (6)$$

The W_H's implied by (5) are very different from those in Table 1, based on calorimetry, and the values of the W_S's implied by (6) are also very different from those in Tables 2 and 3. Equations (5) and (6) then provide another illustration of the difficulties in obtaining accurate values of both enthalpy and entropy

parameters from equilibrium studies alone, particularly when the range of temperature covered by the experiments is small. Even though their enthalpy and entropy parameters are inconsistent with other data, however, the W_G's implied by the formulation of Traetteberg and Flood should be reasonably accurate, at least within the temperature range of their experiments. $\bar{G}_{ex}$, in other words, may be quite well known even when its factoring into $\bar{H}_{ex}$ and $\bar{S}_{ex}$ is not. We have therefore used their formulation, as evaluated at 900°C (the mid-temperature of their experiments), and the enthalpy coefficients for one bar from Table 1, to obtain a revised estimate of $\bar{S}_{ex}$ as based on their experiments and the calorimetric values of $\bar{H}_{ex}$. The results may be written

$$\bar{S}_{ex} \text{ (cal/deg mol)} = 2.372\, N_{Ab}N_{Or}^2$$
$$+ 1.078\, N_{Or}N_{Ab}^2 \quad (7)$$

if $\bar{H}_{ex}$ is taken as symmetric, and as

$$\bar{S}_{ex} \text{ (cal/deg mol)} = 3.892\, N_{Ab}N_{Or}^2$$
$$- 0.263\, N_{Or}N_{Ab}^2 \quad (8)$$

if $\bar{H}_{ex}$ is taken as asymmetric. The values of the W_S's implied by (7) and (8) are much closer to those of Tables 2 and 3 than are those of (6). Equations (7) and (8) are also plotted in Figure 11 for comparison with the results based on Delbove's data. It is possible that the differences between the two sets of data are more apparent than real, inasmuch as different corrections were used to account for the mixing properties of the molten salts. Uncertainties in the mixing properties of the fused salts probably are responsible

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[1] According to Traetteberg (personal communication, 1977) there is an error in the X_1 coefficient for their h-feldspar series as given in their Table 1 on p. 614. The correct value is +15.9, *not* -16.0.
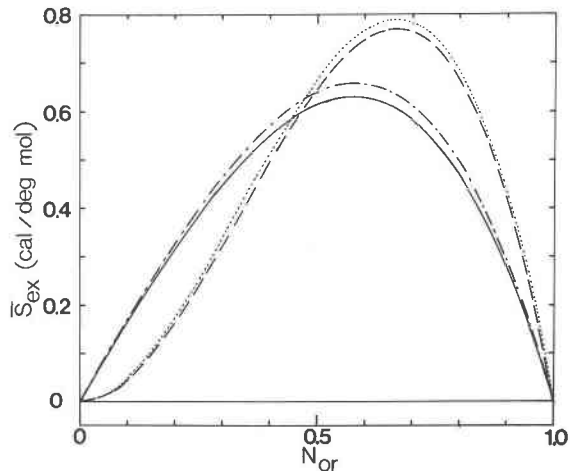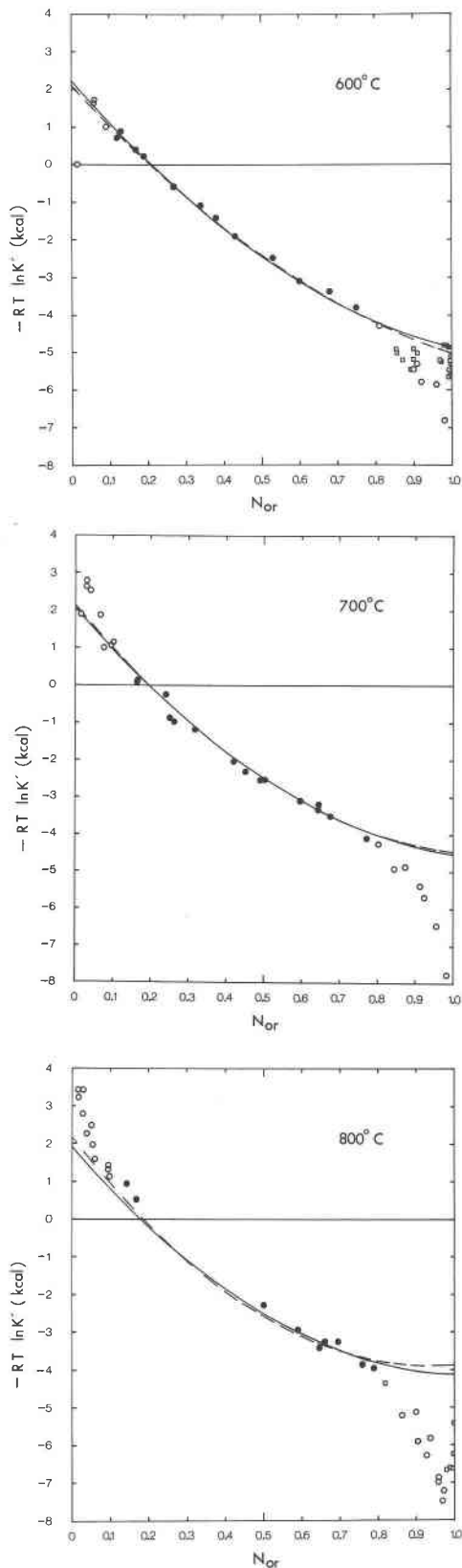
Fig. 10. Molar excess entropy based on W_S's (Tables 2 and 3) calculated from the ion-exchange data of Orville (1963; dot and dash-dot curves) and Iiyama (1965, 1966; dashed and solid curves). The two curves representing relatively larger entropies of mixing assume asymmetric W_H's; the other two curves assume a symmetric W_H.

for the systematic differences distinguishing the aqueous exchange experiments (Fig. 10) from the fused-salt experiments (Fig. 11). All the exchange data except those of Delbove have been fitted to two-parameter Margules expressions. The method of formulation might thus be responsible for the minor differences between the entropy coefficients obtained from Delbove's data and those obtained from the data of Traetteberg and Flood. This cannot, however, explain the larger differences separating both from the aqueous exchange data.

Two-phase data

Calculation of mixing properties from coexisting alkali–feldspar pairs is possible if it is assumed that a two-parameter expression for $\bar{G}_{ex}$ is sufficient, and then if the assumed algebraic form for such an expression is the correct one. In this sense it is comparable to calculating an expression for $R\ln K'$ as a function of N_{or} on the basis of only three data points! The results for the two-phase pairs of Orville (1963) and the peralkaline pairs of Luth and Tuttle (1966) are given in Table 4, using the values of B_G and C_G

Figs. 7 through 9. $-RT \ln K'$ vs. N_{or} isothermal ion-exchange curves at 1 kbar and the stated temperatures (data of Iiyama, 1965, 1966 and personal communication). Solid curves represent calculations assuming symmetric W_H's, dashed curves assume asymmetric W_H's (see our Tables 1 and 3). Solid circles are data points used in the polythermal fit to Iiyama's data. Open squares represent the data of Volfinger (1976).
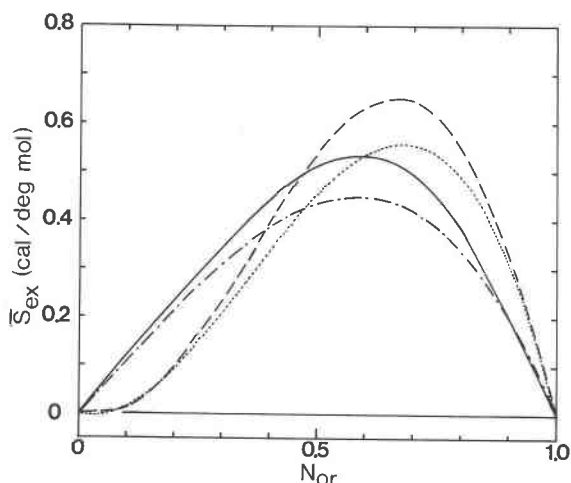
Fig. 11. Molar excess entropy calculated from molten salt ion-exchange data of Delbove (1971; dashed and solid curves) and Traetteberg and Flood (1972; dot and dash-dot curves). The two curves representing relatively larger entropies of mixing assume asymmetric W_H's, the other two curves assume a symmetric W_H.
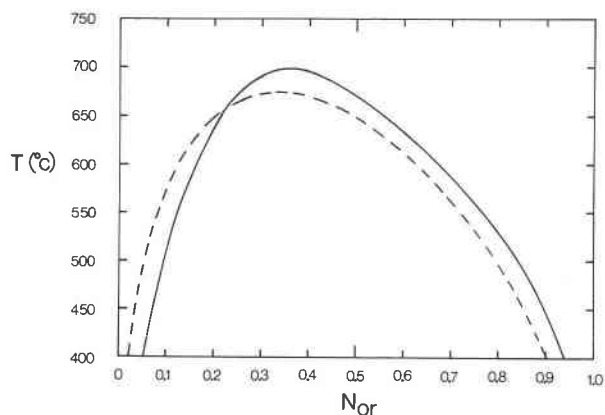

Fig. 12. Alkali feldspar solvus for 2 kbar. Dashed solvus is based on parameters given by Thompson and Waldbaum (1969), as consistent with two-phase data. Solid solvus is based on equation (10).

calculated by Thompson and Waldbaum (1969) and the values of B_H and C_H from Table 1. The values of $\bar{S}_{ex}$ implied by Table 4 are on the whole greater than those based on exchange isotherms, but similar in that the asymmetry in $\bar{S}_{ex}$ is in the same sense. We consider the entropy parameters based on exchange data to be far more reliable and include Table 4 only for comparison.

Discussion

It is evident from the foregoing analysis that excess entropies of mixing in high-temperature alkali feldspars are positive for virtually the entire composition range, and most strongly so in the more K-rich compositions. This asymmetry is strongest when the

Table 4. Entropy coefficients calculated from two-phase data*

T(°C)	P(kbar)	$\bar{H}_{ex}$ Symmetric				$\bar{H}_{ex}$ Asymmetric			
		$W_{S,Ab}$	$W_{S,Or}$	B_S	C_S	$W_{S,Ab}$	$W_{S,Or}$	B_S	C_S
(a) Orville (1963)									
500	2	4.04	.55	1.16	−.88	6.34	−1.48	1.22	−1.97
600	2	3.78	1.52	1.33	−.57	5.83	− .28	1.39	−1.54
650	2	3.58	1.66	1.32	−.49	5.52	− .05	1.38	−1.40
670	2	3.71	1.65	1.35	−.52	5.60	− .02	1.41	−1.41
600	5	4.40	1.08	1.38	−.83	6.45	− .73	1.44	−1.81
(b) Luth and Tuttle (1966), peralkaline									
550	2	3.72	.57	1.21	−.66	5.89	− .82	1.28	−1.69
575	2	4.94	1.27	1.56	−.92	7.04	− .58	1.63	−1.92
577	2	5.33	.68	1.51	−1.17	7.43	−1.17	1.58	−2.17
600	2	4.59	1.05	1.42	−.89	6.63	− .76	1.48	−1.86
625	2	4.03	1.75	1.45	−.58	6.02	− .01	1.51	−1.52
627	2	4.58	1.53	1.54	−.77	6.56	− .22	1.60	−1.71
635	2	4.44	1.38	1.47	−.77	6.41	− .35	1.52	−1.70
642	2	4.33	1.67	1.51	−.67	6.28	− .05	1.57	−1.59
650	2	4.24	1.69	1.49	−.64	6.17	− .02	1.55	−1.56
658	2	3.74	1.75	1.38	−.50	5.66	+ .06	1.44	−1.41
665	2	3.53	1.70	1.32	−.46	5.43	+ .02	1.37	−1.36
650	5	4.51	1.24	1.45	−.82	6.44	− .46	1.50	−1.74
650	10	5.19	.48	1.43	−1.18	7.12	−1.22	1.48	−2.10

*The run data may be found in Table 1 (a) and (b) of Thompson and Waldbaum (1969).

asymmetric formulation for the enthalpy excess is used, which is in fact the one that provides the better fit, statistically, to the heat-of-solution data. Our preferred values of the entropy parameters give

$$\bar{S}_{ex} \text{ (cal/deg mol)} = 5.2 \, N_{Ab} N_{Or}^2 + 0.0 \, N_{Or} N_{Ab}^2 \quad (9)$$

based on the combined results of our analyses of the Orville and Iiyama exchange data, using the asymmetric enthalpy parameters from Table 1. Equation (9) and the parameters in Table 1 imply an expression for $\bar{G}_{ex}$ having the form

$$\bar{G}_{ex} \text{ (cal/mol)} = 0.0862 \, P \, N_{Ab} N_{Or}$$
$$+ (7474 - 5.2 \, T) N_{Ab} N_{Or}^2 \quad (10)$$
$$+ 4117 \, N_{Or} N_{Ab}^2$$

where P is pressure in bars and T is absolute temperature in degrees Kelvin.

A solvus for 2 kbar based on equation (10) is plotted in Figure 12 for comparison with the one based on the formulation obtained by Thompson and Waldbaum (1969). The earlier formulation was weighted fairly heavily by calculations based on two-phase data but without the benefit of calorimetric enthalpies. It thus agrees quite well not only with the data on which it was based, but also with later two-phase experiments of Luth (1974), Luth et al. (1974), and Goldsmith and Newton (1974). The early formulation thus yields a fairly accurate empirical representation of the alkali feldspar miscibility gap, possibly a better one than (10), although the results at 2 kbar as shown in Figure 12 are not drastically different. We are quite confident, however, that equation (10) gives a far more accurate representation of the thermodynamic mixing properties of highly disordered alkali feldspars; hence it should give considerably better results in calculating equilibria between such alkali feldspars and other non-feldspar phases (as, for example, alkali feldspar–quartz–jadeite). Neither formulation is applicable to strongly ordered, triclinic alkali feldspars.

Non-ideal entropies of mixing are commonly attributed to short-range ordering among the substituting species, in this case, a non-random distribution of the Na and K atoms on the alkali sites (all crystallographically equivalent). This, however, can only produce a negative excess entropy, hence if short-range ordering is significant here, it must be overwhelmed by other effects of opposite sign. The most likely explanation is that there is a positive excess in the vibrational heat capacity, probably most significant at very low temperatures. This is consis-

tent with the positive excess volumes, and the asymmetry in $\bar{S}_{ex}$ would be consistent with the argument that a small ion (Na) on a large-ion (K) site would have greater vibrational freedom than a large ion on a small–ion site. Such an excess heat capacity would also lead inevitably to an asymmetry in the excess enthalpy. If the excess enthalpy were symmetric at one temperature, an asymmetric excess heat capacity would make the excess enthalpy asymmetric at other temperatures. Low-temperature heat capacity measurements are clearly needed on Na–K feldspars comparable to those in the experiments discussed above. Only with such vibrational effects removed will it be possible to assess the effects of short-range order or other factors.

Note added in proof

The $W_{E,Ab}$ and $W_{E,Or}$ values for the analbite–sanidine series of Hovis and Waldbaum (1977) recently have been revised slightly from 7474 and 4117 cal/mol (see Table 1) to 7404 and 4078 cal/mol, respectively (Hovis, in preparation). The new values have little effect on the calculations in the present paper. For instance, $W_{S,Ab}$ and $W_{S,Or}$ values listed in Table 2 change from 5.19 and -0.04 to 5.12 and -0.08 cal/deg mol, respectively.

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