A solution calorimetric investigation of K–Na mixing in a sanidine–analbite ion-exchange series

GUY L. HOVIS
Department of Geology, Lafayette College
Easton, Pennsylvania 18042

AND DAVID R. WALDBAUM
Department of Geological and Geophysical Sciences
Princeton University, Princeton, New Jersey 08540

Abstract

Heats of solution have been measured for seven members of a sanidine–analbite ion-exchange series in 20.1 percent HF at 49.7°C under isoperibolic conditions. A cubic least-squares fit to the heat-of-solution data from twenty-eight experiments yields:

$$-H_{\text{sol}}(\text{kcal/mol}) = 154.411 - 6.233 N_{\text{Or}} + 7.474 N_{\text{Ab}}N_{\text{Or}} + 4.117 N_{\text{Or}}N_{\text{Ab}}^2$$

where $N_{\text{Or}}$ and $N_{\text{Ab}}$ are the mole fractions of KA$_2$Si$_3$O$_8$ and NaAlSi$_3$O$_8$, respectively. Excess molar enthalpy of K–Na mixing for this series may be expressed as

$$H_{e}^\circ(\text{kcal/mol}) = W_{H,\text{Ab}}N_{\text{Ab}}N_{\text{Or}}^2 + W_{H,\text{Or}}N_{\text{Or}}N_{\text{Ab}}^2$$

where $W_{H,\text{Ab}}$ and $W_{H,\text{Or}}$ are the Margules parameters for the enthalpy of K–Na mixing and are equivalent to 7.474 and 4.117 kcal/mol, respectively.

This series of feldspars has a topochemically monoclinic, relatively disordered Al–Si distribution. Comparison of the enthalpy of K–Na mixing for these feldspars with that of a microcline-low albite series of feldspars (Waldbaum and Robie, 1971) having a topochemically triclinic, relatively ordered Al–Si distribution shows that $W_{H,\text{Ab}} > W_{H,\text{Or}}$ for both; however $W_{H,\text{Ab}}$ and $W_{H,\text{Or}}$ are 1.8 and 1.0 kcal/mol less, respectively, for the (monoclinic) disordered series than for the (triclinic) ordered feldspars, probably due to a reduction in the strain associated with K–Na substitution in the less dense, disordered feldspar series.

Introduction

In order to characterize the alkali feldspars thermodynamically, it is necessary to obtain enthalpy, entropy, and volume data as functions of both K–Na mixing and Al–Si distribution. Solution calorimetric measurements can provide information on the enthalpy of K–Na mixing and Al–Si exchange. By combining information obtained calorimetrically with data from alkali ion-exchange equilibria (Orville, 1963) information may be obtained on the entropy of K–Na mixing (Thompson and Hovis, in preparation).

In this investigation we have measured heats of solution of a K–Na ion-exchange series of feldspars ranging from sanidine to analbite (as used in the context of Laves, 1952, p. 439; also 1960). This is the first ion-exchange series of feldspars with Al–Si distributions consistent with monoclinic symmetry to be studied calorimetrically. Previously, heats of solution were reported for a triclinic (maximum microcline-low albite) ion-exchange series of feldspars by Waldbaum and Robie (1971). Kracek and Neuvonen (1952) measured heats of solution for various natural feldspars, but not for any ion-exchange series. By comparing the results of the present study with those of Waldbaum and Robie (1971) we now are able to estimate the effects of Al–Si distribution on K–Na mixing properties in the alkali feldspars. This supplements the data of Hovis (1971, 1974), who used the same calorimetric system to determine the enthalpy

---

1 Died, April 11, 1974
HEATS OF SOLUTION FOR SANIDINE CRYSTALLINE SOLUTIONS

Fig. 1. Heat-of-solution data plotted against composition for sanidine-analbite crystalline solutions. Solid curve represents a quadratic fit [equation (1)] to the data, the dashed curve a cubic fit [equation (2)].

of Al–Si exchange for monoclinic potassium feldspars.

Unit-cell dimensions, molar volumes, and chemical compositions for members of this sanidine-analbite series have been reported in the preceding paper (Hovis, 1977; also Hovis and Waldbaum, 1976). Tetrahedral site occupancies for all members of this series are estimated to be $N_{Al(T1)} = 0.271$ and $N_{Al(T2)} = 0.229$ (for nomenclature, see Thompson, 1969, 1970).

Calorimetry

Details of our calorimetric apparatus and procedures have been described elsewhere (Hovis, 1971; 1974, p. 125-127; also see Robie and Hemingway, 1972), and only the most important aspects will be repeated here.

Feldspar crystalline solutions were dissolved in 20.1 weight percent HF (to conform with acid strengths used by previous investigators: King, 1951; Kracek and Neuvonen, 1952; Waldbaum, 1966, p. 18) at 49.7°C (1 atm) under isoperibolic conditions, using an internal sample container (Waldbaum and Robie, 1970). Early experiments were conducted using 940 grams of acid, later ones using 910 grams of acid (Table 1); this had no detectable effect on the resulting heats of solution. Generally, three experiments were conducted using the same acid solution; 0.65 to 1.00 gram of material (~325 mesh) was dissolved during each experiment. This violates the rule of strict stoichiometry (Hovis, 1974, p. 125), but because of the very small amounts of feldspar dissolved, the solutions remained in the ideally dilute range with respect to the ions in solution; this procedure had no detectable effect on the calorimetric results (Hovis, 1974, p. 129).

Thermometry and data reduction are as described by Hovis (1974, p. 126-127; 1971).

Calorimetric results

Calorimetric data for the sanidine-analbite crystalline solutions are shown in Figure 1 and recorded in Table 1. These data represent the results of 28 heat-of-solution experiments on seven different feldspars; two heats of solution are given for most experiments, the first based on the heat capacity of the calorimeter before dissolution, the second on the heat capacity after dissolution. Calorimetric data are not presented.
for the small number of runs where heat capacities were associated with either abnormally high or low $\alpha$ values, because such data are considered unreliable. Values of $\alpha$ are calculated during each calorimetric experiment and indicate the rate at which heat exchange between the reaction vessel and its surroundings changes with temperature during an experiment (Waldbaum, 1966). Abnormal $\alpha$-values may be indicative of problems, such as failure of an experiment to go to completion, and are one criterion used to evaluate a run.

Heat-of-solution values (Table 1) expressed in joules/gram are independent of the assumed feldspar chemical composition. Values given in kcal/mol (where 1 defined calorie = 4.184 joules) are based on atomic weights corresponding to the compositions stated in the preceding paper (Table 3) and assuming such compositions are precisely on the (K,Na)AlSi₃O₈ join. No corrections were made for minor-element content; as stated in the preceding paper, these elements were present in very small amounts and should be nearly constant for all members of the ion-exchange series.

Least-squares fits to the data in Table 1 as a func-
Effect of sample inhomogeneity on calorimetric results

Sample inhomogeneity (Hovis, 1977) has an effect on heats of solution in any chemical system where heats of mixing exist. In such a system, a set of mechanical mixtures about the mean composition would result in a lower absolute value for heat of mixing than would a single homogeneous phase. However, if the mechanical mixture represents a relatively small range of chemical compositions, the effect of inhomogeneity should be small, perhaps negligible.

Of the five feldspars with intermediate chemical compositions, four were inhomogeneous to a minor extent, with ranges of ±3.5 mole percent Or or less. Feldspar 7057 was somewhat more inhomogeneous, with a range of ±11 percent. It is impossible to make rigorous corrections for inhomogeneity without detailed quantitative information about how much of each composition is represented in each of the feldspar samples. However, it is possible to estimate the maximum effect that inhomogeneity would have on the heats of solution. This can be done by assuming that each sample is made up of a mechanical mixture of two feldspars, one at each end of the composition range of each feldspar. Based on equation (1) or equation (2), we may then calculate the heat of solution for a 50:50 mechanical mixture of these two feldspars and compare it with the actual heat of solution for a feldspar in the middle of the composition range. Doing this for feldspars 7059, 7044, 7058, and 7060, we find that the maximum effect on the heats of solution would be approximately 0.01 kcal/mol. Because each feldspar crystalline solution does not consist of a mechanical mixture of two feldspars at either end of the composition range, but rather a whole series of phases along the entire range, any correction to the heats of solution of these four feldspars should be even less than 0.01 kcal/mol; in the present study this is negligible.

Inhomogeneity in sample 7057 was somewhat more serious than in the other samples. Estimating the effect of inhomogeneity in this sample as above indicates an effect of 0.08 kcal/mol. However, this too would be the maximum effect, since this feldspar consists of a whole range of compositions, not just two.

In order to check the maximum effect that inhomogeneity could have on the calculations, least-squares fits to heats of solution were performed after adding 0.08 kcal/mol to the values of \(-H_{\text{soln}}\) for sample 7057 and 0.01 kcal/mol to the values of \(-H_{\text{soln}}\) for all other feldspars except the end members. These calculations resulted in a change of the last coefficient in equation (1) to 5.848 (±0.035) kcal/mol and of the last two coefficients in equation (2) to 7.357(±0.090) and 4.516(±0.080) kcal/mol, respectively.

Comparison of calorimetric data with those of other investigators

The heat-of-solution values for sanidine and analbite may be compared with those of Waldbaum and Robie (1971), who measured the heats of solution of nearly identical end-member samples but used a different HF solution calorimetric data acquisition system. Their values are between 1 and 2 kcal/mol different from the present data, not only for sanidine and analbite, but also for microcline and low albite. Therefore, differences between the two sets of calorimetric measurements are probably systematic. Each system yields internally consistent results, and enthalpy changes due to compositional variations or changes in Al-Si distribution in alkali feldspars are the same as measured on either system. Therefore, the results from either calorimetric system can be considered valid, but at present absolute values of

\[-H_{\text{soln}}(\text{kcal/mol}) = 154.326(±0.080)\]
\[+ 6.033(±0.010)N_{\text{Or}} + 5.691(±0.035)N_{\text{Or}}N_{\text{Ab}}\]
Excess mixing properties of sanidine-analbite crystalline solutions

The excess enthalpy due to K–Na mixing is equal to the difference between the quadratic formulation given by equation (1), or the cubic expression of equation (2), and the associated line corresponding to mechanical mixtures of end-member feldspars. For the sanidine-analbite series of the present investigation, equations of $H_{ex}$ corresponding to equations (1) and (2) above are

$$H_{ex}(\text{kcal/mol}) = 5.691(\pm 0.035)N_{Or}N_{Ab}$$ (3)

and

$$H_{ex}(\text{kcal/mol}) = 7.474(\pm 0.085)N_{Ab}N_{Or}^2 + 4.117(\pm 0.080)N_{Or}N_{Ab}^2$$ (4)

Curves corresponding to equations (3) and (4) are plotted in Figures 2a and 2b.

Excess molar volume data for the same feldspar series are given in the preceding paper [Hovis, 1977, equation (7)]. Using the thermodynamic relationship, $\Delta E_{ex} = H_{ex} - PV_{ex}$ (Thompson, 1967), we can develop general expressions for excess internal energy of K–Na mixing:

$$\Delta E_{ex}(\text{kcal/mol}) = (5.691 - 0.0862P)N_{Or}N_{Ab}$$ (5)

and

$$\Delta E_{ex}(\text{kcal/mol}) = (7.474N_{Or} + 4.117N_{Ab} - 0.0862P)N_{Or}N_{Ab}$$ (6)

where pressure is expressed in kilobars. For pressures up to 10 kbar and more, the excess enthalpy and internal energy of K–Na mixing are virtually identical, owing to the very small value of $W_v$, the Margules parameter for molar volume.

Excess mixing properties as functions of Al–Si distribution for alkali feldspars

Excess internal energies of mixing for the low albite–microcline ion-exchange series investigated by Waldbaum and Robie (1971) and also for the analbite–sanidine series of the present study are recorded in Table 2. Because differences in the mixing properties for the two series are the combined result of changes in Al–Si distribution over four tetrahedral sites, it is impossible to factor these heat-of-solution differences into effects due to changes in the Al–Si population of each site. However, we can make some general comments about K–Na mixing properties in alkali feldspars as a whole:

1. Excess internal energy and enthalpy are positive for all alkali feldspar ion-exchange series, regardless of Al–Si distribution.

2. $W_{H,Ab} > W_{H,Or}$ (and $W_{E,Ab} > W_{E,Or}$) for asymmetric fits to the heat-of-solution data of ordered and disordered ion-exchange series.
(3) \( W_{E,Ab} \) and \( W_{E,Or} \) are 1.8 and 1.0 kcal/mol less, respectively, for the (topochemically monoclinic) disordered series than for the (triclinic) ordered series of feldspars, based on the cubic fits to heat of solution data. \( W_E \) is 1.4 kcal/mol less for the disordered series, based on the quadratic fits to the same data.

**Interpretation of the results**

Asymmetry of the heats of K–Na mixing in the alkali feldspars is probably related to strain created by the substitution of ions of unequal size into the "M" crystallographic position in the structures of these minerals. In both of the alkali feldspar series studied calorimetrically, the heat effect resulting from the substitution of a potassium ion into a sodic feldspar (reflected by the value of the Margules parameter, \( W_{H,Ab} \)) is greater than that resulting from the substitution of a sodium ion into a potassic feldspar (reflected by \( W_{H,Or} \)). Put simply, less strain is created when a small ion occupies a cavity than when a relatively large ion occupies the same (or a slightly smaller) cavity.

Differences in the K–Na mixing properties between topochemically monoclinic, disordered and topochemically triclinic, ordered alkali feldspars can also be explained as a function of strain. The disordered feldspars have slightly greater molar volumes (Orville, 1967; Hovis, 1971 and 1974), and therefore lower densities, than more ordered compositionally-equivalent feldspars. Because their structures are more open, the strain created by ionic substitution of potassium and sodium ions in the "M" crystallographic position is not as great as in the relatively ordered feldspars. The less strain, the smaller the effect of K–Na mixing.

A more detailed analysis of these results will be given in a later report (Thompson and Hovis, in preparation), where excess enthalpy and excess molar volume data are combined with data based on Orville’s (1963) ion-exchange experiments (Thompson and Waldbaum, 1968) to give excess entropy relationships for sanidine–analogite crystalline solutions.

**Acknowledgments**

We wish to thank Professor James B. Thompson, Jr., for his continuing interest in our work on the feldspars, for his encouragement, and for his helpful criticism on a preliminary version of this manuscript. We thank Dr. James Woodhead and Dr. Ronald Openshaw for their cooperation in various aspects of the work. Messrs. Harold Ames and Arthur Ames were instrumental in helping to get the calorimetric research started in fabricating part of the system; Mr. Maurice Campion helped debug electronic problems which developed and also helped maintain some of the apparatus.

**Table 2. Internal energies of K–Na mixing at 1 atm for feldspar crystalline solutions**

<table>
<thead>
<tr>
<th>Feldspar Series</th>
<th>( U_{E,Or} ) (kcal/mol)</th>
<th>( U_{E,Ab} ) (kcal/mol)</th>
<th>( W_{ex/50:50} ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low albite - microcline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Waldbaum and Robie, 1971, asymmetric or cubic fit to the data)</td>
<td>5.928 ( \pm 0.085 )</td>
<td>8.147 ( \pm 0.099 )</td>
<td>1.798</td>
</tr>
<tr>
<td>Low albite - microcline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Waldbaum and Robie, 1971, symmetric or quadratic fit to the data)</td>
<td>7.075 ( \pm 0.044 )</td>
<td>7.075 ( \pm 0.044 )</td>
<td>1.768</td>
</tr>
<tr>
<td>Analbite - sanidine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(This investigation, asymmetric or cubic fit to the data)</td>
<td>4.117 ( \pm 0.080 )</td>
<td>7.474 ( \pm 0.085 )</td>
<td>1.449</td>
</tr>
<tr>
<td>Analbite - sanidine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(This investigation, symmetric or quadratic fit to the data)</td>
<td>5.691 ( \pm 0.035 )</td>
<td>5.691 ( \pm 0.035 )</td>
<td>1.423</td>
</tr>
</tbody>
</table>

One of us (GLH) extends his gratitude to Professors Sheldon Judson and Lincoln Hollister of Princeton University for their cooperation in preserving the data herein reported and the calorimetric apparatus during the period after Dr. Waldbaum’s death.

We thank Dr. Richard A. Robie and Dr. Bruce Hemingway for their helpful comments on a preliminary version of this manuscript. Dr. Gordon E. Brown and Dr. Alexandra Navrotsky made very helpful comments on the final version of the manuscript. We thank Mrs. Mary Alice Skinner, who typed preliminary and final versions of this manuscript.

This work was supported financially by the Higgins Fund of Harvard University and by the Earth Sciences Section of the National Science Foundation, NSF Grants GA–1171, GA–12869, GA–31165, and EAR75–21852.

**References**


*Manuscript received, August 19, 1976; accepted for publication, March 11, 1977.*