

THERMODYNAMICS OF THE DISORDERING
PROCESS IN ALBITEJ. L. HOLM AND O. J. KLEPPA, *Department of Chemistry and The James
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ABSTRACT

The enthalpies of solution, in lead-cadmium-borate at 700°C, of samples of Amelia albite heated for 0–35 days at $1045 \pm 5^\circ\text{C}$ have been measured. For the transformation low albite→high albite at 700°C we obtained $\Delta H = 3.4 \pm 0.25$ kcal/mole. The heat content of high albite at 700°C was measured by “transposed temperature” drop calorimetry. This permits a comparison of the enthalpy of transformation at 700°C with corresponding data determined near room temperature.

The enthalpy of solution data indicate that the process low albite→high albite takes place in two steps. The first step, which in our samples was essentially complete after three days at 1045°C, is associated with an enthalpy change of about 2.4 kcal/mole. The second step of about 1 kcal/mole was nearly complete after three weeks at 1045°C. We attribute the first step in the transformation to partial disordering of the Al+Si atoms to form an “intermediate” albite, $\text{Na}[\text{Al}_{0.5}\text{Si}_{0.5}]_2\text{Si}_2\text{O}_8$.

Based on various assumptions regarding the configurational entropies in low, intermediate and high albite, we have estimated approximate temperatures of transformation for the process low albite→high albite and for low albite→intermediate albite. The calculated transformation temperatures are consistent with the work of McConnell and McKie, who suggested the existence of a “smeared” polymorphic transformation around 600°C.

INTRODUCTION

Sodium feldspar, $\text{NaAlSi}_3\text{O}_8$, is known to exist in at least two crystalline modifications, a low-temperature form stable below 500–700°C (“low-albite” or simply “albite”) and a high-temperature form (“high-albite”). While the low-temperature form is one of the most common minerals in plutonic rocks, the high-temperature modification has been found only in some acid lavas, usually with considerable potassium and calcium content. However, this form may readily be produced by heating the low-temperature modification for extended periods of time at temperatures near the melting point. X-ray structural analysis by Ferguson, Traill and Taylor (1958), revised by Ribbe (1963), has proved beyond doubt that the main structural difference between the two forms of albite is related to the distribution of Al and Si atoms in the tetrahedrally coordinated framework of the feldspars. In low albite there is nearly complete long range order in the mutual arrangement of 1Al+3Si atoms, while in the high albite the distribution is nearly random.

The published literature on the crystallographic and mineralogical properties of the feldspars is extremely extensive. In contrast to this the thermodynamic information is quite sparse. From the point of view of the present work it is of interest to note that White (1919) determined the high-temperature enthalpy of low albite and of albite glass. Similar

data for high albite are not available in the literature. Kracek and Neuvonen (1952) reported heat of solution measurements for a series of feldspars in aqueous hydrofluoric acid at 74.7°C. From these data they derived values of the enthalpy of transformation of low albite to high albite (2.3 kcal/mole). Very recently Waldbaum and Robie (1966), on the basis of heat solution measurements in aqueous HF at 49.7°C, have found an enthalpy of transformation of 2,633 cal/mole, with an estimated uncertainty of about ± 200 cal/mole.

In the present work we report the results of a series of heat of solution measurements for Amelia albite in a lead-cadmium-borate melt at 698°C. The albite samples have been heated for periods of 0–35 days at $1045 \pm 5^\circ\text{C}$. The results permit a calculation of the heat of transformation of low albite to high albite at 698°C, and give some insight into the kinetics of the transformation.

In order to compare our results with those of Waldbaum and Robie (1966) and of Kracek and Neuvonen (1952) we have also determined the heat content of high and low albite at 698°C by means of "transposed temperature" drop calorimetry.

EXPERIMENTAL AND RESULTS

Materials. We had available a small sample of Amelia albite, kindly furnished by Dr. Stefan Hafner. Prior to use, the small clean crystalline chunks of the mineral were crushed in a mullite mortar to about 250 mesh. This powder was subsequently used for all heating-solution measurements and for the determination of the heat content of low albite. The heat content measurements on high albite (heated Amelia albite) were performed on a small powdered sample lent by Dr. D. R. Waldbaum. This is the same material used by Waldbaum and Robie (1966). A description of the material and details of the procedures used in its preparation are given by Waldbaum (1966).

Apparatus and Procedures. During the heating experiments the albite powder was contained in a platinum capsule of about 6 mm I.D. \times 30 mm length. The capsule was closed by a tight-fitting lid and placed inside a fused silica protection tube which in turn was inserted, always at the same location, into the heat-treating furnace. This was a horizontal, Kanthal-wound unit with a mullite core of about 1 1/4" I.D. \times 20" long. The furnace temperature was stabilized by means of a Sorensen Constant Voltage Regulator, and measured by means of a Pt-Pt 13 percent Rh thermocouple which had been checked against a N.B.S. calibrated couple. Throughout the period of the heating experiments (about 2 months) the furnace temperature remained constant at $1045 \pm 5^\circ\text{C}$.

The calorimetric measurements were performed in a single unit Calvet-type differential micro-calorimeter similar to the apparatus previously described by Hersh and Kleppa (1965). The experimental procedures were analogous to those used in the work on the aluminum silicates by Holm and Kleppa (1966). The solvent was a lead-cadmium-borate of approximate composition $9\text{PbO}:3\text{CdO}:4\text{B}_2\text{O}_3$. In each solution experiment a small sample, 0.2–0.3 mmole of $\text{NaAlSi}_3\text{O}_8$ was dissolved in about 40 g of solvent (about 250 mmoles of oxides). The experimentally determined heats of solution (kcal/mole) are recorded in Table 1. In Figure 1 the average values of the heat of solution are plotted *versus* the length of heat-treatment at $1045 \pm 5^\circ\text{C}$.

TABLE 1. HEATS OF SOLUTION OF ALBITE IN LEAD-CADMIUM-BORATE MELT AT 698°C

Heating time	Heats of solution kcal/mole	Mean ^a kcal/mole
0	18.35, 18.3, 18.15, 18.0	18.2
23 hours	17.2, 17.1	17.15
48 hours	16.3, 16.1, 15.9	16.1
8 days	15.8, 15.8, 15.7	15.8
13 days	15.8, 15.8	15.8
14 days	15.8, 15.5	15.65
21 days	14.85, 14.8, 14.8	14.8
28 days	14.8, 14.75	14.8
35 days	14.85, 14.75	14.8

^a The uncertainty in the quoted mean values is estimated to be about $\pm 1\%$, *i.e.*, ± 0.15 to ± 0.20 kcal/mole.

From Figure 1 it is apparent that the heat of solution varies significantly with the heating time, ranging from 18.2 ± 0.2 kcal/mole for the unheated albite to 14.8 ± 0.15 kcal/mole for a sample which has been heated for three weeks or more. The difference between these two values, 3.4 ± 0.25 kcal, represents the enthalpy of transformation for the process low albite \rightarrow high albite at 971°K .

It is interesting to note that the data given in Figure 1 seem to indicate that the heating of low albite to form high albite occurs in two steps. The first step, which involves an enthalpy change of the order of 2.4 kcal/mole, is largely completed in as short a time as about three days, while the second step involves about 1 kcal/mole and is fairly complete after about three weeks at 1045°C .

In the calorimetric drop experiments 250 mgs of (low or high) albite were placed in a Pt-capsule of 5 mm diameter, 25 mm length and 0.07

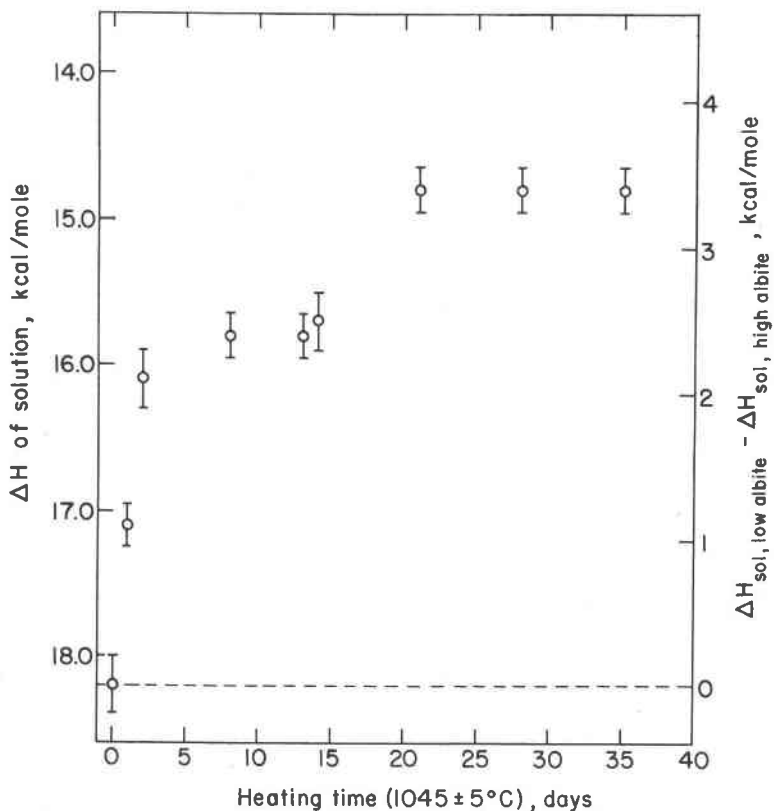


FIG. 1. Enthalpies of solution in lead-cadmium-borate at 700°C of samples of Amelia albite heated for various periods of time at 1045 ± 5°C.

mm wall. After the capsule was filled the open end was squeezed shut by means of a three-jaw chuck. The sample was then dried to constant weight at 150°C.

In the actual calorimetric experiments the filled capsule was dropped from near 25°C into the calorimeter at 698°C, through a fused silica tube of 8 mm I.D. In the calorimeter proper it was received in a well (lined with silica glass) in a silver cylinder of 16 mm O.D. × 100 mm length. The results of these experiments are recorded in Table 2.

From the data quoted by Kelley (1960) we calculate the enthalpy difference $H_{971^\circ} - H_{298^\circ}$ for low albite to be 44.09 kcal/mole, in good agreement with our own result 44.03 ± 0.10 . The corresponding value obtained for high albite was 44.82 ± 0.22 . From these values, and the heat of

solution data given above, we calculate the enthalpy of transformation of low albite to high albite at 298°K to be 2.6 ± 0.35 kcal/mole. This is in good agreement with the results of Waldbaum and Robie (1966) and of Kracek and Neuvonen (1952).

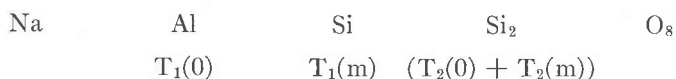
DISCUSSION

X-ray structural analysis has shown that the Al/Si positions in triclinic alkali feldspars consist of four different sites. These are referred to as $T_1(0)$, $T_1(m)$, $T_2(0)$ and $T_2(m)$ by Megaw (1956). In the ordered low-albite form the Al-atoms are concentrated in the $T_1(0)$ sites while the Si atoms occupy the other three positions. In the disordering process strong Al-O and Si-O bonds must be broken, which accounts for the generally sluggish character of this process.

TABLE 2. TRANSPOSED TEMPERATURE HEAT CONTENT MEASUREMENTS ON LOW AND HIGH ALBITE

	$H_{971}^{\circ} - H_{298}^{\circ}$ kcal/mole				
	I	II	III	IV	Mean
Low albite	44.08	44.03	43.92		44.03 ± 0.10
High albite	45.02	44.96	44.70	44.60	44.82 ± 0.22

From the heat of solution data reported in the present work it may be inferred that the kinetics of the disordering process in albite involves (at least) two different steps which proceed at somewhat different rates. This is believed to be related to the fact that the three Si-sites are not crystallographically equivalent in the low albite structure. With this in mind let us write the formula for low albite in the form



If we assume that the interchange of Al-atoms on $T_1(0)$ with Si-atoms on $T_1(m)$ occurs with greater ease than the interchange between atoms on T_1 and T_2 sites, the two step process indicated by Figure 1 is readily explained. If this interpretation is correct, the intermediate albite which results from partial disordering of the Al and Si atoms may be referred to, structurally, as $\text{Na}[\text{Al}_{0.5}\text{Si}_{0.5}]_2\text{Si}_2\text{O}_8$, while the fully disordered form is $\text{Na}[\text{Al}_{0.25}\text{Si}_{0.75}]_4\text{O}_8$.

For the potassium feldspars, Hafner and Laves (1956 and 1957), on the basis of infrared absorption measurements, have argued that ortho-

classes and adularias are stable members of a continuous series, and structurally intermediate between the low-temperature, ordered form KAlSi_3O_8 (microcline) and the disordered, high-temperature form $\text{K}[\text{Al}_{0.25}\text{Si}_{0.75}]_4\text{O}_8$ (sanidine). Similar ideas also have been expressed by Barth (1959).

However, in the sodium feldspars the existence of stable intermediate forms between low and high albite is much more doubtful. For example it appears that intermediate albites are quite rare in nature [see *e.g.*, Baskin (1956)].

In recent years the most comprehensive experimental study of phase transformations in the albites was carried out by MacKenzie (1957). This study emphasized the kinetics of the slow ordering process which occurs in high albite when this modification is heated under hydrothermal conditions at temperatures of the order of 500°–700°C. In MacKenzie's work a wide range of different intermediate albites were produced, and recognized through their X-ray patterns. However, due to the extremely sluggish character of the ordering process, this process cannot be brought to completion under laboratory conditions. Thus no one has as yet succeeded in synthesizing completely ordered low albite or in reversing the low-high albite transformation in the laboratory.¹

MacKenzie's work in itself provides no arguments for or against a possible stability range for intermediate albites. On the other hand, from a careful analysis of MacKenzie's kinetic data, McConnell and McKie (1960) conclude that the data indicate the existence of a "smeared" polymorphic transformation (Ubbelohde (1957)) in the temperature range around 600°C. The "smearing" of the transformation might be a consequence of a single phase transformation which is of higher order than one, or it might be the result of the superposition of two or more phase transformations which occur within a limited range of temperature.

THERMODYNAMIC CALCULATIONS

For the purpose of the present discussion let us first make the simplifying assumption that the disordering of low albite, to form either high albite or intermediate albite, may be treated thermodynamically as if the processes were one-step, first order phase transformations.

While this assumption may or may not be valid, it offers the only possible approach to the thermodynamics of these transformations on the basis of the available data. Specifically it allows us to associate with each transformation a characteristic latent heat, ΔH , a characteristic

¹ According to a report which has come to our attention since the present paper was completed Martin (1967) recently has succeeded in synthesizing low albite in the presence of $\text{Na}_2\text{Si}_2\text{O}_5$ at 200°C and 10 kb water pressure.

entropy change, ΔS , and a characteristic temperature, T . We may equate the latent heat of the transformation, Low albite \rightarrow High albite, with the difference in the heats of solution of these two modifications in lead-cadmium-borate at 700°C, 3.4 ± 0.25 kcal/mole. Our heat content data for low and high albite suggest that this value will change relatively little over a modest range in temperature.

If we assume, as a zeroth approximation, that low albite is *fully ordered*, while high albite is fully disordered, the change in configurational entropy on going from the low to the high form is simply¹

$$\Delta S_{\text{conf}} = -4R(0.75 \ln 0.75 + 0.25 \ln 0.25) = 4.47 \text{ cal/deg mole}$$

If other possible contributions to the entropy of transformation are neglected, we may now estimate the equilibrium transformation temperature from the requirement

$$\Delta G = \Delta H - T\Delta S_{\text{conf}} = 0$$

This yields $T = 760 \pm 70^\circ\text{K}$ or $490 \pm 70^\circ\text{C}$. The quoted uncertainty reflects only the estimated error in the enthalpy of transformation. For reasons which will be discussed next, this estimate may be considered to represent a lower bound on the transformation temperature.

The recent structural work on albite by Ferguson, Ribbe, Traill and Taylor, quoted by Bragg and Claringbull (1965), indicates that low albite may not in fact be fully ordered. High albite similarly may not be completely disordered, even after lengthy heat treatment near 1050°C. These authors give the following distribution of Al-atoms in Amelia albite, *i.e.*, the same type of albite which was used in our experiments.

	Site				Total
	$T_1(0)$	$T_1(m)$	$T_2(0)$	$T_2(m)$	
Low Albite	0.96	0.00	0.03	0.02	1.01
High Albite	0.29	0.27	0.20	0.22	0.98

In view of the many experimental uncertainties associated with the determination of these numbers, they must be accepted with reservations. It also is entirely possible that other specimens of Amelia albite may show slightly different Al-Si distributions. Nevertheless, it will be

¹ Very recently Fyfe, Turner and Verhoogen (1967) and following them, Orville (1967), have given the entropy change for Al-Si disorder in the alkali feldspars as 1.12 cal/deg mole. This estimate fails to take into account that at high temperature one mole of feldspar actually contains four moles of structurally equivalent (Al+Si) sites.

noted that our suggestion above regarding the relative ease of atomic interchange between T_1 and T_2 sites is entirely consistent with these data, which show a higher than random population (0.25) of Al-atoms on the $T_1(0)$ and $T_1(m)$ sites in high albite.

These data also offer the possibility of making a perhaps somewhat improved estimate of the configurational entropy difference between low and high albite. For this purpose we shall assume that in each case the total configurational entropy of the two albites may be represented by the sum of the random entropies of mixing of Al and Si atoms located on each of the four lattice sites.¹ Thus we have

$$\begin{aligned} S_{\text{conf}}(\text{high albite}) &= -R[0.29 \ln 0.29 + 0.71 \ln 0.71] \\ &\quad - R[0.27 \ln 0.27 + 0.73 \ln 0.73] \\ &\quad - R[0.20 \ln 0.20 + 0.80 \ln 0.80] \\ &\quad - R[0.22 \ln 0.22 + 0.78 \ln 0.78] \\ &= 4.41 \text{ cal/deg mole} \end{aligned}$$

and similarly

$$\begin{aligned} S_{\text{conf}}(\text{low albite}) &= -R[0.96 \ln 0.96 + 0.04 \ln 0.04] \\ &\quad + 0 \\ &\quad - R[0.03 \ln 0.03 + 0.97 \ln 0.97] \\ &\quad - R[0.02 \ln 0.02 + 0.98 \ln 0.98] \\ &= 0.81 \text{ cal/deg mole} \end{aligned}$$

It will be recognized that any uncertainty in the adopted occupation numbers for the four sites will carry over into the calculated configurational entropies. For this reason we do not argue that these entropy values necessarily are more "correct" than those estimated in the zeroth approximation above. On the other hand, the new entropy values serve the purpose of illustrating two very important points:

It is in the nature of the functional dependence of the entropy of mixing on composition that moderate departures from completely random mixing will give rise only to small deviations from the theoretically calculated entropy values. This situation is reflected in the fact that the "improved" value of S_{conf} for high albite (4.41 cal/degree mole) is quite close to that calculated for completely random mixing (4.47 cal/deg mole). On the other hand, even small errors in the quoted occupation

¹ In making these calculations we have adopted the reported Al-distributions, *i.e.*, we have *not* normalized the Al-content to Al=1.00. The small difference in the calculated entropies would be of no significance for the present discussion.

numbers for low albite could change the calculated entropy for this phase very significantly. Keeping these points in mind our "improved" estimate of the difference in configurational entropy between low and high Amelia albite is $4.41 - 0.81 = 3.6$ cal/deg mole. Based on this value we make a new estimate of the equilibrium transformation temperature

$$T = \frac{3400}{3.6} = 940 \pm 70^\circ\text{K} \quad \text{or} \quad 670 \pm 70^\circ\text{C}$$

In arriving at this value, as well as the zeroth approximation value given above, we have completely neglected all non-configurational contributions to the entropy of transformation. Since the volume change associated with the considered transformation is small (about 0.54 cm^3/mole , Waldbaum and Robie (1966)), these contributions are expected to represent at most a few per cent of the configurational entropy and accordingly to *lower* the calculated transformation temperatures to this extent. We conclude that the actual transformation temperature should fall somewhere in the range 490°C to 670°C but most probably in the upper part of this interval.

So far we have made no attempt to take into account the possible existence of the intermediate albite, $\text{Na}_3[\text{Al}_{10.5}\text{Si}_{0.5}]_2\text{Si}_2\text{O}_8$. If this phase in fact has a separate temperature range of stability we may calculate the equilibrium transformation temperature, low albite \rightarrow intermediate albite, by application of the same thermodynamic method. From our calorimetric data it is indicated that the enthalpy change for this reaction is about 2.4 kcal/mole. In the zeroth approximation the entropy of transformation is simply $2R\ln 2 = 2.76$ cal/mole degree. From these values we estimate the transformation temperature to be about 870°K or 600°C . If we again take the residual disorder in low albite into account, our calculated transformation temperature may be some 100° higher. Thus it appears that the separate stability range for intermediate albite, if it exists, must be of very limited extent. In view of the uncertainties both in the calorimetric data and in the entropy estimates we do not consider it justified to pursue this problem further. Note that our calculated transformation temperatures are consistent with the "smeared" polymorphic transformation around 600°C suggested by McConnell and McKie (1960). On the other hand, since their analysis refers to Al/Si ordering in a *hydrothermal* environment, it should not necessarily be compared to the *dry disordering* process considered in the present work.

Finally it should be mentioned that the present discussion, although relating to an albite which had in fact been disordered in the laboratory at temperatures of about 1045°C , has no bearing on the existence of a monoclinic form of pure albite between 900°C and the melting point

(Grundy, Brown and MacKenzie (1966)). Since the triclinic-monoclinic transformation is reversible and quite rapid, it will not affect our calorimetric measurements at 700°C.

ACKNOWLEDGMENTS

We are particularly indebted to Professor S. Hafner, who furnished us with the specimens of Amelia albite, and to Dr. D. R. Waldbaum who lent us a sample of high albite for the heat content measurements and who kindly carried out the X-ray work on our small powdered albite samples. We have benefitted greatly from discussions with and comments on the manuscript by Professors S. Hafner, J. R. Goldsmith and J. V. Smith and by Drs. R. A. Robie and D. R. Waldbaum.

This work has been supported by the Army Research Office, Durham. It also has benefitted from the support of Material Science at the University of Chicago provided by the Advanced Research Projects Agency, Department of Defense.

APPENDIX: STRUCTURAL EXAMINATION OF THE ALBITES

On the basis of our small powdered samples an X-ray structural study of the various albites was carried out by Dr. David Waldbaum. He kindly provided us with the following information:

The X-ray data for our unheated Amelia albite are in excellent agreement with all previous data for other specimens from this locality. From these data it is estimated that our sample contains less than three mole percent KAlSi_3O_8 or $\text{CaAl}_2\text{Si}_2\text{O}_8$. Similarly, the structural data on our heated albites are in good agreement with previously published lattice parameters and with results obtained recently by Waldbaum (1966).

Plots of γ^*, c_0 and other parameters for our albites *versus* heating time indicate a fast initial process, which takes place over a period of 1–2 days at $1045 \pm 5^\circ$. This process is followed by a very slow change which may not yet have reached its ultimate final state even after 35 days at 1045°C .

REFERENCES

- BARTH, T. F. W. (1959) The interrelation of the structural variants of the potash feldspars. *Z. Kristallogr.* **112**, 263–274.
- BASKIN, Y. (1956) Observations on heat-treated authigenic microcline and albite crystals. *J. Geol.* **64**, 219–224.
- BRAGG, SIR L. AND G. F. CLARINGBULL (1965) *Crystal structures of minerals, vol. IV*. G. Bell and Sons, Ltd., London, pp. 338–339.
- FERGUSON, R. B., R. J. TRAILL, AND W. H. TAYLOR (1958) The crystal structures of low-temperature and high-temperature albites. *Acta Crystallogr.* **11**, 331–348.
- FYFE, W. S., F. S. TURNER AND J. VERHOOGEN (1967) Metamorphic reactions and metamorphic facies. *Geol. Soc. Amer. Mem.* **72**, 32.
- GRUNDY, H. D., W. L. BROWN, AND W. S. MACKENZIE (1967) On the existence of monoclinic $\text{NaAlSi}_3\text{O}_8$ at elevated temperatures. *Mineral. Mag.*, **36**, 83.
- HAFNER, S. AND F. LAVES (1957) Ordnung/Unordnung und Ultrarotabsorption. II. Variation der Lage und Intensität einiger Absorptionen von Feltspäten. Zur Struktur von Orthoklas und Adular. *Z. Kristallogr.* **109**, 204–225.

- HERSH, L. S. AND O. J. KLEPPA (1965) Enthalpies of mixing in some binary liquid halide mixtures. *J. Chem. Phys.* **42**, 1309-1322.
- HOLM, J. L. AND O. J. KLEPPA (1966) The thermodynamic properties of the aluminum silicates. *Amer. Mineral.* **51**, 1608-1622.
- KELLEY, K. K. (1960) Contributions to the data on theoretical metallurgy. U. S. Bur. Mines Bull. **584**.
- KRACEK, F. C. AND K. J. NEUVONEN (1952) Thermochemistry of plagioclase and alkali feldspars. *Amer. J. Sci.*, Bowen Volume, 293-318.
- LAVES, F. AND S. HAFNER (1956) Ordnung/Unordnung und Ultrarotabsorption. I (Al, Si) Verteilung in Feltspäten. *Z. Kristallogr.* **108**, 52-63.
- MACKENZIE, W. M. S. (1957) The crystalline modifications of $\text{NaAlSi}_3\text{O}_8$. *Amer. J. Sci.* **255**, 481-516.
- MARTIN, R. F. (1967) The synthesis of low albite. *Trans. Amer. Geophys. Union* **48**, 225.
- MCCONNELL, J. D. C. AND D. MCKIE (1960) The kinetics of the ordering process in triclinic $\text{NaAlSi}_3\text{O}_8$. *Mineral. Mag.* **32**, 436-454.
- MEGAW, HELEN D. (1956) Notation for feldspar structures. *Acta Crystallogr.* **9**, 56-60.
- ORVILLE, PHILIP M. (1967) Unit-cell parameters of the microcline-low albite and the sanadine-high albite solid solution series. *Amer. Mineral.* **52**, 55.
- RIBBE, P. H. (1963) *Structural studies of plagioclase feldspars*. Diss. Cambridge Univ., England.
- UBBELOHDE, A. R. (1957) Thermal transformation in solids. *Quart. Rev. Chem. Soc.* **11**, 246-272.
- WALDBAUM, D. R. (1966) *Calorimetric investigation of the alkali feldspars*. Ph.D. Thesis, Harvard University, 247 pp.
- AND R. A. ROBIE (1966) Thermodynamics of K/Na-mixing and Al/Si-disordering in the system KAlSi_3O_8 (alkali feldspars). *21st Calorimetry Conference, Boulder, Colorado, June 22-24, 1966*.
- WHITE, W. P. (1919) Silicate specific heats. *Amer. J. Sci.* **47**, 1-59.

Manuscript received, May 19, 1967; accepted for publication, August 14, 1967.