

## High-Temperature Thermodynamic Properties of Alkali Feldspars\*

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*Abstract.* Recent hydrofluoric acid solution calorimetric data are used to derive standard enthalpies and Gibbs free energies of formation of low-albite, high-albite,  $\text{NaAlSi}_3\text{O}_8$  glass, microcline, sanidine, and  $\text{KAlSi}_3\text{O}_8$  glass. The data are presented as high-temperature functions from 298.15 to 1400°K.

Despite many laboratory studies on the feldspars, only a small amount of quantitative thermochemical data are available for calculations of geological interest. In most experimental thermodynamic studies of feldspars, emphasis has been on determining phase relations of crystalline solutions relative to the end-member phases (BOWEN and TUTTLE, 1950; ORVILLE, 1963; LUTH and TUTTLE, 1966) or other phases. WHITE (1919) and KELLEY, TODD, ORR, KING, and BONNICKSON (1953) measured the low-temperature heat capacities and values of  $(H_T^\circ - H_{298.15}^\circ)$  for adularia,  $\text{KAlSi}_3\text{O}_8$  glass, low-albite, and  $\text{NaAlSi}_3\text{O}_8$  glass. GARRELS (1957) and REESMAN and KELLER (1965) have estimated the Gibbs free energies of formation of "orthoclase" and microcline from solubility measurements. TAMMANN (1903), MULERT (1912), and KRACEK and NEUVONEN (1952) measured the heats of solution of several alkali feldspars in hydrofluoric acid. In each of these studies, however, the crystallographic properties of the samples were not adequately described, and in view of the complex Al/Si order-disorder relations in the feldspar structure, the usefulness of the derived thermodynamic data is somewhat limited.

WALDBAUM and ROBIE (1966) recently reported solution calorimetric data for alkali feldspars which are utilized in this paper to derive standard thermodynamic functions for end-member compositions in the system  $\text{NaAlSi}_3\text{O}_8$ - $\text{KAlSi}_3\text{O}_8$ . The materials were prepared by fused-salt ion-exchange, and were dissolved in 20.1 weight per cent hydrofluoric acid using a vacuum-jacketed solution calorimeter (ROBIE, 1965). Details of this investigation are reported elsewhere (WALDBAUM, 1966).

The following enthalpies of transition (at 49.7°C) were derived from the heat of solution measurements on samples synthesized initially from Amelia (Virginia, U.S.A.) albite:

microcline $\rightarrow$ sanidine,	$\Delta H = +1.89 \pm 0.44$ kcal gfw <sup>-1</sup>
sanidine $\rightarrow$ $\text{KAlSi}_3\text{O}_8$ glass,	$\Delta H = +11.10 \pm 0.37$ kcal gfw <sup>-1</sup>
low-albite $\rightarrow$ high-albite,	$\Delta H = +2.63 \pm 0.28$ kcal gfw <sup>-1</sup>
high-albite $\rightarrow$ $\text{NaAlSi}_3\text{O}_8$ glass,	$\Delta H = +11.89 \pm 0.40$ kcal gfw <sup>-1</sup> .

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The data for low-albite, high-albite, and  $\text{NaAlSi}_3\text{O}_8$  glass are in excellent agreement with the results of KRACEK and NEUVONEN (1952) and HOLM and KLEPPA (in press). No previous determinations have been made on the enthalpy differences between microcline, sanidine, and  $\text{KAlSi}_3\text{O}_8$  glass.

Combining the above results with heat capacity data (KELLEY, et al., 1953) and the heats of solution of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{SiO}_2$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{HCl} \cdot n\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}$  in 20.1% hydrofluoric acid (KING, 1951; KELLEY, BARANY, KING, and CHRISTENSEN, 1959; and BARANY, 1962), one can derive the standard enthalpies of formation of alkali feldspars at 298.15°K. The values thus derived in Tables 1—6 are to be preferred over existing values of the enthalpies of formation of alkali feldspars inasmuch as the compositions and X-ray crystallographic properties of the calorimetric samples are accurately known (WALDBAUM, 1966).

Table 1. *Molar (gram formula weight, gfw) enthalpy ( $H_T^\circ - H_{298.15}^\circ$ ), entropy ( $S_T^\circ$ ), free energy function [ $-(G_T^\circ - H_{298.15}^\circ)/T$ ], standard enthalpy of formation ( $\Delta H_f^\circ, T$ ), and standard Gibbs free energy of formation ( $\Delta G_f^\circ, T$ ) of low-albite at high temperatures and 1.013 bars pressure*

$T$ °K	$H_T^\circ - H_{298}^\circ$ (kcal gfw <sup>-1</sup> )	$S_T^\circ$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$-(G_T^\circ - H_{298}^\circ)/T$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_f^\circ, T$ $\Delta G_f^\circ, T$	
				(kcal gfw <sup>-1</sup> )	
298.15	0.000	50.20	50.20	-937.146	-883.988
		$\pm 0.40$	$\pm 0.40$	$\pm 0.740$	$\pm 0.760$
400	5.410	65.75	52.22	-938.146	-865.822
500	11.390	79.07	56.29	-938.100	-847.598
600	17.900	90.93	61.10	-937.706	-829.536
700	24.690	101.40	66.13	-937.192	-811.555
800	31.690	110.74	71.13	-936.614	-793.643
900	38.870	119.19	76.00	-936.002	-775.802
1000	46.220	126.94	80.72	-937.873	-757.839
1100	53.720	134.08	85.24	-937.101	-739.866
1200	61.340	140.71	89.59	-959.510	-721.521
1300	69.060	146.89	93.77	-958.429	-701.740
1400	76.860	152.67	97.77	-957.315	-682.027

Table 2. *High-temperature thermodynamic properties of high-albite*

$T$ °K	$H_T^\circ - H_{298}^\circ$ (kcal gfw <sup>-1</sup> )	$S_T^\circ$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$-(G_T^\circ - H_{298}^\circ)/T$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_f^\circ, T$ $\Delta G_f^\circ, T$	
				(kcal gfw <sup>-1</sup> )	
298.15	0.000	54.67	54.67	-934.513	-882.687
		$\pm 0.45$	$\pm 0.45$	$\pm 0.770$	$\pm 0.790$
400	5.530	70.56	56.74	-935.393	-864.995
500	11.627	84.14	60.89	-935.230	-847.263
600	18.254	96.21	65.78	-934.719	-829.715
700	25.162	106.85	70.90	-934.087	-812.264
800	32.279	116.33	75.99	-933.392	-794.897
900	39.576	124.91	80.94	-932.663	-777.614
1000	47.044	132.78	85.73	-934.416	-760.220
1100	54.661	140.02	90.33	-933.527	-742.824
1200	62.398	146.74	94.74	-955.819	-725.067
1300	70.236	153.01	98.98	-954.620	-705.882
1400	78.153	158.86	103.04	-953.389	-686.773

Table 3. *High-temperature thermodynamic properties of NaAlSi<sub>3</sub>O<sub>8</sub> glass*

$T$ °K	$H_T^\circ - H_{298}^\circ$ (kcal gfw <sup>-1</sup> )	$S_T^\circ$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$-(G_T^\circ - H_{298}^\circ)/T$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_f^\circ, T$ $\Delta G_f^\circ, T$	
				(kcal gfw <sup>-1</sup> )	
298.15	0.000	62.95 ±0.60	62.95 ±0.60	-922.609 ± 0.760	-873.252 ± 0.790
400	5.468	78.66	64.99	-923.551	-856.393
500	11.536	92.08	69.01	-923.417	-839.419
600	18.167	104.26	73.98	-922.902	-822.730
700	25.118	114.98	79.09	-922.227	-806.093
800	32.321	124.59	84.19	-921.446	-789.552
900	39.751	133.33	89.16	-920.584	-773.110
1000	47.400	141.40	94.00	-922.156	-756.578
1100	55.254	148.87	98.64	-921.030	-740.066
1200	63.286	155.86	103.12	-943.027	-723.219
1300	71.480	162.42	107.44	-941.472	-704.972
1400	79.820	168.60	111.59	-939.818	-686.832

To derive the standard Gibbs free energies of formation at 298.15°K, the third-law entropies,  $S_{298.15}^\circ$ , of the phases are needed. KELLEY et al. (1953) measured the heat capacities of low-albite (Amelia, Virginia) and adularia (Switzerland) down to 50°K. From these measurements they obtained  $50.20 \pm 0.40$  cal deg<sup>-1</sup> gfw<sup>-1</sup> and  $52.47 \pm 0.60$  cal deg<sup>-1</sup> gfw<sup>-1</sup>, for the entropies at 298.15°K, but these represent only vibrational entropies ( $S_{298.15}^\circ - S_0^\circ$ ). Crystallographic and kinetic data (TAYLOR, 1965; WALDBAUM, 1966; MACKENZIE, 1957) for alkali feldspars indicate that in addition to vibrational entropy obtained by cryogenic calorimetry, a certain amount of Al/Si configurational entropy is frozen in at 0°K. This kind of configurational contribution to the entropy cannot be determined by heat capacity measurements, hence must be derived from phase equilibrium data which depend on the total third-law entropy of the substance. Configurational entropy can also be calculated from considerations based on simple solution theory, as shown below, when the Al/Si-distribution is known.

Table 4. *High-temperature thermodynamic properties of (maximum) microcline*

$T$ °K	$H_T^\circ - H_{298}^\circ$ (kcal gfw <sup>-1</sup> )	$S_T^\circ$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$-(G_T^\circ - H_{298}^\circ)/T$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_f^\circ, T$ $\Delta G_f^\circ, T$	
				(kcal gfw <sup>-1</sup> )	
298.15	0.000	52.47 ±0.80	52.47 ±0.80	-946.265 ± 0.930	-892.817 ± 0.970
400	5.500	68.28	54.53	-947.146	-874.504
500	11.550	81.76	58.66	-947.032	-856.210
600	17.950	93.42	63.50	-946.753	-838.073
700	24.800	103.97	68.54	-946.189	-820.001
800	32.000	113.58	73.58	-945.428	-802.026
900	39.400	122.29	78.51	-944.618	-784.144
1000	46.900	130.19	83.29	-946.370	-766.150
1100	54.500	137.44	87.89	-964.439	-747.152
1200	62.200	144.14	92.31	-963.325	-727.454
1300	70.000	150.37	96.52	-962.164	-707.836
1400	77.900	156.23	100.59	-960.950	-688.315

Table 5. *High-temperature thermodynamic properties of (high) sanidine*

$T$ °K	$H_T^\circ - H_{298}^\circ$ (kcal gfw <sup>-1</sup> )	$S_T^\circ$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$-(G_T^\circ - H_{298}^\circ)/T$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_f^\circ, T$	$\Delta G_f^\circ, T$
				(kcal gfw <sup>-1</sup> )	
298.15	0.000	56.94 ±1.00	56.94 ±1.00	-944.378 ± 0.930	-892.263 ± 0.980
400	5.500	72.75	59.00	-945.259	-874.405
500	11.550	86.23	63.13	-945.145	-856.558
600	17.950	97.89	67.97	-944.866	-838.868
700	24.800	108.44	73.01	-944.302	-821.243
800	32.000	118.05	78.05	-943.541	-803.715
900	39.400	126.76	82.98	-942.731	-786.280
1000	46.900	134.66	87.76	-944.483	-768.733
1100	54.500	141.91	92.36	-962.552	-750.182
1200	62.200	148.61	96.78	-961.438	-730.931
1300	70.000	154.84	100.99	-960.277	-711.760
1400	77.900	160.70	105.06	-959.063	-692.686

The lattice parameters of the low-albite studied by WALDBAUM and ROBIE (1966) given in Table 7 indicate it to be highly ordered, if not completely ordered within the limits of detectability. Thus the value of KELLEY et al. (also for Amelia albite) can be adopted for  $S_{298.15}^\circ$  (low-albite). Similarly, the X-ray data indicate that the heated Amelia albite is completely disordered (or very nearly so). Hence, we obtain the configurational entropy from the relation:

$$S_{\text{cfg}}^\circ = -R \sum_i (N_{\text{Si}} \ln N_{\text{Si}} + N_{\text{Al}} \ln N_{\text{Al}}) \\ = 4.47 \text{ cal deg}^{-1} \text{ gfw}^{-1}$$

where  $i$  is the number of Al-Si crystallographic sites (4),  $N_{\text{Al}}$  is the mole fraction of Al in each site (0.25), and  $N_{\text{Si}} = 1 - N_{\text{Al}}$ . Adding this configurational entropy to  $S_{298.15}^\circ$  (low-albite) we obtain 54.67 for  $S_{298.15}^\circ$  (high-albite). This calculation assumes that the vibrational entropy of high-albite is equal to the calorimetric entropy of ordered low-albite at 298.15°K, that is, it assumes the vibrational properties of

Table 6. *High-temperature thermodynamic properties of KAlSi<sub>3</sub>O<sub>8</sub> glass*

$T$ °K	$H_T^\circ - H_{298}^\circ$ (kcal gfw <sup>-1</sup> )	$S_T^\circ$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$-(G_T^\circ - H_{298}^\circ)/T$ (cal deg <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_f^\circ, T$	$\Delta G_f^\circ, T$
				(kcal gfw <sup>-1</sup> )	
298.15	0.000	63.28 ±1.00	63.28 ±1.00	-933.276 ± 0.910	-883.051 ± 0.960
400	5.542	79.20	65.35	-934.115	-865.841
500	11.743	93.01	69.53	-933.850	-848.655
600	18.341	105.03	74.47	-933.373	-831.662
700	25.391	115.89	79.62	-932.609	-814.767
800	32.772	125.74	84.78	-931.667	-797.997
900	40.331	134.64	89.83	-930.698	-781.342
1000	47.988	142.71	94.72	-932.293	-764.591
1100	55.783	150.14	99.43	-950.167	-746.854
1200	63.777	157.10	103.95	-948.759	-728.438
1300	72.049	163.70	108.28	-947.126	-710.133
1400	80.702	170.12	112.48	-945.159	-691.972

the feldspar structure below 298.15°K to be independent of Al/Si-distribution. The recent work of HOLM and KLEPPA (in press) shows that changes in Al/Si-disorder appreciably affect the heat capacity of albite above 298.15°K. This was somewhat unexpected inasmuch as there are no differences in symmetry or topology of the crystal structures or in the bulk compositions of high- and low-albite. In view of HOLM and KLEPPA's results, it is likely that low-temperature heat capacity measurements on high-albite will show that the vibrational entropies of high- and low-albite at 298.15°K differ by several cal deg<sup>-1</sup> gfw<sup>-1</sup>, hence the entropies in Table 2 are at best minimum values of the true third-law entropy of high-albite.

Table 7. *Lattice parameters of end-member alkali feldspars studied in calorimetric investigation of WALDBAUM and ROBIE (1966). Cell dimensions in Angstroms; angles in degrees*

Material	<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	$\beta$	$\gamma$
Low-albite (Amelia, Virginia)	8.1414 ±0.0016	12.7836 ±0.0020	7.1571 ±0.0011	94.233 ±0.016	116.592 ±0.012	87.680 ±0.015
Microcline (Amelia albite heated in fused KCl, 25 hours at 910°C)	8.5836 ±0.0016	12.9723 ±0.0015	7.2238 ±0.0009	90.619 ±0.013	115.924 ±0.010	87.650 ±0.012
High-albite (Amelia albite heated for 668 hours at 1060°C)	8.1627 ±0.0020	12.8729 ±0.0016	7.1141 ±0.0010	93.545 ±0.019	116.460 ±0.011	90.131 ±0.023
Sanidine (high-albite heated in fused KCl, 24 hours at 910°C)	8.6079 ±0.0012	13.0354 ±0.0011	7.1817 ±0.0009	90.0	116.012 ±0.008	90.0

To obtain the entropies of microcline and high-sanidine it is assumed that the heat capacity data of KELLEY et al. (1953) represent the vibrational properties of both Al/Si-ordered and -disordered K-feldspars. The entropy of microcline is therefore taken to be  $52.47 \pm 0.80$  and for Al/Si-disordered high-sanidine,  $56.94 \pm 1.00$  cal deg<sup>-1</sup> gfw<sup>-1</sup>.

Combining these results with  $\Delta H_f^\circ_{298.15}$  gives the standard Gibbs free energies of formation of the crystalline end-member alkali feldspars in Tables 1, 2, 4 and 5. Auxiliary data for the elements were taken from the compilation of ROBIE and WALDBAUM (in press).

The melting point of high-albite is 1118°C at 1 atm (BOYD and ENGLAND, 1963). Using the high-temperature enthalpy functions in Tables 2 and 3 derived from the data of WHITE (1919), KELLY et al. (1953), and HOLM and KLEPPA (in press), the entropy of fusion of high-albite is calculated to be  $9.75$  cal deg<sup>-1</sup> gfw<sup>-1</sup> at 1118°C<sup>1</sup>. This result yields a third-law entropy of  $62.95 \pm 0.60$  cal deg<sup>-1</sup> gfw<sup>-1</sup> for NaAlSi<sub>3</sub>O<sub>8</sub> glass at 298.15°K.

Recent work of SPENGLER and BURNHAM (1962) and LINDSLEY (1966) indicate that the (metastable) congruent melting temperature of sanidine is approximately

<sup>1</sup> This value is in good agreement with the value of  $9.3$  cal deg<sup>-1</sup> gfw<sup>-1</sup> at 1100°C for  $\Delta S_m^\circ$  calculated by BOWEN (1913) from experimentally determined crystal-liquid phase relations in the system NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>. However, this agreement does not imply confirmation of BOWEN's conclusion that liquid and crystalline plagioclase solutions are ideal. Crystallographic data indicate that plagioclase feldspars cannot be ideal solutions in the classical sense. The results in BOWEN's Table 4 suggest only that deviations from "ideality" are nearly the same for both crystal and liquid.

1200° ± 40°C at 1 atm. Using this value and the high-temperature heat capacity data of WHITE (1919) and KELLEY et al. (1953) in Tables 5 and 6,  $S_{298.15}^{\circ}$  (KAlSi<sub>3</sub>O<sub>8</sub> glass) is calculated to be 63.28 ± 1.00 cal deg<sup>-1</sup> gfw<sup>-1</sup>, and the entropy of fusion is 9.98 cal deg<sup>-1</sup> gfw<sup>-1</sup> at 1200°C.

The above entropy values yield sufficient data to calculate all the high-temperature thermodynamic functions in Tables 1—6. Procedures used in the calculations and in the assignment of uncertainties are given in ROBIE and WALDBAUM (in press). Thus far, however, only the thermodynamic properties of pure end-member phases have been considered. WALDBAUM and ROBIE (1966) also reported heat of solution data on 12 highly ordered synthetic K-Na feldspar crystalline solutions (microcline—low-albite series).

These data yield the following equation for calculating  $\Delta H_{f,T}^{\circ}$  (kcal gfw<sup>-1</sup>) for microcline—low-albite solutions of *intermediate* bulk composition:

$$\Delta H_{f,T}^{\circ} = N_{Ab} \Delta H_{f,T}^{\circ}(\text{low-albite}) + N_{Or} \Delta H_{f,T}^{\circ}(\text{microcline}) \\ + 6.244 N_{Ab} N_{Or}^2 + 8.426 N_{Or} N_{Ab}^2$$

where  $N_{Ab}$  is mole fraction NaAlSi<sub>3</sub>O<sub>8</sub>,  $N_{Or}$  is mole fraction KAlSi<sub>3</sub>O<sub>8</sub>, and the standard enthalpies of formation of the end-members are given in Tables 1 and 4. The excess entropy of mixing of either microcline—low-albite solutions or sanidine—high-albite solutions cannot be *accurately* evaluated with existing experimental data (THOMPSON and WALDBAUM, 1967). Hence, the Gibbs function for the binary system NaAlSi<sub>3</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub> cannot now be accurately calculated as a function of temperature, pressure, and composition. Despite the present lack of data on the thermodynamic mixing properties of alkali feldspars, numerous phase equilibrium calculations of interest to petrologists can be made with the data summarized in Tables 1—6.

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## References

- BARANY, R.: Heats and free energies of formation of some hydrated and anhydrous sodium- and calcium-aluminium silicates. U.S. Bur. Mines Rept. Investig. 5900 (1962).
- BOWEN, N. L.: The melting phenomena of the plagioclase feldspars. *Am. J. Sci.* **185**, 577—599 (1913).
- , and O. F. TUTTLE: The system NaAlSi<sub>3</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O. *J. Geol.* **58**, 489—511 (1950).
- BOYD, F. R., and J. R. ENGLAND: Effect of pressure on the melting of diopside CaMgSi<sub>2</sub>O<sub>6</sub>, and albite, NaAlSi<sub>3</sub>O<sub>8</sub>, in the range up to 30 kilobars. *J. Geophys. Research* **68**, 311—323 (1963).
- GARRELS, R. M.: Some free energy values from geologic relations. *Am. Mineralogist* **42**, 780—791 (1957).
- HOLM, J., and O. J. KLEPPA: Thermodynamics of the disordering process in albite (NaAlSi<sub>3</sub>O<sub>8</sub>). *Am. Mineralogist* (in press).
- KELLEY, K. K., R. BARANY, E. G. KING, and A. U. CHRISTENSEN: Some thermodynamic properties of fluorophlogopite mica. U.S. Bur. Mines Rept. Investig. 5436, 16 pp. (1959).
- S. S. TODD, T. L. ORR, E. G. KING, and K. R. BONNICKSON: Thermodynamic properties of sodium-aluminum and potassium-aluminum silicates. U.S. Bur. Mines Rept. Investig. 4955, 21 pp. (1953).
- KING, E. G.: Heat of formation of crystalline calcium orthosilicate, tricalcium silicate and zinc orthosilicate. *J. Am. Chem. Soc.* **73**, 656—658 (1951).

- KRACEK, F. C., and K. J. NEUVONEN: Thermochemistry of plagioclase and alkali feldspars. *Am. J. Sci.*, Bowen Vol., 293—318 (1952).
- LINDSLEY, D. H.: Melting relations of  $\text{KAlSi}_3\text{O}_8$ ; effect of pressure up to 40 kilobars. *Am. Mineralogist* **51**, 1793—1798 (1966).
- LUTH, W. C., and O. F. TUTTLE: The alkali feldspar solvus in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ . *Am. Mineralogist* **51**, 1359—1373 (1966).
- MACKENZIE, W. S.: The crystalline modifications of  $\text{NaAlSi}_3\text{O}_8$ . *Am. J. Sci.* **255**, 481—516 (1957).
- MULERT, O.: Über die Thermochemie der Kieselsäure und der Silicate. *Z. anorg. Chem.* **75**, 198—240 (1912).
- ORVILLE, P. M.: Alkali ion exchange between vapor and feldspar phases. *Am. J. Sci.* **261**, 201—237 (1963).
- REESMAN, A. L., and W. D. KELLER: Calculation of apparent standard free energies of formation of six rock-forming silicate minerals from solubility data. *Am. Mineralogist* **50**, 1729—1739 (1965).
- ROBIE, R. A.: Vacuum-jacketed hydrofluoric acid solution calorimeter. *Rev. Sci. Instr.* **36**, 484—486 (1965).
- , and D. R. WALDBAUM: Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Survey Bull.* (in press).
- SPENGLER, C. J., and C. W. BURNHAM: Compositions in the upper phase region of the system  $\text{KAlSi}_3\text{O}_8-\text{H}_2\text{O}$  at pressures up to 6 kilobars. *Geol. Soc. Am. Spec. Paper* **68**, 277 (1962).
- TAMMANN, G.: *Kristallisieren und Schmelzen*. 348 pp. Leipzig: J. A. Barth 1903.
- TAYLOR, W. H.: Framework silicates; the feldspars. Chap. 14, in: Sir L. BRAGG, and G. F. CLARINGBULL, *The Crystalline State* 4. 409 pp. London: G. Bell & Sons, Ltd. 1965.
- THOMPSON, J. B., jr., and D. R. WALDBAUM: Thermodynamic mixing properties of sanidine/high-albite crystalline solutions. *Trans. Am. Geophys. Union* **48**, 230 (1967).
- WALDBAUM, D. R.: Calorimetric investigation of the alkali feldspars. *U.S. Geol. Survey Open File Report*, Washington, D. C. 1966. 247 pp.
- , and R. A. ROBIE: Thermodynamics of K/Na-mixing and Al/Si-disordering in the system  $\text{KAlSi}_3\text{O}_8-\text{NaAlSi}_3\text{O}_8$  (alkali feldspars). 21st Annual Calorimetry Conference, Boulder (abstract), p. 27—28 (1966).
- WHITE, W. P.: Silicate specific heats. Second series. *Am. J. Sci.* **197**, 1—43 (1919).

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