American Mineralogist, Volume 63, pages 109–123, 1978

Low-temperature heat capacities and entropies of feldspar glasses and of anorthite

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Abstract

The heat capacities of glasses near the feldspar compositions $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$, and of crystalline anorthite were measured between 12 and 380 K by means of an adiabatic calorimeter. Difference plots, C_p°(glass) − C_p°(crystals), show pronounced maxima at 30 K for $KAlSi_3O_8$, at 50 K for $NaAlSi_3O_8$, and at 35 K for $CaAl_2Si_2O_8$, similar to maxima previously observed for other inorganic glass-crystal pairs (*e.g.*, As_2O_3 and SiO_2). The entropy changes, $S_{298}^\circ - S_0^\circ$, for $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$ glasses and for anorthite based on our measurements are 224.3 ± 0.3, 213.8 ± 0.3, 198.7 ± 0.3, and 199.3 ± 0.3 J/(mol·K), respectively.

Approximate values for the zero-point entropies, S_0°, of $NaAlSi_3O_8$, $KAlSi_3O_8$ and $CaAl_2Si_2O_8$ glasses were calculated from our heat-capacity data combined with (1) the high-temperature $H_T^\circ - H_{298}^\circ$ data for these glasses and their crystals; (2) the low-temperature heat capacities of analbite and high sanidine; and (3) the enthalpy changes, obtained by HF(aq) solution calorimetry, for the transformation crystals → glass, ΔH_{323}°.

Our calculated values for the entropies of $KAlSi_3O_8$ glass, $NaAlSi_3O_8$ glass, and $CaAl_2Si_2O_8$ glass at zero Kelvin, that is, the residual or zero-point entropies, are 37.3 ± 2.5, 38.1 ± 1.5, and 38.6 ± 2.2 J/(mol·K), respectively. The entropies of fusion at the melting points of high sanidine, analbite, and anorthite are 33.8, 42.6, and 44.3 J/(mol·K), respectively. The Debye temperature, θ_D, of $CaAl_2Si_2O_8$ glass is 210 ± 10 K, and that of anorthite is 227 ± 15 K.

Introduction

As part of a continuing study of the thermodynamic properties of the feldspar-group minerals, we have used adiabatic calorimetry to measure the heat capacities of $KAlSi_3O_8$ and $NaAlSi_3O_8$ glass between 12 and 385 K and of $CaAl_2Si_2O_8$ glass and anorthite between 6 and 385 K to obtain their standard entropies. K. M. Krupka, R. A. Robie, and B. S. Hemingway (1977) have measured the heat capacities of these same samples of glass and of anorthite between 350 and 1000 K by differential scanning calorimetry.

White (1919) measured the heat contents, $H_T^\circ - H_{273.15}^\circ$, of anorthite and of the three feldspar glasses. The upper limit of White's measurements was 1373.2 K for $KAlSi_3O_8$ glass, 1173.2 K for $NaAlSi_3O_8$ glass, 973.2 K for $CaAl_2Si_2O_8$ glass, and 1673.2 K for anorthite. King (1957) measured the heat capacity of synthetic anorthite between 53.4 and 295.9 K. Ferrier's (1969b) measurements of $H_T^\circ - H_{298}^\circ$ for $CaAl_2Si_2O_8$ glass to 1500 K and of anorthite to 1800 K have an accuracy of about ± 2.0 percent.

Materials

The samples of $KAlSi_3O_8$ and $NaAlSi_3O_8$ glasses used for our heat-capacity measurements were prepared by the Corning Glass Company, Corning, New York. Chemical analyses of these glasses are given in Table 1.

$CaAl_2Si_2O_8$ glass was prepared by James Woodhead, Department of Geological and Geophysical Sciences, Princeton University, by direct fusion of a stoichiometric mixture of CaO, Al_2O_3 (Research Organic/Inorganic Chemical Corporation, reagents A-12 and Al-21), and SiO_2 glass (Spectrosil, Thermal American Fused Quartz Company) at 1850–1875 K for 2 hours in a platinum crucible. Anorthite crystals were prepared from a portion of the $CaAl_2Si_2O_8$ glass crushed to pass a 35-mesh sieve (0.42 mm). The material retained on a 150-mesh (0.104 mm) screen was divided into two separate batches and heated in platinum crucibles. The first batch was heated for 17 hours at 1375 K and then for 1 hour at 1675–1700 K and then was removed from the furnace to air-cool. The second batch was heated for 4½ hours at 1375 K

0003-004X/78/0102-0109$02.00

Table 1. Chemical analyses, in weight percent, of calorimetric samples of feldspar glasses

	1	2	3	4	5	6
SiO_2	64.76	64.75	68.74	66.89	43.19	42.09
Al_2O_3	18.32	18.03	19.44	20.71	36.65	37.05
Fe_2O_3		0.02		0.00		
Na_2O		0.07	11.82	12.41		
K_2O	16.92	16.52		0.00		
CaO				0.02	20.16	20.18
H_2O-		0.19				
H_2O+		0.59		0.15		
Total	100.00	100.17	100.00	100.18	100.00	99.32
Specific gravity at 25°C		2.378		2.395		

1. $KAlSi_3O_8$
2. $KAlSi_3O_8$ glass 95GQA[2] - Prepared by Corning Glass Co. Analyst J. J. Fahey, U.S. Geological Survey (70-WC-8).
3. $NaAlSi_3O_8$
4. $NaAlSi_3O_8$ glass X95GQB[1] - Prepared by Corning Glass Co. Analyst J. J. Fahey, U.S. Geological Survey (69-WC-8).
5. $CaAl_2Si_2O_8$
6. $CaAl_2Si_2O_8$ glass #75015 prepared by James Woodhead, Dept. of Geology, Princeton University. Microprobe analysis by Toby Wiggins, U.S. Geological Survey.

and for 1 hour at 1675–1700 K. The furnace was shut off and the sample was allowed to cool to room temperature for a period of 6 hours. The material that passed the 150-mesh screen was heated for 5 hours at 1375 K and for 1 hour at 1675–1700 K and was then removed from the furnace. The three batches were combined for the heat-capacity measurements.

The refractive indices (measured in white light) of the glasses were 1.487, 1.489, and 1.575 for $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$, respectively. These values agree well with the values of Schairer *et al.* (1956)—1.487, 1.489, and 1.575. The densities for $KAlSi_3O_8$ glass and $NaAlSi_3O_8$ glass, measured on powders by J. J. Fahey (for explanation of technique, see Fahey, 1961) of the U. S. Geological Survey, were 2.378 ± 0.003 and 2.395 ± 0.003 g/cm³, respectively. These values agree to within 0.9 percent with those given by Berman *et al.* (1942). The density of the $NaAlSi_3O_8$ glass was also determined from the volume and mass of a right-circular cylinder of the glass (1.8285 ± 0.0028 cm diameter by 0.9289 ± 0.0025 cm length, and 5.8164 ± 0.0003 g) to be 2.384 ± 0.004 g/cm³. The density of the $CaAl_2Si_2O_8$ glass was obtained by pycnometer at 23.4°C on coarse fragments of the glass as 2.69 ± 0.02 g/cm³.

Unit-cell parameters for this anorthite sample, measured by J. S. Huebner (U. S. Geological Survey) at 23.5°C using BaF_2 (a = 0.61971 ± 0.0001 nm) as an internal standard, were a = 0.8189 ± 0.0006 nm (1 nanometer = 10 angstroms), b = 1.2870 ± 0.0007 nm, c = 1.4167 ± 0.0007 nm, α = 93° 4.1′ ± 3.8′, β = 115° 50.9′ ± 4.1′, and γ = 91° 6.3′ ± 3.6′. The cell dimensions are in reasonable agreement with the values determined by Kroll [as reported by Smith (Table 7-6, p. 309, 1974)], on crystals grown at 1703 K for 3 hours.

The peaks on the diffractometer pattern for our anorthite are considerably broader than those from another synthetic anorthite (sample ANS-305, Stewart, 1967) used as a standard; the ANS-305 anorthite was crystallized from a glass at 1333 K for 2 hours at 10 kbars H_2O pressure. The large uncertainties in the refined cell parameters are a consequence of the broadened lines. Our anorthite was also examined by Gordon Nord of the U. S. Geological Survey using a 200-kV electron microscope. His examination showed that the individual grains were multiply twinned (albite law) and twin widths were between 3 and 20 nm. This is presumably the cause of the line broadening observed in the X-ray diffractometer pattern of our anorthite sample. From his electron-diffraction observations, Nord (written communication, 7/22/76) concluded that "short-range order is >20 nm for the Al–Si framework and less than 3 nm for positional ordering of calcium. The weak intensity seen in the type (b) reflections as compared to slowly grown anorthite suggests that Al/Si order is incomplete."

The samples of the glasses used in our heat-capacity measurements were in the form of shards 1–10 mm long. The $KAlSi_3O_8$ and $NaAlSi_3O_8$ glasses were heated at 775 K for 2 hours in a forced-air furnace and cooled in a desiccator over Drierite prior to being loaded into the calorimeter. Unpublished studies by J. J. Fahey have shown that this treatment is necessary to remove absorbed surface water.

Apparatus

The cryostat used in these studies has been described in detail by Robie and Hemingway (1972). The calorimeter and data acquisition system used for our measurements have been described by Robie *et al.* (1976).

After the measurements on $KAlSi_3O_8$ and

$NaAlSi_3O_8$ glass had been completed, the resistance of the platinum thermometer (Minco type S-1059, serial number 68) was measured at the normal boiling point of helium, 4.215 K, using a current of 0.004 amperes. The resistance at the boiling point of helium was 0.04725 ± 0.00005 ohms. The helium calibration point together with the resistance and dR/dT at 13.0 K from the earlier National Bureau of Standards calibration data on IPTS-68 (International Practical Temperature Scale of 1968) between 13 and 500 K were substituted into the equation given by McCrackin and Chang (1975) to generate a provisional resistance-temperature relation for the temperature range 3 to 13 K. The value of $R_{4.215}/R_{273.15}$ for our thermometer, 4.72×10^{-6}, is in the middle of the range of values considered acceptable by McCrackin and Chang. The value of $R_{373.15}/R_{273.15}$ for this thermometer calculated from the National Bureau of Standards' calibration data was 1.392617. On the basis of McCrackin and Chang's analysis, we believe that temperatures determined by our provisional calibration are accurate to ± 0.03 K between 4 and 13 K. Riddle, *et al.* (1973) gave 0.003 K as the maximum estimated uncertainty in the Bureau of Standards' calibration of a platinum resistance thermometer on the IPTS-68 (Comité Int. des Poids et Mes., 1969) between 13 and 505 K.

Table 2. Experimental specific heats of $KAlSi_3O_8$ glass

TEMP. K	SPECIFIC HEAT J/(G.K)	TEMP. K	SPECIFIC HEAT J/(G.K)
SERIES 1		SERIES 6	
302.68	.7588	184.20	.5405
311.62	.7717	191.50	.5566
319.36	.7826	198.65	.5722
326.71	.7925	205.87	.5876
334.21	.8022	213.15	.6028
341.74	.8115	220.42	.6176
SERIES 2		227.66	.6318
349.32	.8212	234.90	.6457
356.84	.8311	242.04	.6589
364.31	.8405	249.18	.6716
371.73	.8483	256.41	.6843
379.09	.8559	263.74	.6972
386.51	.8668	271.07	.7096
SERIES 3		SERIES 7	
54.66	.1609	266.43	.7017
58.66	.1755	273.84	.7141
63.45	.1924	281.16	.7264
69.28	.2125	288.50	.7378
76.08	.2357	295.96	.7488
83.65	.2611	303.44	.7597
91.69	.2874	310.74	.7700
SERIES 4		SERIES 8	
80.09	.2493	13.30	.01111
85.30	.2666	14.31	.01357
90.74	.2844	15.75	.01737
96.15	.3017	17.50	.02244
101.80	.3196	19.39	.02853
107.64	.3377	21.37	.03523
113.96	.3569	23.40	.04242
SERIES 5		25.52	.05020
113.80	.3564	27.77	.05858
120.70	.3768	30.28	.06814
127.74	.3970	33.06	.07910
135.38	.4181	36.56	.09247
143.52	.4401	40.40	.1070
151.80	.4618	44.92	.1240
159.59	.4818	51.04	.1469
166.94	.5000	56.78	.1684
174.11	.5172		
181.22	.5336		
188.36	.5497		
195.57	.5655		
202.83	.5811		

Table 3. Experimental specific heats of $NaAlSi_3O_8$ glass

TEMP. K	SPECIFIC HEAT J/(G.K)	TEMP. K	SPECIFIC HEAT J/(G.K)
SERIES 1		SERIES 4	
13.87	.00877	163.50	.5145
15.34	.01166	169.87	.5317
17.04	.01544	178.45	.5490
19.12	.02080	182.70	.5649
21.27	.02691	188.92	.5802
23.51	.03376	195.13	.5953
25.81	.04126	201.41	.6104
28.36	.04994	207.74	.6254
31.12	.05980	214.00	.6394
34.05	.07061	220.33	.6535
37.34	.08301	226.75	.6672
40.99	.09689	233.25	.6809
45.04	.1123	239.85	.6946
49.56	.1299	SERIES 5	
54.70	.1505	234.40	.6831
SERIES 2		240.68	.6960
54.34	.1495	247.12	.7088
59.92	.1712	253.60	.7213
65.58	.1927	260.15	.7337
71.41	.2147	266.63	.7459
77.34	.2369	273.00	.7579
83.28	.2589	279.38	.7692
SERIES 3		286.13	.7807
80.73	.2496	293.21	.7924
85.95	.2687	300.22	.8032
91.02	.2870	307.17	.8149
96.04	.3048	314.05	.8257
101.08	.3224	SERIES 6	
106.17	.3399	308.18	.8162
111.36	.3574	315.43	.8277
116.63	.3749	322.52	.8388
122.02	.3925	329.70	.8495
127.55	.4097	337.08	.8600
133.20	.4271	344.46	.8696
138.97	.4444	351.91	.8799
144.82	.4617	SERIES 7	
150.74	.4789	345.26	.8706
156.68	.4955	352.80	.8809
162.58	.5120	360.28	.8916
168.08	.5268	367.70	.9013
		375.07	.9099
		382.29	.9186

Experimental results

Our experimental data for the specific heats of $KAlSi_3O_8$ glass, $NaAlSi_3O_8$ glass, $CaAl_2Si_2O_8$ glass, and crystalline anorthite, in joules/(g·K), are listed in their chronological order of measurement in Tables 2 through 5, respectively. The molar heat capacities are shown graphically in Figures 1 through 4. The

Table 4. Experimental specific heats of $CaAl_2Si_2O_8$ glass

TEMP. K	SPECIFIC HEAT J/(G.K)	TEMP. K	SPECIFIC HEAT J/(G.K)
SERIES 1		SERIES 8	
306.28	.7682	163.88	.4726
312.30	.7777	169.10	.4868
318.44	.7871	174.34	.5009
324.75	.7960	179.70	.5147
331.07	.8064	185.19	.5284
337.32	.8152	190.75	.5424
343.52	.8233	196.30	.5558
SERIES 2		201.81	.5689
349.66	.8311	SERIES 9	
355.74	.8395	207.30	.5817
361.81	.8470	212.79	.5944
367.89	.8544	218.31	.6063
374.01	.8610	223.86	.6185
380.14	.8675	229.43	.6305
386.26	.8760	SERIES 10	
SERIES 3		221.50	.6135
53.41	.1084	227.34	.6239
59.44	.1301	233.34	.6374
SERIES 4		239.26	.6504
65.49	.1517	245.33	.6627
70.64	.1703	251.58	.6750
75.41	.1876	SERIES 11	
80.04	.2043	257.88	.6868
84.67	.2212	264.19	.6989
89.47	.2383	270.52	.7108
SERIES 5		276.96	.7222
94.55	.2559	283.43	.7334
99.92	.2746	289.82	.7440
105.50	.2937	296.14	.7541
111.00	.3123	302.38	.7642
116.26	.3297	SERIES 12	
SERIES 6		6.48	.000232
106.53	.2961	7.31	.000344
112.04	.3146	8.72	.000725
117.23	.3317	10.42	.001440
122.29	.3482	11.73	.002207
127.34	.3639	12.75	.002914
132.45	.3798	13.67	.00372
137.66	.3956	14.63	.00465
142.93	.4116	15.77	.00589
SERIES 7		17.32	.00785
148.14	.4267	19.06	.01045
153.25	.4426	21.28	.01432
158.28	.4569	23.71	.01907
163.27	.4708	25.98	.02406
168.27	.4841	28.71	.03032
173.29	.4975	31.77	.03840
		35.02	.04767
		38.55	.05819
		42.44	.07053
		46.78	.08458
		51.59	.10160

experimental data have been corrected for curvature but not for deviations from the stoichiometric compositions. The sample weights corrected for buoyancy used in these measurements were 34.036, 34.004, 39.709, and 38.130 g for $KAlSi_3O_8$ glass, $NaAlSi_3O_8$ glass, $CaAl_2Si_2O_8$ glass, and anorthite, respectively. The formula weights used in the calculations were based on the 1971 values for the atomic weights (Commission on Atomic Weights, 1972) and were 278.337, 262.224, and 278.210 g/mol for $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$, respectively. The temperatures are those of the International Practical Temperature Scale of 1968. The experimental data have an estimated uncertainty of ± 0.15 percent between 25 and 380 K, ± 1.0 percent at 15 K, and ± 5.0 percent at 6 K.

The experimental data for the potassium aluminosilicate glass were corrected for deviation from the exact composition $KAlSi_3O_8$ by assuming that 283.370 g of anhydrous glass consisted of 1 mole of

Table 5. Experimental specific heats of anorthite, $CaAl_2Si_2O_8$

TEMP. K	SPECIFIC HEAT J/(G.K)	TEMP. K	SPECIFIC HEAT J/(G.K)	TEMP. K	SPECIFIC HEAT J/(G.K)
SERIES 1		SERIES 6		SERIES 11	
302.00	.7662	61.10	.1366	300.59	.7637
307.68	.7756	66.04	.1549	307.14	.7737
313.31	.7843	71.20	.1739	313.68	.7840
318.98	.7927	76.59	.1938	320.25	.7941
324.77	.8009	81.86	.2132	326.81	.8035
330.82	.8097	SERIES 7		333.36	.8125
336.99	.8179	83.72	.2199	339.91	.8209
343.35	.8269	88.97	.2388	346.46	.8396
349.98	.8348	94.24	.2576	353.01	.8383
356.65	.8441	99.43	.2758	SERIES 12	
363.28	.8523	104.49	.2933	342.31	.8243
369.94	.8605	109.67	.3108	348.88	.8331
376.64	.8672	114.96	.3285	355.41	.8418
SERIES 2		SERIES 8		361.93	.8504
55.58	.1164	103.51	.2899	368.45	.8579
60.71	.1352	108.71	.3076	374.98	.8650
65.57	.1525	113.80	.3246	381.50	.8722
70.53	.1715	119.08	.3419		
75.74	.1908	124.36	.3589		
81.08	.2103	129.63	.3754		
86.46	.2300	134.93	.3917		
91.84	.2491	140.16	.4230		
97.27	.2684	145.42	.4230		
102.76	.2875	150.73	.4383		
SERIES 3		156.00	.4535		
303.29	.7678	161.24	.4682		
309.89	.7782	SERIES 9			
316.36	.7882	154.45	.4490		
SERIES 4		159.89	.4644		
55.07	.1144	165.31	.4793		
60.19	.1333	170.97	.4945		
65.24	.1519	176.86	.5101		
70.49	.1713	183.00	.5256		
75.99	.1912	189.37	.5415		
81.28	.2110	195.80	.5572		
SERIES 5		202.12	.5723		
7.31	.000158	208.34	.5865		
7.80	.000277	214.45	.6004		
8.31	.000402	220.56	.6141		
9.16	.000619	SERIES 10			
10.20	.000945	221.94	.6171		
11.18	.001369	228.11	.6304		
12.21	.001920	234.37	.6433		
13.27	.002568	240.64	.6559		
14.38	.003420	246.91	.6686		
15.57	.004402	253.36	.6812		
16.86	.005831	259.99	.6937		
21.83	.01313	273.19	.7181		
23.80	.01688	279.69	.7297		
26.00	.02156	286.21	.7408		
28.45	.02733	292.74	.7516		
31.09	.03422	299.21	.7615		
33.92	.04225	305.63	.7716		
37.10	.05186				
40.89	.06395				
45.38	.07902				
50.29	.09636				
55.64	.1162				

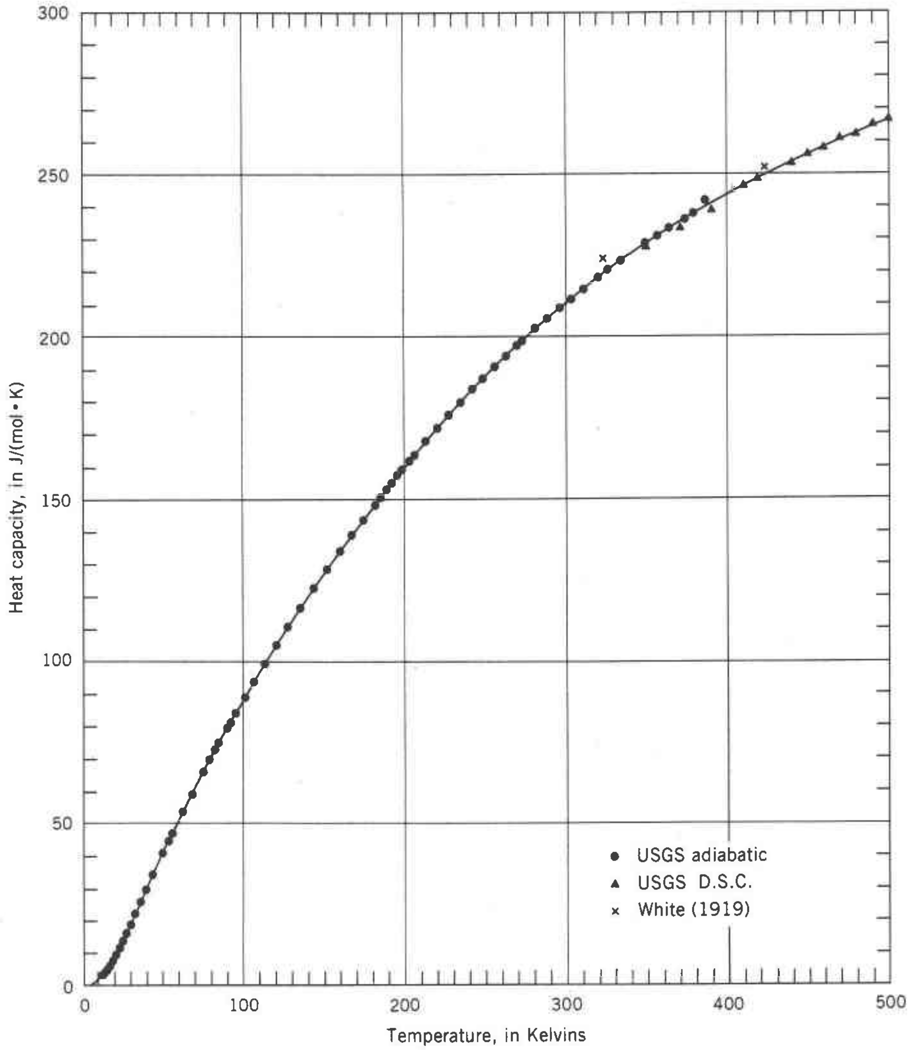

Fig. 1 Molar heat capacities of $KAlSi_3O_8$ glass between 13 and 500 K. Solid line is the least-squares fit to the U.S.G.S. data.

$KAlSi_3O_8$ (278.337 g), and 3.203 g of SiO_2 glass, 1.678 g of $NaAlSi_3O_8$ glass, 0.092 g of Al_2O_3 (corundum), and 0.056 g of Fe_2O_3 (hematite). The heat capacities of these fictive impurity phases were subtracted from the measured heat capacity for 283.370 g of sample to obtain the molar heat capacity of $KAlSi_3O_8$ glass. The correction to C_p° amounted to a maximum of 0.38 percent at 33 K, and was 0.15 percent at 100 K and 0.05 percent or less for all temperatures greater than 150 K. The difference between the calculated values for $S_{298}^\circ - S_0^\circ$ for the corrected and uncorrected C_p° values was less than 0.1 percent.

The experimental data for the sodium aluminosilicate glass were corrected for deviation from the formula $NaAlSi_3O_8$ by assuming that 269.550 g of anhydrous glass consisted of 1 mole of $NaAlSi_3O_8$ (262.224 g) and 6.500 g of $NaAlO_2$, 0.765 g of Al_2O_3 (corundum), and 0.056 g of CaO (lime). The correction to C_p° was a maximum of −0.6 percent at 30 K and decreased to 0.2 percent at 380 K. The difference between the values for $S_{298}^\circ - S_0^\circ$ calculated from the corrected and uncorrected C_p° data was 0.15 percent.

No corrections were applied to the data for either $CaAl_2Si_2O_8$ glass or to anorthite, inasmuch as the uncertainty of the analytical results (microprobe) and the deviations from the ideal formula are of comparable magnitude.

Thermodynamic properties of $KAlSi_3O_8$ glass, $NaAlSi_3O_8$ glass, $CaAl_2Si_2O_8$ glass, and of anorthite

Our measured data were extrapolated smoothly to zero Kelvin using a plot of C_p°/T versus T^2 (Fig. 5).

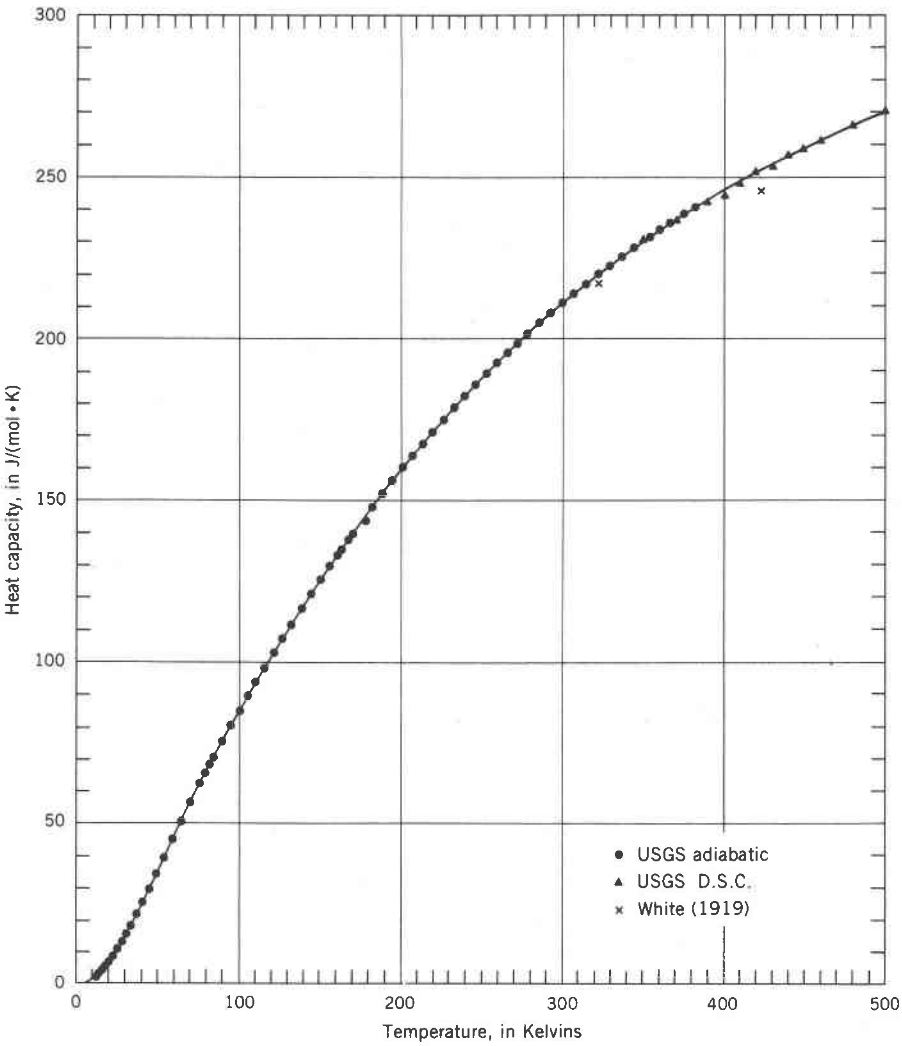

Fig. 2 Molar heat capacities of $NaAlSi_3O_8$ glass between 13 and 500 K. Solid line is the least-squares fit to the U.S.G.S. data.

The data were analytically smoothed using the methods outlined by Westrum *et al.* (1968). For $KAlSi_3O_8$ glass, the average deviation from the fitted curve, above 20 K, was 0.06 percent, and the maximum deviation was 0.39 percent (at 33 K). For $NaAlSi_3O_8$ glass, the average deviation was 0.05 percent and the maximum was 0.38 percent (at 50 K). For $CaAl_2Si_2O_8$ glass, the average and maximum deviations from the fitted curve above 20 K were 0.08 and 0.52 percent (at 29 K), respectively, and for anorthite, 0.04 and 0.35 percent (at 50 K), respectively.

For $KAlSi_3O_8$ glass and $NaAlSi_3O_8$ glass, the contributions to $S^\circ_{298} - S^\circ_0$ caused by the extrapolation of our measurements below 13.8 K were 1.3 and 0.8 J/(mol·K), respectively. For $CaAl_2Si_2O_8$ glass and anorthite the extrapolated portions of the entropies, below 7 K, were 0.02 and 0.01 J/(mol·K), respectively.

Smoothed values of the thermodynamic functions C°_P, $S^\circ_T - S^\circ_0$, $(H^\circ_T - H^\circ_0)/T$, and $(G^\circ_T - H^\circ_0)/T$ for $KAlSi_3O_8$ glass, $NaAlSi_3O_8$ glass, $CaAl_2Si_2O_8$ glass, and anorthite are listed at integral temperatures in Tables 6–9. At 298.15 K, the entropy change $S^\circ_{298} - S^\circ_0$ for the potassic, sodic, and calcic [feldspar] glasses, and anorthite are 224.3 ± 0.3, 213.8 ± 0.3, 198.7 ± 0.3, and 199.3 ± 0.3 J/(mol·K), respectively. For anorthite, S°_0 is zero, and accordingly $S^\circ_{298} = 199.3 \pm 0.3$ J/(mol·K). The values of the Gibbs energy function tabulated for the three glasses do not include the contribution arising from the zero-point entropies.

King (1957) measured the heat capacity of anorthite between 52.4 and 295.9 K. His sample (p. 5437) "was prepared by repeated sintering of a stoichiometric mixture of reagent-grade calcium carbonate, pure hydrated alumina and pure silica, with the usual intervening grinding, mixing, analysis, and adjustment of composition. Nine heats were made, totaling 58 hours at 1100°, 53 hours at 1200°, 6 hours at 1300°, and 10 hours at 1500°. A platinum container was used for the 1500° heats and Alundum for the others. The product analyzed 20.10 % lime, 36.63 % alumina, 43.02 % silica and 0.2 % ferric oxide." King's values differ from ours by no more than 0.3 percent over the common temperature range.

Our value for the entropy of anorthite at 298.15 K is 3.2 J/(mol·K) (1.6 percent) less than the value obtained by King (1957). The difference is almost entirely due to the extrapolation of King's data below 51 K, the lowest temperature for which he measured C_p°. From his measurements, King obtained $S_{298}^\circ - S_{51}^\circ$ = 187.2 J/(mol·K) and by extrapolation $S_{51}^\circ - S_0^\circ$ = 15.5 J/(mol·K). From our data we obtain $S_{298}^\circ - S_{51}^\circ$ = 187.3 in almost exact agreement with the *measured* part of King's result. He extrapolated his data to zero Kelvin using the method of comparison with a fictive standard substance, described by Kelley *et al.* (1953).

The fact that the molar heat capacity of $KAlSi_3O_8$ glass is very much larger than that of $CaAl_2Si_2O_8$ glass below 40 K, even though their formula weights are the same (within 0.05 percent) and both have the same number of atoms per mol., is most probably a consequence of the much lower density of $KAlSi_3O_8$ glass (2.378 g/cm^3) in contrast to $CaAl_2Si_2O_8$ glass (2.69 g/cm^3).

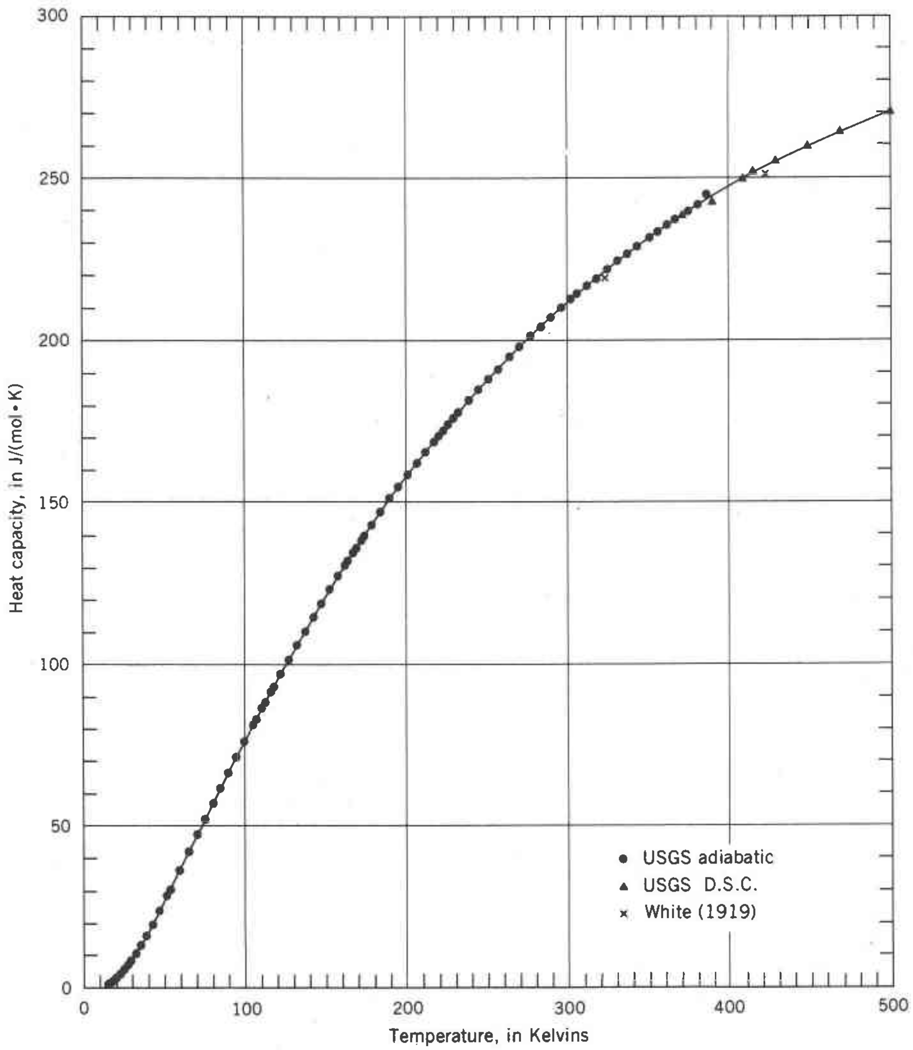

Fig. 3 Molar heat capacities of $CaAl_2Si_2O_8$ glass between 7 and 500 K. Solid line is the least-squares fit to the U.S.G.S. data.

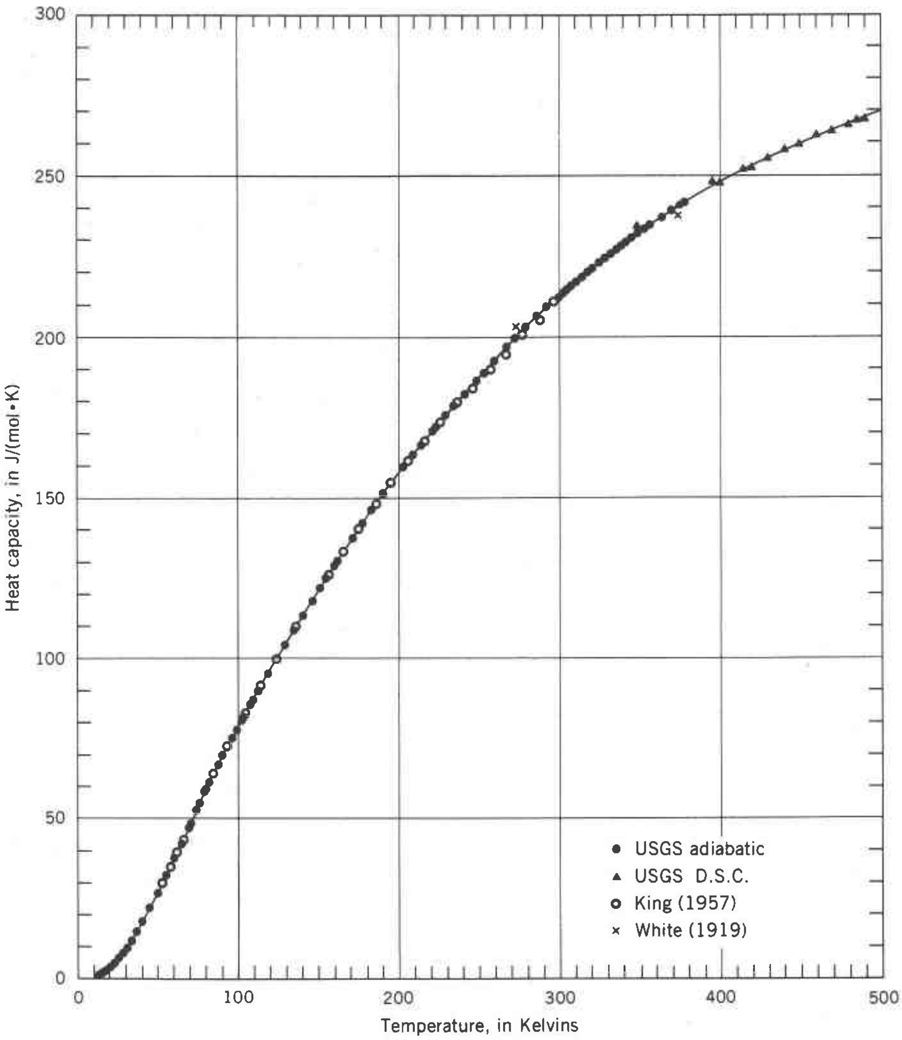

Fig. 4 Molar heat capacities of anorthite between 7 and 500 K. Solid line is the least-squares fit to the U.S.G.S. data.

The general relation that at temperatures below about 30 K the heat capacity of the low-density form is always greater than that of the high-density form is clearly evident in our results for $CaAl_2Si_2O_8$ glass (ρ = 2.69 g/cm^3) and anorthite (ρ = 2.758 g/cm^3). Similar differences are shown by the polymorphs of silica (Holm *et al.*, 1967) and silica glass (Westrum, E. F., Jr., written communication, August, 1957), and between As_2O_3 glass and claudetite and arsenolite (Chang and Bestul, 1971).

In Figure 6 we have plotted the difference, ΔC_P° in the smoothed values of the molar heat capacities of $KAlSi_3O_8$ (glass)–high sanidine, $NaAlSi_3O_8$ (glass)–analbite, and of $CaAl_2Si_2O_8$ (glass)–anorthite as a function of temperature. The data of Openshaw *et al.* (1976) were used for the heat capacity of high sanidine and analbite. This figure shows a marked peak in ΔC_P°. for $KAlSi_3O_8$ at 30 K, at 35 K for $CaAl_2Si_2O_8$, and at 50 K for $NaAlSi_3O_8$. The negative value of ΔC_P° for $CaAl_2Si_2O_8$ above 60 K is in sharp contrast to the positive increase of the ΔC_P° values for $KAlSi_3O_8$ and $NaAlSi_3O_8$ and for most other inorganic glasses. Guttman (1972) attributes the normal increase of ΔC_P° above the peak to the difference in the C_P°–C_V term. In this respect thermal-expansion measurements on $CaAl_2Si_2O_8$ glass and anorthite at temperatures between 50 and 300 K would be most useful.

The entropy difference, $S_{298}^\circ - S_0^\circ$, for $KAlSi_3O_8$ glass is greater than that for high sanidine by 10.2 J/(mol·K), and that of $NaAlSi_3O_8$ glass is greater than $S_{298}^\circ - S_0^\circ$ of analbite by 6.1 J/(mol·K). In contrast,

$S^\circ_{298} - S^\circ_0$ for anorthite exceeds that of $CaAl_2Si_2O_8$ glass by only 0.6 J/(mol·K).

Zero-point entropies of the feldspar glasses

In order to calculate the Gibbs free energies of formation of $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$ glasses from the relation

$$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ \quad (1)$$

we need to know both the enthalpy and entropy of formation of the specific glass from the elements. From our measurements of the heat capacities of the three [feldspar] glasses (extrapolated to zero Kelvin) one cannot calculate their absolute entropies but only the change in the entropy $S^\circ_T - S^\circ_0$. This is because S°_0 is not zero for a glass (Gibson and Giauque, 1923). One way of determining S°_0 for a glass is to measure the heat capacities of both the glass and its crystalline equivalent between approximately zero Kelvin and the melting temperature, T_M, and also to measure the enthalpy of melting, ΔH°_M of the crystal, keeping in mind that the glass changes to a liquid without a change in enthalpy. At T_M, the Gibbs free energies of the liquid and crystal are equal and equation (1) reduces to

$$\Delta H^\circ_M = T_M \Delta S^\circ_M \quad (2)$$

Unfortunately, the enthalpies of melting of the feldspars cannot be measured directly in a calorimeter for the following reasons:

(a) $NaAlSi_3O_8$ (monalbite) readily superheats above its equilibrium melting point, 1391 K.

(b) $KAlSi_3O_8$ (high sanidine) melts incongruently at one bar pressure (10^5Pa) to $KAlSi_2O_6$ (leucite) plus a silica-rich liquid.

(c) The melting point of $CaAl_2Si_2O_8$ (anorthite) is 1830 K and exceeds the normal maximum oper-

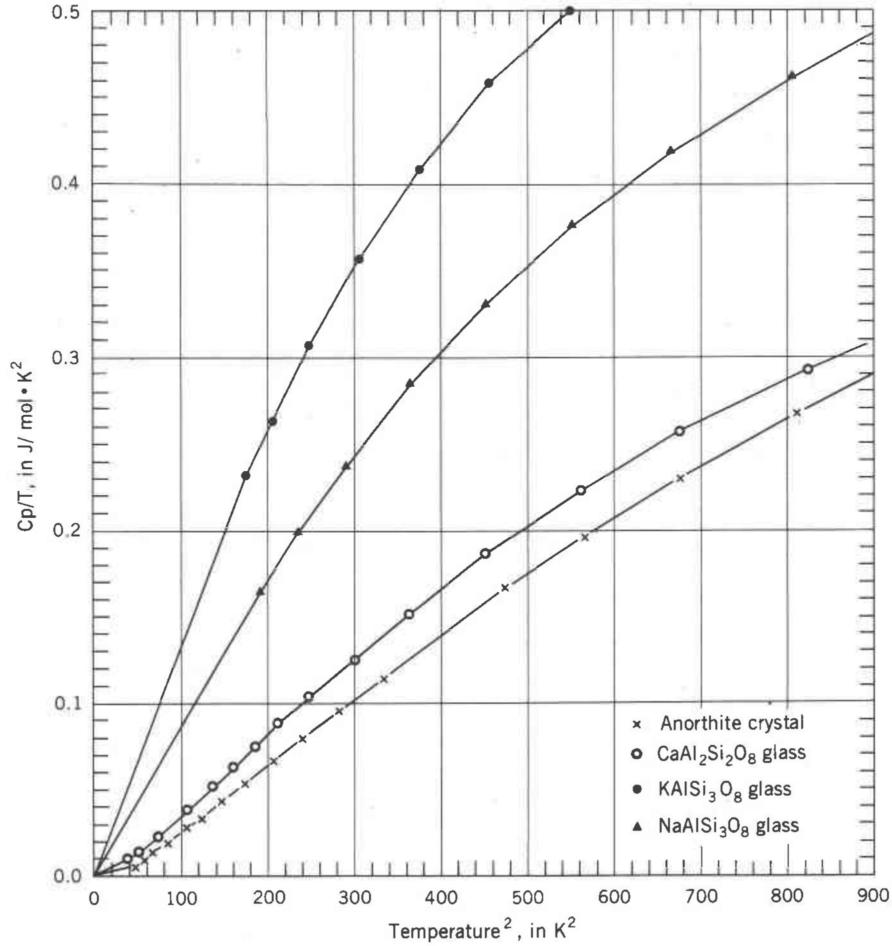

Fig. 5 Extrapolation of the molar heat capacities of $KAlSi_3O_8$ glass, $NaAlSi_3O_8$ glass, $CaAl_2Si_2O_8$ glass, and anorthite to zero Kelvin.

Table 6. Molar thermodynamic properties of $KAlSi_3O_8$ glass, formula weight = 278.337

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p	(S_T-S_0)	$(H_T-H_0)/T$	$-(G_T-H_0)/T$
KELVIN	J/(MOL.K)			
5	0.183	0.058	0.043	0.015
10	1.40	0.468	0.350	0.118
15	4.27	1.518	1.128	0.390
20	8.51	3.289	2.410	0.879
25	13.45	5.709	4.115	1.594
30	18.66	8.619	6.102	2.517
35	24.10	11.91	8.291	3.619
40	29.27	15.48	10.60	4.876
45	34.81	19.26	13.00	6.263
50	40.07	23.20	15.44	7.758
60	50.27	31.41	20.40	11.01
70	60.04	39.90	25.37	14.53
80	69.47	48.54	30.30	18.24
90	78.65	57.25	35.16	22.09
100	87.56	66.00	39.96	26.04
110	96.16	74.75	44.68	30.07
120	104.4	83.48	49.32	34.16
130	112.4	92.15	53.86	38.29
140	120.0	100.8	58.32	42.44
150	127.4	109.3	62.68	46.62
160	134.5	117.7	66.95	50.80
170	141.3	126.1	71.12	54.98
180	147.8	134.4	75.20	59.16
190	154.1	142.5	79.19	63.34
200	160.1	150.6	83.08	67.50
210	166.0	158.5	86.89	71.64
220	171.7	166.4	90.62	75.77
230	177.1	174.1	94.26	79.88
240	182.4	181.8	97.82	83.97
250	187.4	189.3	101.3	88.03
260	192.3	196.8	104.7	92.07
270	197.0	204.1	108.0	96.09
280	201.6	211.4	111.3	100.1
290	205.9	218.5	114.5	104.0
300	210.1	225.6	117.6	108.0
310	214.1	232.5	120.7	111.9
320	218.0	239.4	123.6	115.8
330	221.7	246.2	126.6	119.6
340	225.3	252.8	129.4	123.4
350	228.8	259.4	132.2	127.2
360	232.3	265.9	134.9	131.0
370	235.7	272.3	137.6	134.7
380	238.4	278.6	140.2	138.4
273.15	198.5	206.4	109.1	97.35
298.15	209.4	224.3	117.0	107.2

ating temperature of all but a few drop calorimeters.

(d) The liquids of all three compositions quench to glasses, and the use of the drop calorimetric technique is thus not possible.

The reluctance of $NaAlSi_3O_8$ and $KAlSi_3O_8$ glasses (in the absence of H_2O) to crystallize even at temperatures near their melting points, however, makes it possible to measure the heat contents of the metastable glasses to near T_M by standard drop calorimetry. By combining the $H^\circ_T - H^\circ_{298}$ data (from drop calorimetry) with low-temperature heat capacities, one can determine the entropy change $S^\circ_{T_M} - S^\circ_0$ for both crystals and glass.

Although we cannot measure the enthalpy of melting of the feldspars directly, we can determine ΔH°_M indirectly by combining measurements of the enthalpies of solution of both crystal and glass [measured by either HF solution calorimetry (Waldbaum and Robie, 1971) or fused salt calorimetry (Holm and Kleppa, 1968)], with high-temperature heat-capacity data and using the relation

$$\Delta H^\circ_{T_M} = \Delta H^\circ_T + \int_T^{T_M} \Delta C^\circ_P dT \qquad (3)$$

Waldbaum (1968) used this method to obtain the enthalpies of melting of high sanidine and analbite. Although the stable phase of $NaAlSi_3O_8$ above 1253 K is monalbite (Smith, 1974), no data are available

Table 7. Molar thermodynamic properties of $NaAlSi_3O_8$ glass, formula weight = 262.224

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p	(S_T-S_0)	$(H_T-H_0)/T$	$-(G_T-H_0)/T$
KELVIN	J/(MOL.K)			
5	0.111	0.033	0.025	0.008
10	0.877	0.287	0.216	0.071
15	2.88	0.969	0.727	0.242
20	6.10	2.214	1.643	0.571
25	10.11	3.996	2.925	1.071
30	14.62	6.232	4.493	1.739
35	19.36	8.840	6.277	2.563
40	24.29	11.75	8.219	3.527
45	29.34	14.90	10.28	4.613
50	34.45	18.25	12.45	5.808
60	45.09	25.51	17.04	8.476
70	55.11	33.22	21.76	11.46
80	64.87	41.22	26.54	14.67
90	74.39	49.41	31.33	18.08
100	83.63	57.73	36.10	21.62
110	92.53	66.12	40.83	25.29
120	101.1	74.54	45.50	29.04
130	109.3	82.95	50.09	32.86
140	117.2	91.34	54.60	36.74
150	124.7	99.69	59.02	40.66
160	132.0	108.0	63.36	44.61
170	139.1	116.2	67.61	48.58
180	145.9	124.3	71.77	52.56
190	152.4	132.4	75.84	56.55
200	158.7	140.4	79.83	60.54
210	164.8	148.3	83.73	64.53
220	170.6	156.1	87.55	68.52
230	176.2	163.8	91.28	72.49
240	181.5	171.4	94.93	76.45
250	186.8	178.9	98.50	80.40
260	191.8	186.3	102.0	84.33
270	196.7	193.7	105.4	88.25
280	201.3	200.9	108.8	92.14
290	205.8	208.0	112.0	96.01
300	210.1	215.1	115.2	99.87
310	214.3	222.0	118.3	103.7
320	218.4	228.9	121.4	107.5
330	222.3	235.7	124.4	111.3
340	226.0	242.4	127.3	115.0
350	229.5	249.0	130.2	118.8
360	233.2	255.5	133.0	122.5
370	236.7	261.9	135.8	126.2
380	239.4	268.3	138.5	129.8
273.15	198.2	195.9	106.5	89.47
298.15	209.3	213.8	114.6	99.15

Table 8. Molar thermodynamic properties of $CaAl_2Si_2O_8$ glass, formula weight = 278.210

TEMP. T KELVIN	HEAT CAPACITY C_p J/(MOL.K)	ENTROPY (S_T-S_0) J/(MOL.K)	ENTHALPY FUNCTION $(H_T-H_0)/T$ J/(MOL.K)	GIBBS ENERGY FUNCTION $-(G_T-H_0)/T$ J/(MOL.K)
5	0.255	0.008	0.006	0.002
10	0.333	0.088	0.068	0.020
15	1.401	0.397	0.321	0.086
20	3.346	1.042	0.803	0.239
25	6.442	2.069	1.572	0.497
30	9.386	3.460	2.590	0.870
35	13.20	5.188	3.828	1.360
40	17.43	7.222	5.260	1.962
45	21.97	9.534	6.861	2.673
50	26.74	12.09	8.609	3.485
60	36.68	17.84	12.45	5.384
70	46.77	24.25	16.64	7.615
80	56.83	31.15	21.03	10.12
90	66.77	38.42	25.56	12.86
100	76.46	45.96	30.17	15.79
110	85.82	53.69	34.81	18.88
120	94.83	61.55	39.44	22.11
130	103.6	69.48	44.03	25.45
140	112.1	77.47	48.59	28.88
150	120.3	85.48	53.10	32.39
160	128.4	93.51	57.55	35.96
170	136.1	101.5	61.95	39.58
180	143.4	109.5	66.27	43.24
190	150.4	117.5	70.52	46.94
200	157.1	125.3	74.68	50.66
210	163.5	133.2	78.76	54.40
220	169.7	140.9	82.75	58.16
230	175.6	148.6	86.66	61.92
240	181.3	156.2	90.49	65.69
250	186.8	163.7	94.23	69.46
260	192.2	171.1	97.89	73.23
270	197.5	178.5	101.5	76.99
280	202.5	185.8	105.0	80.75
290	207.1	192.9	108.4	84.49
300	211.4	200.0	111.8	88.23
310	215.5	207.0	115.1	91.95
320	219.6	213.9	118.3	95.65
330	223.8	220.8	121.4	99.34
340	227.8	227.5	124.5	103.0
350	231.5	234.2	127.5	106.7
360	235.0	240.7	130.4	110.3
370	238.4	247.2	133.3	113.9
273.15	199.1	180.8	102.6	78.18
298.15	210.6	198.7	111.2	87.54

for the enthalpy of transition of analbite to monalbite, and we have, therefore, assumed that it is zero in our calculations.

We have reevaluated the enthalpies of melting of sanidine and analbite (assumed to be the same as for monalbite), using the data of Waldbaum and Robie (1971) for the differences in enthalpies between the glasses and crystals at 323 K (obtained by HF solution calorimetry) and the recent measurements of C_P^o at high temperatures by K. M. Krupka, R. A. Robie, and B. S. Hemingway (1977, unpublished data) for the feldspar glasses, anorthite, high sanidine, and analbite. Krupka, Robie, and Hemingway have prepared tables (1977, unpublished data) of the thermodynamic functions for the three feldspar-composition glasses and for sanidine, analbite, and anorthite; the tables combine their measurements of C_P^o for temperatures between 350 and 1000 K (obtained by differential scanning calorimetry), with those of Openshaw *et al.* (1976), and the results of the present investigation, as well as the heat-content data of White (1919), Kelley *et al.* (1953), and Ferrier (1969b). From the above data, we obtain 49800 ± 3000 J/mol at 1473 K and 59280 ± 2000 J/mol at 1391 K for the enthalpies of fusion of high sanidine and analbite, respectively. Kracek and Neuvonen (1952) used HF solution calorimetry to obtain 71800 J/mol for the difference in enthalpy of $CaAl_2Si_2O_8$ glass and anorthite at 298 K. Yoder (1975) has reported unpublished data of O. J. Kleppa and T. V.

Table 9. Molar thermodynamic properties of anorthite, $CaAl_2Si_2O_8$, formula weight = 278.210

TEMP. T KELVIN	HEAT CAPACITY C_p J/(MOL.K)	ENTROPY (S_T-S_0) J/(MOL.K)	ENTHALPY FUNCTION $(H_T-H_0)/T$ J/(MOL.K)	GIBBS ENERGY FUNCTION $-(G_T-H_0)/T$ J/(MOL.K)
5	0.009	0.002	0.002	0.001
10	0.248	0.052	0.043	0.009
15	1.105	0.288	0.239	0.049
20	2.802	0.815	0.642	0.173
25	5.388	1.702	1.318	0.384
30	8.71	2.969	2.265	0.705
35	12.62	4.599	3.458	1.141
40	16.98	6.564	4.871	1.692
45	21.68	8.832	6.475	2.357
50	26.61	11.37	8.240	3.130
60	36.85	17.12	12.15	4.971
70	47.19	23.58	16.42	7.161
80	57.41	30.55	20.91	9.645
90	67.47	37.90	25.52	12.37
100	77.29	45.51	30.21	15.30
110	86.81	53.33	34.93	18.40
120	95.96	61.28	39.63	21.65
130	104.7	69.31	44.31	25.00
140	113.2	77.38	48.93	28.46
150	121.4	85.48	53.49	31.99
160	129.3	93.56	57.98	35.58
170	136.9	101.6	62.40	39.23
180	144.1	109.7	66.74	42.92
190	151.1	117.6	71.00	46.64
200	157.8	125.6	75.17	50.39
210	164.3	133.4	79.26	54.16
220	170.5	141.2	83.27	57.94
230	176.5	148.9	87.19	61.73
240	182.2	156.5	91.03	65.52
250	187.7	164.1	94.78	69.31
260	193.0	171.6	98.46	73.10
270	198.2	178.9	102.1	76.88
280	203.1	186.2	105.6	80.66
290	207.8	193.5	109.0	84.43
300	212.2	200.6	112.4	88.18
310	216.6	207.6	115.7	91.92
320	220.9	214.5	118.9	95.64
330	224.9	221.4	122.1	99.35
340	228.5	228.2	125.1	103.0
350	232.2	234.9	128.1	106.7
360	236.0	241.4	131.1	110.4
370	239.3	248.0	134.0	114.0
273.15	199.8	181.3	103.2	78.07
298.15	211.4	199.3	111.8	87.49

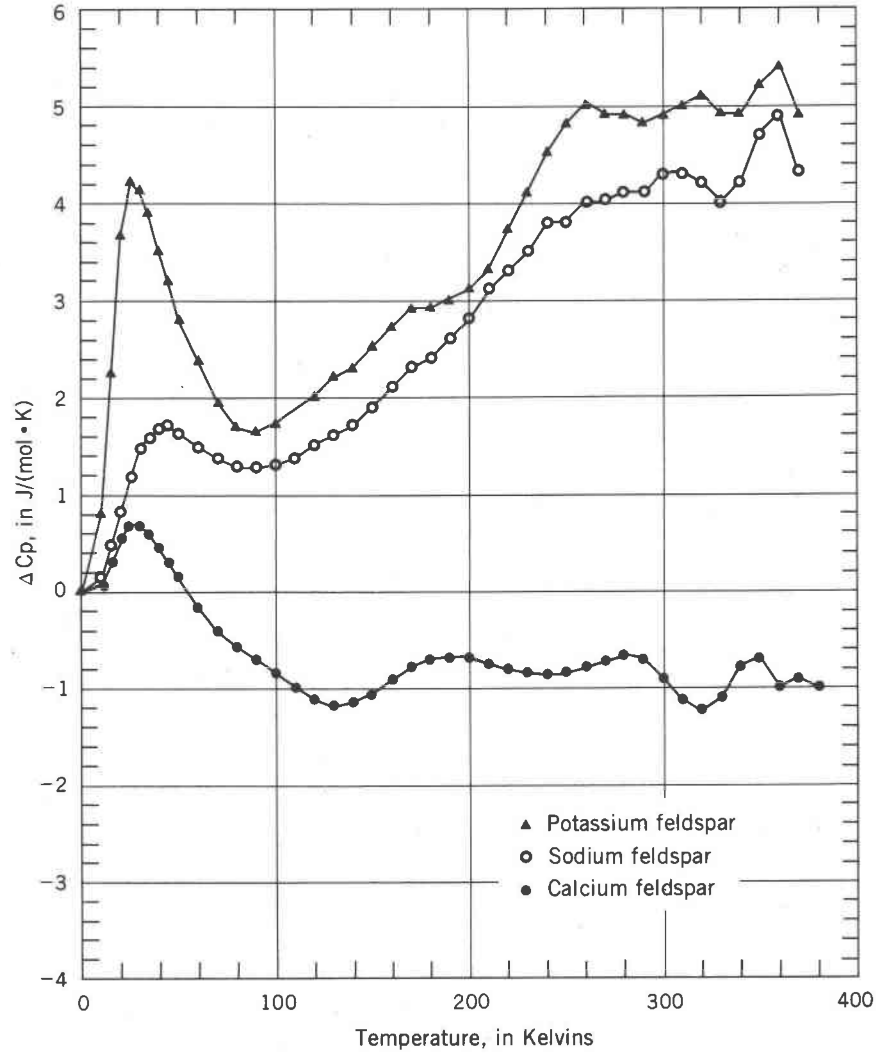

Fig. 6 The difference, ΔC_P°, between the molar heat capacities of $KAlSi_3O_8$ (glass)–high sanidine, $NaAlSi_3O_8$ (glass)–analbite, and $CaAl_2Si_2O_8$ (glass)–anorthite as a function of temperature.

Charlu of the enthalpies of solution of $CaAl_2Si_2O_8$ glass and anorthite in molten $2PbO \cdot B_2O_3$ at 973 K that lead to $\Delta H^\circ_{M,973}$ of 78240 J/mol.

Ferrier (1969a) measured the enthalpy difference by solution calorimetry in HF–HCl at 353 K and corrected this value to the melting point, using his heat-content data (1969b) to obtain 167000 J/mol for the enthalpy of fusion at the melting point of anorthite.

We believe that Ferrier's (1969a) value for $\Delta H^\circ_{M,1830}$ of anorthite is incorrect. We also feel that, until the details of Kleppa and Charlu's measurements are more fully reported, it is best to use the value of $\Delta H^\circ_{M,298}$ for anorthite obtained by Kracek and Neuvonen (1952) for our calculations. The correction of Kracek and Neuvonen's value from 298 to 1830 K was made using the heat-capacity values of anorthite and $CaAl_2Si_2O_8$ glass tabulated by Krupka *et al.* (1977). The difference in the heat contents of the glass minus that of the crystals, $\Delta(H_T - H_{298})$, was plotted as a function of temperature and was extrapolated smoothly to the melting point of anorthite, 1830 K. The resultant value for $\Delta H^\circ_{M,1830}$ is 81000 ± 2500 J/mol, which corresponds to an entropy of melting of 44.3 ± 1.4 J/(mol·K).

The zero-point entropies of the three [feldspar] glasses were calculated from the values of $S^\circ_{T_M} - S^\circ_0$ for the glasses and for high sanidine, analbite, and anorthite, together with the enthalpies of melting of the crystal phases using the relation:

$$[(S^\circ_{T_M} - S^\circ_0)_{\text{crystal}} + H^\circ_M/T_M] - (S^\circ_{T_M} - S^\circ_0)_{\text{glass}} = S^\circ_{0,\text{ glass}} - S^\circ_{0,\text{ crystal}} \quad (4)$$

The data used to calculate S°_0 for the $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$ glasses are summarized in Table 10. For anorthite $S^\circ_0 \equiv 0$, and for high sanidine and analbite, we have adopted the ideal configurational value 18.70 J/(mol·K), given by Holm and Kleppa (1968).

The principal source of the uncertainty in the calculated values of the zero-point entropies is the extrapolation of the heat capacities of the glasses above the glass transition temperature, T_g. At T_g the heat capacity of a glass changes slope. On the basis of thermal expansion measurements, Arndt and Haberle (1973) give 1086 and 1036 K as the glass transition temperatures for $CaAl_2Si_2O_8$ glass and $NaAlSi_3O_8$ glass. Vergano *et al.* (1967) obtained 1088 and 1213 K for T_g of $NaAlSi_3O_8$ glass and $KAlSi_3O_8$ glass also from thermal-expansion studies. Thus our extrapolation of C°_P for $KAlSi_3O_8$ glass and $NaAlSi_3O_8$ glass to T_M contains an unknown error, inasmuch as the heat-content data (upper limit 1373 and 1173 K, respectively) include only a single measurement of $H_T - H_{298}$ above T_g. The extrapolation of C°_P for $CaAl_2Si_2O_8$ glass is quite long and may introduce an uncertainty in ΔH°_M of $\pm$ 2.5 kilojoules (*i.e.*, 1.4 J/(mol·K) in ΔS°_M).

In our calculation of the zero-point entropy we have assumed that anorthite retains its ordered Al/Si distribution up to the melting point, 1830 K. There is, however, some evidence (Smith, p. 540, 1974) that the aluminum and silicon atoms become partially randomized over the tetrahedral positions in the $Al_2Si_2O_8$ framework of anorthite at temperatures above 1525 K. The extent of this disorder is not presently known, and accordingly we have not included this effect in our calculation of S°_0.

If we assume that, at the melting point, equilibrium anorthite is totally disordered with respect to the Al/Si occupancy of the tetrahedral positions, and furthermore that our extrapolation of C°_P for anorthite does not include any contribution due to this disorder, then our calculated value for S°_{1830} for anorthite would be too small by 23.05 J/(mol·K), and therefore our value for S°_0 for $CaAl_2Si_2O_8$ glass would also be too small by this amount.

If, however, anorthite is only partially disordered, the entropy contribution due to disorder would be much less. Until the exact structure of anorthite at a temperature near the melting point is known, we believe it best to assume that Al and Si are ordered. Thus, our value for S°_0 of $CaAl_2Si_2O_8$ glass represents the minimum possible value for S°_0 and can be (though we consider it unlikely) too small by a maximum of 23.05 J/(mol·K). Although our anorthite sample is probably somewhat disordered, we believe, on the basis of a comparison with data for the alkali feldspars, that this would have a trivial effect on our

Table 10. Thermodynamic values used to calculate the residual entropies of feldspar glasses

Formula	Name	T_M kelvins	$S^\circ_{T_M} - S^\circ_0$ J/(mol·K)	ΔH°_M J/mol	ΔS°_M J/(mol·K)	S°_0 J/(mol·K)	S°_{298} J/(mol·K)
$KAlSi_3O_8$	high sanidine	1473*	660.9	49800	33.8	18.7	-
$KAlSi_3O_8$	glass	-	676.1	-	-	37.3	261.6
$NaAlSi_3O_8$	analbite	1391	636.2	59280	42.6	18.7	-
$NaAlSi_3O_8$	glass	-	659.4	-	-	38.1	251.9
$CaAl_2Si_2O_8$	anorthite	1830	739.0	81000	44.3	0.0	-
$CaAl_2Si_2O_8$	glass	-	744.7	-	-	38.6	237.3

*Estimated congruent melting temperature at 1 atmosphere, (see Waldbaum, 1968) derived value for the entropy of anorthite. Openshaw *et al.* (1976) have shown that the difference between the Al/Si ordered and disordered polymorphs of the Na and K feldspars leads to a difference in C_P° below 300 K of less than 0.3 percent and of less than 0.1 percent in $S^\circ_{298} - S^\circ_0$.

Values for the various thermodynamic quantities used to calculate the entropies for the feldspar glasses at zero Kelvin (S°_0) are listed in Table 10. At zero Kelvin S°_0 for $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$ glass are 37.3 ± 2.5, 38.1 ± 1.5, and 38.6 ± 2.2 J/(mol·K), respectively. At 298.15 K, the absolute entropies for $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$ glass are 261.6 ± 2.8, 251.9 ± 1.8, and 237.3 ± 2.5 J/(mol·K), respectively, and are the appropriate values of S°_{298} to be used in thermodynamic calculations. The largest part of the uncertainties assigned to these values for the absolute entropies is due to the extrapolation of the heat capacities of the glasses to the melting point and the consequent uncertainty in the entropy of melting. Our values for the absolute entropies were combined with the $\Delta H^\circ_{f,298}$ data given by Hemingway and Robie (1977), and were used to calculate the Gibbs free energies of formation, $\Delta G^\circ_{f,298}$, for the three feldspar glasses. The Gibbs free energies of formation are −3703500 ± 3500, −3665325 ± 3720, and −3956800 ± 4000 J/mol for $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAlSi_2O_8$ glasses, respectively.

We have calculated the Debye temperature, θ_D, of $CaAl_2Si_2O_8$ glass and of anorthite from our heat capacity measurements using the relation

$$C_V = \frac{12}{5}\pi^4 RT^3/\theta^3 \quad (5)$$

Values of θ_D calculated from our measurements between 6.5 and 12.7 K were extrapolated smoothly to zero Kelvin, using the assumption that equation (5) is exact for temperatures less than approximately θ_D/50. The data point for anorthite at 7.8 K is undoubtedly too low by at least 5 percent. We have not calculated the Debye temperatures of the alkali feldspar glasses because our heat capacity data do not extend to sufficiently low temperatures to provide a satisfactory extrapolation of θ_D to zero Kelvin.

Acknowledgments

We thank our U. S. Geological Survey colleagues D. B. Stewart, for providing us with the samples and analyses of $KAlSi_3O_8$ glass and $NaAlSi_3O_8$ glass, and J. S. Huebner, for determining the unit-cell parameters of the calorimetric sample of anorthite. We are particularly grateful to Gordon Nord for examining our anorthite by electron microscopy and for several enlightening discussions concerning aluminum/silicon disorder in plagioclase feldspars. We are also most grateful to James Woodhead, Princeton University, for preparing the sample of $CaAl_2Si_2O_8$ glass used for our measurements and for determining its refractive index.

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Manuscript received, February 28, 1977; accepted for publication, August 2, 1977.