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Thermodynamic Properties of Potassium Metasilicate and Disilicate

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
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THERMODYNAMIC PROPERTIES OF POTASSIUM METASILICATE AND DISILICATE

by

R. P. Beyer,[1] M. J. Ferrante,[2] R. R. Brown,[2] and G. E. Daut[3]

ABSTRACT

The Bureau of Mines has measured the low-temperature heat capacities and high-temperature enthalpies of crystalline $K_2Si_2O_5$ as part of a program for advancing mineral resources technology with energy economy. High-temperature enthalpies of glassy and liquid $K_2Si_2O_5$ and crystalline K_2SiO_3 were also measured. An adiabatic calorimeter operating over the range 5 to 308 K was used for the heat capacity measurements for $K_2Si_2O_5$ from which the standard entropy at 298.15 K, S°_{298} = 45.55 ±0.05 cal/deg-mole, was calculated. Tabulated values of C_p°, S°, $-(G^\circ - H_0^\circ)/T$, and $H^\circ - H_0^\circ$ from 5 to 300 K are given for $K_2Si_2O_5$. A copper-block drop calorimeter was used in the enthalpy measurements, operating from 298.15 to 1,198 K for K_2SiO_3 and from 298.15 to 1,453.8 K for $K_2Si_2O_5$. No transitions were found for K_2SiO_3. The $K_2Si_2O_5$ showed two reversible first-order transitions, one at 510 K with a heat of transition of 0.29 kcal/mole and one at 867 K with a heat of transition of 0.38 kcal/mole. The heat of fusion for $K_2Si_2O_5$ was calculated to be 8.42 kcal/mole. Relative enthalpies are given in equation form, and high-temperature values are tabulated for C_p°, S°, $-(G^\circ - H^\circ_{298})/T$, and $H^\circ - H^\circ_{298}$. Also tabulated are ΔH°, ΔG°, and log K for formation of K_2SiO_3 and $K_2Si_2O_5$ from both the elements and the oxides.

INTRODUCTION

Two goals of the Bureau of Mines, U.S. Department of the Interior, are to minimize the environmental conflicts and to reduce the energy requirements for mining and mineral processing operations. An essential part of this effort involves the thermodynamic investigation of compounds of mineral and metallurgical interest, such as the potassium silicates. These silicates are found in widespread use in the ceramics industry, and a better understanding of their thermodynamic properties could help improve processing technology. Another benefit of improved knowledge of silicate thermodynamics is a better understanding of the formation of corrosive materials in magnetohydrodynamic power generators.

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In this investigation, the low-temperature heat capacities of crystalline potassium disilicate ($K_2Si_2O_5$) were measured with an adiabatic calorimeter over the range 5 to 308 K. A copper-block drop calorimeter was used to determine the high-temperature enthalpies of crystalline, glassy, and liquid potassium disilicate and crystalline potassium metasilicate (K_2SiO_3). Data from the literature were combined with these experimental data to calculate thermodynamic properties over a wide temperature range. The enthalpies and Gibbs energies of formation and equilibrium constant logarithms for the formation reactions from both the elements and the oxides were calculated.

No low-temperature data for $K_2Si_2O_5$ (crystal) or high-temperature data for K_2SiO_3 (crystal) were found in the literature. High-temperature enthalpies of $K_2Si_2O_5$ have been measured by others (22-23)[4], but by methods inherently less accurate than the method used in this investigation.

MATERIALS

K_2SiO_3, Crystalline

Crystalline potassium metasilicate, K_2SiO_3, was synthesized by reacting a mixture of reagent-grade potassium carbonate and silicic acid containing stoichiometric quantities of K_2O and SiO_2. The reaction was initiated by heating the mixture in a platinum dish at 980 K for 48 hours. Observed weight loss indicated incomplete reaction, so the sample was ground and blended in an argon atmosphere box and then reheated at 1,120 K for 3.5 hours and at 1,270 K for 19.5 hours. Analysis of the sample at this point showed a potassium deficiency, so an appropriate amount of potassium carbonate was added to the sample and the mixture was reheated at 1,070 K for 74 hours and then at 1,200 K for 2 hours.

Analysis of this material indicated a SiO_2 content of 38.87 pct compared to the theoretical 38.94 pct for stoichiometric K_2SiO_3. Since no X-ray powder diffraction pattern was available for K_2SiO_3(c), two portions were heated, one at 1,070 K and the other at 1,170 K, for 4 more hours and checked for changes in their diffraction pattern. X-ray analysis showed patterns for both portions to be the same, with no evidence of starting materials or their decomposition products. To insure complete recrystallization, a final heat treatment was made, first at 1,240 K for 24 hours, then at 1,120 K for 7 days.

Petrographic examination indicated the material to be crystalline and single phase. The index of refraction was determined to be approximately 1.52, which agrees with the data of Kracek (13). Chemical analysis by conversion of the K_2SiO_3 to K_2SiF_6, the method used by Morey (15), indicated the K_2SiO_3 to be essentially stoichiometric, 99.94 pct K_2SiO_3. Optical emission spectrographic analysis showed a total of 200 ppm impurities of copper, nickel, and titanium.

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

$K_2Si_2O_5$, Crystalline

Crystalline potassium disilicate was also prepared by reacting a mixture of reagent-grade potassium carbonate and silicic acid containing stoichiometric quantities of K_2O and SiO_2. The reaction was initiated by heating the mixture in a platinum dish at 810 K for several hours, followed by a 5-day heating period at 1,070 K. After the reaction was completed, the sample was ground and blended in an argon atmosphere and then heated at 1,195 K for 19 hours. This procedure was repeated twice, with a heating period each time of 6 days.

The X-ray analysis of this material was in good agreement with the powder diffraction pattern for $K_2Si_2O_5$(c). Petrographic examination indicated a crystalline, single-phase material with an index of refraction of 1.50, which is in agreement with Kracek (13). Chemical analysis showed an average K_2O content of 43.93 pct and an average SiO_2 content of 56.16 pct, for a mole ratio of 1:2.004. Optical emission spectrographic analysis showed total impurities of less than 100 ppm consisting of aluminum, magnesium, and titanium.

$K_2Si_2O_5$, Glass

The glassy form of $K_2Si_2O_5$ was made by melting the crystal form and rapidly quenching the sample. This procedure is given in more detail in the experimental section.

EXPERIMENTAL WORK AND RESULTS

Energy units of the calorimetric measurements are the thermochemical calorie (1 cal = 4.184 J). The 1973 Table of Atomic Weights (8) gives molecular weights of 154.280 for K_2SiO_3 and 214.365 for $K_2Si_2O_5$.

Low Temperature

The heat capacity measurements were carried out with an adiabatic calorimeter operating over the range 5 to 308 K. The details of construction and method of operation have been reported elsewhere by Stuve (21).

A sample mass of 95.6376 g of $K_2Si_2O_5$(c) was used. Experimental heat capacities are listed in table 1 and shown graphically in figure 1. The overall uncertainty of the heat capacities was estimated to be ±1 pct below 25 K; ±0.5 pct between 25 and 50 K; and ±0.2 pct between 50 and 308 K. Experimental data were smoothed using a curve-fitting routine developed by Justice (9), and the smoothed values of C_p°, S°, $-(G^\circ - H_0^\circ)/T$, and $H^\circ - H_0^\circ$, are listed in table 2. Heat capacity data were extrapolated from 5 to 0 K by using a plot of C_p°/T versus T^2.

TABLE 1. - Low-temperature experimental heat capacities of $K_2Si_2O_5$ (c)

T, K	C_p°, cal/deg-mole	T, K	C_p°, cal/deg-mole	T, K	C_p°, cal/deg-mole
4.80	0.014	37.75	5.891	156.62	26.712
5.21	.017	41.33	6.848	165.97	27.755
5.79	.024	46.07	8.089	176.28	28.841
6.46	.035	50.65	9.253	187.31	29.933
7.10	.049	51.69	9.518	197.55	30.869
7.70	.068	55.93	10.532	211.86	32.134
8.44	.095	59.08	11.260	222.89	33.070
9.28	.135	60.96	11.686	229.44	33.597
9.85	.169	66.23	12.840	243.27	34.664
10.17	.189	68.68	13.322	253.37	35.399
11.28	.270	72.45	14.134	263.28	36.114
12.27	.357	78.21	15.256	273.45	36.811
13.23	.456	84.88	16.506	283.64	37.487
14.21	.568	90.56	17.517	283.83	37.482
15.45	.736	96.95	18.601	288.94	37.838
17.09	.989	104.02	19.739	294.09	38.160
18.73	1.272	110.73	20.775	295.85	38.262
20.71	1.648	118.70	21.928	302.78	38.700
23.05	2.145	127.78	23.173	304.26	38.776
25.68	2.760	137.12	24.402	308.08	39.029
28.43	3.437	146.97	25.602		

High Temperature

Enthalpy measurements above 298.15 K were made with a copper-block drop calorimeter described by Douglas (4). The present drop calorimeter was modified to incorporate a more sensitive potentiometric system capable of detecting a temperature change of ±0.00005 K. The calorimeter was calibrated electrically before and after measurements of a substance. At these times, the entire apparatus was also checked by measuring the enthalpy of MgO, and comparing the results with the values reported by Victor (24) and Pankratz (18).

TABLE 2. - Low-temperature properties of $K_2Si_2O_5$ (c)

T, K	cal/deg-mole			$H°-H_O°$, cal/mole
	$C_p°$	$S°$	$-(G°-H_O°)/T$	
5	0.015	0.005	0.001	0.019
10	.178	.050	.011	.387
15	.673	.204	.047	2.362
20	1.510	.505	.120	7.701
25	2.593	.954	.239	17.870
30	3.843	1.536	.406	33.914
35	5.163	2.227	.615	56.42
40	6.492	3.003	.864	85.56
45	7.812	3.844	1.148	121.32
50	9.096	4.734	1.462	163.61
60	11.468	6.606	2.162	266.64
70	13.624	8.538	2.934	392.26
80	15.60	10.488	3.757	538.5
90	17.42	12.432	4.613	703.7
100	19.10	14.355	5.491	886.4
110	20.66	16.25	6.384	1,085.3
120	22.12	18.11	7.283	1,299.3
130	23.48	19.94	8.192	1,527.3
140	24.76	21.72	9.088	1,768.5
150	25.96	23.47	9.989	2,022.2
160	27.10	25.18	10.883	2,287.5
170	28.18	26.86	11.778	2,564.0
180	29.21	28.50	12.661	2,851.0
190	30.18	30.11	13.542	3,147.9
200	31.11	31.68	14.408	3,454.4
210	31.99	33.22	15.27	3,769.9
220	32.83	34.72	16.11	4,094.0
230	33.64	36.20	16.95	4,426.4
240	34.41	37.65	17.79	4,766.6
250	35.16	39.07	18.61	5,114
260	35.88	40.46	19.42	5,470
270	36.58	41.83	20.23	5,832
273.15	36.79	42.25	20.47	5,948
280	37.25	43.17	21.02	6,201
290	37.90	44.49	21.81	6,577
298.15	38.41	45.55	22.45	6,888
300	38.52	45.79	22.59	6,959

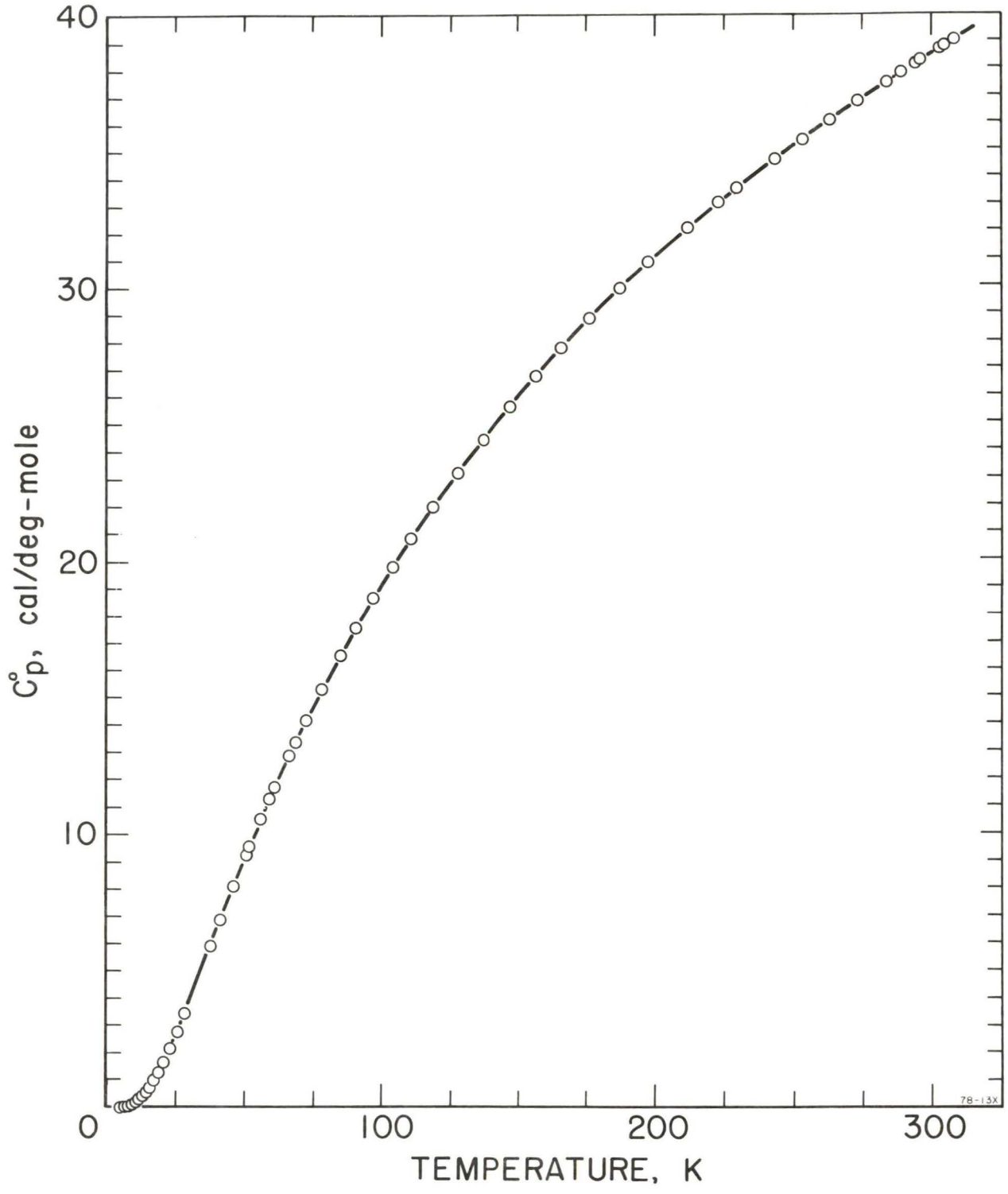

FIGURE 1. - Low-temperature heat capacities of $K_2Si_2O_5$(c).

Enthalpy measurements were conducted with sample containers made of Pt-10 pct Rh. Empty capsules had an approximate weight of 10 g, a nominal volume of 6 cm^3, and a wall thickness of 0.254 mm. The enthalpy contribution of the empty capsule was approximately 17 pct for the glassy and liquid states of $K_2Si_2O_5$, and 25 pct for the crystalline forms of $K_2Si_2O_5$ and K_2SiO_3. Capsules were evacuated in a dry box, backfilled with 1 atmosphere of helium, and filled with powdered samples of crystalline K_2SiO_3 or $K_2Si_2O_5$. After the capsule neck was squeezed gastight, the capsule was removed from the dry box and the neck was sealed by arc welding under an inert gas.

In the case of glassy $K_2Si_2O_5$, the filled capsule was removed from the dry box to melt the crystalline powder in the open capsule for 15 minutes at 25 kelvins above the melting point of 1,318 K. The melt was quenched on an aluminum brick for 15 seconds, and then quickly transferred back to the dry box for further cooling to room temperature while being evacuated. The loading and melting procedure was repeated twice more to nearly fill the capsule. The capsule was sealed as previously described. Under these conditions, molten $K_2Si_2O_5$ solidified completely into the single-phase glassy state as verified by X-ray powder diffraction and petrographic examination. This behavior agrees with the findings of Kracek (13), who found that the glass was readily formed from the liquid even when slowly cooled in a furnace. The composition of the glass was the same as that of the crystals, as shown by no weight change after melting. The resulting sample masses were 9.01419 g and 9.43470 g. A second capsule filling was needed after the first capsule leaked. The sample masses were 6.03396 g for crystalline $K_2Si_2O_5$ and 6.82090 g for crystalline K_2SiO_3.

The mass of the sample and capsule was periodically checked for constancy by weighing during experimental measurements. At these times, the integrity of the capsule wall was also checked by pressurizing the sealed capsule with 2 atmospheres of helium for 1 hour, followed by a quick immersion in isopropyl alcohol to detect any bubbles from small leaks. The temperature of the sample and capsule in the furnace was measured with a Pt-10 pct Rh versus Pt thermocouple, which was calibrated against the melting point of pure gold. Temperatures are based on the IPTS-68 (3).

The experimental enthalpy data are given in table 3. These values were smoothed with the curve-fitting routine described previously. For the crystalline $K_2Si_2O_5$ the high-temperature data were merged with the low-temperature data of this investigation. For crystalline K_2SiO_3 the high-temperature data were merged with the low-temperature data reported by Stull (20). Stull's measurements were made on a sample of questionable purity using an automatic adiabatic calorimeter, which he stated was less accurate than manually operated ones. Due to a small disparity in the two sets of data, Stull's C_p° value at 298.15 K of 28.30 cal/deg-mole was changed to 28.10 cal/deg-mole in order to merge the two sets of data smoothly. This change resulted in a higher than normal deviation of 0.7 pct for the experimental enthalpy measurement at 403.2 K. Smooth values of C_p°, S°, $-(G^\circ - H^\circ_{298})/T$, and $H^\circ - H^\circ_{298}$ are listed in tables 4-6. The standard error of measurement was 0.08 pct for K_2SiO_5 and 0.3 pct for K_2SiO_3. The absolute uncertainty of enthalpies in tables 4-6 is estimated to be $\pm$0.3 pct.

TABLE 3. - High-temperature experimental enthalpies

T, K	$H^\circ - H^\circ_{298}$, kcal/mole	T, K	$H^\circ - H^\circ_{298}$, kcal/mole	T, K	$H^\circ - H^\circ_{298}$, kcal/mole
		K_2SiO_3(c)			
403.2	3.097	703.3	13.238	1,019.4	25.222
503.0	6.304	803.4	16.881	1,103.3	28.653
602.9	9.698	902.8	20.659	[1]1,195.0	32.846
		$K_2Si_2O_5$(c)			
402.5	4.332	704.8	19.303	952.8	33.228
442.0	6.092	782.4	23.431	1,018.8	36.836
473.7	7.538	803.2	24.638	1,103.3	41.425
[2]503.0	9.020	[2]852.6	27.527	1,192.9	46.299
517.7	9.877	872.5	28.806	1,195.0	46.441
531.5	10.564	872.7	28.803	1,258.0	49.917
556.7	11.781	879.6	29.201	[1]1,309.1	53.163
594.1	13.619	890.0	29.785		
605.2	14.205	902.2	30.457		
		$K_2Si_2O_5$(gl, 1)			
403.3	4.387	653.6	16.468	[3]956.0	33.719
453.2	6.644	703.4	19.009	1,363.0	60.089
504.1	9.035	753.2	21.662	1,403.0	62.810
573.6	12.418	[3]805.4	24.614	1,453.8	66.067
606.7	14.083	[3]903.2	30.854		

[1] Possible onset of melting.

[2] Pretransition.

[3] Partial conversion of glass to crystal.

TABLE 4. - High-temperature properties of K_2SiO_3 (c)

T, K	cal/deg-mole			$H°-H°_{298}$, kcal/mole
	$C_p°$	S°	$-(G°-H°_{298})/T$	
298.15	28.10	34.93	34.93	0
300	28.17	35.10	34.93	.052
350	29.74	39.57	35.23	1.501
400	30.97	43.62	36.07	3.020
450	32.00	47.33	37.12	4.595
500	32.90	50.75	38.31	6.218
550	33.72	53.93	39.60	7.884
600	34.48	56.89	40.91	9.589
650	35.20	59.68	42.25	11.330
700	35.89	62.32	43.59	13.110
750	36.57	64.81	44.92	14.920
800	37.22	67.20	46.24	16.765
850	37.87	69.47	47.54	18.640
900	38.50	71.65	48.82	20.550
950	39.13	73.75	50.08	22.490
1,000	39.75	75.78	51.32	24.465
1,050	40.36	77.73	52.53	26.465
1,100	40.97	79.62	53.71	28.500
1,150	[1](41.58)	(81.46)	(54.88)	(30.565)
1,200	(42.18)	(83.24)	(56.03)	(32.655)
[2]1,249	(42.77)	(84.94)	(57.13)	(34.740)

[1]Values in parentheses are extrapolations.

[2]Melting point of K_2SiO_3.

TABLE 5. - High-temperature properties of $K_2Si_2O_5$ (c, l)

T, K	cal/deg-mole			$H°-H°_{298}$, kcal/mole
	$C_p°$	S°	$-(G°-H°_{298})/T$	
298.15	38.41	45.55	45.55	0
300	38.52	45.79	45.55	.071
350	41.66	51.99	46.04	2.083
400	43.80	57.70	47.14	4.223
450	45.40	62.95	48.61	6.454
500	46.67	67.80	50.29	8.757
[1]510	46.90	68.73	50.64	9.225
510	47.92	69.30	50.64	9.515
550	48.91	72.95	52.13	11.450
600	50.13	77.26	54.04	13.930
650	51.31	81.32	55.99	16.465
700	52.47	85.17	57.94	19.060
750	53.62	88.83	59.88	21.710
800	54.76	92.32	61.80	24.420
850	55.89	95.68	63.70	27.185
[1]867	56.27	96.79	64.33	28.140
867	54.51	97.23	64.33	28.520
900	54.54	99.26	65.57	30.320
950	54.59	102.2	67.41	33.050
1,000	54.65	105.0	69.22	35.780
1,050	54.70	107.7	71.02	38.515
1,100	54.75	110.2	72.70	41.250
1,150	54.81	112.7	74.45	43.990
1,200	54.86	115.0	76.06	46.730
1,250	54.91	117.2	77.62	49.475
1,300	54.96	119.4	79.23	52.22
[2]1,318	54.98	120.1	79.73	53.21
1,318	65.80	126.5	79.74	61.63
1,350	65.80	128.1	80.89	63.74
1,400	65.80	130.5	82.62	67.03
1,450	65.80	132.8	84.30	70.32
1,500	[3](65.80)	(135.0)	(85.93)	(73.61)
1,550	(65.80)	(137.2)	(87.59)	(76.90)
1,600	(65.80)	(139.3)	(89.18)	(80.19)

[1]Transition point of $K_2Si_2O_5$.
[2]Melting point of $K_2Si_2O_5$.
[3]Values in parentheses are extrapolations.

TABLE 6. - High-temperature properties of $K_2Si_2O_5$ (gl)

T, K	cal/deg-mole			$H°-H°_{298}$, kcal/mole
	$C_p°$	$S°$	$-(G°-H°_{298})/T$	
298.15	38.41	0	0	0
300	38.56	.238	.001	.071
350	41.83	6.44	.48	2.086
400	44.22	12.19	1.59	4.240
450	46.08	17.51	3.07	6.499
500	47.62	22.45	4.77	8.842
550	48.94	27.05	6.59	11.255
600	50.13	31.36	8.47	13.735
650	51.21	35.42	10.39	16.270
700	52.22	39.25	12.31	18.855
750	53.17	42.88	14.23	21.490
800	[1](54.08)	(46.34)	(16.13)	(24.170)
850	(54.97)	(49.65)	(18.01)	(26.895)
900	(55.82)	(52.82)	(19.86)	(29.665)

[1]Values in parentheses are extrapolations.

The smooth enthalpies in tables 4-6 were also expressed as equations for those who prefer the data in this form. The equations were derived by the method described by Kelley (10). The equations are expressed in kcal/mole, and their temperature ranges of validity and the percent average deviation from the experimental data are shown in parentheses. It should be noted that the average deviation of the experimental data from the smooth curve is less than 0.01 pct. Therefore, little accuracy is lost by using enthalpies calculated from the equations instead of the tabulated values.

K_2SiO_3 (crystal)

$$H° - H°_{298} = 28.418 \times 10^{-3}T + 5.833 \times 10^{-6}T^2 + 3.383 \times 10^2 T^{-1} - 10.126$$

(298 - 1,249 K; 0.2 pct).

$K_2Si_2O_5$ (crystal, liquid)

Base $H^\circ_{298} = \alpha\ K_2Si_2O_5$

α: $H^\circ - H^\circ_{298} = 45.855 \times 10^{-3}T + 4.372 \times 10^{-6}T^2 + 8.883 \times 10^{2}T^{-1} - 17.040$

(298 - 510 K; <0.01 pct),

$\Delta H^\circ_{510}(\alpha-\beta) = 0.29.$

β: $H^\circ - H^\circ_{298} = 37.764 \times 10^{-3}T + 10.854 \times 10^{-6}T^2 + 2.387 \times 10^{2}T^{-1} - 13.035$

(510 - 867 K; 0.1 pct),

$\Delta H^\circ_{867}(\beta-\gamma) = 0.38.$

γ: $H^\circ - H^\circ_{298} = 53.591 \times 10^{-3}T + 0.528 \times 10^{-6}T^2 - 18.340$

(867 - 1,318 K; <0.1 pct),

$\Delta H^\circ_{1318}(\gamma-\ell) = 8.42.$

ℓ: $H^\circ - H^\circ_{298} = 65.800 \times 10^{-3}T - 25.094$

(1,318 - 1,600 K; <0.1 pct).

$K_2Si_2O_5$ (glass)

$H^\circ - H^\circ_{298} = 43.807 \times 10^{-3}T + 7.268 \times 10^{-6}T^2 + 8.649 \times 10^{2}T^{-1} - 16.608$

(298 - 900 K; <0.1 pct).

Enthalpy values of crystalline K_2SiO_3 in tables 3 and 4 are plotted in figure 2 as the mean heat capacity, $(H^\circ - H^\circ_{298})/T - 298.15)$. The curve for K_2SiO_3 changed in a regular manner over the temperature range measured. Evidence of possible onset of melting was found at 1,195 K. No measurements were made for the liquid state, because molten samples that were cooled in the calorimeter to 298 K were not single phase. A mixture of glassy and crystalline forms was found and confirmed by X-ray powder diffraction and petrographic examination.

The enthalpies of crystalline $K_2Si_2O_5$ from tables 3 and 5 are also plotted in figure 2. The crystalline phase was measured prior to the liquid and glass. A reversible transition was found near 510 K, with an isothermal heat absorption of 0.29 kcal/mole. Another reversible transition was also found at about 867 K, with a heat absorption of 0.38 kcal/mole.

When furnace residence times of 2.75 hours were used, valid enthalpy measurements of the glassy phase of $K_2Si_2O_5$ were limited to 753 K. Enthalpies between this temperature and the melting point of 1,318 K showed a partial

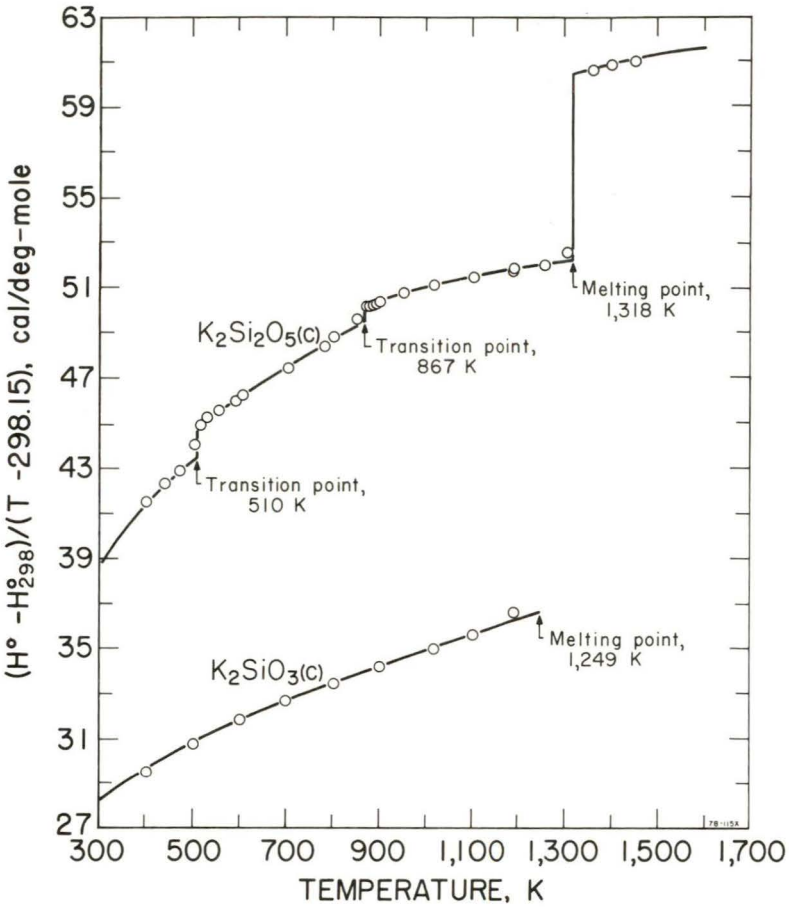

FIGURE 2. - High-temperature mean heat capacities.

conversion of glass to crystal. This partial conversion was shown by the larger than normal thermal effect above the smooth glass curve, equivalent to 0.6 pct at 805.4 K, 3.3 pct at 903.2 K, and 2.7 pct at 956.0 K. The highest measurement at 956.0 K was also 1.0 pct above the smooth crystal curve. These three measurements are listed in table 3, but were given no weight in deriving the smooth enthalpy values of table 6.

The enthalpy measurements of the liquid phase of $K_2Si_2O_5$ were possible because molten samples solidified completely in the glassy state when cooled to 298 K in the calorimeter. This glass was verified as single phase by X-ray diffraction and petrographic examination of a test sample and the contents of the two capsules used in the measurements. In addition, after a measurement above the melting point, it was possible to reproduce enthalpy values previously obtained for the glassy state below 753 K.

STANDARD ENTHALPIES AND GIBBS ENERGIES OF FORMATION

The results of calculations for the standard enthalpies and Gibbs energies of formation and the logarithms of the equilibrium constant for formation reactions of metasilicate and disilicate from both the elements and the oxides are listed in tables 7-12. The sources for data other than the present investigation are listed in table 13.

TABLE 7. - Formation data for $2K(c,l) + Si(c) + 3/2O_2(g) = K_2SiO_3(c)$

T, K	Hf°, kcal	Gf°, kcal	Log Kf	T, K	Hf°, kcal	Gf°, kcal	Log Kf
298.15	-370.0	-347.9	255.02	600	-370.9	-324.7	118.27
300	-370.0	-347.8	253.37	700	-370.6	-317.0	98.97
[1]336.35	-370.1	-345.1	224.24	800	-370.2	-309.4	84.52
336.35	-371.2	-345.1	224.24	900	-369.7	-301.8	73.29
400	-371.2	-340.2	185.88	1,000	-369.1	-294.3	64.32
500	-371.2	-332.4	145.29	[2]1,032	-368.8	-291.9	61.82

[1]Melting point of K. [2]Boiling point of K.

TABLE 8. - Data for $K_2O(c) + SiO_2(quartz) = K_2SiO_3(c)$

T, K	Hr°, kcal	Gr°, kcal	Log Kr	T, K	Hr°, kcal	Gr°, kcal	Log Kr
298.15	-65.9	-66.5	48.75	[1]847	-66.5	-67.3	17.37
300	-65.9	-66.5	48.45	847	-66.7	-67.3	17.37
400	-65.9	-66.7	36.44	900	-66.7	-67.4	16.37
500	-66.0	-66.9	29.24	1,000	-66.6	-67.5	14.75
600	-66.1	-67.0	24.40	1,100	-66.5	-67.5	13.41
700	-66.2	-67.2	20.98	[2]1,154	-66.4	-67.6	12.80
800	-66.4	-67.3	18.39				

[1]Transition point of SiO_2. [2]Decomposition point of K_2SiO_3.

TABLE 9. - Formation data for $2K(c,l) + 2Si(c) + 5/2O_2(g) = K_2Si_2O_5(c)$

T, K	Hf°, kcal	Gf°, kcal	Log Kf	T, K	Hf°, kcal	Gf°, kcal	Log Kf
298.15	-599.4	-564.6	413.86	600	-599.8	-528.4	192.47
300	-599.4	-564.3	411.09	700	-599.3	-516.5	161.26
[1]336.35	-599.5	-560.1	363.94	800	-598.5	-504.8	137.90
336.35	-600.6	-560.1	363.94	[2]867	-598.0	-496.9	125.26
400	-600.7	-552.4	301.82	867	-597.6	-496.9	125.26
500	-600.5	-540.4	236.21	900	-597.3	-493.1	119.74
[2]510	-600.5	-539.1	231.02	1,000	-596.6	-481.5	105.23
510	-600.2	-539.1	231.02	[3]1,032	-596.4	-477.8	101.19

[1]Melting point of K.
[2]Transition point of $K_2Si_2O_5$.
[3]Boiling point of K.

TABLE 10. - Data for $K_2O(c) + 2SiO_2(quartz) = K_2Si_2O_5(c)$

T, K	Hr°, kcal	Gr°, kcal	Log Kr	T, K	Hr°, kcal	Gr°, kcal	Log Kr
298.15	-77.6	-78.4	57.47	[2]847	-77.9	-79.8	20.59
300	-77.6	-78.4	57.11	847	-78.3	-79.8	20.59
400	-77.6	-78.6	42.95	[1]867	-78.3	-78.8	20.12
500	-77.7	-78.9	34.49	867	-77.9	-79.8	20.12
[1]510	-77.7	-78.9	33.81	900	-77.9	-79.9	19.40
510	-77.4	-78.9	33.81	1,000	-78.0	-80.1	17.51
600	-77.5	-79.1	28.81	1,100	-78.1	-80.2	15.93
700	-77.6	-79.4	24.79	[3]1,154	-78.2	-80.4	15.23
800	-77.7	-79.6	21.75				

[1]Transition point of $K_2Si_2O_5$.
[2]Transition point of SiO_2.
[3]Decomposition point of $K_2Si_2O_5$.

TABLE 11. - Formation data for $2K(c,l) + 2Si(c) + 5/2O_2(g) = K_2Si_2O_5(gl)$

T, K	Hf°, kcal	Gf°, kcal	Log Kf	T, K	Hf°, kcal	Gf°, kcal	Log Kf
298.15	-594.9	-546.5	400.60	500	-595.9	-513.1	224.28
300	-594.9	-546.2	397.91	600	-595.5	-496.6	180.89
[1]336.35	-595.0	-540.3	351.07	700	-595.0	-480.1	149.89
336.35	-596.1	-540.3	351.07	800	-594.3	-463.7	126.68
400	-596.1	-529.7	289.41	900	-593.5	-447.5	108.67

[1]Melting point of K.

TABLE 12. - Data for $K_2O(c) + 2SiO_2(quartz) = K_2Si_2O_5(gl)$

T, K	Hr°, kcal	Gr°, kcal	Log Kr	T, K	Hr°, kcal	Gr°, kcal	Log Kr
298.15	-73.1	-60.3	44.20	700	-73.3	-43.0	13.43
300	-73.1	-60.2	43.86	800	-73.5	-38.6	10.55
400	-73.1	-55.9	30.54	[1]847	-73.7	-36.6	9.44
500	-73.1	-51.6	22.55	847	-74.1	-36.6	9.44
600	-73.2	-47.3	17.23	900	-74.1	-34.2	8.30

[1]Transition point of SiO_2.

TABLE 13. - Auxiliary thermodynamic data

Element or compound	Function[1]	Reference[2]
K (c,ℓ).....	H.T.	(7)
	S°_{298}	(2)
O_2 (g).....	H.T.	(6)
Si(c).....	H.T.	(7)
K_2O(c).....	ΔHf°_{298}	(26)
	L.T.	Estimated.
	H.T.	Estimated.
SiO_2 (quartz).....	ΔHf°_{298}	(25)
	L.T.	(25)
	S°_{298}	(25)
	H.T.	(16), (19), (27-28).
K_2SiO_3 (c).....	ΔHf°_{298}	(5)
	L.T.	(20)
$K_2Si_2O_5$ (c, gl).....	ΔHf°_{298}	(1)

[1] H.T. = High-temperature thermodynamic properties; L.T. = low-temperature thermodynamic properties.

[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

DISCUSSION

The low-temperature heat capacities of $K_2Si_2O_5$ (c) showed no transitions from 4.80 K to 308.08 K. Values at 298.15 K were calculated for S° as 45.55 ±0.05 cal/deg-mole, for $-(G^\circ - H^\circ_0)/T$ as 22.45 cal/deg-mole, and for $H^\circ - H^\circ_0$ as 6,888 cal/mole.

Enthalpy measurements of crystalline K_2SiO_3 showed no transitions or other anomalies. No heat of fusion was calculated, because molten samples that were cooled in the calorimeter under the same conditions as those for enthalpy measurements contained a mixture of glassy and crystalline substances. Extrapolation of the enthalpy data from the last valid experimental measurement at 1,103.3 K to the melting point at 1,249 K was based on a reasonable projection of the smooth data. The congruent melting point of 1,249 K was adopted from measurements by Morey (15) that were later confirmed in studies by Kracek (12-13). No previous high-temperature measurements of K_2SiO_3 were found in the literature.

The thermal behavior of crystalline $K_2Si_2O_5$ showed two reversible transitions near 510 and 867 K. Experimental measurements made above and then below both of these temperatures verified the rapid reversibility of the phase transitions by again being on the mean heat capacity curve in figure 2. No other

reports of the transition near 510 K could be found in the literature. The transition at 867 K was determined between 853 and 873 K for an average temperature of 863 K. Nevertheless, 867±2K was adopted for the transition, from the differential thermal analysis conducted by Kracek (12), who had earlier reported (13) this transition at 863 K. His heat of transition of 1.2 ±0.5 cal/g (0.257 ±0.107 kcal/mole) compares with 0.38 kcal/mole measured in the present investigation. Present enthalpy measurements did not determine the melting point of the crystals due to the possible onset of melting observed at 1,309.1 K, which was 0.8 pct above the smooth curve of figure 2. Consequently, the data were extrapolated from the last valid measurement at 1,258 K to the adopted melting point at 1,318 K reported by Kracek (12). The temperature for the fusion point of 1,318 K compares with 1,309 K measured earlier by Kracek (11, 13), 1,314 K by Morey (15), and 1,288 K by Niggli (17).

Enthalpies of glassy $K_2Si_2O_5$ are reported to 900 K. The conversion of the glass to crystal started between 753 and 805 K, and was not completed by 956 K with furnace residence times of 2.75 hours. Kracek (13) reported that the conversion started at about 943 K and was completed near 1,073 K. Kracek used differential thermal analysis with heating rates of about 0.5 to 1.0 kelvin per minute on a sample of $K_2Si_2O_5$ containing a 0.15 pct excess of SiO_2. Obviously, the conversion is temperature-time dependent, and therefore, smooth values for the glassy state in table 6 were extrapolated to 900 K as a compromise. The conversion can be most easily completed by heating just below the melting point for a short time. However, the very rapid cooling of the liquid phase causes the curve to pass over the fusion point to lower temperatures in a continuous line.

Enthalpy measurements of the glassy form of $K_2Si_2O_5$ using a continuous measurement water calorimeter have been reported by Tashiro (23) and later by Takahashi (22). The results of both investigations were higher than those for this investigation by 4 to 8 pct between 373 and 900 K. These calorimeter, with inaccuracies as high as ±3 pct, were some tenfold less accurate than the drop calorimeter used here. Takahashi also reported enthalpies of the crystalline phase that were higher than those of the present investigation by 12 pct at 373 K decreasing to 2 pct between 873 and 1,309 K. The high-temperature data of Takahashi showed poor agreement with the low-temperature heat capacities of the present investigation.

Enthalpy measurements of the liquid phase of $K_2Si_2O_5$ were made to obtain the heat of fusion. This was possible because molten samples solidified completely in the glassy state when cooled in the calorimeter. However, the formation of the glass instead of the crystals required that the heat of fusion be obtained indirectly. This involved combining the heats of solution (in hydrofluoric acid) of the crystal and the glass at room temperature with the enthalpies of the crystal and the liquid at room temperature and the enthalpies of the crystal and the liquid at the melting point. Kracek (14) reported a heat of transition of 4.47 kcal/mole for crystals to glass at 298.15 K. This value combined with the enthalpy of the liquid at the melting point of 57.16 kcal/mole, based on the following equation, and the crystals at the melting point of 53.21 kcal/mole, from table 5, yielded 8.42 kcal for the heat of fusion. The equation for the enthalpy of the liquid, $H^\circ - H^\circ_{298} = 65.800 \times 10^{-3}T - 29.564$,

is in kcal/mole and is with respect to the glass at 298.15 K as the base. The average deviation of the equation is less than 0.1 pct from the experimental measurements over the range 1,318 to 1,600 K. Comparable smooth values for this equation are not shown in tabulated form, because the smooth enthalpy data for the glass with respect to glass at 298.15 K as the base were limited to 900 K. Instead, data in table 5 and figure 2 were corrected for the liquid with respect to crystals at 298.15 K as the base to show the actual heat of fusion.

Takahashi obtained the heat of fusion by the same indirect procedure. His heat of fusion of 7.6 kcal/mole was based on the adopted melting point of 1,309 K from the 1932 work of Kracek (11) and on his own heat of solution measurements that yielded 3.4 kcal/mole for the heat of transition of crystals to glass at 298.15 K.

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