[Contribution from the Western Region, Bureau of Mines, United States Department of the Interior]

High-temperature Heat Contents of Sodium Metasilicate and Sodium Disilicate[1]

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The thermodynamic properties of silicates have, in recent years, received only nominal attention in spite of the importance of these substances as constituents of glasses and metallurgical slags. Earlier publications of the Pacific Experiment Station have dealt with low-temperature specific heats and entropies of several silicates.[3] The present paper reports high-temperature heat content measurements of sodium metasilicate and sodium disilicate. Previous similar data are lacking for both these substances.

Method and Materials

The heat content measurements were made by the "drop" method in an apparatus previously described.[4] The calorimeter was calibrated with electrical energy, measured in international joules, and the results were converted to the conventional thermochemical calorie by the relation,[5] 1 cal. = 4.1833 int. joules (NBS).

The samples were enclosed in platinum-rhodium alloy capsules, the heat contents of which were measured separately. Each capsule was sealed with platinum after filling; however, on reaching the liquid range of either substance, small pin holes developed in the capsule walls. A close check was maintained and weight corrections were made for any loss of sample, which for any single measurement did not exceed 0.1%.

The sodium metasilicate and disilicate were furnished by the Philadelphia Quartz Co. The metasilicate was part of the material used previously by Kelley[3] for low-temperature specific heat measurements. This sample was reheated to 1100° and then slowly cooled to assure complete crystallization. Analysis showed it to be at least 99.5% pure.

The sodium disilicate was a specially decolorized sample which was heated at 700° before using; its purity was 99%.

Results

The results of the experimental measurements are presented in Table I and Fig. 1. The column labeled T, °K., lists the temperature of the sample before dropping into the calorimeter and $H_T - H_{298.16}$, the heat liberated per gram molecular weight in cooling to 298.16°K. The heat content values that appear to involve premelting have been designated "(p)." Sodium disilicate forms a glass upon cooling quickly from the liquid state, and the results for crystals, glass, and liquid have been listed separately.

The sample weights were corrected to vacuum, using the densities sodium metasilicate, 2.61; and sodium disilicate 2.50, g./cc. The molecular weights accord with the 1941 International Atomic Weights. No attempt was made to correct for the impurities present, since they were small and not definitely known.

Sodium metasilicate is represented by curve A in Fig. 1. The melting point, 1361°K., is indicated by a dotted line and the heat of fusion was calculated to be 12,470 calories per mole. Slight premelting was indicated about 100° below the melting point.

The measurements of crystalline sodium disilicate were made before the liquid and glass were studied, care being taken not to melt the sample; the results are plotted as curve B in Fig. 1. Some premelting occurred on approaching the melting point, 1147°K. No heat of fusion is obtainable because of glass formation when the liquid cooled in the calorimeter. The upper portion of curve C represents the heat contents obtained for liquid disilicate, while the lower portion shows the results of measurements made on the glass. The values for the glass from 877°K. to the melting point are not considered reliable, as several erratic results in this temperature range, listed in Table I but not plotted, showed that while heating in the furnace, the glass was transforming spontaneously to crystals. It could, however, be re-formed by heating the sample above 1147°K. and dropping into the calorimeter. This was done before and during the measurements of the glass.

Table I

Heat Contents above 298.16°K.

Na_2SiO_3, mol. wt. = 122.054		$Na_2Si_2O_5$, mol. wt. = 182.114			
T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
360.5	1,890	Crystal		Glass	
496.0	6,170	376.8	3,390	445.5	6,570
664.3	11,990	503.2	9,200	677.4	18,250
750.7	15,060	570.3	12,410	800.6	25,450
804.6	17,060	641.1	16,020	877.3	30,710
891.9	20,400	673.8	17,800	939.2	34,040
1007.0	25,000	719.3	20,170	996.0	36,200
1154.0	31,040	751.4	21,970	1018.5	38,110
1261.1(p)	35,760	838.2	26,890	1120.7	47,450
1304 (p)	38,220	874.6	28,910	Liquid	
1354	51,840	897.1	30,150	1173.2	49,540
1414	54,580	939.5	32,690	1226.5	52,820
1507	58,640	974.7	34,800	1338	59,790
1616	63,270	1009.1(p)	37,270	1447	66,860
1747	68,690	1059.3(p)	40,170	1512	70,920
		1097.9(p)	43,820	1570	74,350
		1100.2(p)	44,120	1670	80,570
				1744	84,990

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(3) K. K. Kelley, This Journal, **61**, 471, 1217 (1939); **63**, 2750 (1941); **65**, 339 (1943).

(4) J. C. Southard, *ibid.*, **63**, 3142 (1941)

(5) E. F. Mueller and F. D. Rossini, *Am. J. Physics*, **12**, 1-7 (1944).

Heat content values read from smooth curves at 100° intervals and corresponding entropy increments are given in Table II.

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	Na_2SiO_3, cryst. and liquid		$Na_2Si_2O_5$, crystal	
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole
400	3,080	8.85	4,410	12.70
500	6,300	16.04	9,040	23.02
600	9,650	22.14	13,980	32.02
700	13,190	27.60	19,160	40.00
800	16,910	32.56	24,670	47.35
900	20,730	37.08	30,400	54.09
1000	24,700	41.24	36,320	60.33
1100	28,770	45.11	42,430	66.15
1147			45,360	68.76
1200	32,940	48.74		
1300	37,210	52.16		
1361	39,870(s)	54.16		
1361	52,340(l)	63.32		
1400	54,010	64.53		
1500	58,290	67.48		
1600	62,570	70.24		
1700	66,850	72.84		
1800	71,130	75.28		

Using the method previously described by Shomate[6] and the specific heats[7] at 298.16°K. (Na_2SiO_3, $C_{p298.16} = 26.72$ and $Na_2Si_2O_5$, $C_{p298.16} = 37.41$ calories per degree), heat content equations were derived for the crystalline state of both silicates. A linear equation based upon heat contents of 54,010 calories at 1400°K. and 62,570 calories at 1600°K. satisfactorily fitted the experimental data for liquid sodium metasilicate, the mean deviation being 0.1%. Assuming that liquid sodium disilicate cooled to the same final state in each measurement, a value was obtained for its specific heat from the slope of the best straight line through the experimental heat content points. The heat content equations, followed by the appropriate temperature range and mean percentage deviation of the equation from the experimental data, are given below. The heat contents influenced by premelting were not used in computing the mean deviation.

$Na_2SiO_3(s)$: $H_T - H_{298.16} = 31.14T + 0.00480T^2 + (647{,}000/T) - 11{,}882$ (298°–1361°K.; 1%)

$Na_2SiO_3(l)$: $H_T - H_{298.16} = 42.80T - 5910$ (1361°–1800°K.; 0.1%)

$Na_2Si_2O_5(s)$: $H_T - H_{298.16} = 44.38T + 0.00843T^2 + (1{,}067{,}000/T) - 17{,}560$ (298°–1147°K.; 1%)

The specific heat equations are

$Na_2SiO_3(s)$: $C_p = 31.14 + 0.00960T - (647{,}000/T^2)$
$Na_2SiO_3(l)$: $C_p = 42.80$
$Na_2Si_2O_5(s)$: $C_p = 44.38 + 0.01686T - (1{,}067{,}000/T^2)$
$Na_2Si_2O_5(l)$: $C_p = 62.35$

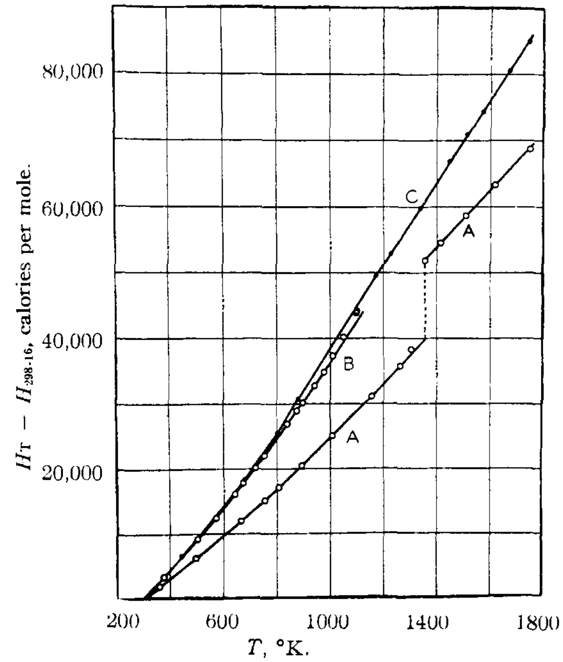

Fig. 1.—Crystalline and liquid Na_2SiO_3, A; crystalline $Na_2Si_2O_5$, B; glassy and liquid $Na_2Si_2O_5$, C.

Summary

High-temperature heat contents above 298.16°K. of sodium metasilicate and sodium disilicate were determined from room temperature to about 1773°K. The heat of fusion of the metasilicate also was obtained, but glass formation precluded a heat of fusion determination for the disilicate. The results have been summarized by algebraic equations and a table giving heat content and entropy increments above 298.16°K. at 100° intervals.

BERKELEY, CALIF. RECEIVED DECEMBER 15, 1944

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(6) C. Howard Shomate, THIS JOURNAL, **66**, 928 (1944).

(7) K. K. Kelley, Bureau of Mines Bull. 434 (1941).