The Specific Heats at Low Temperatures of Crystalline Ortho-, Meta-, and Disilicates of Sodium[1]

BY K. K. KELLEY[2]

As part of its program of supplying fundamental thermodynamic data for metallurgically important substances, the Metallurgical Division of the Bureau of Mines is interested in the specific heats at low temperatures and in the entropies of silicates. This subject has not been studied extensively, only five silicates in all having been investigated adequately—pseudo - wollastonite ($CaSiO_3$) studied by Parks and Kelley[3] and Wagner,[4] wollastonite ($CaSiO_3$) studied by Cristescu and Simon[5] and Wagner,[4] and cyanite, andalusite, and sillimanite (Al_2SiO_5) studied by Simon and Zeidler.[6] In addition, diopside, $CaMgSi_2O_6$, in the temperature range 20 to 40°K., and $MgSiO_3$, in the temperature range 21 to 36°K., were investigated by Wagner.[4]

The present paper reports measurements of the specific heats and entropies of three crystalline sodium silicates, Na_4SiO_4, Na_2SiO_3, and $Na_2Si_2O_5$. Similar measurements for iron, manganese, and magnesium silicates will be undertaken in the near future.

Materials.—The orthosilicate sample was a special preparation made and furnished by the Pennsylvania Salt Co. through the courtesy of Mr. J. E. Underwood. He stated that the sodium orthosilicate content was between 97 and 98%, the remainder for the most part being sodium carbonate. Analysis by the writer checked the sodium orthosilicate content.

The meta- and disilicates were furnished by the Philadelphia Quartz Co. through the courtesy of Mr. T. K. Cleveland. The former, as received, was virtually pure $Na_2SiO_3·6H_2O$. Most of the water was removed at low temperature and the remainder by heating to over 1100° (m. p. of Na_2SiO_3 = 1088°) and holding for about one hour. Subsequently, the temperature was lowered to 1025–1050° for one and one-half hours

and complete crystallization occurred. The disilicate was received in the anhydrous crystalline form and was heated to 700° before the calorimeter was filled. Its purity was 98%.

Specific Heats

The method and apparatus have been described previously.[7]

The specific heat data expressed in defined calories (1 calorie = 4.1833 international joule) are given in Table I and shown graphically in Fig. 1. It may be seen readily that these three substances

TABLE I

SPECIFIC HEAT OF Na_4SiO_4 (184.05 g.)

T	C_p	T	C_p	T	C_p
54.0	7.72	122.1	25.11	222.3	38.28
58.0	8.82	132.1	26.93	232.8	39.22
62.6	10.25	142.4	28.71	242.6	40.10
67.2	11.66	152.2	30.11	252.7	40.92
71.9	13.10	162.4	31.64	262.5	41.67
81.0	15.68	172.3	32.88	272.7	42.49
85.4	16.83	182.2	34.18	283.4	42.96
94.1	19.01	192.5	35.46	294.7	43.57
103.0	21.03	202.4	36.45	298.6	43.37
112.8	23.21	212.6	37.44		

SPECIFIC HEAT OF Na_2SiO_3 (122.05 g.)

T	C_p	T	C_p	T	C_p
53.6	3.95	124.6	14.72	216.0	22.49
58.1	4.70	134.8	15.87	226.8	23.16
62.7	5.49	144.9	16.93	237.5	23.77
67.2	6.31	155.1	17.95	248.4	24.47
72.1	7.21	165.2	18.79	259.7	24.91
81.3	8.73	174.8	19.59	272.0	25.55
85.9	9.40	184.8	20.35	282.7	26.06
95.8	10.89	194.6	21.08	290.5	26.38
105.0	12.23	205.4	21.83	294.5	26.63
114.7	13.51				

SPECIFIC HEAT OF $Na_2Si_2O_5$ (182.11 g.)

T	C_p	T	C_p	T	C_p
54.3	6.40	114.3	18.60	214.7	31.08
58.0	7.16	124.1	20.10	224.6	31.97
62.4	8.15	134.7	21.72	234.8	32.79
67.2	9.27	144.8	23.12	245.0	33.62
72.0	10.39	154.8	24.57	255.3	34.44
76.5	11.39	165.0	25.77	265.5	35.24
81.3	12.10	174.8	26.91	275.3	35.96
85.5	13.10	184.6	28.01	285.1	36.62
95.1	14.97	194.6	29.10	294.7	37.20
104.4	16.72	204.6	30.14		

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(3) Parks and Kelley, *J. Phys. Chem.*, **30**, 1175 (1926).

(4) Wagner, *Z. anorg. Chem.*, **208**, 1 (1932).

(5) Cristescu and Simon, *Z. physik. Chem.*, **B25**, 273 (1934).

(6) Simon and Zeidler, *ibid.*, **123**, 383 (1926).

(7) Millar, THIS JOURNAL, **50**, 1875 (1928); Anderson, *ibid.*, **52**, 2296 (1930).

behave very normally and therefore no discussion appears to be necessary.

Fig. 1.—Specific heats of Na_2SiO_3, $Na_2Si_2O_5$ and Na_4SiO_4.

Entropies

The entropies at 298.1°K. were calculated in the usual manner, the portion between 53.1 and 298.1°K. being obtained graphically and the portion lying below 53.1°K. being obtained by extrapolation by means of combinations of Debye and Einstein functions. The results are given in Table II.

In the case of sodium orthosilicate it was found that the combination

$$D\left(\frac{227}{T}\right) + 4E\left(\frac{256}{T}\right) + 4E\left(\frac{677}{T}\right)$$

fits the specific heat results over the entire temperature range studied. For sodium metasilicate, the combination

$$D\left(\frac{252.5}{T}\right) + 2E\left(\frac{292}{T}\right) + 2E\left(\frac{618}{T}\right)$$

fits the experimental results between 53.1 and 180°K. The data for sodium disilicate for the entire temperature range studied are represented by the combination

$$D\left(\frac{140}{T}\right) + 4E\left(\frac{328}{T}\right) + 2E\left(\frac{802}{T}\right) + 2E\left(\frac{1228}{T}\right)$$

Several years ago Parks and Kelley[3] called attention to the fact that for calcium and magnesium silicates the specific heats above 200°K. are very nearly equal to the sum of those of silicon dioxide glass and the component metal oxides, and more recently Kelley[8] has indicated that as a first approximation the entropy of a silicate at 298.1°K. may be taken as the sum of the entropies of the component oxides. In the present instance, if 11.0 is assigned as the entropy of silicon dioxide contained in a silicate, then $S_{298.1} = 17$ is indicated as the entropy of sodium oxide, this being about the mean of the figures, 17.9, 16.2, and 17.4. This value is of the right magnitude in comparison with the measured entropies of cuprous and silver oxides and is suggested for use until such time as the entropy of sodium oxide is measured.
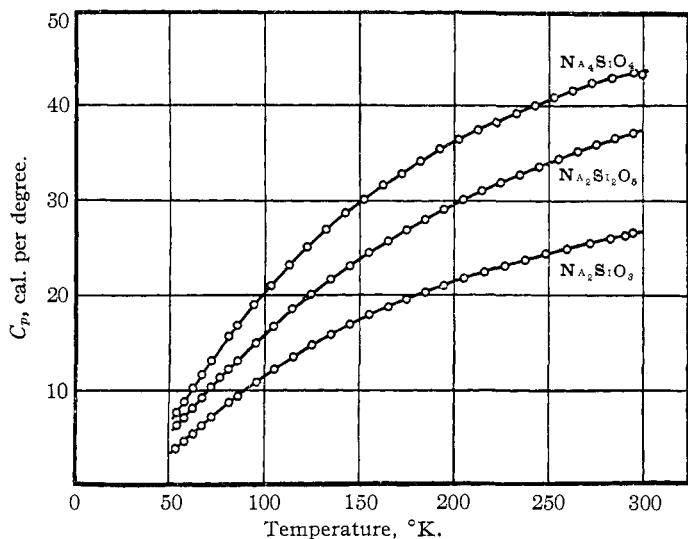
Related Thermal Data

The heat of formation of sodium metasilicate from the work of Matignon has been reported as $\Delta H = -331,400$[9] and $\Delta H = -351,000$.[10] The heat of the reaction $Na_2O + SiO_2 = Na_2SiO_3$ was investigated by Kröger and Fingas[11] and Troitzsch,[11] who obtained $\Delta H = -54,600$ and $\Delta H = -56,500$, respectively, the mean being $\Delta H = -55,600$. The last figure in conjunction with the mean of the results for the heat of formation of sodium oxide based on the work of Rengade[12] and Beketoff[12] $\Delta H = -100,700$ and $\Delta H = -100,260$, respectively, and Roth and Troitzsch's[13] heat of formation of quartz, $\Delta H = -208,300 \pm 350$, yields $\Delta H = -364,400$, in poor agreement with either of the figures derived from Matignon's work. If the value $\Delta H = -364,400$ is accepted, then, by means of the relationship $\Delta F° = \Delta H - T\Delta S$ and the entropies of the elements[14] involved, there is obtained $\Delta F°_{298.1} = -342,000$ as the free energy of formation of sodium metasilicate from the elements, which, of course, must be regarded as uncertain.

TABLE II

ENTROPIES AT 298.1°K.

	Na_4SiO_4	Na_2SiO_3	$Na_2Si_2O_5$
0–53.1°K. (extrapolated)	2.48	1.39	3.43
53.1–298.1°K. (graphical)	44.30	25.80	35.93
$S_{298.1}$	46.8 ± 0.6	27.2 ± 0.3	39.4 ± 0.6

(8) Kelley, Bureau of Mines Bulletin 350, 1932, 63 pp.
(9) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Verlag von Julius Springer, Berlin, First Supplement, 1927, p. 818.
(10) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 380.
(11) Ibid., Third Supplement, Vol. III, 1936, p. 2756.
(12) Ibid., Vol. II, 1923, p. 1504.
(13) Ibid., Third Supplement, Vol. III, 1936, p. 2749.
(14) Kelley, Bureau of Mines Bulletin 394, 1936, pp. 55.

The free energy of formation of sodium oxide corresponding to the mean of the mentioned heats of formation and the suggested entropy value is $\Delta F°_{298.1} = -91,000$.

Summary

Specific heat data covering the temperature range 52.5 to 298.1°K. have been presented for sodium ortho-, meta-, and disilicates in the anhydrous crystalline state. The corresponding entropies at 298.1°K. have been determined as 46.8 ± 0.6, 27.2 ± 0.3, and 39.4 ± 0.6, respectively.

The value $S_{298.1} = 17$ is suggested as an approximation to the entropy of sodium oxide and $\Delta F°_{298.1} = -91,000$ as an approximation to the free energy of formation.


Orientation in the Furan Series. XI. Cleavage-Rearrangements in Friedel–Crafts Reactions

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Introduction

In the Friedel–Crafts alkylation of methyl 2-furoate each of the four butyl chlorides, as well as butylene, gave some of the same product, namely, methyl 5-t-butyl-2-furoate.[1a]

When higher alkyl halides[1b] are used in the alkylation of ethyl 5-bromo-2-furoate, there is not only a rearrangement to the tertiary radical, but also a cleavage to a t-butyl radical, irrespective apparently of both the branching and length of the R group and of the nature of the X in the RX compound. One of the more striking reactions reported at this time is the 46% yield of ethyl 4-t-butyl-5-bromo-2-furoate from n-octadecyl bromide ($C_{18}H_{37}Br$).
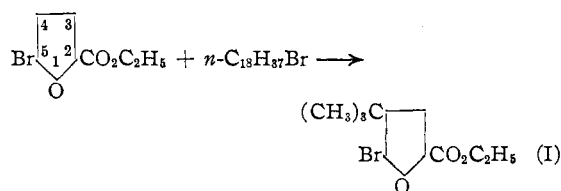
t-Amyl alcohol alkylated after the fashion of the corresponding amyl halides, but no alkylation was observed with some olefins.

Replacement-Alkylation with n-Amyl Bromide.—When ethyl 5-bromo-2-furoate was first treated with n-amyl bromide the usual cleavage and rearrangement to a t-butyl radical took place; however, the t-butyl radical replaced the bromine and entered the 5-position to give ethyl 5-t-butyl-2-furoate in yields between 31 and 40%.

This highly unusual result, when it is considered that a reaction like (I) took place with very closely related halides, prompted experiments in which some factors were varied.[2] It was subsequently found possible, in separate experiments, to obtain not only a mixture of ethyl 5-t-butyl-2-furoate and ethyl 4-t-butyl-5-bromo-2-furoate, but also the latter compound exclusively.

A replacement-substitution reaction has been noted in an acylation. Nitrofuran, propionyl chloride and titanium chloride give 5-chlorofuryl ethyl ketone.[1c]

Alkylation with Other Furan Derivatives. A. Ethyl 5-Chloro-2-furoate.—It seemed reasonable to attribute the cleavage-rearrangement reaction to a mechanism concerned in part with steric hindrance. Accordingly, ethyl 5-chloro-2-furoate was brought into reaction with n-amyl chloride in order to determine whether the smaller nuclear chlorine might permit the introduction of an amyl radical. However, the usual cleavage-rearrangement took place, and a t-butyl radical was substituted in the 4-position to give ethyl 4-t-butyl-5-chloro-2-furoate. A more significant test of the steric factor would be the alkylation of the as yet unknown ethyl 5-fluoro-2-furoate.

B. Ethyl 4-Bromo-2-furoate.—This bromo ester was selected in order to establish whether a cleavage would take place when an α-position in furan is available. It is known that there is apparently no cleavage when methyl 2-furoate is alkylated by n-amyl chloride and n-hexyl bromide, for the products isolated were methyl 5-

(1) (a) Gilman and Calloway, THIS JOURNAL, **55**, 4197 (1933); (b) Gilman and Burtner, ibid., **57**, 909 (1935); (c) Gilman, Burtner, Calloway and Turck, ibid., **57**, 907 (1935); (d) Gilman, Calloway and Burtner, ibid., **57**, 906 (1935).

(2) See Experimental Part.