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The Specific Heats at Low Temperatures of Ferrous Silicate, Manganous Silicate and Zirconium Silicate[1]

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The available low-temperature specific heat data for silicates are rather meager in spite of the wide interest in and importance of these substances as constituents of slags and glasses. Previous measurements that are adequate for entropy calculations have been reported for pseudo-wollastonite ($CaSiO_3$) by Parks and Kelley,[3] wollastonite ($CaSiO_3$) by Wagner[4] and Cristescu and Simon,[5] cyanite, andalusite, and sillimanite (Al_2SiO_5) by Simon and Zeidler,[6] ortho- meta- and di-silicate of sodium by Kelley,[7] and phenacite (Be_2SiO_4) by Kelley.[8] In addition, Wagner[4] has reported data for diopside ($CaMgSi_2O_6$) in the temperature range 20 to 40° K. and for enstatite ($MgSiO_3$) in the range 21 to 36° K.

As part of its program of supplying fundamental data for substances of metallurgical interest, the Metallurgical Division of the Bureau of Mines has undertaken the measurement of low-temperature specific heats of several typical crystalline silicates. The present paper presents data for Fe_2SiO_4, $MnSiO_3$ and $ZrSiO_4$ in the temperature range 51 to 298° K. Subsequent papers will deal with the silicates of lead, silver and magnesium.

Materials[9]

The method of preparation of Fe_2SiO_4 was essentially that described by Bowen, Schairer and Posnjak.[10] Finely powdered silica, ferric oxide and iron (made by the reduction of ferric oxide by hydrogen at 650° in a silica flask) were thoroughly mixed in proportions corresponding to the reaction $2Fe_2O_3 + 2Fe + 3SiO_2 \longrightarrow 3Fe_2SiO_4$, tamped into a nickel cartridge and heated for several days at 1040° in an evacuated silica tube. The resulting product, a stony, yellow material, was crushed to 100-mesh and the small amount of free iron that appears to be inherent in this method of preparation was removed with an electromagnet. The density of the product was measured as 4.35 at room temperature, and analysis gave 54.5% iron and 29.5% silica as compared with the theoretical values, 54.8% iron and 29.5% silica. The material appeared to be identical, except for minor differences in analysis, with a sample of fayalite from Rockport, Mass., available through the courtesy of the United States National Museum. A 241.9-g. sample was used in the specific heat measurements.

The $MnSiO_3$ was prepared from manganese carbonate and silica. The carbonate was obtained by precipitation from manganous chloride solution with ammonium carbonate. After careful washing and drying at 120° it analyzed 58.7% MnO, some hydrated oxide being present. A stoichiometric mixture (based upon analysis) of this material and finely powdered silica were ground together in a porcelain ball mill, tamped in a nickel cartridge and heated for five days at 1035° in a silica tube through which a slow stream of hydrogen was passed continuously. The product was a pale pink, easily crushed material of density 3.69 at room temperature, which agrees with values in the literature for rhodonite. Analysis gave 54.18 and 54.00% MnO as compared with the theoretical value for $MnSiO_3$, 54.15%. A 105.4-g. sample was used in the specific heat measurements.

The $ZrSiO_4$ was zircon sand from Lincoln, Calif., collected by O. C. Ralston, Bureau of Mines, College Park, Md., who kindly furnished a sample that had been purified under his direction by flotation methods. The sample was treated further in this Laboratory, first by digestion with 6 *N* hydrochloric acid to remove iron stains and then by dropping slowly through a column of *sym*-tetrabromoethane to float off any free silica. (Only a small amount was found.) The density at room temperature was 4.65. Analysis gave 66.3% $ZrO_2(HfO_2)$, 0.4% Fe_2O_3, and 33.6% SiO_2. Ignoring the presence of hafnium, these figures correspond to 98.6% $ZrSiO_4$, 0.4% Fe_2O_3 and 1.3% SiO_2, which was the basis adopted in calculating the specific heat results. A 351.7-g. sample was employed in the measurements, and correction was made for the Fe_2O_3 and excess SiO_2.

Specific Heats

The previously described[11] methods and apparatus were employed. The results, expressed in defined calories (1 calorie = 4.1833 int. joules), are given in Table I and shown graphically in Fig. 1. The atomic mass values used are: Fe, 55.85; Mn, 54.93; Zr, 91.22; Si, 28.06; and O, 16.0000.

The $MnSiO_3$ and $ZrSiO_4$ results show normal behavior. The correction for Fe_2O_3 and excess SiO_2 in the latter instance ranges from 2.21% at 52.7° K. to 0.60% at 294.8° K.

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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) Kelley, THIS JOURNAL, **61**, 471 (1939).

(8) Kelley, *ibid.*, **61**, 1217 (1939).

(9) These materials were prepared and analyzed by Dr. G. W. Marks, Metallurgical Division, Bureau of Mines. The author gratefully acknowledges this assistance.

(10) Bowen, Schairer and Posnjak, *Am. J. Sci.*, **25**, 273 (1933).

(11) Kelley, THIS JOURNAL, **63**, 1137 (1941).

Fe_2SiO_4 has a marked "hump" in its specific heat curve, the peak being at 65.0° K. Examination of the measurements just above and just below this temperature shows that the specific heat rises to at least 17.9 calories per gram formula mass or about twice the normal value at this temperature. The total heat absorption between 51.34° K. and 71.68° K. was found to be 225.2 calories per gram formula mass.

There are no previous low-temperature specific heat data with which to compare the present results. Esser, Averdieck and Grass,[12] in the temperature range 100 to 1200°, and Roth and Bertram,[13] in the temperature range 96 to 888°, have measured mean specific heats of Fe_2SiO_4. The two sets of results are in poor agreement. For example, the former obtain 38.8 calories per gram formula mass at an average temperature of 50° (0 to 100°) while the latter obtain 31.5 at an average temperature of 58° (20 to 96°). The present results obviously extrapolate to an intermediate value, which, however, is nearer that of Roth and Bertram.

TABLE I

SPECIFIC HEAT OF Fe_2SiO_4 (203.76 G.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
52.2	8.630	92.3	11.93	205.1	24.98
54.6	9.494	102.1	13.34	214.9	25.73
57.3	10.66	113.0	14.83	224.7	26.60
59.5	11.90	123.5	16.20	235.3	27.44
62.1	13.88	133.5	17.48	245.2	28.19
65.5	12.69	144.2	18.77	255.7	28.97
69.5	9.568	154.1	19.84	265.5	29.69
73.6	9.768	164.5	21.11	275.5	30.25
77.6	10.20	174.4	22.06	285.5	31.01
80.3	10.42	184.7	23.13	295.2	31.57
84.3	10.89	194.8	24.05		

SPECIFIC HEAT OF $MnSiO_3$ (130.99 G.)

52.6	3.591	103.3	8.754	218.1	17.01
55.5	3.847	113.6	9.729	228.3	17.60
59.2	4.227	123.7	10.62	238.3	18.05
63.1	4.643	134.2	11.51	248.1	18.58
67.4	5.105	144.6	12.35	257.9	18.97
72.2	5.625	154.9	13.07	268.2	19.46
80.3	6.452	164.8	13.87	278.1	19.83
84.3	6.857	175.2	14.55	286.8	20.24
93.6	7.768	185.1	15.17	294.8	20.52

SPECIFIC HEAT OF $ZrSiO_4$ (183.28 G.)

52.7	1.857	113.9	9.089	215.4	18.59
55.8	2.158	124.1	10.32	225.2	19.29
59.7	2.536	134.3	11.47	235.7	19.97
64.1	3.031	144.8	12.50	245.6	20.65
68.7	3.572	154.7	13.57	255.4	21.28
73.3	4.124	165.0	14.63	265.8	21.84
80.6	5.000	175.2	15.50	275.8	22.34
84.9	5.520	185.0	16.31	285.5	22.80
93.9	6.654	195.5	17.17	294.8	23.37
103.4	7.835	205.6	17.93		

(12) Esser, Averdieck and Grass, *Arch. Eisenhüttenw.*, **6**, 289 (1933).

(13) Roth and Bertram, *Z. Elektrochem.*, **35**, 297 (1929).

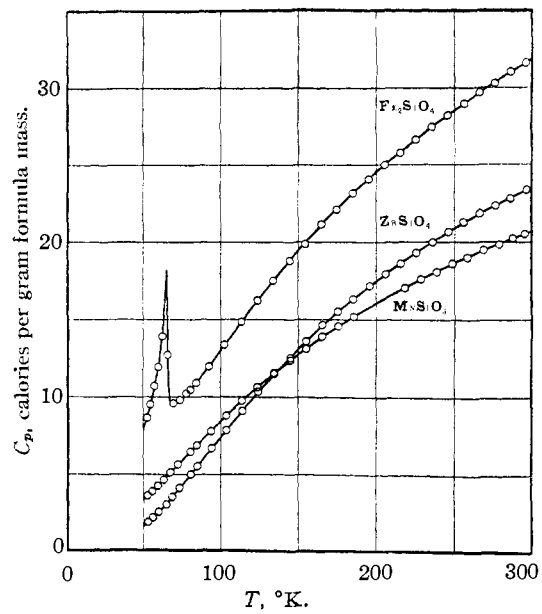

Fig. 1.—Specific heats of Fe_2SiO_4, $MnSiO_3$ and $ZrSiO_4$.

Entropies

The function sum $D(195/T) + 2E(410/T) + 2E(1027/T)$ closely represents the $MnSiO_3$ specific heat results between 51 and 200° K. and differs by only 1% or less from the measurements at higher temperatures. The extrapolated portion of the entropy, below 50.12° K., was computed using this set of functions of which the Einstein terms contribute only an insignificant amount. The entropy increment between 50.12 and 298.16° K. in all instances was computed graphically in the usual manner from a plot of C_p against log T.

Similarly, the results for $ZrSiO_4$ are represented adequately between 51 and 298° K. by $D(321/T) + 2E(407/T) + 2E(796/T) + E(1624/T)$, which was used in computing the extrapolated portion of the entropy.

The maximum in the specific heat of Fe_2SiO_4 at 65.0° K. precludes the fitting of the data by such a function sum, and the extrapolation is necessarily much more uncertain. The procedure in this instance was to extend, in a manner that appeared reasonable, the specific-heat curve below the maximum to bring it into coincidence with a Debye function, $D(138/T)$.

The entropy values are given in Table II. The error in the $S_{298.16°}$ result for Fe_2SiO_4 has been made abnormally large to make allowance for the before-mentioned increased uncertainty in extrapolation to 0° K. The limits of error given apply only to the measurements and extrapolations as made. It is probable that some correction to the values for Fe_2SiO_4 and $MnSiO_3$ will be required in the future, when more information is available, to allow for unextracted magnetic entropy, as illustrated by the very recent work of Stout and Giauque[14] on nickel sulfate heptahydrate and Stout[15] on copper sulfate.

TABLE II

ENTROPIES AT 298.16°K.

	Fe_2SiO_4	$MnSiO_3$	$ZrSiO_4$
0–50.12°K. (extrapolation)	3.74	1.69	0.56
50.12–298.16°K. (graphical)	31.70	19.61	19.53
$S_{298.16}$	35.4 ± 1.4	21.3 ± 0.3	20.1 ± 0.3

Related Thermal Data

The heat of formation of $MnSiO_3$ is not known with high accuracy. Bichowsky and Rossini[16] have adopted $\Delta H_{291.16} = -301,300$, based upon the work of Mulert.[17] The correction to 298.16° K. is negligible. From the entropy of $MnSiO_3$ and the values[18] for Mn, Si, and O_2, respectively (7.61, 4.50 and 49.03), there is computed $\Delta S_{298.16} = -64.4$, which in turn leads to the free energy of formation from the elements, $\Delta F°_{298.16} = -282,100$.

(14) Stout and Giauque, THIS JOURNAL, **63**, 714 (1941).

(15) Stout, *J. Chem. Phys.*, **9**, 285 (1941).

(16) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 94.

(17) Mulert, *Z. anorg. allgem. Chem.*, **75**, 198 (1912).

(18) Kelley, "Bureau of Mines Bulletin 434," 1941, 115 pp.

Troitzsch[19] has obtained $\Delta H_{350.16} = -11,300 \pm 300$ for the reaction $2FeO + SiO_2(\alpha\text{-quartz}) = Fe_2SiO_4$, corresponding to $\Delta H_{298.16} = -11,100$. The heat of formation of α-quartz also was determined by Troitzsch[19,20] as $\Delta H_{293.16} = -208,300 \pm 350$, and the correction to 298.16° K. is negligible. The heat of formation of FeO has been determined several times by Roth and his coworkers. The most recent value, that of Roth and Wienert,[21] is $\Delta H_{293.16} = -64,650$, corresponding to $\Delta H_{298.16} = -64,670$. These figures yield $\Delta H_{298.16} = -348,700$ as the heat of formation of Fe_2SiO_4 from the elements. Employing $S_{298.16} = 6.47$ for $Fe(\alpha)$[18] and the before-mentioned entropies of Fe_2SiO_4, Si and O_2, there is computed $\Delta S_{298.16} = -80.1$. The corresponding free energy of formation from the elements is $\Delta F°_{298.16} = -324,800$.

The free energy of formation of $ZrSiO_4$ cannot be calculated, as heat of formation data are not available.

Summary

Specific heat measurements of Fe_2SiO_4, $MnSiO_3$ and $ZrSiO_4$ have been made in the temperature range 51 to 298° K. Fe_2SiO_4 has a marked maximum in its specific heat curve, with the peak at 65.0° K.

The entropies at 298.16° K. are 35.4 ± 1.4 for Fe_2SiO_4, 21.3 ± 0.3 for $MnSiO_3$, and 20.1 ± 0.3 for $ZrSiO_4$.

The free energies of formation from the elements have been computed for $MnSiO_3$ and Fe_2SiO_4 as, respectively, $\Delta F°_{298.16} = -282,100$ and $\Delta F°_{298.16} = -324,800$.

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(19) Troitzsch, (a) Diss. Braunschweig, 1936; (b) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 3rd suppl. vol. 3, 1936, p. 2776.

(20) Ref. 19(b), p. 2749.

(21) Ref. 19(b), p. 2774.