mixed with DMF, it forms a deliquescent solid which slowly crystallizes on standing in DMF. DMF is readily recovered from these crystals upon hydrolysis. They are slightly soluble in DMF, exhibit fourfold symmetric extinction, but were not isolated since they are decomposed in part by vacuum drying at 56° or by washing with petroleum ether. Approximate analysis places their molar ratios between 1:7 and 1:9. The infrared spectrum of $SiBr_4 \cdot 6.8$ DMF (Fig. 1E) shows bands at 1340 and 780 cm.$^{-1}$ in addition to those of DMF; ν_3 of silicon tetrabromide (487 cm.$^{-1}$) was not active in this compound. The high molar ratio precludes addition. A plausible hypothesis which can explain the lability of some of the DMF is that some or all of the bromine atoms ionize,[4] each forming a silicon substituted quaternary ammonium salt, and that this ionic compound separates from DMF solution with several moles of DMF of crystallization.

Our experiments have confirmed A. Hardin's report of $SiCl_4 \cdot 2NC_5H_5$,[5] but we could find no evidence for addition of tri-*n*-butylamine or dimethylaniline to silicon tetrachloride. Mixing either of the latter two bases with silicon tetrachloride produces no precipitate nor any appreciable heating effect. Thermal analysis of the system silicon tetrachloride–dimethylaniline (Fig. 2) shows that if 1:1 and 1:2 addition compounds do form, they are liquid at room temperature and highly dissociated in the liquid phase. Of the three amines, pyridine has an intermediate basicity and is the least hindered donor, so steric interference seems to offer the only explanation of these results.

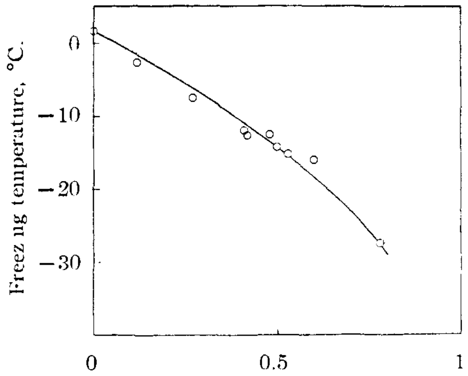

Fig. 2.—The system $SiCl_4$–$(CH_3)_2NC_6H_5$.

Experimental

Forty-five millimoles of DMF absorbed 23 millimoles of gaseous silicon tetrafluoride which was prepared by thermal decomposition of barium fluosilicate; the product was freed of excess silicon tetrafluoride by evaporation under vacuum. *Anal.* Calcd. for $SiF_4 \cdot 2DMF$: C, 28.80; H, 5.64; F, 30.4. Found: C, 28.81; H, 5.81; F, 30.6. Fluorine was determined by titration with thorium nitrate. When 31.0 millimoles of pyridine was added to 8.81 millimoles of silicon tetrachloride in carbon tetrachloride there was an immediate exothermic reaction to produce a white precipitate. The supernant liquid was analyzed for pyridine by separation as the hydrochloride and Volhard titration. The supernatant liquid contained 12.7 millimoles of pyridine; calcd. for a precipitate of $SiCl_4 \cdot 2NC_5H_5$, 13.4 millimoles. The infrared spectra were taken in pressed iodide disks with a Baird double beam recording spectrophotometer.

We take pleasure in expressing our gratitude to Professor M. K. Wilson for his helpful suggestions and his aid in interpreting the infrared spectra.

The financial assistance of the Mallinckrodt Fund is greatly appreciated.

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[4] K. Gingold, F. G. Rochow, D. Seyferth, A. C. Smith, Jr., and R. West, THIS JOURNAL, **74**, 6306 (1952).

[5] A. Hardin, *J. Chem. Soc.*, **51**, 40 (1887).

Low Temperature Heat Capacity, Entropy at 298.16°K., and High Temperature Heat Content of Sphene ($CaTiSiO_5$)

BY E. G. KING, R. L. ORR AND K. R. BONNICKSON

RECEIVED MARCH 31, 1954

This paper covering fundamental research in mineral thermodynamics represents one phase of the Bureau of Mines research and development program directed toward the more effective utilization of our mineral resources.

Sphene ($CaTiSiO_5$) is a common accessory constituent of both igneous and metamorphic rocks, probably the most widely occurring titanium mineral other than ilmenite and rutile. No thermodynamic data have been available previously for this substance. This paper reports heat capacity measurements in the temperature range 51 to 298°K., the entropy at 298.16°K., and high temperature heat content measurements in the temperature range 298 to 1811°K.

Material.—Sphene was prepared from a stoichiometric mixture of reagent grade calcium carbonate, pure (99.95%) silica and pure (99.8%) titania. The mixture was heated in platinum to about 50° above the fusion temperature, held for a time to assure uniform composition and to permit complete evolution of carbon dioxide, and then poured onto a polished nickel plate. The resulting crystalline mass was broken up to a suitable size for filling the calorimeter containers. The X-ray diffraction pattern of the product agreed with that in the A. S. T. M. catalog. Chemical analysis gave 28.59% calcium oxide, 30.66% silica and 40.68% titania, as compared with the theoretical values—28.60, 30.65 and 40.75%. Further evidence regarding purity may be derived from the heat content data below the melting point, as will be mentioned later.

Measurements and Results.—The low temperature heat capacity measurements were made with previously described apparatus.[1] using 252.17 g. mass of sphene. The results, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, appear in Table I. The molecular

TABLE I

LOW TEMPERATURE HEAT CAPACITY OF $CaTiSiO_5$ (MOL. WT., 196.07)

T, °K.	C_p, cal./deg. mole	*T*, °K.	C_p, cal./deg. mole	*T*, °K.	C_p, cal./deg. mole
52.30	3.888	114.30	14.04	216.12	26.89
56.37	4.448	124.31	15.62	226.14	27.82
60.99	5.161	135.90	17.37	235.99	28.67
65.43	5.899	146.05	18.84	245.69	29.49
70.04	6.653	156.20	20.18	255.73	30.28
74.51	7.377	165.86	21.41	265.82	31.04
79.65	8.320	176.14	22.67	278.23	31.94
82.94	8.814	185.86	23.79	287.65	32.60
93.10	10.54	196.01	24.87	296.95	33.09
103.65	12.27	206.19	25.88	298.16	(33.21)

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[1] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

weight is taken as 196.07 g. No unusual behavior of the substance was observed; the heat capacity increases in a regular manner from 3.888 cal./deg. mole at 52.30°K. to 33.09 at 296.95°K.

The entropy increment between 51.00 and 298.16°K. was obtained by Simpson-rule integration of the C_p against log T plot as 29.18 cal./deg. mole. To obtain the entropy below 51.00°K., the measured heat capacity values were fitted with an empirical sum of Debye and Einstein functions, $D(200/T) + 3E(373/T) + 3E(760/T) + E(1551/T)$. This sum represents the data over the entire measured range to within 0.5% and gives 1.70 cal./deg. mole as the entropy at 51.00°K. The entropy at 298.16°K. is $S^\circ_{298.16} = 30.9 \pm 0.2$ cal./deg. mole.

The entropy of sphene at 298.16°K. and other entropy values compiled by Kelley[2] lead to $\Delta S_{298.16} = -0.6 \pm 0.3$ for the entropy of formation from calcium oxide, quartz and rutile. Likewise, the entropy of formation from wollastonite ($CaSiO_3$) and rutile is $\Delta S_{298.16} = -0.7 \pm 0.3$, and from perovskite ($CaTiO_3$) and quartz, $\Delta S_{298.16} = 0.0 \pm 0.3$.

The heat content measurements for the temperature range 298 to 1811°K. also were made with previously described apparatus.[1] The results, expressed in defined calories per mole, are in Table II and Fig. 1.

TABLE II

MEASURED HEAT CONTENT VALUES ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
375.4	2,735	1006.1	30,220	1579.6	59,170[a]
478.4	6,815	1105.4	35,050	1636.0	63,140[a]
579.2	10,980	1194.2	39,310	1665.4	74,740[a]
675.9	15,170	1296.5	44,240	1675.4	92,880
691.9	15,820	1387.8	48,740	1679.5	93,250
811.2	21,330	1495.5	54,110	1748.3	97,800
902.2	25,490	1542.3	56,770[a]	1811.7	102,030

[a] Values show premelting effects.

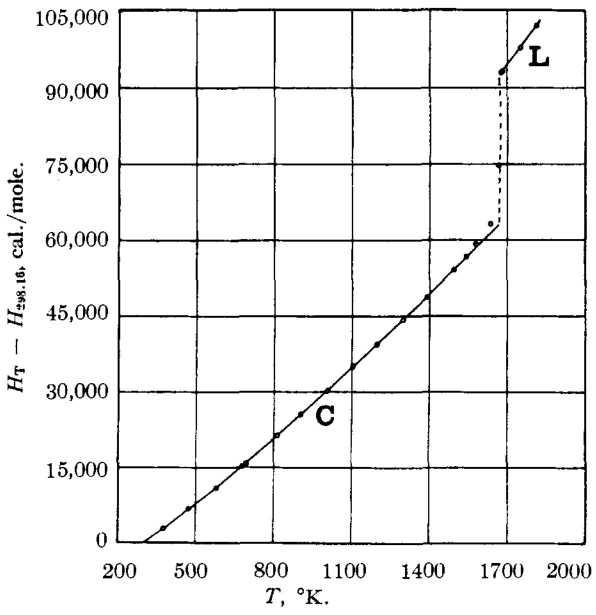

Fig. 1.—Heat content of $CaTiSiO_5$ above 298.16°K.: C, crystals; L, liquid.

The substance melts at 1,670°K., the heat and entropy of fusion being 29,590 cal./mole and 17.72 cal./deg. mole. The heat content of the crystals follows a regular course and averages about 2% less than the heat content sum for the constituent oxides. No evidence of premelting appeared below the 1,542.3°K.-point. This point and others labeled (a) in Table II show premelting effects. Assuming liquid-soluble, solid-insoluble impurities, the reported data indicate the purity of the sphene to be 99.0 mole %.

The heat content of the crystals between 298.16 and 1670°K. is represented by the following equation, with an average deviation of less than 0.3%

$$H_T - H_{298.16} = 42.39T + 2.77 \times 10^{-3}T^2 + 9.63 \times 10^5T^{-1} - 16{,}115$$

The heat content of the liquid increases linearly with temperature between 1670 and 1811°K. The measured results are represented to within 0.1% by the equation

$$H_T - H_{298.16} = 66.80T - 18{,}990$$

Table III contains smooth values of the heat content and entropy increments above 298.16°K. The latter were calculated to match the former by means of the method of Kelley.[3]

TABLE III

HEAT CONTENT AND ENTROPY INCREMENTS ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg. mole	T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg. mole
400	3,750	10.78	1300	44,430	62.87
500	7,690	19.56	1400	49,350	66.51
600	11,860	27.16	1500	54,340	69.96
700	16,230	33.89	1600	59,400	73.22
800	20,750	39.93	1670	62,980(c)	75.41
900	25,380	45.38	1670	92,570(l)	93.13
1000	30,070	50.32	1700	94,570	94.32
1100	34,800	54.83	1800	101,250	98.14
1200	39,580	58.99			

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(2) K. K. Kelley, *U. S. Bur. Mines Bull.*, 477 (1950).

(3) K. K. Kelley, *ibid.*, 476 (1949).

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Studies in Low Concentration Chemistry. IX. Some Investigations on Zinc

BY GEORGE K. SCHWEITZER AND WM. N. BISHOP

RECEIVED APRIL 30, 1954

The purpose of these studies was to investigate the radiocolloidal properties,[1] solvent extraction characteristics[2] and the tendency spontaneously to deposit on platinum foil[3] of zinc in low concentration aqueous solutions using zinc-65 as a radioactive tracer.

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(1) G. K. Schweitzer and W. M. Jackson, *J. Chem. Educ.*, **29**, 513 (1953).

(2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 72; J. F. Steinbach and H. Freiser, *Anal. Chem.*, **25**, 881 (1953); C. B. Cook and J. F. Duncan, "Modern Radiochemical Practice," Oxford University Press, New York, N. Y., 1952, p. 11.

(3) G. K. Schweitzer and D. L. Wilhelm, THIS JOURNAL, **75**, 5432 (1953).