[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low-temperature Heat Capacities and Entropies at 298.16°K. of Crystalline Calcium Orthosilicate, Zinc Orthosilicate and Tricalcium Silicate

BY S. S. TODD

Low temperature heat capacity measurements of crystalline calcium orthosilicate (β-variety), zinc orthosilicate (willemite), and tricalcium silicate were made throughout the temperature range from 51 to 298°K. The entropies at 298.16°K. were obtained as 30.5 ± 0.2, 40.3 ± 0.3 and 31.4 ± 0.3 cal./deg./mole, respectively. Free energies of formation at 298.16°K. from the oxides and from the elements are listed.

Introduction

Several earlier publications[1,2] of this Laboratory have dealt with low-temperature heat capacities and entropies of silicates. This paper presents similar data for calcium orthosilicate (β-variety), zinc orthosilicate (willemite) and tricalcium silicate. No previous heat capacity and entropy data have been reported for these substances, but their heats of formation were determined recently by King.[3]

Materials

The two calcium silicates are identical with those studied by King,[3] who gave details of the methods of preparation and tests for purity. The calcium orthosilicate analyzed 64.47% calcium oxide, 34.68% silica, 0.32% iron and aluminum oxides, 0.14% magnesia, and 0.02% ignition loss, as compared with the theoretical 65.13% calcium oxide and 34.87% silica. Its X-ray diffraction agreed with the pattern given by Clark[4] for the β-variety. The tricalcium silicate analyzed 73.64% calcium oxide, 26.21% silica, 0.13% iron and aluminum oxides, 0.11% magnesia, and 0.05% ignition loss, as compared with the theoretical 73.69% calcium oxide and 26.31% silica. Its X-ray diffraction pattern agreed with the work of Hansen.[5]

The zinc orthosilicate comprised 169.41 g. of the willemite studied by King[3] and 61.85 g. of willemite synthesized here.[6] The latter was made by prolonged (13 days total) heating of an intimate mixture of finely ground, high-purity zinc oxide and silica at temperatures from 1200 to 1350°, part of the time in water vapor and part in air. Intermittent grindings, analyses and adjustments of composition were conducted. The final product contained 26.86% silica, as compared with the theoretical 26.95%.

The major portion of the willemite heat capacity sample, retained from the work of King, showed no evidence of uncombined oxides on X-ray examination. The newly prepared material, which constitutes 26.75% of the total, showed evidence of uncombined silica, variously estimated and possibly as much as 2.7%. The correction of the heat capacity results for the indicated maximum amount of uncombined oxides is virtually negligible (0.00 to 0.09%, depending upon temperature). The composite analysis of the measured sample was 72.95% zinc oxide and 26.92% silica (theoretical, 73.05 and 26.95%, respectively).

Measurements and Results

The heat capacity measurements were made with previously described[7] apparatus. The masses of the substances employed were 207.75 g. of calcium orthosilicate, 231.26 g. of zinc orthosilicate and 124.53 g. of tricalcium silicate.

The measured results, expressed in defined calories per mole (1949 International Atomic Weights) are listed in Table I.

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
Ca_2SiO_4 (mol. wt. 172.22)					
52.66	4.084	114.59	14.77	216.22	25.66
57.02	4.814	124.62	16.21	226.42	26.39
61.61	5.649	138.68	18.08	236.16	27.06
66.24	6.533	146.69	19.05	245.79	27.74
70.92	7.392	155.86	20.08	256.19	28.40
75.66	8.249	165.96	21.20	266.31	29.04
80.72	9.180	175.94	22.19	276.22	29.57
85.20	9.963	185.93	23.14	286.41	30.17
94.81	11.63	195.92	24.01	296.48	30.62
104.39	13.17	206.22	24.82	298.16	(30.74)
Zn_2SiO_4 (mol. wt. 222.82)					
53.01	5.361	114.59	14.46	216.21	24.31
57.34	6.047	124.69	15.68	225.86	25.07
62.00	6.859	136.01	16.98	236.15	25.76
66.68	7.668	146.09	18.08	245.68	26.40
71.55	8.444	155.90	19.06	256.06	27.06
76.37	9.174	165.83	20.04	266.03	27.71
80.63	9.842	175.95	20.96	276.00	28.29
85.08	10.50	185.88	21.86	286.51	28.88
94.71	11.87	195.89	22.68	296.24	29.37
104.42	13.15	206.18	23.49	298.16	(29.48)
Ca_3SiO_5 (mol. wt. 228.30)					
54.26	5.569	114.71	19.28	216.33	34.30
58.11	6.374	124.74	21.26	226.01	35.31
62.13	7.324	136.27	23.40	236.19	36.24
66.58	8.387	146.18	25.15	245.95	37.07
71.20	9.469	156.05	26.68	256.33	37.97
75.83	10.55	166.07	28.20	266.88	38.76
80.73	11.74	176.24	29.60	276.75	39.56
85.62	12.88	186.17	30.90	286.50	40.35
95.10	15.04	196.00	32.06	296.53	40.89
104.67	17.12	206.33	33.18	298.16	(41.08)

It is evident that all three substances behave normally over the entire investigated temperature range. The curves for the orthosilicates are substantially parallel over most of the range. Divergence is evident at the lowest temperatures, zinc orthosilicate tending to maintain the higher heat capacity, as would be expected. The heat capacity of tricalcium silicate does not differ greatly from the sum of those for calcium orthosilicate and calcium oxide in the range from 100 to 298°K. At lower temperatures, however, data for the tricalcium silicate deviate from this sum, being about 10% greater at 50°K.

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[1] K. K. Kelley, THIS JOURNAL, **61**, 471 (1939); **61**, 1217 (1939); **63**, 2750 (1941); **65**, 339 (1943).

[2] S. S. Todd, *ibid.*, **72**, 4742 (1950).

[3] E. G. King, *ibid.*, **73**, 656 (1951).

[4] C. B. Clark, *J. Am. Ceram. Soc.*, **29**, 25 (1946).

[5] W. C. Hansen, *ibid.*, **11**, 68 (1928).

[6] The author expresses his thanks to K. R. Bonnickson, Chemist, Pacific Experiment Station, Bureau of Mines, for the synthesis and tests of this material.

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

Entropies at 298.16°K.

The entropies were calculated in the usual manner. The portions above 51°K. were obtained by Simpson-rule integrations of C_p *vs.* log T plots. The following empirical sums of Debye and Einstein functions, which fit the measured data over the entire temperature range to within the amounts shown in parentheses, were used in making the extrapolations to 0°K.

$$\mathrm{Ca_2SiO_4}:\ D\left(\frac{216}{T}\right) + 3E\left(\frac{340}{T}\right) + 2E\left(\frac{749}{T}\right) + E\left(\frac{1238}{T}\right) \quad (0.5\%)$$

$$\mathrm{Ca_3SiO_5}:\ D\left(\frac{188}{T}\right) + 4E\left(\frac{329}{T}\right) + 3E\left(\frac{714}{T}\right) + E\left(\frac{996}{T}\right) \quad (1.0\%)$$

$$\mathrm{Zn_2SiO_4}:\ D\left(\frac{146}{T}\right) + 3E\left(\frac{343}{T}\right) + 3E\left(\frac{1012}{T}\right) \quad (1.2\%)$$

The entropy results appear in Table II.

TABLE II

MOLAL ENTROPIES

	Ca_2SiO_4	Ca_3SiO_5	Zn_2SiO_4
0–51°K. (extrap.)	1.55	2.08	2.90
51–298 16°K. (meas.)	28.96	38.20	28.46
$S^\circ_{298.16}$	30.5 ± 0.2	40.3 ± 0.3	31.4 ± 0.3

Related Thermal Data

Employing the heat of formation values obtained by King[3] and entropy values from the compilation of Kelley,[8] the free energies of formation at 298.16° K. from the oxides (quartz and calcium oxide) and from the elements may be calculated. The results are given in Table III. For comparison, values for calcium metasilicate (wollastonite), the heat of formation of which was determined by Torgeson and Sahama,[9] also are included.

TABLE III

FREE ENERGIES OF FORMATION

Substance	$\Delta H_{298.16}$	$\Delta S_{298.16}$	$\Delta F^\circ_{298.16}$
	From oxides		
$CaSiO_3$	−21,250	−0.4	−21,130
Ca_2SiO_4	−30,190	1.5	−30,640
Ca_3SiO_5	−26,980	1.8	−27,520
Zn_2SiO_4	−6,990	0.5	−7,140
	From elements		
$CaSiO_3$	−378,600	−68.4	−358,200
Ca_2SiO_4	−539,500	−91.9	−512,000
Ca_3SiO_5	−688,100	−116.6	−653,300
Zn_2SiO_4	−378,700	−91.0	−351,600

It is evident that tricalcium silicate is thermodynamically unstable at room temperature with respect to the β-variety of the orthosilicate and calcium oxide ($\Delta F^\circ_{298.16} = 3{,}120$); but the orthosilicate is stable with respect to wollastonite and calcium oxide ($\Delta F^\circ_{298.16} = -9{,}510$). The much greater stability of calcium orthosilicate with respect to the oxides, as compared with zinc orthosilicate, is striking and in line with the known chemistry of these substances.

BERKELEY 4, CALIF. RECEIVED JANUARY 22, 1951

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[8] K. K. Kelley, *U. S. Bur. Mines Bulletin*, 477 (1950).

[9] D. R. Torgeson and Th. G. Sahama, THIS JOURNAL, **70**, 2156 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

The Occurrence of Plutonium in Nature

BY CHARLES A. LEVINE* AND GLENN T. SEABORG

Plutonium has been chemically separated from seven different ores and the ratios of plutonium to uranium determined. This ratio was found to be fairly constant ($\sim 10^{-11}$) in pitchblende and monazite ores, in which the uranium content varied from 50 to 0.24%, and substantially less in carnotite and fergusonite. All the plutonium obtained was Pu^{239}, probably formed by the U^{238} in the ore through capture neutrons and decay by $U^{238} + n \longrightarrow U^{239} \xrightarrow{\beta^-} Np^{239} \xrightarrow{\beta^-} Pu^{239}$. The sources of neutrons include the spontaneous fission of uranium, (α,n) reactions caused by the action of α particles from the heavy radioactive elements on the nuclei of light elements in the ore, and cosmic rays. In the cases of the pitchblende ores, the spontaneous fission of uranium and (α,n) reactions contribute the major portion of the neutrons. In thorium ores which contain a low abundance of uranium, neutrons from (α,n) reactions are probably dominant. The lower concentration of plutonium in carnotite and fergusonite is a result of the presence of neutron absorbing impurities in these ores. No isotopes of plutonium other than Pu^{239} were found. An upper limit for Pu^{238} in Canadian and Belgian Congo pitchblendes was set at one part Pu^{238} in 4×10^{15} parts ore. An upper limit for the hypothetical Pu^{244} in Brazilian monazite was set (assuming a half-life of 10^8 years for Pu^{244}) at one part Pu^{244} in 3.6×10^{11} parts ore. It is postulated that U^{233} and the "missing" neptunium (4n + 1) radioactive series are present in nature in minute quantities, formed by the absorption of neutrons by Th^{232}, thus: $Th^{232} + n \longrightarrow Th^{233} \xrightarrow{\beta^-} Pa^{233} \xrightarrow{\beta^-} U^{233}$. Smaller amounts of Np^{237}, from the reactions $U^{238}(n,2n)U^{237} \xrightarrow{\beta^-} Np^{237}$, are also present. The amounts of transplutonium elements present in nature seem to be too small to detect by present means unless some unknown, very long-lived isotopes exist.

I. Introduction

The discovery of naturally occurring plutonium was reported in 1942 by Seaborg and Perlman[1] who chemically separated the plutonium from a sample of Canadian pitchblende concentrate and estimated the plutonium content of the ore to be roughly one part in 10^{14} by weight. From considerations of possible methods of formation of plutonium, it was assumed that the plutonium was Pu^{239}.

Because of the more complete knowledge of the chemical properties of plutonium and the availability of the multi-channel differential pulse

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* Now at the Dow Chemical Company, Pittsburg, Calif.

[1] G. T. Seaborg and M. L. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 1.3 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949); THIS JOURNAL, **70**, 1571 (1948).