[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low-temperature Heat Capacities and Entropies at 298.15°K. of Crystalline Lead Metasilicate, Lead Orthosilicate and Cadmium Metasilicate

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Heat capacities of lead metasilicate, lead orthosilicate and cadmium metasilicate were measured between 51 and 298°K. The entropies at 298.15°K. are 26.2 ± 0.3, 44.6 ± 0.5 and 23.3 ± 0.2 cal./deg. mole, respectively.

The literature contains no low temperature heat capacity data or experimental entropy values for crystalline silicates of lead and cadmium. This paper supplies values for the metasilicates of lead and cadmium, and the ortho silicate of lead. Kelley[2] has reported similar data for lead amorphous metasilicate.

Materials

Lead metasilicate was prepared from natural quartz (99.9% pure) and lead carbonate. (Lead carbonate was obtained by treating a solution of reagent grade lead nitrate with a solution of reagent grade ammonium carbonate, washing the precipitate and drying at 140°.) A stoichiometric mixture of the carbonate and quartz was heated for a total of 9 days at 700°, 5 days at 650° and 9 days at 500°, with grinding and mixing between heats. Analysis of the product gave 78.78% lead oxide and 21.20% silica, as compared with the theoretical 78.79 and 21.21%. The X-ray diffraction pattern agreed with that reported by McMurdie and Bunting.[3] There was no evidence of unreacted oxides.

Lead orthosilicate also was prepared from the natural quartz and lead carbonate. The proper stoichiometric mixture was heated for 36 days at 680–700°. The material was ground and mixed six times during this treatment. The final product analyzed 88.16% lead oxide (theory, 88.14%) and 11.83% silica (theory, 11.86%). The X-ray diffraction pattern matched that of McMurdie and Bunting[3]; no lines of the constituent oxides were present.

Cadmium metasilicate was prepared by heating a mixture of reagent grade cadmium oxide and natural quartz (99.9% pure) for 23 days at temperatures between 900 and 1050°. The material was ground and mixed three times during this treatment. Analysis of the product gave 68.12% cadmium oxide (theory, 68.12%) and 31.94% silica (theory, 31.88%). The X-ray diffraction pattern agreed with the ASTM catalog.

Measurements and Results

The apparatus and method have been described.[4] Table I contains the experimental heat capacity values, expressed in defined calories per deg. mole (1 cal. = 4.1840 abs. joules). Molecular weights accord with the 1954–55 Report on Atomic Weights.[5]

No abnormal behavior was observed for any of the substances in the measured temperature range. The heat capacity values for crystalline lead metasilicate are lower at all temperatures than those reported by Kelley[2] for the amorphous substance, by amounts ranging from 0.67 cal./deg. mole at 50°K. to 0.91 at 298.15°K. This deviation is in the direction which is to be expected from a consideration of the theory.

Entropies at 298.15°K.—The entropy increments between 51 and 298.15°K. were calculated by Simpson-rule integrations of C_p against log T plots. The increments between 0 and 51°K. were obtained by extrapolation, using the following empirical combinations of Debye and Einstein functions, which fit the measured heat-capacity data between 51 and 298°K. within the limits indicated.

TABLE I

HEAT CAPACITIES (CAL./DEG. MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		$PbSiO_3$ (mol. wt., 283.30)			
53.25	6.161	114.57	11.86	216.15	18.15
58.01	6.674	124.68	12.64	226.19	18.62
62.79	7.174	135.99	13.46	236.11	19.04
67.35	7.658	145.70	14.16	245.61	19.45
72.01	8.135	156.08	14.85	256.29	19.91
76.60	8.572	166.01	15.47	266.17	20.30
80.11	8.909	175.81	16.02	276.10	20.67
83.77	9.250	185.81	16.60	286.45	21.08
94.51	10.21	195.85	17.11	296.03	21.45
104.69	11.07	205.98	17.66	298.15	(21.52)
		Pb_2SiO_4 (mol. wt., 506.51)			
53.07	11.04	114.56	19.34	216.14	28.33
57.33	11.72	124.87	20.49	226.05	28.97
61.80	12.43	135.95	21.68	236.16	29.51
66.44	13.13	145.67	22.70	245.86	30.07
71.18	13.81	155.85	23.63	256.18	30.63
75.96	14.50	166.18	24.58	266.33	31.24
81.28	15.22	175.68	25.37	276.26	31.77
86.15	15.86	185.75	26.18	286.46	32.17
94.86	16.99	195.90	26.91	295.99	32.67
105.15	18.26	206.10	27.69	298.15	(32.78)
		$CdSiO_3$ (mol. wt., 188.50)			
53.19	4.663	114.41	10.87	216.23	17.66
57.35	5.165	124.65	11.73	225.79	18.14
61.74	5.715	135.81	12.62	235.94	18.57
66.27	6.234	145.55	13.35	245.61	19.02
71.07	6.716	155.60	14.08	256.39	19.51
75.96	7.212	165.71	14.76	266.23	19.93
80.84	7.713	175.87	15.38	276.16	20.34
85.08	8.138	185.89	16.00	287.01	20.74
94.70	9.076	195.85	16.57	296.04	21.11
104.65	10.02	206.29	17.15	298.15	(21.17)

$PbSiO_3$:

$$D(140/T) + E(213/T) + 2E(596/T) + E(1440/T), \quad (0.7\%)$$

Pb_2SiO_4:

$$D(78.5/T) + 2E(164/T) + 3E(547/T) + E(1379/T), \quad (0.8\%)$$

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

(3) H. F. McMurdie and E. N. Bunting, *J. Research Natl. Bur. Standards*, **23**, 543 (1939).

(4) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686, 1941.

(5) E. Wichers, THIS JOURNAL, **78**, 3235 (1956).

$CdSiO_3$:

$$D(192/T) + E(246/T) + 2E(630/T) + E(1366/T),\ (0.7\%)$$

The entropy calculations are summarized in Table II.

Table II

Entropies at 298.15°K. (cal./deg. mole)

Substance	$S^0_{51} - S^0_0$ (extrap.)	$S^0_{298.15} - S^0_{51}$ (meas.)	$S^0_{298.15}$
$PbSiO_3$	3.40	22.85	26.2 ± 0.3
Pb_2SiO_4	7.80	36.84	44.6 ± .5
$CdSiO_3$	2.02	21.25	23.3 ± .2

The entropy of crystalline lead metasilicate is 2.5 units lower than obtained by Kelley[2] for the amorphous substance. Using the entropy values for cadmium oxide and quartz listed by Kelley[2] and that for PbO(red) given by the author,[6] the following entropies of formation from the constituent oxides are obtained for the crystalline silicates: $PbSiO_3$, $\Delta S_{298.15} = 0.6$; Pb_2SiO_4, $\Delta S_{298.15} = 3.4$, and $CdSiO_3$, $\Delta S_{298.15} = 0.2$ cal./deg. mole.

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[6] E. G. King, This Journal, **80**, 2400 (1958).

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Heats of Combustion and Formation of Metal Carbonyls. III. Iron Pentacarbonyl; The Nature of the Bonding in Metal Carbonyls[1]

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The heat of combustion of iron pentacarbonyl has been measured by bomb calorimetry and leads to a value of −182.6 ± 1.7 kcal./mole for ΔHf^0_{298} of liquid $Fe(CO)_5$. In the combustion process metallic iron and several iron oxides are produced and each of these was determined analytically. The heat of formation of $Fe(CO)_5$ together with the heats of formation of the carbonyls of Ni, Cr, Mo and W permit calculation of the mean bond dissociation energies in all of these compounds. When these energies are corrected for the valence state promotion energies according to the classical view of the bonding in metal carbonyls, it is found that the energies of dissociation of the metal–carbon bonds to valence states are of reasonable magnitude, thus suggesting that the assumed picture of the bonding is reasonable.

I. Introduction

In previous papers we have reported the heats of combustion and heats of formation of the carbonyls of the group VI[2] elements, *i.e.*, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, and subsequently of $Ni(CO)_4$.[3] In the present paper we report the same quantities for $Fe(CO)_5$. With all of these data it is now possible to draw certain conclusions concerning the nature and strengths of the metal–carbon bonds in these molecules, and this is done in section IV.

Previous efforts to determine the heat of formation of iron pentacarbonyl have also utilized combustion calorimetry. In discussing these previous results and those presented in this paper, the following thermochemical equations are pertinent

$$Fe(CO)_5(l) = Fe(CO)_5(g) \quad \Delta H_v = 8.9 \text{ kcal./mole} \quad (1)$$

$$Fe(CO)_5(l) + 13/4O_2(g) = 1/2Fe_2O_{3(s)} + 5CO_2(g) \quad (\Delta H_{\text{comb.}}) \quad (2)$$

$$Fe(s) + 5C(s) + 5/2O_2(g) = Fe(CO)_5(l) \ (\Delta Hf^0) \quad (3)$$

In all cases the temperature is taken to be 298°K. and the substances are in their standard states according to present conventions.[4] The heat of vaporization of $Fe(CO)_5$ has been determined by several workers, the quoted value being that given in the NBS tables,[4] where references to the original papers may be found. About thirty years ago Roth[5] reported some work by Doepke on the heat of combustion of iron pentacarbonyl in which samples sealed in glass were ignited by the burning of Vaseline. It was stated that almost pure Fe_3O_4 was formed; no mention was made of an examination for metallic iron or Fe_2O_3 or of an analysis of the gaseous combustion products. The average heat of combustion from two experiments was reported to be −372.5 kcal./mole, presumably involving liquid $Fe(CO)_5$ and with Fe_3O_4 as the only iron containing product. From this, presumably using the old Berthelot and Thomsen value for the heat of formation of CO, Roth obtained for the reaction, $Fe(\alpha) + 5CO \rightarrow Fe(CO)_5$ (*sic*), an energy of −54.4 kcal., a result stated by him to be in good agreement with Mittasch's value of −54.2 ± 0.7 kcal.[6] Presumably, since Roth makes this comparison and since Mittasch's figure applied to liquid $Fe(CO)_5$, Roth's equation should also specify the liquid state for $Fe(CO)_5$. Mittasch's result appears in the text of a speech and only as an entry in an extensive table of the physical properties of iron pentacarbonyl. It is disconcerting that Mittasch also reports a heat of combustion (states and experimental details unspecified) of −384.5 kcal./mole, 12 kcal./mole higher than Roth's, although their quoted heats of formation agree. From these data the NBS tables[4] derived a value of ΔHf^0_{298} according to equation 3 of −187.8 kcal./mole. The uncertainty and possible error in this value indicated the need for a redetermination before attempting any thermochemical arguments concerning the bonding in this substance.

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[1] Presented before the Division of Inorganic Chemistry, 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

[2] F. A. Cotton, A. K. Fischer and G. Wilkinson, This Journal, **78**, 5168 (1956).

[3] A. K. Fischer, F. A. Cotton and G. Wilkinson, *ibid.*, **79**, 2044 (1957).

[4] Selected Values of Chemical Thermodynamic Properties, U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

[5] W. A. Roth, *Angew. Chem.*, **42**, 981 (1929).

[6] A. Mittasch, *ibid.*, **41**, 827 (1928).