The results with zinc amalgam and eight oxidizing agents reveal no general relationship of rate to electrode potential; but there is some basis for the belief that such a relationship exists provided the nature of the oxidizing agent (metal ions as contrasted with other substances) is taken into consideration.

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A Modified Calorimeter for High Temperatures. The Heat Content of Silica, Wollastonite and Thorium Dioxide Above 25°[1,2]

BY J. C. SOUTHARD[3]

Introduction

The thermodynamic properties of metallurgically important substances have been investigated for a number of years at the Pacific Experiment Station of the Federal Bureau of Mines. Data are now available which permit the calculation of reaction free energies, at room temperature, of a large number of such substances. However, the high-temperature heat content data necessary to calculation of equilibria and heat balances at the elevated temperatures at which most metallurgical processes occur are lacking in a large number of instances. This is particularly true of oxides and sulfides.

Description of Apparatus

The present apparatus for heat contents at high temperatures (to 1500°) is a modification of the standard one in which a capsule containing the sample is heated in a furnace to a determined temperature and at a given moment dropped into a calorimeter of known heat capacity. The modifications described below were introduced primarily to remove the necessity for dismantling a considerable portion of the apparatus to return the sample to the furnace in preparation for another determination. This permits more rapid operation than has previously been consistent with good work.

Capsule (A) (Fig. 1) containing the sample is a 2.0 × 2.0-cm. cylinder made of 0.2-mm. 90% platinum–10% rhodium alloy.

The furnace (B) has a heating element made of B. and S. no. 20 80% platinum–20% rhodium alloy wire wound on a 1 × 14 inch alundum tube. The furnace is surrounded by a water jacket, except for a 1-inch hole at the top and at the bottom for passage of the capsule. When the capsule is in position the top hole is closed with a refractory plug 3 inches long, and the bottom hole with a water-cooled gate (D) which rotates on a shaft (E) eccentric with the center line of the furnace. The heat exchange of the furnace with the calorimeter is thus made virtually zero even when the furnace is at 1500°.

The temperature distribution in the furnace at 1100° is such that a 1.25-inch length is isothermal to 1°. This length is sufficient to hold the capsule and thermocouple junction. This isothermal space is made possible without elaborate precautions by the favorable length to bore ratio of 14 to 1.

The temperature of the capsule was measured by a platinum–platinum–10% rhodium thermocouple (not shown in Fig. 1) which was within 0.25 inch of the top of the capsule and within the above-mentioned isothermal space. The thermocouple was first calibrated by comparison with another bearing a Bureau of Standards certificate and during the course of the determinations on each substance by melting a 0.25-inch length of gold wire and a similar one of palladium wire between the elements of the couple as described in Bureau of Standards Research Paper 768. All calibrations were made with the thermocouple in its usual place in the furnace. Repeated calibration was necessary when working at 1500°.

The capsule is suspended in the furnace by a B. and S. no. 32 90% platinum–10% rhodium alloy wire. The wire is led out through a small hole in the top of the furnace and attached to a steel plunger fastened by a spring trigger at the top of a vertical brass tube. The brass tube is slotted throughout most of its length to permit free fall of the plunger. The lower 6 inches (15 cm.) is not slotted, so that the fall of the plunger

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(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

(2) Not copyrighted.

(3) Chemist, Metallurgical Division, Bureau of Mines.

is checked by an air cushion relieved by the slow escape of air through the small hole which provides passage for the suspension wire. Dimensions are so arranged that the capsule falls from the furnace with nearly the acceleration of gravity until it is entering the calorimeter, where its fall is checked by the plunger coming against the air cushion. The water-cooled furnace gate is provided with a thin slot on an arc of the proper radius which permits the suspension wire to pass through the gate when the latter is closed.

The calorimeter proper (C) is a gold-plated cylindrical copper 5-by-8-inch (12.6 × 20.3 cm.) block, supported by three bakelite knife edges in a gold-plated brass case. The calorimeter assembly is immersed to the level (H) in an oil-bath maintained at 25.00 ± 0.01°. The receiving well is closed, except for the brief interval during transfer of the capsule, by a circular copper gate 0.75 inch (1.9 cm.) thick. This gate is mounted on the same shaft as the water-cooled furnace gate and has a similar slit for accommodating the capsule suspension wire. The receiving well itself is in a removable tapered plug bearing a 100-ohm manganin wire heater, which is used in the electrical calibration of the heat capacity of the calorimeter. The calorimeter thermometer is a transposed bridge arrangement of two copper and two manganin resistances suggested by Maier[4] and used previously in a heat-of-solution calorimeter.[5] It covers about half the cylindrical surface of the copper block and is protected by a tapered copper sleeve which has a driving fit onto the similarly tapered surface of the block itself. The thermometer is calibrated in terms of the amount of electrical energy in defined calories (1 cal. = 4.1833 int. joules) required to increase the thermometer e. m. f. 1 μv. All electrical measurements were made with a shielded White double potentiometer. Standard resistances used had been compared with one calibrated by the Bureau of Standards. The e. m. f. of the standard cell was checked by comparison with a group of three standard cells used only for reference. Time was measured with a calibrated stop watch. The average deviation for a set of eight determinations of the thermometer e. m. f.–calibration energy relationship was 0.03%.

An atmosphere of carbon dioxide was maintained in the calorimeter and furnace by a con-

tinuous flow of about 50 cc. a minute. This reduced the heat exchange rates to about 60% of those obtained in air. The heat exchange rate amounts to 0.002° per minute-degree and is reproducible from day to day to about 0.00002° per minute-degree. The equilibrium time is about six minutes during electrical calibration and eight to twenty minutes during actual determinations, depending on the thermal conductivity of the material under investigation.

The apparent heat content above 25° of the empty capsule was determined by actual experiment. It is assumed, as by White,[6,7] that the loss of heat from the full capsule is the same as for the empty, during the time required for it to fall from the furnace to the calorimeter.

Fig. 1.—Capacities for heat contents above 298°K., showing copper block calorimeter (C), platinum–rhodium high temperature furnace (B), and capsule dropping mechanism (A-F).

Materials

The wollastonite (CaSiO₃) used in this work was a naturally occurring mineral from Riverside County, Calif. By analysis, it was found to contain 51.52% SiO₂, 47.85% CaO, and 0.36% R₂O₃; total, 99.73%. No correction was made for the impurities.

The silica glass sample was prepared from transparent "vitreosil" glass tubing by crushing and screening out the fines. A residue of only 0.05% was obtained on treating this sample with a mixture of sulfuric and hydrofluoric acids in the usual manner.

The thorium dioxide was purified by G. W. Marks of this laboratory from a Kahlbaum product. The latter was dissolved in concentrated hydrochloric acid solution by digestion on a hot-plate overnight. Pure thorium dioxide was
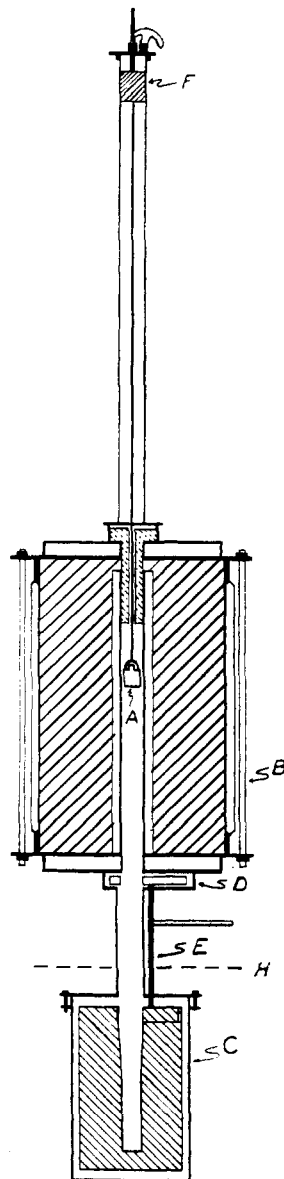
(4) C. G. Maier, J. Phys. Chem., 34, 2860 (1930).

(5) J. C. Southard, Ind. Eng. Chem., 32, 442 (1940).

(6) W. P. White, quoted by Sosman, ref. 7.

(7) "The Properties of Silica," Chemical Catalog Co., 1927, pp. 832–833.

obtained from this solution by the analytical procedure of Meyer and Speter described by Hillebrand and Lundell,[8] using an iodate precipitation for separation from rare earths. The original Kahlbaum sample was found to contain 5.1% rare earths. Analysis of the purified product as used gave ThO_2 99.40, 99.17%, common metals 0.29, 0.23%, rare earths (by difference) 0.31, 0.60%. Again no correction was made for impurities.
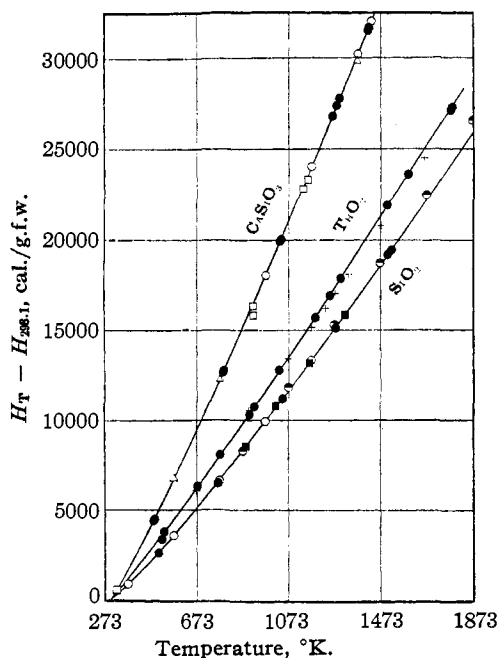

Fig. 2.—Heat contents above 298.1°K. of wollastonite, thorium dioxide and silica glass: ●, This work; O, White; □, Roth and Bertram; △, Wagner; +, Jaeger and Veenstra; ◐, Wietzel; ■, Schläpfer and Debrunner.

Results

The results of the measurements are presented in Fig. 2 and Tables I, II and III as the difference

TABLE I

WOLLASTONITE (G. F. W. = 116.14)

(1) This work; (2) White; (3) Wagner; (4) Roth and Bertram; (5) von Gronow and Schwiete.

Temp., °K.	$H_T - H_{298.1}$ Obsd.	Obsd. − Calcd.	Investigator
1294.8	27,770	+ 47	(1)
1293.1	27,680	+ 9	(1)
1418.9	31,540	− 50	(1)
1041.4	20,010	− 20	(1)
1036.7	19,910	+ 18	(1)
790.8	12,740	+ 22	(1)
787.4	12,620	− 13	(1)
488.4	4,470	− 16	(1)
484.6	4,390	0	(1)
1423.1	31,700	− 23	(1)
1265.8	26,790	− 40	(1)
1261.7	26,810	+107	(1)
1282.5	27,380	+ 36	(1)
973.1	18,004	− 5	(2)
1173.1	24,017	+ 22	(2)
1373.1	30,200	+ 43	(2)
1433.1	32,060	+ 22	(2)
573.1	6,726	+ 18	(3)
773.1	12,228	+ 2	(3)
973.1	18,058	+ 49	(3)
1173.1	23,925	− 70	(3)
1373.1	29,846	−307	(3)
323.1	518	− 7	(4)
778.1	12,125	−243	(4)
978.1	18,051	−101	(4)
977.1	18,133	+ 6	(4)
919.1	16,305	−121	(4)
1135.1	22,784	− 58	(4)
1157.1	23,304	−205	(4)
573.1	6,710	+ 2	(5)
773.1	12,230	+ 4	(5)
973.1	18,050	+ 41	(5)
1173.1	23,890	−105	(5)
1373.1	29,770	−387	(5)

(8) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis." John Wiley & Sons, New York, N. Y., 1929, p. 420.

TABLE II

THORIUM DIOXIDE (G. F. W. = 264.12)

(1a) This work, 1st series; (1b) this work, 2d series; (6) Jaeger and Veenstra.

Temp., °K.	$H_T - H_{298.1}$ Obsd.	Obsd. − Calcd.	Investigator
1301.3	17,850	+ 18	(1a)
1299.0	17,810	+ 22	(1a)
1031.8	12,760	+ 56	(1a)
1029.6	12,730	+ 67	(1a)
777.3	8,090	+ 45	(1a)
776.5	8,060	+ 28	(1a)
1505.2	21,900	+ 66	(1a)
1511.8	21,960	− 5	(1a)
1780.1	27,100	−290	(1a)
522.6	3,430	−171	(1a)
532.1	3,770	+ 8	(1a)
926.3	10,740	− 10	(1a)
924.2	10,720	+ 8	(1a)
1786.6	27,280	−243	(1a)
677.3	6,310	+ 38	(1a)
675.9	6,230	− 17	(1a)
1190.7	15,680	− 24	(1b)
1186.7	15,650	+ 22	(1b)
1591.6	23,660	+100	(1b)
1593.1	23,590	− 1	(1b)
1252.6	16,900	+ 8	(1b)
904.8	10,300	− 56	(1b)
671.3	6,060	−105	(6)
774.1	7,952	− 37	(6)
903.9	10,329	− 10	(6)
904.0	10,309	− 32	(6)
1074.0	13,398	− 97	(6)
1173.3	15,164	−208	(6)
1232.7	16,217	−291	(6)
1274.2	17,025	−282	(6)
1335.4	18,097	−396	(6)
1335.4	18,130	−363	(6)
1476	20,788	−482	(6)
1664.3	24,485	−457	(6)

TABLE III

SILICA GLASS (G. F. W. = 60.06)

(1) This work; (2a) White, 1919; (2b) White, 1933; (7) Schläpfer and Debrunner.

Temp., °K.	$H_T - H_{298.1}$ Obsd.	Obsd. − Calcd.	Investigator
1046.1	11,180	+ 36	(1)
1044.3	11,140	+ 27	(1)
507.1	2,580	−102	(1)
506.4	2,540	−132	(1)
1279.6	15,100	− 23	(1)
766.0	6,490	− 99	(1)
763.1	6,440	−103	(1)
1280.4	15,100	− 36	(1)
1507.3	19,160	+ 16	(1)
1522.3	19,420	+ 7	(1)
373.1	857	− 17	(2a)
573.1	3,575	− 64	(2a)
773.1	6,664	− 37	(2a)
973.1	9,935	+ 4	(2a)
1173.1	13,326	+ 53	(2a)
773.4	6,623	− 82	(2b)
874.3	8,260	− 57	(2b)
1173.2	13,305	+ 25	(2b)
573.0	3,547	− 91	(2b)
371.5	841	− 13	(7)
577.1	3,648	− 50	(7)
764.1	6,576	+ 17	(7)
886.1	8,521	+ 13	(7)
1019.1	10,766	+ 73	(7)
1163.1	13,173	+ 55	(7)
1319.1	15,760	+ 51	(7)

in the heat content at the initial furnace temperature, $t_1°$, and the final calorimeter temperature, $t_2°$, which in each instance has been corrected to 25°. The data have been fitted with equations of the type used in Bureau of Mines Bull. 371 in representing previous high-temperature data. These equations are expressed in degrees absolute so that they may be used conveniently in thermodynamic calculations. Their derivatives with respect to temperature are given as "true" specific heat equations, and they will show no points of inflection in the temperature range covered by the data.

A detailed analysis of the accuracy of the data will not be attempted here. However, it should be pointed out that the principal source of error lies in the determination of the temperature of the sample as it hangs in the furnace. This is due both to (1) lack of isothermality of the region containing the capsule and the thermocouple, and (2) the lack of constancy of the e. m. f.–temperature relationship of the thermocouple. In fact, if care is not taken, the latter uncertainty may outweigh the first. Although data are given here to 0.1° for purposes of comparison with the equations set up,

an accuracy of better than 1° below the gold point (1063°) and several degrees above this temperature cannot be claimed. The necessity for repeated checking of the thermocouple calibration, when working at high temperatures, cannot be overemphasized.

The present data on wollastonite, together with those of White,[9] Wagner,[10] Roth and Bertram,[11] and von Gronow and Schwiete[12] are presented in Table I. The equations

(Eq. 1) $H_T - H_{298.1} = 26.64_3 T + 1.796 \times 10^{-3} T^2 + (6.517 \times 10^5 / T) - 10,288$ (273 to 1450 °K.)

(Eq. 1a) $C_p = 26.64 + 3.992 \times 10^{-3} T - (6.517 \times 10^5 / T^2)$ (273 to 1450 °K.)

represent the present data to within about 0.25% from room temperature to the transition temperature of wollastonite to pseudo-wollastonite (about 1180°). Column (5) of Table I gives the deviation of this equation from the experimental data. Equation (1) is based upon the values $H_{973.1} - H_{273.1} = 18,500$ cal., $H_{1433.1} - H_{273.1} = 32,530$ cal., and $C_{p298.1} = 20.38$ cal./deg. It fits the present data within their limit of accuracy and also those of White and Wagner. The data of Roth and Bertram are in general lower, while those of von Gronow and Schwiete are in good agreement below 900°.

The data on thorium dioxide are summarized in Table II. The only previous work on this substance is that of Jaeger and Veenstra.[13] The equations

Eq. 2) $H_T - H_{298.1} = 16.44_7 T + 1.173 \times 10^{-3} T^2 + (2.124 \times 10^5 / T) - 5720$ (298 to 1790 °K.)

(Eq. 2a) $C_p = 16.45 + 2.346 \times 10^{-3} T - (2.124 \times 10^5 / T^2)$ (298 to 1790 °K.)

represent the present data to 0.5% except at 1500°, where the deviation is about 1%. Equation 2 is based upon the values $H_{533.1} - H_{298.1} = 3,780$ cal., $H_{1173.1} - H_{298.1} = 15,370$ cal., $H_{1773.1} - H_{298.1} = 27,250$ cal. The data of Jaeger and Veenstra are always lower than the value given by Equation (2), the deviation from their data being over 2% at 1200°. Jaeger and Veenstra made their determinations primarily to enable them to correct for the oxide content of a sample of thorium metal they were using, and they fur-

(9) W. P. White, Am. J. Sci., 47, 1 (1919).

(10) H. Wagner, Z. anorg. Chem., 208, 1 (1932).

(11) W. A. Roth and W. W. Bertram, Z. Elektrochem., 35, 297 (1929).

(12) H. E. von Gronow and H. E. Schwiete, Z. anorg. Chem., 216, 185 (1933).

(13) F. M. Jaeger and W. A. Veenstra, Proc. Acad. Sci. Amst., 37, 327 (1934).

nish no description of the method of purification or of the analysis of their sample of thorium oxide. The large hump that they give in their "true" specific heat curve would seem to be largely a product of the six-term equation with which they fit their mean specific heat data. No evidence of it could be found in this work.

The present data on silica glass are given in Table III, with those of White[14] and Schläpfer and Debrunner.[15] The data of Magnus[16] and Roth and Bertram[17] on "amorphous" silicon dioxide are not included, nor are the data of Bornemann and Hengstenberg,[18] while those of Wietzel[19] are shown only in Fig. 2. The equations (3)

(Eq. 3) $H_T - H_{298.1} = 14.784T + 1.111 \times 10^{-3}T^2 +$
(4.306 $\times 10^{-5}/T$) $- 5950$ (298 to 1520°K.)

(Eq. 3a) $C_p = 14.78 + 2.222 \times 10^{-3}T - (4.306 \times 10^{-5}/T^2)$ (298 to 1520°K.)

represent the data of this work and of White within 0.4% above 700°C. but may deviate by about 100 calories in the region 200–500°. The equation represents the data of Schläpfer and Debrunner more closely, in general. The values $H_{973.1} - H_{298.1} = 9930$ cal., $H_{1473.1} - H_{298.1} = 18,530$, and $C_{p298.1} = 10.60$ cal./deg. were used in deriving equation (3).

It may be noted that the more recent data of White are lower and in better agreement with the present work than the earlier. This may be due to a difference in samples. His earlier work was on quartz that had been fused in the laboratory, while the more recent work was on clear silica tubing, as was the present investigation. This suggests that there may be a small variation in the

(14) W. P. White, *Am. J. Sci.*, **47**, 1 (1919); This Journal, **55**, 1050 (1933).

(15) P. Schläpfer and P. Debrunner, *Helv. Chim. Acta*, **7**, 31 (1924).

(16) A. Magnus, *Physik. Z.*, **14**, 5 (1913).

(17) W. A. Roth and W. W. Bertram, *Z. Elektrochem.*, **35**, 297 (1929).

(18) K. Bornemann and O. Hengstenberg, *Metall u. Erz*, **17**, 339 (1920).

(19) R. Wietzel, *Z. anorg. Chem.*, **116**, 75 (1921).

heat content above room temperature of silica glass, depending on its history. However, such variations amounted to only about 0.5% in White's work, and the good agreement of the three sets of data in Table III indicates they should never amount to much.

The use of 1000°K. instead of the conventional 298.1°K. has been recommended as a reference temperature for metallurgical calculations. The difference in heat content and entropy between 1000°K. and 298.1°K. accordingly is given in Table IV.

TABLE IV

Substance	$H_{1000°K.} - H_{298.1°K.}$	$S_{1000°K.} - S_{298.1°K.}$
Wollastonite	18,800	31.5
Thorium dioxide	12,160	20.5
Silica glass	10,380	17.2

The values of $H_{1000} - H_{298.1}$ were obtained from equations 1, 2, and 3 after applying a small correction for deviation of the equations from the data. The values of $S_{1000°K.} - S_{298.1°K.}$ were obtained both by integration of the equations 1a, 2a, 3a and by graphic integration from a plot of H vs. $1/T$. The two methods gave results agreeing within 0.1 entropy unit.

Summary

1. A calorimeter for high-temperature specific heats has been constructed which possesses improved ease of manipulation and gives results that agree with the best previous work.

2. The heat content above room temperature has been determined for wollastonite (to 1150°), thorium dioxide (to 1514°), and silica glass (to 1250°). The data have been fitted with simple equations and the heat capacity derived therefrom.