[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

High Temperature Thermodynamic Properties of Molybdenum Trioxide[1]

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RECEIVED OCTOBER 20, 1952

The high temperature heat content of molybdenum trioxide has been measured from 273.16 to 1300°K. using an ice calorimeter in conjunction with a dropping furnace. From these data, the high temperature thermodynamic properties have been calculated. To present the complete picture in one place, the same properties were calculated for temperatures below 273.16°K. Thus, data from 0 to 1300°K. are tabulated.

Material.—The molybdenum trioxide used in these measurements was a high purity material obtained from a commercial supplier. This material was then sublimed at low pressures yielding a coarse crystalline solid in which the assayed molybdenum was 66.8 ± 0.07%; insoluble in NH_3, 0.001%; non-volatile with HCl at 450°, 0.005%; heavy metals and alkali metals, spectroscopic trace.

Apparatus.—The ice calorimeter used in this work was essentially similar to that developed by Ginnings[2] and co-workers at the National Bureau of Standards. To accommodate larger quantities of heat, the calorimeter was enlarged somewhat over the dimensions used by Ginnings. In addition, the crucible and well were made with a slight taper thus permitting better contact between them. A slow, constant stream of helium gas was passed through the calorimeter well during operation of the instrument.

To check the calibration factor of the ice calorimeter, a heater was constructed to fit snugly in the tapered well. This consisted of a hollow copper block on whose outside tapered surface a recess was machined in which the heater winding was placed. The resistance of the heater approximated 130 ohms. The heater block made metallic contact with the calorimeter well above and below the winding. Since the results obtained in the calibration were within the uncertainty associated with the revised value obtained by Ginnings,[3] it was decided to use his value of 270.46 absolute joules per gram of mercury.

The furnace used to heat the sample was a somewhat conventional vertical tube furnace wound with heavy gage nichrome wire. To obtain a section in the center of the heated zone as nearly isothermal as possible, a 24 inch length of heavy wall copper pipe was placed within the refractory tube of the furnace. The length of winding in the furnace was 24 inches, giving a ratio of length to bore of about 18 calibers. With this construction, it was felt that constant temperature conditions obtained. Actually, if the thermocouple in the furnace was positioned so as to be near, but not touching, the crucible, the fluctuations amounted to several tenths of a microvolt. With the couple in definite, but light, contact with the crucible, no fluctuations within the sensitivity (about 0.2 microvolt) of the potentiometer system could be detected. Throughout the measurements purified nitrogen was passed through the furnace.

The thermocouple used for temperature measurements consisted of the usual platinum–platinum–10% rhodium combination. Since the recommendations for the International Temperature Scale (1948)[4] do not advise the use of a thermocouple below 630°, special pains were taken in the calibration of the couple. To this end, use was made of standard samples of tin, lead, aluminum and copper obtained from the National Bureau of Standards. In addition the silver point was used. For this purpose high purity silver was prepared in this Laboratory by means of repeated chemical purification of silver metal. Furthermore, to obtain a better fitting curve at lower temperatures, the sulfur and steam points were also used. These measurements resulted in two temperature–e.m.f. equations to cover the range from 0 to 1100°. The two curves were made to coincide at the sulfur point.

Energy measurements during calibration, as well as temperature measurements, were made with a White double potentiometer. A fifth decade of the Lindeck-Rothe[5] type was used with the "White," making measurements to 0.2 microvolt possible. During calibration, use was made of standard resistances and standard cells which had been calibrated at the National Bureau of Standards.

Experimental Results

Enthalpy of MoO_3.—To obtain the heat content of MoO_3 using the value at 273.16°K. as a reference, 68.1865 g. of compound was packed in a platinum–3% rhodium crucible. Using 143.95 as the molecular weight, this corresponds to 0.47368 mole of MoO_3. The measured values of relative heat content obtained[6] were used to give the smoothed values recorded in Table I in the manner described below. The data recorded in Table I are based on the "defined calorie" which is assumed to have a value of 4.1840 absolute joules.

Melting Point of MoO_3.—In view of the fact that the heat content measurements extended into the liquid range, it was necessary to determine the melting point of MoO_3. This was done after completion of the calorimetric measurements by the method of thermal analysis. Time–temperature curves were taken, starting with the sample a few degrees above the melting point. From these determinations, it was found that the melting point of MoO_3 under one atmosphere pressure is 1068.36°K. The extreme variations of the individual determinations from this average were somewhat less than 0.1 degree. This compares favorably with a previous value[7] of 795°.

Heat of Fusion of MoO_3.—Using the smoothed values of heat content for solid and liquid at the melting point recorded above, it was found that

$$\Delta H_{1068.36}\ (\text{fusion}) = 12{,}540\ \text{cal./mole}$$

Thermodynamic Properties of MoO_3.—As was mentioned above, the smoothed values of heat content are entered in column 2 in Table I in the form of the function $(H_T - H_0)/T$. To prepare this column, different smoothing methods were used above and below the melting point. The measured data from 273.16 to 1068.36°K. were plotted and a smooth curve drawn from which the values leading to column 2 were obtained. For the liquid data the method of least squares was used as outlined by Milne.[8] The equation obtained by this process is

$$H_T - H_{273.16} = 1.25151 \times 10^5 - 2.19714 \times 10^2 T + 1.47790 \times 10^{-1} T^2 - 2.33333 \times 10^{-5} T^3 \ (\text{per mole of liquid}) \quad (1)$$

Differentiating this expression gives C_p for the liquid. These values are recorded in column 3, Table I. The equation is

$$C_p = -2.19714 \times 10^2 + 2.95580 \times 10^{-1} T - 7.00000 \times 10^{-5} T^2 \ (\text{per mole of liquid}) \quad (2)$$

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(1) From a thesis submitted by Lee A. Cosgrove to the Carnegie Institute of Technology, in partial fulfilment of the requirements for the degree of Doctor of Science. This work was performed under Contract N 6 ori-47 T.O.8 between the U. S. Office of Naval Research and Carnegie Institute of Technology.

(2) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 583 (1947).

(3) D. C. Ginnings, T. B. Douglas and A. F. Ball, *ibid.*, **45**, 23 (1950).

(4) H. F. Stimson, *ibid.*, **42**, 209 (1949).

(5) H. B. Brooks and A. W. Spinks, *ibid.*, **9**, 781 (1932).

(6) A table of the measured data can be obtained from the senior author by addressing an inquiry to him at Carnegie Institute of Technology.

(7) F. Hoermann, *Z. anorg. allgem. Chem.*, **177**, 145 (1928).

(8) W. E. Milne, "Numerical Calculus," Princeton University Press, Princeton, N. J., 1949, p. 242.

TABLE I

THERMODYNAMIC PROPERTIES OF MoO_3

T, °K.[a]	$(H_T - H_O)/T$, cal./degree mole	C_p, cal./degree mole	S_T, cal./degree mole	$-(F_T - H_O)/T$, cal./degree mole
70[b]	1.9470	4.720	2.9539	1.0070
75	2.1458	5.132	3.2937	1.1479
100	3.2214	7.403	5.0777	1.8563
125	4.2671	9.385	6.9618	2.6947
150	5.2603	11.05	8.8244	3.5641
175	6.1973	12.58	10.641	4.4435
200	7.0733	13.79	12.400	5.3270
225	7.8811	14.88	14.087	6.2059
250	8.6326	15.90	15.707	7.0741
273.16	9.2854	16.75	17.152	7.8669
275	9.3357	16.82	17.265	7.9294
298.16	9.9482	17.60	18.656	8.7082
300[c]	9.9953	17.66	18.765	8.7695
350	11.167	19.13[d]	21.565	10.399
400	12.251	20.13	24.210	11.959
450	13.192	20.91	26.648	13.456
500	14.003	21.55	28.894	14.891
550	14.730	22.10	30.990	16.260
600	15.372	22.59	32.942	17.569
650	15.954	23.03	34.779	18.824
700	16.476	23.45	36.502	20.026
750	16.941	23.84	38.118	21.178
800	17.371	24.22	39.655	22.285
850	17.778	24.58	41.128	23.350
900	18.170	24.93	42.547	24.377
950	18.541	25.27	43.910	25.369
1000	18.885	25.60	45.213	26.328
1050	19.209	25.93	46.466	27.257
1068.36(c)	19.324	26.05	46.823	27.499
1068.36(1)[e]	31.062	16.02	58.561	27.499
1100	30.702	20.72	59.101	28.399
1150	30.419	27.63	60.176	29.756
1200	30.441	34.18	61.491	31.050
1250	30.716	40.39	63.014	32.298
1300	31.201	46.24	64.713	33.512

[a] 0°C. is taken as 273.16°K. [b] By Debye and Einstein extrapolation. See reference 10. [c] Values to and including 300°K. from low temperature measurements. [d] Solid C_p values from 350°K. to melting point from equation 4. [e] Values for the liquid in columns 2 and 3 obtained from equations 1 and 2, respectively.

In view of the fact that there is considerable use for heat content data, for the solid, in the form of equations as given by Kelley,[9] his method was used to obtain the following equation for one mole of solid MoO_3

$$H_T - H_{298.16} = 20.07T + 2.95 \times 10^{-3}T^2 + 3.68 \times 10^{-5}T^{-1} - 7481 \text{ (1.0\% 298–1068°K.)} \quad (3)$$

Differentiation yields for one mole of solid

$$C_p = 20.07 + 5.90 \times 10^{-3}T - 3.68 \times 10^{5}T^{-2} \quad (4)$$

Values of solid heat capacity obtained from this last equation are entered in column 3, Table I.

By making an appropriate plot[9] of the measured heat content data, it was possible to obtain, by graphical integration, entropy values which are entered in column 4. Combination of entropy and heat content in the usual way gave the data in column 5 for the function $(F_T - H_O)/T$.

In view of the fact that low temperature measurements were available from this Laboratory,[10] it was felt that a useful purpose would be served by including these data in the table, thereby having in one place values for the four thermodynamic functions from 0 to 1300°K. Accoridngly, these data were replotted and recalculated to give the values listed from 70 to 300°K. Obviously, the low temperature data are combined with the high temperature values thereby using the 0°K. values as the reference point for H_T, S_T and F_T in the table.

In Table I the three functions S_T, $(H_T - H_O)/T$ and $(F_T - H_O)/T$ are given to five significant figures for future calculation purposes only. This also applies to the constants in equations 1 and 2 for the liquid. Investigation of the experimental technique and the curve smoothing process in the case of the high temperature entropy and enthalpy shows that these values have an average precision of about 0.1%. This value would be higher at lower temperatures and lower in the neighborhood of 1300°K.

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(9) K. K. Kelley, United States Bureau of Mines Bulletin No. 476.

(10) H. Seltz, F. J. Dunkerley and B. J. DeWitt, THIS JOURNAL, **65**, 600 (1943).