are held less firmly. The removal of rare earth ions by regeneration of the base-exchange material may also be carried out in a fractional manner with the largest, most loosely-held ions being removed first.

WEST LAFAYETTE, INDIANA RECEIVED OCTOBER 15, 1942

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

Heat Capacities and Entropies of Molybdenum and Tungsten Trioxides

BY HARRY SELTZ, F. J. DUNKERLEY AND B. J. DEWITT[1]

The heat capacity measurements reported in this paper were carried out in a calorimeter described in a previous publication.[2] Several improvements have been made, however, in this apparatus. A new calorimeter can has been constructed, wound with no. 40 double silk insulated gold wire containing 0.175% of silver, and the heavy calorimeter shield was rewound with the same wire. These windings have shown consistently constant temperature-resistance readings over a period of a year. To increase the mass of the shield a heavy copper screw top was added, giving a total mass of 4890 g. The vacuum vessel for the calorimeter was rebuilt with a seal in the form of a V, which was partly filled with eutectic composition solder and into which the lid fitted loosely. The solder in this well was melted by a coil of chromel wire wound around the outside. With this type of seal no vacuum difficulties, such as were sometimes encountered with a bolted lid, appeared, and pressures between 10^{-5} and 10^{-6} mm. were readily maintained using a two-stage vapor pump backed by a Cenco Hyvac. For pumping off liquid nitrogen a second large capacity container, completely inclosing the calorimeter set-up, was made vacuum tight by a similar type of seal, and a high capacity three-stage steam ejector was employed in this pumping-off operation. Temperatures as low as 58°K. have been reached by this means.

Materials.—The molybdic oxide used in these measurements was Baker's Analyzed, containing less than 0.1% of impurities. Under the microscope it consisted of very small transparent rhombic crystals. This material was dried in an oven to constant weight and was kept in a desiccator until ready for use. The total charge in the calorimeter was 139.055 g. *in vacuo*, or 1.0316 moles.

The tungstic oxide was prepared by the method described by Schumb and Hartford.[3] A hot solution of reagent grade sodium tungstate was treated with hydrochloric acid, and the precipitated tungstic acid was washed free from chlorides. This was dissolved in hot ammonium hydroxide, and ammonium tungstate was crystallized from this solution. After three recrystallizations the hot solution of the purified tungstate was treated with nitric acid and the precipitated tungstic acid was digested on a water-bath for several hours. This material, which filtered readily, was washed, dried in an oven and finally ignited to 775° for ten hours. It was kept in a desiccator in the dark until ready for use. Under the microscope it showed very fine rhombohedral crystals. The charge of the oxide used in the heat capacity measurements was 135.446 g. *in*

TABLE I

MOLAL HEAT CAPACITIES OF MoO_3

Temp., °K.	Molal C_p	Temp., °K.	Molal C_p	Temp., °K.	Molal C_p
70.05	4.73	134.07	10.00	212.87	14.35
74.48	5.09	142.25	10.40	220.05	14.66
79.75	5.53	144.65	10.68	224.12	14.79
83.95	5.90	151.50	11.12	230.39	15.08
87.70	6.27	154.87	11.32	234.69	15.25
91.15	6.48	159.51	11.66	240.15	15.53
97.55	7.20	163.47	11.90	250.67	15.96
101.79	7.58	169.45	12.30	254.86	16.15
105.58	7.90	179.40	12.78	260.30	16.31
109.22	8.23	182.50	13.08	268.20	16.60
114.00	8.61	186.37	13.16	280.32	17.01
117.65	8.75	192.46	13.47	294.72	17.50
124.72	9.19	201.05	13.85	298.73	17.60
129.30	9.70	208.92	14.21		

TABLE II

MOLAL HEAT CAPACITIES OF WO_3

Temp., °K.	Molal C_p	Temp, °K.	Molal C_p	Temp., °K.	Molal C_p
62.90	4.21	120.52	9.58	212.20	15.75
63.37	4.34	126.86	10.18	216.13	15.99
68.98	4.87	136.30	10.90	230.95	16.70
71.55	5.21	144.96	11.43	236.40	16.90
75.25	5.44	152.88	12.06	242.85	17.25
79.68	5.94	160.16	12.68	251.79	17.50
84.20	6.26	167.68	13.15	267.50	18.19
88.90	6.68	177.86	13.75	273.68	18.46
93.80	7.18	183.46	14.09	287.03	19.10
105.22	8.30	189.08	14.40	299.20	19.55
112.44	8.73	203.95	15.26		

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(1) Abstracted, in part, from a thesis presented by B. J. DeWitt to the committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science, June, 1941.

(2) McDonald and Seltz, THIS JOURNAL, **61**, 2405 (1939).

(3) Schumb and Hartford, *ibid.*, **56**, 2613 (1934).

vacuo, or 0.5840 mole, which was the maximum capacity of the calorimeter.

Experimental Results.—In Tables I and II the experimental heat capacities for the two oxides are given. The conversion from electrical energy to defined calories was made on the basis of 1 calorie = 4.1833 international joules. The over-all accuracy of the heat capacity measurements is believed to be ±0.3%. The results are plotted in Fig. 1.

Entropies and Free Energies of Formation.—A graphical evaluation of the entropy change for MoO_3 from 70.05 to 298.1°K. gave a value of 15.710 cal./°C. The extrapolation from 70.05 to 0°K. was made by the usual method. It was found that the experimental C_p curve could be fitted by the expression

$$C_v = D\left(\frac{195}{T}\right) + 2E\left(\frac{480}{T}\right) + E\left(\frac{1160}{T}\right)$$

This Debye and Einstein summation fitted the curve up to 260°K. At 70.05°K. the entropy contribution of the Debye function was 2.864 cal./°C., the two equal Einstein functions, $2E(480/T)$, contributed 0.102 cal./°C., while the contribution of the $E(1160/T)$ was negligible. The sum of these values gave for the entropy of the oxide: $S^0_{298.1} = 18.68$ cal./°C., with an uncertainty of ±0.3 cal./°C. Combining this value with the entropies of molybdenum and oxygen[4] we obtain for the entropy of formation of the oxide; $\Delta S^0_{298.1} = -61.70$ cal./°C. The most reliable value for the $\Delta H_{298.1}$ of formation of the oxide seems to be from the measurements of Moose and Parr,[5] who obtained −176,500 cal. We thus calculate for the standard free energy of formation; $\Delta F^0_{298.1} = -158{,}100$ cal.

$$Mo(s) + 3/2\ O_2(g) = MoO_3(s);\ \Delta H_{298.1} = -176{,}500 \text{ cal.};$$
$$\Delta S^0_{298.1} = -61.70 \text{ cal./°C.};\ \Delta F^0_{298.1} = -158{,}100 \text{ cal.}$$

To establish the equation of ΔF^0 as a function of temperature, the heat capacity equations for Mo(s) and O_2(g) recommended by Kelley[6] were used. For MoO_3(s) his estimated equation was used after correction to agree with the experimental value obtained in this work at 298.1°K. The three equations are

$$MoO_3(s);\ C_p = 14.1 + 12.1 \times 10^{-3}T$$
$$Mo(s)\ ;\ C_p = 5.69 + 1.88 \times 10^{-3}T - 0.503 \times 10^5T^{-2}$$
$$O_2(g)\ ;\ C_p = 8.27 + 0.258 \times 10^{-3}T - 1.877 \times 10^5T^{-2}$$
$$\Delta C_p = -4.0 + 9.8 \times 10^{-3}T + 3.3 \times 10^5T^{-2}$$

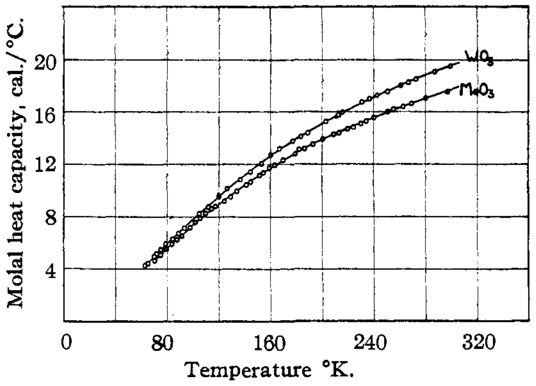

Fig. 1.—Molal heat capacities of molybdic and tungstic oxides.

Combining these data with the $\Delta H_{298.1}$ of formation we calculate $\Delta H_0 = -174{,}634$, and from the value of $\Delta F^0_{298.1}$ we obtain for I the value 35.89. The complete ΔH and ΔF^0 equations thus become

$$\Delta H = -174{,}600 - 4.0T + 4.9 \times 10^{-3}T^2 - 3.30 \times 10^5T^{-1}$$
$$\Delta F^0 = -174{,}600 + 4.0T \ln T - 4.9 \times 10^{-3}T^2 - 1.65 \times 10^5T^{-1} + 35.89T$$

The graphical evaluation of the entropy change for tungstic oxide from 62.90°K. to 298.1°K. gave a value of 17.508 cal./°C, and the C_p curve was fitted up to 220°K. by the summation

$$C_v = D\left(\frac{200}{T}\right) + 2E\left(\frac{450}{T}\right) + E\left(\frac{880}{T}\right)$$

which gave for the entropy at 62.90°K.

$$S_{62.90} = 2.328 + 2 \times 0.030 + 0.000 = 2.388 \text{ cal./°C.}$$

The entropy at 298.1°K. is thus: $S^0_{298.1} = 19.90 \pm 0.2$ cal./°C. The heat of formation of the oxide, from the combustion measurements of Moose and Parr,[5] is: $\Delta H_{298.1} = -195{,}700$ cal., and hence

$$W(s) + 3/2\ O_2(g) = WO_3;\ \Delta H_{298.1} = -195{,}700 \text{ cal.};$$
$$\Delta S^0_{298.1} = -61.65 \text{ cal./°C.};\ \Delta F^0_{298.1} = -177{,}300 \text{ cal.}$$

Again, using the C_p equation for W(s), recommended by Kelley, and correcting the equation for WO_3(s) to agree with our experimental value

$$W(s);\ C_p = 5.65 + 0.866 \times 10^{-3}T$$
$$WO_3(s);\ C_p = 17.33 + 7.74 \times 10^{-3}T$$
$$\Delta C_p = -0.73 + 6.48 \times 10^{-3}T + 2.816 \times 10^5T^{-2}$$

The value of ΔH_0 is found to be −194,800 and I is 57.10, and finally

$$\Delta H = -194{,}800 - 0.73T + 3.24 \times 10^{-3}T^2 - 2.816 \times 10^5T^{-1}$$
$$\Delta F^0 = -194{,}800 + 0.73T \ln T - 3.24 \times 10^{-3}T^2 - 1.408 \times 10^5T^{-1} + 57.10T$$

Summary

1. The heat capacities of MoO_3 and WO_3 have been determined from about 65 to 298°K.

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[4] K. K. Kelley, "Bureau of Mines Bulletin 434."

[5] Moose and Parr, THIS JOURNAL, **46**, 2656 (1924).

[6] K. K. Kelley, "Bureau of Mines Bulletin 371."

2. The entropy at 298.1°K. of MoO_3 is found to be 18.68 ± 0.3 cal./°C. and of WO_3 is 19.90 ± 0.2 cal./°C.

3. The complete ΔF^0 equations of formation of the two oxides have been computed.

PITTSBURGH, PA. RECEIVED JANUARY 2, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE JOHNS HOPKINS UNIVERSITY]

The Carbides of Magnesium[1]

BY WALTER H. C. RUEGGEBERG

The carbides of magnesium have attracted the attention of investigators for many years.[2]

The work of Novak[3] on these compounds is by far the most illuminating to date. Novak allowed acetylene, methane, *n*-pentane, *n*-octane, benzene, toluene and xylenes to react with magnesium metal at elevated temperatures. This work led to the conclusion that there were two carbides of magnesium, namely, the acetylide MgC_2 and a carbide which, upon hydrolysis, gave methylacetylene. To this latter substance, Novak assigned the formula Mg_2C_3, in which, according to this investigator, there should exist discrete C_3^{-4} units in the crystal lattice. Unfortunately, the results of Novak are based upon the hydrolysis products, rather than upon the identification of the crystal modifications.

This paper will constitute a reconsideration of the magnesium carbide problem.

Preparation of the Carbide Mg_2C_3

Four to five grams of powdered magnesium metal was placed in a porcelain boat and the boat and its contents were heated in a stream of gaseous *n*-pentane at 700°. The hydrocarbon was brought to the metal by bubbling dry hydrogen through *n*-pentane, thus carrying the vapors through the resistance furnace. It is simply a modification of the general method of the preparation of the alkaline earth carbides, namely

$$\text{Metal} + \text{Carbon} \longrightarrow \text{Carbide}$$

It may be mentioned that magnesium carbide forms in large amounts, if: 1. A hydrocarbon is used which decomposes into large quantities of carbon at the melting point of magnesium (651°). 2. The absence of oxygen is assured. Either gaseous oxygen or an oxide reactant will poison the formation of the carbide by forming the oxide of magnesium. 3. The hydrocarbon does not polymerize into oils or solids to cover the surface of the metal.

X-Ray powder pictures were taken of the carbide resulting from *n*-pentane and magnesium at 712°. Two separate pictures were made, one of a sample from the surface material in the boat (Table I), the other from the material near the bottom of the boat (Table II). The results clearly indicate complete reaction on the surface, while the lower regions contain large quantities of unchanged magnesium.

TABLE I

Powder Photograph Data of Mg_2C_3 prepared from *n*-Pentane and Magnesium at 712°

Filtered Cu radiation; sample from top of boat

Relative intensity	*d*, Å.
Strong	3.21
Very weak	3.05
Very weak	2.74
Strong$^-$	2.43
Strong$^-$	2.20
Very very weak	2.11
Very very weak	1.97
Medium	1.85
Weak	1.79
Weak	1.75
Weak	1.54
Very weak	1.48

The results here obtained are in full agreement with those previously published for the same substance.[4a,b]

Hydrolyses of the Carbides.—The hydrolyses of the carbides and the identification of the acetylene and methylacetylene were carried out in a manner similar to that described by Novak.[3]

Reaction of Mg_2C_3 with Nitrogen.—Dry oil-pumped nitrogen was passed over magnesium carbide at 620° for two hours. At the end of this time, considerable decomposition of the carbide

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[1] From a dissertation submitted by Walter H. C. Rueggeberg in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Johns Hopkins University. Original manuscript received November 29, 1941.

[2] For a review of earlier work on this subject, see Gmelin's "Handbook," 8th edition: Magnesium, part B, pp. 299–301 (1939).

[3] Novak, *Ber.*, **42**, 4209 (1909); *Z. physik. Chem.*, **73**, 513 (1910).

[4] (a) Hanawalt, Rinn and Frevel, *J. Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 457 (1938). (b) Franck, *et al.*, *Z. anorg. Chem.*, **232**, 111 (1937).