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

The Heats of Combustion and Formation of Two Manganese Nitrides, Mn_5N_2 and Mn_4N

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The heats of combustion of Mn_5N_2 and Mn_4N to manganomanganic oxide were determined by bomb calorimetry to be −504.0 ± 0.4 and −411.4 ± 0.2 kcal./mole, respectively. These results, in conjunction with the heat of formation of manganomanganic oxide, lead to the following heats of formation at 298.15°K. (kcal./mole): Mn_5N_2, −48.2 ± 0.6; and Mn_4N, −30.3 ± 0.4.

Thermodynamic data for the nitrides of manganese are scanty and indefinite, as is apparent from the reviews of Brewer and co-workers[1] and Kubaschewski and Catterall.[2] There are no experimental entropy or high temperature heat capacity data, and existing heat of formation values are uncertain. In this paper, heat of combustion and heat of formation results are reported for manganese nitrides of composition Mn_5N_2 and Mn_4N. The only previous heat of combustion measurements are those of Neumann and co-workers[3] for a nitride approaching Mn_4N in composition.

Materials.—The two manganese nitrides were made in this Laboratory by K. C. Conway. Electrolytic manganese, analyzing 99.92%, was obtained from the Boulder City Station of the Bureau of Mines and used as one starting material; the other was nitrogen which was purified by passing it over hot copper, titanium and manganese metals and drying it with magnesium perchlorate.

The nitride Mn_5N_2 was obtained by heating the metal in a stream of nitrogen for 162 hr. at 700–850°, followed by 54 hr. at 635°. Analysis for manganese, by conversion to the sulfate, was 90.76% (theory, 90.75%). Nitrogen, by the Kjeldahl method, was 9.14% (theory, 9.25%). The remaining 0.10% was assumed to be oxygen. The X-ray diffraction pattern showed no evidence of uncombined manganese.

The nitride Mn_4N was made by heating the metal in a stream of nitrogen for 31 hr. at 900–970°. Analysis gave 94.02% manganese and 5.89% nitrogen, as compared with the theoretical 94.01 and 5.99%. The remaining 0.09% was assumed to be oxygen. The X-ray diffraction pattern agreed with the ASTM catalog.

Both nitrides were in coarsely crystalline form; about 90% of the particles were larger than 40-mesh and only a minor fraction smaller than 100-mesh.

Experimental

The combustion calorimeter was described previously.[4] The mean calibration value, obtained with National Bureau of Standards benzoic acid sample No. 39g, was 32495.3 ± 0.01% cal./ohm. All weights were corrected to vacuum and heat values are in terms of the defined calorie (1 cal. = 4.1840 abs. joules).

Containers for the combustion samples were prepared by placing heavy liners of manganous oxide in silica crucibles and igniting for 16 hr. at 960°. Weight increases indicated over 99.8% conversion to manganomanganic oxide by this treatment. The combustions were made at 30 atm. pressure of oxygen. Ignition was by means of an electrically heated platinum spiral and a filter paper fuse.

Oxygen deficiencies in the combustion products, relative to manganomanganic oxide, were obtained from the weight increases during combustion. The samples were tested for oxidation prior to ignition; no weight increase was observed when the nitrides were placed under 30 atm. pressure of oxygen for several hours. The bomb gases after combustion contained negligible quantities of oxides of nitrogen.

The amounts of combustion product remaining in the crucibles averaged 92% for Mn_5N_2 and 90% for Mn_4N. The other 8 and 10% were deposited on the bomb walls. X-Ray diffraction patterns of the combustion products in the crucibles and on the walls, and also of the liner material, agreed with that for manganomanganic oxide in the ASTM catalog.

Results

The experimental data are in Table I. The successive columns show the mass of the substance burned, the total energy evolved, the correction for ignition, the oxygen deficiency in the combustion product, the correction for oxygen deficiency and, finally, the corrected energy of combustion per gram.

TABLE I

ENERGIES OF COMBUSTIONS AT 30°

Mass of substance, g.	Total heat evolved, cal.	Cor. for EIt, fuse, cal.	Oxygen deficiency, g.	Cor. for incomplete comb., cal.	$-\Delta U_B$, cal./g.
		Mn_5N_2			
1.49965	2333.26	11.38	0.04741	162.62	1656.7
1.51370	2349.30	8.19	.04786	164.16	1655.1
1.00421	1645.80	7.52	.00720	24.70	1656.0
1.49725	2464.15	8.86	.00702	24.08	1655.9
1.50935	2489.30	8.35	.00531	18.21	1655.8
1.00306	1650.16	8.29	.00589	20.20	1657.0
				Mean	1656.1 ± 0.6
				Cor. for impurities	3.4 ± 0.7
					1659.5 ± 1.0
		Mn_4N			
2.00151	3524.82	8.53	−0.00289	−9.91	1751.9
1.90055	3330.13	8.33	+ .00174	+5.97	1751.0
2.00131	3505.99	7.21	.00170	5.83	1751.2
2.00109	3502.86	7.13	.00171	5.87	1749.8
2.00206	3511.73	6.93	.00023	0.79	1751.0
2.00218	3511.12	6.31	.00000	0.00	1750.5
				Mean	1750.9 ± 0.6
				Cor. for impurities	2.7 ± 0.5
					1753.6 ± 0.8

The energy corrections for incomplete combustion were obtained by multiplying the oxygen deficiencies by the energy evolved (3430 cal./g. of oxygen, under bomb conditions) in the oxidation of manganous oxide to manganomanganic oxide. This energy of oxidation value was derived from Southard and Shomate's[5] heat of formation value for manganous oxide (−92,040 ± 110 cal./mole)

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(1) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Paper 4 of National Nuclear Energy Series Vol. IV-19B, Edited by L. L. Quill, McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

(2) O. Kubaschewski and J. A. Catterall, "Thermochemical Data of Alloys," Pergamon Press, 1956, p. 142.

(3) B. Neumann, C. Kröger and H. Haebler, *Z. anorg. Chem.*, **196**, 65 (1931).

(4) G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).

(5) J. C. Southard and C. H. Shomate, *ibid.*, **64**, 1770 (1942).

and Shomate's[6] heat of formation value for manganomanganic oxide (−331,300 ± 250 cal./mole, after applying a minor correction).

The impurity corrections also were calculated from the above heat of formation values. The compositions assumed for these corrections were: for Mn_5N_2, 0.44% MnO, 0.80% Mn and 98.76% Mn_5N_2; for Mn_4N, 0.40% MnO, 1.30% Mn and 98.30% Mn_4N. These proportions conform with the chemical analyses.

The mean value of the heat of combustion of Mn_5N_2 corresponds to $\Delta E_{303 \cdot 15} = -502.36$ kcal./mole under bomb conditions. Corrections to unit fugacities of oxygen and nitrogen (−215 cal.), to a constant pressure process (−1406 cal.), and to 298.15°K. (−6 cal.) gives $\Delta H_{298 \cdot 15} = -503.99 \pm 0.40$ kcal./mole as the standard heat of combustion of Mn_5N_2. Combination with the heat of formation of manganomanganic oxide (−331.3 kcal.) leads to $\Delta H_{298 \cdot 15} = -48.2 \pm 0.6$ kcal./mole as the standard heat of formation of Mn_5N_2 from the elements.

Similarly, the mean heat of combustion of Mn_4N yields $\Delta E_{303 \cdot 15} = -409.94$ kcal./mole under bomb conditions. Corrections to unit fugacities (−195 cal.), to constant pressure (−1305 cal.) and to 298.15°K. (−4 cal.) gives $\Delta H_{298 \cdot 15} = -411.44 \pm 0.20$ kcal./mole as the standard heat of combustion of Mn_4N. Again, combining with the heat of formation of manganomanganic oxide gives $\Delta H_{298 \cdot 15} = -30.3 \pm 0.4$ kcal./mole as the standard heat of formation of Mn_4N from the elements.

The value of the heat of formation of Mn_4N does not differ greatly from that similarly obtained by Neumann and co-workers[3] for material of composition $Mn_{4 \cdot 74}N$ (−31.2 kcal.). The present value for Mn_5N_2, however, deviates widely from their result (−57.8 kcal.), which was obtained by the direct nitriding of manganese (containing 0.25% hydrogen) in a bomb calorimeter.

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[6] C. H. Shomate, THIS JOURNAL, **65**, 785 (1943).

[CONTRIBUTION FROM ARTHUR D. LITTLE, INC., WESTERN DIVISION]

The Nature of Uranyl 8-Quinolinolate[1]

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It is shown that the three moles of 8-quinolinol in the uranyl 8-quinolinolate are coördinated in an equivalent manner and that the acidic nature of this chelate is best represented by the formula $H(UO_2(C_9H_6NO)_3)$, where the anions, $UO_2(C_9H_6NO)_3^{-1}$, are linked together by hydrogen bonding of the uranyl oxygens. The uranyl tri-8-quinolinolate anion is shown to be stable in alkaline solutions and to form stable salts with cations, such as Na^+, R_4N^+ and $(C_6H_5)_4As^+$. The absorption spectra of aqueous alkaline solutions of the uranyl tri-8-quinolinolate anion and chloroform solutions of the tetraphenylarsonium salt of this anion are reported. The chemical behavior of the uranyl di-8-quinolinolate is reported and discussed with respect to its possible structure.

It has long been known that uranium forms two compounds with 8-quinolinol, one of which contains an "added mole of reagent."[2] The red compound of composition $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ is easily obtained by direct precipitation at controlled *p*H and is converted into the green "normal" chelate $UO_2(C_9H_6NO)_2$ by heating at 210–215°.[3] In the course of an investigation in this Laboratory concerning possible uranium chelating agents,[4] it was observed that the addition of 8-quinolinol to sodium carbonate solutions of the very stable uranium complex, $UO_2(CO_3)_3^{-4}$, causes the uranium to precipitate as an orange solid, which contains sodium. This interesting precipitate, later identified as $Na(UO_2(C_9H_6NO)_3)$, and the fact that the precipitation only occurs in carbonate solutions at an elevated *p*H (11–12) led to the studies presented below.

Treatment of solid $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ with dilute sodium hydroxide (~0.01 *M*) leads to its dissolution and the formation of an intense red solution. Such solutions are decomposed at higher hydroxide ion concentrations to yield the familiar yellow solutions of the 8-quinolinolate ion and a precipitate of orange U(VI) uranates.[5] This behavior of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ leads to the strong presumption that this chelate is an acid. In support of this presumption, it was found that the soluble red complex could be precipitated from alkaline solution by providing suitable concentrations of various cations, *e.g.*, Na^+, R_4N^+, $(C_6H_5)_4As^+$.[6] These precipitates were shown by analysis to have the general composition $M^IUO_2(C_9H_6NO)_3$ where M^I is a monovalent cation. It was further observed that the soluble red complex could be extracted readily from aqueous alkaline solutions into organic solvents ($CHCl_3$, MIBK) when quaternary ammonium or arsonium cations were present, *but not when these organic cations were absent.* This fact, when considered in conjunction with the analyses mentioned above, certainly implies that the soluble red complex is the anion, $UO_2(C_9H_6NO)_3^{-1}$.

Titration of the red uranyl 8-quinolinolate, $H(UO_2(C_9H_6NO)_3)$, in acetonitrile with potassium methoxide led to the results in Fig. 1. Here the acidity of the chelate is compared under identical conditions with 8-quinolinol and benzoic acid. These results demonstrate conclusively that the ex-

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[1] Work reported here was carried out under Contract AT(49-6)-923, for the Atomic Energy Commission.

[2] F. J. Frere, THIS JOURNAL, **55**, 4362 (1933).

[3] T. Moeller and D. H. Wilkins, *Inorg. Syntheses*, **4**, 101 (1953). See also ref. 10 for earlier references.

[4] W. E. Clifford, P. Noble, Jr., and E. P. Bullwinkel, A. E. C. Report RMO-2623.

[5] J. E. Ricci and F. J. Loprest, THIS JOURNAL, **77**, 2119 (1955).

[6] Salts prepared by this method are not of high purity. Improved methods of synthesis are presented in the Experimental Section.