through formation of metal–metal bonds. It may be significant in this connection that the dimeric carbonyls, and the monomeric carbonyl iodides which can have no bridging groups, have very similar bands in the region about 5 μ.

Acknowledgments.—We wish to acknowledge the assistance of Dr. Clair M. Birdsall and the Infrared-Group of this Laboratory for recording the infrared spectra and of Mr. L. G. Dowell for his X-ray study of these compounds and interpretation of these results.

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Heats of Formation of Nickel and Cobalt Oxides (NiO and CoO) of Combustion Calorimetry

BY B. J. BOYLE, E. G. KING AND K. C. CONWAY

The heats of formation of nickel and cobalt oxides (NiO and CoO) were determined as $\Delta H_{298.16} = -57.3 \pm 0.1$ and $\Delta H_{298.16} = -57.1 \pm 0.3$ kcal./mole, respectively, by combustion calorimetry. The corresponding free energies of formation from the elements are -50.6 and -50.4 kcal./mole.

The heats of formation of nickel and cobalt oxides have been determined previously by combustion calorimetry and from reaction equilibria. The data, summarized by Brewer[1] and in the N. B. S. tables,[2] cover ranges of 2.8 and 3.1 kcal./mole, respectively; and those from combustion calorimetry are not of high precision. This paper reports new experiments in combustion calorimetry, which yield heats of formation of these oxides valid to within ± 0.1 and ± 0.3 kcal./mole.

Materials.—The nickel was a specially purified product in the form of a small bar.[3] Analysis showed 0.03% iron, 0.003% silicon, 0.001% cobalt and 0.002% sulfur as the only detectable impurities. In a series of preliminary experiments, using filings and fine lathe turnings from this bar, the metal either failed to ignite or showed only superficial combustion under conditions prevailing in the calorimeter bomb. It was discovered, however, that the presence of a small amount (ca. 0.1%) of cobalt had a markedly beneficial effect in promoting combustion.[4] This led to adoption of the following procedure for preparing the metal used in the reported measurements. Lathe turnings from the bar (cut with a Carboloy tool) and pure cobalt sponge, in amount equal to 0.1% of the nickel, were dissolved in concentrated reagent grade nitric acid, and the solution was diluted and filtered. The filtrate was evaporated to dryness and the resulting cake transferred to a porcelain dish and ignited at 1,150°. The oxide from this process was finely ground and reduced to metal in a stream of pure hydrogen at 650°. When reduction was complete, the hydrogen stream was discontinued and replaced by a stream of pure helium in which the metal was allowed to cool to room temperature. This metal, consisting of 99.9% nickel and 0.1% cobalt, was used in all the reported measurements. X-Ray diffraction showed only lines corresponding to the normal nickel structure.

The cobalt was a Johnson, Matthey and Co. product. Their analysis showed 0.003% silicon, 0.0005% aluminum, 0.0002% magnesium, 0.0001% copper, 0.0001% manganese and less than 0.001% iron. Other metallic impurities, including nickel, were not present in amounts large enough for detection. The metal, as received, contained a small amount of oxygen. This was eliminated by reduction in a stream of pure hydrogen at 750°, followed by cooling to room temperature in a stream of pure helium. The X-

ray diffraction pattern contained no lines other than those of the normal cobalt structure.

Measurements and Results.—The measurements were conducted with the calorimetric equipment described by Humphrey.[5] Benzoic acid (N. B. S. sample No. 39g) was used in determining the energy equivalent of the calorimeter, which was 32,415.1 (± 0.01%) cal./ohm for the nickel combustions and 32,435.4 (± 0.01%) for the cobalt combustions, the difference being attributable to minor apparatus repairs. All weighings were reduced to vacuum and all heat values are expressed in defined calories (1 cal. = 4.1840 abs. joules).

The metal samples for combustion were held in unlined silica-glass capsules, the use of nickel and cobalt oxide linings being precluded by possible changes in composition resulting from exposure to oxygen in the bomb during combustion of the metal. The capsules were attacked by the combustion products, superficially in the nickel combustions and appreciably in the cobalt combustions. In the latter case, a special procedure for correcting for silica contamination of the combustion products was devised, as will be described later.

All heat measurements were made at a calorimeter temperature of 303.16°K. The initial oxygen pressure in the bomb was 40 atm. for the nickel combustions and 25 and 30 atm. (mostly 30 atm.) for the cobalt. In all instances the bomb walls remained clean, the total combustion product being contained in the capsule. Ignition was by means of an electrically heated platinum spiral and a filter paper fuse, for which appropriate corrections were applied. The bomb gases after combustion were tested for oxides of nitrogen. The amount found was negligible, yielding a correction of less than 0.001% in the heat values. Exposure tests of the metals to oxygen, conducted under bomb conditions, showed that no oxidation occurred before ignition of the fuse.

Completion of combustion was determined from the difference in mass of the combustion product and the metal sample. The percentage completions of the nickel combustions ranged from 87.33 to 92.92, the average O:Ni atomic ratio of the combustion products being 0.9036. X-Ray diffractions of the nickel combustion products showed the lines of ordinary nickel oxide (NiO) and a few faint lines of nickel. The energy values were corrected to correspond with complete formation of NiO by assuming direct proportionality with the oxygen contents of the combustion products. It was mentioned previously that the attack of the silica-glass capsules by the nickel combustion products was only superficial. This was confirmed by analysis of these products for silica.

The cobalt combustion products had O:Co atomic ratios greater than unity in all instances. They ranged from 1.0312 to 1.0365, the average being 1.0338. Correction of the results to correspond to

(1) L. Brewer, *Chem. Revs.*, **52**, 1 (1953).

(2) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Natl. Bur. Standards Circular* 500, 1952.

(3) This metal was furnished by T. H. Hazlett, Division of Mineral Technology, University of California.

(4) This phenomenon was first noted by G. L. Humphrey, formerly of this Laboratory.

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

CoO was made upon the assumption that the excess oxygen was combined as Co_3O_4, using 35.7 kcal./g.-atom as the energy of combination of the excess oxygen, in accordance with unpublished information compiled by Coughlin[6] of this Laboratory. X-Ray diffractions of the cobalt combustion products showed the lines corresponding to CoO plus a few faint lines attributable either to Co_3O_4 or to the effect of silica contamination (silicate formation).

The cobalt combustion products attacked the silica-glass capsules to an appreciable extent. Each combustion product was analyzed specifically for silica. As a means of correction for silicate formation, some of the combustions were conducted in a manner that deliberately increased the silica content, either by using previously etched capsules or by addition of powdered silica (ground up capsule) to the cobalt before combustion. In this way the silica contents of the combustion products were made to cover the range 2.52 to 10.16 wt. %. A plot of the energy of combustion per g. of metal (after correction for excess oxidation beyond CoO) against the mass of silica in the combustion product gave a straight line, within an average deviation of 0.05%. The slope of this line yields 128.1 cal./g. of silica as the correction factor.

by the platinum spiral and filter paper fuse, (4) the correction for incomplete combustion, (5) the net corrected total energy, and (6) the energy evolution in the combustion of 1 g. of nickel to nickelous oxide. A small correction (−0.013%) has been applied to the mean result for the iron, cobalt, and silicon contents of the metal.

The mean value in Table I corresponds to an energy evolution of 56.92 kcal. for the combustion of 1 gram-atom of nickel to nickelous oxide under bomb conditions. To obtain the standard heat of formation of nickelous oxide, three corrections are required. The correction to unit fugacity of oxygen (−59 cal.) is obtained from a suitable modification of Washburn's[7] equation. Correction to a constant pressure process (−301 cal.) employs the relationship $\Delta H = \Delta E - 0.5\,RT$, and correction to 298.16°K. (−5 cal.) accords with data assembled by Kelley.[8] The final result for the standard heat of formation of nickelous oxide is $\Delta H_{298.16} = -57.3 \pm 0.1$ kcal./mole. The uncertainty interval allows for errors associated with the following items: combustion energy of benzoic acid, calibration of the calorimeter, combustion measurements of nickel, determinations of completion of combustion, and correction for impurities.

The measured results for cobalt are summarized in Table II. The information reported is the same as for nickel, except that a column of corrections for the silica contents of the combustion products is included and a column of corrections for over-oxidation (beyond CoO) replaces that for incomplete combustion.

The mean value in Table II corresponds to 56.70 kcal. energy evolution for the combustion of 1 gram-atom of cobalt to cobaltous oxide, under bomb conditions. Corrections to unit fugacity of oxygen, to a constant pressure process, and to 298.16°K., made as previously described, amount to −45, −301 and −5 cal., respectively. Thus, the standard heat of formation of cobaltous oxide becomes $\Delta H_{298.16} = -57.1 \pm 0.3$ kcal./mole, the uncertainty interval

TABLE I
COMBUSTION DATA FOR NICKEL

Mass of Ni, g.	Total energy, cor. to 303.16° K., cal.	Cor. for fuse and E_{it}, cal.	Cor. for in-comp. comb., cal.	Net total energy, cal.	$-\Delta H_B$, cal./g.
3.50528	3185.00	−27.66	240.58	3398.0	969.4
3.44745	3047.36	−17.92	315.05	3344.5	970.1
2.64029	2361.07	−16.78	216.93	2561.2	970.0
3.59989	3146.92	−17.02	361.34	3491.2	969.8
3.59962	3066.26	−16.75	442.43	3491.9	970.1
3.60588	3110.69	−20.77	409.03	3498.9	970.3
3.46220	3113.81	−19.31	261.43	3355.9	969.3

				Mean	969.9 ± 0.3
				Cor. for impurities	−0.1
				(−0.013%)	969.8 ± 0.3

TABLE II
COMBUSTION DATA FOR COBALT

Mass of Co, g.	Total energy, cor. to 303.16°K., cal.	Cor. for fuse and E_{it}, cal.	Cor. for overoxid., cal.	Cor. for silica, cal.	Net total energy, cal.	$-\Delta U_B$, cal./g.
3.42534[a]	3398.88	−13.34	−70.54	−20.93	3294.1	961.7
3.41831[a]	3402.62	− 9.00	−70.60	−36.83	3286.2	961.4
3.41785[a]	3409.59	−13.81	−68.73	−36.87	3290.2	962.7
3.41785[a]	3425.19	− 9.98	−64.59	−60.25	3290.4	962.7
3.41887[a]	3386.52	−11.76	−66.68	−20.26	3287.8	961.3
3.41983[a]	3427.48	−18.44	−73.12	−42.40	3293.5	963.1
3.36433[b]	3347.41	−10.31	−74.38	−24.82	3237.9	962.4
3.41508[b]	3378.03	−11.36	−67.02	−13.78	3285.9	962.2
3.41521[b]	3387.07	−13.30	−73.23	−14.58	3286.0	962.2

					Mean	962.2 ± 0.5
					Cor. for impurities	−0.2
					(−0.024%)	962.0 ± 0.5

[a] Combustion in 30 atm. oxygen. [b] Combustion in 25 atm. oxygen.

The measured combustion data for nickel are summarized in Table I. The columns from left to right contain (1) the amount of nickel used in each experiment, (2) the total energy evolved at 303.16°K., (3) the correction for energy generated

taking account of items analogous to those listed for nickel.

Related Data.—The present value for nickelous oxide differs by 0.7 kcal./mole from that listed in

(6) J. P. Coughlin, personal communication.

(7) E. W. Washburn, Natl. Bur. Standards J. Research, 10, 525 (1933).

(8) K. K. Kelley, U. S. Bur. Mines Bull., 477 (1950).

Brewer's[1] compilation (-58.0 ± 0.5) and by 1.1 kcal./mole from that listed in the N. B. S. tables[2] (-58.4). These values were selected from data ranging from -57.1 to -59.9 kcal./mole.

The present value for cobaltous oxide is in good agreement with that listed by Brewer (-57.0 ± 0.5) and also with the N. B. S. listing (-57.2). These values were selected from data ranging from -54.5 to -57.6 kcal./mole.

The present heat of formation of nickelous oxide, together with entropy values listed by Kelley,[8] leads to $\Delta F^0_{298.16} = -50.6 \pm 0.1$ kcal./mole as the free energy of formation from the elements. The entropy of cobaltous oxide has not been determined. If it is assumed that this oxide has the same entropy of formation as nickelous oxide, then the free energy of formation becomes $\Delta F^0_{298.16} = -50.4$ kcal./mole.

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Thermodynamic Properties of Thorium Tetrafluoride from 5 to 300°K. and the Magnetic Entropy of Uranium Tetrafluoride

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RECEIVED MARCH 20, 1954

The heat capacity of thorium tetrafluoride was measured from 5 to 300°K., and the enthalpy, entropy and free energy were calculated from these data. At 298.16°K. the values of C_p, $H^0 - H_0^0$, and S^0 are 26.46 ± 0.03 cal. deg.$^{-1}$ mole^{-1}, 5113.8 ± 6 cal. mole^{-1}, and 33.953 ± 0.04 cal. deg.$^{-1}$ mole^{-1}, respectively. On the assumption that the heat capacity of thorium tetrafluoride is equal to the lattice heat capacity of uranium tetrafluoride, the magnetic entropy of uranium tetrafluoride was evaluated by subtracting the entropy of thorium tetrafluoride from the entropy of uranium tetrafluoride given by Brickwedde, Hoge and Scott. At 298.16°K. the value of the magnetic entropy obtained in this way, 2.17 cal. deg.$^{-1}$ mole^{-1}, is 0.87 cal. deg.$^{-1}$ mole^{-1} lower than the magnetic entropy of uranium dioxide, and this suggests that the extrapolation of the heat capacity of uranium tetrafluoride below 20°K. may be in error.

The measurements of the low temperature heat capacity of thorium tetrafluoride that are presented in this paper were made both to provide thermodynamic data which should be useful in thorium chemistry and to resolve the lattice and magnetic contributions to the heat capacity and entropy of uranium tetrafluoride.

It has been found that an anomaly or "hump" occurs in the heat capacity curve of uranium dioxide at 28.7°K.[2] and in that of neptunium dioxide at 25.3°K.[3] The anomalies are believed to be related to the magnetic behavior of these substances. However, there is no hump in the heat capacity curve of uranium tetrafluoride between 20 and 350°K.,[4] and the question arises as to whether the magnetic contribution is spread out over a wide range of temperature or whether it is concentrated in a hump in the heat capacity curve below 20°K. In the latter case the entropy obtained by extrapolating the heat capacity curve from 20 to 0°K. with a Debye function might be in error by 2 or 3 cal. deg.$^{-1}$ mole^{-1}.

Because the electronic structure of the Th^{+4} and F^- ions are of the rare gas type, with a $^1S_0$ ground state, so that thorium tetrafluoride is diamagnetic, the heat capacity of this compound depends only upon the lattice vibrations. Both thorium tetrafluoride and uranium tetrafluoride are monoclinic and isostructural with zirconium tetrafluoride, and the lattice dimensions of thorium tetrafluoride are only about 2.5% larger than those of uranium tetrafluoride.[5] In view of the small per-

centage difference in the atomic masses as well as in the lattice dimensions it seems reasonable to assume that the molal heat capacity of thorium tetrafluoride is very nearly equal to the lattice contribution to the molal heat capacity of uranium tetrafluoride, and hence that the molal entropy of thorium tetrafluoride is very nearly equal to the lattice contribution to the molal entropy of uranium tetrafluoride. The magnetic contribution to the heat capacity or entropy of uranium tetrafluoride can then be obtained by subtracting the lattice contribution, as given by the heat capacity or entropy of thorium tetrafluoride, from the total heat capacity or entropy of uranium tetrafluoride.

Thorium Tetrafluoride Sample.—The thorium tetrafluoride for this investigation was prepared by hydrofluorination of a pure sample of electrically fused thorium dioxide that had been used for the determination of the heat capacity of the latter substance.[6] The oxide charge was placed in a platinum boat, which was contained in a nickel reaction tube attached to a nickel vacuum line. Anhydrous, high purity, gaseous hydrogen fluoride was passed over the sample at 750° until constant weight was attained; this required a reaction time of 132 hours.

Weighing of the sample before and after hydrofluorination indicated that the amount of unconverted thorium dioxide was less than 0.13% by weight. Thorium determinations by gravimetric oxalate precipitation gave 75.40 and 75.26% (theoretical, 75.33%). Fluorine analysis by a method involving pyrohydrolysis in a platinum apparatus followed by titration with a standard base gave 24.6% fluorine (theoretical, 24.67%). The only significant amounts of impurities found by spectrochemical analysis of the thorium tetrafluoride were, in p.p.m.: 70 of Ca, 10 of Mg, less than 10 of K, 5

(1) Department of Chemistry, University of Michigan, Ann Arbor, Mich.

(2) W. M. Jones, J. Gordon and E. A. Long, J. Chem. Phys., 20, 695 (1952).

(3) E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, ibid., 21, 419 (1953).

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(5) W. H. Zachariasen, Acta Cryst., 2, 388 (1949).

(6) D. W. Osborne and E. F. Westrum, Jr., J. Chem. Phys., 21, 1884 (1953).