Both compounds dissolved fairly rapidly in a solution that was about 1 *M* in both aluminum nitrate and nitric acid. Some gas evolution occurred in both cases. The gas may have been oxygen produced by the oxidation of water.

Efforts to determine the partial pressure of $F_{2(g)}$ in equilibrium with the solid tetrafluorides by an effusion technique were not successful, but it was noted that samples of cerium tetrafluoride heated in prefluorinated nickel crucibles in vacuum (10^{-6} mm.) were largely converted to the trifluorides at 230° in ten minutes. These results are not inconsistent with the work of Klemm and Henkel,[4] who reported an equilibrium pressure of 2 mm. over cerium tetrafluoride at 400°. These workers, however, could not have observed a true pressure of $F_{2(g)}$ since their work was done in an apparatus of silica. In our own case, we cannot exclude the possibility that reduction to $CeF_{3(c)}$ of the small samples used was due to traces of reducing substances liberated in the vacuum line during the heating period.

Although it is thus not possible from present data to compute accurate free energy values for the trifluoride–fluorine reactions for cerium and terbium, we can conclude that the partial pressure of fluorine over the tetrafluorides of these elements is less than one atmosphere at about 320°. Since all other rare earths which might reasonably be expected to form simple tetrafluorides were examined in our study we also conclude that, except for cerium and terbium, the pressure of fluorine over all rare earth tetrafluorides exceeds one atmosphere at 320°.

This last conclusion is inconsistent with the view of Perros, Munson and Naeser,[8] who compute that the free energy of the reaction is negative to the extent

$$PrF_{3(c)} + {}^1/_2F_{2(g)} = PrF_{4(c)}$$

of at least 48 kcal. mole^{-1} at 298°K. From Latimer's[15] rules ΔS for the reaction is about -16 e.u. and praseodymium tetrafluoride therefore should be stable in an atmosphere of fluorine even at very high temperatures. The fact that it was not formed under conditions which yielded CeF_4 and TbF_4 suggests that the data used by Perros, Munson and Naeser in their calculations may contain large errors.

If our view that PrF_4 is not thermodynamically stable with respect to PrF_3 and $F_{2(g)}$ is correct, the situation is unusual in that a higher oxide (PrO_2) is more stable than the corresponding higher fluoride (PrF_4). However, it is quite conceivable that a small highly charged cation (Pr^{+4}) with eight nearest neighbor O^{--} ions might form a more stable structure relative to the sesquioxide (coördination number 6) than does the tetrafluoride relative to the trifluoride. Crystal energy calculations on this point would be highly interesting, although the low symmetry of TbF_4 would make such calculations tedious.

In any event, the extreme difficulty of reducing CeO_2 to Ce_2O_3 and the ready reduction of CeF_4 suggest that the free energy of the reaction

$$CeO_2 \longrightarrow Ce_2O_3 + {}^1/_4O_{2(g)}$$

may be more positive than that for

$$CeF_4 \longrightarrow CeF_3 + {}^1/_2F_{2(g)}$$

Since PrO_2 is less stable than CeO_2, the free energy of the reaction

$$PrF_4 \longrightarrow PrF_3 + {}^1/_2F_{2(g)}$$

may very well be negative.

Acknowledgment.—The authors take pleasure in expressing their gratitude to Dr. F. H. Spedding of Iowa State College for supplying certain of the rare earths used in this work.

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[15] W. M. Latimer, "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Chromium Oxide and Cadmium Oxide from Combustion Calorimetry

BY ALLA D. MAH

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Calorimetric combustions of pure chromium and cadmium metals were conducted at 303.16°K. under 30 atm. pressure of oxygen. The energies of combustion under these conditions are 2611.0 cal./g. of chromium and 541.5 cal./g. of cadmium. The corresponding standard heats of formation from the elements are $\Delta H_{298.16} = -272.7 \pm 0.4$ kcal./mole for chromic oxide and $\Delta H_{298.16} = -61.2 \pm 0.2$ kcal./mole for cadium oxide.

Literature values[1,2] of the heats of formation of both chromic oxide and cadmium oxide show variations and uncertainties that are large enough to warrant new determinations. New values, based upon combustion calorimetry, are reported in this paper, and it is believed that the uncertainties have been very significantly reduced.

Materials.—The chromium was produced at the Albany, Oregon, Station of the Bureau of Mines and supplied by S. M. Shelton. The metal as received was in the form of a machined bar that had been produced by hydrogen purification of electrolytic chromium, followed by arc melting under helium and annealing for four hours at 1200° before machining. Spectrographic analysis showed 0.01% iron and 0.04% silicon; other impurity elements were not detected. Nitrogen was found to be 0.001% by chemical means, and hydrogen was 0.0005% by the vacuum fusion method. Fine lathe turnings (*ca.* 0.001 inch), cut with a Carboloy tool, were used in the measurements.

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[1] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffé, *Natl. Bur. Standards Circ.*, 500 (1952).

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

The cadmium was the super-purity grade supplied in the form of small lumps by the New Jersey Zinc Company. Their spectrographic analysis showed very faint traces of magnesium and copper, and no other impurities were detectable. Carefully prepared and cleaned, fine filings of the metal were used in the measurements.

Measurements and Results.—The combustion calorimeter was described previously by Humphrey.[3] Calibration was made by use of National Bureau of Standards benzoic acid (Sample No. 39g), the mean value being 32,417.8 (±0.01%) cal./ohm. All weighings were reduced to vacuum and all heat values are expressed in defined calories (1 cal. = 4.1840 abs. joules). The combustions were conducted at 30 atm. oxygen pressure.

The chromium metal samples for combustion were held in silica glass capsules that were heavily lined with chromic oxide and baked at 1050°. An exposure test of the chromium to the oxygen in the bomb gave no evidence of oxidation before ignition. Ignition was by means of a heated platinum spiral and a filter-paper fuse. Correction in the heat values was made for the energy supplied to the spiral and for the energy evolved by combustion of the fuse; this combined correction never exceeded 0.3%.

The bomb gases after combustion were tested for oxides of nitrogen; only an entirely negligible amount was found, resulting in a correction of the heat values by less than 0.002%. In all instances the bulk of the combustion product remained in the capsule, but a small amount (less than 0.6%), was deposited on the walls of the bomb. X-Ray diffractions[4] showed the combustion product in the capsule, the wall deposit, and the capsule liner to be the normal, hexagonal variety of chromic oxide. The wall deposits were carefully collected and added to the bulk of the combustion product in the capsule.

The percentage completion of combustion was determined from the mass of the combustion product in comparison with the original mass of chromium. Some difficulty, due to moisture adsorption, was encountered in weighing the combustion products. This was circumvented by heating first at 135° and then for 5 minutes at 1050°, and transferring to a closed container before weighing. (A test of this procedure showed that it resulted in no additional oxygen pickup by the combustion products.) Completions of combustion ranged from 95.30 to 98.90%.

Data for the combustions of chromium are in Table I. The mean value for the energy of combustion is 2612.8 ± 1.1 cal./g., which becomes 2611.0 ± 1.1 cal./g. after correcting for impurities. Data from the N. B. S. Tables[1] were used in the impurity corrections. The molal energy of combustion of chromium oxide at 303.16°K. and 30 atm. oxygen pressure is 271.60 kcal.

TABLE I

COMBUSTION DATA FOR CHROMIUM

Mass o Cr, g.	Total energy, cor. to 30°, cal.	Cor. for fuse and *EIt*, cal.	Cor. for incomp. comb., cal.	Net total energy, cal.	$-\Delta U_B$, cal./g.
2.60293	6733.11	−19.29	87.46	6801.3	2612.9
2.60242	6749.95	−19.56	74.78	6805.2	2614.9
2.60245	6731.04	−18.78	87.99	6800.2	2613.0
2.60225	6718.82	−19.64	101.05	6800.2	2613.2
2.60126	6726.68	−17.96	80.31	6789.0	2609.9
2.60170	6731.20	−18.74	85.24	6797.7	2612.8
2.60057	6494.07	−18.58	319.64	6795.1	2612.9
				Mean	2612.8 ± 1.1
				Cor. for impurities	−1.8
				(−0.069%)	2611.0 ± 1.1

Correction to unit fugacity of oxygen, −130 cal., was made by applying Washburn's[5] equation to the exact conditions of the present experiments. Correction to a constant pressure process, −904 cal., was made by the relationship $\Delta H = \Delta E + nRT$. Correction to 298.16°K., −33 cal., utilized heat capacity data given by Kelley.[6] The final result for the heat of formation of chromic oxide is $\Delta H_{298.16} = -272.7 \pm 0.4$ 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 chromium, determinations of completion of combustion and correction for impurities.

The cadmium metal samples for combustion were held in silica glass capsules that were heavily lined with cadmium oxide and baked at 950°. It was determined experimentally that no oxidation of cadmium occurred merely on standing in the bomb in the presence of 30 atm. of oxygen pressure.

The usual platinum spiral-filter paper fuse combination alone failed to ignite the cadmium. After trying several schemes, it was decided to adopt the expedient of adding a small amount of titanium to the cadmium, to serve as a kindling agent in conjunction with the spiral and fuse. The energy of combustion of titanium under bomb conditions to form rutile is known from the work of Humphrey,[3] 4679.38 cal./g. However, it was expected and found experimentally that the use of titanium results in an additional energy evolution because of interaction of the titanium and cadmium oxides formed by combustion. This additional energy was determined by varying the amount of titanium added to cadmium between the limits of 0.75 and 2.0%. The additional energy was found to be directly proportional to the amount of titanium and necessitated an additional correction of 2.86 to 7.57 cal./g. of cadmium burned.

The bomb gases after combustion showed the same negligible amount of nitrogen oxides as mentioned for the chromium combustions. About 88% of the cadmium oxide combustion product remained in the combustion capsule and 12% was deposited upon the walls of the bomb. The wall deposit was cleanly removed and added to the contents of the capsule. X-Ray diffractions[4] showed the combustion product in the capsule, the wall deposit, and the capsule liner to have the same normal cadmium oxide structure. Completion of combustion was evaluated from the mass of the combustion product, which was heated at 135° before weighing. Combustion completions ranged from 96.71 to 98.30%.

Table II gives the combustion data for cadmium. The mean energy of combustion is 541.5 ± 0.7 cal./g. In this instance no correction for impurities was considered necessary as only traces were present. The molal energy of combustion at 303.16°K. and 30 atm. of oxygen pressure is 60.87 kcal.

Methods of reduction to standard conditions are the same as indicated for chromium. The corrections are −44 cal. for oxygen fugacity, −301 cal. for constant pressure process and −3 cal. for temperature. The standard heat of formation of cadmium oxide from the elements is, therefore,

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

(4) The X-ray diffractions were conducted by K. C. Conway and C. J. O'Brien.

(5) E. W. Washburn, *Natl. Bur. Stands. J. Res.*, **10**, 525 (1933).

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

TABLE II

COMBUSTION DATA FOR CADMIUM

Mass. of Cd, g.	Total energy, cor. to 30°, cal.	Cor. for fuse and *EIt*, cal.	Cor. for Ti, cal.	Cor. for incomp. comb., cal.	Net total energy, cal.	$-\Delta U_B$, cal./g.
6.99965	4221.98	−20.19	−534.22	126.12	3793.7	542.0
7.00033	4093.46	−19.21	−355.12	69.43	3788.6	541.2
7.00007	4412.99	−20.61	−709.37	115.94	3799.0	542.7
7.00008	4182.91	−20.15	−442.49	64.91	3785.2	540.7
6.99986	4335.34	−17.39	−616.88	77.25	3778.3	539.8
7.00023	4010.38	−19.03	−267.51	70.57	3794.4	542.0
7.00022	4345.23	−19.86	−623.15	87.86	3790.1	541.4
6.99968	4087.81	−19.60	−355.35	80.21	3793.1	541.9
					Mean	541.5 ± 0.7

$\Delta H_{298.16} = -61.2 \pm 0.2$ kcal./mole. The uncertainty interval allows for items corresponding to those listed above for chromium.

Recent compilers[1,2] of data have adopted −269.7 and −270.0 kcal./mole as the heat of formation of chromium oxide and −60.86 and −62.2 kcal./mole as the heat of formation cadmium oxide. The present results are considered superior from the viewpoint of experimental technique, precision and metal purity.

Combination of the new heat of formation values with entropy data listed by Kelley[6] leads to $\Delta F^\circ_{298.16} = -253.2 \pm 0.5$ kcal./mole for the free energy of formation of chromic oxide and $\Delta F^\circ_{298.16} = -54.1 \pm 0.3$ kcal./mole for cadmium oxide.

BERKELEY 4, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Activation Energy for the Solid State Reaction γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$

BY FRANK E. DEBOER[1] AND P. W. SELWOOD

RECEIVED MARCH 15, 1954

Thermomagnetic measurements have been made on gamma ferric oxide prepared in several ways and with the addition of alumina, lanthana and gallia. The experimental data have been used to calculate the activation energy for the transformation γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$. The activation energy for this reaction depends on previous heat treatment. It is raised by the presence of alumina, lowered by lanthana, and unaffected by gallia.

Quantitative description of reactions in the solid state has recently been facilitated by the demonstration by Parkins, Dienes and Brown[2] that activation energies for rate processes may, under certain conditions, be calculated from the isothermal variation of a measured physical property, without knowledge of the order of the reaction.

The method used in the present study was isothermal variation of the specific magnetization, in a manner similar to that used by Hofer[3] in a study of the decomposition of cobalt carbide. The method is based on the assumption that in a mixture of gamma and alpha ferric oxides the specific magnetization is linear with the mass of the ferromagnetic gamma phase.

Ferromagnetic ferric oxide has the spinel structure and alpha ferric oxide has the corundum structure. Thus in order for the transition to occur the oxygen lattice must shift from cubic close packed to hexagonal close packed and some of the iron ions must migrate from tetrahedral to octahedral positions. There have been several investigations of this reaction since the gamma oxide was characterized, in 1925. It has been established that aging[4] and purity govern the rate of transition. In particular it has been shown that alumina and other substances in small amounts may stabilize the gamma oxide.[5] The most nearly quantitative of these studies was that of Sachse and Haase.

Experimental

Preparations.—Series N was prepared in a conventional manner by precipitation of hydrous Fe_3O_4 which was then oxidized to γ-Fe_2O_3. Fifty grams of ferric ammonium sulfate hydrate in 0.5 l. of boiling water was added to 61.5 g. of ferrous ammonium sulfate hydrate in a like amount of boiling water. The solution so formed was poured into 2 l. of dilute ammonium hydroxide. The resulting jet black precipitate was washed by decantation six times with 4 l. of water each time. It was then filtered, dried at 110° for several hours and crushed to pass a 150-mesh screen. The gel was then divided into several portions and these were oxidized in air at 230° for varying lengths of time as shown in Table I.

Series PY was prepared from a pyridine complex according to the directions of Baudisch and Hartung.[6] About 120 g. of the complex, $Fe[py]_4Cl_2$ was added to 6 l. of water. Clean air was bubbled through this solution to oxidize and convert the mixture to gamma ferric oxide hydrate, γ-$Fe_2O_3{\cdot}H_2O$. The precipitated monohydrate was dried in air at 110° for 24 hours, crushed in an agate mortar to pass a 150-mesh screen, then heated in air for varying lengths of time as shown in Table I.

Series AL was made as follows: 110 g. of ferrous sulfate hydrate was dissolved in 1.1 l. of water. To this solution, in different preparations, there was added from 0 to 16 g. of aluminum sulfate hydrate. The solution was brought

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(1) This work was initiated under contract with the Office of Naval Research and continued on the Visking Corporation Fellowship, receipt of which is gratefully acknowledged.

(2) W. E. Parkins, G. J. Dienes and F. W. Brown, *J. Appl. Phys.*, **22**, 1012 (1951).

(3) L. J. E. Hofer, E. M. Cohn and W. C. Peebles, *J. Phys. Colloid Chem.*, **53**, 661 (1949).

(4) H. Sachse and R. Haase, *Z. physik. Chem.*, **A148**, 401 (1930).

(5) P. H. Emmett and K. S. Love, *J. Phys. Chem.*, **34**, 41 (1930).

(6) O. Baudisch and W. H. Hartung, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 184.