Fluorine Bomb Calorimetry

Enthalpy of Formation of Nickel Difluoride

EDGARS RUDZITIS, ERVEN H. VAN DEVENTER, and WARD N. HUBBARD
Chemical Engineering Division, Argonne National Laboratory, Argonne, Ill.

The energy of formation of nickel difluoride was measured by direct combination of the elements in a bomb calorimeter. From these measurements, the standard enthalpy of formation $\Delta Hf^{\circ}_{298.15}$ (NiF_2,c) was -157.2 ± 0.4 kcal. per mole.

IN VIEW OF the widespread use of nickel in research and technology related to fluorine, including fluorine bomb calorimetry, a determination of the energetics of the nickel-fluorine reaction appeared desirable. The previously accepted value (*20*) of the enthalpy of formation of nickel fluoride, −159.5 kcal. per mole, was derived from studies of chemical equilibria at elevated temperatures; the present authors' estimate of the uncertainty of this value is ±3 kcal. per mole. In the present work, a more accurate value was obtained by direct combination of the elements in a bomb calorimeter. A valuable by-product of this investigation was the development of a fluorine combustion technique suitable for substances which exhibit a degree of passivity toward fluorine.

EXPERIMENTAL

Materials. High-purity Nivac nickel, produced by the Crucible Steel Co., was rolled to foil about 0.1 mm. thick. This material was supplied by R. L. Jarry, who has reported (*13*) kinetics of its reaction with fluorine. The foil, although self supporting, was soft enough to be perforated, folded, and cut into disks, strips, and wire. Chemical and spectrochemical analysis showed the following significant impurities (in p.p.m.): N, 58; C, 36; O, 20; and H, 2. The Ni was preconditioned by exposure to fluorine; the typical weight gain was 0.08 mg. per gram.

The fluorine was purified by distillation (*23*). Its impurity content was less than 0.1%.

Anhydrous nickel fluoride, obtained from the City Chemical Corp., contained about 1% of oxygen as determined by the $KBrF_4$ method (*6*). Repeated autoclaving with chlorine trifluoride at 300° C. under autogenous pressure effectively removed the oxygen impurity.

Apparatus and Procedures. The calorimeter and calorimetric procedures have been described earlier (*7*). The bomb, designated Ni-4B, with an internal volume of 0.365 liter, was lined with nickel fluoride in a manner similar to that described for magnesium combustions (*22*). After a number of trials, the following arrangement overcame the problems of obtaining ignition and sustaining combustion. The edge of a circular, perforated nickel foil was folded to form a basket which was filled with strips of nickel and suspended from a post by a nickel wire. In addition, three or four circular pieces of nickel foil, whose diameter was slightly larger than the inside diameter of the nickel fluoride liner, were stacked under the basket about 1 cm. apart. The bomb was evacuated and charged with 15 to 25 atm. of fluorine. Electrical ignition of a cadmium wire-and-foil fuse initiated the combustion. (Cadmium was chosen for the fuse material because x-ray investigations of heated synthetic NiF_2-CdF_2 mixtures disclosed no significant interaction.) The burning proceeded in several steps as the strips, basket, and stacked foils ignited successively. This arrangement tended to minimize the amount of molten nickel that dropped onto the nickel fluoride liner, melted it, and submerged.

Postcombustion Analysis. Unreacted nickel, which typically amounted to 50% of the introduced sample, was mostly in the form of beads imbedded in the liner. Its presence was readily detected by the color and glassy appearance of the nickel fluoride which had solidified around the molten droplets. These portions of the liner were finely ground, and the unreacted nickel was then mechanically and magnetically separated and weighed. Small amounts of nickel fluoride on the surface of, or occluded in, the beads were determined by chemical analysis (*9, 18*) for fluoride. The amount of reacted nickel was determined by difference. The combustion product, NiF_2, was identified by its x-ray diffraction pattern.

Analysis was made also of the postcombustion gases, which typically contained more than 99% fluorine. After combustion, the bomb gases were discharged into an analytical train where fluorine was removed by reaction with mercury; the residual gases were then transferred by a Toepler pump into a gas buret where the total amount was determined. The relative amounts of the component gases were determined subsequently by mass spectrometry and by gas chromatography.

In each series of fluorine bomb calorimetric combustions in which compressed fluoride powder has been used to support the sample or line the bomb, the investigators have been plagued with interpretation of the fact that oxygen is liberated during the combustion experiment. In this investigation, additional evidence was sought which would indicate that, if the fluoride powder is pretreated by high-temperature, high-pressure autoclaving with anhydrous HF and/or ClF_3 to minimize the oxygen content of the powder, then a thermal correction is not required for liberation of oxygen during the combustion. Experiments 8, 9, and 11 were performed in such a manner that the fluoride liner in the bomb was not exposed to air; between experiments the bomb was opened only in a helium-filled glovebox.

RESULTS

Eleven calorimetric combustions were performed; incomplete analysis invalidated two experiments and one additional value was rejected because of excessive deviation from the mean. The results of the remaining experiments, summarized in Table I, are expressed in terms of the defined calorie equal to (exactly) 4.184 absolute joules. Item 1, the mass of nickel burned, was obtained by correcting the mass of the Ni sample for the amount fluorinated during the preconditioning in fluorine and correction for the amount of Ni recovered after the experiment. Also listed is the amount of Ni burned, expressed as % of sample introduced into the bomb. For the calculation of item 3, $\mathcal{E}$(Calor.) was taken to be 3423.00 ± 0.23 cal. per degree from a series of five benzoic acid calibration experiments which immediately followed the nickel combustions. For calculation of item 4, the following values were used (calories per degree per mole): C_p—Ni, 6.23 (*11*); NiF_2, 15.31 (*3*);

Table I. Results of Nickel Combustion Experiments[a]

		Combustion Number							
		1	2	3	4	6	8	9	11
1.	*m′*, grams (% burned)	1.0656_3 (42.3)	1.1428_9 (58.7)	1.4442_4 (48.3)	1.9517_6 (42.3)	2.3200_4 (53.4)	1.0937_2 (48.4)	0.9803_7 (47.6)	0.9883_4 (43.3)
2.	Δt_c, degree	0.84698	0.94959	1.13080	1.51193	1.79807	0.85439	0.76163	0.77069
3.	$\mathfrak{E}$(Calor.) ($-\Delta t_c$), cal.	−2899.2	−3250.5	−3870.7	−5175.3	−6154.8	−2924.6	−2607.2	−2638.1
4.	$\Delta E_{\text{contents}}$, cal.	−102.5	−114.2	−134.9	−178.0	−205.3	−92.5	−80.5	−77.9
5.	$\Delta E_{\text{ignition}}$, cal.	1.8	2.4	2.4	2.4	3.4	2.3	2.6	2.3
6.	ΔE_{gas}, cal.	−1.3	−1.3	−1.5	−2.8	−3.0	−1.1	−1.4	−1.3
7.	ΔE_{fuse}, cal.	158.4	306.4	155.2	159.3	143.3	90.6	91.2	86.1
8.	$\Delta Ec^\circ/M$, cal./gram	−2667.7	−2674.9	−2665.4	−2661.4	−2679.4	−2674.5	−2647.2	−2659.8

Mean $\Delta Ec^\circ/M$(Sample) = −2666.3 cal./gram
Std. dev. of mean = 2.9 cal./gram
Impurity correction = −0.6 cal./gram
$\Delta Ec^\circ/M$(Ni,c) = −2666.9 cal./gram

[a] The calculations and symbols are from reference (*10*) except that $\Delta t_c = t_f - t_i - \Delta t_{\text{corr}}$ and items 3 + 4 + 5 = $\Delta E_{\text{I.B.P.}}$, the energy of the isothermal bomb process.

CdF_2, 15.8 (*21*); and C_v—F_2, 5.50 (*5*). The contents of the bomb, in addition to the sample, fuse, and fluorine were: 429.3 grams of nickel, in the form of liner, electrodes, etc.; and varying amounts of nickel fluoride liner weighing 470.5, 466.8, 459.6, 446.5, 424.4, 390.8, 372.3, and 343.5 grams for the eight experiments as listed. Item 7, ΔE_{fuse}, was calculated from the amount of cadmium burned and its energy of combustion in fluorine (*21*), −1483.9 cal. per gram. Item 8, $\Delta Ec^\circ/M$, is the sum of items 3 through 7 divided by *m′*. The impurity correction was made with the assumption that oxygen was in the form of NiO and the other impurities were dissolved in their elemental states without significant heat effects. The reaction products were assumed to be NiF_2, O_2, N_2, CF_4, and HF. The following ΔHf° values were used (in kilocalories per mole): NiO, −57.3 (*1*); HF, −64.8 (*24*); and CF_4, −221 (*24*). An estimated uncertainty of ±0.1 cal. per gram in the impurity correction includes allowances for variations in the analyses and the assigned chemical states of the impurities.

The Student's *t*-test failed to show a significant trend in the results attributable to the variation in *m′* or the percentage burned.

The results of gas analysis showed that the oxygen concentration changed from 0.05% before the combustion to 0.5% after the combustion for experiments 1 through 6 when the bomb was handled in air. In experiments 8 through 11, the bomb did not contact air and the oxygen concentration decreased to 0.1%. The difference in postcombustion oxygen levels would represent a thermal effect of ~150 cal. if the liberated oxygen had been due to a fluorine-oxide reaction. The fact that such a large thermal effect is not observed strengthens the belief that the liberated oxygen is due primarily to an oxygen-fluorine exchange near the reaction zone.

The following standard thermal data were derived for the reaction

$$Ni(c) + F_2(g) \rightarrow NiF_2(c) \qquad (1)$$

with the reactants and products in their standard states at 25° C. (in kilocalories per mole): $\Delta Ef^\circ = -156.6$; $\Delta Hf^\circ = -157.2$; and $\Delta Gf^\circ = -145.9$. An uncertainty interval of ± 0.4, which equals twice the combined standard deviation resulting from the scatter of $\Delta Ec^\circ/M$ values, calibration data, and impurity corrections, was assigned to each of the derived values. In the calculation, the atomic weight of nickel was taken as 58.71 and the following entropies, S°_{298}, were used (in calories per degree per mole): Ni, 7.14 (*16*); F_2, 48.5 (*16*); and NiF_2, 17.6 (*3*).

DISCUSSION

Table II presents a comparison of the calorimetrically obtained value of $\Delta Hf^\circ_{298}(NiF_2)$ with previously determined values, all of which were derived from high-temperature equilibrium studies by the transpiration method. In the data of Jellinek and Rudat (*14*) for reaction 1 of Table II, the concentration of the HF in H_2 was dependent on the flow rate. To interpret their data, Jellinek and Rudat

Table II. Derived Enthalpies of Formation of NiF_2

No.	Reaction	Temperature, ° K.	ΔH_{298} Kcal.	$\Delta Hf^\circ_{298}(NiF_2)$ Kcal./Mole
1.	$H_2 + NiF_2 \rightarrow Ni + 2\ HF$[a]	573, 673, 723, 773,	30.0, 30.0, 30.3, 30.3,	−160
2.	$H_2O + NiF_2 \rightarrow NiO + 2HF$[b]	773, 823, 873, 923, 973	29.1, 28.7, 28.8, 29.3, 28.8	−155
3.	$NiCl_2 + 2\ HF \rightarrow NiF_2 + 2\ HCl$[c]	477, 520, 589, 623, 684, 735, 801, 830,	3.1, 3.0, 2.9, 2.9, 2.8, 2.6, 2.6, 2.5	−156
4.	$Ni + F_2 \rightarrow NiF_2$[d]	298	−157.2	−157.2

[a] (*14*). [b] (*4*). [c] (*8*). [d] This work.

extrapolated the concentration to zero flow rate. Because this is no longer considered sound practice (*17, 19*), the result is suspect. Domange (*4*) calculated the data for reaction 2 by the same method; however, on re-examination of the data the authors find an apparent "plateau region" at flow rates of approximately 10 ml. per minute. Recalculation of the data that apply in this region leads to the value given in the table. The data of Hood and Woyski (*8*) for reaction 3 were obtained in a plateau region, and the equilibrium was approached from both directions; nevertheless, the present authors' calculation of the heats of reaction by the third-law method shows a small but distinct trend. For these calculations, free energy functions for the gases were taken from the JANAF Tables (*12*) and those for solids, except NiF_2, from Kelley's compilation (*15*). The free energy functions for NiF_2 were calculated from the extraploated low-temperature heat capacity data according to Catalano and Stout (*3*). The auxiliary ΔHf° values used for calculating $\Delta Hf_{298}(NiF_2)$ are (in kilocalories per mole): $NiCl_2$, −73.04 (2); H_2O, −57.8 (*24*); and HCl, −22.1 (*24*).

CONCLUSION

For the reasons given above, the authors believe that the earlier values of $\Delta Hf^\circ_{298}(NiF_2)$ based on equilibria data are suspect and that their value, based on the direct combustion of nickel in fluorine, is preferable. In spite of the difficulties of burning nickel in fluorine and incomplete combustions, the precision obtained is acceptable.

Recent solid-state e.m.f. measurements (Lofgren, N. L., McIver, E. J., U. K. Atomic Energy Establishment, Rept. **AERE-R-5169**, 1966) on the cell Mg, $MgF_2|CaF_2|NiF_2$, Ni, in combination with the value ΔHf°_{298} (MgF_2, c) = −268.7 kcal. per mole (*22*), yielded the values $\Delta Hf^\circ_{298}(NiF_2,c)$ = −156.7 or −157.6 kcal. per mole, respectively, depending on whether the calculations were made by the second- or third-law methods. The latter values are in excellent agreement with the value reported.

ACKNOWLEDGMENT

The authors thank F. J. Karasek for rolling of the nickel sample into foil, R. Juvinall and L. Ross for the postcombustion determinations of NiF_2 in nickel, and H. M. Feder for his interest and help. The assistance of M. Ader in preparation of the manuscript is gratefully acknowledged.

LITERATURE CITED

(1) Boyle, B.J., King, E.G., Conway, K.C., *J. Am. Chem. Soc.* **76**, 3835 (1954).
(2) Busey, R.H., Giauque, W.F., *Ibid.*, **75**, 1791 (1953).
(3) Catalano, E., Stout, J.W., *J. Chem. Phys.* **23**, 1284 (1955).
(4) Domange, L., *Ann. chim. (Paris)* [11] **7**, 225 (1937).
(5) Evans, W.H., Munson, T.R., Wagman, D.D., *J. Research Natl. Bur. Standards* **55**, 147 (1955).
(6) Goldberg, J., Meyer, A.S., Jr., White, J.C., *Anal. Chem.* **32**, 314 (1960).
(7) Greenberg, E., Settle, J. L., Feder, H.M., Hubbard, W.N., *J. Phys. Chem.* **65**, 1168 (1961).
(8) Hood, G.C., Woyski, M.M., *J. Am. Chem. Soc.* **73**, 2738 (1951).
(9) Horton, A.D., Thomason, P.F., Miller, F.J., *Anal. Chem.* **24**, 548 (1952).
(10) Hubbard, W.N., in "Experimental Thermochemistry," H.A. Skinner, Ed., Vol. **II**, Chap. 6, Interscience, London, 1961.
(11) Hultgren, R., Orr, R.L., Anderson, P.D., Kelley K.K., "Selected Values of Thermodynamic Properties of Metals and Alloys," Wiley, New York, 1963.
(12) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1960 - 1965.
(13) Jarry, R.L., Fischer, J., Gunther, W.H., *J. Electrochem. Soc.* **110**, 346 (1963).
(14) Jellinek, K., Rudat, A., *Z. anorg. u. allgem. Chem.* **175**, 281 (1928).
(15) Kelley, K.K., *U. S. Bur. Mines, Bull.* **584**, 1960.
(16) Kelley, K.K., King, E.G., *Ibid.*, **592**, 1961.
(17) Merten, U., Bell, W.E., General Atomic, Report, **GA-2144** (Rev.), 1961.
(18) Mengregian, S., *Anal. Chem.* **26**, 1161 (1954).
(19) Richardson, F.D., Alcock, C.B., in "Physicochemical Measurements at High Temperatures," Chap. 6, J.O'M. Bockris, J.L. White, J.D. MacKenzie, Eds.; Academic Press, New York, 1959.
(20) Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., Jaffe, I., *Natl. Bur. Std. (U. S.), Circ.* **500**, 1952.
(21) Rudzitis, E., Feder, H.M., Hubbard, W.N., *J. Phys. Chem.* **67**, 2388 (1963).
(22) *Ibid.*, **68**, 2978 (1964).
(23) Stein, L., Rudzitis, E., Settle, J.L., "Purification of Fluorine by Distillation," Argonne National Laboratory, **ANL-6364**, 1961.
(24) Wagman, D.D., Evans, W.H., Halow, I., Parker, V.B., Bailey, S.M., Schumm, R.H., *Natl. Bur. Std. (U. S.), Techn. Notes*, **270-1**, 124 pp., 1965.

RECEIVED for review August 5, 1966. Accepted September 2, 1966. Work performed under the auspices of the U. S. Atomic Energy Commission. Operated by The University of Chicago under Contract No. W-31-109-eng-38. This paper is Part XIX in a series on Fluorine Bomb Calorimetry.

Thermochemistry of Cobaltous Hydroxide

L. M. GEDANSKY, G. L. BERTRAND, and L. G. HEPLER
Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pa.

The heat of solution and heat of precipitation of $Co(OH)_2$(pink) were determined calorimetrically. Combination of the calorimetric data with appropriate heats of formation yield $\Delta H_f^\circ = -129.4$ kcal. per mole for $Co(OH)_2$(pink). This ΔH_f° was combined with $\Delta G_f^\circ = -110.0$ kcal. per mole for $Co(OH)_2$(pink) from solubility data to yield $S^\circ_{298} = 22.3$ cal. per degree per mole for $Co(OH)_2$(pink).

ALTHOUGH there are many solubility data for the slightly soluble hydroxides of the transition elements, there are very few reliable heats of formation or entropies available for these important compounds. This investigation was undertaken to remedy this lack of information for $Co(OH)_2$, and also to acquire data that may be useful guides in estimating thermochemical properties of other hydroxides.

Bichowsky and Rossini (*2*) listed $\Delta H_f^\circ = -131.5$ kcal. per mole and, more recently, Rossini *et al.* (*10*) have listed $\Delta H_f^\circ = -131.2$ kcal. per mole for $Co(OH)_2$. Both of these values are based on the heats of precipitation determined calorimetrically by Thomsen. Latimer (*8*) cited $\Delta H_f^\circ = -129.3$ kcal. per mole, apparently on the basis of an estimated entropy and ΔH_f° derived from a solubility product. All of these values (and our values cited later) depend on the thermochemical properties assigned to Co^{+2} or some compound of Co(II).

The authors have investigated the thermochemical properties of $Co(OH)_2$ by way of calorimetric determination of both heats of precipitation and heats of solution in acid.

EXPERIMENTAL

The calorimeter (*9*) consists of a Dewar vessel suspended in a brass can submerged in a water bath maintained at