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 $\Delta Hf^\circ_{298}(NiF_2)$ 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 $\Delta Hf^\circ_{298}(MgF_2, c) = -268.7$ 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.

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Thermochemistry of Cobaltous Hydroxide

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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 $\Delta H^\circ_f = -129.4$ kcal. per mole for $Co(OH)_2$(pink). This ΔH°_f was combined with $\Delta G^\circ_f = -110.0$ 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 $\Delta H^\circ_f = -131.5$ kcal. per mole and, more recently, Rossini *et al.* (*10*) have listed $\Delta H^\circ_f = -131.2$ 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 $\Delta H^\circ_f = -129.3$ 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 constant temperature. Temperatures in the calorimetric system were determined with a nickel resistance thermometer connected to a Leeds and Northrup Mueller G-2 bridge and a Beckman Model 14 breaker amplifier. The resistance thermometer and the calibration heater were contained in a glass spiral filled with mineral oil. Stirring was effected by means of a glass stirrer that passed through the center of the glass spiral. A fragile glass bulb attached to the end of the stirrer contained the weighed calorimetric sample, which was introduced to the solution by depressing the stirrer and breaking the bulb. All the calorimetric data reported here were obtained with 950 ml. of solution at 25.0° ± 0.2° C.

The calorimetric samples of $Co(OH)_2$ were prepared from Baker Analyzed reagent grade $CoSO_4 \cdot 7H_2O$ and $CoCl_2 \cdot 6H_2O$. The general procedure was to mix rapidly, with continuous stirring, 100 ml. of a 1*M* Co(II) salt solution with 150 ml. of a 2*M* NaOH solution. After about 15 minutes, during which the original blue precipitate changed to pink, the $Co(OH)_2$ was filtered on paper and washed thoroughly with water. The pink $Co(OH)_2$ precipitate was then washed with 100 ml. of 95% ethanol and finally dried and stored in a vacuum system. Deoxygenated water prepared by boiling distilled water for 10 minutes and then cooling with bubbling N_2 was used in all of the preparations and calorimetric measurements. The entire preparation procedure was carried out in a N_2 atmosphere.

The various samples were analyzed as cobalt pyrophosphate and corresponded to 100 ± 1% $Co(OH)_2$. Samples of hydrated cobalt sulfate used in heat of precipitation measurements were prepared and analyzed as described previously (*4*).

RESULTS AND CALCULATIONS

Heats of solution of pink $Co(OH)_2$ in excess dilute perchloric acid were carried out with the results shown in Table I, where the ΔH_1 values refer to the calorimetric reaction

$$Co(OH)_2(\text{pink}) + 2\ H^{+}(\text{aq.}) = Co^{+2}(\text{aq.}) + 2\ H_2O(\text{liq.}) \qquad (1)$$

Total calorimetric uncertainty in the ΔH_1 values listed in Table I is no more than 0.05 kcal. per mole. With the aid of data from NBS Circ. 500 (*10*), the authors estimate the small heats of dilution that are required for use with ΔH_1 values to obtain $\Delta H_1^\circ = -21.2 \pm 0.3$ kcal. per mole of $Co(OH)_2$. The indicated uncertainty in ΔH_1° includes contributions from possible impurities in the $Co(OH)_2$, heats of dilution, and calorimetric uncertainties.

The precipitation reaction represented by Equation 2

$$Co^{+2}(\text{aq.}) + 2\ OH^{-}(\text{aq.}) = Co(OH)_2(\text{pink}) \qquad (2)$$

was investigated in two ways. The first method involved the addition of 2 to 5 ml. of 6*M* NaOH to 950 ml. of a dilute solution of cobalt sulfate, as indicated in Equation 3:

$$CoSO_4(\text{dilute}) + 2\ NaOH(\text{concd.}) = Co(OH)_2(\text{pink}) + Na_2SO_4(\text{dilute}) \qquad (3)$$

Separate determination of the combined heat of bulb breaking and dilution of the NaOH permitted calculation of the experimental results in terms of the desired reaction 2 as shown in Table II.

To obtain the desired standard heat of precipitation from the data in Table II, heat of dilution data from Lange (7) were used to calculate $\Delta H_2^\circ = -5.7$ kcal. per mole.

The second method involved addition of samples of hydrate of $CoSO_4$ (of known composition) to 0.030*M* solutions of NaOH as in Equation 4:

$$CoSO_4 \cdot nH_2O(\text{c.}) + 2\ NaOH(\text{dilute}) = Co(OH)_2(\text{pink}) + Na_2SO_4(\text{dilute}) \qquad (4)$$

Separate determination of the heats of solution of these hydrates—results in good agreement with those of an earlier investigation (*4*)—permitted calculation of the experimental results in terms of the desired Reaction 2 as shown in Table III.

The ΔH_2 values in Table III were used with heats of dilution (*7, 10*) to calculate the desired standard heat of precipitation as $\Delta H_2^\circ = -5.5$ kcal. per mole of $Co(OH)_2$.

Calorimetric uncertainties in ΔH_2 values are about 0.1 kcal. per mole. The total uncertainty also includes contributions from heats of dilution and especially that due to uncertainty about the physical state of the precipitated cobalt hydroxide. The authors adopt $\Delta H_2^\circ = -5.6 \pm 0.5$ kcal. per mole.

The above $\Delta H_2^\circ = -5.6$ kcal. per mole was combined with the heat of ionization of water (*5*) to obtain a calculated value of $\Delta H_1^\circ = -21.3 \pm 0.5$ kcal. per mole, compared to the $\Delta H_1^\circ = -21.2 \pm 0.3$ kcal. per mole from heats of solution. The authors combine two earlier heats of precipitation from concentrated solutions that were determined by Thomsen (2) with large heats of dilution to obtain approximate ΔH_1° values of −20.6 and −21.8 kcal. per mole.

Before completing the calculations for $Co(OH)_2$, the thermodynamic properties of Co^{+2}(aq.) must be considered. Adami and King (*1*) reported $\Delta H = -14.28$ kcal. for the reaction

$$CoO(\text{c.}) + H_2SO_4 \cdot 7.068\ H_2O(\text{liq.}) = CoSO_4(\text{c.}) + 8.068\ H_2O(\text{liq.})$$

Combination of this value with $\Delta H_f^\circ = -57.1$ kcal. per mole for CoO(c.) and data from NBS Circ. 500 (*10*) led (*1*) to $\Delta H_f^\circ = -212.0$ kcal. per mole for $CoSO_4$(c.). The standard heat of solution of $CoSO_4$(c.)—$\Delta H^\circ = -18.8$ kcal.

Table I. Heats of Solution of Pink $Co(OH)_2$ in $HClO_4$(aq)

$Co(OH)_2$, G.	$HClO_4$, M	$-\Delta H_1$, Kcal./ Mole $Co(OH)_2$
0.2354	0.0119	21.19
0.2395	0.0119	21.02
0.2505	0.0119	21.11
0.2363	0.0238	21.26
0.2927	0.0238	21.15
0.2298	0.0595	21.25
0.2439	0.0595	21.14
0.2487	0.0595	21.07
0.2538	0.0595	21.29
0.2414	0.119	21.03
0.2587	0.119	21.07
0.2656	0.119	20.98

Table II. Heats of Precipitation of Pink $Co(OH)_2$

Moles of $CoSO_4$	Mole of OH^-	$-\Delta H_2$ Kcal./ Mole $Co(OH)_2$
5.067×10^{-3}	0.0120	5.83
6.642	0.0210	6.28
10.668	0.0300	6.26

Table III. Heats of Precipitation of Pink $Co(OH)_2$

Moles of $CoSO_4$	$-\Delta H_2$, Kcal./ Mole $Co(OH)_2$
9.190×10^{-3}	6.35
10.153	6.13
10.160	5.88
10.944	5.98
11.043	5.96
11.566	5.99

per mole—has been combined (*4*) with this ΔH_f° and that for SO_4^{-2}(aq.) from NBS Circ. 500 (*10*) to yield ΔH_f° = −13.9 kcal. per mole for Co^{+2}(aq.). Subsequent publication of part of the successor to NBS Circ. 500 by Wagman *et al.* (*11*) suggests that these calculations should be revised to conform with new data for sulfuric acid and sulfate ion. These calculations yield $\Delta H_f^\circ = -212.55$ kcal. per mole for $CoSO_4$(c.), which is then combined with the ΔH° of solution of $CoSO_4$(c.) and the new ΔH_f° for SO_4^{-2}(aq.) to yield $\Delta H_f^\circ = -14.0$ kcal. per mole for Co^{+2}(aq.). Combination of this ΔH_f° with the previously reported $\bar{S}_2^\circ$ gives ΔG_f° = −13.4 kcal. per mole for Co^{+2}(aq.).

Combination of our ΔH_1° with the ΔH_f° cited above for Co^{-2}(aq.) and ΔH_f° for H_2O (*11*) gives $\Delta H_f^\circ = -129.4$ kcal. per mole for pink $Co(OH)_2$. Feitknecht and Schindler (*3*) have reviewed solubility data for cobalt hydroxide and recommend $K_{sp} = 2 \times 10^{-16}$ for pink $Co(OH)_2$. This K_{sp} leads to $\Delta G^\circ = 21.4$ kcal. per mole for the standard free energy of solution. By combination with ΔG_f° values for Co^{+2}(aq.) cited above and OH^-(aq.) (*11*) we obtain ΔG_f° = −110.0 kcal. per mole for pink $Co(OH)_2$. Further combination of ΔG_f° with ΔH_f° and entropies (*6*) of Co, H_2, and O_2 leads to $S_{298}^\circ = 22.3$ cal. per degree per mole for pink $Co(OH)_2$.

This S_{298}° for $Co(OH)_2$ is 9.6 cal. per degree per mole greater than the entropy (*6*) of CoO. Reliable third law entropies (*11*) for MgO, $Mg(OH)_2$, CaO, and $Ca(OH)_2$ lead to corresponding differences of 8.5 and 10.4 cal. per degree per mole for these pairs of compounds. Less certain entropies for $Cd(OH)_2$ and $Zn(OH)_2$ calculated by combination of ΔH_f° and K_{sp} data (*8, 10*) and third law entropies (*6*) for CdO and ZnO lead to entropy differences between the hydroxide and oxide of 9.7 (Cd) and 9.4 (Zn) cal. per degree per mole. Therefore, apparently, entropies of $M(OH)_2$ compounds can be estimated reliably by adding ~9.5 cal. per degree per mole to the S_{298}° value of the corresponding oxide.

It has long been believed that the MO and $M(OH)_2$ compounds of transition elements are about equally stable in contact with water, which means that $\Delta G^\circ \cong 0$ for reactions of the type

$$MO + H_2O(liq.) = M(OH)_2$$

Free energies of formation lead to ΔG° values of −1.9, −2.0, and +0.2 kcal. per mole for reactions of this type involving Co, Cd, and Zn, respectively. Similar, but less certain, calculations can also be made for several compounds of transition elements in higher oxidation states. Thus, the free energy of hydration (by liquid water) of many oxides of transition elements apparently have small (usually negative) ΔG° values. However, ΔG° values for hydration of MgO and CaO are −6.5 and −13.2 kcal. per mole.

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Fluorine Bomb Calorimetry

Enthalpies of Formation of the Diborides of Zirconium and Hafnium

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The energies of combustion in fluorine of zirconium diboride ($ZrB_{1.993\pm0.006}$) and hafnium diboride ($HfB_{2.003\pm0.006}$) were measured in a combustion bomb calorimeter. These results, when combined with the enthalpies of formation of ZrF_4, HfF_4, and BF_3 previously obtained by similar techniques, gave $\Delta Hf_{298.15}^\circ$ values of $-77._9 \pm 1._5$ and $-78._6 \pm 2._1$ kcal. (g.f.m.)$^{-1}$ for $ZrB_{1.993\pm0.006}$ and $HfB_{2.003\pm0.006}$, respectively.

RECENT interest in refractory borides for possible high temperature applications has prompted a number of concurrent studies of the thermodynamic properties of zirconium and hafnium diborides. Some of these studies deal with vaporization processes (*2, 19, 21, 23, 44, 51*), oxygen bomb calorimetry (7, 14), low- (*47, 49*) and high- (*45*) temperature heat capacities, and relative stabilities (*4, 33, 38*). In this work accurate values of the enthalpies of formation were sought by the method of fluorine bomb calorimetry.

EXPERIMENTAL

Preliminary Observations. Kuriakose and Margrave (*22*) have observed the fluorination of zirconium and hafnium diborides in low-pressure fluorine at elevated temperatures.