[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY HARVARD UNIVERSITY]

Heats of Combustion and Formation of Metal Carbonyls. II. Nickel Carbonyl[1]

BY A. K. FISCHER, F. A. COTTON[2] AND G. WILKINSON

RECEIVED DECEMBER 10, 1956

The heat of combustion of liquid nickel carbonyl, $Ni(CO)_4$, has been determined as $\Delta H^\circ_{298} = -282.2 \pm 0.5$ kcal./mole. For the reaction $Ni(s) + 4CO$ (g, 1 atm.) $= Ni(CO)_4$ (g, 1 atm.) a value of -39.1 ± 0.5 kcal./mole is calculated for ΔH°_{298} (the error does not include errors in auxiliary data). The relation of these values to the various highly divergent results previously reported is discussed.

Introduction

The unsatisfactory status of the value of ΔH° for the reaction $Ni(s) + 4CO(g) = Ni(CO)_4(g)$ was recently emphasized by Spice, Staveley and Harrow,[3] who surveyed the field, checked some of the earlier calculations, and tabulated the values which they recalculated so as to be consistent among themselves in respect to the various supplementary quantities. They indicated that values for ΔH°, as determined by several methods, ranged from -26.0 to -52.6 kcal./mole, with the more recent values tending to center toward -35 kcal./mole, and this figure was accepted as the best then available. Because of possible uncertainties attending equilibrium studies involving finely divided nickel metal, it seemed that combustion calorimetry might assist a resolution of the difficulties. Shortly after the paper by Spice, *et al.*, there appeared a report of a combustion study by Smagina and Ormont[4] giving the value of ΔH° as -47.3 ± 1 kcal./mole. This Russian work appeared to be of doubtful reliability not only because of a paucity of experimental data and inadequately described experimental technique, but also because of the rather large deviation of their result from the region in which the value might be expected to lie as a result of the discussion by Spice, *et al.* The discordance therefore remained, and a redeterminaation of the heat of combustion of nickel carbonyl was included in the present series of combustion studies.

Experimental

The nickel carbonyl used in this work was obtained from a cylinder bottled by The Matheson Co., Inc., and was purified by repeated bulb-to-bulb distillation *in vacuo*. The purified nickel carbonyl was shown not to contain iron by testing with thiocyanate. Immediately before use, the samples were distilled into thin-walled Pyrex bulbs about 1.5 cm. in diameter. Two types of bulb (see below) were used, and the stems of either type were fused to a standard taper joint fitting into the vacuum system. After degassing the sample by means of thawing followed by freezing and pumping, the bulb was sealed by touching a small flame to the constricted stem about 1.5 cm. above the bulb at the same time that the bulb was drawn aside with tweezers. During this operation the sample was kept frozen by having the bulb just immersed in liquid nitrogen; also, the space above the sample was evacuated. Heat was further kept away from the sample by several layers of slotted asbestos paper slipped around the bulb stem. Nevertheless, slight decomposition of carbonyl vapor occurred just at the point of sealing, but analysis showed that the resulting nickel mirror weighed only 0.1 to 0.2 mg.; in a 1 to 2-g. sample the error thus introduced is negligible.

The calorimetric apparatus and technique were the same as described previously.[1] In the first of two series of combustions which were performed, the sample was fired with the aid of a benzoic acid pellet placed next to the bulb. In the second series, bulbs with 4.0 cm. of electrically heated no. 32 platinum wire sealed in (Fig. 1) were used in order to check on the hydration effect of the water present in the first set.[5]

Although incomplete combustion represented by unburned nickel metal in the final state was the rule, in a few preliminary runs a more serious difficulty was encountered in the form of residual nickel carbonyl; this was evident from the abnormally small temperature rises and spontaneous ignition upon venting the bomb gases. Subsequently, therefore, all runs were checked for residual nickel carbonyl and for unburned carbon monoxide by slowly releasing the bomb gases into a train consisting, in order, of a Dry Ice trap, an iodine pentoxide tube maintained at 150°, and two carbon tetrachloride traps. The Dry Ice trap serves to condense out any nickel carbonyl, and any carbon monoxide reacts in the iodine pentoxide tube: $5CO + I_2O_5 = I_2 + 5CO_2$.[6] Carbon dioxide and oxygen from the bomb then sweep any liberated iodine into the carbon tetrachloride traps where the characteristic violet color should develop. Nickel carbonyl was tested for by removing the Dry Ice and adding bromine water to the still cold trap; after debromination by boiling, the resulting solution was tested with dimethylglyoxime. Any run which revealed residual nickel carbonyl or unburned carbon monoxide was rejected. Three of the twenty-one runs done failed this test; none in the internally fired series did so.

The solid combustion products consisting of NiO and some unburned nickel metal were found in the combustion cup and on the bomb walls with the nickel metal concentrated as a black underlying layer almost exclusively on the lower half of the walls and in the cup. The solids were brushed out so as to recover all of the nickel metal and most of the nickel oxide, weighed and dissolved in concentrated nitric acid. To recover any traces of nickel metal occluded in fused glass, the glass was pulverized and leached with concentrated hydrochloric acid. The total nickel in these solutions was determined gravimetrically with dimethylglyoxime. To calculate the quantity of unburned metal, it was assumed that a fraction x of the solid material is nickel metal and a fraction $1 - x$ is nickel oxide; the nickel content expressed in terms of x was equated to the total nickel determined and the operation solved for x. The weight of unburned nickel metal was used to calculate a correction for incomplete combustion of nickel, using -57.3 kcal./mole as the enthalpy of formation of nickel oxide.[7]

No X-ray studies were made on the solid combustion products, but the presence of significant amounts of higher oxides of nickel was unlikely. Smagina and Ormont,[4] in runs made under conditions similar to those employed here, reported that X-ray powder patterns of the products of combustion were consistent with the presence of only NiO and

---

[1] Part I: F. A. Cotton, A. K. Fischer and G. Wilkinson, THIS JOURNAL, **78**, 5168 (1956).

[2] Chemistry Department, Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

[3] J. E. Spice, L. A. K. Staveley and G. A. Harrow, *J. Chem. Soc.*, 100 (1955).

[4] E. I. Smagina and B. F. Ormont, *J. Gen. Chem. U.S.S.R.*, **25**, 207 (1955). (In the English translation edition published by Consultants Bureau, Inc., New York, N. Y.)

[5] A few runs (not reported) were made with magnesium ribbon as a fuse, but this mode of operation was abandoned when it was realized that unknown heat effects might attend the possible formation of mixed oxides of magnesium and nickel and, indeed, the ΔH° values for the carbonyl obtained in these runs were well outside the ranges of the ones reported below.

[6] M. C. Teague, *Ind. Eng. Chem.*, **12**, 964 (1920).

[7] B. J. Boyle, E. G. King and K. C. Conway, THIS JOURNAL, **76**, 3835 (1954).

TABLE I

DATA FOR COMBUSTION OF $Ni(CO)_4$ WITH BENZOIC ACID FUSE

Run	Vac. wt. sample, g.	Cor. temp. change, °C.	Uncor. heat of combustion, kcal./mole	Cor. for incomplete combustion, kcal./mole	Fuse cor. kcal./mole	Washburn cor. kcal./mole	Fully cor. $\Delta E^{\text{comb.}}_{298°}$
1	1.86885	1.4278	−305.42	−11.12	+33.68	+0.48	−283.03[a]
2	1.71979	1.2955	−301.05	−14.70	+24.79	+ .48	−290.48
3	2.32480	1.7571	−302.04	−11.68	+28.28	+ .48	−284.96
4	2.40332	1.8752	−311.81	−13.98	+41.07	+ .47	−284.25
5	1.96039	1.7171	−350.01	−10.75	+75.89	+ .45	−284.42
6	1.25641	1.9568	−336.22	−11.02	+63.26	+ .46	−283.52

[a] This value includes a correction of −0.15 kcal. for the reduction to 25° (see text).

TABLE II

DATA FOR COMBUSTION OF $Ni(CO)_4$ WITH INTERNAL FIRING

Run	Vac. wt. sample, g.	Cor. temp. change, °C.	Uncor. heat of combustion, kcal./mole	Cor. for incomplete combustion, kcal./mole	Washburn cor. kcal./mole	Fully cor. $\Delta E^{\text{comb.}}_{298°}$
1	2.45808	1.6979	−276.03	− 4.87	+0.50	−280.40
2	2.65744	1.8163	−273.11	−10.16	+ .50	−282.77
3	2.16307	1.4761	−272.66	− 8.75	+ .50	−280.91
4	2.10515	1.5186	−287.86	− 5.95	+ .50	−293.31
5	2.95059	1.9963	−270.32	−14.34	+ .50	−284.16

Ni. Moreover, higher oxides of nickel are said not to exist in the anhydrous state.[8] Hence, although the non-anhydrous final state resulting in the runs fired with benzoic acid might conceivably permit slightly higher oxide formation, the borderline significance of the difference between this series of runs and the internally fired series would belie this; indeed, the difference can in greater likelihood be ascribed to hydration effects.

The heat input (*e.i.t.*) correction for the internally fired series was estimated in control runs with an empty sample bulb and its enclosed fuse wire in the following way. The slopes of the time *vs.* resistance curves for the fore- and after-periods, together with an allowance of an average time of 7 minutes for attainment of maximum temperature rise in a combustion run, permitted calculation of the correction, using the method of Dickenson.[9] This heat effect is such as to raise the resistance of the platinum resistance thermometer 0.0004 ohm and is included in the corrected temperature rise in Table II. Washburn corrections were calculated in one case by the original method of Washburn[10] which applies to 20° and also by the modified method of Hubbard, *et al.*,[11] which applies to 25°. The difference between the two values was insignificant for the present purposes, and all subsequent calculations were made by Washburn's simpler method. It was found that the correction differs negligibly from run to run and the same value, +0.50 kcal./mole, was applied to all.[12]

In Table I, run no. 2, and in Table II, run no. 4 were rejected as being obviously out of line with the other values. Thus, the remaining values in Table I give a mean value for $\Delta E^{\text{comb.}}_{298°}$ of −284.00 kcal./mole with an average deviation from the mean of ±0.61 kcal./mole and a standard deviation of the mean of ±0.34 kcal./mole. The mean of the remaining values in Table II is −282.06 kcal./mole with an average deviation from the mean of ±1.41 kcal./mole and a standard deviation of the mean of ±0.87 kcal./mole.

Results

An analysis of errors in the various operations leads to a maximum expected random error of ±0.80 kcal./mole in the benzoic acid ignited runs, and an error of ±0.90 kcal./mole in the internally fired series. In the latter case, the error is larger because of uncertainties in the *e.i.t.* correction. The error in the determination of unburned nickel metal is taken as ±0.006 g., leading to an error in ΔE of ±0.50 kcal./mole for an average 2-g. sample. The percentage of nickel metal in the solid combustion products varies from 16 to 21% in the benzoic acid fired series, and from 9 to 21% in the internally fired series; this is also about the range reported by Smagina and Ormont.[4]

Initial temperatures for the accepted runs ranged from 21.6° for run no. 1 in Table I to 27.9° for run no. 5 in Table II, but calculation of the temperature coefficients of these runs showed that neglecting to reduce the data to 25° introduced an error of −0.15 kcal./mole for the former and only 0.02 kcal./mole for the latter. Therefore, the temperature being assigned to the measured reaction is 25°, run no. 1 in Table I being corrected to this temperature and the other runs standing as they are.[13]

Discussion

If the means are expressed as −284.0 and −282.1 kcal./mole for the series with and without benzoic acid, respectively, and if allowance is made for the expected maximum random error, these values fail to coincide by 0.2 kcal./mole, and the separation is 0.7 kcal./mole if the standard deviations are considered. It is doubtful if much significance can be attributed to or explanation given for this difference at the present time, save ascribing it to slight, exothermic hydration of the NiO by the water produced from the combustion of benzoic acid, and/or, less likely, to the formation of a small amount of a higher oxide of nickel in the same runs. If it is assumed that the two series do indeed measure the same thing, then together they have a mean of $\Delta E^{\text{comb.}}_{298°}$ = −283.1 kcal./mole with a standard deviation of the mean[14] of ±0.5 kcal./mole; this grand average was used in the subsequent calculations.

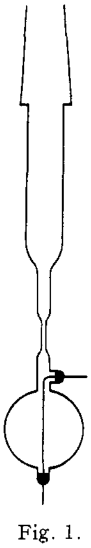

Fig. 1.

For the reaction

$$Ni(CO)_4(l) + 5/2O_2\ (g,\ 1\ atm.) = NiO(s) + 4CO_2\ (g,\ 1\ atm.)$$

$$\Delta H°_{298} = -282.2 \pm 0.5\ \text{kcal./mole}$$

---

[8] N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, Oxford, England, 1951, p. 1450.

[9] H. C. Dickenson, *Bull. Bur. Standards*, **11**, 189 (1914).

[10] E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

[11] W. N. Hubbard, D. W. Scott and G. Waddington, *J. Phys. Chem.*, **58**, 152 (1954).

[12] For the benzoic acid fired series, the fuse correction was calculated from the heat of combustion of benzoic acid under the standard conditions specified by the National Bureau of Standards. The actual conditions here, however, differed from the standard ones in that 1 ml. of water was omitted from the bomb. It can be calculated that this gives rise to a correction of −0.066% of the fuse correction. This has been included in Table I with the general Washburn corrections thus lowering them from 0.50 to the values listed. The effect is seen to be practically negligible, but has been treated to avoid uncertainty in the matter.

[13] Calculation of the correction utilized heat capacity data from National Bureau of Standards Circular 500, except for $Ni(CO)_4$, for which the value $C_p^{298°}$ = 48.9 cal./mole was taken from reference 2.

[14] In part I a typographical error occurred in the definition of this quantity. The reported standard deviations of the means were calculated from the correct expression involving Σd_i^2.

For the reaction

$$Ni(s) + 4CO(g, 1\ atm.) = Ni(CO)_4(g, 1\ atm.),\quad \Delta H°_{298} = -39.1 \pm 0.5\ kcal./mole^{15}$$

The enthalpies of formation used in the calculations are from reference 13 for CO and CO_2 and from reference 7 for NiO. The heat of vaporization of $Ni(CO)_4$ was taken as 6.5 kcal./mole.[3] From the foregoing, $\Delta Hf°_{298} = -145.1$ kcal./mole was calculated for the reaction Ni(s) + 4C (graphite) + $2O_2$ (g, 1 atm.) = $Ni(CO)_4$ (g, 1 atm.). Taking $S°_{298}$ of nickel carbonyl as 96.0 cal./°mole,[16] $\Delta Ff°_{298} = -140.0$ kcal./mole was calculated for the same reaction. The values quoted for Mittasch's work are those recalculated by Spice, *et al.*, from the corrected mathematical expressions; Reicher's value had also been recalculated by the same authors using more modern values for the relevant heats of formation and for the heat of vaporization of $Ni(CO)_4$. Of the listed figures, Reicher's is the most divergent and since the technique used is of doubtful reliability, this value perhaps need not be considered further.

The results obtained from equilibrium studies involving finely divided nickel metal may, as Spice, *et al.*, pointed out, suffer from an effect demonstrated by Giauque,[22] namely, that sometimes it may be impossible to identify equilibrium data obtained with finely divided solids with the equilibrium obtaining with the macrocrystalline phase, presumably because of the higher energy content of the more open structure of the finer material. The direct determination and the heat of combustion studies should be free from this difficulty. Mittasch's direct determination agrees fairly well with Smagina and Ormont's combustion value, but Mittasch's result conflicts markedly with the more modern direct determinations by Tomlinson and by the Mond Nickel Company, the latter agreeing well and contrasting with Mittasch's 30% higher figure. Smagina and Ormont's value was based on only three combustion runs, the average of which can be expressed to only two-figure significance and the result appears to be of doubtful reliability. In the present work, pains were taken to eliminate systematic errors, one noteworthy source of which could be incomplete detection of unburned nickel metal; an error of this sort would lead to a high value for $\Delta H°$. Consequently, it appears reasonable to regard previous values greater than −40 kcal. as erroneous.

TABLE III

SUMMARY OF $\Delta H°$ VALUES FOR $Ni(s) + 4CO(g) = Ni(CO)_4(g)$ (IN KCAL./MOLE)

Mittasch—direct determination[17]	−45.7
Tomlinson—direct determination[18]	−32.0
Mond Nickel Co.—direct determination[19]	−34.5
Mittasch—equilibrium study[17]	−26.0
Mittasch—equilibrium study[17]	−27.5
Mittasch—equilibrium study[17]	−30.0
Sykes and Townshend—indirect determination[20]	−36.3
Reicher—heat of combustion study[21]	−52.6
Smagina and Ormont—heat of combustion study[4]	−47.3
This research—heat of combustion study	−39.1

Acknowledgment.—One of us (A.K.F.) wishes to express his thanks to the Mallinckrodt Chemical Company for a grant toward research expenses.

---

(15) The ±0.5 kcal. represents the standard deviation of the mean in $\Delta E°_{298}$ and does not include errors in the auxiliary data from refs. 3, 7 and 13.

(16) B. L. Crawford, Jr., and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938), report a spectroscopically determined value of 97.0 e.u. The expected error was stated as not greater than 2%. Recently L. H. Jones, *ibid.*, **23**, 2448 (1955), reinvestigated the infrared spectrum and in a preliminary report suggests some reassignments of bands in the neighborhood of 300-400 cm.$^{-1}$ which may lower the entropy value. Spice, *et al.*,[3] found 95.4 (probably ±2 e.u.) calorimetrically, the uncertainty arising in a long low temperature extrapolation.

(17) A. Mittasch, *Z. physik. Chem.*, **40**, 1 (1902).

(18) J. R. Tomlinson, Abstract of Papers Presented at the 125th Meeting of the American Chemical Society, March, 1954, p. 18-Q.

(19) Private communication to Spice, *et al.*, see reference 3.

(20) K. W. Sykes and S. C. Townshend, *J. Chem. Soc.*, 2528 (1955). In line 2, p. 2529, a typographical error omitted a factor of 4 from the denominator of the expression for *C*, but the result was obtained from the correct formula.

(21) R. Reicher, "Werken von het Genootschap ter befordering der naturgenees-en heelkunde," Amsterdam, 2nd series, Vol. II, 1896, p. 296.

(22) W. F. Giauque, THIS JOURNAL, **71**, 3192 (1949).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

A Polarographic Study of the Formate Complexes of Cadmium, Copper, Lead, Thallium and Zinc[1]

BY HERBERT M. HERSHENSON,[2] RUTH THOMPSON BROOKS AND MARY E. MURPHY

RECEIVED OCTOBER 8, 1956

Cadmium, lead and zinc have been found to form weak but definite complexes of the types $M(HCOO)^+$, $M(HCOO)_2$, $M(HCOO)_3^-$ and $M(HCOO)_4^=$ with formate ion concentrations ranging from 0 to 1.98 *M* in solutions held at a constant ionic strength of 2.00 with perchlorate. Copper forms similar complexes which appear to be more stable, while thallium shows no complexing tendency except at very high formate concentrations. The formation constants at 25° for the $M(HCOO)^+$, $M(HCOO)_2$, $M(HCOO)^-_3$ and $M(HCOO)_4^=$ complexes, respectively, were determined to be 3, 13, 22 and 16 for cadmium, 6, 23, 27 and 15 for lead, 4, 9, 3 and 6 for zinc and 37, 116, 112 and 283 for copper. No constants could be determined for thallium.

Introduction

The formate complexes of metal ions have not been investigated extensively; however, a few complex formates of iron and chromium have been

---

(1) Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 20, 1956. Taken from the M.S. dissertations of Ruth Thompson Brooks, June, 1954, and Mary E. Murphy, June, 1956.

(2) Fox Project, Pratt & Whitney Aircraft, East Hartford, Conn.