For the reaction

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

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, $\Delta Hf^\circ_{298} = -145.1$ 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] $\Delta Ff^\circ_{298} = -140.0$ 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.

TABLE III

SUMMARY OF ΔH° 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

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 ΔH°. Consequently, it appears reasonable to regard previous values greater than −40 kcal. as erroneous.

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(15) The ±0.5 kcal. represents the standard deviation of the mean in ΔE°_{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).

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

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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

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(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.

known for some time.[3–5] Brintzinger and coworkers[5] employed dialysis measurements to establish the existence of the following complexes: $Cd(HCOO)_4^{=}$, $Cu(HCOO)_4^{=}$ and $M(HCOO)_6^{-4}$ where M may be Co^{++}, Ni^{++} or Zn^{++}.

As part of a program involving the complexing tendencies of certain anions in aqueous solution, the formate complexes of cadmium, copper, lead, thallium and zinc have been studied using the polarographic technique developed by DeFord and Hume.[6]

Experimental

Half-wave Potential Measurements.—A Sargent Recording Polarograph, Model XXI, was used throughout this study. The span voltage was normally set at 0.5 volt, the sensitivity at 0.040 μa./mm. and no damping was employed. The initial and final applied voltages were measured to ±0.1 mv. with a Rubicon potentiometer and the resistance of the cell system was determined by means of an Industrial Instruments conductivity bridge. A Beckman Model G *p*H meter was used to determine the acidity of all solutions. Nitrogen was bubbled through the sample solution before each run in order to remove dissolved oxygen. All polarograms were run at 25.0 ± 0.2°. The method employed for determining the half-wave potential, slope and diffusion current for each polarogram was essentially that described by Hume and co-workers.[7]

Electrode Assembly.—The dropping mercury electrode, made from Corning marine barometer tubing, served as cathode. Because of the possibility of precipitation of potassium perchlorate,[8] it was decided to avoid the use of a conventional saturated calomel reference electrode. Instead a reference solution saturated with quinhydrone and hydroquinone was used. The sample solution, containing 0.001 *M* metal ion, 0.01 *M* perchloric acid, and various concentrations of sodium perchlorate and sodium formate, was placed in one arm of a U-shaped cell. The other arm, separated by a sintered-glass disk, contained the reference solution and 100 cm. of 0.0014″ platinum wire wound into a 3″ coil. The reference solution consisted of the same concentrations of perchloric acid, sodium perchlorate and sodium formate as in the sample solution, but contained no metal ion, and was saturated with quinhydrone and hydroquinone by shaking with the solids immediately before use. This assembly had the advantage of reducing to a minimum the unknown junction potential. Since the *p*H of the reference solution varies with the sodium formate concentration, it was necessary to measure the *p*H of each solution in order to calculate the potential of the reference electrode in each case. The standard potential of the quinhydrone–hydroquinone electrode was taken as +0.6123 volt *vs.* hydrogen.[9] Half-wave potential values were converted to S.C.E. as reference.

Chemicals.—All chemicals were reagent grade except for C.P. quinhydrone and hydroquinone. The nitrate salts were used to supply the metal ions, sodium formate to supply the formate ions and sodium perchlorate to adjust the ionic strength.

Results and Discussion

It is generally true that, if the half-wave potential of a metal ion shifts in a more negative direction as the concentration of ligand is increased, formation of complexes is indicated. Experiments were performed, therefore, to discover the direction and magnitude of the half-wave potential shift for each metal as the concentration of formate was increased. The results are shown in Fig. 1. It may be seen that in each case except thallium, there was a pronounced shift to more negative potentials with increasing formate concentration. Thus it appeared that complex formation does occur with cadmium, copper, lead and zinc. However, the observed shift in half-wave potential is due to two factors: the increased amount of complex formation at higher formate concentrations and the change in activity coefficients due to changing ionic strength. In order to obtain quantitative results, another series of determinations was performed for each metal during which the ionic strength was maintained at a constant value of 2.00 while the formate concentration was varied. The data obtained were calculated and plotted as directed by DeFord and Hume.[6] The analysis of the data is shown in Tables I, II, III and IV.

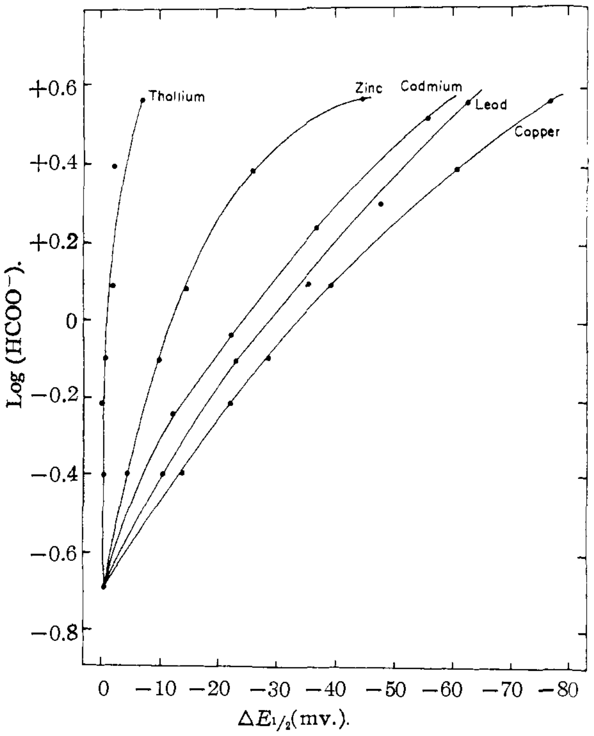

Fig. 1.—Shift in half-wave potential of the metals as a function of sodium formate concentration (based arbitrarily on the half-wave potential in 0.20 *M* formate as the initial value).

TABLE I

ANALYSIS OF $E_{1/2}$ OF CADMIUM IN FORMATE MEDIUM WITH $\mu = 2.00$

($HCOO^-$), *M*	$E_{1/2}$, v.	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.00	−0.5687	(1.00)	...	...	...	...
.09	.5730	1.40	4.4	16	...	...
.19	.5790	2.28	6.7	19	...	...
.49	.5965	9.53	17.4	29	33	...
.79	.6102	26.6	32.4	37	30	10
.89	.6140	37.0	40.4	42	33	12
.99	.6193	55.2	54.8	52	39	17
1.79	.6421	349	194	107	53	17
1.98	.6465	525	265	132	60	19
			$K_1 =$ 3	$K_2 =$ 13	$K_3 =$ 22	$K_4 =$ 16

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[3] R. Weinland and H. Reihlen, *Ber.*, **46**, 3144 (1913).

[4] W. D. Treadwell and W. Fisch, *Helv. Chim. Acta*, **13**, 1219 (1930).

[5] H. Brintzinger, H. Plessing and W. Rudolph, *Z. anorg. Chem.*, **242**, 197 (1939).

[6] D. D. DeFord and D. N. Hume, THIS JOURNAL, **73**, 5321 (1951).

[7] D. N. Hume, D. D. DeFord and G. C. B. Cave, *ibid.*, **73**, 5323 (1951).

[8] H. M. Hershenson, M. E. Smith and D. N. Hume, *ibid.*, **75**, 507 (1953).

[9] J. B. Conant and L. F. Fieser, *ibid.*, **45**, 2194 (1923).

TABLE II

ANALYSIS OF $E_{1/2}$ OF LEAD IN FORMATE MEDIUM WITH μ = 2.00

(HCOO$^-$), M	$E_{1/2}$ v.	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.00	−0.3890	(1.00)	...	...	...	...
.04	.3921	1.30	7.5	...	...	...
.09	.3917	1.32	3.6	...	...	...
.19	.4029	3.18	11.5	29	...	...
.29	.4100	5.48	15.5	33	...	...
.49	.4216	14.5	27.6	44	...	...
.79	.4347	40.5	50.0	56	42	19
.89	.4384	51.7	57.0	57	38	12
1.29	.4507	146	112	82	46	15
1.59	.4581	256	160	97	47	13
1.79	.4637	411	229	125	57	17
1.98	.4681	570	287	142	60	17
			$K_1 =$ 6	$K_2 =$ 23	$K_3 =$ 27	$K_4 =$ 15

TABLE III

ANALYSIS OF $E_{1/2}$ OF ZINC IN FORMATE MEDIUM WITH μ = 2.00

(HCOO$^-$), M	$E_{1/2}$ v.	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.00	−0.9975	(1.00)	...	...	...	...
.04	1.0009	1.34	8.5	...	...	...
.09	1.0090	1.8	8.9	5.5	...	...
.19	1.0095	1.8	4.2	1.0	...	...
.29	1.0101	2.8	6.2	7.6	...	...
.49	1.0183	5.4	8.4	10.1	4.3	6.7
.69	1.0239	12.8	17.1	13.2	1.6	...
.89	1.0318	16.0	16.9	14.5	7.3	7.1
1.09	1.0386	23.3	20.5	13.7	3.4	3.1
1.29	1.0425	37.9	28.6	19.1	8.6	5.9
1.49	1.0503	68.8	45.5	27.8	13.3	8.2
1.69	1.0531	88.7	51.9	28.3	12.1	6.7
1.84	1.0597	145	78.5	40.5	17.7	9.1
1.98	1.0667	259	130	66.0	29.3	14.8
			$K_1 =$ 4	$K_2 =$ 9	$K_3 =$ 3	$K_4 =$ 6

TABLE IV

ANALYSIS OF $E_{1/2}$ OF COPPER IN FORMATE MEDIUM WITH μ = 2.00

(HCOO$^-$), M	$E_{1/2}$ v.	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.00	+0.0318	(1.00)	...	...	...	...
.04	.0198	2.96	48	...	...	...
.19	.0024	10.3	49	68	...	...
.29	− .0128	34	114	236	242	448
.49	.0246	87	175	284	240	261
.69	.0366	226	326	420	369	370
.89	.0445	421	472	490	364	283
1.09	.0527	799	731	630	425	286
1.29	.0652	2197	1700	1290	870	510
1.49	.0625	1807	1210	790	419	210
1.69	.0746	4550	2685	1570	830	424
1.84	.0747	4630	2510	1320	630	282
1.98	.0809	7725	3900	1960	956	428
			$K_1 =$ 37	$K_2 =$ 166	$K_3 =$ 112	$K_4 =$ 283

Plots of the calculated values of $F(X)$ against the formate ion concentration for each of the elements resulted in straight lines for $F_3(X)$ and $F_4(X)$. This indicates the presence of complexes of the forms $M(HCOO)^+$, $M(HCOO)_2$, $M(HCOO)_3^-$ and $M(HCOO)_4^=$ in each case.

The formation constants for the formate complexes and their estimated uncertainties are summarized in Table V. These uncertainties are primarily the result of the difficulty in determining very precisely half-wave potential shifts ranging from 10 to 100 mv. Examination of the data in Table V will show that the order of complexing with formate is Cu >> Pb > Cd > Zn >> Tl. This agrees with the order predictable from the results of the preliminary experiment shown in Fig. 1.

TABLE V

CALCULATED FORMATION CONSTANTS FOR FORMATE COMPLEXES AT 25°

Complex type	Zinc	Cadmium	Lead	Copper
$M(HCOO)^+$	4 ± 1	3 ± 1	6 ± 1	37 ± 8
$M(HCOO)_2$	9 ± 2	13 ± 1	23 ± 4	166 ± 22
$M(HCOO)_3^-$	3 ± 1	22 ± 7	27 ± 10	112 ± 40
$M(HCOO)_4^-$	6 ± 3	16 ± 4	15 ± 4	283 ± 23

Burns and Hume[10] have reported recently that lead forms only the $Pb(OAc)^+$, $Pb(OAc)_2$ and $Pb(OAc)_3^-$ complexes with acetate under comparable conditions. However, the evidence for the presence of the tetraformato complex at high formate concentrations is quite definite. Also, the $Cd(HCOO)_4^=$ and $Cu(HCOO)_4^=$ complexes identified by Brintzinger and co-workers[5] have been confirmed but no indication of a $Zn(HCOO)_6^{-4}$ complex was observed.

The formate complexes of cadmium, lead and particularly zinc are obviously very weak. The validity of the constants is therefore somewhat questionable. Nevertheless, the data presented strongly suggest the tendency for complex formation with formate and represent at least a reasonable measure of the magnitude of this tendency.

MIDDLETOWN, CONN.

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(10) E. A. Burns and D. N. Hume, THIS JOURNAL, **78**, 3958 (1956).