excess against standard KCNS in aqueous solution. The concentrations were calculated in molarity.

The hydrogen electrode assembly and the silver–silver chloride electrode employed were the same as those described before.[9]

After preparation the silver–silver chloride electrodes were kept short-circuited for some time and finally preserved in dilute aqueous solution of KCl in the dark. The electrodes were usually washed thoroughly with water and then with the desired solvent prior to use in non-aqueous solutions. Before and after the experiments, the electrodes (*viz.*, the hydrogen and the silver–silver chloride electrodes) were checked in aqueous solutions of known activities of hydrogen or halide ions as the case may be.

The e.m.f.'s were recorded at intervals of about 30 minutes for 3 to 4 hours at 35 ± 0.25° with the help of a Leeds and Northrup Type K2 potentiometer and a Hartmann Braun galvanometer till the values were constant within ±0.0001 volt. An additional thermionic amplifier was used to aid the measurements in acetic acid solutions because of their high resistance.

Results and Discussions

The results obtained in the present study together with the relevant details are given in Table I. The E^0 of silver–silver chloride (relative to hydrogen electrode as zero) is found to be −0.11995 and −0.61800 volt, respectively, in formic and acetic acids.

TABLE I

E^0 Ag/AgCl = −0.11995 v. (molar); −0.13022 v. (molal) (formic acid) = −0.61800 v. (molar); −0.62084 v. (molal) (acetic acid). $AgCl + {}^1/_2H_2 \rightleftharpoons Ag + H^+ + Cl^-$; temp. = 35°

Formic acid pK_{HCl} = 1.398, D = 58.5 (16°), a^0 = 6 Å.		Acetic acid pK_{HCl} = 9.292, D = 6.15 (20°), a^0 = 5 Å.	
Concn. of HCl, M	E.m.f. obsd. (v.) cor. to 1 atm. H_2 press.	Concn. of HCl, M	E.m.f. obsd. (v.) cor. to 1 atm. H_2 press.
0.00033	0.17695	0.00090	0.14000
.00120	.15100	.00098	.13770
.00146	.14690	.00125	.13165
.00187	.14065	.00139	.12900
.00273	.13140	.00144	.12515
.00362	.11570	.00226	.10100
.00468	.10730	.00311	.08130
.00563	.09910	.00533	.04970
.00655	.09410		
.00844	.08155		
.01690	.05500		

It follows from a consideration of the actual values of the standard reduction potentials for the silver–silver chloride electrode in the two solvents, *viz.*, formic and acetic acids, that the reaction $AgX + {}^1/_2H_2 \rightarrow Ag + H^+ + X^-$ is more likely to occur in the former solvent than in the latter. The reason for this difference in behavior probably lies in the combined effect of the dielectric constant and the autoprotolysis constant both of which are relatively high in the case of formic acid (D = 58.50 and pK_s = 6.20 for formic acid; D = 6.15 and pK_s = 14.45 for acetic acid). It appears that the effect due to its large autoprotolysis constant acts in such a way that the influence of the fairly high dielectric constant is substantially reduced. This is also evident from the large difference in the E^0 value of the silver–silver chloride electrode obtained in formic acid and that secured in a 20 wt. % of dioxane–water mixture—a medium of nearly the same dielectric constant as that of formic acid but of much lower proton activity which seems almost equal to that of water.

Conclusions

1. The E^0 of the Ag/AgCl electrode relative to hydrogen electrode is found to be −0.11995 v. in formic acid and −0.61800 v. in acetic acid in the molar scale.

2. The large difference in E^0 obtained in the two solvents probably can be ascribed to the combined role of the dielectric constant as well as the autoprotolysis constant of the solvents concerned and not simply to the influence of any one of these two factors.

Acknowledgments.—My grateful thanks are due to Dr. S. K. Mukherjee, Reader, Department of Applied Chemistry, University of Calcutta, and to Dr. A. K. Ganguly, Senior Research Officer, Department of Atomic Energy, Govt. of India, for helpful suggestions and valuable criticism of the work.

CALCUTTA 9, INDIA

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[9] L. M. Mukherjee, *J. Phys. Chem.*, **58**, 1042 (1954).

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING COMPANY]

The Hydrogen Fluoride Solvent System. IV. Metallic Complexes in Liquid HF[1]

BY A. F. CLIFFORD[2] AND J. SARGENT

RECEIVED MARCH 28, 1957

Evidence is presented for the existence in liquid HF of complexes of Co(II), Co(III), Ni(II), Cu(II), Zn(II), Hg(II) and Pb(II). In particular the system $Ni(II)–CH_3CN$ is discussed and evidence presented for the existence of the ions $NiCH_3CN^{+2}$ and $Ni(CH_3CN)_{1+x}^{+2}$. The instability constant for the former was found to be 1.4×10^{-3}.

Introduction

The existence of metallic complexes in a solvent so extremely acidic as liquid hydrogen fluoride, in which the complexing agents themselves must exist largely in cationic form, is of practical and theoretical interest.[3]

As one of the commonest types of complex ion in water is the ammono complex, such as $Cu(NH_3)_4^{+2}$, so in the search for complexes in liquid HF, one

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[1] Presented before the Division of Physical and Inorganic Chemistry, 119th National A.C.S. Meeting, Cleveland, Ohio, April 10, 1951.

[2] Department of Chemistry, Purdue University, West Lafayette, Indiana.

[3] The acid–base relationships in liquid HF have been treated by A. F. Clifford, *et al.*, in Parts I, II and III of this Series, *J. Inorg. Nucl. Chem.*, in press.

may first think of aquo complexes, such as $Cu(H_2O)_x^{+2}$. Indeed, evidence for these does exist. Thus, it is found[4] that several metallic fluorides, whose solubility in water solution is decreased by increasing the concentration of potassium fluoride, on the other hand become more soluble as the concentration of hydrofluoric acid is increased. After a maximum is reached, however, the solubility decreases as anhydrous hydrogen fluoride is approached (*i.e.*, as the concentration of water is decreased). Thus the compounds CoF_2, NiF_2, CuF_2, ZnF_2 and MnF_2 are found to decrease in solubility in aqueous solutions of KF and NH_4F, obviating the formation of complex ions such as CuF_3^-, and yet their solubility increases in aqueous HF solutions. The solid phases in equilibrium with the HF solutions of high water concentration are found generally to be hydrated, and often contain a ratio of water molecules per metal ion that might be expected for a complex aquo ion. Examples of these are $CoF_2 \cdot 4H_2O$, $NiF_2 \cdot 4H_2O$, $CuF_2 \cdot 2H_2O$ and $ZnF_2 \cdot 4H_2O$. It is to be noted that none of these contain "HF of crystallization" in contrast to the substances which form anionic fluoro complexes. An example of the latter case is AlF_3[4] which forms $AlF_3 \cdot 3H_2O \cdot 3HF$ and $AlF_3 \cdot 6H_2O \cdot 3HF$, which are presumably $[H_3O^+]_3[AlF_6^{-3}]$ and $(H_3O^+]_3[AlF_6^{-6}] \cdot 3H_2O$.

An exact parallel is found in the case of ammono complexes. Thus, the oxides and hydroxides of most metals are quite insoluble in anhydrous ammonia.[5] With the transition metal hydroxides, however, as the concentration of water increases, the solubility increases to a maximum (*i.e.*, a solution of the "ammono complex" is produced), finally decreasing again to a minimum as pure water is approached. The available data do not permit actual calculation of constants of the aquo complexes in HF.

It might be expected, however, that more strongly complexing groups than the aquo group could form complexes of reasonable stability in liquid HF. This paper is a report on some of those which were found.

Discussion of Results

A wide variety of complexes was investigated. In most cases the complexes were not sufficiently stable to withstand isolation of solid phases, so that most of the work was confined to the observation of what complexes were capable of formation in solution. In general this was accomplished by observing simply whether a metallic fluoride could be taken into solution by addition of the complexing agent.

In Table I are listed the results of the reactions between various metal–agent pairs. As nearly as possible the metals and the agents are listed in order of increasing ability to form *covalent* or *inner* complexes.

It can be seen from this table that many complexes which form in aqueous solution apparently do not do so in HF. Moreover, those which do survive in HF are the most "covalent" in nature—*i.e.*, those of Ni, Cu, Zn, Pb, which also involve nitrogen and sulfur.

TABLE I

METALLIC COMPLEXES IN LIQUID HF[a]

Increasing electronegativity of metal →

← Decreasing electronegativity of ligand

Agent	Th^{+4}	Mg^{+2}	Mn^{+2}	Zn^{+2}	Pb^{+2}	Fe^{+2}	Co^{+2}	Ni^{+2}	Fe^{+3}	Hg^{+2}	Co^{+3}	Cu^{+2}
KNO_3	O	O										
CF_3CO_2H	O	O			X							
CH_3CO_2H	O	O			X							
Anth.		O	O					?				
Citric		O							?			
EtAcAc		O							O			X
Tart.		O										X
$O(CH_2CO_2H)_2$		O				X			X			
Ophen.	O	O				?		?	?			X
Dmg.		O										
NH_4F		O									X	
8-OH		O										X
CH_3CN		O		X		X	X	X		X	X	X
$(CH_2CN)_2$		O						X				X
α-NO		O					X[b]				X	
Dithizone		O			X							
Thiosal.		O			X							X
CO		O				X		O				

[a] X = complex formed; O = no evidence of complex formation; Anth. = anthranilic acid; Citric = citric acid; EtAcAc = ethyl acetoacetate; Tart. = tartaric acid; Ophen = orthophenanthroline; Dmg = dimethylglyoxime; 8-OH = 8-hydroxyquinoline; α-NO = α-nitroso-β-naphthol; Thiosal. = thiosalicylic acid. [b] Gives Co(III) complex.

The colors of the complexes were generally close to those of their aqueous counterparts and are listed in Table II. The colors of lead complexes with thiosalicylic acid and diphenylthiocarbazone (dithizone) could not be observed because of the intensity of the red-brown solutions of the reagents themselves.

The complexes of iron were for the most part weak and ill-defined. It was found that diglycolic acid was precipitated from its solution in HF on

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(4) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Ed., Vol. 1, D. Van Nostrand Co., Inc., New York, N. Y., 1940.

(5) E. C. Franklin, "The Nitrogen System of Compounds," Reinhold Pub. Corp., New York, N. Y., 1935, p. 21.

TABLE II

COLORS AND SOLUBILITIES OF COMPLEXES[a]

Complex	Solubility	Color	Complex	Solubility	Color
Fe–CO					
Less stable	s	Emerald	Cu(II)–ophen	s	Blue-green
More stable	s	Yellow	Cu(II)–tart	s	Blue-green
			Cu(II)–EtAcAc	s	Deep-blue
Fe–$O(CH_2COH)_2$					
From Fe	i	Colorless	Cu(II)–CH_3CN	s	Cobalt
From FeF_3	i	Tan	Cu(II)–$(CH_2CN)_2$	s	Green
Fe(II)–CH_3CN	s	Colorless	Cu(II)–8–OH	i	Yellowish-green
Co(II)–CH_3CN	s	Red	Cu(II)–thiosal	i	Dark brown
Co(III)–CH_3CN	s	Cherry	Zn–CH_3CN	s	Colorless
Co(III)–NH_4F	i	Red-orange	Hg–CH_3CN	s	Colorless
Co(III)–α-NO	i	Deep red	Pb(II)–CH_3COOH	s	Colorless
Ni–CH_3CN	s	Steel blue	Pb(II)–CF_3COOH	s	Colorless
Ni–$(CH_2CN)_2$	s	Dark blue	Pb(II)–dithizone	i	Obscured
			Pb(II)–thiosal	s	Obscured

[a] See footnote *a* of Table I.

addition of FeF_3, although no iron could be detected in the solution. The composition of the solid phase was variable and corresponded to no definite ratio of acid to iron. A typical analysis was Fe 32%, F 25% corresponding to an atom ratio of F to Fe of 2.3 (theoretical for FeF_3, Fe 49%). Apparently reaction took place on the surface of the ferric fluoride or iron metal to form an insoluble complex.

When iron pentacarbonyl was mixed with liquid HF a two phase system resulted, at the interface of which gas was evolved in a somewhat more rapid reaction than was observed with nickel tetracarbonyl. If the solution were at least as cold as 0°, and not acidified (*e.g.*, with BF_3), a clear emerald green solution resulted. If the solution were warmed to 20°, acidified with BF_3 or allowed to stand at 0°, or if the initial reaction were carried out under these conditions, a bright yellow solution resulted. Neither of these colors was extractable into CCl_4. This solution partially decomposed in a matter of hours, precipitating FeF_2 and FeF_3 (the latter probably resulting from oxidation by atmospheric oxygen). Complete decomposition to these products resulted when either solution was evaporated. Both of these solutions when treated with solid KI became deep purple. When the purple solution was shaken with CCl_4, the color was extracted into the CCl_4, giving a deep red solution which was found to contain iron tetracarbonyl iodide. This was identified by means of its pyridine complex. The fact that both of these solutions yielded $Fe(CO)_4I_2$ shows that both the green and yellow complexes must contain at least four carbonyl groups. Since both solutions were found to be electrolytic, the complexes must have been ionized.

Nickel tetracarbonyl differed from $Fe(CO)_5$ in decomposing at the liquid–liquid interface directly to NiF_2 with no evidence for the formation of an intermediate complex. For this reason it was used in some experiments as a source of pure, fresh NiF_2.

As in water, the α-nitroso-β-naphthol complex of Co(III) was insoluble. It is interesting that this could be prepared from Co(II) just as in aqueous solution, as well as directly from Co(III). The reaction also proceeded with Co(II) in 48% aqueous HF. Because of the heterogeneous nature of these reactions, however, the products were of variable composition.

Certain of the complexes were strong enough that the free metals would dissolve in solutions of the complexing agents with liberation of hydrogen. Thus in acetonitrile solution zinc dissolved vigorously; nickel, readily; and cobalt and iron, slowly, the last with subsequent precipitation of white iron(II) fluoride. This probably indicates decreasing stability of the complexes of Ni(II), Co(II) and Fe(II) in this order. The greater vigor of dissolution of zinc, on the other hand, may be related to its more electropositive character. Acetonitrile dissolved CoF_3, giving a cherry red solution which on evaporation gave a red solid which oxidized hydrochloric acid and was 46.1% Co (theoretical for CoF_3, 50%; for $CoF_3.CH_3CN$, 37.5%). The solid resulting from evaporation of the Cu(II)–acetonitrile solutions contained a white phase analyzing 0% Cu, 31% F (theoretical for CH_3CNHF, 33.7% F) and a blue phase analyzing 44.2% Cu (theoretical for $CuF_2 \cdot CH_3CN$, 45% Cu).

The gummy solid residue from the Cu(II)–ethyl acetoacetate complex analyzed Cu 10%, F 27%. (A mixture of one part CuF_2 to 3.1 parts $[C_6H_{10}O_3H_2]F_2$ would analyze Cu 10%, F 28%.)

In the case of the acetate and trifluoroacetate complexes of lead, the fact that the residue from evaporation of solutions of the former approximated $Pb(C_2H_3O_2)F$, (75% Pb, theoretical 73% Pb) and of the latter, PbF_2 (83% Pb, theoretical 84.5%), may indicate greater stability of the former. This would accord with expectation based on the relative strengths of the free acids. That these were not oxonium fluoroplumbates was shown by the nonreaction of PbF_2 with HF solutions of water, ethanol and KF.

Since none of the metals involved is amphoteric in HF, as shown by the inability of NaF solutions to dissolve the metal fluorides, reaction can in no case be attributed to that cause. That none of the reagents acted as an acid is attested by the complete lack of reaction with the magnesium vessel.

Chromium.—In addition to the complexes already discussed, it was attempted to form an ethyl acetoacetate complex of chromium(III). It was found that CrF_3 dissolved in ethyl acetoacetate solution in HF to give a deep green solution identical in appearance with that of CrF_3 in KF solutions in HF. The solid obtained on evaporation of the solution corresponded in analysis to no simple cationic complex, Cr 23%, F 29%.

Quantitative Studies.—The nickel-acetonitrile complex was made the subject of a quantitative study by observing the concentration of nickel taken into solution when introduced as metal powder into HF solutions of known acetonitrile concentration. A plot of the curve obtained is shown in Fig. 1. The numerical data are given in Table III.

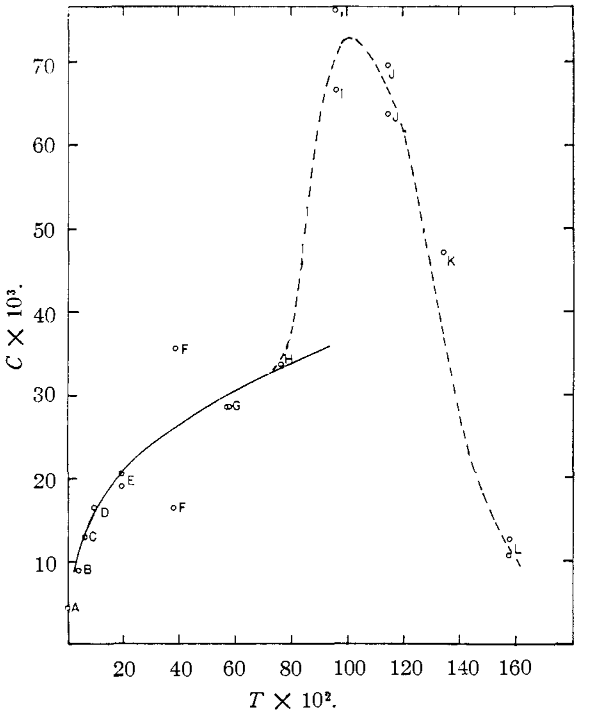

Fig. 1.—Solubility of Ni in HF *vs.* concentration of CH_3CN at −10°. Solid curve: $(T - C)/C^3 = 2.0 \times 10^4$; C = molar concentration of Ni(total); $T = [CH_3CN]_{total}$.

The reaction times quoted show that equilibrium was attained in at least one hour.

If the ionization of acetonitrile as a base ($CH_3CN + HF \rightleftarrows CH_3CNH^+ + F^-$) is ignored, the equations involved in this system are

(1) $F = 2C$ where $F = [F^-]$, C = [complex]

(2) $T = nC + A$ where $T = [CH_3CN]_{total}$, $A = [CH_3CN]$

(3) $MF^2 = s$ where $M = [Ni^{+2}]$, $s = K_{sp}(NiF_2) = 2.81 \times 10^{-7}$ at −10° (calcd. from ref. 6)

(4) $MA^n = jC$ where j = instability constant of complex, n = coördination no

from which $(T - nC)^n/C^3 = 4j/s$ = const.

It can be seen from Table III that up to point H the value of $(T - nC)^n/C^3$ is very nearly constant for $n = 1$. Consequently, for concentrations of CH_3CN up to 0.60 *M*, the predominant complex in solution must be $[Ni(CH_3CN)]^{+2}$.

Eliminating point B, and points above H, an average value is found for $4j/s$ of $2.0 \pm 0.2 \times 10^4$.

TABLE III

SOLUBILITY OF NICKEL *versus* CONCENTRATION OF CH_3CN AT −10°[a]

Point	$T \times 10^2$, *M*	Stirring time, hr.		$C \times 10^3$, *M*	$\frac{(T - C)}{C^3} \times 10^{-4}$	$\frac{(T - 2C)^2}{C^3} \times 10^{-3}$
A	0			4.1 (ref. 6)		
B	3.8	3.00		9.2	3.8	0.52
C	5.7	2.00		12.9	2.1	0.45
D	9.5	2.00		16.5	1.7	0.86
E	19.1	0.75 2.00	19.1 20.4	19.7	2.3	3.0
F	38.1	2.00 2.00	35.5 16.3	26.4	1.9	5.9
G	57.2	1.00 3.00	28.4 28.5	28.5	2.3	11.0
H	76.2	3.00		33.5	1.9	13.0
I	95.4	0.75 3.0C	66.4 76.0	71.2	0.24	1.8
J	114.3	3.00 3.00	69.5 63.5	66.5	0.37	3.5
K	133.3	3.00		47.0	1.3	15.0
L	157.5	2.00 3.00	12.7 10.6	11.4	12.0	1700

[a] T = total concentration of CH_3CN; C = total concentration of nickel.

From this the instability constant is found to be $j = 1.4 \times 10^{-3}$.

(If the alternative simplification is made, that the basic ionization of CH_3CN is large, the concentration of fluoride ion therefore being primarily the result of this ionization and also the concentration of free nitrile as a result being negligible in comparison to the nitrile in other forms, then the following calculations result

(5) $F = H$ where $H = [CH_3CNH^+]$

(6) $T = H + nC$

(7) $HF = bA$ where b = ionization constant of CH_3CN, which in conjunction with (3) and (4) give

$$\frac{(T - nC)^{2n-2}}{C} = \frac{b^n j}{s} = \text{const.}$$

This is constant for no integral value of n.)

The portion of the curve from H to I corresponds to the formation of a higher complex. However, the data are not sufficient to determine the nature of the complex. Since in this region the concentration of $[Ni(CH_3CN)]^{+2}$ cannot be considered negligible, the mathematical equation for the curve—even with the same simplification as before—is necessarily complicated. It takes the form

$$(8) \quad k = \frac{js(4jC^2)^{n-1}\,(T - nC)^{n-2}}{[4jC^3 - s(T - C)][4jC^2 - s(n - 1)]^{n-1}}$$

where k is the instability constant of the new complex. The values of this expression calculated from points H and I are not consistent for any value of n.

The portion of the curve from I to L appears to correspond to the formation of an insoluble phase, presumably $Ni(CH_3CN)_nF_2$. Since with the available data the value of n cannot be determined, however, it is not possible to treat this quantitatively.

Experimental

Apparatus.—The cell employed for these experiments was a magnesium cylinder, 6 cm. in internal diameter and 5 cm.

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(6) A. W. Jache, Ph.D. Thesis, University of Washington, 1952.

deep, closed at top and bottom with Teflon-gasketed Kel-F plates for visibility. The top window was removable. Connections to a reflux condenser of coiled polyethylene tubing, to drainage and to an inlet for liquid HF were provided through magnesium fittings in the walls. These were protected from atmospheric moisture with anhydrous $CaSO_4$ and could be closed by means of magnesium bodied stopcocks with Teflon plugs held in place by spring tension. The drainage outlet was used for obtaining samples of supernate. The HF (General Chemical Company, sulfur-free) was led through a copper coil condenser to a cooled calibrated magnesium reservoir with a Kel-F window from which measured quantities of HF could be delivered to the cell. The cell itself was provided with a cooling coil which maintained the temperature close to −10°.

Thorough mixing of the solutions was ensured by use of a magnetic stirrer. The internal magnet was sealed in a polyethylene capsule for protection.

The Nickel-Acetonitrile Complex.—A portion of pure nickel powder weighed with the magnet, and known volume of acetonitrile, measured by pipet, were placed in the dry cell through the top window, which was then closed tightly. One hundred ml. of HF was now delivered to the cell and stirring begun. In most cases the evolution of hydrogen, brisk at first, was no longer observable after 30 minutes. Stirring was maintained for a longer period (Table III) to ensure attainment of equilibrium. When equilibrium was deemed to have been reached, the cell was drained and washed out with HF until the washes were colorless. The magnet with the unreacted nickel clinging to it was then removed quickly to an anhydrous potassium fluoride desiccator and subsequently weighed. From the loss in weight of the nickel the concentration of nickel in solution was calculated. In two blank runs in the absence of acetonitrile and with different weights of nickel, it was found that complete transfer of the nickel could be accomplished by this method. Because of the formation of a fluoride coating on the metal, the weight increased each time exactly 3.62%, agreeing within the accuracy of the analytical balance. All weights of nickel found during the course of the investigation were corrected by this amount before calculation of the concentration of nickel in solution. The data so obtained are those appearing in Fig. 1 and Table III.

Reagents.—The complexing agents used were of reagent grade in all cases except that of the diglycolic acid, which was of technical grade.

The metal powders were of reagent grade. The metal fluorides were commercial materials obtained from Penn Salt. The $Ni(CO)_4$ was obtained from the International Nickel Company, and the $Fe(CO)_5$ from Chemical Commerce.

Analytical.—All analyses were done by the analytical laboratories of the Central Research Department of Minnesota Mining and Manufacturing Company.

In all cases where analyses were carried out on solutions, the solution of complexing agent was treated with an excess of the solid metallic fluoride.

ST. PAUL, MINN.

[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Heats of Formation of Potassium Chromate, Potassium Dichromate, Chromate and Dichromate Aqueous Ions. Entropy of Dichromate Ion

BY C. N. MULDROW, JR., AND L. G. HEPLER

RECEIVED FEBRUARY 28, 1957

We have determined the heats of solution of $K_2CrO_4(c)$, $K_2Cr_2O_7(c)$ and $(NH_4)_2Cr_2O_7(c)$ and the heats of reaction of $K_2Cr_2O_7(c)$ and $CrO_3(c)$ with aqueous alkali and of $K_2CrO_4(c)$ with aqueous acid. From the results of these determinations we have calculated the heats of formation of $K_2CrO_4(c)$, $K_2Cr_2O_7(c)$, $(NH_4)_2Cr_2O_7(c)$, $CrO_4^{=}(aq)$ and $Cr_2O_7^{=}(aq)$ to be, respectively, −331.9, −486.4, −425.0, −207.6 and −345.2 kcal./mole. From our heats of formation and reaction, equilibrium constants and entropy data from the literature, we have calculated the entropies of $Cr_2O_7^{=}(aq)$ and $HCrO_4^-(aq)$ to be 70.5 and 47.8 cal./deg. mole, respectively. The standard free energies of $CrO_4^{=}(aq)$, $Cr_2O_7^{=}(aq)$ and $HCrO_4^-(aq)$ have also been calculated to be −170.1, −303.4 and −179.0 kcal./mole, respectively.

Investigation of the experimental data on which the thermodynamic properties of $CrO_4^{=}(aq)$ and $Cr_2O_7^{=}(aq)$ as given by the Bureau of Standards,[1] Bichowsky and Rossini[2] and Latimer[3] are based showed that these values were not reliably known. Especially, it became apparent that the heats of formation of these ions and of various chromates and dichromates (*e.g.*, K_2CrO_4, $K_2Cr_2O_7$, etc.) were based on questionable heats of reaction of CrO_3 and heats of solution of chromates and dichromates. Calculation of standard heats of formation at 298°K. from the results of many of the pertinent earlier investigations is difficult because most of that work was carried out under such conditions that heats of dilution and heat changes in correcting observed heats of reaction to 298°K. are both large and uncertain. Therefore we have undertaken an investigation of the thermochemistry of $K_2Cr_2O_7(c)$, $Cr_2O_7^{=}(aq)$, $K_2CrO_4(c)$ and $CrO_4^{=}(aq)$ by means of solution calorimetry. This work also has involved the study of $CrO_3(c)$ and $(NH_4)_2Cr_2O_7(c)$.

Experimental

Our high-precision solution calorimeter used in previous investigations[4,5] has been improved by several changes. The rate of stirring has been increased and more efficient stirrers have been used. This improved stirring has markedly lessened the time required to attain thermal and reaction equilibrium in the calorimeter, without significantly changing the calorimetric drifts, and has therefore reduced extrapolation uncertainties. A second improvement has been more accurate timing of the heating periods. The calibrated stopwatch has been replaced by a Standard electrical timer read to 0.01 second. The timer is wired through a triple pole-double throw switch that is used to switch the electrical power from the dummy heater to the calorimeter heater. We estimate that the total uncertainty in elapsed time for the heating periods due to variation in the frequency of the local 60 cycle a.c. current, etc., is no more than 0.05 second.

All of the reactions investigated have been rapid. In every experiment the reaction was completed and steady after-period drifts were obtained less than five minutes after breaking the sample bulbs. The heating periods varied from 55–200 seconds.

All of the heats have been determined at 25.0 ± 0.3°.

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[1] "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

[2] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

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

[4] R. L. Graham and L. G. Hepler, THIS JOURNAL, **78**, 4846 (1956).

[5] C. N. Muldrow, Jr., and L. G. Hepler, *ibid.*, **78**, 5989 (1956).