of magnesium ortho- and dititanates from their constituent oxides are −0.4 and −0.2 cal./deg. mole, as compared with −0.7 for magnesium metatitanate. Thus, the entropies of the compounds in this system do not deviate markedly from the sums of the entropies of the oxides. Similar behavior for magnesium meta- and orthosilicates was noted by Kelley.[6]

(6) K. K. Kelley, THIS JOURNAL, **65**, 339 (1943).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Heats of Solution and Formation of Some Iron Halides

BY JAMES C. M. LI AND N. W. GREGORY

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Heats of solution have been determined for $FeCl_2$, $FeCl_3$, $FeBr_2$, $FeBr_3$ and $FeBrCl_2$ at concentrations of the order 10^{-3} molal. Heats of formation calculated from these data agree with quantities measured by independent methods when corrections are applied for hydrolysis and complex ion formation in the iron(III) solutions.

The complex nature of the ionic species in aqueous iron halide solutions makes interpretation of heats of solution of these compounds difficult. A question arises concerning the reported value for the heat of formation of iron(III) chloride based on determination of its heat of solution.[1,2] A correction for complex ion formation and hydrolysis does not appear to have been included in the interpretation of data and the value obtained is not in good agreement with that determined from equilibrium studies in anhydrous systems.[3] We have reinvestigated the heats of solution of $FeCl_2$ and $FeCl_3$ at low concentrations and have obtained similar results for $FeBr_2$, $FeBr_3$ and $FeBrCl_2$. Taken in conjunction with the reported characteristics of iron(III) solutions,[2] these data lead to heats of formation which are in good agreement with quantities observed in equilibrium studies.

Experimental Part

Thermal measurements were made in a simple adiabatic calorimeter, consisting of a dewar flask equipped with stirrer and sample-holding and breaking device. 750 ml. of water, carefully saturated with and maintained under a nitrogen atmosphere to minimize oxidation of iron(II), served as the solvent. The calorimeter thermometer was constructed from 6-mm. Pyrex glass tubing in the form of a spiral of 17 turns, 2 inches in diameter and 5.5 inches long, filled with toluene and a small amount of mercury. The lower end was connected to a capillary of 0.4 mm. diameter which turned upward and served as the thermometer stem. The sensitivity, as measured with a cathetometer read to 0.1 mm., corresponded to 0.0004 degree, or 0.36 calorie.

The entire device was placed in an air-bath controlled to ±0.01° at 25° with only the stirring rod, breaking rod and thermometer stem extending out of the thermostat. In tests for temperature drift the thermometer reading was observed to stay within the error of the cathetometer for periods of more than two hours during blank runs under normal operating conditions.

Samples were carefully prepared, purified by vacuum sublimation where possible, analyzed, and transferred to small Pyrex capsules in a dry-box. The capsules were evacuated and sealed and the quantity of material present determined by subsequent analysis of the solution. The calorimeter was calibrated by measuring heats of solution of LiCl, NaCl, KCl, KBr and KI.[2] For each compound various amounts were used to give approximately 36, 72, 108, 144 and 180 calories. Deviation of results for the various substances was within ±0.3 calorie.

The heat conductivity of toluene is much lower than that of mercury which offsets some of the advantage gained by its greater coefficient of thermal expansion. However, our experience confirms an approximate calculation of the time required (somewhat less than two minutes with efficient stirring) to reduce the temperature differential between the center of the liquid column and the outer edge of the glass tube to 0.001 of the original value produced on dissolving the sample. Stirring appears to be the major factor in the problem of heat transfer; in the absence of stirring in the calorimeter, more than 30 minutes was required for the system to reach uniform temperature. Thermal equilibrium in times of the order of two minutes was considered satisfactory for the purpose of the present work.

It should also be noted that the compressibility of toluene is sufficiently large to require a correction in the temperature reading if barometric pressure varies appreciably. The error becomes significant for variations of the order of 2 cm.

The heat of stirring at the rate employed was of the order of 0.2 calorie per minute. Allowance for this was included in the calibration by adjusting the temperature of the air-bath so that the heat leaking out of the calorimeter matched the input from stirring (*i.e.*, the calorimeter remained at constant temperature with a constant rate of stirring). This steady state was maintained for a period of 15 minutes or more before breaking the sample holder. After solution of the sample the temperature would again stay constant at its maximum value and was observed for a period of 10 minutes or more. Hence it was assumed that the heat of stirring was exactly compensated by heat leakage during the run and no correction applied for either. The change of heat of stirring while the sample was dissolving was neglected inasmuch as these compounds dissolved almost immediately in water.

As an illustration of the temperature behavior during a run, the following examples are observations made with $FeBr_3$ samples.

Time, minutes	Cathetometer reading	Time, minutes	Cathetometer reading
0 to 19	94.665	0 to 8	94.720
Capsule broken		Capsule broken	
20	95.855	9	95.925
21 to 28	95.865	10 to 20	95.940

Results and Discussion

Iron(II) Chloride.—Samples were prepared by thermal decomposition of the hydrate with subsequent sublimation of anhydrous $FeCl_2$ in high vacuum at 550°. After the thermal measurements, solutions were tested for Fe^{+++} ion with negative results in all cases. Data are shown in Table I. An average value for the heat of solution

$$FeCl_2(s) = Fe^{++}(aq) + 2Cl^-(aq)$$

has been taken as −19.5 ± 0.2 kcal./mole, neglecting the small contribution accompanying fur-

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(1) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

(2) F. D. Rossini, *et al.*, Natl. Bur. Stds. Circ. 500, U. S. Govt. Printing Office, Washington, D. C., 1950.

(3) W. Kangro and E. Petersen, *Z. anorg. Chem.*, **261**, 157 (1950).

ther dilution of the solution. Assuming that the aqueous solution of $FeCl_2$ involves only Fe^{++} ($\Delta H^\circ = -21.0^2$) and Cl^- ($\Delta H^\circ = -40.0^2$), the heat of formation of $FeCl_2(s)$ is found to be −81.5 ± 0.2 kcal./mole at 25°. This value is in good agreement with other results, including those based on independent methods.[2,3,4,5]

Iron(II) Bromide.—The heat of formation of $FeBr_2$ reported by Hieber and Woerner[4] is not based on a direct determination of the heat of solution and the latter has not been reported. Three independently prepared samples were studied, including vacuum sublimed material and $FeBr_2$ obtained by thermal decomposition of $FeBr_3$ at 100°. Data are shown in Table I. A slight trend toward larger negative values observed with decreasing concentration; however, the change is of the order of experimental error and in as much a similar behavior was not observed with $FeCl_2$ an average value for the heat of solution of −20.1 ± 0.4 kcal./mole has been taken rather than extrapolating the data. Using $\Delta H^\circ = -28.93^2$ for Br^-, a heat of formation for $FeBr_2(s)$ of −58.7 ± 0.4 kcal./mole is obtained. Whereas this is somewhat less than −60.02 given by the N.B.S. tables,[2] our value is consistent with results for $FeBr_3$ when compared with the difference in heats determined from thermal dissociation equilibrium data.[6]

TABLE I

HEATS OF SOLUTION FOR IRON(II) HALIDES

$FeCl_2$ Molality	$FeCl_2$ Heat of solution, kcal./mole	$FeBr_2$ Molality	$FeBr_2$ Heat of solution, kcal./mole
0.0117	−19.5	0.00828	−19.7
.0029	−19.5	.00652	−20.2
.0022	−19.8	.00386	−20.3
.00167	−19.5	.00316	−20.3
.00139	−19.5	.00247	−20.4

Iron(III) Chloride.—The heats of solution which have been reported for $FeCl_3$ were determined in rather concentrated solution.[7,8] In the present work measurements have been made at lower concentrations using samples prepared by resublimation of Fisher C.P. anhydrous $FeCl_3$. Solutions were carefully tested for Fe^{++} with negative results. The heat of formation of $FeCl_3(s)$ has been estimated from these data by considering the reactions

$$\begin{array}{ccccccc} Fe^{+++} & + & H_2O & = & FeOH^{++} & + & H^+ \\ m(1-\alpha-\beta) & & & & m\alpha & & m\alpha \end{array} \qquad (1)$$

$$\begin{array}{ccccc} Fe^{+++} & + & Cl^- & = & FeCl^{++} \\ m(1-\alpha-\beta) & & m(3-\beta) & & m\beta \end{array} \qquad (2)$$

where α is the fraction of Fe^{+++} hydrolyzed and β that fraction complexing with chloride ion. We have used values for ΔF° and ΔH° characterizing these equilibria as given by the N.B.S. tables.[2,9] Corresponding quantities for the second stages of these reactions indicate that they may be neglected for the purposes of this treatment.

The equilibrium constants for (1) and (2) were expressed as functions of ionic strength of the solutions by the approximation given by the Debye–Huckel limiting law.

$$\log K_1 = -2.43 - 2\mu^{1/2};\ \Delta H^\circ_1 = 12.32 \text{ kcal.}$$
$$\log K_2 = 1.49 - 3\mu^{1/2};\ \Delta H^\circ_2 = 8.52 \text{ kcal.}$$
$$\text{where } \mu = m(6 - 2\alpha - 3\beta).$$

With these three equations and the expressions for the equilibrium constants in terms of m, α and β, one may solve for α and β for various values of the concentration m.

The heat of reaction (defined as λ)

$$FeCl_3(s) = Fe^{+++}(aq) + 3Cl^-(aq)$$

may be calculated from the experimental heat of solution and ΔH°_1 and ΔH°_2. Data are summarized in Table II. The constancy of λ over a rather wide range of values of α and β tends to support the validity of the assumptions made in this treatment. An average value of λ is −38.0 ± 0.2 kcal./mole at 25°, which leads to −93.4 kcal./mole for the heat of formation of $FeCl_3(s)$ (using ΔH° for Fe^{+++} as -11.4^2). This is 3.4 kcal. smaller than the value previously reported from heats of solution but is in good agreement with −93.5 obtained by Kangro and Petersen[3] from equilibrium studies in the iron–chlorine system.

TABLE II

HEATS OF SOLUTION FOR IRON(III) HALIDES

Molality	α	β	Exptl. heat of solution, kcal./mole	λ, kcal./mole
		$FeCl_3$		
0.00318	0.53	0.05	−31.1	−38.1
.00311	.535	.049	−30.8	−37.8
.00221	.615	.035	−30.1	−38.0
.00150	.69	.024	−29.7	−38.4
.000766	.81	.012	−27.8	−37.9
		$FeBr_3$		
0.00736	0.36	0.0127	−29.0	−33.5
.00307	.555	.005	−29.2	−36.1
.00271	.58	.005	−28.6	−35.8
.00220	.63	.0038	−26.4	−34.2
.00206	.645	.0035	−28.3	−36.3
.00191	.66	.003	−27.6	−35.7
.00098	.78	.0017	−24.3	−33.9

The heats of solution measured by us are consistent with earlier data[7,8]; however, a quantitative comparison involves rather uncertain approximations concerning ionic strength and composition in extrapolating to the higher concentrations.

Iron(III) Bromide.—Heats of solution of $FeBr_3$ have not been reported previously. Preparation and analysis of samples have been described.[6] Techniques employed were the same as with $FeCl_3$, including the corrections for hydrolysis and complex formation. The equations

$$\log K_1 = -2.43 - 2\mu^{1/2};\ \Delta H^\circ_1 = 12.32 \text{ kcal.}$$
$$\log K_2' = 0.59 - 3\mu^{1/2};\ \Delta H^{\circ\prime} = 6.10 \text{ kcal.}$$

(K_2' referring to the equilibrium involving Fe^{+++},

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[4] H. Hieber and A. Woerner, *Z. Elektrochem.*, **40**, 287 (1934).

[5] Kokiti Sano, *J. Chem. Soc. Japan*, **59**, 1069 (1938).

[6] N. W. Gregory and B. A. Thackrey, THIS JOURNAL, **72**, 3176 (1950).

[7] G. Lemoine, *Ann. Chim. Phys.*, **30**, 373 (1893).

[8] W. Kangro and R. Flugge, *Z. physik. Chem.*, **A175**, 187 (1935).

[9] For a discussion of the hydrolysis problem see A. B. Lamb and A. G. Jacques, THIS JOURNAL, **60**, 1215 (1938), and others. On chloride complexes, C. Brosset, *Svenk. Kem. Tid.*, **53**, 434 (1941); J. Badozlambling, *Bull. soc. Chim.*, 552 (1905), and others.

Br^- and $FeBr^{++}$ [2]) were used with the results shown in Table II.

Four independent samples lead to an average value for λ of −35.3 ± 1.0 kcal./mole. This gives −62.8 ± 1.0 kcal./mole for the heat of formation of $FeBr_3(s)$ at 25°. The difference between the heats of formation of $FeBr_3(s)$ and $FeBr_2(s)$ obtained in this work is in good agreement with that found from equilibrium studies,[6] 4.1 ± 1.2 kcal. and 4.0 ± 0.3 kcal., respectively.

The somewhat greater scatter of data for $FeBr_3$ as compared with those for the chloride is thought to be due largely to the greater difficulty of purifying the bromide. Solutions gave negative tests for Fe^{++}, however.

Iron(III) Monobromodichloride.—This substance was prepared by bromination of $FeCl_2$.[10] Its thermal instability makes purification difficult and varying amounts of Fe^{++} were found in the solutions following thermal measurements. The Fe^{++} ion was assumed to represent $FeCl_2$ in the original sample and the heat of solution corrected for the amount present as determined by analysis. Interpretation of results was carried out as for the other iron(III) compounds. The fraction of iron in the form of $FeBr^{++}$ predicted in these solutions is very small; hence only $FeOH^{++}$ and $FeCl^{++}$ were considered. Results are shown in Table III, where m' represents the molality of $FeCl_2$ in the solution and λ is again defined as $\Delta H°$ for the reaction $FeBrCl_2(s) = Fe^{+++}(aq) + Br^-(aq) + 2Cl^-(aq)$. An average value for λ of −37.4 ± 0.3 kcal./mole is obtained; this leads to −82.9 ± 0.3 kcal./mole for the heat of formation of $FeBrCl_2$ which agrees well with −83 kcal. obtained from equilibrium studies of the thermal dissociation of $FeBrCl_2$ into $FeCl_2$ and bromine.[10]

Values for heats of formation of substances involving bromine are based on the liquid Br_2 as the standard state.

TABLE III

HEATS OF SOLUTION FOR $FeBrCl_2$

Molality	Molality m'	α	β	Exptl. heat of solution, kcal./mole	λ, kcal./mole
0.00585	0.00212	0.38	0.10	−31.8	−37.3
.00420	.00100	.46	.07	−30.9	−37.2
.00197	.00037	.63	.03	−29.5	−37.5
.00125	.00013	.73	.02	−28.6	−37.8

Conclusions.—Whereas several assumptions are involved in the interpretation of measured heats of solution of the iron halides in order to estimate heats of formation, the agreement of the values obtained with those from independent methods offers some support to the validity of the treatment.

A linear relation between the heats of formation of $FeCl_3$, $FeBrCl_2$ and $FeBr_3$ and the number of Cl or Br atoms per atom of iron is observed which is not apparent if one uses the higher value for the heat of formation of $FeCl_3$ previously reported. This relationship also applies to the heats of solution (λ) and might be anticipated from the close similarity in structure of the mixed halide to $FeCl_3$ and $FeBr_3$ as discussed in an earlier paper.[10]

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(10) N. W. Gregory, THIS JOURNAL, **73**, 5433 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

Spectrophotometric Study of the Phosphorus–Interhalogen Complexes in Carbon Tetrachloride and Acetonitrile[1]

BY ALEXANDER I. POPOV AND EDWARD H. SCHMORR

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Spectrophotometric study of phosphorus hexachloroiodide and phosphorus hexabromoiodide reveal that in carbon tetrachloride solutions the complexes dissociate into component molecules $PCl_6I \leftrightarrows PCl_5 + ICl$; $PBr_6I \rightleftarrows PBr_3 + IBr + Br_2$. In polar solvents, like acetonitrile, the dissociation is ionic: $PCl_6I \rightleftarrows PCl_4^+ + ICl_2^-$ and $PBr_6I \rightleftarrows PBr_4^+ + IBr_2^-$. Phosphorus pentabromide–carbon tetrachloride complex $PBr_5 \cdot 2CCl_4$ is prepared by a new method, and its decomposition point is determined.

Introduction

Although a large number of phosphorus–halogen complexes have been reported in the literature, it seems that relatively little work has been done on the elucidation of their structure and their physical and chemical properties.

In recent years Fialkov and Kuz'menko[2] have studied the addition of iodine, iodine chloride and iodine bromide to phosphorus tri- and pentahalides. It was found that stable solid complexes, phosphorus hexachloroiodide (PCl_6I) and phosphorus hexabromoiodide (PBr_6I) can be obtained by the simple addition of iodine chloride and iodine bromide to the respective phosphorus pentahalides. Likewise Fialkov and Kuz'menko have verified the reaction reported by Baudrimont[3] in which phosphorus hexachloroiodide is formed by the addition of iodine to phosphorus pentachloride.

A study was made on the electrical conductivity of these complexes in various organic solvents.[2d] It was found that while acetonitrile, nitrobenzene, ethyl bromide and chloroform yield conducting solutions—benzene, toluene, carbon tetrachloride and dioxane solutions do not. These results were based on a study of saturated solutions of these complexes in the respective solvents, and it must be noted that in the case of non-conducting solutions

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(1) Abstracted from a thesis presented by Edward H. Schmorr to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Master of Science, February, 1952.

(2) (a) Ya. A. Fialkov and A. A. Kuz'menko, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 812 (1949); (b) **19**, 997 (1949); (c) **21**, 433 (1951); (d) A. A. Kuz'menko and Ya. A. Fialkov, *ibid.*, **21**, 473 (1951).

(3) M. E. Baudrimont, *Ann. chim. phys.*, [4] **2**, 8 (1864).