greenish-yellow fluorescence. Hence it may be concluded that this fluorescence must originate in the formation of the complexes of the metal ions with the substituted 8-hydroxyquinoline, as in the case with 8-hydroxyquinoline itself.

(B) **Resolution of Zinc Derivative of 8-Hydroxyquinoline-5-sulfonic Acid.**—A conclusive proof that the zinc derivative of 8-hydroxyquinoline-5-sulfonic acid is covalent and has a tetrahydral configuration lies in the resolution of the complex salt into its optically active isomers. Strychnine was found to be a satisfactory resolving agent. It gave nice crystals from a boiling aqueous solution.

Strychnine (0.01 mole or 3.344 g.) and the complex zinc acid (0.01 mole or 5.14 g.) were dissolved in 300 ml. of hot water. The solution was concentrated to 100 ml. and allowed to cool, whereupon crystals slowly formed. These were dissolved in pyridine and fractionally precipitated by the addition of ether. After each ether addition, the solution was allowed to stand overnight, the resulting light yellow crystals were filtered, washed with ether, and dried. In this manner, five fractions were obtained.

Fraction no.	Observed rotation (α_D) of 0.5% soln. in pyridine	Specific rotation $[\alpha]_D$	Dec. temp., °C.
1	−0.22	−44	258–262
2	− .27	−54	235–240
3	− .32	−64	233–238
4	− .35	−70	222–228
5	− .36	−72	178–185

The rotation of the solutions did not change on standing for two days at room temperature.

X-Ray diffraction patterns of these fractions did not coincide exactly, indicating them to be of a different nature.

The removal of strychnine from the complex salt was accomplished by grinding the dry salt in a mortar with a slight excess of potassium iodide, followed by extraction with enough water to give 0.5% solutions. Such solutions, prepared from the first, fourth and fifth fractions gave specific rotations ($[\alpha]_D$) of −10, −40 and −35°, respectively. The slightly smaller value obtained from the fifth fraction, in comparison with the fourth, is attributed to slight decomposition during recrystallization, as shown by its heterogeneous shade. The value of 40° (fourth fraction) is probably close to the specific rotation of the levo form of the zinc complex.

After a four-hour digestion at 100°, 0.5% solutions of the fourth and fifth fractions of the strychnine complex salt gave a specific rotation of −32° which was doubtless contributed by the strychnine itself. An aqueous solution of the potassium salt, obtained from the fourth fraction, completely lost its optical activity when digested for four hours.

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

Thermodynamic and Structural Characteristics of the Iron(III) Phase Formed by Bromination of Iron(II) Chloride

BY N. W. GREGORY

X-Ray powder patterns indicate that the iron(III) phase ($FeBrCl_2$) formed by bromination of $FeCl_2$ is essentially isostructural with $FeCl_3$ and $FeBr_3$, closely approximating that expected for a solid solution of the two. Thermodynamic properties, determined from equilibrium studies, are also reasonably consistent with those anticipated for such a solid solution. The sublimation of $FeCl_2$ in a bromine atmosphere at relatively low temperatures has been observed.

Introduction

Preparation of iron(III) monobromodichloride by bromination of $FeCl_2$ was reported by Lenormand in 1893.[1] The behavior of ionic substances such as the alkali halides (sodium chloride and sodium bromide form a complete series of solid solutions with essentially random distribution of the halide ions) suggests that metallic compounds of the mixed halide type may not be clearly defined. Whereas the bonds in $FeCl_3$ and $FeBr_3$ undoubtedly possess considerable covalent character, their crystal structures are very similar[2,3] and one would anticipate formation of solid solutions in this system. Both structures are of the layer type, typified by BiI_3, in which the crystal parameters are effectively determined by close packing of the halogens with the metal atoms (ions) in the interstices.

The relationship of thermodynamic and structural properties of the mixed halide phase to those of the simple halides has been investigated to determine whether these properties indicate $FeBrCl_2$ to be a distinct compound or a phase indistinguishable from a solid solution of $FeCl_3$ and $FeBr_3$. The equilibrium between $FeCl_2$ and bromine has been studied in the temperature interval between 30 and 97°, and X-ray powder patterns from the mixed halide phase compared with those of the simple halides.

Experimental Part

(a) **Preparation of Materials.**—Lenormand[1] reported complete conversion of $FeCl_2$ into $FeBrCl_2$ by reaction with bromine in a sealed tube at 100° for a period of five days. This observation was essentially confirmed in the present work. It was found difficult, however, to ensure complete separation of excess bromine from the product without some decomposition. This is to be anticipated as the equilibrium decomposition pressure of bromine over the solid is quite large even at room temperature (35 mm.). It was also observed that larger crystals of $FeCl_2$ were not completely brominated in this period of time.

Two of the samples used in the equilibrium studies were prepared directly in the apparatus. Others were prepared independently by Lenormand's method and transferred to the apparatus or powder tubes in a carbon dioxide dry-box. Excess bromine was removed by subjecting the samples to high vacuum at −20°. The composition of Sample III (treated in this manner) did not correspond to complete bromination; however, it was desired to ensure absence of excess adsorbed bromine before undertaking equilibrium measurements.

Analyses were performed by heating samples slowly in vacuum, eventually at 200°, and collecting the liberated bromine in a trap cooled with liquid air. The quantity of $FeCl_2$ remaining was determined by standard analytical methods and its identity confirmed by X-ray powder patterns. The amount of bromine released was determined by dissolving the condensed material in KI solution and titrating the liberated iodine with standard thiosulfate.

(b) **Determination of Equilibrium Pressures of Bromine.**—Pressures were measured by means of a thin glass membrane manometer. The gage was a modification of the Daniels type[4] in which the membrane was arranged to support a mirror. With a suitable beam of light the null position of the membrane could be established with an uncertainty of less

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[1] M. C. Lenormand, *Compt. rend.*, **116**, 820 (1893).

[2] Nora Wooster, *Z. Krist.*, **83**, 35 (1932).

[3] N. W. Gregory, THIS JOURNAL, **73**, 472 (1951).

[4] F. Daniels, *ibid.*, **50**, 1115 (1928).

than 1 mm. differential in pressure. The volume of the gage was approximately 50 ml.

The temperature of the system was controlled within one-half degree variation at a given point until the pressure remained constant for a minimum of 12 hours. At lower temperatures, several days were allowed to make certain equilibrium had been established. The temperature was varied randomly during each series.

Three independent sets of measurements were made with quite different bulk compositions: Sample I was prepared by subliming (under high vacuum) approximately 2 g. of $FeCl_2$ directly into the manometer. An amount of bromine sufficient to convert 51 mole per cent. of the $FeCl_2$ to $FeBrCl_2$ was permitted to enter the system (composition determined following the measurements). Data were obtained between 30 and 87°. Sample II was prepared in a similar manner, with introduction of a small excess of bromine. In this experiment, a residual pressure of bromine of 500 mm. remained in the system at temperatures below 75°. Equilibrium measurements were made between 80 and 97°. The third series of values was obtained using material formed in a separate reaction tube at 100° and transferred to the manometer in a dry-box. The composition of this sample corresponded to 81% $FeBrCl_2$. An insufficient amount was used to establish the equilibrium pressure of bromine in the system above 75°. Data were obtained between 35 and 70°.

Results

The experimental results are given in Table I. A comparison of data from samples with widely varying mole fraction of bromine in the solid indicates that the system is univariant. The iron(III) phase formed must be the same in all cases and appreciable solid solution between the iron(III) and iron(II) phases does not appear to occur. The entire pressure measured in the system has been attributed to bromine. There has been no evidence observed to indicate that the iron(III) halides possess a significant vapor pressure in the temperature range of interest.

Table I

Equilibrium Pressures of Bromine above Iron(II) Chloride

Sample I				Sample II		Sample III	
, °C.	$P_{mm.}$	t, °C.	$P_{mm.}$	t, °C.	$P_{mm.}$	t, °C.	$P_{mm.}$
30	48	72	403	81.5	630	35	61
40	86	76	482	86	721	44.5	105
50	145	79	558	87	775	55	179
59	224	80.5	592	89	900	60	230
65	307	84	698	90.5	951	65	290
69.5	353	87	770	94.5	1050	70	371
71.5	410	88	781	97	1175	80	Insuff. Br_2

A least squares treatment of all values leads to the equation $\log P_{mm.} = -2332/T + 9.369$. The average deviation of P (experimental) from that given by the equation was found to be 2%. The heat of the reaction (1) $2FeBrCl_{2(s)} = 2FeCl_{2(s)} + Br_{2(g)}$ is 10.6 kcal., with an estimated uncertainty of ±0.4 kcal. (The iron(III) phase is represented by the formula $FeBrCl_2$.) These results have been combined with other data currently available for the iron halides to construct Table II. There is a discrepancy in the value for the heat of formation reported for $FeCl_3$ by Kangro and Petersen[5] (based on equilibrium studies) and that given in the National Bureau of Standards Tables of Selected Values.[6]

Table II

Thermodynamic Properties of Chlorides and Bromides of Iron at 25°

The standard state for the halogens has been chosen as the gas at one atmosphere.

Substance (solid phase)	Reference	ΔH^0, kcal./mole	ΔF^0, kcal./mole	S^0, cal./mole/deg.
$FeCl_2$	6	−81.5	−72.2	28.6
$FeBr_2$	7	−67	−57	32
$FeCl_3$	5	−93.5	−78.6	36.9
	8	−96.8	−82	38.5
$FeBr_3$	9	−75	−59	42
$FeBrCl_2$	10	−87	−73	43

An examination of the structure of the mixed halide phase has been made by a study of X-ray powder patterns. Samples were ground and sealed in Pyrex capillary tubes and exposures made with Cu radiation, filtered by nickel, for a 24-hour period. Three independent samples were studied with satisfactory agreement. The results in Table III were taken from the best pattern. The eleven lines observed indicate that the mixed halide is essentially iso-structural with $FeCl_3$ and $FeBr_3$. Indices were assigned using a hexagonal cell comparable to that of $FeCl_3$ (this neglects possible symmetry effects due to dissimilar halogens). Although the powder data are not sufficient to define the structure completely, it is evident that the mixed halide must be an iron(III) phase which involves a packing of halogen atoms essentially the same as that in the simple iron(III) halides.

Table III

Powder Pattern Data for $FeBrCl_2$

Observed d's are compared with those calculated for a hexagonal cell with $a = 6.17$ and $c = 17.88$.

$d_{obsd.}$	Est. relative intensity	hkl	$d_{calcd.}$
5.960	8	0 0 3	5.960
3.083	1	1 1 0	3.085
2.976	3	0 0 6	2.980
2.741	10	1 1 3	2.740
2.145	8	1 1 6	2.143
1.783	6	3 0 0	1.780
1.670	5	1 1 9	1.669
1.496	3	2 2 3	1.493
1.490	3	0 0 12	1.490
1.370	2	2 2 6	1.369
1.145	3	3 0 12	1.143

Average deviation of d(calcd.) from d(obsd.) is 0.1%.

Discussion of the Mixed Halide Phase

The cell dimensions given in Table III are very close to those which are anticipated by application of Vegard's rule[11] to a solution of $FeCl_3$ and $FeBr_3$. For $FeCl_3$: $a = 6.06$, $c = 17.47$; $FeBr_3$: $a = 6.42$, $c = 18.40$; for a 2:1 mixture: $a = 6.18$, $c = 17.88$, as compared with 6.17 and 17.88 found in Table

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(5) Kangro and Petersen, *Z. anorg. Chem.*, **261**, 157 (1950).

(6) "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Standards, Circ. 500, Series I. Table 47, U. S. Gov. Printing Office, Washington, 1950.

(7) Heat of formation from ref. 6 (based on Br_2 gas as std. state); entropy estimated by Brewer, *et al.*; see L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Materials; Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

(8) Heat of formation from ref. 6; entropy estimated by Brewer.[7]

(9) Values calculated from data for $FeBr_2$ and results of N. W. Gregory and B. A. Thackrey, This Journal, **72**, 3176 (1950).

(10) Values calculated from data in this paper and those for $FeCl_3$.

(11) L. Vegard, *Z. Physik*, **5**, 17 (1921).

III. However, these parameters might be considered equally consistent with values anticipated for a mixed halide with definite orientation of bromine atoms. It was not found possible to prepare single crystals suitable for a more detailed study of the structure.

The univariance of the system in the equilibrium study does not rule out the possibility that the mixed halide phase is a solid solution. The iron (III) phase was formed in every case by reaction of bromine with $FeCl_2$ and hence has the same composition. Unfortunately, the thermal instability of $FeCl_3$ and $FeBr_3$ effectively prohibits an attempt to prepare solid solutions of varying known compositions.

Careful analysis of the iron(II) residue obtained by thermal decomposition of the mixed halide in high vacuum has shown repeatedly that bromine is not present. Powder patterns taken of samples of the mixed halide which were partially decomposed were found to show the three most intense lines characteristic of $FeCl_2$ in addition to those for $FeBrCl_2$. If the mixed halide phase is assumed to have a random distribution of bromine atoms, it is apparent that a mechanism must exist whereby decomposition occurs according to an over-all reaction of the type

$$4/3FeCl_3 + 2/3FeBr_3 = 2FeCl_2 + Br_2 \qquad (2)$$

However, it is somewhat misleading to write such an equation for reaction in the solid phase since each iron(ion) is surrounded by an octahedron of halogens in the crystal with each halogen shared by two ions in the iron(III) state and by three in the iron(II) state.

The thermodynamic properties of $FeCl_3$ and $FeBr_3$ are not sufficiently well defined to permit a significant comparison of characteristics expected for reaction (2) with the properties of the mixed halide observed in the current work. Data from references (8) and (9) lead to a value of the entropy of a mixture of $FeCl_3$ and $FeBr_3$ in good agreement with that presented in Table II by inclusion of an ideal entropy of mixing of the halide atoms. However, the enthalpy and free energy of (2) differ from that observed by 4 kcal. On the other hand, the heat of formation of $FeCl_3$ observed by Kangro and Petersen[5] leads to a value of ΔH for (2) in close agreement with that observed for decomposition of $FeBrCl_2$.

Slow sublimation of iron(II) chloride at a temperature of 250° has been found to occur if a pressure of bromine of approximately 500 mm. is maintained over the solid. A crystalline deposit of $FeCl_2$ may be collected in an adjacent zone at 150°. Direct sublimation of $FeCl_2$ under high vacuum will not occur at an appreciable rate until the temperature is well above 400°. One may explain the transfer of $FeCl_2$ by assuming that $FeBrCl_2$ is formed at very low concentration in the vapor phase and subsequently undergoes decomposition on condensation in the 150° zone. An alternate mechanism such as equation (2) is not ruled out but seems less likely.

Anderson[12,13] has shown that mixed halides of carbon and silicon undergo redistribution reactions quite readily in the vapor phase at temperatures of the order of 200°. In experiments described above and in others in which $FeCl_2$ was heated in an atmosphere of bromine for prolonged periods at higher temperatures, no evidence for exchange of halogen in the iron(II) phase could be found. This may be due largely to the fact that it is impossible to form a high concentration of mixed halide in the vapor phase. The vapor pressure curve for liquid bromine crosses the curve representing the equilibrium bromine pressure above solid $FeCl_2$ at approximately 150°. This means that the solid mixed halide phase cannot be formed above this temperature and hence the vapor will be stable only at pressures below the equilibrium vapor pressure of the solid. This is probably of the order of 10^{-3} mm. at 150°.

An attempt to determine the nature and thermodynamic characteristics of the vapor phase of the mixed halide as well as the properties of solid solutions in this system is being made in a continuation of this work.

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[12] H. H. Anderson, THIS JOURNAL, **72**, 2091 (1950), and related work.

[13] G. S. Forbes and H. H. Anderson, *ibid.*, **66**, 931 (1944).