there appears to be always at least one B–H$_{bond}$ bond from each boron atom, i.e., there are 4 H atoms in bridges and therefore 8B–H$_{bridge}$ bonds), then the equation

$$0.598(5 + 8) + 0.541(\text{no. B–B bonds}) = 12.00$$

which expresses equality between the sum of the bond numbers in the molecule and the sum of the bonding electrons, leads to 7.8 as the number of B–B bonds, a value which is certainly satisfactorily close to the actual value of eight. The accuracy of a result derived by a calculation of this sort depends principally upon the correctness of the assumed number of B–H bonds and upon the closeness of the assumed values of r_B to the best value for the compound; it depends to a lesser extent upon the use of average values for what may actually be a distribution of distances. To illustrate using the B$_5$H$_9$ example, for the case 7 B–H$_{bond}$, 4 B–H$_{bridge}$, r_B = 0.795 Å.; 5 B–H$_{bond}$, 8 B–H$_{bridge}$, r_B = 0.800 Å.; and 5 B–H$_{bond}$; 8 B–H$_{bridge}$, r_B = 0.795 Å., but with the B–H bonds split 0.13 Å.; one calculates 10.0, 7.2 and 8.2 B–B bonds, respectively.

It is to be noted that consistent values for the boron radius may be obtained only from compounds in which boron has high ligancy, 5 or 6; compounds of lower boron ligancy give values over the wide range 0.896 to 0.751 Å.[30] At present little can be said about the reasons for this lack of consistency, but certainly a wider range of calculated boron radii are to be expected for compounds of low ligancy, where in bonding the use of both three and four boron orbitals are encountered, than for compounds of high ligancy when usually only three are used.

Note added in proof.—The dipole moment of B$_{10}$H$_{14}$ has recently been reported [A. W. Laubengayer and R. Bottei, This Journal, 74, 1618 (1952)] as 3.52 D. Although this value and the value for B$_5$H$_9$ (mentioned above) are considerably greater than the calculated values, they cannot be regarded as invalidating the treatment. The sizes of these two molecules and the nature of the calculated charge distributions are such as to require shifting only relatively small amounts of charge to bring about complete agreement. Indeed, considering the sensitive dependence of atom charge on bond distance the observed and calculated values are satisfactorily close.

(30) These values are derived from borazole, B$_3$N$_3$H$_3$ (S. H. Bauer, This Journal, 60, 524 (1938)) and BF$_1$ (D. M. Gage and E. F. Barker, J. Chem. Phys., 7, 455 (1939)), respectively.

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[A Contribution of the Department of Chemistry, The University of Wisconsin]

Addition Compounds of Zirconium and Hafnium Tetrachlorides with Phosphorus Oxyhalogen Compounds[1]

By Edwin M. Larsen, John Howatson,[2] Adrian M. Gammill and Layton Wittenberg

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Zirconium and hafnium tetrachlorides react with POCl$_3$ and POFCl$_2$ to give addition products of the composition 2 POX$_3$·MCl$_4$ which decompose under reduced pressure at 50 to 60° to give POX$_3$·MCl$_4$. With POF$_2$Cl and POF$_3$, the metal tetrahalides give only POX$_3$·MCl$_4$ at room temperature. All the 1:1 products when heated decompose with the evolution of the phosphorus oxyhalide, with the temperature at which the decomposition is first observed decreasing with increasing fluorine content of the POX$_3$. No significant difference is observed in the behavior of the zirconium and hafnium compounds. If the contact time of the MCl$_4$ with excess POFCl$_2$ or POF$_2$Cl is long enough, complete halogen exchange within the phosphoryl molecule occurred and 2POCl$_3$·MCl$_4$ was crystallized from solution.

Addition compounds of zirconium (hafnium) tetrachloride with phosphorus pentachloride and phosphorus oxychloride[3] can be distilled and consequently are of interest since they can be employed[3,4] to separate zirconium from hafnium by a fractional distillation process. It was therefore thought desirable to make a study, wider in scope, of the reactions of zirconium and hafnium tetrachlorides with phosphorus oxyfluorides and oxychlorides to determine whether there were other distillable compounds formed.

All of the substances concerned in this work reacted readily with moisture, so operations involving transfer of solid materials were performed in a "dry-box," while all transfers of the volatile reactants were made in a vacuum system. The physical properties of the reactants are: POCl$_3$, m.p. 1.25°, b.p. 105.1°; POFCl$_2$, m.p. −80.1°, b.p. 52.9°; POF$_2$Cl, m.p. −96.4°, b.p. 3.1°; POF$_3$, m.p. −39.4°, b.p. −39.8°.

Experimental Procedure

Materials Used.—The zirconium and hafnium tetrachlorides were prepared by the action of gaseous chlorine on a sugar charcoal–metal oxide mixture, in a manner similar to that for the preparation of zirconium tetrabromide by Young.[5] The crude tetrachloride was heated in hydrogen at 450° and then sublimed under reduced pressure at 350°. Analysis of the purified product gave a Cl/Zr atomic ratio of 3.98. The zirconium oxide contained only 0.04% hafnium, and the hafnium oxide 0.75% zirconium according to spectrographic analyses.[6]

(1) (a) Supported, in part, by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation, and in part by the Office of Naval Research under Task Order 4 of Contract N7onr-28504 between the Office of Naval Research and the University of Wisconsin. (b) Presented, in part, at the Detroit Meeting of the American Chemical Society, April 17, 1950. (c) Based on the dissertations of John Howatson and Adrian Gammill in fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) W.A.R.F. research assistant, 1947–1949. Recipient of du Pont grant-in-aid, Summer, 1949.

(3) A. E. Van Arkel and J. H. de Boer, Z. anorg. Chem., 141, 289 (1924).

(4) D. M. Gruen and J. J. Katz, This Journal, 71, 3843 (1949).

(5) R. C. Young and H. G. Fletcher, Inorganic Syntheses, 1, 49 (1939).

(6) C. Feldman, Oak Ridge National Laboratory.

Phosphoryl chloride was purified by fractional distillation in an all-glass apparatus, the first fraction was discarded, and the middle fraction was collected in a new dry receiver. *Anal.* Calcd.: P, 20.22; Cl, 69.36. Found: P, 20.02; Cl, 68.5.

The phosphoryl dichlorofluoride, phosphoryl chlorodifluoride and phosphoryl fluoride were prepared by the fluorination of boiling phosphoryl chloride with hydrogen fluoride.[7] The equilibrium mixture was fractionated in a column with a low temperature head. Each component was then redistilled, and delivered into a storage vessel. The purity of the phosphoryl fluoride was determined by analyzing an unknown weight of material for both phosphorus and fluorine. The F/P ratio obtained was 3.09. The analyses of the other compounds gave: POF_2Cl, Calcd.: P, 25.7; F, 31.6; Cl, 29.5. Found: P, 25.6; F, 30.0; Cl, 29.5; $POFCl_2$, Calcd.: P, 22.63; F, 13.98; Cl, 51.80. Found: P, 22.72; F, 13.85; Cl, 50.54.

Analytical Methods.—Two types of samples were analyzed, the liquid reactant or volatile decomposition product, and the solid addition compound. A liquid sample was first frozen in liquid air and then, as with the regular solid samples, the weighed reaction tube was cut open, and the parts dropped into a flask containing 100 ml. of frozen 1 N sodium hydroxide. After the hydrolysis reaction was complete, the parts of the ampule were recovered and weighed again to determine the weight of the sample. Hydrolysis of a phosphorus oxyhalogen compound gave a clear, colorless solution which was subsequently analyzed for phosphorus, chlorine and fluorine. The hydrolysis of the addition compound resulted in a solution in which was suspended a mixed precipitate of the metal hydroxide and phosphate which required further treatment before the analysis could be carried out.

The precipitate was separated from the bulk of the liquid, washed by decantation until free of chloride, and then converted to an acid-soluble zirconium (hafnium) peroxy compound.[8] The washings were filtered, combined in a volumetric flask with the liquor initially separated, and this solution then analyzed for phosphorus, fluorine and chlorine.

For the phosphate analyses, aliquots of the solution contained in a platinum dish were heated with 60% perchloric acid or concentrated sulfuric acid until the solution fumed, to ensure complete hydrolysis of any intermediate fluophosphate to the ortho phosphate.[9] The phosphate content was determined by the magnesium ammonium phosphate method.

The fluorine analyses were carried out by distilling an aliquot of the solution in the presence of 60% perchloric acid and glass beads to volatilize the fluorine as fluosilicic acid.[10] The fluorine in the distillate was then titrated with 0.1 N thorium nitrate solution[11] which had been standardized with sodium fluoride. Sodium alizarin sulfonate was used as the internal indicator.

Chloride was determined by the Volhard method after acidification of an aliquot of the solution. These halide values usually ran low, probably due to the loss of volatile products during the solution of the sample, or incomplete separation of the halide from the metal precipitate. Since we were mainly interested in establishing the exchange or non-exchange of the halogens, the data are reported in terms of Cl/F ratios (Table I).

For the metal analysis, the insoluble peroxy zirconium (hafnium) compound, along with any of the peroxy compound collected on the filter paper, was dissolved in hydrochloric acid, the solution filtered to remove filter paper threads, and finally boiled to decompose any remaining peroxide. The metal content of an aliquot was determined by precipitating and igniting the hydrated oxide. Filter papers from all the operations were collected, ignited, the residues leached with water and reignited. The values for the metal analysis were corrected accordingly assuming that any residue was the oxide and filter paper ash. The results expressed in terms of the P/metal ratio are given in

(7) M. Woyski, unpublished data

(8) E. M. Larsen, W. C. Fernelius and L. L. Quill, *Inorganic Syntheses*, **3**, 67 (1950).

(9) G. Tarbutton, E. P. Egan, Jr., and S. G. Frary, This Journal, **63**, 1782 (1941).

(10) H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(11) R. J. Rowley and H. V. Churchill, *ibid.*, **9**, 551 (1937).

Table I. These data are average values representing a minimum of four results, two for each experimental sample.

Apparatus.—Two types of reaction vessels were used. The first, type A, was made from 14 mm. × 14.5 cm. Pyrex test-tubes and 8-mm. Pyrex glass tubing. The body part of the resulting ampule was approximately 6 cm. long with a neck of 8-mm. tubing about 15 cm. long. To the 8-mm. tubing was sealed a $^{12}/_{30}$ inner ground glass joint, by means of which the ampule could be attached to a vacuum manifold. Another type of reaction tube, designated as type B, was constructed in the same manner, except that a right angled side-arm containing a thin glass diaphragm was sealed on the body of the tube just below the shoulder of the ampule.

General Procedure.—The weighed reaction ampule, containing a one to two gram sample of the tetrachloride, was attached to the vacuum manifold and an ampule containing the phosphoryl halide was similarly attached and frozen. After evacuation of the system to less than 0.1 mm. the phosphoryl halide was melted and distilled on to the metal tetrachloride by cooling the reaction tube in liquid air. After a 6–10 molar excess of the phosphoryl halide had condensed in the tetrachloride tube, the latter was closed off and the reactants were allowed to stand for the given period of time at the desired temperature. The excess reactant was then distilled off, dry air was admitted to the system, the reaction tube removed from the manifold, and reweighed. This process was repeated until no further gain in weight was observed. The sample was then analyzed.

To study the thermal stability of the compounds, the initial reaction product was usually prepared in a Type B reaction tube which was then sealed to an all glass vacuum manifold bearing the collection ampules. With the system at atmospheric pressure, the thin glass diaphragm separating the ampule and the manifold was broken with a piano wire probe. The probe and its fittings were then replaced with a cork, the system was evacuated, the side arm sealed and the manifold cut off from the pump with a torch. The reaction vessel was then immersed in an oil-bath at 50°, and one of the collecting bulbs was immersed in liquid air. The temperature of the oil-bath was raised gradually so that the temperature at which condensation of the volatile decomposition products was first observed was approximately the temperature at which the vapor pressure of the POX_3 first became significant. This observed temperature was a function of the rate of heating, and therefore the observations were reproducible only if the rate of heating was reproducible. The reaction vessel was finally heated until no additional volatile product was collected in a new collection ampule. For analysis, the reaction ampule and collection ampules were sealed off from the apparatus with a torch.

Summary of Results

Initial Products (for analytical data see Table 1). **A.** $POCl_3$.—From a supersaturated solution, small, transparent crystals were deposited which were converted to a white powder upon removal of the excess solvent. The composition of the product was $2POCl_3 \cdot MCl_4$.

B. $POFCl_2$.—When the reactants were in contact for long periods of time, exchange occurred between the phosphoryl halide molecules. When excess phosphoryl dichlorofluoride was removed from the metal tetrahalide within one hour after solution, the composition of the white powder resulting was $2POFCl_2 \cdot MCl_4$.

C. POF_2Cl.—When excess phosphoryl difluorochloride was removed from the metal tetrachloride within ten minutes after solution, the white powder resulting had a composition which was less than that necessary for $2POF_2Cl \cdot MCl_4$. Continued pumping for a week resulted in loss in weight until the composition $POF_2Cl \cdot MCl_4$ was reached. For the hafnium compound especially, it was most difficult to remove the last trace of the phosphoryl halide. This is reflected in the analytical results in the form of low Cl/F ratios and for the hafnium product by the high P/metal ratio.

D. POF_3.—The solid metal tetrachloride was treated repeatedly with a large excess of liquid phosphoryl fluoride at −40° until no further gain in weight was observed; complete solution was never obtained. The white solid resulting had the composition $POF_3 \cdot MCl_4$.

Thermal Decomposition Products (at pressures less than 0.1 mm.). **A.** $POCl_3$ (1).—The 2:1 compounds began to decompose at 60° with the evolution of phosphoryl chlo-

ride. When held at 105° until no further evolution was observed, the composition of the resulting product was $POCl_3 \cdot MCl_4$ (Table I). No melting was observed.

(2).—At 130°, sublimation of the 1:1 compounds was observed but further decomposition was not apparent until 145° was reached. The decomposition was complete after the sample had been held at 205° for several hours. The sublimate from the hafnium compound was analyzed and found to have nearly the composition $POCl_3 \cdot HfCl_4$ (Table II, 1a) although the P/Hf ratio was low owing to the sublimation of hafnium tetrachloride as a decomposition product. The non-volatile residue remaining had a high P/Hf ratio which could not be explained. Under the conditions of the experiment, the $2POCl_3 \cdot 3MCl_4$ compound was never observed as a decomposition product of the 1:1 compound.

B. $POFCl_2$ (1).—The 2:1 compounds when heated to 50–55° evolved phosphoryl dichlorofluoride. As the temperature was increased the zirconium compound gave a melt at 74–78°, and the hafnium product at 80–83°. When heated finally at 115° until the gaseous evolution had ceased, the composition of the resulting product was $POFCl_2 \cdot MCl_4$ (Table I). The Cl/F ratios for the zirconium compound were high owing to some halogen exchange while the sample was molten.

(2).—At 130° the 1:1 compounds showed evidence of decomposition, but the evolution of volatile products became rapid only when a melt was obtained: at 161–163° for the zirconium compound, and 165–167° for the hafnium compound. If the temperature was raised slowly, the molten state was maintained, and at 260–270° a distillate was obtained. Under these conditions the halogen exchange between the phosphoryl dichlorofluoride molecules was almost complete, and the distillate approached the composition $2POCl_3 \cdot 3ZrCl_4$ (Table II, 2c). If the heating was rapid, the liquid range was short, no exchange occurred, and the decomposition products at 250° were the metal tetrachloride as a sublimate and residue, contaminated by some of the 1:1 compound (Table II, 2a,b), and the phosphoryl halide. Complete analytical data were available for the zirconium compound only.

C. POF_2Cl.—The 1:1 products when heated evolved no phosphoryl halide until the sample melted, which occurred at 106–109° for the zirconium compound and 110–113° for the hafnium compound. When heated to a still higher temperature (240°), a white sublimate appeared and the melt became dark. The maximum temperature attained was 325° after which no further change was observed. The sublimate gave an analysis which approached that for the
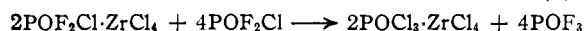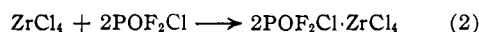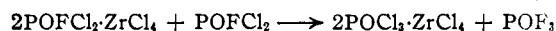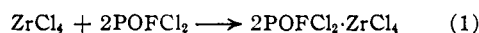
metal tetrachloride itself, and the non-volatile residue had a high F/M ratio indicating that some of the chlorine in the tetrachloride had been exchanged for fluorine (Table II, 3a,b). The data were available for the zirconium compound only.

D. POF_3.—The 1:1 compounds lost about 20% of the phosphoryl fluoride while being brought up to 85°, the temperature at which both the zirconium and the hafnium compounds melted. Analysis of the vapors collected over this period showed that about 7% halogen exchange had occurred. Upon heating to 250°, a white sublimate and a black residue were obtained. The sublimate was essentially the metal tetrachloride (Table II, 4a,b), while the residue showed evidence for fluorination of the tetrachloride. If the decomposition was carried out rapidly so that no melt was obtained, the decomposition products were only the metal tetrachloride (Table II, 4c), and the phosphoryl fluoride. The analyses of the hafnium products were not made.

Discussion

It is apparent that the introduction of fluorine in the donor molecule reduced the thermal stability of the resulting addition compounds, and introduced the possibility of halogen exchange reactions.

Although the exchange of halogens between POF_xCl_y molecules had never been observed in the pure liquids at room temperature, reactions such as the following must have occurred in the presence of zirconium tetrachloride.

$$ZrCl_4 + 2POFCl_2 \longrightarrow 2POFCl_2 \cdot ZrCl_4 \qquad (1)$$

$$2POFCl_2 \cdot ZrCl_4 + POFCl_2 \longrightarrow 2POCl_3 \cdot ZrCl_4 + POF_3$$

$$ZrCl_4 + 2POF_2Cl \longrightarrow 2POF_2Cl \cdot ZrCl_4 \qquad (2)$$

$$2POF_2Cl \cdot ZrCl_4 + 4POF_2Cl \longrightarrow 2POCl_3 \cdot ZrCl_4 + 4POF_3$$

Additional steps to these reactions could be written but no real evidence was at hand for the presence of intermediate reactions. These exchange data were carefully confirmed by comparing the analyses of the excess reactant removed from the reaction system, with the per cent. fluorine and chlorine calculated to be present from a knowledge of the initial weight and composition of the starting POF_x-Cl_y, the fluorine and chlorine content of the addition compound prepared, and the weight of the excess POF_xCl_y. In all cases, the excess fluorine and the deficiency of the chlorine in the excess reactant, checked the calculated values.

Several reaction systems were studied as a function of time at room temperature in which the mole ratio of reactants was approximately the same. The halogen exchange, based on the deficiency of fluorine in the solid addition compound, appeared to be more rapid in the solution of phosphoryl difluorochloride (36% exchange in two hours), than in the solution of phosphoryl dichlorofluoride (18% exchange in 22 hours). Because of this exchange phenomenon, the time of contact of the metal tetrahalides with POF_xCl_y was kept at a minimum in the synthesis of the molecular addition compounds.

This same halogen exchange was observed whenever the molten state was obtained in addition compounds of $POFCl_2$. If the compound was held at the melting point for a long period of time, then the temperature range over which the system remained liquid increased, and as the temperature increased complete exchange occurred with $2POCl_3 \cdot 3ZrCl_4$ formed as a distillable product. On the other hand, if the temperature was high enough so

TABLE I

Compound	Gain in wt. data[a] MCl₄, % Hf Exptl.	Calcd.	Zr Exptl.	Calcd.	Analytical data[a] Atomic ratios P/metal Hf	Zr	Cl/F Hf	Zr
$2POCl_3 \cdot MCl_4$	51.0	51.0	43.3	43.2	1.94	..	9.96	..
$POCl_3 \cdot MCl_4$	66.7	67.6	60.8	60.5	1.02	..	6.98	..
$2POFCl_2 \cdot MCl_4$	54.2	53.9	46.1	46.0	2.00	1.80	4.01	3.96
$POFCl_2 \cdot MCl_4$	69.4	70.0	62.7	63.0	1.00[b]	0.97	5.81[b]	6.78
$POF_2Cl \cdot MCl_4$	72.6	72.6	65.3	65.9	1.15	0.98	2.04	2.18
$POF_3 \cdot MCl_4$	75.9	75.5	69.3	69.2	0.99	1.01	1.37	1.36

[a] Average results. Corrected for known zirconium–hafnium ratios. [b] Single result.

TABLE II

THERMAL DECOMPOSITION PRODUCTS OF $POX_3 \cdot MCl_4$ COMPOUNDS

Compound		Atomic ratios P/M	Cl/M	F/M
(1) $POCl_3 \cdot HfCl_4$	(a) Sublimate	0.88	7.05	..
	(b) Residue	3.06	4.76	..
(2) $POFCl_2 \cdot ZrCl_4$	(a) Sublimate	0.27	4.37	0.16
	(b) Residue	0.09	3.74	0.12
	(c) Distillate	0.58	5.2	0.3
(3) $POF_2Cl \cdot ZrCl_4$	(a) Sublimate	0.27	4.04	0.84
	(b) Residue	0.67	3.37	2.0
(4) $POF_3 \cdot ZrCl_4$	(a) Sublimate	0.10	4.35	0.28
	(b) Residue	0.41	1.52	3.4
	(c) Residue	0.12	3.93	0.51

that the rate of decomposition was more rapid than the rate of exchange, then only the metal tetrachloride and the phosphoryl halide were obtained as decomposition products.

At the melting points of the $POF_2Cl \cdot MCl_4$ and $POF_3 \cdot MCl_4$ compounds, however, the metal tetrahalide was fluorinated as evidenced by the fact that the non-volatile residues resulting from the thermal decomposition were always high in fluorine and low in chlorine. Fluorination with phosphoryl fluoride was also observed when the initial reaction mixture was warmed up to −15° under pressure.

For this reason the reactions with phosphoryl fluoride were carried out at −40°.

No significant difference in the behavior of zirconium and hafnium compounds was noted except that the hafnium compounds usually melted at slightly higher temperatures than the corresponding zirconium compounds.

Studies Pertaining to Soluble Silver Iodide Species

BY EDWARD L. KING, HARRY J. KRALL AND MARY L. PANDOW

The increase of the solubility of silver(I) iodide with an increasing concentration of silver(I) ion or iodide ion indicates the existence in solution of cationic and anionic complex ions. Solubility measurements, ion mobility determinations, and spectral studies have been employed to elucidate the nature of these complex ions. These studies indicate the existence of anionic complex ions which contain varying numbers of silver(I) ions and the existence of cationic complex ions which contain varying numbers of iodide ions. It appears that the solutions contain not merely monomeric and dimeric species but a large variety of these polymeric species.

In this work solubility measurements, ion mobility determinations and spectra studies have been utilized for the purpose of elucidating the equilibria which exist in solutions containing silver (I) and iodide. It will be seen that a wide variety of soluble species containing silver(I) and iodide must exist. While the methods utilized here are inadequate in completely describing the system, several important conclusions can be drawn from the observations.

Solubility Studies

The manner in which the solubility of a slightly soluble compound is affected by the concentration of a complexing agent provides valuable information regarding the species existing in the solutions. The interpretation is particularly straightforward if each of the soluble species contains only one ion or atom of the one kind. In the case of the solubility of silver(I) iodide in solutions of sodium iodide, the various possible equilibria would be

$$AgI(s) + nI^- \rightleftarrows AgI_{1+n}^{-n}$$
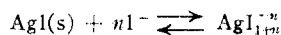
and the dependence of the solubility on the iodide ion concentration in media in which the activity coefficients could be assumed to be constant would allow a calculation of the average value of n, the charge on the complex. If the value of n is known as a function of the iodide concentration, the formulas of the species existing in solution over that concentration range can be established. If several complex species containing different numbers of silver(I) ions[1] exist, the situation is more complicated. The dependence of the solubility on the iodide ion concentration still gives the average

value of the charge on the complex but no information regarding the number of silver(I) ions per unit is provided. If complexes containing varying numbers of silver(I) ions do exist, the solutions saturated with silver(I) iodide will have as important a contribution from the species containing the largest numbers of silver(I) ions as is possible for any solution of that particular iodide ion concentration.

W. Erber[2] has studied the solubility of silver(I) iodide in aqueous solutions of hydrogen iodide and found the solubility to be proportional to the fourth power of the iodide concentration over a wide concentration range. The interpretation that the species $Ag_2I_6^{-4}$ was present in the saturated solutions is of rather dubious validity. The ionic strength was not held constant and therefore the activity coefficients of the various species were not constant. No evidence was presented to prove the existence of a species containing a single number of silver(I) ions.

In an attempt to remove one of the factors contributing to the uncertainty in interpretation, the solubility of silver(I) iodide has been measured in media of varying sodium iodide concentration and approximately constant ionic strength (2 molar) at approximately 25°. This device of maintaining the ionic strength constant is not, of course, assurance that the activity coefficients of all of the species will remain constant.[3] In these studies the ionic strength was maintained constant with sodium perchlorate; calculations using the equation developed by Glueckauf[4] indicate that the mean activity coefficient of sodium iodide varies

(1) The bonding in the silver(I) iodide complex ions undoubtedly has a great deal of covalent character. In this paper, the constituents of the complex ions will be referred to as silver(I) ions and iodide ions, nevertheless.

(2) W. Erber, Z. anorg. allgem. Chem., 248, 36 (1941).

(3) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," second ed., Reinhold Publishing Company, New York, N. Y., 1950, pp. 454-461.

(4) E. Glueckauf, Nature, 163, 414 (1949).