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**INVESTIGATIONS RELATING TO THE CHEMISTRY
OF URANIUM**

**Contribution of the Metcalf Research Laboratory of
Brown University, Providence, Rhode Island**

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**PART I. SOME PROPERTIES OF SOLUTIONS OF CERTAIN
URANYL SALTS**

**Investigations Carried Out Between
January 1, 1942 and March 15, 1946**

May 1, 1946

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Part I of BT-68 (A-2329)

PART I

SOME PROPERTIES OF SOLUTIONS OF CERTAIN URANYL SALTS

By Charles A. Kraus

Contribution of the Metcalf Research Laboratory

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PART I

SOME PROPERTIES OF SOLUTIONS OF CERTAIN URANYL SALTS

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PART I

SOME PROPERTIES OF AQUEOUS SOLUTIONS OF CERTAIN URANYL SALTS

FOREWORD

Our knowledge of the properties of aqueous solutions of uranyl salts is extremely limited. It seemed worth while, therefore, to study certain of the more common of these salts. The properties of solutions of uranyl chloride have been studied in some detail. These studies include the phase relations of the system $\text{UO}_2\text{-HCl-H}_2\text{O}$, the conductance, the viscosity and the density of these solutions as well as the determination of transference numbers and of pH values. Phase relations have been determined for the systems $\text{UO}_2\text{-HNO}_3\text{-H}_2\text{O}$ and $\text{UO}_2\text{-HClO}_4\text{-H}_2\text{O}$. As the results of these studies will show, the $\text{UO}_2\text{-HCl-H}_2\text{O}$ system is much the most complex of the three.

Various analytical and preparative procedures are described. A few test experiments were made on the properties of solutions of UO_2Cl_2 in pyridine and in antimony trichloride. The results indicate that uranyl salts are relatively weak electrolytes.

Chapter I

ANALYTICAL METHODS

An accurate and fairly rapid method for the analysis of uranium must be available before any reliable investigation of its chemical properties can be made. Accordingly, some time was spent in developing the necessary technique and in checking three independent methods of analyses against each other.

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The first gravimetric method consisted in precipitating the uranium with carbon dioxide-free ammonium hydroxide, washing the precipitate and igniting to U_3O_8 . The second gravimetric method involved the evaporation of a weighed sample of the solution to dryness in a porcelain crucible and ignition to U_3O_8 .

Since the volumetric method of analysis for uranium is more rapid than either of the two gravimetric methods, and is in good agreement with them, it was more generally used. The method employed was that developed by Kolthoff and Lingane (J.Am.Chem.Soc., 55, 1871 (1933)). A quantity of the unknown solution was withdrawn from a weight burette, diluted to 100 ml. with dilute sulfuric acid (1 part conc. H_2SO_4 to 20 parts H_2O) and reduced in the Jones Reductor. The sample was washed out of the Reductor with three 30 ml. portions of 1:20 sulfuric acid followed by three 30 ml. portions of distilled water. Air was then bubbled through the solution for approximately ten minutes in order to oxidize any U^{III} to U^{IV} . After adding 25 ml. of 2 percent $FeCl_3$ solution, 15 ml. of 85 percent H_3PO_4 and 4-5 drops of a 0.2 percent aqueous solution of barium diphenylamine sulfonate as an indicator, the sample was titrated with 0.1 N $K_2Cr_2O_7$ solution from a weight burette to the first violet color that persisted for at least one minute. It was found advisable to use samples that would require not more than 20 grams of 0.1 N $K_2Cr_2O_7$ for titration. If this amount was exceeded, it became more difficult to determine the end point precisely. When performed under carefully duplicated conditions, an experienced analyst can attain an accuracy of 0.1 to 0.2 percent. Larger deviations were only occasionally observed.

Chapter II

MATERIALS AND PREPARATIONS

The oxides of uranium which were studied in some detail are uranium tetroxide, UO_4 , uranium trioxide, UO_3 , and uranium dioxide, UO_2 .

1. Uranium Trioxide. Pure uranium trioxide is of particular interest, since a convenient method for preparing solutions of uranyl salts consists in dissolving this oxide in the correct amount of a given acid.

Uranium trioxide can be obtained by thermally decomposing uranyl nitrate. This method necessarily requires a pure starting material and leads to the formation of a rather dense oxide. Attempts to prepare the oxide by adding ammonium hydroxide to a uranyl nitrate solution followed by calcination of the resulting precipitate were not successful. The precipitate obtained in this way contained ammonia which could not be removed at sufficiently low temperatures to prevent the formation of U_5O_8 .

The thermal decomposition of uranium tetroxide was found to be the most satisfactory method of preparing pure uranium trioxide. This method is described in the following paragraphs.

2. Uranium Tetroxide. The precipitation of uranium tetroxide from a uranyl nitrate solution by means of hydrogen peroxide has been found to yield a very pure product. The trioxide can be readily obtained by thermal decomposition of the tetroxide. The reactions involved are:

Reaction (1) is practically quantitative, and the precipitate of UO_4 formed in the acid solution shows little tendency to be contaminated by ordinary impurities. If the reaction is carried out at room temperatures, the resulting precipitate filters extremely slowly. An easily filterable precipitate is obtained when the reaction is carried out at 75°C ; the following procedure gives satisfactory results:

A filtered solution of 210 grams of uranyl nitrate in 1 liter of water is heated to 75°C , and after removing the source of heat, 1 liter of 3 percent hydrogen peroxide is added slowly with stirring. After allowing the mixture to stand for 10 to 20 minutes, the resulting precipitate is washed on a Buchner filter with 6 to 8 liters of water.

Experiments were performed to determine how completely foreign salts can be removed from UO_4 by washing. Several preparations were made using solutions containing known amounts of iron and sodium salts. Three ml. of these solutions contained 540 mg. of UO_2^{++} , 5 mg. of Na^+ , and 5 mg. of Fe^{+++} . In experiments where chloride was present, the solutions were first evaporated to dryness in the presence of nitric acid. After precipitating and washing the UO_4 , it was dissolved in concentrated hydrochloric acid, the solution was evaporated to dryness, and the residues taken up in 6 N acetic acid. The resulting solutions were then tested with thiocyanate for the presence of iron and, with zinc uranyl acetate, for the presence of sodium. In this way, 0.01 mg. of iron or sodium could be detected. The data obtained are listed in Table 1. In experiments in which 3 ml.

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samples were used, the precipitate was separated from the mother liquor and wash water by centrifuging, and the liquid was withdrawn by means of a capillary dropper. The UO_4 obtained from the 75 ml. sample was washed on a small sintered glass Buchner funnel. The last two columns of Table 1 list the percentages of the initially added sodium and iron which remained in the UO_4 .

TABLE 1

Separation of Na and Fe from Uranium
by a Peroxide Precipitation

Amount and Nature of Sample	Amount of Washing	Amount of Added Impurity Remaining in UO_4	
		Na	Fe
3 ml. $\text{UO}_2(\text{NO}_3)_2$	2-10 ml. portions	3%	1-5%
" " "	" " "	1	3
3 ml. UO_2Cl_2	3-10 ml. portions	0.2	0.4
" " "	" " "	0.2	0.4
75 ml. UO_2Cl_2	400 ml.	0.1	0.2

It is evident that sodium washes out more readily than does iron, and that both can be nearly completely removed from the precipitate.

Uranium tetroxide can be dried at $60^\circ\text{--}70^\circ\text{C}$ for 13 hours without appreciable loss of oxygen. At higher temperatures, decomposition takes place, and the extent of this reaction was followed. The procedure employed consisted in heating a sample of the tetroxide at a particular temperature for three hours in a stream of oxygen. A fresh sample of the tetroxide was used for each temperature. The amount of uranium and water present in the original material was determined by igniting samples to U_3O_8 . The analysis gave 85.77 percent UO_4 and 14.23 percent H_2O , corresponding

closely to the trihydrate, $\text{UO}_2 \cdot 3\text{H}_2\text{O}$. The amount of uranium actually present as UO_2 was determined by a permanganate titration and found to be 85.53%. The change in oxygen content of a sample after heating was determined by titration, since both UO_2 and U_3O_8 will reduce potassium permanganate in sulfuric acid solution. In order to avoid possible loss of oxygen from the tetroxide, due to heating, the solutions were chilled in an ice bath before adding sulfuric acid and titrating. The data obtained are tabulated in Table 2 and illustrated graphically in Figure 1.

TABLE 2

Thermal Decomposition of UO_2
Three-hour Heating Time

Temperature °C	Amount Uranium as:		Atom Ratio, O/U (By Analysis)
	<u>UO_2</u>	<u>U_3O_8</u>	
initial sample	99.72%	--	3.998 (UO_2)
65°C			
100	98.25	--	3.981
150	81.22	--	3.804
175	21.56	--	3.206
200	0.19	--	3.003 (UO_3)
250	0.19	--	3.000
300	0.09	--	3.000
400	--	0.41	2.998
500	--	14.48	2.951
575	--	21.48	2.927

FIG. 1. THE DECOMPOSITION OF UO_4 AS A FUNCTION OF TEMPERATURE.

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As may be seen from Figure 1, the decomposition of UO_4 to UO_3 begins at slightly below $100^\circ C$, and is nearly complete at $200^\circ C$. It is apparent that by heating for three hours at temperatures between 250° and $300^\circ C$, UO_4 can be completely decomposed to UO_3 . An analysis of UO_3 prepared in this fashion showed it to be 99.97 percent pure UO_3 . Above $400^\circ C$, U_3O_8 is formed slowly. It should be pointed out that these data are valid only for UO_4 prepared and decomposed as described in the preceding paragraphs. Furthermore, the transition from one oxide to another is not abrupt, nor is it independent of the time of heating.

In carrying out investigations relating to the preparation of UO_3 for use in the liquid and vapor phase chlorination reactions, it was found that the presence of $2H_2O$ as an impurity interfered with the conversion of UO_4 to UO_3 by calcination, whereas H_2SO_4 and $Ca(NO_3)_2$ did not affect the conversion. In the presence of $\frac{1}{2}$ H_2O , based on the uranium content, the conversion to UO_3 was only approximately 50% complete on extended heating at $350^\circ C$. Unlike the original peroxide-oxygen in UO_4 dried in an oven at $110^\circ C$, which may be determined by titration with a suitable reagent, such as permanganate, the peroxide-oxygen in the virtually anhydrous calcined product is evolved immediately on contact with H_2O and can only be determined by measuring the volume of oxygen evolved. Presumably, such a product contains anhydrous UO_4 . Preparations with similar properties may be made by dehydrating UO_4 in vacuo, or by heating the diurate rapidly to $400^\circ-450^\circ C$ in a

stream of air or oxygen. Investigations relating to the properties of oxides used in chlorination reactions as affected by the conditions employed in their preparation and studies on the dehydration of UO_3 are presented in Part III, Chapter IV.

3. Uranium Dioxide. When UO_3 is heated between 400-550°C in a stream of purified hydrogen, reduction to UO_2 takes place with the liberation of sufficient heat to cause the mass to glow. The brown product is insoluble in hydrochloric acid. It reacts exothermally with the oxygen of the air presumably to form U_3O_8 .

The possibility of using UO_2 as anode material in the electrolysis of uranyl chloride solutions was briefly investigated. An electrode was prepared by packing 27 g. of UO_2 into a Soxhlet thimble containing a cylindrical platinum gauze 1 cm. in diameter and 2 cm. long. While serving as an anode during the electrolysis of 0.6 N HCl , it carried a current of 0.1 amp for 10 hours without gassing. Hydrogen was liberated at the cathode, and the yellow solution which formed at the anode proved to be uranyl chloride. The reaction may be written as:

A detailed study of this reaction was not undertaken. However, it was qualitatively observed that the more concentrated the uranyl chloride solution at the anode became, the greater was the tendency for chlorine gas to be evolved.

4. Uranyl Chloride. The preparation of uranyl chloride containing a minimum amount of water is necessary if the

behavior of this salt is to be studied in solvents other than water. An attempt to carry out this preparation by passing commercial, dry chlorine over pure UO_2 at 500°C resulted in the formation of a mixture of UO_2Cl_2 and U_2O_7 . It is probable that a small amount of oxygen was present in the chlorine. Due to the difficulty of purifying chlorine, this method was abandoned in favor of a simpler one.

Gaseous HCl reacts readily with uranium trioxide to form UO_2Cl_2 . The reaction is exothermic, and proceeds at room temperature provided that some moisture is present. If anhydrous uranium trioxide is used, the reaction with HCl is extremely slow. The hydrated uranyl chloride formed can be dried without decomposition in a current of dry HCl at 500°C . Material prepared in this way contained 79.85 percent UO_2 and 20.35 percent Cl . After grinding and again treating the salt with dry HCl at 500°C , analysis yielded 79.24 percent UO_2 and 20.32 percent Cl , corresponding to 1.94 percent unreacted UO_3 and 0.29 percent water.

By modifying the reaction conditions, a more nearly complete conversion may be obtained. A closed system, containing a charge of partially hydrated UO_3 , is evacuated without heating in order to remove from the system as much air and as little water as possible. Gaseous HCl is then introduced at a rate sufficient to maintain a pressure of one atmosphere in the system. The reaction requires from 15 to 24 hours at room temperature for completion, and may be followed by the change in color from orange uranium

trioxide to yellow uranyl chloride. Material prepared in this way showed an analysis of 94.69 percent UO_2Cl_2 , 0.51 percent UO_3 , and 4.80 percent H_2O .

The above material was entirely suitable for use in studies of aqueous solutions of UO_2Cl_2 . Pure anhydrous UO_2Cl_2 may be prepared by the oxidation of UCl_4 by oxygen. Investigations relating to the preparation and properties of anhydrous UO_2Cl_2 may be found in Chapter X, Part III of this report.

Chapter III

PROPERTIES OF URANYL CHLORIDE SOLUTIONS

1. Phase Relations in the System $\text{UO}_3\text{-HCl-H}_2\text{O}$. The solubility of uranium trioxide in aqueous uranyl chloride solutions has been measured over a wide range of concentration. Up to chloride ion concentrations of about 6 N , the solutions were prepared by shaking UO_3 with HCl solutions of various concentrations. Above 6 N , varying amounts of gaseous HCl and solid UO_2Cl_2 were also used in the preparations. All of the solutions were shaken for 24 to 48 hours, and, except as noted in the tables, were prepared at 25°C.

The analyses of the solid phases were performed by Schreinemakers' method (*Zeit.phys.Chem.* 11, 61 (1893)). This method consists essentially in determining the composition of the solution and of a mixture of the solution and the solid phase. The analyses give two points on a triangular phase diagram. This procedure is repeated for a solution having a different concentration but mixed with the same solid phase. The point of intersection of the

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straight lines drawn through each pair of points gives the composition of the solid.

The experimental data are given in Table 3, Parts A and B. Density values appearing with an asterisk were interpolated. In Part B of Table 3, experiment numbers followed by a t, indicate that samples were taken at room temperature; all others were taken at 25°C.

TABLE 3

The System $\text{UO}_3\text{-H}_2\text{O}$

A. Liquid Phase Analyses

<u>Exp.</u> <u>No.</u>	<u>Temp.</u> <u>of</u> <u>Prep.</u>	<u>Equiv.</u> <u>UO_3 per</u> <u>1000 g.</u> <u>solution</u>	<u>Equiv.</u> <u>H_2O per</u> <u>1000 g.</u> <u>solution</u>	<u>Den-</u> <u>sity</u> <u>g/cm^3</u>	<u>H_2O</u> <u>Con-</u> <u>cent</u>	<u>Equiv.</u> <u>Ratio</u> <u>$\text{UO}_3/\text{H}_2\text{O}$</u>	<u>Solid</u> <u>Phase</u>
1	Am.T.	0.1769	0.09716	1.022*	0.09930	1.821	$\text{UO}_3 \cdot \text{H}_2\text{O}$
2	"	0.3272	0.2887	1.076*	0.3106	1.826	"
3	"	0.8758	0.4599	1.136*	0.5224	1.904	"
4	"	1.329	0.6802	1.224*	0.8326	1.954	"
5	"	1.628	0.8162	1.278*	1.043	1.995	"
6	"	2.646	1.249	1.372	1.963	2.118	"
7	"	3.138	1.453	1.761	2.359	2.160	"
8	25°C	3.662	1.651	1.988	3.242	2.246	"
9	"	4.070	1.772	2.193	3.885	2.297	"
10	"	4.064	1.780	2.221	3.953	2.285	"
11	"	4.217	1.803	2.308	4.161	2.359	"
12	Am.T.	4.062	1.820	-	-	2.252	$\text{UO}_3 \cdot \text{H}_2\text{O}$
13	25°C	4.100	1.832	-	-	2.238	"
14	"	4.100	1.837	2.243*	4.120	2.232	"
15	"	4.121	1.927	-	-	2.139	"
16	"	4.146	2.051	2.155*	4.379	2.021	"
17	"	4.118	2.100	-	-	1.961	"
18	"	4.140	2.192	-	-	1.889	"
19	"	4.218	2.274	2.097*	4.769	1.854	"
20	"	3.870	2.299	-	-	1.685	$\text{UO}_2 \cdot 0.8\text{H}_2\text{O} \cdot x\text{H}_2\text{O}$
21	"	3.778	2.392	-	-	1.579	"
22	"	3.528	2.842	1.973	5.607	1.242	"
23	"	3.509	3.104	1.978	6.138	1.151	"
24	"	3.568	3.250	2.011	6.536	1.098	"
25	"	3.979	3.927	2.306	9.030	1.016	"
26	"	4.018	3.985	2.313	9.077	1.004	"
27	"	4.066	4.001	2.357	9.430	1.016	"
28	"	4.058	4.004	2.365	9.469	1.013	"
29	"	4.328	4.268	2.560	10.95	1.014	"
30	"	4.380	4.316	2.598	11.21	1.015	"
31	"	4.454	4.415	2.685	11.85	1.009	"
32	"	4.510	4.443	2.720	12.09	1.015	"
33	"	4.522	4.508	-	-	1.003	"
34	"	4.548	4.550	2.842	12.95	0.9995	$\text{UO}_2 \cdot 0.12 \cdot x\text{H}_2\text{O}$
35	"	4.490	4.582	-	-	0.9799	"
36	"	4.296	5.083	2.603	13.23	0.8450	"
37	"	4.140	5.574	2.521	14.05	0.7427	"
38	"	4.086	5.747	2.484	14.28	0.7110	"
39	"	4.030	6.077	2.459	14.94	0.6652	"

*Density Values interpolated from plot in Figure 4.

TABLE 3 (continued)

**B. Analysis of Solution and of Mixtures of
Solution and Solid Phase**

Exp. No.	Solution		Mixture of Solution and Solid	
	Equiv. HCl/1000 g.	Equiv. UO ₂ /1000 g.	Equiv. HCl/1000 g.	Equiv. UO ₂ /1000 g.
2 t	0.2887	0.5272	0.2160	1.6610
12 t	1.880	4.062	0.6842	5.612
7 t	1.453	3.138	1.116	5.914
10	1.780	4.064	1.453	5.741
15	1.987	4.121	1.642	5.161
20 t	2.229	3.870	2.527	4.660
21 t	2.392	3.778	2.569	4.590
28 t	4.004	4.058	3.541	4.650
31	4.415	4.454	3.923	4.746
34 t	4.550	4.548	4.853	4.888
38	5.747	4.086	5.446	4.577

t, sample taken at room temperature, all
others at 25°C.

A triangular phase diagram of the UO₂-HCl-H₂O system is shown in Figure 2. The data for Figure 2 are computed from Table 3, and are given in Table 18 of the Appendix. In Figure 2, the triangular coordinates represent the percent by weight of each of the three components. Along the HCl axis, the scale has been doubled in order to reveal the detail of the curve. The solid phase analyses have been omitted in order to simplify the figure.

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FIG. 2. THE SYSTEM UO₃-HCl-H₂O; 25 °C.

For chloride ion concentrations ranging from 0.09930 $\underline{N}$ to 4.161 $\underline{N}$, analyses indicate that the solid phase in equilibrium with the solution is probably $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. The solid phase analysis of solution No. 2 does not give an accurate estimate of the amount of water present in the oxide since the resultant points lie too close to the base of the triangle. A microscopic examination of the solid phases associated with the solutions in this concentration range showed that they consisted of small, amorphous particles.

From 4.161 $\underline{N}$ to 4.769 $\underline{N}$, the saturating phase is $\text{UO}_3 \cdot \text{H}_2\text{O}$. The solid phases in this region were sometimes found to be crystalline and sometimes amorphous. Both amorphous and crystalline structures have been reported for this compound (Gmelin, Handbuch d. Anorg. Chem., 55, 103 (1926)). In addition, both $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_3 \cdot \text{H}_2\text{O}$ have been prepared by Kuttig and Schroeder (Z. anorg. Chem., 121, 243 (1922)).

Hydrated, basic uranyl chloride, probably the dihydrate, $\text{UO}_2\text{OHCl} \cdot 2\text{H}_2\text{O}$, was found in the region from 4.769 $\underline{N}$ to 12.4 $\underline{N}$. This phase consisted of yellow crystals having a large, positive temperature coefficient of solubility.

From 12.4 $\underline{N}$ to 14.94 $\underline{N}$, the saturating phase is hydrated, normal uranyl chloride, UO_2Cl_2 . The degree of hydration was not determined.

A smoother representation of the experimental data is obtained when the ratio of the number of equivalents of UO_3 per equivalent of HCl in the solution is plotted as a function

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of the concentration expressed in terms of equivalents of chloride per 1000 g. of solution. This is shown in Figure 3.

FIG. 3. RATIO OF EQUIVALENTS OF UO_3/HCl AS A FUNCTION OF HCl CONCENTRATION.

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Some points have been omitted for the sake of clarity.

Along the isotherm $\overline{AB}$, the solid phase has the composition $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. Between B and C, the solid phase is $\text{UO}_3 \cdot \text{H}_2\text{O}$. Along $\overline{CD}$ and $\overline{DE}$, the solid phases are $\text{UO}_2\text{O} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ and $\text{UO}_2\text{Cl}_2 \cdot x\text{H}_2\text{O}$, respectively. The points at which discontinuities occur in the curve, representing changes in the composition of the saturating phase, are uncertain to the extent of the experimental error.

It will be observed that along the isotherm $\overline{AB}$, the equivalent ratio increases from 1.80 to 2.34. It is evident that one equivalent of hydrochloric acid may dissolve as much as 2.34 equivalents of uranium trioxide. In such a solution, the ionic structures must be extremely complex. A qualitative indication of the formation of complex ions is given by the fact that in the vicinity of the peak B, from approximately 1.45 to 2.39 equivalents of HCl per 1000 g. of solution, the color of the solutions is orange-yellow, whereas in all other regions of the curve, varying intensities of yellow are observed. It appears that as the ratio of equivalents of UO_3 to HCl decreases with increasing chloride ion concentration, the complex ions in the solution are converted into simple ions characteristic of uranyl chloride.

In Figure 4, the density data of Part A of Table 3 are shown as a function of the HCl concentration in equivalents per 1000 g. of solution. It is of interest to note the similarity between Figure 4 and the UO_3/HCl ratio vs. HCl concentration curve of Figure 3. The densities of these

solutions are determined almost entirely by the amount of CO_2 present in them.

FIG. 4. THE SYSTEM UO_3 - HCl - H_2O ; DENSITY AT 25°C. AS A FUNCTION OF HCl CONCENTRATION.

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2. The Solubility of UO_3 in Aqueous HCl and HNO_3

Solutions. The solubility of UO_3 in aqueous HCl and HNO_3 solutions is due chiefly to the stability and insolubility of the potassium uranates. Thus, a possible mechanism for the solution of UO_3 in HCl solutions is given by the following equations:

The data for HCl solutions are given in Table 4. The uranium analyses were carried out volumetrically. Analyses for HCl were made by precipitating the uranium in a sample with ammonium hydroxide and filtering to obtain a clear solution. Evaporation of the filtrate to dryness in a platinum dish and ignition at $350^\circ C$ to volatilize any ammonium chloride present left a residue of pure HCl. The values in parentheses in Table 4 were not experimentally determined, but are calculated, on the basis of the above equations, from the equivalents of UO_3 found per liter of solution.

TABLE 4

The Solubility of UO_3 in Aqueous HCl Solutions

Expt. No.	Initial Equivs. HCl Per Liter of Solution	Equivs. UO_3 per Liter of Solution	Equivs. K^+ Pre- cipita- ted	% HCl Reacted	Time of Shaking Hrs.	Temp. °C
1	0.01	0.0240	(0.0240)	(240)	48	room
2	0.025	0.0210	(0.0210)	(84)	48	"
3	0.3621	0.0364	0.0376	9.6	24	80
4	0.3746	0.0254	0.0266	7.1	66	80
5	0.4679	0.0238	(0.0238)	(5.1)	36	80
6	0.5706	0.0280	0.0361	6.3	24	80
7	1.0	0.0538	(0.0538)	(5.4)	24	room
8	2.0	0.0470	(0.0470)	(2.4)	24	"
9	3.0	0.0204	(0.0204)	(0.68)	30	"

The exact composition of the precipitate of potassium uranates formed in equation (1), above, is not known. Regardless of this fact, equations (1) and (2) are valid to the extent that the equivalents of UO_3 found per liter of solution should be equal to the equivalents of K removed from the solution by precipitation in the form of potassium uranates. In Experiments 3 and 4, in which the initial and final HCl concentrations of the solutions were accurately determined, this is found to be very nearly true. Experiment 6 is apparently in error. Some discrepancies may be due to the solubility of UO_3 in UO_2Cl_2 solutions, resulting in the formation of complex ions. Although the majority of the values are not precise, the data of Table 4 indicate in general that the fraction of UO_3 reacting with HCl is a function of the concentration of HCl , and decreases as the HCl concentration increases. The solubility of UO_3 appears to be limited, regardless of the temperature or concentration of the HCl solution.

Further investigations are required in order to determine whether the reaction is a function of the time or a true equilibrium is established.

Only one measurement of the solubility of UO_3 in aqueous KNO_3 was made. A 1.0 N KNO_3 solution shaken with UO_3 for 24 hours at room temperature contained 0.0161 moles of UO_3 per liter of solution.

3. Conductance Measurements.

a. The Conductance of Aqueous Uranyl Chloride Solutions at 25°C. The specific conductance of aqueous uranyl chloride solutions has been measured at 25°C over a wide range of concentration and composition. Values of the specific and equivalent conductances are given in Table 5. The solution with an equivalent UO_2/HCl ratio of 1.954 became supersaturated with respect to uranyl hydroxide when it was diluted but no precipitate was formed. The solutions obtained, however, were quite stable, and the absence of erratic behavior contrasted strikingly with that shown by the pH measurements.

Since the density data were available for these solutions, calculations were made to determine the volume change which results when 1 mole of the normal and basic uranyl chlorides is dissolved in water. The results are given in Table 2 of the Appendix. The volume increase refers to the difference between the volume of the solution containing one mole of solute and the volume of the pure solvent.

The equivalent conductivities of aqueous uranyl chloride solutions at 25°C, as a function of the square root of the chloride normality, are shown graphically in Figure 5 for various equivalent ratios of UO_2 to HCl. The values of the conductance obtained for a solution having an equivalent ratio of 1.000 are in excellent agreement with similar data obtained at the Rockefeller Institute. The conclusions to be drawn from Figure 5 are limited; namely, (1) the equivalent conductance decreases rapidly with increasing concentration. Except for a sharp increase in the equivalent conductance below 0.01 N, due to hydrolysis, the trend of the curve is similar to that exhibited by other 2-1 valent strong electrolytes such as $BaCl_2$; (2) the equivalent conductance decreases with an increase in the equivalent ratio of UO_2 to HCl.

TABLE 5

The Equivalent Conductance of Aqueous UO_2Cl_2 Solutions at 25°C

A. Equivalent ratio = 1.000 (specific conductance of solvent = 0.88×10^{-6})

<u>Equiv.</u> <u>Cl/1000 g.</u>	<u>Density</u> <u>g./ml.</u>	<u>Equiv.</u> <u>Cl/liter</u>	<u>Sp. con-</u> <u>ductance mho</u>	<u>Equiv.</u> <u>Conductance.</u>
0.7915	1.128	0.8928	0.05301	59.37
0.5991	1.093	0.6548	0.04313	63.87
0.2582	1.037	0.2678	0.02162	80.75
0.07726	1.008	0.07788	0.007334	96.74
0.01854	0.9998	0.01854	0.002090	112.8
0.004543	0.9981	0.004534	0.0005771	127.5
0.001271	0.9971	0.001267	0.0001788	141.1

B. Equivalent ratio = 1.0056 (specific conductance of solvent = 1.78×10^{-6})

0.7886	1.128	0.8895	0.05177	58.20
0.1720	1.023	0.1760	0.015013	85.30
0.01411	1.000	0.01411	0.0016109	114.2
0.008550	0.999	0.008541	0.0010205	119.5
0.004271	0.998	0.004262	0.0005409	126.9

TABLE 5 (Continued)

C. Equivalent ratio = 1.099 (specific conductance of solvent = 0.79×10^{-6})

<u>Equiv.</u> <u>Cl/1000 g.</u>	<u>Density</u> <u>g./ml.</u>	<u>Equiv.</u> <u>Cl/liter</u>	<u>Sp. Con-</u> <u>ductance sho</u>	<u>Equiv.</u> <u>Conductance</u>
0.2919	1.044	0.3047	0.02315	75.98
0.1686	1.023	0.1725	0.01439	83.42
0.08814	1.0097	0.08899	0.008121	91.26
0.02273	1.0001	0.02273	0.002388	105.1
0.005680	0.9975	0.005666	0.0006701	118.27
0.001472	0.9971	0.001463	0.0001933	131.7
0.0003860	0.9972	0.0003849	0.00005726	148.8

D. Equivalent ratio = 1.396 (specific conductance of solvent = 1×10^{-6})

0.8295	1.1934	0.9899	0.05111	51.63
0.6203	1.139	0.7063	0.04154	58.80
0.3825	1.0787	0.4126	0.02826	68.49
0.1349	1.0243	0.1382	0.01150	83.21
0.03498	1.0038	0.03311	0.003406	97.01
0.006175	0.9978	0.006161	0.0006845	111.0
0.001297	0.9975	0.001286	0.0001587	123.4

E. Equivalent ratio = 1.657 (specific conductance of solvent = $.88 \times 10^{-6}$)

1.0703	1.3550	1.429	0.05438	38.05
0.9158	1.2731	1.166	0.05058	43.38
0.5530	1.0884	0.5842	0.02543	66.19
0.1092	1.0238	0.1118	0.009304	83.22
0.03550	1.0049	0.03366	0.003214	95.48
0.009431	0.9990	0.009422	0.0009957	105.7
0.004693	0.9984	0.004685	0.0005179	110.5

F. Equivalent ratio = 1.954 (specific conductance of solvent = $.98 \times 10^{-6}$)

0.6802	1.2236	0.8323	0.03955	47.52
0.4221	1.1264	0.4755	0.02802	58.93
0.1380	1.0357	0.1429	0.01108	77.54
0.03342	1.0060	0.03362	0.005142	93.46
0.006051	0.9981	0.006020	0.0006425	106.7
0.001412	0.9974	0.001408	0.0001632	115.9

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FIG. 5. THE EQUIVALENT CONDUCTANCE OF AQUEOUS UO_2Cl_2 SOLUTIONS CONTAINING UO_3 . 25 °C.

Additional information may be gained from Figure 6, which follows, in which the equivalent conductances for given chloride ion concentrations are plotted as a function of the equivalent ratio. The data for Figure 6 are given in Table 20 of the Appendix. For solutions having a chloride ion concentration of approximately 0.1 N , or greater, the equivalent conductance decreases rapidly as the amount of UO_3 in the solution increases. As the excess of UO_3 is increased still more, the decrease in conductance becomes approximately linear. The initial sharp drop in the conductance is due principally to the repression of the hydrolysis of the solution by the addition of excess UO_3 (actually, uranyl hydroxide, $\text{UO}_2(\text{OH})_2$). Approximately 10 percent excess UO_3 is required to repress the hydrolysis of a 0.1 N uranyl chloride solution. For more concentrated solutions, Figure 6 indicates that a 0.6 percent excess of UO_3 is sufficient. The linear decrease in the equivalent conductance is due partly to an increased viscosity of the solution and partly to the formation of less mobile ions. For uranyl chloride solutions less than approximately 0.1 N , the amount of UO_3 necessary to repress the hydrolysis of the solution becomes greater. Thus, approximately 55 percent excess UO_3 is required for a 0.04 N solution. Consequently, the linear portion of the curve becomes shorter with increasing dilution, and disappears at a chloride ion concentration of approximately 0.0049 N .

FIG. 6. THE EQUIVALENT CONDUCTANCE AT 25 °C. OF AQUEOUS UO_2Cl_2 SOLUTIONS CONTAINING UO_3 , AS A FUNCTION OF THE RATIO OF EQUIVALENTS, UO_3/HCl .

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b. The Temperature Coefficient of Conductance of Aqueous Uranyl Chloride Solutions. The temperature coefficient of conductance of aqueous uranyl chloride solutions has been determined by a series of conductance measurements at 0°C and 25°C. The results are given in Table 6. The temperature coefficients listed in the last column were calculated on the basis of the specific conductances at 0°C.

TABLE 6

The Temperature Coefficient of Conductance of Aqueous Uranyl Chloride Solutions

Conc. Cl ⁻ Equivalency	Ratio of Equivs. UO ₂ /MCl	Sp. Cond. 25°C-25°C	Sp. Cond. 0°C-25°C	$\frac{\Delta K \times 100}{\Delta T}$
0.009508	1.099	0.01082	0.009545	3.81
0.3047	1.099	0.02384	0.01861	3.37
0.9029	1.904	0.03044	0.01607	3.22

No abnormalities were observed in the temperature coefficient of conductance for these solutions. For a solution having an equivalent ratio of 1.099, the percent increase in conductance with increasing temperature is of the same order of magnitude as that obtained for common salts. Thus, in Table 6, from 0° to 25°C, the mean temperature coefficient is 3.81 percent for a chloride ion concentration of 0.0095 M and 3.37 percent at 0.3047 M . A similar calculation for a 0.1 M NaCl solution gives a value of 3.68 percent.

c. The Conductance of Uranyl Chloride in Pyridine at 25°C. The conductance of uranyl chloride dissolved in pyridine at 25°C has been measured. The uranyl chloride

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used gave an analysis of 79.24 percent UO_2 and 20.32 percent Cl, corresponding to 1.94 percent unreacted UO_3 and 0.29 percent water. The data are given in Table 7.

TABLE 7

The Conductance of UO_2Cl_2 in Pyridine at 25°C Solvent
Specific Conductance = 5×10^{-10} mhos

<u>(Molar Con.) $\times 10^4$</u>	<u>Sp. Cond. $\times 10^6$</u>	<u>Eqv. Cond.</u>
379.3	100.32	1.735
336.9	62.344	1.821
189.5	35.600	1.879
118.1	22.329	1.908
51.48	9.9681	1.936
22.97	4.3472	1.980
14.66	2.9711	2.027
9.23	1.9443	2.107
4.94	1.1441	2.316
3.50	0.8718	2.492
2.03	0.5031	2.872

The extremely low values obtained for the equivalent conductance indicate that uranyl chloride behaves as a weak electrolyte when dissolved in pyridine.

4. The Conductance of UO_2Cl_2 in Molten SnCl_4 . A rough measurement was made to determine the conductance of uranyl chloride in molten SnCl_4 . The SnCl_4 used had a specific conductance of 1.3×10^{-3} mhos at 25°C. The specific conductance of a 0.0047 M solution of UO_2Cl_2 was 4.2×10^{-5} mhos at 25°C, corresponding to an equivalent conductance of approximately 6 mhos. The solution was nearly saturated with respect to UO_2Cl_2 . Because of the very low conductivity of this solution, no further measurements were made.

4. The Viscosity of Aqueous Uranyl Chloride Solutions at 25°C. The relative viscosities were determined for aqueous uranyl chloride solutions having the following

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equivalent ratios of UO_3 to HCl : 2.339, 1.634, 1.027, 1.024 and 0.9402. Measurements were made at 25° over a wide range of concentrations. All of the measurements were carried out with an Ostwald type viscosimeter. Each of the initial solutions was analyzed volumetrically for uranium and gravimetrically for chloride, the remaining concentrations being calculated from the dilution data. The values of the relative viscosities, together with the corresponding densities of the solutions are given in Table 8.

TABLE 8

Relative Viscosities and Densities of Aqueous
 UO_2Cl_2 Solutions at 25°C .

A. Equivalent Ratio $\text{UO}_3/\text{HCl} = 0.9402$

<u>Equivs. $\text{Cl}^-/1000$ g. Sol'n.</u>	<u>Equivs. $\text{UO}_3/1000$ g. Sol'n.</u>	<u>Density</u>	<u>Cl^- Normality</u>	<u>Relative Viscosity</u>
0.4703	0.4422	1.065	0.5009	1.16
0.8823	0.8295	1.133	0.9996	1.34
1.246	1.171	1.202	1.498	1.53
1.885	1.772	1.342	2.530	2.03
2.676	2.516	1.566	4.191	3.09
3.055	2.872	1.697	5.184	3.98
3.944	3.708	2.119	8.357	9.84

B. Equivalent Ratio $\text{UO}_3/\text{HCl} = 1.024$

1.226	1.255	1.230	1.508	1.61
1.944	1.991	1.406	2.734	2.28
2.584	2.646	1.616	4.175	3.44
3.174	3.250	1.870	5.936	5.90
3.925	4.019	2.313	9.077	17.2

C. Equivalent Ratio $\text{UO}_3/\text{HCl} = 1.027$

0.06995	0.07184	1.009	0.07058	1.02
0.2338	0.2402	1.034	0.2417	1.08
0.4516	0.4636	1.071	0.4837	1.16
0.8466	0.8692	1.141	0.9960	1.32
1.195	1.227	1.215	1.452	1.54

TABLE 8 (continued)

<u>Equiva.</u> <u>Cl⁻/1000</u> <u>g. Sol'n.</u>	<u>Equiva.</u> <u>SO₃/1000</u> <u>g. Sol'n.</u>	<u>Density</u>	<u>Cl⁻</u> <u>Normality</u>	<u>Relative</u> <u>Viscosity</u>
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B. Equivalent Ratio SO₃/HCl = 1.654

0.07898	0.1306	1.017	0.08032	1.03
0.5539	0.9162	1.146	0.6348	1.29
0.7428	1.229	1.205	0.8951	1.41
0.8587	1.387	1.241	1.040	1.49
0.9786	1.619	1.291	1.263	1.64
1.079	1.785	1.331	1.436	1.79
1.158	1.915	1.363	1.578	1.91

C. Equivalent Ratio SO₃/HCl = 2.559

0.03933	0.09198	1.014	0.03987	1.02
0.4179	0.9774	1.155	0.4819	1.27
0.7185	1.680	1.298	0.9326	1.59
1.034	2.417	1.491	1.541	2.24
1.442	3.573	1.842	2.656	4.60
1.683	3.975	2.130	3.584	9.59
1.803	4.216	2.308	4.161	16.51

The viscosity data of these tables are shown graphically in Figure 7, the equivalent chloride ion concentrations being plotted as abscissas against relative viscosities as ordinates. Some points have been omitted for the sake of clarity.

FIG. 7. RELATIVE VISCOSITY OF AQUEOUS UO_2Cl_2 SOLUTIONS AT 25 °C. AS A FUNCTION OF Cl^- NORMALITY.

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A relative viscosity of 16.51 was observed for the solution having an equivalent ratio of 2.539 and a UO_3 concentration of 4.216 equivalents per 1000 g. of solution. The solution of this composition is represented by point B in Figure 3, and has the highest equivalent ratio observed in the study of the $\text{UO}_3\text{-HCl-H}_2\text{O}$ system. In such a solution, complex ionic structures are undoubtedly present. A solution having approximately the same UO_3 content, 4.019 equivalents per 1000 g. of solution, but with an equivalent ratio of 1.024, was found to have a relative viscosity of 17.15. The simpler ions characteristic of uranyl chloride exist in this solution. From these two measurements, it may be concluded that the relative viscosity of uranyl chloride solutions depends mainly upon the quantity of UO_3 dissolved in the solution, and not upon any changes in the type or complexity of the ions that may occur in the solution.

In order to estimate the contribution of viscosity to the decrease in conductance caused by an increase in the equivalent ratio of UO_3 to HCl , the relative viscosity as a function of the equivalent ratio is plotted in Figure 8 for various chloride normalities. The data for Figure 8 are given in Table 21 of the Appendix. The changes occurring in the relative viscosity and equivalent conductance between an equivalent ratio of 1.03 and 1.65 for a solution 1 N with respect to HCl are given in Table 9.

TABLE 9

Conductance and Viscosity of Aqueous UO_2Cl_2 Solutions
as a Function of the Equivalent Ratio
 Cl^- Concentration = 1.0 N

<u>UO_2/HCl, Equivs.</u>	<u>Λ_{25}</u>	<u>Relative Viscosity</u>
1.03	55.2	1.33
1.65	47.2	1.47

For the solution of Table 9, the ratio of the equivalent conductances is 1.17, while the reciprocal of the ratio of the relative viscosities is 1.09. Ordinarily, the conductance of a solution decreases at approximately the same rate as the viscosity increases. In this case, however, it is seen that the decrease in conductance is more rapid than the increase in viscosity. Consequently, it is necessary to assume that other factors, such as the formation of entities of lower mobility, are contributing to the decrease in conductance.

FIG. 8. RELATIVE VISCOSITY OF AQUEOUS UO_2Cl_2 SOLUTIONS AT 25 °C. AS A FUNCTION OF THE EQUIVALENT RATIO, UO_3 / HCl .

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5. The pH of Aqueous Uranyl Chloride Solutions at 25°C. Measurements of the pH of aqueous solutions of UO_3 in uranyl chloride were undertaken to determine the nature of the hydrolytic reaction of uranyl chloride. A Leeds and Northrup glass electrode apparatus was used. Dilution curves were obtained for solutions having UO_3/HCl ratios of 0.9944, 1.000 and 1.0056, and the measurements were reproducible. Values of the pH, percent hydrolysis and hydrolysis constants are given in Table 10.

TABLE 10

pH, Percent Hydrolysis and Hydrolysis Constants
of Uranyl Chloride Solutions

Ratio of Equivs. UO ₂ /HCl	Cl ⁻ Normality	pH	% Hydrolysis	K ₁ × 10 ⁴	K ₂ × 10 ⁶	log ₁₀ (Cl ⁻ Normality)
0.9944	0.5185	2.13	3.7	2.7	6.6	-0.4969
"	0.08499	2.64	4.3	1.0	2.9	-1.071
"	0.01748	3.03	9.3	1.0	3.9	-1.757
"	0.003569	3.41	21	1.0	14	-2.447
"	0.001109	3.66	40	1.4	44	-2.955
1.000	0.8928	1.92	2.68	-	-	-0.04925
"	0.09202	2.73	4.04	-	-	-1.036
"	0.02307	3.11	6.72	-	-	-1.637
"	0.006408	3.46	10.82	-	-	-2.193
1.0036	0.8895	2.08	1.9	2.6	2.45	-0.0506
"	0.1760	2.61	2.8	1.0	1.5	-0.7545
"	0.01411	3.29	7.3	0.47	2.3	-1.851
"	0.008541	3.47	8.0	0.27	1.5	-2.069
"	0.004262	3.64	11	0.31	1.9	-2.571

In general, values of the pH of aqueous uranyl chloride solutions as determined in this laboratory with a glass electrode assembly have proven to be unreliable in spite of the fact that every precaution was observed in carrying out the measurements. Reproducible measurements could not be made with solutions having ratios of 1.515 and 1.954.

In both cases, the measurements were extremely erratic, and deviations of as much as 0.8 pH unit were observed. Further examination of the data reveals additional discrepancies.

In Table 10 are given values of the percent hydrolysis calculated from the pH measurements. These values are shown in Figure 9 as a function of the logarithm of the chloride ion concentration, and indicate inconsistencies in the data.

FIG.9. PER CENT HYDROLYSIS OF AQUEOUS UO_2Cl_2 SOLUTIONS AS A FUNCTION OF $\text{Log}_{10} (\text{Cl}^- \text{ NORMALITY})$.

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Curve A, Figure 9, represents the percent hydrolysis of a uranyl chloride solution containing excess acid, while Curve C is for a solution containing excess UO_3 . The percent hydrolysis of a uranyl chloride solution having an equivalent ratio of UO_3 to HCl of 1.000 is shown by Curve B. Since the addition of either HCl or UO_3 to a uranyl chloride solution should repress the hydrolysis of the salt, both Curve A and Curve C should lie below Curve B. Curve A, however, lies above Curve B, which throws doubt on the reliability of the pH measurements. Conductance measurement indicate a degree of hydrolysis much lower than that obtained from pH measurements. Since the pH measurements are obviously in error for uranyl chloride solutions containing excess acid, it is not unlikely that all of the pH values given in Table 10 are unreliable.

Using the pH data of Table 10, hydrolysis constants have been calculated according to the equations:

The latter reaction was suggested by Dr. Longworth. In Table 10, K_1 and K_2 are the hydrolysis constants calculated on the basis of equations (1) and (2), respectively. K_1 is reasonably constant for the solution having an equivalent ratio of 0.944, but varies from 2.6 to 0.27 when the ratio is 1.0056. On the other hand, values of K_2 are fairly constant for the solution having an equivalent ratio of 1.0056. If we assume the data to be correct and significant, it becomes necessary to assume one hydrolytic reaction

when the equivalent ratio is less than unity and another when the ratio is greater than unity.

Conductance measurements provide one of the most reliable methods for obtaining the hydrogen ion concentration of certain solutions. In Table 11 are given values of the equivalent conductance of a 0.1 N uranyl chloride solution as a function of the equivalent ratio of UO_2 to HCl .

TABLE 11

Equivalent Conductance of 0.1 N Aqueous UO_2Cl_2 Solution as a Function of the Equivalent Ratio, UO_2/HCl

<u>Equiv. Ratio</u> <u>UO_2/HCl</u>	<u>Equiv. Cond.</u>
1.000	93.7
1.006	92.6
1.099	89.8
1.396	86.8
1.657	84.4
1.954	81.9

Data of this type were discussed in the section on conductance measurements, and the form of the curve is almost identical to that shown in Figure 6 for a solution having a 0.09 N chloride ion concentration. From the data of Table 11, the H^+ concentration of a 0.1 N uranyl chloride solution having an equivalent ratio of 1.000 may be calculated. In Table 11, the equivalent conductance of such a solution is seen to be 93.7. This value includes the contribution to the conductance made by the hydrogen ions resulting from hydrolysis of the solution. By a graphical extrapolation of the data of Table 11, the equivalent conductance of the solution without hydrolysis is found to be 90.5 mhos.

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Hence, the conductance due to hydrolytic products, chiefly H^+ , in the solution, is 3.2 mhos. The limiting ionic equivalent conductance of H^+ at $25^\circ C$ in water is approximately 350 mhos. Consequently, the amount of H^+ present in the uranyl chloride solution is $(3.2/350)(0.1) = 0.001 \text{ } H^+$. According to the pH measurements on this solution, the hydrogen ion concentration is approximately $0.004 \text{ } H^+$.

In view of these considerations, it appears likely that the pH measurements performed in this laboratory with a glass electrode and calomel electrode do not give reliable information regarding the nature of uranyl chloride solutions.

6. Transference Numbers of Aqueous Uranyl Chloride Solutions at $25^\circ C$. Hittorf transference measurements on aqueous uranyl chloride solutions were carried out at $25^\circ C$. The solutions used were approximately $0.1 \text{ } N$ with respect to chloride, and the ratio of equivalents of UO_2 to Cl ranged from 0.98 to 1.954. A $0.05 \text{ } N$ solution having a ratio of exactly 1.000 was also measured.

The apparatus employed is illustrated in Figure 10. The internal diameter of the cell is 30 mm., and the bore is as uniform as possible throughout. Holes drilled in the stopcock keys permitted the circulation of water through them while the apparatus was in the thermostat. The silver chloride cathode and silver anode were prepared according to the directions of Jones and Dale (J. Am. Chem. Soc. 51, 1973 (1927)). The length of path between the electrodes was 97 cm. No gas was formed at the electrodes during an experiment.

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FIG. 10. CELL FOR TRANSFER NUMBER DETERMINATIONS.

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The results of the transport experiments are given in Table 12. The transference numbers, T_U and T_{Cl} , refer to the equivalents of U and Cl, respectively, which are transferred per equivalent of current. T_U is calculated on the basis of the assumption that the concentrations of U and Cl ions are equivalent. Run 1 was not included in the table, since the coulometers failed. Concentration variations which took place in the middle compartment during the first three experiments indicated that too much current was being passed through the cell. It was possible to reduce the time of electrolysis and minimize these variations and still obtain sufficient concentration changes in the anode and cathode compartments. Experiments 3 and 4 were carried out on solutions supersaturated with respect to uranium trioxide, and deposits of uranium formed on both electrodes. In Experiment 12, a deposit formed on the cathode but not on the anode. The amount of uranium compound on the electrodes was determined and taken into account in the calculation of T_{UO_2} . The uranium compound which deposited on the anode in Experiment 3 was not determined, and the value of T_U obtained in that case is too high. The uranium compound deposited on the cathode was assumed to be U_3O_8 , since calculations showed that this was necessary in order that the transference numbers obtained for the chloride ion be the same at both electrodes.

TABLE 12

Transference Numbers at 25.00°C

Ratio of				
Equiv. UO_2/HCl	2 % excess HCl	1.000	1.006	1.006
Exp. No.	10	7	2	5
Milliamperes	6	6	6	6
Volts	36	40	38	38
Time, hours	12	12	18	12
Anode Coul., g. Ag.	0.5718	0.6224	0.8589	0.5617
Cathode Coul., g. Ag.	0.5718	0.6227	0.8634	0.5613
Wt. Anode Portion, g.	97.254	97.443	101.956	98.814
Wt. Cathode "	117.158	117.219	117.032	116.852
Equivs. $\text{UO}_2/1000$ g. Soln.				
Anode I	0.08054	0.08212	0.07550	0.08310
II	0.08050	0.08206	0.07532	0.08314
Anode Mid.	0.09658	0.09988	0.09890	0.09906
Mid. Mid.	0.09626	0.09986	0.09958	0.09888
Cathode Mid.	0.09626	0.09978	0.09826	0.09884
Cathode I	0.1084	0.1139	0.1169	0.1121
II	0.1088	0.1140	0.1168	0.1121
Equivs. $\text{Cl}^-/1000$ g. Soln.				
Anode I	0.07837	0.07884	0.07071	0.07967
II	0.07838	0.07878	0.07078	0.07958
Anode Mid.	0.09787	0.09954	0.09797	0.09804
Mid. Mid.	0.9866	0.09984	0.09786	0.09787
Cathode Mid.	0.09859	0.09981	0.09835	0.09843
Cathode I	0.1149	0.1167	0.1196	0.1134
II	0.1149	0.1166	0.1198	0.1134
T_{U} Anode value	0.296	0.305	0.305	0.305
Cathode "	0.275	0.291	0.268	0.300
T_{Cl^-} Anode value	0.626	0.641	0.647	9.644
Cathode "	0.628	0.650	0.679	0.653
Ratio of				2% excess
Equivs. UO_2/HCl	1.006	1.099	1.313	UO_3
Exp. No.	6	8	11	12
Milliamperes	6	6	6	6
Volts	40	40	40	40
Time, hours	12	12	12	12
Anode Coul., g. Ag.	0.6065	0.6135	0.6150	0.5795
Cathode Coul., g. Ag.	0.6064	0.6135	0.6151	0.5785
Wt. Anode Portion, g.	95.384	97.238	96.981	97.472
Wt. Cathode Portion, g.	117.137	117.326	117.575	117.984

TABLE 12 (continued)

Equivs. UO_2 /1000 g. Soln.

Anode I	0.08130	0.08952	0.1093	0.1365
II	0.08128	0.08970	0.1081	0.1366
Anode Mid.	0.09926	0.1086	0.1312	0.1599
Mid. Mid.	0.09950	0.1086	0.1312	0.1598
Cathode Mid.	0.09916	0.1086	0.1311	0.1599
Cathode I	0.1126	0.1228	0.1475	0.1743
II	0.1132	---	0.1483	0.1743

Equivs. Cl^- /1000 g. Soln.

Anode I	0.07755	0.07925	0.08139	0.08271
II	0.07757	0.07921	0.08132	0.08271
Anode Mid.	0.09834	0.09915	0.1001	0.09942
Mid. Mid.	0.09859	0.09898	0.1001	0.09940
Cathode Mid.	0.09870	0.09926	0.1001	0.09950
Cathode I	0.1143	0.1133	0.1139	0.1115
II	0.1144	0.1131	0.1139	---

Wt. U_2O_5 on Cathode, g. --- --- --- 0.2178

T_U Anode Value	0.311	0.331	0.391	0.434
Cathode Value	0.288	0.297	0.353	0.423

T_{Cl} Anode Value	0.639	0.634	0.675	0.689
Cathode Value	0.665	0.703	0.709	0.698

Ratio of			
Equivs. UO_2 /MCl	1.954	1.954	1.000
Experiment No.	3	4	9
Milliamperes	6	6	3
Volts	42	42	35
Time, hours	15.3	12	12
Anode Coul., g. Ag.	0.7211	0.5898	0.3090
Cathode Coul., g. Ag.	0.7208	0.5902	0.3088
Wt. Anode Portion, g.	101.956	98.414	95.729
Wt. Cathode Portion, g.	117.032	117.894	116.128

Equivs. UO_2 /1000 g. Soln.

Anode I	0.1537	0.1530	---
II	0.1526	0.1541	0.04278
Anode Mid.	0.1899	0.1890	0.05210
Mid. Mid.	0.1900	0.1890	0.05196
Cathode Mid.	0.1899	0.1893	0.05194
Cathode I	0.02036	0.1920	0.05930
II	0.1989	0.1919	0.05930

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Equivs. $\text{Cl}^-/1000 \text{ g. Soln.}$

Anode I	0.07597	0.07871	0.04046
II	0.07527	0.07875	0.04046
Anode Mid.	0.09620	0.09660	0.05181
Mid. Mid.	0.09526	0.09614	0.05202
Cathode Mid.	0.09614	0.09673	0.05196
Cathode I	0.1088	0.1066	0.06066
II	0.1091	0.1068	0.06067
Wt. UO_3 on Anode, g.	?	0.1268	---
Wt. U_3O_8 on Cathode, g.	0.7369	0.9293	---
T_{U} Anode Value	(0.5787)	0.479	0.511
Cathode Value	0.469	0.466	0.303
T_{Cl} Anode Value	0.683	0.671	0.615
Cathode Value	0.680	0.644	0.643

The results of the data in Table 12 for 0.1 N solutions are shown graphically in Figure 11 which follows. The chloride transference increases from 0.627 to 0.679 as the equivalent ratio increases from 0.98 to 1.10. This is at least in part due to the repression of hydrolysis caused by the addition of UO_3 . It will be recalled that the conductance data showed that the hydrolysis of a 0.1 N uranyl chloride solution was sharply repressed by the addition of approximately 10 percent excess UO_3 . Further addition of UO_3 causes only a slight rise in T_{Cl} . Because of the uncertainties introduced by the deposition of uranium compounds on the electrodes when the equivalent ratio is 1.954, the drop in the chloride transference at this point is not necessarily significant. The uranium transference increases approximately linearly with increasing ratio of UO_3 to HCl .

FIG. II. AVERAGE VALUES OF THE TRANSFER NUMBERS OF AQUEOUS UO_2Cl_2 SOLUTIONS AT 25°C . AS A FUNCTION OF THE EQUIVALENT RATIO, UO_3 / HCl .

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Using the values of T_{Cl} taken from Figure 11, and the measured equivalent conductances of uranyl chloride solutions, the equivalent conductance due to the chloride ion has been computed as a function of the equivalent ratio. The results are given in Table 13.

TABLE 13

Chloride Conductance at 25°C as a Function of the
Equivalent Ratio
Concentration = 0.1 N with respect to Cl^-

<u>Equiv. Ratio, UO_2/HCl</u>	<u>Equiv. Conductance</u>	<u>Chloride Transference</u>	<u>Chloride Conductance</u>
1.000	93.7	0.643	60.4
1.006	92.6	0.634	60.6
1.099	89.8	0.679	61.0
1.396	86.8	0.690	59.9
1.657	84.4	0.695	58.7
1.954	81.9	0.700	57.3

In Table 13, the values calculated for the chloride ion conductance in these solutions agree fairly well with the accepted experimentally determined value of 59.3 for the chloride ion in a 0.1 N $HClO_4$ solution at 25°C. This suggests that the chloride ion is not present to any appreciable extent in the form of complex intermediate ions.

Table 14 lists the ratio of equivalents of UO_2 to HCl found in the middle, anode and cathode compartments at the completion of an experiment. The ratios for the initial solutions are also given for those experiments in which they were accurately determined.

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TABLE 14

Change of Equivalent Ratio for UO_3 -HCl
Solutions which Occurs During Electrolysis

Exp. No.	Approx. Normality	Ratio of Equivalents, UO_3/HCl			
		Initial	Average for Middle	Anode	Cathode
10	0.1	2% excess HCl	0.980	1.027	0.945
7	"	1.000	1.001	1.042	0.976
1	"	1.006	1.016	1.052	0.974
2	"	1.006	1.009	1.066	0.976
5	"	1.006	1.008	1.044	0.988
6	"	1.006	1.008	1.048	0.987
8	"	1.099	1.095	1.131	1.084
11	"	1.315	1.310	1.336	1.298
12	"	60% excess UO_3	1.608	1.651	1.565
3	"	1.954	1.981	2.025	1.847
4	"	1.954	1.960	1.965	1.799
9	0.05	1.000	1.002	1.057	0.979

A decrease in the ratio occurs at the cathode and an increase at the anode. For solutions containing a large excess of UO_3 , the deposition of U_3O_8 is the primary factor in bringing about the decrease. In order to account for the changes which take place in other cases, it is necessary to assume that several cations are present in the solution. As shown by the conductance data, solutions containing less than 15 percent excess UO_3 possess an appreciable hydrogen conductance, and these ions, carrying positive current from the anode to the cathode, bring about a change in the equivalent ratio. The hydrogen conductance in solutions containing larger amounts of excess UO_3 is very small and the fact that a change in ratio still occurs, indicates that the cation formed when UO_3 dissolves in uranyl chloride possesses a smaller mobility than the uranyl ion.

It is of interest to compare the experimental values of the transference numbers for a 0.1 N solution having an equivalent ratio of 1.000 with the values calculated from the conductance data. The equivalent conductance of 0.1 N uranyl chloride solution having an equivalent ratio of 1.000 is 93.7 mhos, while the hydrogen ion conductance was found to be 3.2 mhos. The equivalent chloride ion conductance in 0.1 N BaCl_2 solution is 59.5 mhos. Hence, the cation conductance is $(93.7 - 59.5 - 3.2)$, or 31.2 mhos. The computed and experimental values of the chloride transference numbers are compared in Table 15.

TABLE 15

Comparison of the Calculated and Observed Chloride
Transference Numbers

<u>Calculated Values</u>	<u>Experimental Values</u>
$T_{\text{Cl}} = \frac{29.5}{93.7} = 0.633$	0.630
$T_{\text{U}} = \frac{51.2}{93.7} = 0.333$	0.290
$T_{\text{H}^+} = \frac{3.2}{93.7} = 0.034$	$(1.000 - 0.940) = 0.060$

The experimental value of T_{H^+} corresponds to an equivalent conductance of 5.6 mhos, or a hydrogen ion concentration of 0.0016 N , as compared to 0.001 N H^+ and 0.004 N H^+ determined from conductance and pH measurements, respectively.

Chapter IV

PHASE RELATIONS IN THE SYSTEM $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$

The solubility of uranium trioxide in aqueous solutions of uranyl nitrate at 25°C has been measured for concentrations from 0.05638 to 6.322 equivalents of HNO_3 per 1000 g.

of solution. The solutions were prepared by shaking uranium trioxide with varying concentrations of HNO_3 for 24-48 hours. Each preparation was thermostated for several hours at 25° before samples for analysis were withdrawn. Schreinemaker's method (Z. phys. Chem., 11, 81 (1893)) was employed for the solid phase analyses. The method is briefly described in the discussion of the $\text{UO}_3\text{-H}_2\text{O}$ system. The results of both liquid and solid phase analyses are given in Table 16, together with the data of A. Gelani (Bull. soc. Chim. (4), 32, 1243 (1926)) for the liquid phases for concentrated solutions of UO_3/HNO_3 ratios less than 1.0 (See Part B of Table 16).

TABLE 16

The System $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$
A. Liquid Phase Analyses, 25°

Exp. No.	Equiv. HNO_3 per 1000 g. Soln.	Equiv. UO_3 per 1000 g. Soln.	Ratio of UO_3/HNO_3	Density 25°	HNO_3 Normality	% UO_3	% HNO_3	% H_2O	Solid Phase
1	0.05638	0.1062	1.883	1.012	0.05706	1.52	0.36	98.1	$\text{UO}_3 \cdot x\text{H}_2\text{O}$
2	0.1303	0.2290	1.737	1.033	0.1346	3.28	0.82	95.9	"
3	0.2878	0.4688	1.629	1.073	0.3008	6.71	1.81	91.5	"
4	0.4340	0.6958	1.603	1.114	0.4835	9.95	2.74	87.3	"
5	0.7373	1.187	1.609	1.214	0.8951	17.0	4.65	78.4	"
6	0.7458	1.204	1.614	1.213	0.9407	17.2	4.70	78.1	"
7	0.8102	1.293	1.596	1.241	1.005	18.5	5.11	76.4	$\text{UO}_3 \cdot y\text{H}_2\text{O}$
8	1.280	1.971	1.540	1.419	1.816	28.2	8.07	63.7	"
9	2.058	2.886	1.373	1.732	3.606	40.4	13.0	46.6	"
10	2.519	3.450	1.370	2.088	5.260	49.4	13.9	34.8	"
11	2.533	3.480	1.374	2.101	5.322	49.8	16.0	34.3	"
12	2.723	3.054	1.122	1.900	5.174	43.7	17.2	39.2	$\text{UO}_2(\text{HNO}_3)_2 \cdot 6\text{H}_2\text{O}$
13	2.892	2.862	0.9896	1.821	5.266	40.9	18.2	40.8	"
14	6.322	1.769	0.2798	1.681	10.63	25.5	39.8	34.9	"

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TABLE 16 (Continued)

B. Liquid Phase Analyses, 25°C
Date of A. Calami (Coll. Soc. Chim. (b),
39, 1243 (1966))

<u>Equiv. HNO₃</u> <u>per 1000 g.</u> <u>Solution</u>	<u>Equiv. UO₃</u> <u>per 1000 g.</u> <u>Solution</u>	<u>Ratio of</u> <u>Equiv.</u> <u>UO₃/HNO₃</u>	<u>%</u> <u>UO₃</u>	<u>%</u> <u>HNO₃</u>	<u>%</u> <u>H₂O</u>	<u>Solid</u> <u>Phase</u>
2.846	2.846	1.000	40.7	17.9	41.4	UO ₂ (HNO ₃) ₂ ·4H ₂ O
4.008	2.048	0.5110	29.3	25.3	45.4	"
5.526	1.557	0.2781	22.0	34.8	43.2	"
6.055	1.505	0.2486	21.5	38.2	40.3	"
6.382	1.587	0.2510	22.7	39.8	37.5	"
6.692	1.863	0.2784	26.7	42.2	31.1	"
6.712	1.988	0.2782	27.6	42.3	30.1	"
6.968	1.841	0.2642	26.3	43.9	29.8	UO ₂ (HNO ₃) ₂ ·3H ₂ O
8.698	1.379	0.1585	19.7	54.8	25.5	"
9.312	1.309	0.1406	18.7	58.7	22.6	"
9.801	1.359	0.1387	19.4	61.8	18.8	"
9.918	1.355	0.1407	20.0	62.5	17.5	"
10.15	1.382	0.1362	19.8	64.0	16.2	UO ₂ (HNO ₃) ₂ ·2H ₂ O
10.78	1.200	0.1113	17.2	67.9	14.9	"
11.72	1.131	0.09653	16.2	73.8	10.0	"
12.06	1.141	0.09458	16.3	76.0	7.7	"

C. Solid Phase Analyses, 25°C

<u>Exp.</u> <u>No.</u>	<u>Equivs. HNO₃</u> <u>per 1000 g.</u>	<u>Equivs. UO₃</u> <u>per 1000 g.</u>	<u>%</u> <u>UO₃</u>	<u>%</u> <u>HNO₃</u>	<u>%</u> <u>H₂O</u>
1	0.000	0.2096	3.00	0.13	96.9
3	0.2252	1.308	18.7	1.44	79.9
5	0.3451	4.312	61.7	2.17	36.2
7	0.5097	3.110	44.5	3.21	32.3
9	1.687	3.404	48.7	10.6	40.7
10	1.840	4.144	60.7	11.6	27.7
11	2.872	3.960	36.6	18.1	25.3
12	3.646	3.762	53.8	25.0	25.2
13	3.767	3.542	50.7	23.7	25.6
14	4.711	3.288	47.0	29.7	23.3

The data of Table 16 are shown graphically on a triangular diagram in Figure 12. For the sake of clarity, the solid phase analyses have been omitted from the figure.

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FIG. 12. THE SYSTEM UO₃ - HNO₃ - H₂O; 25 °C.

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Along the Curve AC, extending to approximately 5.0 H HNO_3 , the solid phase analyses indicate the presence of hydrated uranium trioxide. The saturating phases above 5.0 H , in the regions OD, DE and EF, are the hexahydrate, trihydrate and dihydrate of uranyl nitrate, respectively. It is of interest to note that there is no evidence of the formation of a basic uranyl nitrate, $\text{UO}_2\text{OHNO}_3 \cdot x\text{H}_2\text{O}$. This is in contrast to the $\text{UO}_3\text{-HCl-H}_2\text{O}$ system, in which the basic uranyl chloride, $\text{UO}_2\text{OHCl} \cdot 2\text{H}_2\text{O}$, appears.

The ratio of the equivalents of UO_3 to HNO_3 as a function of the equivalents of HNO_3 per 1000 g. of solution is shown graphically in Figure 15. Changes occurring in the composition of the solid phases are indicated in the figure and correspond to those shown in Figure 12.

FIG.13. THE SYSTEM $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$; RATIO OF EQUIVALENTS, UO_3/HNO_3 AS A FUNCTION OF HNO_3 CONCENTRATION. 25 °C.

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Chapter V

PHASE RELATIONS EXISTING IN THE SYSTEM $\text{UO}_3\text{-HClO}_4\text{-H}_2\text{O}$.

The solubility of uranium trioxide in aqueous uranyl perchlorate solutions has been measured over a wide range of concentrations. The solutions were prepared by shaking UO_3 with various concentrations of HClO_4 for 24 to 48 hours at room temperature. Before withdrawing samples for analysis, each preparation was thermostated for several hours at 25°C. The data obtained are given in Table 17.

TABLE 17

The System $\text{UO}_3\text{-HClO}_4\text{-H}_2\text{O}$

A. Liquid Phase Analyses, 25°C

Exp. No.	Equiv. ClO_4^- per 1000 g. Soln.	Equiv. UO_3 per 1000 g. Soln.	Equiv. Ratio $\text{UO}_3/\text{HClO}_4$	Density	ClO_4^- Normality	% HClO_4	% UO_3	% H_2O
1	0.09787	0.1687	1.663	1.080	0.09983	0.983	2.33	96.7
2	0.1764	0.2940	1.666	1.049	0.1850	1.77	4.28	94.0
3	0.4019	0.6390	1.590	1.116	0.4483	4.04	9.14	86.8
4	0.4298	0.6902	1.606	1.126	0.4840	4.32	9.87	85.8
5	0.7899	1.208	1.530	1.247	0.9850	7.93	17.3	74.8
6	0.9120	1.368	1.501	1.293	1.179	9.16	19.6	71.3
7	1.063	1.550	1.459	1.344	1.428	10.7	22.2	67.1
8	1.187	1.717	1.447	1.401	1.663	11.9	24.6	63.5
9	1.297	1.848	1.423	1.446	1.873	13.0	26.4	60.5
10	1.393	1.974	1.417	1.493	2.083	14.0	28.2	57.8
11	1.681	2.246	1.336	1.610	2.707	16.9	32.1	51.0
12	2.038	2.368	1.249	1.788	3.679	20.7	36.7	42.6
13	2.252	2.840	1.261	1.949	4.389	22.6	40.6	36.8
14	2.723	3.206	1.164	2.263	6.233	27.7	45.9	26.3
15	2.886	3.286	1.138	2.346	6.771	29.0	47.0	24.0
16	3.106	3.088	0.9732	2.243	6.973	31.2	43.3	25.5
17	4.334	2.088	0.4818	1.978	8.373	43.3	29.9	26.6
18	5.522	1.401	0.2537	1.983	10.63	33.3	20.0	46.5

B. Solid Phase Analysis

4	0.2123	3.592	---	---	---	2.13	51.4	46.5
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Figure 14 presents the data of Table 17 in a triangular diagram. Only one solid phase analysis was made which indicated that the saturating phase along AB in Figure 14 is hydrated uranium trioxide, probably $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. The solid phase along the line BC was not determined, but is doubtless the normal perchlorate, since a large excess of HClO_4 is present in this region.

The ratio of equivalents of UO_3 to HClO_4 as a function of the equivalents of HClO_4 per 1000 g. of solution is shown graphically in Figure 15. The solubility of UO_3 in uranyl perchlorate decreases steadily as the concentration of uranyl perchlorate increases.

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FIG. 14. THE SYSTEM UO_3 - HClO_4 - H_2O ; 25 °C.

FIG. 15. THE SYSTEM $\text{UO}_3\text{-HClO}_4\text{-H}_2\text{O}$; RATIO OF EQUIVALENTS, $\text{UO}_3/\text{HClO}_4$ AS A FUNCTION OF HClO_4 CONCENTRATION. 25°C .

The form of the curves in Figures 14 and 15 indicate that the $\text{UO}_3\text{-HClO}_4\text{-H}_2\text{O}$ system is less complex and contains fewer solid phase compounds than either the $\text{UO}_3\text{-HCl-H}_2\text{O}$ or $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$ systems. At infinite dilution, the equivalent ratio of the $\text{UO}_3\text{-HClO}_4\text{-H}_2\text{O}$ system has a limiting value of 1.7, as compared to approximately 2.0 for the $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$ system, and 1.8 for the $\text{UO}_3\text{-HCl-H}_2\text{O}$ system. In Figure 15, the equivalent ratio decreases rapidly to 1.00 as the HClO_4 concentration increases to approximately 7.0 N . Similarly, the equivalent ratio of UO_3 to HNO_3 in the $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$ system decreases to 1.00 as the HNO_3 concentration increases to approximately 5.0 N . In the $\text{UO}_3\text{-HCl-H}_2\text{O}$ system, however, an increase in the HCl concentration to approximately 4.0 N causes the equivalent UO_3/HCl ratio to increase to 2.5. From these differences in the behavior of the various systems, it appears that, for dilute solutions, at least, the properties of the systems are determined not only by the uranyl ion, but also by the negative ion with which the uranyl ion is associated.

Chapter VI

CONCLUSION

The ionic structures existing in aqueous uranyl chloride solutions are extremely complex. Conductance, pH and transference measurements indicate that dilute uranyl chloride solutions having an equivalent ratio of UO_3 to HCl of 1.00 are considerably hydrolyzed. Consequently, in any electrolysis of such a solution, a considerable amount of

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current is passing through the solution, due to the conductance of the hydrogen ion. According to the conductance data, at least a 33 percent excess of UO_3 is required to repress the hydrolysis of a 0.04 N uranyl chloride solution. Unfortunately, this increases the ionic complexity of the solution. If, however, it is possible to work with at least a 1.0 N solution, only 0.6 percent excess UO_3 is required to repress the hydrogen conductance. This would also increase the complexity of the ions, but to a lesser degree than in the case of the 0.04 N solution. According to the solubility data, it is possible to increase the concentration beyond 1.0 N to a point where the equivalent ratio of UO_3 to HCl is approximately 1.00. In such a solution, the simple uranyl ion is predominant and hydrolysis is at a minimum.

The phase relations in the systems $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$ and $\text{UO}_3\text{-HClO}_4\text{-H}_2\text{O}$ are less complex than in the $\text{UO}_3\text{-HCl-H}_2\text{O}$ system. No basic salts are present. Since the equivalent ratios UO_3/HNO_3 and $\text{UO}_3/\text{HClO}_4$ approach unity at lower concentrations than the UO_3/HCl ratio, more dilute solutions will retain the characteristics of the simple uranyl ion.

APPENDIX

TABLE 18

The System $\text{UO}_2\text{-HCl-H}_2\text{O}$ A. Percentage Composition of Liquid Phases

Exp. No.	% HCl	% UO_2	% H_2O	Exp. No.	% HCl	% UO_2	% H_2O
1	0.354	2.53	97.1	21	8.72	54.0	37.2
2	1.05	7.54	91.4	22	10.4	50.5	39.2
3	1.68	12.5	85.8	23	11.3	50.2	38.5
4	2.48	19.0	78.5	24	11.9	51.0	37.1
5	2.98	23.3	73.7	25	14.3	56.9	28.8
6	4.55	37.9	57.6	26	14.3	57.5	28.2
7	5.30	44.9	49.8	27	14.6	58.2	27.3
8	5.95	52.4	41.7	28	14.6	58.0	27.4
9	6.46	58.2	35.3	29	15.6	61.9	22.5
10	6.49	58.1	35.4	30	15.7	62.7	21.6
11	6.58	60.3	33.1	31	16.1	63.7	20.2
12	6.64	58.1	35.2	32	16.2	64.5	19.3
13	6.68	58.6	34.7	33	16.4	64.7	18.9
14	6.70	58.6	34.7	34	16.6	65.1	18.4
15	7.03	58.9	34.0	35	16.7	64.2	19.1
16	7.48	59.3	33.2	36	18.5	61.5	20.0
17	7.66	58.9	33.4	37	20.3	59.2	20.5
18	7.99	59.2	32.8	38	21.0	58.4	20.6
19	8.29	60.3	31.4	39	22.2	57.6	20.2
20	8.38	55.4	36.3				

B. Percentage Composition of Mixtures of Solid
and Liquid Phases

Exp. No.	% HCl	% UO_2	% H_2O
2	0.788	23.8	75.5
12	2.50	80.3	17.2
7	4.07	56.0	39.9
10	5.30	82.1	12.6
15	5.99	73.8	20.2
20	9.58	66.7	23.8
21	9.37	65.7	25.0
28	12.9	66.5	20.6
31	14.3	67.9	17.8
34	17.7	69.1	13.2
38	19.9	65.5	14.7

TABLE 18 (Continued)

C. Percentage Composition of Assumed Solid Phases

<u>Compound</u>	<u>% HCl</u>	<u>% UO₃</u>	<u>% H₂O</u>	<u>M.Wt.Comp'd.</u>
UO ₃ ·H ₂ O	---	94.08	5.92	---
UO ₃ ·2H ₂ O	---	88.81	11.19	---
UO ₃ ·HCl	11.30	88.70	---	---
UO ₃ ·HCl·H ₂ O	10.70	84.01	5.29	---
UO ₃ ·HCl·2H ₂ O	10.16	79.78	10.05	---
UO ₃ ·HCl·3H ₂ O	9.68	75.96	14.35	376.58
UO ₃ ·2HCl	20.31	79.69	---	---
UO ₃ ·2HCl·H ₂ O	19.34	75.88	4.78	---
UO ₃ ·2HCl·2H ₂ O	18.46	72.42	9.12	---

TABLE 19

Volume Increase Resulting when UO₂Cl₂ and
UO₂(OH)Cl are Dissolved in Water

<u>Moles of</u> <u>UO₂Cl₂</u> <u>per Liter</u>	<u>Volume</u> <u>Increase</u> <u>cc.</u>	<u>Moles of</u> <u>UO₂(OH)Cl</u> <u>per Liter</u>	<u>Volume</u> <u>Increase</u> <u>cc.</u>
0.103	44	0.211	43
0.212	48	0.448	53
0.328	48	0.718	48
0.452	49	1.003	50

TABLE 20

Equivalent Conductance as a Function of the
Equivalent Ratio, UO₃/HCl

<u>Equiv.</u> <u>Ratio</u> <u>UO₃/HCl</u>	<u>Equivalent Conductance (Interpolated)</u>			
	<u>Cl⁻ =</u> <u>0.0016 N</u>	<u>Cl⁻ =</u> <u>0.0049 N</u>	<u>Cl⁻ =</u> <u>0.004 N</u>	<u>Cl⁻ =</u> <u>0.009 N</u>
1.000	138.4	126.4	104.4	94.9
1.006	137.8	125.2	103.3	93.9
1.099	130.5	119.7	99.6	91.0
1.396	121.9	112.6	95.8	87.9
1.657	117.6	110.4	94.0	85.6
1.954	115.4	108.2	91.7	83.1

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Part I

TABLE 20 (continued)

Equiv. Ratio UO_2/HCl	Equivalent Conductance (Interpolated)			
	Cl^- 0.16 N	Cl^- 0.36 N	Cl^- 0.64 N	Cl^- 1.0 N
1.000	87.9	76.6	66.2	56.8
1.006	86.6	74.9	64.8	55.5
1.099	84.4	73.5	63.6	54.2
1.396	81.4	70.5	60.8	51.5
1.657	78.5	67.1	56.9	47.2
1.954	76.0	63.7	53.2	43.0

TABLE 21

Relative Viscosity of Aqueous UO_2Cl_2 Solutions
at 25°C as a Function of the Equivalent Ratio, UO_2/HCl

Equiv. Ratio UO_2/HCl	Relative Viscosities (Interpolated Graphically)					
	Cl^- 0.04 N	Cl^- 0.09 N	Cl^- 0.16 N	Cl^- 0.36 N	Cl^- 0.64 N	Cl^- 1.0 N
0.9402	1.010	1.026	1.050	1.114	1.206	1.335
1.027	1.011	1.027	1.050	1.117	1.212	1.351
1.654	1.015	1.034	1.063	1.147	1.277	1.470
2.339	1.020	1.045	1.083	1.197	1.397	1.648