S 57. *The Hydrolysis of the Uranyl Ion. Part I.*

By J. Sutton.

Cryoscopic measurements prove conclusively that the hydrolysis of uranyl salts leads to the formation of the ions $U_2O_5^{++}$ and $U_3O_8^{++}$, and not $UO_2(OH)^+$ and $UO_2(OH)_2$.

Measurements of pH of solutions of UO_3 in solutions of uranyl salts, pH titrations of uranyl perchlorate with sodium hydroxide, and the conductivity and absorption spectra of these solutions, point to the formation of further ions $U_3O_8(OH)^+$, $U_3O_8(OH)_2$, and $U_3O_8(OH)_3^-$. More highly charged anions may be formed but the evidence is still inconclusive. The equilibrium constants for the formation of some of these ions have been determined.

Sexavalent uranium forms a series of salts, derived from the trioxide, which contain the bivalent uranyl cation, UO_2^{++}. In solution these salts behave like strong electrolytes (Robinson, Wilson, and Ayling, *J. Amer. Chem. Soc.*, 1942, **64**, 1479; Dittrich, *Z. physikal. Chem.*, 1899, **29**, 449), and from the low entropy of the uranyl ion Coulter, Pitzer, and Latimer (*J. Amer. Chem. Soc.*, 1940, **62**, 2845) concluded that it would attract water much more strongly than most other bivalent cations, which suggests that the ion in solution might be $U(OH)_4^{++}$. Crandall (U.S. Atomic Energy Commission Report MDDC–1294) has, however, recently shown on the basis of ^{18}O exchange experiments that the ion in solution is UO_2^{++}.

The configuration of the ion is still open to question. *X*-Ray diffraction data for sodium uranyl acetate (Fankuchen, *Physical Rev.*, 1933, **43**, 327; *Z. Kryst.*, 1935, **91**, 473), uranyl fluoride (Zachariasen, *Acta Cryst.*, 1948, **1**, 277), and various uranates (*idem, ibid.*; Samson and Sillén, *Arkiv Kemi, Min., Geol.*, 1947, **25**, No. 21) in which the UO_2 is retained as part of the anion, indicate that the group is linear, the two oxygen atoms being covalently held at 1·91 A. from the uranium atom. On the other hand, infra-red absorption spectra of crystalline uranyl salts (Conn and Wu, *Trans. Faraday Soc.*, 1938, **34**, 1483; Lecompt and Freymann, *Bull. Soc. chim.*, 1941, **8**, 622) indicate a bent uranyl ion, and the Raman spectra of saturated solutions of uranyl salts point to the same conclusion (Conn and Wu, *loc. cit.*; Satyanarayana, *Proc. Indian Acad. Sci.*, 1942, **15**, *A*, 414; Crandall, *loc. cit.*). In view of the unequivocal nature of the spectrographic evidence, and taking into account the fact that the oxygen positions cannot be directly deduced from the *X*-ray data but must be derived from spatial considerations, it appears that the uranyl ion is bent.* Neutron-diffraction experiments may throw more light on this point.

When a solution of a uranyl salt is diluted with a large excess of water, or when uranium trioxide is dissolved in a uranyl salt solution, the colour changes from yellow to deep orange. A similar colour change takes place when sodium hydroxide is added to a uranyl salt solution, precipitation occurring immediately unless the solutions are very dilute. The orange precipitate formed in concentrated solutions is called sodium diuranate, but its exact composition is doubtful. These results indicate extensive hydrolysis of the uranyl ion.

When the orange solution obtained by adding excess of 0·01M-sodium hydroxide to 0·01M-uranyl perchlorate is electrolysed with platinum electrodes in a three-compartment cell, the compartments being separated by sintered-glass plates, the concentration of uranium decreases around both electrodes. Over a period of several hours the pH of the anode solution decreases to 2—3, that of the solution in the central compartment decreases to approx. 10, but that of the cathode solution remains at the original value of 11—11·5. These results can be explained only if the hydrolysis of the uranyl ion leads to the formation of an anion at high pH values, the equilibrium between the two depending on pH. Around the cathode, the comparatively mobile sodium ions will be preferentially discharged, and, reacting with water, will ensure that a high hydroxyl-ion concentration is maintained. Therefore the uranium in this compartment will be chiefly in the anionic form and will migrate into the central compartment. In the anode compartment the hydroxyl ions will be preferentially discharged, leading to the large decrease in pH and hence to the formation of uranyl ions which will migrate away from the anode. The hydrogen ions formed in the anode compartment will migrate towards the cathode more quickly than the hydroxyl ions will leave the cathode compartment, and this accounts for the slight decrease in pH of the central compartment.

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* *Added in proof.* Since this paper was written, a critical survey of old and new data (Dieke and Duncan, " Spectroscopic Properties of Uranium Compounds," McGraw-Hill Book Co. Inc.) indicates that the uranyl ion is linear.

The simplest and most obvious explanation of the hydrolysis would involve the successive addition of hydroxyl ions to the uranyl ion, thus :

$$UO_2^{++} + OH^- \rightleftharpoons UO_2(OH)^+$$
$$UO_2(OH)^+ + OH- \rightleftharpoons UO_2(OH)_2$$
$$UO_2(OH)_2 + OH^- \rightleftharpoons UO_2(OH)_3^- \quad \text{etc.}$$

or, the equations being written to include the hydrogen ion :

$$UO_2^{++} + H_2O \overset{K_1}{\rightleftharpoons} UO_2(OH)^+ + H^+ \qquad K_1 = [UO_2(OH)^+][H^+]/(UO_2^{++}]$$
$$UO_2(OH)^+ + H_2O \overset{K_2}{\rightleftharpoons} UO_2(OH)_2 + H^+ \qquad K_2 = [UO_2(OH)_2][H^+]/[UO_2(OH)^+]$$
$$UO_2(OH_2) + H_2O \rightleftharpoons UO_2(OH)_3^- + H^+ \quad \text{etc.}$$

FIG. 1.

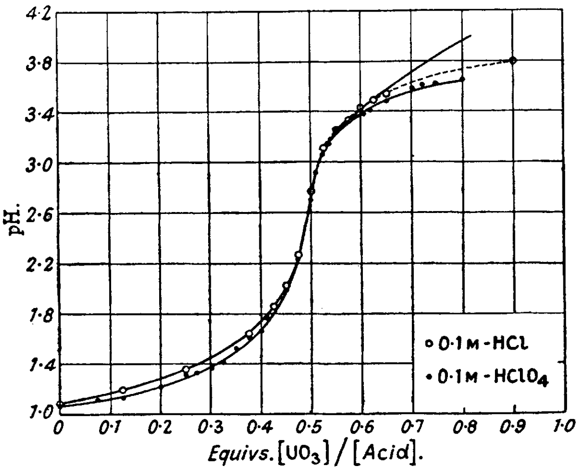
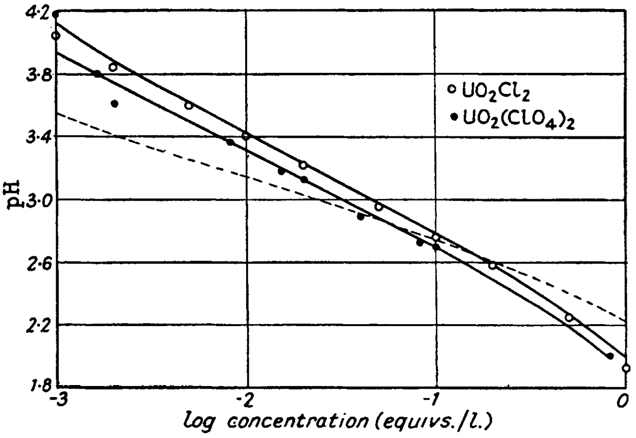


FIG. 2.



Using the first two steps of this mechanism as a basis for their calculations, Longsworth *et al.* (Manhattan Project Report MDDC–911) determined appropriate equilibrium constants from the pH values of solutions of uranium trioxide in hydrochloric acid, the chloride-ion concentration being kept constant at 0·1M. Their results are shown in Fig. 1, in which pH values are plotted against the ratio (equivalents of UO_3)/(equivalents of HCl). The broken line represents the calculated results using $K_1 = 4{\cdot}6 \times 10^{-4}$ and $K_2 = 6{\cdot}0 \times 10^{-5}$, and it coincides with the upper full line below the ratio 0·5. Difficulties arose when the same equilibrium constants were used in an attempt to explain the variation of pH with concentration in stoicheiometric uranyl chloride solutions. Fig. 2 shows pH plotted against log concentration for these solutions, the broken curve being calculated.

Another serious disadvantage was that, these two constants being used, the calculated concentrations of $UO_2(OH)_2$ in some of the solutions with a high UO_3/HCl ratio were greater than the solubility of UO_3,H_2O in water.

Longsworth therefore suggested another mechanism to account for the results. This involved oxygen bridging, a process which has recently been used to explain the hydrolysis of Bi^{3+} ions (Granér and Sillén, *Acta Chim. Scand.*, 1947, **1**, 631). The first two stages of the hydrolysis are then

$$2UO_2^{++} + H_2O \rightleftharpoons U_2O_5^{++} + 2H^+$$
$$U_2O_5^{++} + UO_2^{++} + H_2O \rightleftharpoons U_3O_8^{++} + 2H^+$$

and the equilibrium constants are

$$K_1 = [U_2O_5^{++}][H^+]^2/[UO_2^{++}]^2 \qquad K_2 = [U_3O_8][H^+]^2/[U_2O_5^{++}][UO_2^{++}]$$

Using only the first of these reactions, Longsworth *et al.* were able to calculate an equilibrium constant which explained the variation of pH with the UO_3/HCl ratio and with concentration for the stoicheiometric solutions over a considerable range. The calculated values are the full curves in Figs. 1 and 2.

Three points should be raised with regard to the above work. First, there is certainly an error in all the calculations owing to neglect of the complexing of the uranyl ion with chloride ions. That this complexing takes place is shown by adding hydrochloric acid to a uranyl perchlorate solution, whereupon a deepening colour indicates the occurrence of a reaction which cannot be hydrolytic. Secondly, whereas the continuation of the oxygen bridging process can never lead to the production of an anion as required by the experimental observations, the OH^- addition mechanism does so in the third stage. Thirdly, the difference between the observed and the calculated results for the stoicheiometric solutions might be explained on the basis of the first mechanism if the activity coefficients of the various ionic species are taken into account. Which mechanism applies, therefore, is still an open question.

To avoid the errors due to formation of anionic complexes, Longsworth's experiments were repeated, uranyl perchlorate and perchloric acid being used. The results are the lower full curves plotted in Figs. 1 and 2. That no complexing occurred between uranyl and perchlorate ions was shown by the constancy of the absorption spectra between 3400 and 5000 A. of a set of solutions 0·5M. in uranyl perchlorate and containing varying amounts of excess perchlorate ion up to a concentration of 7M. supplied in the form of perchloric acid and sodium perchlorate. The pH's of these solutions were kept between 0 and 1 in this way, thus preventing hydrolysis.

Activity coefficient data for the UO_3–HCl system are not available, so the third point cannot be easily or directly answered. The problem of deciding which is the more satisfactory mechanism must therefore be approached from another angle. Transference-number and conductivity data will not differentiate between the two mechanisms but, as Longsworth suggested (*loc. cit.*), cryoscopic measurements should clearly decide which alternative is correct, and the following work was carried out for this purpose.

When uranium trioxide is dissolved in a stoicheiometric uranyl perchlorate solution, then, by the first mechanism, it does so thus :

$$UO_3 + UO_2^{++} + H_2O \rightleftharpoons 2UO_2(OH)^+ \quad \text{etc.}$$

and according to the second mechanism thus :

$$UO_3 + UO_2^{++} \rightleftharpoons U_2O_5^{++}$$

If the original concentration of the solution is M moles per l. and the added UO_3 corresponds to a concentration N moles per l., then the ionic concentration will increase from $3M$ to $3M + N$ according to the first reaction, but will remain constant according to the second, except for negligible factors due to the volume and pH changes of the solution. The following table shows the freezing-point depressions of a number of uranyl perchlorate solutions with and without dissolved uranium trioxide. For the former solutions the depressions expected on the basis of the first mechanism are also tabulated for comparison. The results clearly indicate that the preliminary stages of the hydrolysis take place in accord with the second mechanism. London (private communication) arrived at the same conclusion in the case of a uranyl nitrate solution with added uranium trioxide, for which he measured both the freezing-point depression and the boiling-point elevation.

Freezing-point depressions for uranyl perchlorate solutions with and without added uranium trioxide.

Molarity	0·500	0·250	0·125	0·0625	0·0313
$UO_3/HClO_4 = 0{\cdot}5$: F. p. obs.	3·504°	1·447	0·662	0·334	0·162
$UO_3/HClO_4 = 0{\cdot}645$: F. p. obs.	3·502°	1·452	0·665	0·335	0·173
$UO_3/HClO_4 = 0{\cdot}645$: F. p. calc.	3·84°	1·588	0·726	0·366	0·178

It is now necessary to determine how far this reaction proceeds. In the case of Bi^{3+} Granér and Sillén showed that the oxygen-bridging process can lead to the formation of large flat ionic plates, this being in agreement with the *X*-ray crystallographic observations which show that bismuth oxyhalides consist of parallel cationic layers of BiO with the anions between them (Bannister and Hey, *Min. Mag.*, 1935, **24**, 1949; Sillén, *Naturwiss.*, 1942, **30**, 318). That the mechanism does not proceed so far in the case of uranyl salts is suggested by four experimental facts: (1) the existence of anions containing uranium in alkaline solutions of uranyl salts, (2) the shape of the pH titration curves for uranyl perchlorate and sodium hydroxide, (3) the shape of the conductivity titration curve for the same system, (4) the changes in the absorption spectrum of uranyl perchlorate solutions with addition of aqueous sodium-hydroxide.

Experimental evidence supporting the first point has already been discussed.

pH *Data*.—Titration of uranyl salts with sodium hydroxide have been carried out by a number of investigators. Britton (*J.*, 1925, **127**, 2148) showed that for uranyl nitrate in dilute nitric acid there were three inflexions in the curve of pH against c.c. of alkali solution added, one at the point of neutralization of the excess acid, another when the composition of the solution corresponded to $U(NO_3)_{2\cdot38}(OH)_{3\cdot62}$, and the third at the point where precipitation commenced. The deepening in colour which occurred before precipitation was, he suggested, due to the formation of large particles of uranium hydroxide. Substantially similar results were found for uranyl chloride solutions (Britton and Young, *J.*, 1932, 2467).

Guiter (*Bull. Soc. chim.*, 1947, **14**, 275) found two inflexions at pH 6·8—8·6 and at pH 9·3—9·9 in the plot of pH against c.c. of sodium hydroxide added to a solution of uranyl acetate, and attributed them to the formation of $UO_2(OH)_2$ and $Na_2O,8UO_3$, respectively. In the case of uranyl nitrate (*ibid.*, 1946, **13**, 403; 1947, **14**, 64; *Ann. Chim.*, 1947, **12**, 72) he postulated the formation of $(UO_2{\cdot}OH)_2^{++}$, $UO_2NO_3{\cdot}OH^+$, and $UO_2(NO_3)_2{\cdot}OH^-$ in different concentration ranges. His pH values were obtained colorimetrically and this throws some doubt on their accuracy.

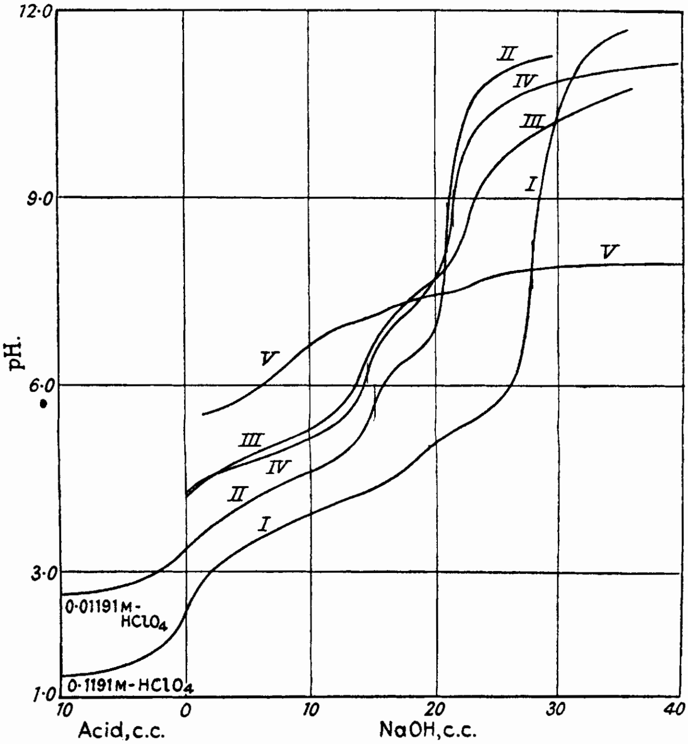
Kraus and Nelson (U.S. Atomic Energy Commission Report AECD. 1864) carried out similar titrations using a glass electrode and showed that there is a marked " hysteresis " effect when the final solution is back-titrated with acid owing to the formation of large particles which do not quickly redistribute themselves. They attribute failure to interpret the curves in terms of the acid constants of the hydrated complexes of UO_2^{++} to polymerisation of the hydrolysed ions, even in the first few units % of hydrolysis. Their curves show the same inflexions as Britton's.

Faucherre (*Compt. rend.*, 1948, **227**, 1367), using the relationship for " condensation " reactions of ions, $d\mathrm{pH}/d\log V = n/(q + 1)$, derived by Geloso and Faucherre (*ibid.*, p. 200), where V is the dilution, n the number of cations condensing, and q the number of hydrogen ions formed in the condensation reaction, has shown that for uranyl solutions $n = 2$, and has given the equilibrium constant for the formation of the dimer as $1{\cdot}07 \times 10^{-6}$ and $1{\cdot}90 \times 10^{-6}$ at ionic strengths 0·6 and 0·06, respectively.

These investigations, although concordant among themselves that complex ions of the type visualized by Longsworth are formed in the hydrolysis of uranyl solutions, do not present a complete or coherent picture of the process. The work described here forms part of a programme undertaken with a view to improving this situation. In addition to the freezing-point depression investigations already described, pH measurements have been made on solutions of uranium trioxide dissolved in perchloric acid, and pH titrations of uranyl perchlorate with sodium hydroxide and perchloric acid have been carried out. The absorption spectra of some of these solutions have been measured, and preliminary conductivity titration data obtained.

The pH titrations were performed for the concentration range 1·000 to 10^{-4}M-uranyl perchlorate, the concentration of the alkali and acid being used in general of the same order as that of the uranyl salt. Under these conditions, the titration of 1·00M-uranyl perchlorate with 0·848M-sodium hydroxide was unsatisfactory, as precipitation occurred after addition of a few c.c. of alkali. The initial pH of 10^{-4}M-uranyl perchlorate was so high (5·3) and that of the corresponding alkali was so low (7·8) that this titration was also of little value. In the concentration range 0·100—0·001M., however, reproducible curves were obtained, all of which showed the same characteristic features. Fig. 3 shows some of these curves. The abscissæ represent the number of c.c. of sodium hydroxide or perchloric acid added to 10 c.c. of the uranyl perchlorate solution.

FIG. 3.



pH titration curves of uranyl perchlorate solutions against sodium hydroxide and perchloric acid.

Uranyl concn., M.	1st inflexion NaOH, c.c.	1st inflexion $(OH^-)/(UO_2^{++})$	2nd inflexion NaOH, c.c.	2nd inflexion $(OH^-)/(UO_2^{++})$
0·1	19·5	1·65	27·7	2·35
0·01	15·2	1·68	21·0	2·32
0·001	14·8	1·63	21·5	2·37

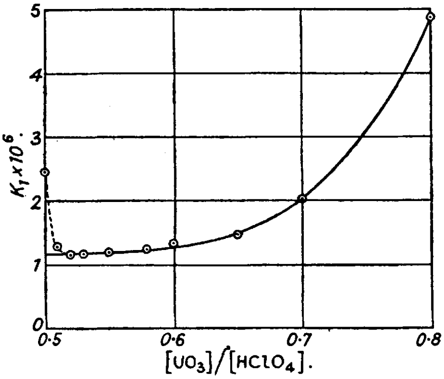
I. 0·1M-$UO_2(ClO_4)_2$ v. 0·848M-NaOH.
II. 0·01M-$UO_2(ClO_4)_2$ v. 0·01104M-NaOH.
III. 0·001M-$UO_2(ClO_4)_2$ v. 0·001104M-NaOH.
IV. 0·001M-$UO_2(ClO_4)_2$ v. 0·00552M-NaOH.
V. 0·0001M-$UO_2(ClO_4)_2$ v. 0·0001104M-NaOH.

The general features are the same as those found by Britton, and by Kraus and Nelson. Besides the inflexion corresponding to the stoicheiometric uranyl salt, two other inflexion points are present in the curves, a small one at lower and a large one at higher pH values. These two inflexions occur at pH values which vary with the concentrations of the solutions used in the titration but their significant property is that the ratios (moles of UO_2^{++}) : (equiv. of NaOH corresponding to the first inflexion) : (equivs. of NaOH corresponding to the second inflexion) are the same for all the curves and are 1 : 1·66 : 2·33 or 3 : 5 : 7. The equivalents of sodium hydroxide are estimated for the points of greatest slope in the inflexions so that the results indicate reactions involving 3 uranyl and 5 hydroxyl ions for the first inflexion and 3 uranyl and 7 hydroxyl ions for the second. These observations can be explained if the first two stages of hydrolysis occur according to the oxygen-bridging mechanism, followed by the addition of hydroxyl ions to the resultant $U_3O_8^{++}$ unit. The reactions being written in terms of hydrogen ions the complete scheme is

$$\begin{aligned}
2UO_2^{++} + H_2O &\rightleftharpoons U_2O_5^{++} + 2H^+ \\
U_2O_5^{++} + UO_2^{++} + H_2O &\rightleftharpoons U_3O_8^{++} + 2H^+ \\
U_3O_8^{++} + H_2O &\rightleftharpoons U_3O_8(OH) + H^+ \\
U_3O_8(OH)^+ + H_2O &\rightleftharpoons U_3O_8(OH)_2 + H^+ \\
U_3O_8(OH)_2 + H_2O &\rightleftharpoons U_3O_8(OH)_3^- + H^+ \\
U_3O_8(OH)_3^- + H_2O &\rightleftharpoons U_3O_8(OH)_4^- + H^+ \quad \text{etc.}
\end{aligned}$$

The shape of the titration curves can now be interpreted. The initial rise and flattening out from the pH of the stoicheiometric solution is due to the two stages of oxygen bridging. Since the addition of the hydroxyl ion to the $U_3O_8^{++}$ ions is a different type of process, it is to be expected that the equilibrium constant for the formation of $U_3O_8(OH)^+$ will be of a different order of magnitude from the constants for the first two stages. The build-up of the hydroxyl ion concentration over the region corresponding to the formation of $U_3O_8(OH)^+$ is large, and the equilibrium is thus less favourable to the products than in the preceding reactions. Addition of the sixth hydroxyl ion to form $U_3O_8(OH)_2$ is more favourably inclined towards the products, so the curve flattens out again. The next stage, the addition of the seventh hydroxyl ion, is accompanied by a sharp rise in pH and leads to the formation of an anion as demanded by experiment. Where the process of hydroxyl-ion addition ends cannot be decided by an inspection of the curves, and quantitative calculations are needed to throw light on this point.

FIG. 4.



Variation of equilibrium constant for formation of $U_2O_5^{++}$ *with the ratio* $[UO_3]/[HClO_4]$ *for* 0·1M-$HClO_4$.

Calculation. The analyses of the curves of pH plotted against the $UO_3/HClO_4$ ratio (Fig. 1) and of pH plotted against c.c. of sodium hydroxide added to uranyl perchlorate solution (Fig. 3) were carried out along similar lines. Considering the UO_3 in perchloric acid first, and assuming that two oxygen-bridging stages are followed by hydroxyl-ion addition to the $U_3O_8^{++}$ ion, let the concentrations of the various ionic species be written as follows : $UO_2^{++} = u$; $U_2O_5^{++} = v$; $U_3O_8^{++} = w$; $U_3O_8(OH)^+ = x$; $U_3O_8(OH)_2 = y$; $U_3O_8(OH)_3^- = z$; $H^+ = h$[*]; $OH^- = k_w/h$; and $ClO_4^- = a$. Then, in general, for a solution of UO_3 of concentration b moles/litre in $HClO_4$ of concentration a moles/litre, and on the assumption that the first complex only is formed :

$$\begin{aligned}
&K_1 = vh^2/u^2 \\
&u + 2v = b \qquad \text{(Total base)} \\
&2u + 2v + h = a \qquad \text{(Electrical neutrality)} \\
\therefore\ &K_1 = (2b - a + h)h^2/2(a - h - b)^2
\end{aligned}$$

This enables values of K_1 to be found for various values of the ratio b/a. The results in Fig. 4 show K_1 plotted against the $UO_3/HClO_4$ ratio for solutions in which the ClO_4^- concentration was 0·1M. Extrapolation to the ratio 0·5, which corresponds to a 0·05M. stoicheiometric uranyl perchlorate solution, gives a value of $1{\cdot}14 \times 10^{-6}$ for K_1.

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[*] The values of h were obtained from the pH measurements with the aid of the relationship $\mathrm{pH} = -\log\,[H^+]\gamma$, where γ is a correction factor for ion interaction and liquid-junction potential effects. The values of γ used in the calculations were taken from the data of Longsworth (*loc. cit.*), and were 0·92 for 0·05M-uranyl perchlorate solutions and 0·96 for 0·10M-solutions.

Above the ratio 0·6, the values of K_1 increase rapidly, showing that the second complex is forming. In this region

$$u + 2v + 3w = b; \quad 2a + 2v + 2w + h = a; \quad K_2 = wh^2/uv$$

Elimination of w gives a quadratic in u, and the resulting values of u can be used to determine K_2. Extrapolation of the results gives $K_2 = 1{\cdot}1 \times 10^{-7}$ at ratio 0·5. The rapid increase of K_2 with increasing $UO_3/HClO_4$ ratio shows that the third complex is forming. By adding a term in x to the equations for total base and electrical neutrality, and using the relationship $K_3 = xh/w$, a cubic in u can be derived, and the solution of this gives values of u which enable K_3 to be determined. The extrapolated value is $7{\cdot}5 \pm 1 \times 10^{-4}$. The analysis was discontinued at this stage.

For the titration curves, if q c.c. of sodium hydroxide of concentration c moles/l. are added to p c.c. of uranyl perchlorate of concentration m moles/l., then for the total base present, it being assumed that only one complex is formed :

$$u + 2v = pm/(p + q)$$

and for electrical neutrality

$$2u + 2v + h + qc/(p + q) = 2pm/(p + q) + Kw/h$$

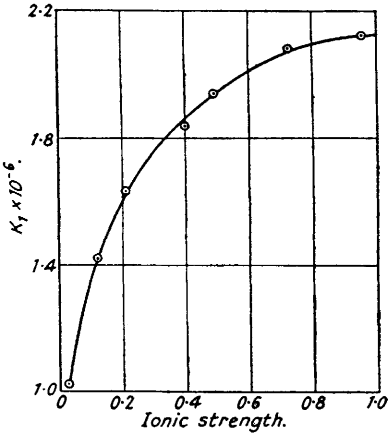
where $qc/(p + q)$ is the sodium-ion concentration and $2pm/(p + q)$ is the perchlorate-ion concentration. For values of q less than 20, the term K_w/h may be neglected. These equations were solved for values of q from 0 to 7 c.c., and the resultant values of K_1 were extrapolated to 0 c.c., the value $1{\cdot}02 \times 10^{-6}$ being obtained.

This value of K_1 being used, and the formation of the second complex $U_3O_8^{++}$ being assumed, the equations

$$u + 2v + 3w = pm/(p + q)$$
$$2u + 2v + 2w + h = (2pm - qc)/(p + q)$$

lead to a quadratic in u, solution of which enables K_2 to be determined. Below $q = 5$, values for K_2 are non-existent or very inaccurate owing to the low concentration of $U_3O_8^{++}$ in the solutions. From 5 to 12 c.c. they lie on a rapidly ascending curve, and extrapolation to 0 c.c. presents difficulty. To overcome this, titrations of 0·01M-uranyl perchlorate containing various concentrations of sodium perchlorate against 0·01104M-sodium hydroxide and 0·00844M-perchloric acid containing the same concentration of sodium perchlorate were carried out, and the values of K_1 and K_2 were calculated for each set of results in the manner outlined above. Fig. 5 shows the extrapolated values of K_1 plotted against initial total ionic strength of the uranyl solution, and in Fig. 6 the values of log K_2 are plotted against c.c. of sodium hydroxide added. By interpolation, a set of values of K_2 corresponding to an initial ionic strength of 0·15 was obtained, and these values are also plotted in Fig. 6. Since this ionic strength is the same as that for the uranium trioxide in perchloric acid experiments, the two sets of results should

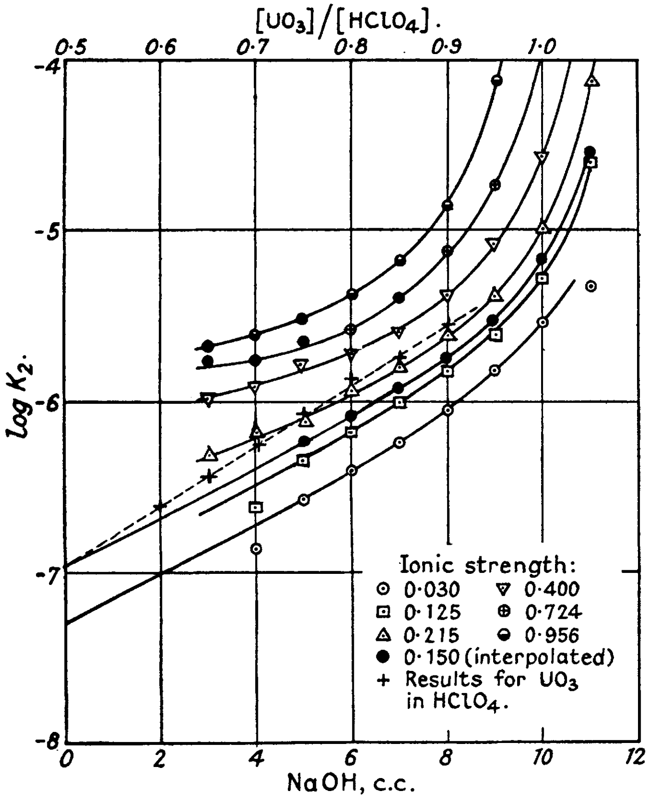
FIG. 5.



extrapolate to the same point. This extrapolation is shown in Fig. 6, and by means of it as a guide, the log K_2 values for the titration of 0·01M-uranyl perchlorate against 0·01104M-sodium hydroxide were extrapolated in a parallel fashion to give $K_2 = 5 \times 10^{-9}$.

From 6 c.c. of sodium hydroxide onwards, equations were set up involving K_3 and x, the $U_3O_8(OH)^+$ concentration, leading to a cubic in u which was conveniently solved by successive approximation. Values of K_3 were then deduced and plotted, the extrapolated result being $2{\cdot}8 \times 10^{-4}$.

FIG. 6.



Variation of the equilibrium constant K_2, for the formation of $U_3O_8^{++}$ *with volume of added* NaOH *at various ionic strengths.*

The differences between the values of K_1, K_2, and K_3 from the two experimental sources is due to the difference in concentration between the uranyl solutions involved. The variation of K_1 with concentration has been considered, but sufficient data are not yet available to make confident predictions about the behaviour of K_2 and K_3.

For determination of the equilibrium constants for the succeeding reactions a cubic in u is always obtained, but terms involving higher powers of h appear in this equation and these terms increase the errors in the values of K_4, K_5, K_6, etc.

The values of K_4, the constant for the formation of $U_3O_8(OH)_2$, determined in the same way as K_3, etc., is 3×10^{-7}.

From 16 c.c. of sodium hydroxide onwards, the concentrations of UO_2^{++}, $U_2O_5^{++}$, and $U_3O_8^{++}$ become negligible, so they are ignored in the determination of K_5. The value obtained for K_5 is 4×10^{-8}.

Above 21 c.c. the concentration of the hydroxyl ion becomes appreciable, and that of $U_3O_8(OH)^+$ negligible. On this basis the extrapolation of the calculated values for K_6 gives 1×10^{-11}. The values of K_6 increase from 24 c.c. upwards, indicating a probable further stage in the hydrolysis. Assuming the same mechanism continues, this would be

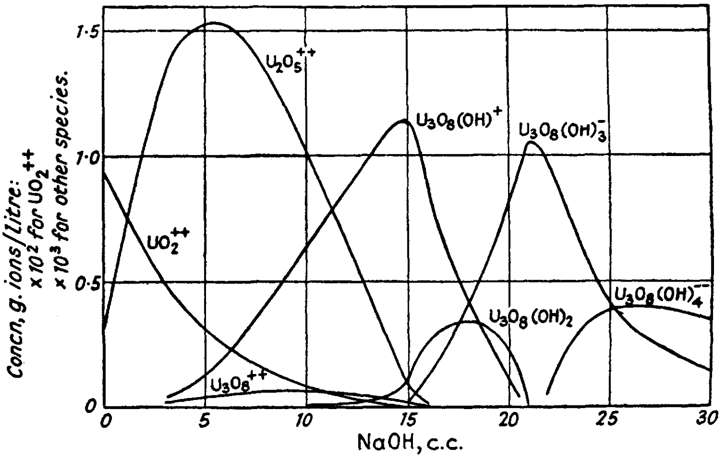
$$U_3O_8(OH)_4^{2-} + H_2O \rightleftharpoons U_3O_8(OH)_5^{3-} + H^+$$

and K_7 for this reaction is 4×10^{-12}.

In the absence of more definite evidence it is impossible to interpret the upper portion of the titration curve with any certainty. Diffusion data should indicate any gross changes in ionic size which occur in these regions, but it is doubtful if addition of hydroxyl ions will be detectable.

Fig. 7 shows the variation in concentration of the different ionic species with addition of sodium hydroxide, calculated with the aid of the above equilibrium constants.

FIG. 7.

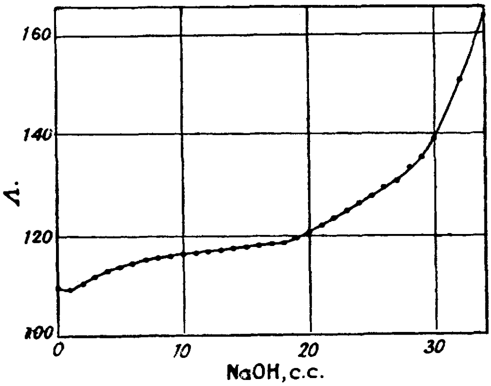


Concentrations of various ionic species plotted against volume of 0·00848M-NaOH *added to* 10 *c.c. of* 0·01M-*uranyl perchlorate.*

Conductivity Data.—The conductivity titration curve for uranyl chloride and sodium hydroxide was recorded by Britton and Young (*loc. cit.*). Two changes in slope were observed, one at the point where the excess of acid present in the uranyl solution was neutralised, and a second near the precipitation point.

A typical curve for the titration of 0·01M-uranyl perchlorate against 0·00848M-sodium hydroxide is shown in Fig. 8. The initial rise is due to the gradual increase in concentration of the sodium ions, which are much more mobile than the uranyl ion and its complexes.

FIG. 8.



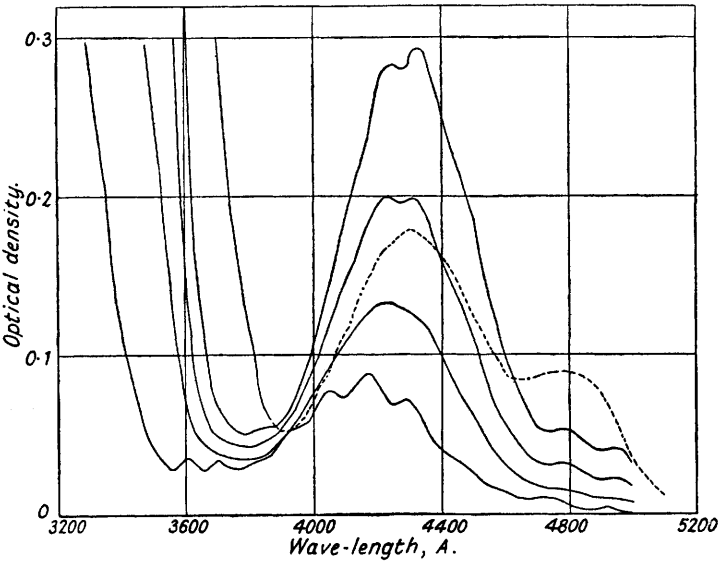
Conductivity titration curve for 0·01M-*uranyl perchlorate and* 0·00848M-NaOH.

From 8 to 18 c.c., where the pH titration curve is flatter, the conductivity increases more slowly. The sharp change in slope which occurs at 18—19 c.c. corresponds to the first inflexion in the pH curve and is caused by the sudden increase in concentration of hydroxyl ions in the solution. The second change of slope, corresponding to the rapid rise of the hydroxyl-ion concentration from the point of formation of $U_3O_8(OH)_3^-$ onwards, is not so sharply defined, being spread over the region 26—30 c.c. Thus, the general features of the curve are in agreement with the hydrolysis scheme proposed above.

Spectroscopic Data.—Many studies have been made of the absorption spectra of the uranyl ion in its solid salts at various temperatures, in uranium glass, and in solutions of salts in various solvents (Jones *et al.*, *Physikal. Z.*, 1909, **10**, 499; *Amer. Chem. J.*, 1910, **43**, 37; 1911, **45**, 114, 159; 1912, **47**, 45; 1913, **49**, 16; Carnegie Inst., 1910, No. 130, 99—111; 1911, No. 160, 43, 81, etc.; Nicholls *et al.*, *Physical Rev.*, 1911, **33**, 354; 1915, **6**, 358; 1917, **9**, 113; 1918, **11**, 285; 1919, **14**, 201, 293; Carnegie Inst., 1919, No. 298, 72, etc.; van Heel, *Comm. Phys. Lab. Univ. Leiden*, 1925, Suppl. No. 55B to Nos. 169—180, 7; Freymann, Freymann *et al.*, *Compt. rend.*, 1946, **223**, 543, 547; 1947, **225**, 529; 1948, **226**, 332, 1029; 1948, **227**, 1096; *J. Phys. Radium*, 1948, **9**, 158; Levshin, *Acta Physicochim. U.R.S.S.*, 1937, **6**, 661, Shibata *et al.*, *J. Chem. Soc. Japan*, 1935, **56**, 13; 1936, **57**, 171).

Most of these investigations have been concerned with the fine structure, which appears in both the absorption and the fluorescence spectra at low temperatures, and the explanation of the observed sharp bands in terms of the vibration frequencies of the normal and excited uranyl ion. Recently, Nyiri (*Acta Univ. Szegediensis, Acta Chem. Phys.*, 1942, **1**, 35) and Betts *et al.* (this vol., p. S 286) have used the absorption spectra of solutions at room temperatures to investigate complexing of the uranyl ion with various anions, a subject which has also been studied polarographically by Kolthoff and Harris (*J. Amer. Chem. Soc.*, 1947, **69**, 446).

Fig. 9.



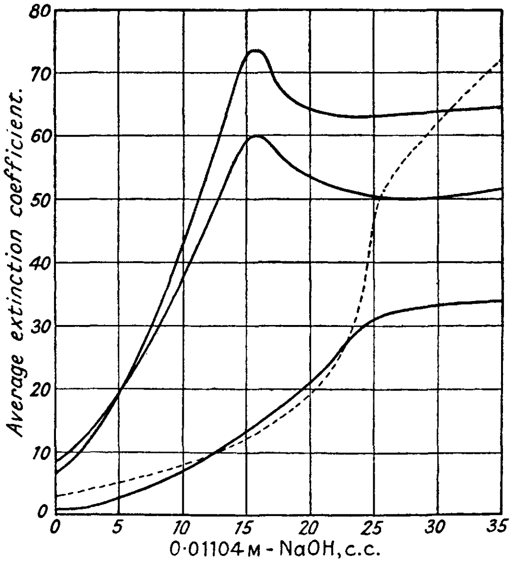
I, no NaOH. II, 5 c.c. of NaOH. III, 9 c.c. of NaOH. IV, 15 c.c. of NaOH. V, 25 c.c. of NaOH.

Variation of absorption spectrum of 0·01M-*uranyl perchlorate with addition of* 0·01104M-NaOH.

Mention had already been made of the fact that the uranyl ion exhibits no tendency to complex with the perchlorate ion. Measurements on solutions of uranyl perchlorate have shown that between 3600 and 5000 A. the spectrum consists of eleven distinct bands (Fig. 9) with a maximum extinction coefficient of 7·79 at the peak of the central band, λ 4160 A. Below 3600 A. the absorption increases rapidly and becomes continuous, but the edge still shows traces of continuation of the band structure. The electronic transition, of which the bands represent associated vibration levels, is forbidden, as the low values of the extinction coefficients indicate (Kasha, *J. Chem. Physics*, 1949, **17**, 349).

Beer's law holds over the range from 3400—5000 A. up to concentrations as high as 3M. provided that the pH is kept below 2·0 to prevent hydrolysis. Above pH 2, the absorption at all wave-lengths increases rapidly. Although the solutions in the region of the maximum concentrations of $U_3O_8(OH)_2$ were metastable, depositing a yellow precipitate when kept for a few hours, especially if the containing vessels were not perfectly clean, it was found possible to measure the absorption spectra for additions up to 30 c.c. of 0·01104M-sodium hydroxide to 10 c.c. of 0·01M-uranyl perchlorate. None of these solutions showed the Tyndall effect, and this was taken to indicate the absence of particles large enough to cause considerable errors by scattering. Fig. 9, in which optical density is plotted against wave-length, shows some of the results. There are three distinct regions observable. Below 3800 A. and above 4700 A. the absorption rises continuously with addition of sodium hydroxide, and between these limits the absorption rises to a maximum value at 15—16 c.c., decreases to a minimum, and then slowly increases again. This variation can be followed in Fig. 10, in which the average extinction coefficient is plotted against the volume of sodium hydroxide added, for a few selected wave-lengths. It is seen that the maxima in the curves for 4300 and 4160 A. occur at the position of the first inflexion in the pH titration curve.

FIG. 10.



Variation of absorption spectrum of 0·01M-*uranyl perchlorate with addition of* 0·01104M-NaOH.

From the initial rapid increase in the average extinction coefficients, it follows that the species $U_2O_5^{++}$ and $U_3O_8^{++}$ are much more strongly absorbing over all wave-lengths than is UO_2^{++}. Therefore, if the oxygen-bridging process continued beyond the formation of $U_3O_8^{++}$ this upward trend should continue. The fact that a maximum is reached shows that a competing process of a different kind is occurring. This must be the addition of hydroxyl ions to $U_3O_8^{++}$, an assumption which is strengthened by the position of the maximum. There is no clearly defined minimum corresponding to the second inflexion in the pH titration curve, and the final steady increase of the average extinction coefficient at all wave-lengths indicates that the hydrolysis process is not complete even after addition of 2 equivs. of sodium hydroxide to one of uranyl perchlorate.

EXPERIMENTAL.

Recrystallisation of uranyl perchlorate gives a slightly acid product. The standard solutions used in this work were therefore prepared by dissolving an excess of a pure commercial uranium trioxide in " AnalaR " perchloric acid, analysing the filtered liquid for uranium and perchlorate, and adding appropriate amounts of standard acid to portions of this solution to make up the required $UO_3 : HClO_4$ ratio. In this way standard solutions with base : acid ratios ranging from 0·7472 to 0·5000 were prepared and stored at 25° in Pyrex flasks.

Uranium analyses were made by evaporating weighed amounts of the solution in a platinum crucible and igniting the crystals at 900°, leaving U_3O_8.

Perchlorate analysis involved diluting the solution until the uranium concentration was less than 0·2 g./c.c., precipitating the uranium with a slight excess of 20-vol. hydrogen peroxide (B.D.H. " AnalaR "), and electrometrically titrating the free acid with standard alkali, with methyl-orange or bromocresol-green as indicator. The concentration of uranium must be kept below the limit quoted in order to prevent errors due to adsorption of acid on the uranium peroxide (Spence *et al.*, unpublished; National Research Council of Canada, Atomic Energy Project).

The cryoscopic determinations were made in an apparatus of the conventional design with a cooling bath of alcohol and solid carbon dioxide which was kept at 0·2—0·5° below the freezing point of the solution. 100-c.c. portions of solution were used, and the freezing points were measured with a Beckmann thermometer which was calibrated at the freezing point of pure water before each determination.

To investigate the variation of pH with the UO_3 : $HClO_4$ ratio for values less than 0·5, solutions were made by adding 0·1M-perchloric acid to a 0·05M-solution of uranyl perchlorate. For values higher than 0·5, weighed amounts of solid uranium trioxide were dissolved in aliquots of the 0·05M-uranyl perchlorate, any volume changes which occurred in this process being neglected.

The solutions used in the investigation of pH variation with concentration were made by suitably diluting a stock 1·000M-solution of stoicheiometric uranyl perchlorate.

Uranyl solutions for the pH titrations were also prepared from this stock solution. The standard hydroxide solution was made by dissolving washed sticks (B.D.H. " AnalaR ") in carbon dioxide-free water. This solution was standardised against recrystallised sulphamic acid and stored under carbon dioxide-free conditions. For the actual titrations it was diluted to the desired concentration with carbon dioxide-free water. The perchloric acid used in the titrations was diluted 72% acid. It was standardised against recrystallised borax and checked with the standard alkali.

All pH measurements were made with a Beckman model G pH meter. For the determination of acid in the uranyl solutions, external glass and calomel electrodes were used, but for the pH titrations and measurements shown in Figs. 1—3 the smaller internal electrodes were employed. In order to remove errors caused by the diffusion of potassium chloride from the calomel electrode and the resulting precipitation of potassium perchlorate in the solution, the electrode was emptied, washed, and refilled with saturated sodium chloride. Measurements made before and after the change on buffer solutions covering the entire pH range showed maximum variations of ±0·02 pH unit. These were ignored in subsequent measurements.

As a general rule, 10-c.c. portions of uranyl perchlorate solution were titrated against acid or alkali of the corresponding concentration, and pH measurements were made after addition of each c.c. All the titrations were repeated at least once and average values were plotted. The maximum differences between the values in Fig. 3 and the observed values were ±0·03 pH unit, but generally the agreement was within ±0·01 unit. Slight drifting occurred in the flat region after the second inflexion; this was reduced by stirring the solution as the alkali was added, but could not be completely avoided. The equilibrium values were reached after 30—60 seconds and these values were used in the calculations.

The sodium perchlorate used in experiments on the variation of K_1 with ionic strength was a commercial product containing small amounts of iron. It was purified by addition of sodium hydroxide, filtration, neutralisation with perchloric acid, and three recrystallisations from water.

Absorption spectra were measured with a Beckman U.-V. spectrophotometer using silica cells. The cell length was varied according to the concentration of the solution and the wave-length region to give transmission values between 20 and 70%, but for the purposes of calculation and for Fig. 10 the optical densities corresponding to a 1-cm. cell length were used.

With the slit fully opened and for visible light, the instrument was also employed to detect the formation of large particles in the solutions by light scattering. With 0·01104M-sodium hydroxide the complete titration was performed without any precipitation although the solutions were metastable in the region where $UO_2(OH)_2$ is a predominating species.

Preliminary conductivity titrations were carried out in a beaker, a pair of platinised platinum electrodes and a conventional A.C. bridge with a Wagner earth being used. A standard potassium chloride solution was used to determine the cell constant.

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