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Acidity Measurements at Elevated Temperatures.

I. Uranium(VI) Hydrolysis at 25 and 94°^{1b}

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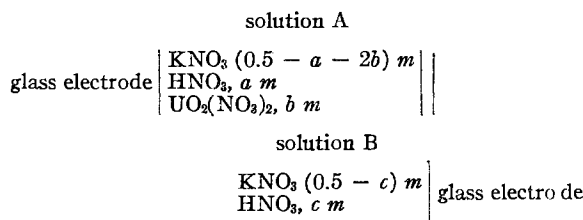
The hydrolysis of uranium(VI) has been measured in potassium nitrate solutions ($I = 0.5\ m$) at 94.4°, using a glass electrode concentration cell with a vibrating reed electrometer null detector. With allowance for the glass electrode asymmetry potential drift, better than ± 0.1 mv. precision was obtained. Similar hydrolysis measurements were made at 25° to better establish the hydrolysis mechanism, which was found to be inconsistent with the proposed "core-links" series of hydrolysis products. Instead the results are consistent with the formation of only three species, UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{++}$, and $(\text{UO}_2)_3(\text{OH})_3^+$, before precipitation occurs, for which equilibrium quotients of formation from uranyl ion and water ($2 \times 10^{-6}\ m$, $1.2 \times 10^{-6}\ m$, and $6 \times 10^{-17}\ m^3$ at 25°; $6.5 \times 10^{-5}\ m$, $3.1 \times 10^{-5}\ m$, and $1.8 \times 10^{-13}\ m^3$ at 94°, respectively) were evaluated. From these, the heats of formation were estimated to be 11, 10.2, and 25.1 kcal., respectively. Over-all hydrolysis increases rapidly with temperature, with the initial monomeric product, UO_2OH^+ , becoming more stable with respect to dimerization to $(\text{UO}_2)_2(\text{OH})_2^{++}$. The trimeric species also becomes more stable with respect to the dimeric species; however, it is also the least stable with respect to precipitation of uranium trioxide and so (because of the decreasing solubility of the oxide) is of decreasing importance in the hydrolysis process with increasing temperature.

The present study is the initial phase in a program of high temperature acidity measurements. The techniques used will, it is hoped, be applicable to the study of a variety of acid dependent equilibria such as hydrolysis, acid association, and some ion association reactions. A knowledge of these could contribute significantly to interpretations of the thermodynamic behavior of aqueous systems at elevated temperatures.

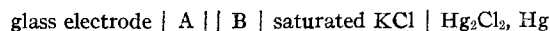
1. Precise Measurements with the Glass Electrode.—Kraus, *et al.*,³ have described use of the vibrating reed electrometer as a detector to obtain precise e.m.f. measurements to a few hundredths of a mv. on glass electrode cells at room temperature. Covington and Prue⁴ subsequently reported similar precision using a conventional potentiometer circuit with glass electrodes of unusually low resistance ($3\text{--}6 \times 10^5$ ohms). The latter investigators pointed out that, when the drift with time often found in glass electrode potentials (probably the result of changing asymmetry potential) is allowed for by a simple extrapolation procedure, the response of the glass

electrode to changes in acidity is comparable in accuracy to that obtainable with the hydrogen electrode.

In the present measurements a vibrating reed electrometer was used as a detector with modified commercial glass electrodes in the concentration cell



designed to test the temperature limitations of the glass electrode. This arrangement has the obvious advantage that the solution measured is in contact with only the relatively inert glass electrodes and the containing vessel. For the room temperature measurements a more conventional arrangement



was used.

2. Uranium(VI) Hydrolysis.—While the hydrolysis of uranium(VI) has been extensively studied at room temperature by numerous investigators,⁵ it has been well established only that

(1) (a) Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission; (b) presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961 (paper no. 105, Inorganic Division).

(2) Summer research participant with the Oak Ridge National Laboratory, 1960–1961, sponsored by the Oak Ridge Institute of Nuclear Studies.

(3) K. A. Kraus, R. W. Holmberg, and C. J. Borkowski, *Anal. Chem.*, **22**, 341 (1950).

(4) A. K. Covington and J. E. Prue, *J. Chem. Soc.*, 3696, 3701 (1955).

(5) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants; Part II, Inorganic Ligands," The Chemical Society, London, 1958, p. 9.

$(\text{UO}_2)_2(\text{OH})_2^{++}$ (or $\text{U}_2\text{O}_8^{++}$) is the principal product of initial hydrolysis. Though it is clear that other products are formed, none has been as well established. In the early stages, $\text{UO}_2\text{OH}^{+6-8}$ and $(\text{UO}_2)_2(\text{OH})^{+3,9}$ may be present. To account for the latter stages of hydrolysis, Ahrland, Hietanen, and Sillén¹⁰ proposed a "core-links" mechanism in which all the important species formed are members of the series: $(\text{UO}_2)_2(\text{OH})_2^{++}$, $(\text{UO}_2)_3(\text{OH})_4^{++}$, . . . $(\text{UO}_2)_n(\text{OH})_{2n-2}^{++}$ or $\text{U}_2\text{O}_8^{++}$, $\text{U}_3\text{O}_8^{++}$, $\text{U}_n\text{O}_{3n-1}^{++}$. What members of this series, if any, are absent could not definitely be decided. However, Ahrland's data⁸ and those of Gustafson, *et al.*,⁷ show systematic deviations from this scheme. Sutton,¹¹ who was able to reach unusually basic solutions before immediate precipitation, proposed a series in which $(\text{UO}_2)_2(\text{OH})_2^{++}$ is followed by the successive trimeric species, $(\text{UO}_2)_3(\text{OH})_4^{++}$, $(\text{UO}_2)_3(\text{OH})_5^+$, . . . $(\text{UO}_2)_3(\text{OH})_8^-$. His titration curves showed inflections corresponding to the stoichiometry of $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_3(\text{OH})_7^-$.

In the present study, it was decided to examine once again the hydrolysis of uranium(VI) at room temperature as well as at the previously unstudied higher temperature in the hope that, with the greater precision offered by the potentiometer circuit used, the specific reactions as well as the temperature dependence of the hydrolysis process could be more clearly established.

Experimental

1. **Uranium(VI) Nitrate Stock Solution.**—All uranium-containing solutions were prepared from a single 0.2 *m* uranyl nitrate solution, made by dissolving a weighed amount of purified uranium trioxide in somewhat less than the equivalent amount of standardized nitric acid. The calculated amount of nitric acid then was added to the resulting filtered solution. The final solution, however, was found to contain *ca.* 2 mole % excess acid; this later was traced to nitrate initially present in the uranium trioxide. Since this fractional excess *X* of acid is an important quantity in such a hydrolysis study, it was estimated by a variety of methods, which included: (1) replacement of the uranyl ion with hydrogen ion by resin ion exchange (giving *X* = 0.057); (2) solvent extraction of the uranyl ion by di-(2-ethylhexyl)-phosphoric acid (giving *X* = 0.020); (3) nitrate analysis of the uranium trioxide used (giving *X* = 0.023); (4) direct titration of the final stock

solution with standard base. Methods 2 and 3 are thought to be the most accurate direct analyses; the solvent extraction reagent was specific for uranyl ion, and the nitrate analysis of UO_3 gave a direct measure of the non-stoichiometry of the final solution, provided cations other than those containing uranium(VI) could be neglected. Method 4 has been used by several previous investigators, on the assumption that the inflection point of the first break in the titration curve is the equivalence point. However, by calculating a titration curve from the most accepted initial hydrolysis reaction, it was found that this assumption is incorrect. The equivalence point instead is expected to occur somewhat above the point of greatest slope. Thus, estimates of *X* will be low (typically 0.04 in *X*). In the present case, the chosen value of *X* (0.023) was most accurately estimated (see below) from the hydrolysis results.

2. **Other Reagent Solutions.**—All stock solutions were prepared by weight from reagent grade chemicals. The 1 *m* potassium nitrate stock solution was found to contain 4×10^{-5} *m* bicarbonate, by careful titration with acid. The potassium hydroxide stock solution contained some carbonate. Its total basicity ($M_{\text{OH}^-} + 2M_{\text{CO}_3^{2-}}$) was determined by titration *vs.* standard acid. In most cases measurements were done in sufficiently acid solution so that it could be assumed that all bicarbonate and carbonate introduced was converted to carbon dioxide. Where the acidity was too low to assume this, the solution was sufficiently buffered that the effect of bicarbonate could be neglected.

All titrations were done on a volume basis. The compositions at each point in the titrations then were converted to molalities, using measured densities of the reagent solutions.

3. **Glass Attack.**—As the temperature increases, alkali metal oxides are leached from glass at an increasing rate. At 94° this rate was found to be *ca.* 1×10^{-4} mmole/hr. (1.6×10^{-4} mmole/hr./cm.² of exposed glass). Since this meant a $<10^{-5}$ mole/l./hr. decrease in the acid concentration of unbuffered solutions, it could be neglected in the present measurements. Limited results at 148° have shown that over 1 hr. at this temperature the glass attack rate is high enough to affect appreciably the acidity of solutions less than 0.01 *M* in acid. Interestingly enough, it was not the pH-sensitive glass (Beckman General Purpose glass) but the lead glass shell (of which most glass electrodes seem to be made) which was most attacked.

4. **High Temperature Cell.**—Figure 1 shows the high temperature cell, which (aside from the limitations of the glass electrode) was designed for temperatures exceeding 200°. The Teflon titration vessel C contained a Teflon covered magnet M, driven by a stirrer unit which was directly beneath the bomb into which the cell was placed. The quartz reference compartment T was provided with an extra-fine porosity quartz frit F at which the liquid junction was made. Two Beckman General Purpose glass electrode bodies G contained silver-silver chloride electrodes and a pH 7 phosphate buffer solution to which potassium chloride and a few crystals of silver chloride were added. All compartments of the cell were fitted with Teflon covers which were vented to assure pressure equilibration throughout. The cell was pressurized (*ca.* 400 p.s.i.) with an inert gas to minimize distillation of water vapor from the cell. Electrical leads passed through insulating

(6) J. A. Hearne and A. G. White, *J. Chem. Soc.*, 2168 (1957).

(7) R. L. Gustafson, C. Richard, and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 1526 (1960).

(8) S. Ahrland, *Acta Chem. Scand.*, **3**, 374 (1949).

(9) S. Hietanen and L. G. Sillén, *ibid.*, **13**, 1828 (1959).

(10) S. Ahrland, S. Hietanen, and L. G. Sillén, *ibid.*, **8**, 1907 (1954).

(11) J. Sutton, *J. Chem. Soc. Suppl. Issue No. 2*, S-275 (1949).

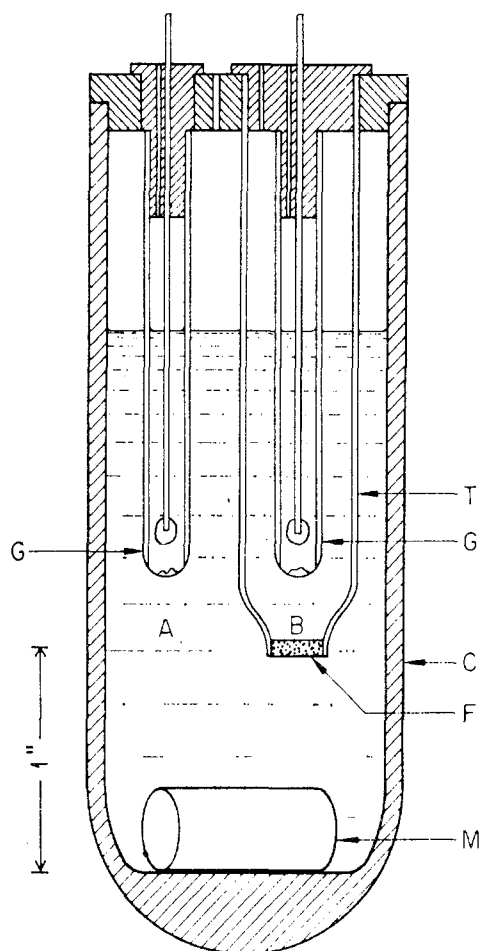


Fig. 1.—High temperature glass electrode cell: C, Teflon cell; G, glass electrodes; T, quartz tube; F, quartz frit; M, stirring magnet; A, test solution; B, reference solution.

Teflon double-cone seals in the bomb head and terminated in shielded coaxial connectors.

Titrating solution was delivered from a High Pressure Equipment Company "pressure generator" (a screw driven piston-cylinder assembly of stainless steel with Teflon packing) for which the volume delivered per turn at 25° was carefully determined. The solution was carried to the cell by a 0.020 in. i.d. titanium capillary which was wound around the outside of the bomb to pre-heat the solution and then passed through the bomb head. The bomb was fitted into an aluminum furnace liner, grooved to position the delivery capillary, in a vertically mounted 5-in. Marshall furnace. Temperature control at 94.4° was provided by a Leeds and Northrup Series 60 DAT controller. During measurements the recorded output of the calibrated iron-constantan control thermocouple inserted in the furnace liner varied less than ± 0.002 mv. ($\pm 0.04^\circ$). A calibrated internal thermocouple, inserted into a Teflon covered well (not shown in Fig. 1), which dipped into the stirred cell solution agreed with the control thermocouple to within 0.1° and showed similar constancy.

5. **Room Temperature Cell.**—Here, the more conventional glass electrode-calomel electrode cell was assembled from glass components. It was mounted inside an alu-

minum cabinet, which like the bomb was part of the electrostatic shield. A pre-saturated inert gas was bubbled through the solution being titrated. Temperature control was provided by a small incandescent light, placed near the cell assembly, and connected to the output of the Leeds and Northrup controller. The control thermocouple was immersed in the stirred cell solution. With the temperature of the air-conditioned room adjusted to about 23.5°, this arrangement gave control to $\pm 0.02^\circ$ at 25°.

6. **Potentiometer Circuit.**—An arrangement similar to that described by Kraus, *et al.*,³ was used. One shielded electrode lead was connected directly to the high-impedance input of a Cary Model 31 vibrating reed electrometer; the other was connected to the G terminal of a Leeds and Northrup K-3 potentiometer. The W1 terminal was connected to the feed-back terminal of the vibrating reed. The potentiometer was used to supply a bucking potential to nearly balance the cell potential. The potential difference (in the range ± 5 mv.) which appeared across the vibrating reed was plotted by a Brown recorder.

Since the vibrating reed electrometer would not measure grounded potentials, it was necessary that the entire cell assembly be well insulated (by Teflon) from ground. For this reason the delivery capillary in the cell could not be dipped directly into the solution.

Results

Three kinds of titrations were made: (1) a control titration in which the concentration of nitric acid was varied in a known way to test the response of the glass electrode and to examine the effect of hydrogen ion on the liquid junction potential; (2) titrations in which uranium(VI) was added to a uranium-free solution of known acidity (the titrant was of a similar acidity so that the hydrogen ion concentration remained nearly constant) to study the early stages of hydrolysis and, with a relatively high acidity, to examine the effect of uranyl ion on the liquid junction potential; (3) titrations in which the acidity was varied while the uranium(VI) concentration remained relatively constant (in the 94° measurements usually the cell solution initially contained potassium hydroxide— $m_{\text{KOH}}/m_{\text{U}} \sim 0.5$ —and acid was added; in one titration at 94° and all those at 25°, the cell solution was initially acid and potassium hydroxide was added until precipitation occurred).

1. **Notation.**—These symbols will be used:

E	e.m.f.
ΔE	the rapid change in e.m.f. when solution acidity is changed
ΔE_j	the corresponding change in liquid junction potential
S	$2.303(RT/nF)$, the Nernst slope
A, B	constants related to the liquid junction potential effect of hydrogen and uranyl ions
m_{H}	the formal acidity; <i>i.e.</i> , that expected in the absence of hydrolysis
h	the equilibrium acidity

m_U the total uranium(VI) concentration
 u the equilibrium concentration of uranyl ion
 u_{xy} the equilibrium concentration of the hydrolysis product $(UO_2)_x(OH)_y^{(2x-y)+}$
 Q_{xy} the formation quotient $(u_{xy}h^y/u^x)$
 X the fractional excess of acid (m_H/m_U) in the uranium(VI) stock solutions
 Δh $h - m_H$, the concentration of OH^- present in hydrolysis products (*i.e.*, $\Sigma y u_{xy}$)
 \bar{n} the hydroxyl number $\Delta h/m_U$, the average number of hydroxyl ions per uranyl ion

The formal acidity m_H includes a term Xm_U , *i.e.*, the fractional excess or deficiency of acid added with the uranyl nitrate. An error in X yields a corresponding opposite error in $\Delta h/m_U$, the hydroxyl number.

2. **Potential Measurements.**—Figure 2 shows a strip chart record of a typical titration. The difference between the cell potential and the opposing e.m.f. from the potentiometer (indicated by the numbers along the zero axis) did not exceed 1 mv. Between additions of titrant, the cell potential is seen to drift uniformly at the rate of *ca.* 1 mv./hr. The effect of this drift is virtually eliminated by determining the *change* in potential ΔE upon each addition of titrant. Each sharp upward break in the plot denotes such a change, whereupon the bucking potential was adjusted to a new balancing value. These sudden changes in E , ΔE , could be measured to a few hundredths of a mv. by a short extrapolation of the subsequent drift back to the point of titrant addition. The procedure is analogous to that used by Covington and Prue.⁴

For solutions in which hydrolysis was negligible (and thus $h = m_H$ and $u = m_U$), the relation between the sum of such potential changes and the solution composition was found to be

$$\Sigma \Delta E = -S \log (h^0/h) + A(h^0 - h) + B(u^0 - u) \quad (1)$$

where h^0 and u^0 were concentrations at the reference point (usually at the beginning or at the end) of the titration to which $\Sigma \Delta E$ was referred. The coefficients A and B were constants at a given temperature and ionic strength. The linear terms in which they appear represent the observed small deviation (<2 mv.) of $\Sigma \Delta E$ from the ideal value given by the Nernst term. Similar corrections have been noted by Ahrlund⁸ and by Sillén and co-workers.⁹

Application of the Henderson equation¹² indicates that these linear terms arise from variation in the liquid junction potential

$$\Delta E_j = \frac{RT}{F} \left[\frac{\Sigma (m_i^0 - m_i) \lambda_i / Z_i}{\Sigma m_i \lambda_i} \right] \quad (2)$$

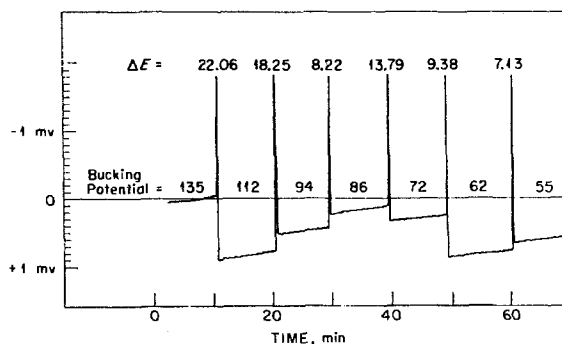


Fig. 2.—Strip chart record of potentiometric titration.

(Here m_i , λ_i , and Z_i are, respectively, the concentrations, equivalent conductance, and charge (with sign) of the *i*th ion.) Thus, the change in liquid junction potential ΔE_j between the reference and a given point in the titration is expected to vary linearly with the change in concentration ($m_i^0 - m_i$) of each ion, provided the total ionic composition and concentration remains approximately constant (*i.e.*, provided $\Sigma m_i \lambda_i$ is *ca.* constant) as is the case here. Introducing charge balance requirements, it can be shown that (for negligible hydrolysis) A and B in eq. 1 are given by

$$A = \frac{RT}{0.5F} \left[\frac{\lambda_{H^+} - \lambda_{K^+}}{\lambda_{K^+} + \lambda_{NO_3^-}} \right];$$

$$B = \frac{RT}{0.5F} \left[\frac{0.5\lambda_{UO_2^{2+}} - 2\lambda_{K^+}}{\lambda_{K^+} + \lambda_{NO_3^-}} \right] \quad (3)$$

if they arise from liquid junction potential changes alone. Table I compares measured values of A

TABLE I
LIQUID JUNCTION POTENTIAL EFFECTS, 0.5 *m* (K)NO₃

Temp., °C.	A^a (mv./m)		B^a (mv./m)	
	Obsd.	Calcd. ^b	Obsd.	Calcd. ^b
25.0	105	98	-46	-43
94.4	71	71	-63	-50

^a Constants in eq. 1. ^b From eq. 3.

and B with those given by these equations. The agreement is good, considering that limiting conductances were used in the calculations. Equa-

(12) Applying the Henderson equation (*cf.* G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier Publishing Co., 1951, Vol. I, pp. 271-272) for liquid junction potential, E_j

$$E_j = \frac{RT}{F} \left[\frac{\Sigma (m_i^0 - m_i) \lambda_i / Z_i}{\Sigma (m_i^0 - m_i) \lambda_i} \ln \left(\frac{\Sigma m_i^0 \lambda_i}{\Sigma m_i \lambda_i} \right) \right]$$

to a junction between solutions (' and ") containing the same principal electrolyte at nearly equal concentrations, the ratio in the logarithmic term is near unity and so the logarithmic term may be replaced by $[\Sigma m_i^0 \lambda_i / \Sigma m_i \lambda_i] - 1$, giving

$$E_j = \frac{RT}{F} \left[\frac{\Sigma (m_i^0 - m_i) \lambda_i / Z_i}{\Sigma m_i \lambda_i} \right]$$

Since in a titration the reference solution (' terms remained constant, changes in E_j which occur are given by eq. 2.

tion 1 was found to relate \bar{h} and u to $\Sigma\Delta E$ in control titrations (in which these concentrations were known) to ca. 0.1 mv., confirming the observation of Covington and Prue⁴ that the response of the glass electrode (corrected for drift) was excellent.

3. Treatment of the Data.—In terms of the ions actually present in a hydrolyzed solution, eq. 2 becomes

$$\Delta E_j = \frac{RT}{0.5F(\lambda_{K^+} + \lambda_{NO_3^-})} [(h^0 - h)\lambda_{H^+} + (m_{K^+} - m_{K^+})\lambda_{K^+} + (u^0 - u)\lambda_{UO_2^{2+}} + \Sigma(u_{xy}^0 - u_{xy})\lambda_{(UO_2)_x(OH)_y^{(2x-y)^+}}] \quad (4)$$

Thus a dilemma appears; *i.e.*, in order to estimate the liquid junction potential effect previous knowledge of the hydrolysis process being studied is required. This difficulty could be overcome in the present case, however, since ΔE_j was small. A preliminary calculation using the experimental data was made assuming $(UO_2)_2(OH)_2^{2+}$ to be the only hydrolysis product and assuming $\lambda_{(UO_2)_2(OH)_2^{2+}}$ to equal $\lambda_{UO_2^{2+}}$. This gave the expression for $\Sigma\Delta E$

$$\Sigma\Delta E = -S \log(h^0/h) + \frac{A(h^0 - h) + B(u^0 + u_{22}^0 - u - u_{22})}{B(u^0 + u_{22}^0 - u - u_{22})} \quad (5)$$

which was first solved for h , neglecting the last (B) term. This first approximation of h then was used to estimate \bar{n} and thus u and u_{22} . These, in turn, were introduced into eq. 5 and a better approximation of h was found. This iterative procedure was continued until the calculated value of h was suitably constant. Interpretation of the results of this preliminary treatment of the data (by the methods described below) led to the conclusion that in addition to $(UO_2)_2(OH)_2^{2+}$, the only other hydrolysis products formed in appreciable amounts were UO_2OH^+ and $(UO_2)_3(OH)_5^+$. If it is assumed that $\lambda_{UO_2OH^+}$ and $\lambda_{(UO_2)_3(OH)_5^+}$ are equal to λ_{K^+} , these new species do not directly affect ΔE_j , and eq. 5 remains the correct expression for $\Sigma\Delta E$. However, in the final calculation of the data by this equation, estimations of u^0 , u_{22}^0 , u , and u_{22} were made from the complete hydrolysis scheme, using increasingly better approximations of the formation quotients Q_{11} , Q_{22} , and Q_{35} .

This final treatment of the data was carried out on an electronic computer (IBM-7090), which was programmed to yield h , Δh , \bar{n} , u_{11} , u_{22} , and u_{35} from given values of the solution compositions, $\Sigma\Delta E$, A , B , X , Q_{11} , Q_{22} , and Q_{35} . The program provided the calculation of \bar{n} directly from $(h - m_H)/m_U$ and also from h and the assumed values of Q_{11} ,

Q_{22} , and Q_{35} . Comparison of the two sets of \bar{n} values gave a check on the consistency of the Q values being used.

4. Summary of Data.—Table II is a partial list of ΔE_j , m_U , h , and \bar{n} values from various hydrolysis titrations. The liquid junction potential correction though small (<2 mv.) was felt to be necessary and desirable, since its neglect would have introduced an error which often would have exceeded the uncertainty of the measurements. At the same time it was felt that the procedure used did not prejudice the interpretation of the result, first, because the total correction was small and, second, because the principal hydrolysis product present in most solutions was indeed quite probably the dimer $(UO_2)_2(OH)_2^{2+}$.

5. Initial Hydrolysis.—From the previous studies three possible species, UO_2OH^+ , $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ will be considered in the early stages of hydrolysis. If the first two are the only ones formed, then it is readily shown¹³ that

$$\frac{h\Delta h}{m_U - \Delta h} = Q_{11} + 2Q_{22} \left(\frac{m_U - \Delta h}{h} \right) \quad (6)$$

so that a plot of the term on the left *vs.* $(m_U - \Delta h)/h$ should yield, in the first stages of hydrolysis, a straight line of slope $2Q_{22}$ and intercept Q_{11} (such plots were used by Hearne and White⁶ and by Gustafson, *et al.*⁷). If the third species $(UO_2)_3(OH)_5^+$ is present and if the acidity is decreased at constant m_U , this plot gives initially the same slope $2Q_{22}$, but the intercept is increased by $Q_{35}m_U$. If instead the acidity is held constant and m_U is increased from zero, then the intercept is again Q_{11} , but the initial slope is increased by $Q_{22}h$.

In Fig. 3, the results at approximately constant acidities are so plotted, yielding straight lines with finite intercepts at both 25 and 94°. This indicates the formation of UO_2OH^+ and the dimeric $(UO_2)_2(OH)_2^{2+}$. At 25°, the intercept is quite close to zero, in terms of the experimental uncertainty. Here the effect on the results at 0.001 *m* acid of a 0.5% error in X is indicated by the dashed lines. However, the results at 0.0005 *m* would be shifted only about half as much, yielding a systematic scatter in the data. Since, as has just been noted, these data should have a common intercept, this plot was used to arrive at the

(13) This relation is obtained as follows: the concentrations of the 1:1 and 2:2 hydrolysis products are given by $u_{11} = Q_{11}(u/h)$; $u_{22} = Q_{22}(u^2/h^2)$. If only these are formed, $\Delta h = u_{11} + 2u_{22}$; $m_U = u + u_{11} + 2u_{22}$, and so $\Delta h = Q_{11}(m_U - \Delta h)/h + 2Q_{22}(m_U - \Delta h)^2/h^2$. Equation 6 is obtained upon multiplying through by $h/(m_U - \Delta h)$.

TABLE II
 URANIUM(VI) HYDROLYSIS DATA IN 0.5 *m* (K)NO₃

25.0°				94.4°			
ΔE_j (mv.)	$m_U \times 10^2$	$-\log h$	\bar{n}	ΔE_j (mv.)	$m_U \times 10^2$	$-\log h$	\bar{n}
	1.989 ^a	1.999 ^b	...		1.998 ^a	1.550 ^b	...
0.83	1.746	3.039	0.049	1.58	1.998	3.052	0.528
.78	1.659	3.485	.231	1.63	1.998	2.971	.442
.65	1.555	3.788	.507	1.68	1.998	2.869	.347
.48	1.443	4.072	.860	1.71	1.998	2.734	.240
.29	1.327	4.428	1.287	1.71	1.998	2.552	.137
	0.9953 ^a	2.300 ^b	...	1.65	1.998	2.360	.071
				1.52	1.998	2.198	.039
0.41	0.9049	3.200	0.056		1.202 ^a	1.900 ^b	...
.38	.8582	3.705	.301				
.29	.8030	4.047	.677	0.52	1.084	2.402	0.035
.20	.7545	4.331	1.061	.59	1.060	2.585	.100
.12	.7115	4.706	1.446	.61	1.033	2.803	.203
	0.5010 ^a	2.310 ^b59	1.011	2.970	.325
0.41	0.4613	3.118	0.022	.54	.9867	3.144	.489
.45	.4495	3.678	.181	.50	.9666	3.277	.639
.43	.4382	3.973	.436	.44	.9473	3.405	.795
.40	.4275	4.176	.704		0.4019 ^a	1.700 ^b	
.33	.4076	4.572	1.249	1.31	0.4036	3.403	0.588
	0.1981 ^a	2.713 ^b	...	1.32	.4036	3.317	.488
0.15	0.1748	3.433	0.039	1.32	.4036	3.215	.387
.17	.1698	3.767	.129	1.32	.4035	3.076	.270
.16	.1628	4.106	.377	1.30	.4034	2.868	.142
.15	.1544	4.387	.756	1.26	.4033	2.677	.079
.13	.1468	4.650	1.145	1.18	.4032	2.487	.043
.12	.1399	5.068	1.536		0.1992 ^a	2.004 ^b	...
	0.09905 ^a	3.015 ^b	...	0.64	0.1995	3.559	0.634
0.07	0.09342	3.591	0.035	.64	.1995	3.484	.532
.08	.09002	4.165	.319	.64	.1995	3.380	.416
.08	.08685	4.488	.764	.62	.1994	3.212	.278
.07	.08390	4.808	1.228	.59	.1994	3.009	.153
.06	.08250	5.061	1.462	.53	.1994	2.801	.084
						2.604	.040

^a Total uranium(VI) concentration at reference point. ^b Negative logarithm of equilibrium acidity at reference point.

most consistent value of X which gives this result. The results at 94° are less sensitive to the same variation in X because of the relatively greater stability of the mononuclear complex.

In Fig. 4 the results of titrations in which the acidity was varied at constant m_U (94°) and roughly constant m_U (25°) are plotted in the same way. Here the reference acidity (h^0 in eq. 5) was chosen so that each curve gave a point on the straight line, from the plots in Fig. 3, in the acidity range of the previous titrations. These reference acidity values agreed, within experimental error, with the initial estimate from the composition of these relatively acidic solutions. This procedure ensured only that the two kinds of titration would have a point in common (as they should); it did not ensure that the linear portion of the curves at constant m_U also would be common with those at

constant h . The fact that they are common within experimental error indicates that $(UO_2)_2(OH)^{+3}$ is not present in detectable amounts (Q_{21} is estimated to be $<2 \times 10^{-4}$ at 25°¹⁴ and $<1 \times 10^{-3}$ at 94°).

6. Further Hydrolysis.—From each titration plotted in Fig. 4, a sharp positive deviation from linear behavior occurs with increasing hydrolysis, indicating the appearance of one or more additional hydrolysis products.

In Fig. 5, the measurements (here plotted in the manner of Sillén¹⁰) are extended to, or near to, hydrolytic precipitation. If the "core-links" mechanism of Sillén were correct, this plot of \bar{n} vs. $\log(m_U/h^2)$ should yield a single curve at

(14) From measurements in 0.4 and 1.4 *M* uranyl perchlorate at 25°, Hietanen and Sillén (ref. 9) report $Q_{21} = 2.2 \times 10^{-4}$ and 2.0×10^{-4} , respectively.

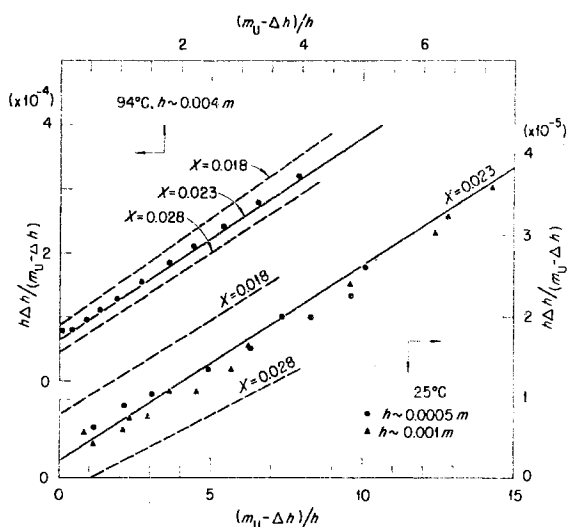


Fig. 3.—Initial hydrolysis of uranium(VI) at approximately constant acidity: the broken lines indicate effect of error in X on the results at $h \sim 0.004 m$ (94.4°) and at $h \sim 0.001 m$ (25.0°). The solid line is calculated from the quotients in Table III (intercept = Q_{11} , slope = $2Q_{22}$).

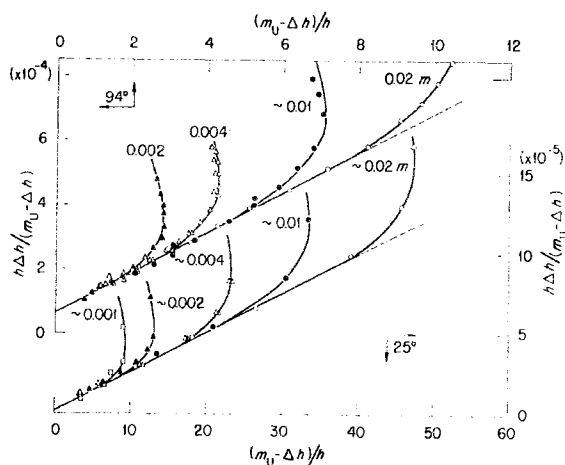


Fig. 4.—Initial hydrolysis with m_U constant, or approximately constant: the solid curves are calculated from the quotients in Table III; the broken lines indicate the limiting slope ($2Q_{22}$).

each temperature.¹⁵ Of course, the presence of UO_2OH^+ (not in the "core-links" series) causes some spread at low hydroxyl numbers, but the curves for various m_U values should subsequently tend to converge. Instead they diverge. The previous extensive results of Ahrlund⁸ showed a

(15) Sillén has pointed out (*Acta Chem. Scand.*, **8**, 300 (1954)) that if all the hydrolysis products of a cation M can be represented by a single formula $M[(OH)_yM]_{x-1}$ in which y is constant, then (provided all activity coefficients are constant) a plot of \bar{n} vs. $\log(m_H/h^y)$ will yield a single curve which is independent of the value of m_M . Thus, in the present case, if only $(UO_2)_2(OH)_2^{++}$ (which may be written $UO_2[(OH)_2UO_2]^{++}$) or if one or more additional dipositive species are the only ones formed, the plots at each temperature in Fig. 5 would coincide.

similar spread, which Ahrlund, *et al.*,¹⁰ attributed partly to experimental scatter and partly to activity coefficient and liquid junction potential effects. Gustafson, *et al.*,⁷ note a similar systematic trend in their results at low uranium concentrations. In the present case, the scatter is considerably smaller than the spread in the curves. Further, the spread is too large to be explained by any reasonable variation in activity coefficients and/or liquid junction potentials.¹⁶ Thus, it can be concluded that the further hydrolysis of uranium(VI) does not proceed by the "core-links" mechanism.

Assuming that only one hydrolysis product in addition to UO_2OH^+ and $(UO_2)_2(OH)_2^{++}$ need be considered here, the following reasoning may be applied: from the direction of the spread of the data at both temperatures in Fig. 5, it appears that the formation of this third species from $(UO_2)_2(OH)_2^{++}$ involves more than two added hydroxyl ions per added uranyl ion. Thus its charge is less than +2. Since neutral species cannot reasonably be expected (in view of the low solubility of UO_3 in pure water), then this third product is expected to have a charge of +1 (*e.g.*, $(UO_2)_2(OH)_3^+$ or $(UO_2)_3(OH)_5^+$ or $(UO_2)_4(OH)_7^+$). Trial hand calculations showed that the only such species which accounts for the present results is $(UO_2)_3(OH)_5^+$. This, it will be recalled, was in the sequence of species originally proposed by Sutton,¹¹ whose titration curves showed inflections corresponding to its formation. The plots in Fig. 5, which are analogous to plots of pH vs. mmoles of added base, show the appearance of this inflection at the higher values of $\Delta h/m_U$, where the curves flatten out. A hydroxyl number of 1.67 (corresponding to complete formation of $(UO_2)_3(OH)_5^+$) could not be reached in the present measurements without precipitation.

7. Summary of Results.—Table III lists the three hydrolysis reactions proposed from the present measurements, their equilibrium quotients

(16) To attribute the deviations from the "core-links" mechanism shown in Fig. 5 to activity coefficient variations alone would require that the activity coefficient quotient $\gamma_{UO_2^{++}}/\gamma_{H^+}$ vary by as much as a factor of two as m_U is varied from 0 to 0.02 *m* in 0.5 *m* nitrate. While no direct measurements of these activity coefficients in 0.5 *m* KNO_3 are available, it has been estimated from equations given by Johnson, Scatchard, and Kraus (*J. Phys. Chem.*, **63**, 793 (1959)) for $\gamma_{Ba^{++}}$ and γ_{H^+} in $BaCl_2$ -HCl mixtures that the analogous quotient $\gamma_{Ba^{++}}/\gamma_{H^+}$ varies about 0.5% when the medium is changed from 0.5 *m* HCl to 0.02 *m* $BaCl_2$ -0.48 *m* HCl (the individual activity coefficients vary about 1%). From this it seems quite unlikely that the quotient $\gamma_{UO_2^{++}}/\gamma_{H^+}$ can be sufficiently variable. Similarly, the liquid junction error required to account for the spread in the curves is much larger (~ 10 mv.) than the estimated total liquid junction potential effects (ΔE_j in Table II).

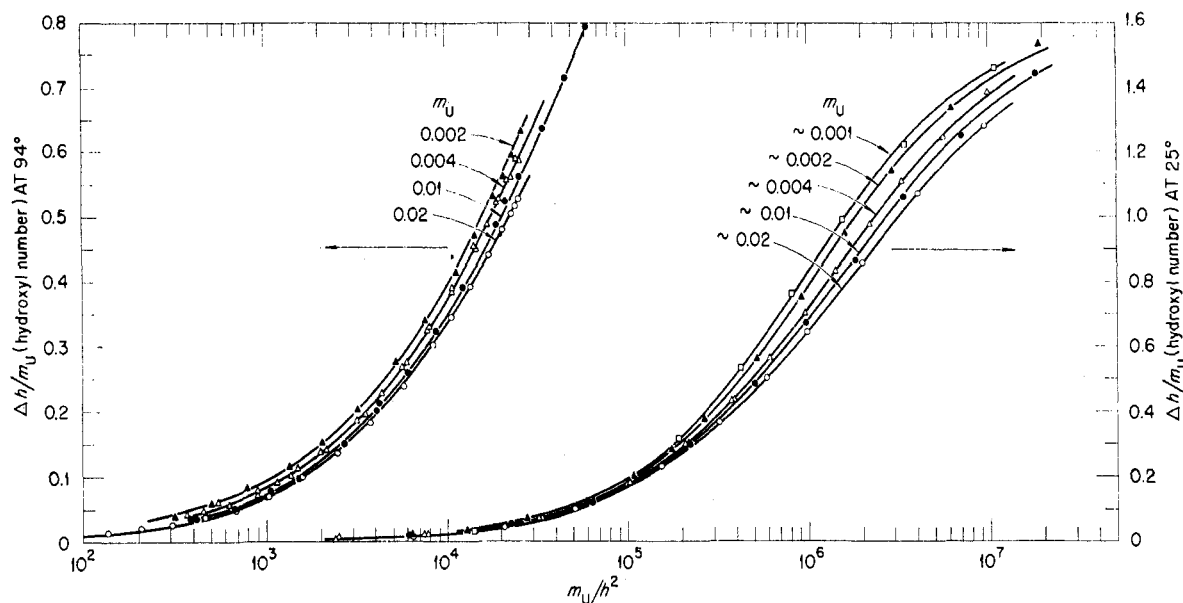


Fig. 5.—Dependence of hydrolysis on m_U ; the spread of the data at each temperature indicates the presence of hydrolysis products other than $UO_2[UO_2(OH)_2]_{x-1}^{++}$. The curves are calculated from the quotients in Table III.

TABLE III
U(VI) HYDROLYSIS AT 25 AND 94.4°

Reaction	Equilibrium quotient ($I = 0.5 m$)		ΔH (kcal.)	ΔF_{25}°	ΔS_{25}° (cal./ °K.)
	25°	94.4°			
(1) $UO_2^{++} + H_2O \rightleftharpoons UO_2OH^+ + H^+$	$Q_{11} = (2 \pm 1) \times 10^{-6}$	$(6.5 \pm 1) \times 10^{-6}$	11 ± 2	7.8 ± 0.5	11 ± 5
(2) $2UO_2^{++} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{++} + 2H^+$	$Q_{22} = (1.2 \pm 0.1) \times 10^{-6}$	$(3.1 \pm 0.2) \times 10^{-6}$	10.2 ± 0.5	8.08 ± 0.05	7.1 ± 2
(3) $3UO_2^{++} + 5H_2O \rightleftharpoons (UO_2)_3(OH)_5^{++} + 5H^+$	$Q_{36} = (6 \pm 1) \times 10^{-17}$	$(1.8 \pm 0.5) \times 10^{-18}$	25.1 ± 1.5	22.1 ± 0.1	10 ± 5

($I = 0.5 m$) at 25 and 94°, and estimates of the enthalpies, free energies, and entropies of reaction. The latter, of course, are not the standard thermodynamic quantities since they were estimated directly from the quotients (uncorrected to $I = 0$; ΔH assumed constant). These equilibrium quotient values are "best values" obtained by an electronic (IBM-7090) computer using a Fortran least squares program¹⁷ to yield the best fit of this hydrolysis scheme to the data. The resulting standard deviation of calculated from observed \bar{n} values was 0.0046 at 25° and 0.0041 at 94° (in each set of more than 80 data points only two points show a difference between calculated and observed \bar{n} values >0.01). The deviations were fairly random and in the range of experimental uncertainty. The quality of the fit is indicated by

(17) We are indebted to R. M. Rush of the Chemistry Division, Oak Ridge National Laboratory, for use of this "Hydrolysis Constant Program." It consists of the "General Least Squares" program written by W. R. Busing and H. A. Levy and a subroutine "Calculation of Hydroxyl Number" written by R. M. Rush, who may be contacted by those interested in the details of this useful computer code.

the solid curves, based on these three equilibrium quotients, which are shown in Fig. 3, 4, and 5. The uncertainties which have been assigned to the Q values (Table III) were estimated from probable uncertainties in X , A , B , and $\Sigma \Delta E$.

Discussion

The present results are adequately accounted for by the set of three hydrolysis products (UO_2^{++} : $OH^- = 1:1, 2:2, \text{ and } 3:5$) shown in Table III. This conclusion is generally in agreement with a recent ultracentrifuge and e.m.f. study of uranium-(VI) hydrolysis in chloride solution at 25° by Rush, Johnson, and Kraus¹⁸ (all of this Laboratory). Their results, however, show evidence of the formation of an additional trimeric species ($UO_2)_3(OH)_4^{++}$ (they propose either 1:1-2:2-3:4-3:5 or 2:2-3:4-3:5 schemes in chloride solution). In a test of the present data (using the Fortran least squares code), assumption of

(18) R. M. Rush, J. S. Johnson, and K. A. Kraus, *Inorg. Chem.*, **1**, 378 (1962).

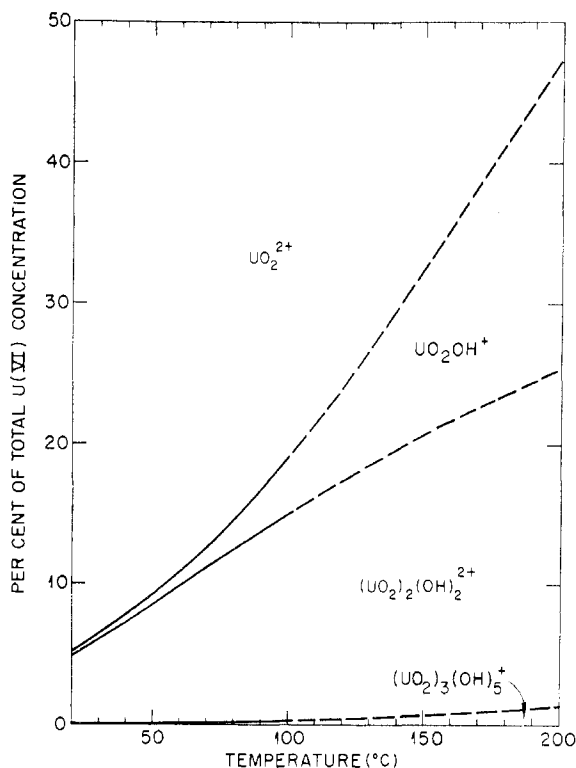


Fig. 6.—Estimated temperature dependence of 0.01 m $\text{UO}_2(\text{NO}_3)_2$ hydrolysis ($I = 0.5 m$).

this additional species failed to improve the fit and the resulting $Q_{3,4}$ value was virtually zero, indicating that $(\text{UO}_2)_3(\text{OH})_4^{++}$ is not formed in detectable amounts in nitrate solution. Thus, as Rush, *et al.*, point out,¹⁸ there appears to be a distinct medium effect on the mechanism of uranium(VI) hydrolysis. In a test of Ahrland's data⁸ in perchlorate solutions, while Rush, *et al.*, find a better fit of a 1:1-2:2:-3:5 (the present) scheme than that given by the previously proposed "core-links" scheme,¹⁰ the addition of $(\text{UO}_2)_3(\text{OH})_4^{++}$ did not further improve the fit. Similarly Sutton's earlier interpretation (2:3-3:4-3:5-3:6-3:7-3:8) of results in perchlorate solution of variable ionic strength indicated relatively small amounts of the 3:4 species (ref. 11, Fig. 7). Finally, in contrast, the recent results of Peterson¹⁹ (of Sillén's laboratory) on uranium(VI) hydrolysis in sulfate solution—which he interprets in terms of either a limited (2:2-3:4-4:6-5:8) or an unlimited core links scheme—might well prove by similar analysis to be consistent with the mechanisms (1:1-2:2-3:4-3:5 or 2:2-3:4-3:5) which Rush, *et al.*,¹⁸ find in chloride solution. This suggestion is ventured from the appearance of Peterson's plot of $\bar{n}/2$ vs. m_{U}/h^2 . . .

(19) A. Peterson, *Acta. Chem. Scand.*, **15**, 101 (1961).

(y vs. x in his notation) which shows a similar but much smaller spread from a single curve (required by the "core-links" scheme of dipositive species only) than is shown by the present results in Fig. 5. It should be emphasized that Sutton's original conclusion that the principal initial 2:2 hydrolysis product is followed by a series of trimers appears essentially correct, insofar as it can be checked by other results which do not extend to the high \bar{n} values he reached. The interesting new conclusion appears to be that the 3:4 species is identifiable in chloride and perhaps in sulfate solutions, but is too unstable to be identified (at least by e.m.f. measurements) in nitrate and perchlorate solutions.

The quotient Q_{11} is difficult to evaluate accurately at 25° owing to the strong tendency of UO_2OH^+ to dimerize ($Q_d = Q_{22}/Q_{11}^2 \cong 3 \times 10^5$). The present value is in adequate agreement with the results of Hearne and White ($Q_{11} = 4 \times 10^{-6}$ at $I = 0.347 M$), who measured the pH of successive dilutions of stoichiometric uranyl perchlorate. It also is consistent with the value (2.3×10^{-6}) found by Rush, *et al.*,¹⁸ in chloride solution. Ahrland's original estimate⁸ of 2×10^{-5} for Q_{11} probably is high because of an error in X (estimated to be *ca.* -0.04) which was based on titration curves (*cf.* Experimental, section 1). Similarly the value of 0.8×10^{-6} ($I = 0.1 M$) reported by Gustafson, *et al.*,⁷ may be low because of an appreciable X correction (assumed to be zero). The present value of Q_{22} at 25° is in adequate agreement with most previous determinations (which fall in the range 0.6 – 1.5×10^{-6}). Sutton's analysis¹¹ yields $Q_{35} = 1.4 \times 10^{-18}$ in 0.15 I perchlorate solution; Rush, *et al.*,¹⁸ find 1×10^{-17} in 1 M chloride.

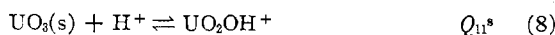
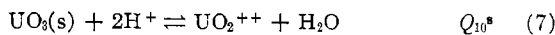
The only previous measurements above room temperature are those of Hearne and White⁶ at 40°, who estimated ΔH values of 20.8 and 6.7 kcal. for reactions 1 and 2, respectively. The lack of agreement with the present values (11 and 10.2 kcal.) may be attributed in part to their short temperature interval and to the possible effect in their dilution method of $(\text{UO}_2)_3(\text{OH})_5^+$ formation in the more dilute solutions. This would raise the apparent value of Q_{11} and lower the apparent value of Q_{22} .

Possible ion-pair (or complex ion) formation of the divalent cation UO_2^{++} with nitrate has been ignored here. If such occurs, the proposed mechanism would not be affected (in view of the relatively high and constant nitrate concentration);

its only effect would be to alter the Q values somewhat. Similarly, no correction has been made for possible incomplete dissociation of nitric acid at 94°. A dissociation constant of *ca.* 5 is estimated from Young's equation,²⁰ giving a dissociation quotient of *ca.* 10 at $I = 0.5 m$. If correct, this would mean that all acid concentrations measured are *ca.* 5% high, resulting in no appreciable change (5%) in Q_{11} , approximately a 10% decrease in Q_{22} , and a 30% decrease in Q_{35} .

Hydrolysis at Elevated Temperatures.—Figure 6 presents the calculated composition of a stoichiometric 0.01 M uranyl nitrate solution ($I = 0.5 m$) as a function of temperature (extrapolated to 200° on the assumption that $\log Q$ is proportional to $1/T(^{\circ}K.)$ for all three hydrolysis reactions). This shows graphically not only the rapid increase of hydrolysis with temperature (6, 19, and 47% hydrolysis at 25, 100, and 200°, respectively), but also the increasing proportion of the monomeric hydrolysis product. This trend was predicted some years ago by Kraus²¹ and first confirmed by Hearne and White.⁶ The trimeric species can predominate in dilute solutions of low acidity at 25°, but it becomes rapidly less important as the temperature increases. This is evident from Fig. 5, in which it is seen that at 94° the maximum hydroxyl number reached is *ca.* 0.7. Precipitation occurs soon thereafter.

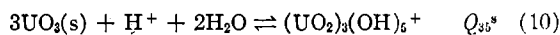
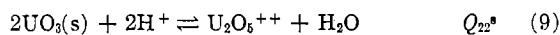
A final comparison which indicates the superiority of the present proposed hydrolysis mechanism over the "core-links" mechanism can be made from Marshall and Slusher's²² solubility measurements of uranium trioxide in nitric acid from 25 to 350°. To compare the two mechanisms with their results, these equilibria should be considered



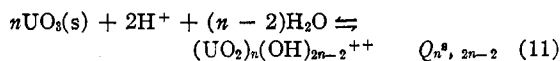
(20) T. F. Young, L. F. Moranville, and H. M. Smith, "The Structure of Electrolyte Solutions," W. J. Hamer, ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 46.

(21) K. A. Kraus, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **7**, 245 (1945).

(22) W. L. Marshall and R. Slusher, ORNL-3127, May 3, 1960, p. 47.



and



(here the corresponding equilibrium quotients are denoted Q_{xy}^s) where eq. 11 includes equilibria for all members (including $n = 1$) of the proposed "core-links" series. If the present proposed mechanism applies, eq. 7-10 are significant, and from charge balance and material balance relations

$$\frac{m_U}{m_{NO_3}} = \frac{Q_{11}^s + 3Q_{35}^s + (Q_{10}^s + 2Q_{22}^s)h}{1 + Q_{11}^s + Q_{35}^s + (2Q_{10}^s + 2Q_{22}^s)h} \quad (12)$$

For the "core-links" mechanism, eq. 11 applies and yields the relationship

$$\frac{m_U}{m_{NO_3}} = \frac{h \sum n Q_{n, 2n-2}^s}{1 + 2h \sum Q_{n, 2n-2}^s} \quad (13)$$

The data of Marshall and Slusher are in qualitative agreement with eq. 12 and in distinct disagreement with eq. 13, since they found the ratio of m_U/m_{NO_3} to be nearly constant in dilute saturated solutions ($h \rightarrow 0$). Under these conditions, eq. 12 reduces to $m_U/m_{NO_3} \rightarrow (Q_{11}^s + 3Q_{35}^s)/(1 + Q_{11}^s + Q_{35}^s)$, which would be constant, while eq. 13 reduces to $m_U/m_{NO_3} \rightarrow 0$, which was not observed.

Considering only eq. 7-10, since the concentration of monovalent cations in UO_3 -saturated solutions varies directly as the first power of the acidity, and the concentration of the divalent cations varies as the second power of the acidity, it is to be expected that at low m_{NO_3} ($\log h$) the predominant cations will be H^+ , UO_2OH^+ , and $(UO_2)_3(OH)_6^+$, while at high m_{NO_3} (high h) the predominant cations will be UO_2^{++} and $U_2O_6^{++}$.

Acknowledgments.—It is a pleasure to thank C. E. Roberts for valuable technical assistance in these measurements. Our thanks also are due to R. J. McNamee, J. L. Gabbard, Jr., and R. L. Matlock of the Operations Analysis Division, Oak Ridge Gaseous Diffusion Plant, who prepared the computer program used in processing the data.