

## Studies on the Hydrolysis of Metal Ions

17. The Hydrolysis of the Uranium(IV) ion,  $U^{4+}$ 

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The hydrolysis of  $U^{4+}$  has been studied in a 3 M (sodium) perchlorate medium at 25°C by two series of electrometric titrations; in one,  $[H^+] = h$  was measured with glass or hydrogen electrodes, in the other,  $b = [U^{4+}]$  was measured with a Pt-Pd redox electrode, after the addition of  $UO_2^{2+}$ .

The data could be explained, assuming the mononuclear reaction  $U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$ , equilibrium constant  $\beta_1$ , and a polynuclear "core+links" reaction, according to hypothesis IIIa:  $(n+1)U^{4+} + 3n H_2O \rightleftharpoons U((OH)_3U)_n^{4+n} + 3n H^+$ , equilibrium constant  $k_n = k_0 k^n$ . The best agreement was found with  $\log \beta_1 = -2.00 \pm 0.1$ ,  $\log k_0 = -1.2 \pm 0.3$ ,  $\log k = -3.4 \pm 0.1$ .

By analogy with  $Th^{4+}$  and considering the crystal structure of  $U(OH)_2SO_4$  it seems plausible that the complexes are chain-like, of formula  $U(OH)_n^{4+n}$ .

Lawrence<sup>1</sup> found that the magnetic susceptibility of uranium(IV) solutions decreases with decreasing  $[H^+]$  and ascribed this effect to the hydrolysis of  $U^{4+}$  to form  $UO^{2+}$ . From his magnetic data he estimated the equilibrium constant  $K = [UO^{2+}][H^+]^2[U^{4+}]^{-1} = 5 \times 10^{-3} \sim 10^{-2.3}$  M<sup>2</sup> in perchlorate solutions. The effect of ionic strength on the activity factors was not considered. (From Lawrence's data one may calculate values of  $K$  varying from  $10^{-3.41}$  to  $10^{-1.41}$ . In the range studied by Lawrence,  $U^{4+}$  forms predominantly mononuclear complexes according to the present investigation.)

Kraus and Nelson<sup>2</sup> have studied the hydrolytic behavior of  $U^{4+}$  by spectrophotometric measurements on chloride and perchlorate solutions. They described the first stages of hydrolysis in terms of the formation of the mononuclear complex  $UOH^{3+}$  and calculated the acidity constant  $K_a = [H^+][UOH^{3+}][U^{4+}]^{-1}$  for various ionic strengths. For instance, for 2.004 M perchlorate they found  $K_a = 2.36 \times 10^{-2}$  M. By extrapolation to zero ionic strength they estimated the true (activity) constant  $K_a^0 = 0.21 \pm 0.02$ . According to Kraus, Nelson and Johnson<sup>3</sup>, further hydrolysis occurs above  $pH = 2$ , to give a polymer of approximate composition  $U(OH)_4$ ; no intermediate product be-

tween  $\text{UOH}^{3+}$  and the polymer was found. The same authors have found that plutonium(IV) gives a similar polymer, approximately  $\text{Pu}(\text{OH})_4$  at 0.2 mM Pu(IV) and a pH as low as 1.5.

Kraus and Nelson<sup>4</sup> found the acidity constant 0.0125 at 10°C and 0.100 at 43°C with U(IV) perchlorate solutions on further spectrophotometric investigations for 0.5 ionic strength.

The aim of the present work was to investigate the hydrolysis of uranium(IV) by the methods developed in this laboratory<sup>7,9,12,13</sup>. Among other things, it seemed interesting to compare its behavior with the mechanism previously found for thorium.

#### METHOD

The hydrolysis of uranium(IV) was studied by two series of potentiometric titrations at 25°C, referred to below as  $Z$  and  $\eta$  titrations. We shall denote the concentrations of free  $\text{H}^+$  and  $\text{U}^{4+}$  by

$$[\text{H}^+] = h; [\text{U}^{4+}] = b \quad (1)$$

$B$  is the total concentration of uranium(IV), whether hydrolyzed or not, and  $H$  is the analytical excess concentration of  $\text{H}^+$ , assuming all uranium(IV) to be present as  $\text{U}^{4+}$ ; thus  $H$  may be negative. The quantities  $B$  and  $H$  for each solution are known from the analytical data.

In each  $Z$  titration,  $B$  was kept constant, and  $h$  was measured for varying  $H$ . Then one could calculate  $Z$ , the average number of OH bound per U(IV) (= the number of  $\text{H}^+$  split off per U(IV)):

$$Z = (h - H)/B \quad (2)$$

Curves  $Z(\log h)_B$  could thus be calculated from this type of titration.

In the  $\eta$  titrations, both  $b$  and  $h$  were measured, the former using redox emf:s in the presence of a comparable amount of  $\text{UO}_2^{2+}$ . From these titrations, each of which was also carried out at constant  $B$ , one obtained

$$\eta = \log \frac{B}{b} \quad (3)$$

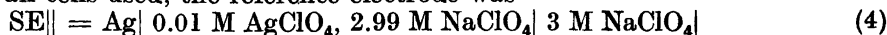
as a function of  $h$ , thus  $\eta(\log h)_B$ .

By addition of  $\text{NaClO}_4$ , all solutions were made to contain 3 M  $\text{ClO}_4^-$ , and no other anions. Since  $h$  and  $B$  were always small compared with  $[\text{Na}^+]$  and  $[\text{ClO}_4^-]$ , the activity factors of all species were assumed to be constant so that true stoichiometric equilibrium constants could be obtained.

The acidity of the solutions was increased by adding  $\text{H}^+\text{ClO}_4^-$ , and decreased by adding  $\text{Na}^+\text{HCO}_3^-$ .  $\text{NaOH}$  was avoided, since local high pH might cause a precipitate which would be hard to redissolve.

#### Types of cells

In all cells used, the reference electrode was



The three types of cell used, and expressions for their emf:s, were

$$-\text{Pd, H}_2(\text{g})|\text{H}^+||\text{SE}+; E_h = E_{0h} + jh - 59.16 \log h \quad (5)$$

$$-\text{glass electrode}|\text{H}^+||\text{SE}+; E_g = E_{0g} + jh - 59.16 \log h \quad (6)$$

$$-\text{Pd}|\text{U}^{4+}, \text{UO}_2^{2+}||\text{SE}+; E_r = E_{0r} + jh - 29.58 \log [\text{UO}_2^{2+}] + 29.58 \log b - 118.32 \log h \quad (7)$$

In eqns. (5) to (7),  $E$  is the measured emf,  $E_{0g}$ ,  $E_{0h}$  and  $E_{0r}$  are constants in each titration (although  $E_{0r}$  was found to vary between different titrations). In the liquid junction potential  $E_j = jh$ , the constant  $j$  was 15 mV M<sup>-1</sup> for  $E_h$ , 22 mV M<sup>-1</sup> for  $E_g$ .

In the pH and concentration range studied, the hydrolysis of  $\text{UO}_2^{2+}$  is negligible according to the data of Ahrlund<sup>5</sup>.

For the  $Z$  titrations,  $E_g$  or sometimes  $E_h$  was measured; the  $\eta$  titrations required measurements of  $E_r$  and  $E_g$ , usually in a range of higher acidity. If  $j$  is known, the  $E_0$  can be calculated from data at higher acidities (negligible hydrolysis); then one may readily obtain  $h$  from  $E_h$  or  $E_g$ , and  $b$  from  $E_r$ .

### Reagents

The starting material for the *uranyl perchlorate* and *uranium(IV) perchlorate* solutions was an ammonium uranyl hydroxide, which had been precipitated from uranyl nitrate, purified by ether extraction. The hydroxide was heated to form  $\text{U}_3\text{O}_8$ , which was dissolved in  $\text{HNO}_3$ , and the uranyl nitrate so obtained was repeatedly evaporated with 70–72 %  $\text{HClO}_4$  under an infrared lamp until no trace of  $\text{HNO}_3$  could be detected. This product was used for preparing uranyl perchlorate solutions.

Uranyl perchlorate solution was adjusted to contain about 0.5 M  $\text{UO}_2^{2+}$  and 2.5 M  $\text{HClO}_4$ ; it was then reduced to uranium(IV) by electrolysis, using a mercury cathode and a platinum anode, separated by a diaphragm of sintered glass<sup>6</sup>. Air was kept away with a stream of  $\text{CO}_2$ . The potential difference between the electrodes was 4–5 V, and the current 0.15–0.25 A. With 6 V and about 1.0 A, chloride ions could be detected after 10 min. The acidity of the  $\text{UO}_2(\text{ClO}_4)_2$  solution to be reduced is important. If it is too low, a black solid (probably  $\text{UO}_2$ ) will precipitate during the electrolysis; if it is too high,  $H$  will be unnecessarily high in the uranium(IV) solution, and it is then hard to determine  $Z$  accurately.

The uranium(IV) perchlorate solution finally obtained was stored under purified  $\text{CO}_2$  in an automatic buret.

*Perchloric acid* solutions were prepared from 70–72 %  $\text{HClO}_4$  (Kebo p.a.) and analyzed using  $\text{HgO} + \text{KI}$ , or recrystallized hydrazine sulfate.

*Sodium hydrogen carbonate* solutions were prepared from  $\text{NaHCO}_3$  (Riedel-de-Haen p.a.) and titrated with  $\text{HClO}_4$ .

*Silver perchlorate* solutions were prepared as described in previous papers from this laboratory<sup>7</sup>.

*Sodium perchlorate* solutions were prepared by mixing  $\text{HClO}_4$  and  $\text{Na}_2\text{CO}_3$ . No  $\text{Cl}^-$  could be detected. The stock solutions were analyzed as described before<sup>7</sup>.

*Carbon dioxide, nitrogen, and hydrogen* were purified as described previously<sup>7</sup>.

### Analysis

The *total uranium* in the uranium(IV) or uranyl stock solutions was determined by precipitating with oxine, igniting, and weighing as  $\text{U}_3\text{O}_8$ . The concentration of *uranium(IV)* had to be checked repeatedly, since it may easily decrease by oxidation. After each titration, the following convenient method was used: Equal volumes of uranium(IV) solution and conc.  $\text{HCl}$  were mixed in a measuring cylinder fitted with a glass stopper; then  $\text{ICl}$  solution and 10 %  $\text{FeCl}_3$  solution were added, and the free  $\text{I}_2$  titrated with  $\text{KIO}_3$ .

using  $\text{CHCl}_3$  as indicator. — Another method was to add excess of  $\text{FeCl}_3$  solution, which oxidizes  $\text{U}^{4+}$  to  $\text{UO}_2^{2+}$ , and to determine the  $\text{Fe}^{2+}$  formed by potentiometric titration with  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

The perchlorate ion concentration was determined by ion exchange. First  $\text{U}^{4+}$  was oxidized to  $\text{UO}_2^{2+}$  with a stream of air or oxygen, and then the solution was passed through a column of the  $\text{H}^+$  form of Amberlite IR 120. The total amount of  $\text{ClO}_4^-$  was found by titrating the eluate ( $\text{H}^+\text{ClO}_4^-$ ) with  $\text{NaOH}$  solution. — When uranium(IV) solution was passed through the same type of ion exchange column without previous oxidation, nevertheless the same total amount of  $\text{ClO}_4^-$  was found. This shows that uranium(IV) on the ion exchange resin is not associated with any  $\text{ClO}_4^-$ .

### Apparatus

The cell was of the type described by Forsling, Hietanen and Sillén<sup>9</sup>. It was kept in a paraffin oil thermostat at  $25.0 \pm 0.1^\circ\text{C}$ , and the titrations were carried out in a room thermostated at approximately  $25^\circ\text{C}$ .

The hydrogen electrodes were lightly palladinised Pt foils<sup>8</sup>. Two glass electrodes were used, a commercial Radiometer electrode, and one prepared by Mr Erik Blomgren in Uppsala. The redox electrodes were palladinised Pt foils. In measurements of  $E_r$  and  $E_g$ , air was kept out of the titration vessel by bubbling purified  $\text{N}_2$  through the solution.

The emfs of the cells were measured with a Vernier compensator (Cambridge Instrument Co.) and a Multiflex galvanometer type MG 2, or with a valve potentiometer (Radiometer PHM 3i).

### PROCEDURE AND DATA

#### Z Titrations

The data from  $Z$  titrations with a glass electrode are given in Fig. 1, those with a hydrogen electrode in Fig. 3, both in the form of plots of  $Z(\log h)_B$ . As an example, the primary data for a titration with a hydrogen electrode for  $B = 10.00$  mM are given in Table 1.

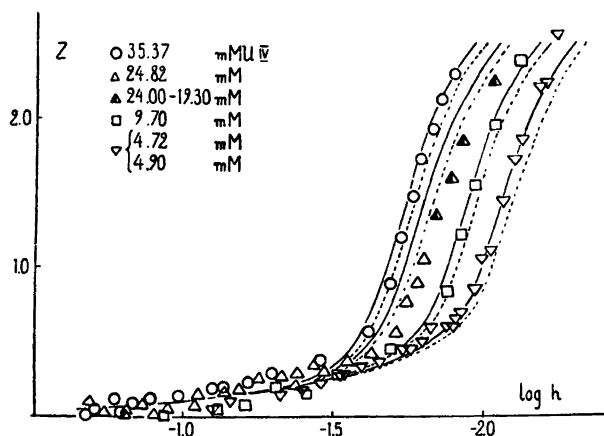


Fig. 1. Data for glass electrode measurements. Vertical axis:  $Z$  = average number of  $\text{OH}^-$  bound per  $\text{U(IV)}$  atom. Horizontal axis:  $\log h$  ( $M$  scale). Full drawn curve: calculated for the various values of  $B$  with "hypothesis IIIa"  $K_0 = 0.06$ ,  $\log k = -3.37$ , assuming one mononuclear step with  $\log \beta_1 = -1.98$ . Broken curve: calculated for  $k_0 = 0.06$ ,  $\log k = -3.45$ ,  $\log \beta_1 = -1.95$ .

Table 1.

Uranium solution	20.00 mM U <sup>4+</sup>	} <i>v</i> ml	HClO <sub>4</sub>	97.80 mM	<i>v</i> <sub>1</sub> ml
	0.55 mM UO <sub>2</sub> <sup>2+</sup>		NaHCO <sub>3</sub>	273.6 mM	<i>v</i> <sub>2</sub> ml
	182.00 mM H <sup>+</sup>				

Acid-base titration. In titration vessel 35.00 ml HClO<sub>4</sub>

<i>v</i> <sub>1</sub>	<i>H</i>	<i>E</i> <sub>0</sub> '	<i>E</i> <sub>h</sub>
0.00	97.80	837.17	719.42
1.00	87.48	836.76	721.88
2.00	77.72	836.54	724.70
3.00	68.48	836.54	727.95
4.00	59.70	836.07	731.00
6.00	43.44	835.32	738.42
10.00	25.26	834.51	764.50
12.00	2.97	835.00	807.05

Uranium addition 47.00 ml

<i>v</i>	<i>v</i> <sub>2</sub>	<i>H</i>	<i>h</i>	<i>E</i> <sub>h</sub>	<i>E</i> <sub>0</sub> '	<i>Z</i>
0.00	0.00	46.98	47.93	735.30	835.1	0.10
2.00	2.00	41.34	43.24	738.10	834.9	0.19
4.00	4.00	36.14	38.50	740.89	834.7	0.24
10.00	10.00	22.72	25.97	750.60	834.3	0.32
15.00	15.00	13.53	18.03	759.78	834.1	0.45
20.00	20.00	5.70	13.77	766.50	833.9	0.81
24.00	24.00	0.24	12.22	769.67	833.9	1.20
26.00	26.00	-2.27	11.51	771.11	833.9	1.38
28.00	28.00	-4.64	10.81	772.62	833.8	1.54
30.00	30.00	-6.90	10.21	774.03	833.8	1.71
32.00	32.00	-9.03	9.62	775.62	833.8	1.87
34.00	34.00	-11.06	9.01	777.20	833.7	2.01
36.00	36.00	-13.00	8.39	779.03	833.7	2.14

The correction for uranyl is made by reducing *E*<sub>0</sub>' with 0.50 mV.

The titration procedure was practically the same as that used for thorium <sup>7</sup>. Usually, as in Table 1,  $E_0' = E_0 + jh$  was obtained from an immediately preceding acid-base titration with no uranium present; sometimes  $E_0'$  was calculated from  $E$  values measured in the most acidic solutions containing U, where the hydrolysis of U<sup>4+</sup> could be neglected.

The accuracy of the  $Z$  values is lower than for many other ions studied in this series, especially at the highest acidities. At 100 mM H<sup>+</sup>, where  $Z$  is already about 0.1, an error of 0.2 or 0.3 mV in  $E$  will make an error of 0.8 to 1.2 mM in  $h$ , which makes the  $Z$  value for the lowest values of  $B$  (2 or 5 mM) very uncertain. For higher  $B$ , and lower  $h$ , the accuracy increases.

*Influence of uranyl ions.* It was practically unavoidable that the uranium(IV) solutions contained 1–2 % of the total uranium in the form of uranyl ions UO<sub>2</sub><sup>2+</sup>. Fig. 2 shows measurements with glass and hydrogen electrodes on a solution, where the analytical H<sup>+</sup> and uranium(IV) concentrations,  $H$  and  $B$ , were kept constant, while the concentration of UO<sub>2</sub><sup>2+</sup> was increased by adding from a buret a uranyl solution, of the same  $H$  and  $B$  as the original solution. The presence of uranyl ions does not seem to affect the glass electrode,

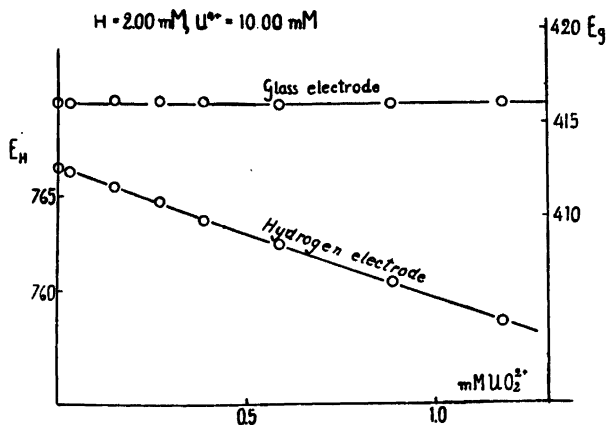


Fig. 2. Influence of uranyl ion on glass and hydrogen electrodes.

whereas  $E_h$  (and thus  $E_{0h}$ ) are seen to decrease. The difference amounted to about 7 mV for 1 mM  $UO_2^{2+}$ ; in experiments with other values for  $B$  and  $H$ , approximately the same slope was obtained.

The glass electrode data would thus seem more reliable. To evaluate the hydrogen electrode data,  $E_{0h}$  was taken from points of high acidity ( $Z = 0$ ) and assumed to be constant.

### $\eta$ Titrations

In preliminary experiments, various redox electrodes were tried: Pt, Pt—Ir, platinised Pt, palladinised Pt, gilded Pt, Au, and Hg. The emf obtained using Hg electrodes was usually about 6—7 mV lower than with the others. Equilibrium was reached most quickly with the palladinised and platinised Pt electrodes. If a few drops of indigo tetrasulfonate solution was added<sup>11</sup>, the gilded Pt electrodes also came to equilibrium rather rapidly.

Palladinised Pt electrodes were used, since they were most easily prepared. New electrodes were palladinised for each titration.

The data, calculated in the form  $\eta(\log h)_B$  are given in Fig. 4. Full data for two titrations are given in Table 2, one in which  $h$  was increased and one in which  $h$  was decreased.

The procedure for  $\eta$  titrations was similar to that of the  $Z$  titrations. The hydrogen ion concentration was sometimes measured directly with the glass electrode; in such cases, an acid-base titration preceded the uranium titrations. In other cases,  $h$  was calculated as  $h = H + BZ$ . The correction term  $BZ$  for the  $H^+$  split off from  $U^{4+}$  was assumed to be a function of  $h$  and  $B$  and was interpolated from previous  $Z$  titrations.

*Variation of  $E_{or}$ .* When the values of  $E_{or}$  for different titrations were compared, they were found to differ, usually by about 1 mV although sometimes deviations up to 6—8 mV were observed. However, in each titration  $E_{or}$  seemed to be constant, since the difference in  $E_r$  values found in parallel

Table 2.

Uranium solution	20.00 mM U <sup>4+</sup>	} v ml	HClO <sub>4</sub>	504.4 mM	v <sub>1</sub> ml
	20.42 mM UO <sub>2</sub> <sup>2+</sup>		NaHCO <sub>3</sub>	273.6 mM	v <sub>2</sub> ml
	102.1 mM H <sup>+</sup>				

In titration vessel 20.00 ml uranium solution + 20.00 ml 3 M NaClO<sub>4</sub>

v	v <sub>1</sub>	v <sub>2</sub>	-E <sub>r</sub>	E <sub>j</sub>	H	h	η
3.00		3.00	488.6	0.6	33.20	35.48	0.111
1.00	1.00		476.5	0.8	44.46	46.24	0.067
2.00	2.00		467.4	0.9	54.81	56.24	0.041
3.00	3.00		460.0	1.1	64.36	65.32	0.035
4.00	4.00		454.2	1.2	73.21	73.96	0.019
6.00	6.00		445.1	1.5	89.07	89.64	0.004
8.00	8.00		438.0	1.7	102.9	102.9	0.010
10.00	10.00		432.6	1.9	115.0	115.3	0.001
12.00	12.00		428.4	2.1	125.8	125.9	0.000
15.00	15.00		423.2	2.3	139.8	139.8	0.000
20.00	20.00		416.9	2.6	158.8	158.8	0.000

In titration vessel 20.00 ml uranium solution + 20.00 ml 3 M NaClO<sub>4</sub>

v	v <sub>2</sub>	-E <sub>r</sub>	E <sub>j</sub>	H	h	η
2.00	2.00	482.0	0.7	38.61	40.74	0.099
3.00	3.45	492.0	0.5	30.23	32.59	0.143
4.00	4.00	494.8	0.5	28.25	30.72	0.149
5.00	5.00	500.6	0.4	23.69	26.45	0.210
6.00	6.00	507.7	0.4	19.48	22.39	0.258
7.00	7.00	514.1	0.3	15.58	19.16	0.310
8.00	8.05	521.3	0.3	11.95	16.64	0.311
9.00	8.95	526.7	0.2	8.83	14.62	0.353
10.00	10.07	530.7	0.2	5.12	13.26	0.388
11.00	11.00	532.2	0.2	2.50	12.28	0.468
12.00	12.05	534.1	0.2	-0.47	11.35	0.541
13.00	13.00	534.7	0.2	-2.84	10.69	0.623
14.00	14.04	535.0	0.2	-5.44	10.03	0.725

titrations was always constant. Since in (7) only the difference  $E_{0r} - E_r$  is important, and not the absolute value of  $E_{0r}$ ,  $\eta$  could still be calculated. It is hard to understand the reason for this deviation. The equilibria between U(IV), U(V), and U(VI) should be reached within the times used. There may be differences in the surface of the electrode, but when two electrodes were immersed in the same solution, they gave the same emf within  $\pm 0.2$  mV at low values of  $Z$  (or  $\eta$ ) and within 0.5 mV close to the point of precipitation.

The equilibrium  $E_r$  or  $E_n$  was obtained within 20-30 min. and  $E_g$  much more quickly; it was sometimes checked that  $E$  did not change after two hours.

A number of back-titrations were made, adding H<sup>+</sup>:  $Z$  titrations for  $B = 9.81$  mM (from  $Z = 0.50$ ) and  $9.74$  mM (from  $Z = 0.40$ ) with the hydrogen electrode, and for  $B = 4.90$  (from  $Z = 0.85$ ) with the glass electrode; and  $\eta$  titrations for  $B = 10.00$  (from  $\eta = 0.11$ )  $B = 9.32$  mM (from  $\eta = 0.260$ ),  $B = 5.00$  (from  $\eta = 0.163$  and for  $B = 4.78$  (from  $\eta = 0.167$ ). They seem to agree well with titrations in the other direction.

*Influence of carbonate.* To make sure that no error was caused by carbonate complexes formed on the addition of  $\text{NaHCO}_3$ , the following experiment was carried out. A solution was prepared with  $H = 22$  mM,  $B = 35$  mM and  $[\text{UO}_2^{2+}] = 7$  mM. In this solution,  $Z \approx 0.35$ , and  $\eta \approx 0.17$ . The redox emf  $E_r$  was measured in the cell (7), and then a stream of  $\text{CO}_2$  was bubbled through the solution.  $E_r$  increased by 1 mV, which may indicate a weak complex formation with uranium(IV). However, when  $\text{N}_2$  was again bubbled through the solution, after 10 min.  $E_r$  had attained the same value as before the treatment with  $\text{CO}_2$ . The experiment was repeated and found to be fully reproducible. Thus there is no indication of strong or irreversible complex formation with carbonate.

*Precipitation.* In order to study the tendency to slow precipitation, four series of solutions were prepared; in each series, the total concentrations of uranium(IV) and uranyl ions were kept constant, whereas the excess of  $\text{H}^+$ ,  $H$ , was varied. The solutions which were initially clear were stored in flasks under paraffin oil to avoid oxidation, and the  $E_r$  with each solution was measured daily. The flasks were also scrutinized for a possible precipitate.

The maximum change in  $E$  was 2 mV, and the variations were usually less than 1 mV. In the most acidic solutions,  $E$  often varied by 1 mV during the first day.

The results may be summarized as follows:

$B$ , mM	$[\text{UO}_2^{2+}]$ , mM	Precipitate at $H$ , mM	no ppt at $H$ , mM
5.05	4.61	0, 2, 5	10, 30, 50...200
10.00	8.65	-10, 0, 5	10, 30...200
25.00	25.00	-10, 0, 5	10, 30...200
50.00	50.00	-20, -15	- 10...

In the most concentrated solution, the black precipitate appeared after three days and in the other solutions after one day. In these experiments, the uranium(IV) perchlorate contained some  $\text{Cl}^-$ , which had formed on electrolytic reduction of  $\text{UO}_2^{2+}$ .

In other experiments it was noticed that the presence of  $\text{UO}_2^{2+}$  ions favored precipitation, which was observed at higher acidities than in the absence of  $\text{UO}_2^{2+}$ .

The polynuclear mechanism: first approximation

From the plots of  $Z(\log h)_B$  in Figs. 1 and 3 or of  $\eta(\log h)_B$  in Fig. 4 it is seen that for different values of  $B$  the steep part of the curves do not coincide but are parallel. This shows that polynuclear complexes are formed and indicates, as a first approximation, that they can be written in a "core + links" form<sup>12</sup>. The spacing between the curves indicates  $t = 3$ , whence the formula of the complexes would be  $\text{U}((\text{OH})_3\text{U})_n^{4+n}$ . As a test, the data of the  $Z$  and  $\eta$  titrations were recalculated and plotted as functions of the variable

$$x = \log B - 3 \log h \quad (8)$$

For convenience,  $Z$  was replaced by the variable

$$y = Z/t = Z/3 \quad (9)$$



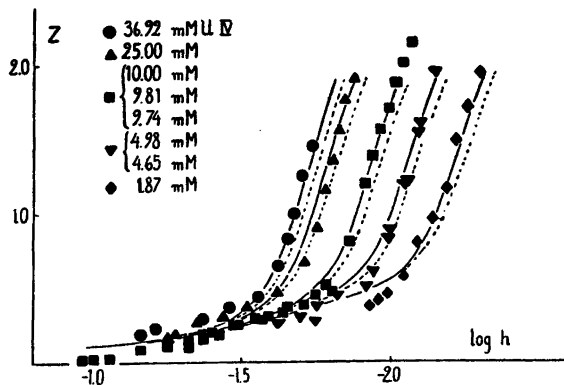


Fig. 3. Data for hydrogen electrode measurements. Vertical axis:  $Z$  = average number of  $\text{OH}^-$  bound per  $\text{U(IV)}$  atom. Horizontal axis:  $\log h$  ( $M$  scale). Full-drawn curve: calculated for the various values of  $B$  with "hypothesis III a"  $k_0 = 0.06$ ,  $\log k = -3.37$ , assuming one mononuclear step with  $\log \beta_1 = -1.98$ .

The data  $y(x)$  are seen to fall on single curves, independent of  $B$ , at least in the steep parts of the curves. In the flat part, for higher  $h$  (lower  $x$ ), the agreement is less good; on the other hand, the experimental inaccuracy is also much greater.

It would thus seem that a "core + links" mechanism would give a good approximation.

For two of the titrations in Fig. 5, the values of  $E'_0$  taken differed from those used for calculating  $Z$  for Figs. 1 and 3. In one of them, with  $B = 4.72$  mM,  $E'_{\text{og}} = 202.7$  mV (giving  $Z = 0.11$  at  $H = 45.88$  mM) was used in Fig. 1, and  $E'_{\text{og}} = 202.8$  mV (giving  $Z = 0.15$ ) in Fig. 5. In the other, with  $B = 36.92$  mM, we used  $E'_{\text{oh}} = 834.62$  (giving  $Z = 0.195$  at  $H = 62.26$ ) in Fig. 3, and  $E'_{\text{oh}} = 832.25$  (giving  $Z = 0.030$ ) in Fig. 5. These

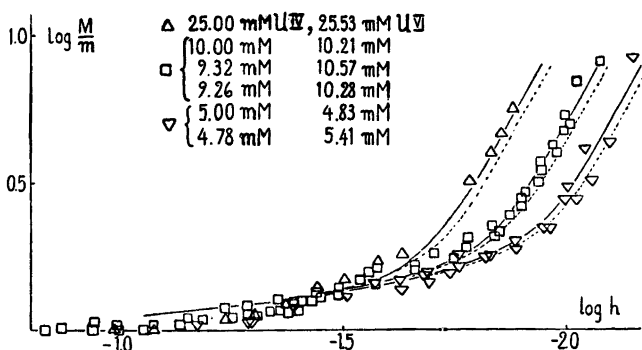


Fig. 4. Data for redox titrations. Vertical axis:  $\eta = \log(B/b)$ ; horizontal axis:  $\log h$  ( $M$  scale.) Full-drawn curve: calculated for the various values of  $B$  with "hypothesis III a"  $k_0 = 0.06$ ,  $\log k = -3.37$ , assuming one mononuclear step  $\log \beta_1 = -1.98$ . Broken curve: calculated for  $k_0 = 0.06$ ,  $\log k = -3.45$ ,  $\log \beta_1 = -1.95$ .

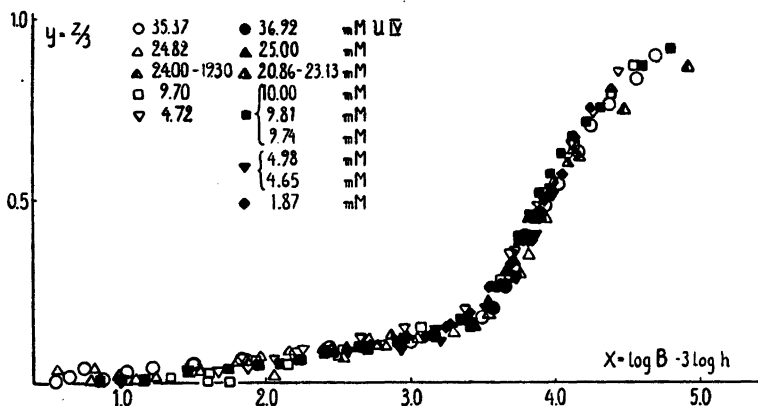
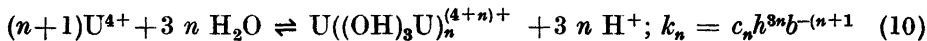


Fig. 5. Data for glass electrode measurements (circles) and hydrogen electrode measurements (dots) recalculated to the form  $y(x)$  assuming  $t = 3$ ,  $x = \log B - 3 \log h$  ( $M$  scale),  $y = Z/3$ .

adjustments were attempted to make the  $Z(x)$  curves coincide more closely; large as they may seem, they will influence the  $Z$  very little in the steep part of the curve: by about 0.01 in the former case and 0.04 in the latter.

*Comparison with simple mechanisms.* The  $y(x)$  curve was now compared with those calculated for a number of simple mechanisms discussed in AB II<sup>12</sup> and in part 8<sup>13</sup>. The steep part gave no fit with hypothesis I (no soluble complex, precipitate formed) or II (single complex formed, with  $n = N$ ). An acceptable fit was found with hypothesis IIIa, for values of  $k_0$  between 0.1 and 0.01. In mechanism IIIa it is assumed that complexes with all values of  $n$  are formed, and that the equilibrium constant  $k_n$  for the formation of the  $n$ :th "core + links" complex (concentration =  $c_n$ ) in this case



is given by

$$k_n = k_0 k^n \quad (11)$$

where  $k$  and  $k_0$  are constants.

A better value of  $k_0$  was found using the equation (AB II, 37)

$$k_0 = y[1 - 10^x(1-y)]^2(1-2y)^{-2} \cdot 10^{-x} \quad (12)$$

The abscissa  $x$  was measured for  $y = 0.7, 0.5(x_{\frac{1}{2}}), 0.3, 0.2$  and, for each value,  $10^x = 2 \cdot 10^{(x-x_{\frac{1}{2}})}$  was calculated. This gave  $k_0 = 0.042$ ,  $\log k_0 = -1.38$  when  $y = 0.7$ ,  $k_0 = 0.06$ ,  $\log k_0 = -1.22$  when  $y = 0.3$  and  $k_0 = 0.134$ ,  $\log k_0 = -0.87$ ,  $y = 0.2$ .

To estimate the uncertainty in  $k_0$  the difference  $x(y = 0.633, Z = 1.9) - x(y = 0.267, Z = 0.8)$  was plotted against  $k_0$ . The experimental value of this difference varied between 0.45 and 0.55, which would correspond to  $\log k_0 = -1.2 \pm 0.3$ .

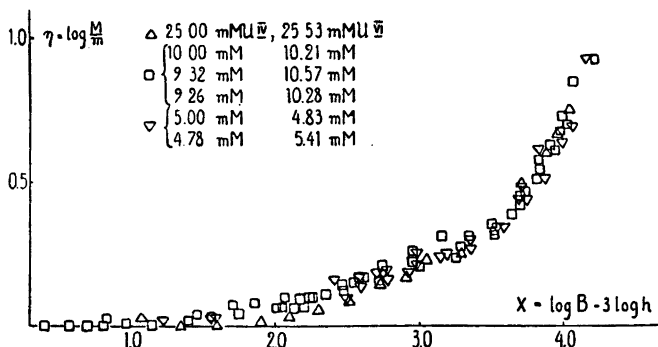


Fig. 6. Data for redox titrations recalculated to the form  $\eta(X)$  assuming  $t = 3$ ,  $\eta = \log(B/b)$ ,  $x = \log B - 3 \log h$  ( $M$  scale).

From  $x_{\frac{1}{2}}$  one also finds  $\log k = \log 2 - x_{\frac{1}{2}} = 3.6 \pm 0.1$ .

*Direct analysis of the curve  $y(x)$ .* A smooth curve  $y(x)$  was drawn through the points of Fig. 5. This curve was used to calculate

$$\log F = y \log e + \int_{-\infty}^x y dx = \eta \quad (13)$$

$$g = (1-y)F^{-1}; \quad u = 10^x F^{-1} \quad (14)$$

In this case

$$u = bh^{-t} = bh^{-3}; \quad g = \sum k_n u^n \quad (15)$$

The average number of  $U(OH)_3$  links per complex is defined by

$$\bar{n} = \frac{\sum n c_n}{\sum c_n} \quad (16)$$

One may calculate  $\bar{n}$  either by differentiating  $\log g(\log u)$ , or directly from  $y$  and  $F$ . (The second formula may be derived from eqns. 5, 6 and 7 in part 10<sup>5</sup> and eqns. 13 and 14 in this paper)

$$\bar{n} = \frac{d \log g}{d \log u} = \frac{y}{1-y-F^{-1}} \quad (17)$$

The squares ( $\square$ ) in Fig. 7 were obtained in this way. Whatever the details of the "core + links" reaction, one would expect  $\bar{n}$  to start at 1.0 for low  $x$  and then to increase with increasing  $x$ . The absurd behavior of the function  $\bar{n}(x)$  in Fig. 7, with a minimum less than 1, was at first ascribed to analytical errors. So, new  $\bar{n}(x)$  curves were calculated, subtracting 0.04 ( $\circ$ ) or 0.08 ( $\times$ ) units from each value of  $y$ . The  $\bar{n}$  curves are still senseless for low  $x$ ; moreover, these corrections would correspond to a very improbable error in the value of  $H$  for the original uranium(IV) solution.

So it was concluded that in the first stages of the hydrolysis, some species other than the "core + links" complexes must be formed. The values of  $\bar{n}$

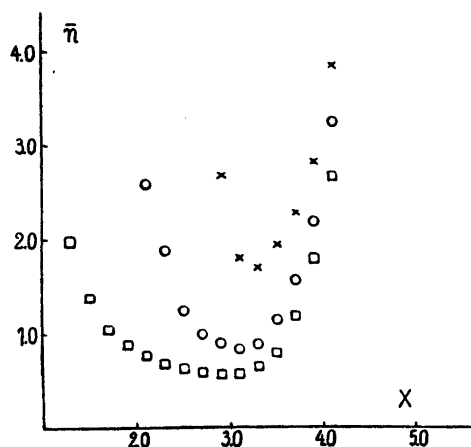
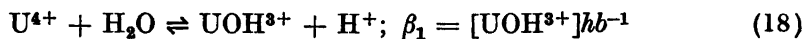


Fig. 7. Direct analysis of  $y(x)$  curve:  $\bar{n}$  as a function of  $x$ .  $y = 0$  ( $\square$ ),  $y = 0.04$  ( $\circ$ ),  $y = 0.08$  ( $\times$ ).

for high values of  $x$ , where the "core + links" mechanism seems to predominate, indicate that complexes with  $\bar{n}$  greater than 3, *i.e.* with more than 4 U, are present.

#### Correction for mononuclear reaction

It was found that the  $Z$  curves could be explained on the reasonable and simple assumption that, in addition to the "core + links" complexes, the mononuclear complex  $\text{UOH}^{3+}$  is formed



To determine the best values for the constants  $\beta_1$  for the mononuclear reaction and  $k$  for the "core + links" mechanism, a normalized projection map was used as indicated by Biedermann and Sillén<sup>14</sup>. If the "core + links" complexes with  $t = 3$ , and in addition only the first mononuclear complex are formed, then the total concentration of uranium(IV) is

$$B = b(1 + \beta_1 h^{-1} + \sum (n+1)k_n u^n) \quad (19)$$

and the concentration of OH bound by uranium(IV) is

$$BZ = \beta_1(h^{-1} + 3 \sum nk_n u^n) \quad (20)$$

We shall introduce the auxiliary normalized variables

$$\alpha = \beta_1 h^{-1}; \mathbf{B} = k\beta_1^{-3}B; v = ku \quad (21)$$

$$\text{and the function } g(v) = \sum k_n u^n; vg'(v) = \sum nk_n u^n \quad (22)$$

For the special case of hypothesis IIIa (with an integer value of  $t$ ) we have

$$g(v) = k_0 v(1-v)^{-1}; \quad vg'(v) = k_0 v(1-v)^{-2} \quad (22a)$$

Introducing (21) and (22) we find from (19) and (20)

$$B = b(1+\alpha+g+vg'); \quad BZ = b(\alpha+3vg') \quad (19a, 20a)$$

$$\mathbf{B} = v\alpha^{-3}(1+\alpha+g+vg'); \quad \mathbf{BZ} = v\alpha^{-3}(\alpha+3vg') \quad (19b, 20b)$$

The method consists in preparing a projection map of the experimental data in the form of curves  $y(x)_z$ , with the experimental variables

$$x = \log B - 3 \log h; \quad y = \log B \quad (23)$$

This plot is moved parallel to the axes across a projection map of calculated curves  $\bar{Y}(X)_z$  where the normalized variables are

$$X = \log \mathbf{B}\alpha^3 = x + \log k; \quad Y = \log \mathbf{B} = y + \log k - 3 \log \beta_1 \quad (24)$$

In the position which gives the best fit one can at once read the best values of  $X - x = \log k$  and  $Y - y = \log k - 3 \log \beta_1$

For calculating the normalized projection map one may eliminate  $\alpha$  from (19a) and (20a), to find

$$\alpha = (Z(1+g+vg') - 3vg')(1-Z)^{-1} \quad (25)$$

$$X = \log v + \log(1+g-2vg') - \log(1-Z) \quad (26)$$

$$Y = X - 3 \log \alpha = \log v + 2 \log(1-Z) + \log(1+g-2vg') - 3 \log(Z(1+g+vg') - 3vg') \quad (27)$$

Thus for a constant value of  $Z$ , corresponding values of  $X$  and  $Y$  can be calculated for various values of the auxiliary variable  $v$ . On applying this method (always using  $k_0 = 0.01$ ) and (21a) we found

$$\log k = X - x = -3.40 \pm 0.10 \quad (28)$$

$$\log k - 3 \log \beta_1 = Y - y = 2.5 \pm 0.3$$

$$\log \beta_1 = -1.95 \pm 0.10$$

The constants  $k$  and  $\beta_1$  can be determined independently from the  $\eta$  titrations, also using normalized projection maps<sup>14</sup>. In this case, an experimental plot  $\log B(\log h)_\eta$  and calculated curves  $\log \mathbf{B}(\log \alpha)_\eta$  were used. From (19a) and (19)

$$\eta = \log(1+\alpha+g+vg'); \quad \alpha = 10^\eta - (1+g+vg') \quad (29)$$

and from (19b)

$$\log \mathbf{B} = \log v + \eta - 3 \log \alpha \quad (30)$$

From the positions of best agreement, we found

$$\log k = \log \mathbf{B} - \log B = -3.30 \pm 0.05$$

$$\log \beta_1 = \log \alpha - \log h = -2.00 \pm 0.10$$

In order to test whether some other value of  $k_0$  could be used successfully, the family of curves  $y(x)_Z$  was constructed from the experimental data, when  $x = \log B - 3 \log h$  and  $y = \log B$ . This diagram was compared with projection maps of calculated curves when  $k_0$  was 0.00 and 0.20. These two values could be eliminated in the region of vertical lines, their spacing in the calculated projection map was much too narrow with  $k_0 = 0$ , and too broad with  $k_0 = 0.20$ .

A diagram  $\log k(\log \beta_1)$  was made in which for each value of  $\log k$ , the range of  $\log \beta_1$  which gave the best fit with the  $Z$  and  $\eta$  data, was marked out. From the common area, a middle set and two extreme sets were selected:

$$\begin{array}{ll} \log k = -3.30, \log \beta_1 = & -2.00 \\ & -3.37 \quad -1.98 \\ & -3.45 \quad -1.95 \end{array}$$

With these three sets, theoretical curves  $Z(\log h)_B$  were calculated for the different  $B$  values used in the  $Z$  titrations with hydrogen and glass electrodes. The second (full-drawn) and the third (broken) sets gave the best agreement (Figs. 1 and 3).

The same three sets of constants were also used to calculate curves  $\eta(\log h)_B$  (Fig. 4) for the  $B$  values used in the titrations. Here also, the second and third set gave the best agreement. It may thus be assumed that

$$\log k = -3.4 \pm 0.1; \log \beta_1 = -2.0 \pm 0.1; \log k_0 = -1.2 \pm 0.3$$

The constant of the mononuclear reaction,  $\beta_1$ , agrees reasonably well with Kraus's constant  $^2 \log \beta_1 = -1.63$  in 2 M perchlorate solution. The constant  $\log \beta_1 = -1.63$  in 2 M perchlorate is somewhat higher than  $\log \beta_1 = -2.0 \pm 0.1$  in 3 M perchlorate as one would expect, especially when one compares it with the constants of Kraus  $^2$  at other ionic strengths:

$\log \beta_1 = -1.56$  for 1 M,  $= -1.45$  for 0.55 M, and  $= -1.23$  for 0.1 M  $\text{ClO}_4^-$

It was tested whether the experimental data could be explained by assuming only the second mononuclear complex  $\text{U}(\text{OH})_2^{2+}$ . The projection map  $\log \mathbf{B}(X)_Z$  was calculated when  $\mathbf{B} = v\alpha^{-3}(1 + \alpha^2 + g + vg')$  (31)

$$\mathbf{BZ} = v\alpha^{-3}(2\alpha + 3 vg') \quad (32)$$

The experimental data  $\log B(x)_Z$  were compared with these curves. The fit was somewhat satisfactory with the high  $Z$  values but not with the low  $Z$  values.

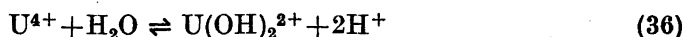
Then it was assumed that both the mononuclear complexes  $\text{UOH}^{3+}$  and  $\text{U}(\text{OH})_2^{2+}$  are formed. The projection map (14)  $\log \mathbf{B}(X)_Z$  was constructed for

$$\log \mathbf{B} = \log v + \log (1 + \alpha + l\alpha^2 + g + vg') - B \log \alpha \quad (33)$$

$$X = \log v + \log (1 + \alpha + l\alpha^2 + g + vg') \quad (34)$$

$$\text{Here } l = \beta_2\beta_1^{-2} \quad (35)$$

where  $\beta_1$  is the equilibrium constant for the reaction



The statistical value  $l = 1/4$  was assumed, which means that both protons are split off equally easily. As before,  $g$  was taken from (22 a).

The agreement of experimental data with these theoretical curves was somewhat less satisfactory than with the curves when only the first complex  $\text{UOH}^{3+}$  was assumed. The following constants were calculated from glass electrode and hydrogen electrode measurements.

$$\begin{aligned} \log \beta_1 &= -1.7 \pm 0.2 \\ \log \beta_2 &= -4.0 \pm 0.2 \end{aligned}$$

The data of the redox electrode measurements were treated in the same way. Only the second complex was at first assumed and the projection map was calculated when

$$\log \alpha = \frac{1}{2} \log (10^\eta - (1 + g + vg')) \quad (37)$$

and

$$\log \mathbf{B} = \log v + \eta - 3 \log \alpha \quad (38)$$

The experimental data did not fit in this case either and therefore the both complexes with  $l = 1/4$  were assumed. The projection map was constructed with

$$\log \mathbf{B} = \log v + \log (1 + \alpha + l\alpha^2 + f + vg') - 3 \log \alpha \quad (39)$$

$$\log \alpha = \log (2\sqrt{1 - (1 + g + vg' - 10^\eta) - 2}) ; \quad \eta = \log \frac{B}{b} \quad (40)$$

Also here the fit was not so good as with the assumption that only one mononuclear complex  $\text{UOH}^{3+}$  is formed. The constants obtained on testing were:

$$\begin{aligned} \log \beta_1 &= -1.7 \pm 0.1 \\ \log \beta_2 &= -4.0 \pm 0.1 \end{aligned}$$

*Influence of uranium (V).* In the previous calculations on the  $\eta$  titration data, the presence of uranium(V),  $\text{UO}_2^+$ , was neglected. According to Kraus<sup>15</sup>,  $K = 9.6 \times 10^7$  for the reaction  $2\text{UO}_2^+ + 4\text{H}_3\text{O}^+ \rightleftharpoons \text{UO}_2^{2+} + \text{U}^{4+} + 6\text{H}_2\text{O}$  in 1.96 M perchlorate medium; a specific solution contained 0.361 mM U(IV), 0.536 mM U(V), 2.41 mM U(VI), and 4.95 mM  $\text{H}^+$ . A rough calculation, using  $K = 10^9$ , indicates that appreciable amounts of U(V) are present in solutions which contain both U(IV) and U(VI) and  $[\text{H}^+]$  approximately equal to or less than 10 mM. Then the correct  $\eta(x)_B$  curves would be slightly to the left of these now used. The correction would in our experiments be at most of an order of magnitude corresponding to about 1 mV in  $E_r$ , which is still within the limits of the experimental error.

## STRUCTURE OF THE COMPLEXES

The equilibrium data give no information about the shape of the complexes  $U((OH)_3U)_n^{(4+n)+}$ . Lundgren<sup>16,17</sup> has studied the crystal structures of two uranium(IV) hydroxide sulfates. In  $U_6O_4(OH)_4(SO_4)_6$  he found separate groups,  $U_6O_4(OH)_4^{12+}$ ; on the other hand, in  $U(OH)_2SO_4$  he found infinite chains  $(U(OH)_2^+)_n$ , which are analogous to the chains in the isomorphous compound  $Th(OH)_2SO_4$ .

It therefore seems reasonable to assume that the uranium(IV) complexes are thread-like,  $U(OH)_n^{4+n}$ , by analogy with the thorium structure.

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