

## Studies on the Hydrolysis of Metal Ions

### 24. Hydrolysis of the Uranyl Ion, $\text{UO}_2^{2+}$ , in Perchlorate Self-Medium

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The hydrolysis of  $\text{UO}_2^{2+}$  has been studied in perchlorate self-medium at 25°C, using quinhydrone or glass electrodes, which gave concordant results. The data indicate the two main reactions:  $2\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{OH}^{3+} + \text{H}^+$  (equilibrium constant  $\beta_{12}$ ) and  $2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$  (equilibrium constant  $\beta_{22}$ ). Small deviations at low acidities could be explained assuming the reaction  $3\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$  (equilibrium constant  $\beta_{43}$ ). The values obtained were: in the medium 0.4  $\text{UO}_2^{2+}$ , 1.0  $(\text{Na})\text{ClO}_4$ ,  $\log \beta_{12} = -3.66 \pm 0.20$ ,  $\log \beta_{22} = -6.02 \pm 0.03$ . In 1.4  $\text{UO}_2^{2+}$ , 3.0  $(\text{Na})\text{ClO}_4$ ,  $\log \beta_{12} = -3.68 \pm 0.20$ ,  $\log \beta_{22} = -6.31 \pm 0.03$ ,  $\log \beta_{43} \approx -12.6$  (quinh.),  $-12.9?$  (glass). The values for  $\beta_{22}$  and  $\beta_{43}$  are of the same order as obtained in an inert medium. The concentration of  $(\text{UO}_2)_2\text{OH}^{3+}$  is appreciable only at high  $\text{UO}_2^{2+}$  concentration.

In an earlier paper<sup>1</sup> in this series, it was suggested that added information on the complex formation between two reagents, A and B, can be gained by equilibrium studies in what was termed as "self-medium". This means that one of the reagents, say B, which is charged, is kept at a high and constant total concentration and forms the major part of the ions of this sign of charge; the inert ions of opposite charge are kept at constant concentration. Self-medium measurements should especially give information on complexes  $\text{A}_p\text{B}_q$  with a higher ratio  $q/p$  than may be studied with the usual "inert medium" method.

The principle was applied to the hydrolysis of the thorium ion,  $\text{Th}^{4+}$ , in chloride self-medium. The data could be explained assuming the two complexes  $\text{Th}_2(\text{OH})_2^{6+}$  and  $\text{Th}_2\text{OH}^{7+}$ ; for the first, a formation constant was found which agreed well with inert-medium data, the second complex was discovered by the self-medium work<sup>1</sup>.

In the present work, the self-medium method has been applied to the hydrolysis of the uranyl ion in perchlorate self-medium. Denoting as usual the total concentration of B by  $B$ , and the "analytical" excess concentration of  $H^+$  by  $H$ , which was negative in the majority of our solutions, the equilibrium solutions were composed as follows:

Medium	$E$	$H$	$[Na^+]$	$[ClO_4^-]=I$
0.4 $UO_2^{2+}$ , 1.0 (Na)ClO <sub>4</sub>	0.4	$H$	0.2 - $H$	1.0
1.4 $UO_2^{2+}$ , 3.0 (Na)ClO <sub>4</sub>	1.4	$H$	0.2 - $H$	3.0

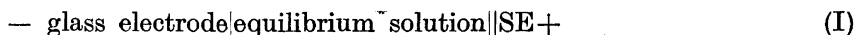
The experiments were performed as titrations, starting with a certain solution S and adding from a buret measured amounts of another solution T. The compositions of the various solutions S and T followed the scheme above; Table 1 gives the values for  $H$  in S, T, and the final solution in the various experiments.

Table 1. Survey of titrations.

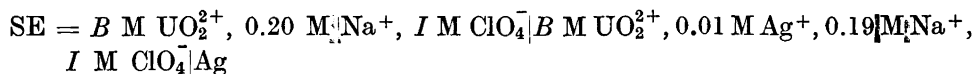
$B$	$I$	$H$		[Final	$H$	Corr	mV	Symbol	
		S	T	quinh.	glass	quinh.	glass	quinh.	glass
0.4	1.0	0.20	-0.30	0.08	-0.06	-	-	+	○
		-0.14	0.20	0.09	0.09	0.5	-	×	□
1.4	3.0	-0.20	0.20	0.05	0.05	0.5	-1.8	+	□
		0.20	-0.20	0.04	0.04	0.5	-1.8	+	□
		0.22	-0.18	0.02	0.02	-	-	×	●
		-0.18	0.22	0.02	0.02	-0.7	-	×	●
		0.20	-0.20		0.00		+50		○
		-0.20	0.20		0.04		+49.5		○

Rounded values are given for  $H$ . The two last titrations were made with a different type of glass electrode. In each solution,  $[UO_2]_{total} = B$ ,  $[ClO_4^-] = I$ ,  $[Na^+] = 0.2 - H$ .

After each addition of T, the hydrogen ion concentration,  $h$ , was measured with one of the cells



Separate experiments were made with cells I and II. The reference electrode was



It so happens that the predominating species for  $UO_2^{2+}$  seem to have the same types of formula as for  $Th^{4+}$ ; for the calculations one may then take over a number of equations which were derived and applied in the previous paper <sup>1</sup>.

## S y m b o l s

A, B = reactants, here  $\text{OH}^-$  ( $-\text{H}^+$ ) and  $\text{UO}_2^{2+}$ ;  $a$  = concentration of free A, here  $a = h^{-1}$ ;  $b$  = concentration of free B;  $B$  = total concentration of B;  $E$  = electromotive force of cell (I) or (II);  $E_0$  = constant in eqn. (1);  $f = 2u^2 + 2ku$ , eqn (6);  $F(h) = BZ + \Delta$ , eqn (2);  $h = [\text{H}^+]$ ;  $H$  = analytical excess of  $\text{H}^+$ , often negative;  $I = [\text{ClO}_4^-]$  in medium;  $j$  = constant in term for liquid junction potential, eqn (1);  $k$  = parameter defined by eqn (6);  $p, q$  = coefficients in formula of complex  $\text{A}_p\text{B}_q$ ;  $u$  = normalized variable, corresponding to  $a$ , eqn (6);  $Z$  = average number of A (here  $\text{OH}^-$ ) bound per B (here  $\text{UO}_2^{2+}$ );  $\beta_{pq}$  = equilibrium constant for formation of  $\text{A}_p\text{B}_q$ , eqn (3);  $\Delta$  = analytical error in  $H$ , eqn (2).

In the equilibrium constants, and figures, the unit M (mole/liter) is used throughout.

## REAGENTS

*Uranyl perchlorate.* In our first experiments, with  $B = 0.4$ , we started from ammonium uranyl hydroxide. This substance had long ago been precipitated from uranyl nitrate, which had been purified by ether extraction. The hydroxide was ignited, and the  $\text{U}_3\text{O}_8$  formed was dissolved in  $\text{HNO}_3$ . The solution was evaporated repeatedly with  $\text{HClO}_4$  under an infrared lamp, until no trace of nitrate ion could be detected.

For the experiments with  $B = 1.4$ , we started with spectroscopically pure  $\text{UO}_3$ , obtained from AB Atomenergi. A possible impurity of  $\text{NH}_3$  was removed by igniting the oxide to  $\text{U}_3\text{O}_8$ , which was then dissolved in 6 M  $\text{HClO}_4$ , 30 %  $\text{H}_2\text{O}_2$  being added. The excess of acid was removed by evaporation under an infrared lamp.

The total uranium concentration was determined by precipitating with oxine or  $\text{NH}_3$  at pH = 7, igniting the precipitate, and weighing as  $\text{U}_3\text{O}_8$ . The results obtained with oxine or  $\text{NH}_3$  agreed within 0.1 %.

Total perchlorate was determined by passing a known amount of solution through a  $\text{H}^+$ -saturated ion exchanger (Wofatit KPS-200), and titrating the eluate with NaOH.

The hydrogen ion excess,  $H$ , in the stock solutions was determined by emf titration with NaOH, after diluting to 0.02, 0.04, or 0.08 M  $\text{UO}_2^{2+}$ , using diagrams according to Gran<sup>2</sup>. The values for  $H$  from experiments of different dilutions were consistent, and the estimated uncertainty in  $H$  will correspond to an error in  $Z$  of at most 0.004, probably only 0.002. The  $H$  so determined came out slightly higher than  $[\text{ClO}_4^-] - 2B$ , which is the difference between two much larger numbers and cannot be determined with sufficient accuracy.

*Sodium perchlorate* was prepared from sodium carbonate p.a. and perchloric acid p.a. *Perchloric acid* was standardized against solid  $\text{KHCO}_3$  and standard NaOH. *Sodium hydroxide* solution was prepared as described earlier<sup>3</sup>.

*Apparatus.* The Ag, AgCl electrodes were prepared according to Brown<sup>4</sup>. In the quinhydrone half-cell, a bright Pt foil was used. The glass electrodes were Radiometer "red" electrodes G 202A (for  $B = 0.4$ ), G 202 BT57, and G 202 B38 (for  $B = 1.4$ ). The electrode vessel was of the usual "Wilhelm" type<sup>5</sup>, and the cells were kept in a paraffin oil thermostat at  $25.0 \pm 0.1^\circ\text{C}$  in a thermostated room. The emfs were measured with a Vernier compensator, or with a Radiometer potentiometer PHM 3.

With the medium 0.4  $\text{UO}_2^{2+}$ , 1.0 (Na)ClO<sub>4</sub>,  $E$  became constant within 5 min; in general, the reading was taken 10 min after each addition. In the medium 1.4  $\text{UO}_2^{2+}$ , 3.0 (Na)ClO<sub>4</sub>, the emfs stabilized somewhat more slowly, especially with the glass electrodes, so one had to wait 15–30 min for a constant reading.

TREATMENT OF DATA

The primary data given by each titration were sets of values ( $E, H$ ), where  $E$  is the emf of cell (I) or (II), and  $H$  is the analytical excess of hydrogen ions calculated for each point; (in the range with appreciable hydrolysis,  $H$  was negative). The fundamental equations are

$$E = E_0 - 59.15 \log h + jh \tag{1}$$

$$H = h - BZ - \Delta = h - F(h) \tag{2}$$

Here,  $E_0$  and  $j$  are constants;  $jh$  is the liquid junction potential, which is expected to be linear with  $h$ .  $BZ$  is the amount of  $\text{OH}^-$  bound by B per liter of solution, and may be expressed as a function of  $h$  applying the law of mass action, eqns (4) and (5) below;  $\Delta$  is the analytical error in  $H$ .

The  $E(H)$  plots for various titrations did not coincide exactly, which might be ascribed either to variations in  $E_0$ , or to variations in  $\Delta$ . In the same way as described in our previous paper <sup>1</sup>, it was checked graphically that the spread is in  $E_0$  and not in  $\Delta$ . Indeed, there was no reason to assume an appreciable

Table 2. Medium 0.4  $\text{UO}_2^{2+}$ , 1 (Na)ClO<sub>4</sub>. Experimental data  $H$  and  $E$  (corrected) for four titrations. Every other point given,  $\log h$  calculated from  $E$  with  $E_0 + 3.59.15 = 164.9$  mV for quinhydrone titrations, and  $E_0 + 3.59.15 = 493.7$  for glass electrode titrations,  $j = 51.0$  mV M<sup>-1</sup>.

<i>quinhydrone electrode</i>							
$H$	$E$	$\log h$	$Z$	$H$	$E$	$\log h$	$Z$
symbol +				symbol ×			
0.2020	38.6	-0.691	-0.006	-0.1450	165.2	-3.005	0.360
0.1671	41.9	-0.777	0.000	-0.1136	159.2	-2.904	0.282
0.1275	47.0	-0.897	-0.002	-0.0760	150.8	-2.760	0.189
0.0866	54.8	-1.064	-0.001	-0.0421	140.2	-2.580	0.107
0.0529	65.3	-1.270	0.001	-0.0191	128.0	-2.372	0.053
0.0246	82.0	-1.578	0.005	0.0029	104.5	-1.970	0.015
0.0005	110.4	-2.079	0.020	0.0275	78.1	-1.506	0.004
-0.0202	129.9	-2.408	0.060	0.0561	63.3	-1.232	0.001
-0.0383	139.0	-2.562	0.103	0.0919	53.2	-1.030	-0.001
-0.0627	147.3	-2.702	0.162				
<i>glass electrode</i>							
$H$	$E$	$\log h$	$Z$	$H$	$E$	$\log h$	$Z$
symbol ○				symbol □			
0.2020	367.4	-0.691	0.004	-0.1430	494.8	-3.017	0.360
0.1671	370.7	-0.777	0.000	-0.1116	488.8	-2.917	0.282
0.1275	375.8	-0.897	-0.002	-0.0740	480.1	-2.770	0.189
0.0866	383.4	-1.061	0.001	-0.0401	469.3	-2.587	0.107
0.0529	394.2	-1.272	0.002	-0.0171	457.2	-2.383	0.053
0.0246	411.1	-1.582	0.004	0.0049	433.4	-1.977	0.014
0.0005	440.1	-2.094	0.019	0.0295	407.0	-1.509	0.004
-0.0202	459.7	-2.425	0.060	0.0581	392.0	-1.230	0.002
-0.0383	468.8	-2.579	0.102	0.0939	381.9	-1.029	-0.001
-0.0599	476.1	-2.702	0.155				

Table 3. Medium 1.4  $\text{UO}_2^{2+}$ , 3 (Na)ClO<sub>4</sub>. Experimental data  $H$  and  $E$  for six titrations. Every other point given,  $\log h$  calculated from  $E$  with  $E_0 + 3 \cdot 59.15 = 157.2$ ,  $j = 8.0$  mV M<sup>-1</sup> for quinhydrone titrations, and  $E_0 + 3 \cdot 59.15 = 260.7$ ,  $j = 8.8$  mV M<sup>-1</sup> for glass electrode titrations.

<i>quinhydrone electrode</i>							
$H$	$E$	$\log h$	$Z$	$H$	$E$	$\log h$	$Z$
symbol +				symbol ×			
-0.1960	125.6	-2.466	0.142	0.2220	19.8	-0.647	0.002
-0.1710	122.9	-2.420	0.125	0.2091	21.2	-0.672	0.002
-0.1490	120.2	-2.374	0.109	0.1856	24.2	-0.726	0.001
-0.1204	116.1	-2.305	0.089	0.1649	26.9	-0.775	0.002
-0.0819	109.1	-2.187	0.063	0.1297	32.7	-0.878	0.002
-0.0489	100.4	-2.040	0.041	0.0887	41.4	-1.030	0.003
-0.0145	86.3	-1.801	0.022	0.0620	49.2	-1.166	0.004
0.0320	61.3	-1.375	0.007	0.0220	66.4	-1.462	0.009
0.2034	22.1	-0.689	0.000	-0.1780	123.5	-2.430	0.131
0.1905	23.7	-0.718	0.000	-0.1651	122.1	-2.407	0.121
0.1670	26.8	-0.773	0.001	-0.1416	119.5	-2.363	0.105
0.1463	29.8	-0.826	0.002	-0.1208	116.4	-2.310	0.090
0.1111	36.2	-0.943	0.002	-0.0857	109.9	-2.200	0.066
0.0701	46.5	-1.118	0.004	-0.0446	98.8	-2.013	0.039
0.0434	56.1	-1.286	0.006	-0.0180	87.7	-1.825	0.024
				0.0183	67.9	-1.489	0.010
<i>glass electrode</i>							
$H$	$E$	$\log h$	$Z$	$H$	$E$	$\log h$	$Z$
symbol □				symbol ● contd.			
-0.1960	230.2	-2.484	0.142	-0.1781	229.5	-2.473	0.130
-0.1710	227.3	-2.435	0.125	-0.1502	225.9	-2.412	0.111
-0.1490	224.4	-2.386	0.109	-0.1185	221.0	-2.329	0.088
-0.1204	220.1	-2.314	0.090	-0.0798	213.2	-2.197	0.062
-0.0819	213.0	-2.194	0.063	-0.0539	206.2	-2.079	0.045
-0.0489	203.7	-2.036	0.041	-0.0280	196.8	-1.919	0.029
-0.0145	189.9	-1.801	0.022	-0.0003	182.6	-1.678	0.015
0.0320	164.8	-1.374	0.007	0.0220	170.0	-1.463	0.009
0.2034	125.9	-0.691	0.000	symbol ○			
0.1905	127.3	-0.716	0.001	0.2040	125.9	-0.691	0.000
0.1670	130.3	-0.770	0.002	0.1790	128.8	-0.743	0.001
0.1463	133.3	-0.824	0.003	0.1468	133.7	-0.831	0.001
0.1111	139.6	-0.936	0.003	0.1117	139.8	-0.939	0.002
0.0701	150.2	-1.122	0.004	0.0767	148.0	-1.083	0.004
0.0434	160.0	-1.291	0.006	0.0440	159.2	-1.277	0.006
				0.0040	179.8	-1.632	0.014
symbol ●							
0.2215	123.5	-0.648	0.004	-0.1960	230.2	-2.484	0.142
0.2122	124.6	-0.667	0.002	-0.1710	227.4	-2.437	0.125
0.1856	127.8	-0.726	0.002	-0.1489	224.6	-2.390	0.109
0.1553	131.9	-0.799	0.002	-0.1203	220.4	-2.319	0.089
0.1297	136.0	-0.873	0.003	-0.0817	213.0	-2.194	0.063
0.1027	141.7	-0.975	0.002	-0.0513	204.8	-2.055	0.043
0.0800	147.2	-1.071	0.003	-0.0183	192.0	-1.837	0.023
0.0573	154.5	-1.196	0.005	0.0040	180.0	-1.632	0.014
0.0353	163.2	-1.347	0.007	0.0316	164.9	-1.375	0.007
0.0220	169.9	-1.462	0.009				

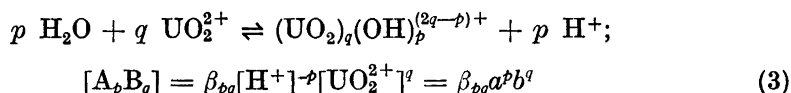
error  $\Delta$ . Since  $\text{UO}_2^{2+}$  hydrolyses at lower acidities than  $\text{Th}^{4+}$ , one may determine  $H$  accurately by acid-base titration and Gran plot, which was not possible for  $\text{Th}^{4+}$ . In the following,  $\Delta = 0$  was assumed.

The quinhydrone and glass electrode measurements for  $B = 0.4$  were made to coincide by applying shifts along the  $E$  axis, whereas for  $B = 1.4$ , data with glass and quinhydrone were treated separately. Thus three separate curves  $E(H)$  were obtained for the calculations. These corrected data are given in Tables 2 ( $B = 0.4$ ) and 3 ( $B = 1.4$ ).

Just as in the case of thorium, a preliminary treatment showed that the data for the lowest  $Z$  agreed well with a mechanism with a complex containing one OH group, whereas for higher  $Z$ , they indicated a complex with 2 OH. Data up to about  $Z = 0.15$  were used in the calculations.

It was concluded that the main products are the complexes  $\text{AB}_2 = (\text{UO}_2)_2\text{OH}^{3+}$  and  $\text{A}_2\text{B}_2 = (\text{UO}_2)_2(\text{OH})_2^{2+}$ . The assumption of 2 B per complex will be justified in the discussion below. Later on also the complex  $\text{A}_4\text{B}_3$  had to be included to account for certain deviations.

We denote by  $\beta_{pq}$  the equilibrium constant for the formation of  $\text{A}_p\text{B}_q$ :



The law of mass action, and the definitions, then give

$$B = b + 2 \beta_{12}ab^2 + 2 \beta_{22}a^2b^2 (+ 3 \beta_{43}a^4b^3) \quad (4)$$

$$BZ = \beta_{12}ab^2 + 2\beta_{22}a^2b^2 (+ 4\beta_{43}a^4b^3) \quad (5)$$

In the calculations, eqns (1) and (2) were used alternately for successive approximations, as described in the thorium paper<sup>1</sup> until a theoretical function  $F(h)$ , and values for  $E_0$  and  $j$ , had been found which generated each other on application of (1) and (2) to the experimental data ( $E, H$ ).

In the calculations, the auxiliary normalized variable  $u$ , the parameter  $k$ , and the abbreviation  $f(u)$  were used<sup>1</sup>:

$$u^2 = 2\beta_{22}a^2B; ku = 2\beta_{12}aB; f = 2u^2 + 2ku \quad (6)$$

One may then derive an expression (Ref<sup>1</sup>, eqn 13) for  $Z$  as a function of  $u$ , and construct plots of  $Z(\log u)_k$  for a number of values for  $k$ , which may be compared with experimental curves  $Z(\log a)$ . From the value of  $k$ , and the difference of coordinates ( $\log u - \log a$ ), at the position of the best fit,  $\log \beta_{22}$  and  $\log \beta_{12}$  could be obtained, using (6) above or Ref.<sup>1</sup>, eqns 14 and 15.

When this method was applied, it was seen that for the very lowest acidities there was an unavoidable bend in the plot ( $E + 59.15 \log h$ ) versus  $h$ , indicating the existence of at least one more complex. Now, the data in inert medium<sup>6,7</sup> had indicated the existence of a series of complexes,  $\text{B}(\text{A}_2\text{B})_n$ . The first member,  $\text{A}_2\text{B}_2$ , had already been found with self-medium. It was then reasonable

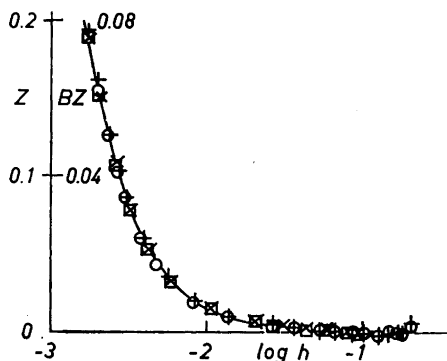


Fig. 1. Hydrolysis of  $\text{UO}_2^{2+}$ , medium 0.4  $\text{UO}_2^{2+}$ , 1.0  $(\text{Na})\text{ClO}_4$ .  $Z$  versus  $\log h$ . Points: calculated from experimental data  $E(H)$ , Table 2, using  $E_0$  and  $j$  from Table 4. Curve: calculated  $Z$ , assuming values for  $\beta_{22}$  and  $\beta_{12}$  from Table 4.

to assume that the deviations are due to the second member,  $\text{A}_4\text{B}_3$ , and on this assumption,  $\beta_{43}$  was calculated using (5), which gives

$$BZ - \beta_{12}ab^2 - 2\beta_{22}a^2b^2 = 4\beta_{43}a^4b^3 \quad (7)$$

The value for  $b$  in each point was obtained from  $B$ ,  $a$ , and eqn (4). In this way,  $\log \beta_{43}$  was estimated for the stronger medium ( $B = 1.4$ ); if this correction was applied to  $BZ$  in  $F(h)$ , the  $E_0$  plots were found to be more nearly linear (Fig. 4, Fig. 5). Because of the greater spread of the glass electrode data, the value for  $\beta_{43}$  derived from them is especially uncertain. For the weaker medium ( $B = 0.4$ ), the deviation is smaller, and no attempt was made to estimate  $\beta_{43}$ .

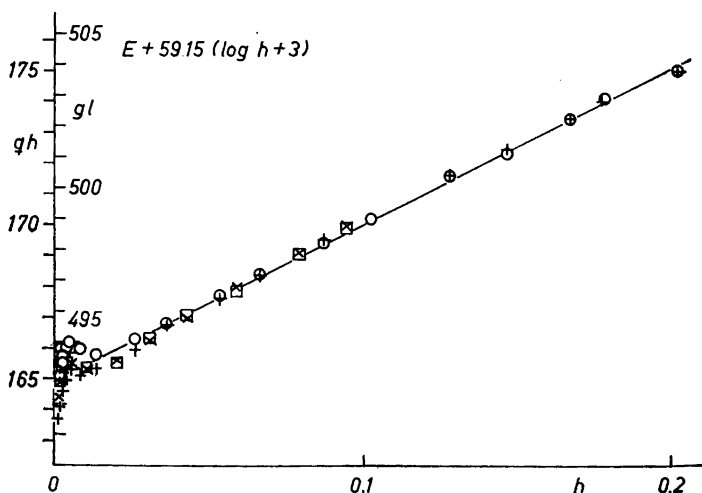


Fig. 2. Medium 0.4  $\text{UO}_2^{2+}$ , 1.0  $(\text{Na})\text{ClO}_4$ . Abscissa:  $\log h$ , calculated from  $H$  and  $Z$ , using values for  $\beta_{12}$  and  $\beta_{22}$  in Table 4. Ordinate:  $E + 59.15 (\log h + 3)$ . Straight line: given by values of  $j$  and  $E_0$  in Table 4.

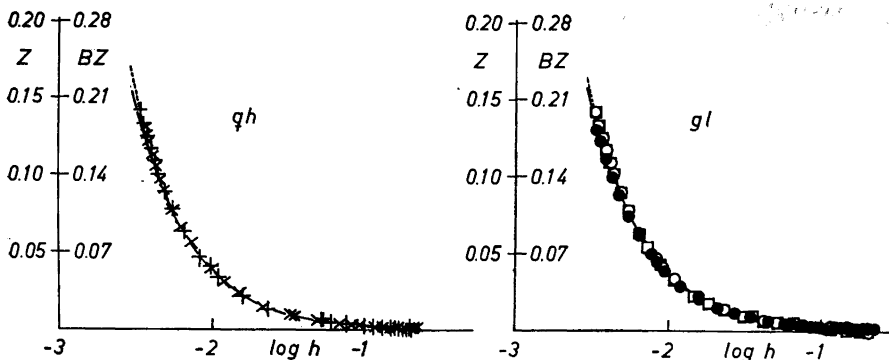


Fig. 3. Hydrolysis of  $\text{UO}_2^{2+}$ , medium 1.4  $\text{UO}_2^{2+}$ , 3.0 (Na)ClO<sub>4</sub>. Experimental points and full-drawn curve obtained as in Fig. 1. Left: quinhydrone electrode data, right: glass electrode data. The dotted lines show the correction obtained by assuming the complex  $\text{A}_4\text{B}_3$ .

It has been pointed out by Professor Robert Connick that if the liquid junction potential is calculated from the Henderson equation, a plot like Fig. 2 would show an upward bend of  $(E + 59.15 \log h)$  at the lowest values for  $h$ , because in this range  $\text{Na}^+$  ions replace a considerable part of the  $\text{UO}_2^{2+}$  ions. Rough estimates of the ionic mobilities, using unpublished data of Dr George Biedermann, indicate that this effect would be of the order of a few 0.1 mV thus much less than the observed effect, which we have ascribed to  $\beta_{43}$ . Although this estimate is too uncertain to justify any correction, it shows that one should be careful not to press the data too much in this region.

The values finally obtained for equilibrium constants,  $E_0$ , and  $j$ , are given in Table 4. The calculated values for  $h$  and  $Z$  are given in Tables 2 and 3

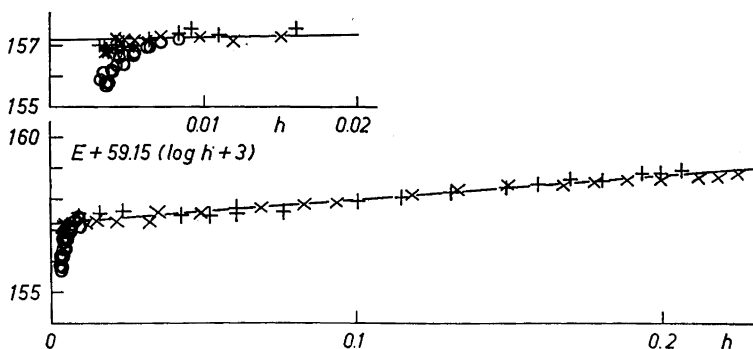


Fig. 4. Medium 1.4  $\text{UO}_2^{2+}$ , 3.0 (Na)ClO<sub>4</sub>, quinhydrone electrode. Plots for  $E_0$  and  $j$ , calculated as in Fig. 2. Crosses: corrected for  $\beta_{43}$ . Circles: not corrected for  $\beta_{43}$ , shown only for  $h < 10$  mM; for higher  $h$ , the difference is negligible.



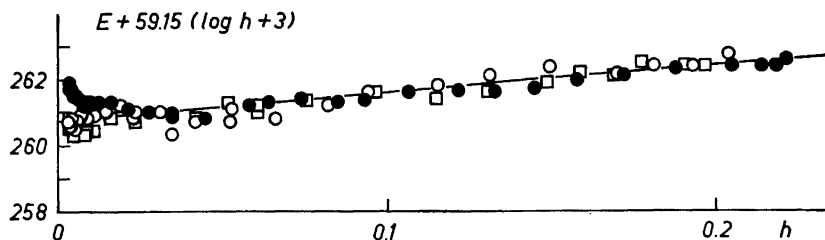


Fig. 5. Medium: 1.4  $\text{UO}_2^{2+}$ , 3.0  $(\text{Na})\text{ClO}_4$ , glass electrode. Plot of  $E + 59.15 (\log h + 3)$  versus  $h$ , calculated as in Fig. 2, assuming  $\log \beta_{43} = -12.9$ . Difference between series indicates spread in glass electrode data.

(every other point given), and the corresponding diagrams are given in Figs. 1, 2 ( $B = 0.4$ ), 3, 4, and 5 ( $B = 1.4$ ).

It has been asked, whether the assumption of  $\text{AB}_2$  is necessary and whether the whole effect could not be explained by  $\text{A}_2\text{B}_2$ , and some deviation of the liquid junction potential from linear behavior. To answer this question, it was assumed that  $\text{A}_2\text{B}_2$  is the only complex present; assuming various values for  $\beta_{22}$ , eqn (2) makes it possible to calculate  $h$  directly from  $H$ ; inserting this in (1), one might plot  $E + 59.15 \log h$  versus  $h$ ; the results for  $B = 1.4$  M are shown in Fig. 6. Deviations from linearity of the order of 10–15 mV cannot be avoided, whatever value for  $\beta_{22}$  is chosen, and so it does not seem possible to dispense with  $\text{AB}_2$  in the explanation.

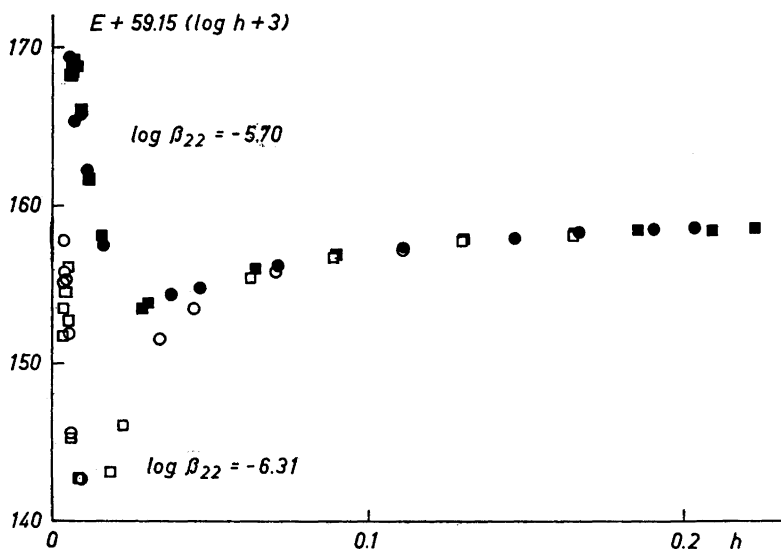


Fig. 6. Medium: 1.4  $\text{UO}_2^{2+}$ , 3.0  $(\text{Na})\text{ClO}_4$ . Plots for  $E_0$  and  $j$ , calculated neglecting  $\text{AB}_2$  and assuming  $\log \beta_{22} = -5.70$  (black symbols) and  $-6.31$  (open symbols). Quinhydrone electrode; circles correspond to  $+$  in Fig. 4, squares to  $\times$ . Non-linearity of plot indicates that the data cannot be explained by  $\text{A}_2\text{B}_2$  alone.

Table 4. Equilibrium constants etc obtained by successive approximations from the experimental data  $E(H)$ . Emfs in mV, concentrations in M.

Quantity	0.4 $\text{UO}_2^{2+}$ , 1.0 (Na)ClO <sub>4</sub>		1.4 $\text{UO}_2^{2+}$ , 3.0 (Na)ClO <sub>4</sub>	
			quinh	glass
$\log k$	-0.7		-0.3	-0.3
$\log u - \log a$	-3.06		-2.93	-2.94
$\log \beta_{22}$	-6.02		-6.31	-6.32
$\log \beta_{12}$	-3.66		-3.68	-3.69
$\log \beta_{43}$	(not est.)		-12.6	(-12.9)
$j$	51.0		8.0	8.8
$E_0 + 3 \cdot 59.15$	164.9 (qh), 493.7 (gl)		157.2	260.7

Estimated uncertainty: approximately  $\pm 0.2$  in  $\log k$  and  $\log \beta_{12}$ ,  $\pm 0.03$  in  $\log \beta_{22}$ . Different type of glass electrode was used in the two media. Of the  $j$  values 8.0 and 8.8, that for "quinh" was more accurately determined. The difference is within the limits of error of the "glass" values.

### DISCUSSION

When equilibria A—B are studied in a self-medium with a high and constant concentration of B, the data allow a rather certain conclusion on the values of  $p$  in the predominating complexes  $A_pB_q$ , whereas the assignment of  $q$  cannot be made with certainty from self-medium data alone.

From the data presented in this paper one may conclude that there are species with 1 OH, 2 OH, and probably 4 OH. The formulas ascribed above have been  $AB_2$ ,  $A_2B_2$ , and  $A_4B_3$ , thus  $(\text{UO}_2)_2\text{OH}^{3+}$ ,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ , and  $(\text{UO}_2)_3(\text{OH})_4^{2+}$ , as usual with unknown amounts of  $\text{H}_2\text{O}$  and  $\text{ClO}_4^-$ .

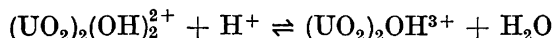
For the uranyl ion, just as in the case of thorium<sup>1</sup>, the predominating complexes cannot reasonably be mononuclear. If they had been, the measurements at lower  $B$  in an inert medium<sup>6,7</sup> would have come out much differently from what is actually observed: hydrolysis would have set in at higher acidities, and moreover, one would have obtained a single curve ("mononuclear wall") instead of a family of parallel curves.

The assignment of the formula  $A_2B_2$  rather than, say,  $A_2B_3$ , or  $A_2B_4$ , is made probable by the fact that the  $\log \beta_{22}$  so obtained is of the same order of magnitude as the  $\log \beta_{22}$  obtained for other ionic media: 1 (Na)ClO<sub>4</sub>, -6.05 to -6.10<sup>7,8</sup>, 0.1 ClO<sub>4</sub><sup>-</sup> -5.94<sup>9</sup>, and similar values in other media studied in this laboratory.

The value for  $\log \beta_{43}$ , which appears only as a correction term, also is of the same order as obtained in earlier work, -12.4 to -12.5 *etc.*<sup>7,8</sup>.

It seems reasonable for structural reasons that the complex with one A is  $AB_2$ . Had it been, say,  $AB_3$ , one might also have expected " $\log \beta_{12}$ " to be about 0.5 units higher in 1.4 than in 0.4 M uranyl medium.

Two of the ions inferred from the self-medium measurements are the same as those observed in inert medium, whereas  $AB_2$  is new. It is understandable that it has not been observed in the earlier inert medium measurements, if it is noticed that the equilibrium constant for



will give

$$[(\text{UO}_2)_2\text{OH}^{3+}][(\text{UO}_2)_2(\text{OH})_2^{2+}]^{-1} = \beta_{12}\beta_{22}^{-1}h \approx 10^{2.5}h$$

Thus,  $[\text{AB}_2] > [\text{A}_2\text{B}_2]$  only for  $h > \beta_{22}\beta_{12}^{-1} \approx 10^{-2.5}$ . Hydrolysis at such a high acidity is appreciable only at rather high concentrations of uranyl. For instance, at  $h = \beta_{22}\beta_{12}^{-2}$ ,  $Z \approx 3 B\beta_{12}^2\beta_{22}^{-1} \approx 0.2 B$ . Even at  $B = 0.1$  M, a high value for inert medium measurements,  $Z$  is then only 0.02.

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