364. *Electrometric Studies of the Precipitation of Hydroxides. Part VI. Sexavalent Uranium Chloride Solutions.*

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With one exception, *viz.*, uranic fluoride, the stable salts of sexavalent uranium exist in the uranyl form. On the other hand, the existence of uranyl kations in solution is by no means proven (see Dittrich, *Z. physikal. Chem.*, 1899, **29**, 449; Kohlschütter, *Annalen*, 1900, **311**, 1; Ley, *Ber.*, 1897, **30**, 193; 1900, **33**, 2659). Britton (Part IV; J., 1925, **127**, 2151) carried out an oxygen-electrode titration of a nitric acid solution of sexavalent uranium to ascertain whether uranic hydroxide was able to combine with more than 2 equivs. of nitric acid, but the results were vitiated by the uncertainties inherent in the use of the electrode. The quinhydrone electrode, having now been found to function reversibly in the presence of sexavalent uranium, has been used in this work, which consists of potentiometric and conductometric titrations with alkali of hydrochloric acid solutions of uranyl chloride.

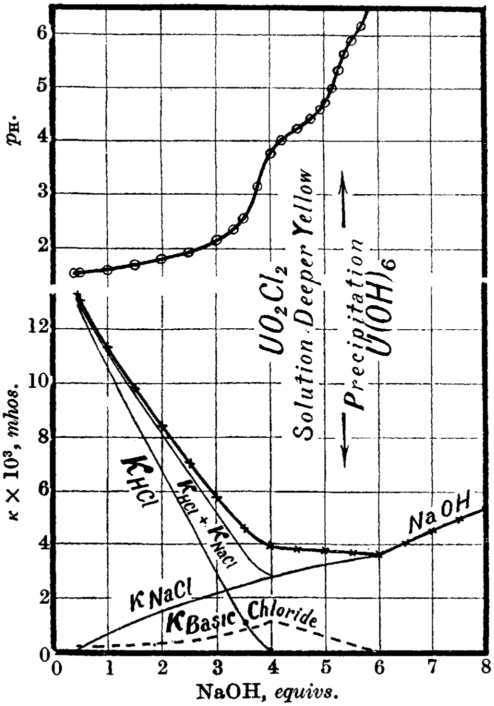
A typical pair of electrometric titrations is that of a solution containing sufficient HCl to form $U(OH)_{0\cdot40}Cl_{5\cdot60}$, some of the data of which are given in cols. 4 and 5 of the table.

The p_H curve is plotted in the upper part of Fig. 1 and the corresponding conductometric curve in the lower part. The first section of both curves corresponds to the neutralisation of free acid, which, in both cases, terminates

Quinhydrone electrotitration at 18° *and conductometric titration at* 25° *of* 100 *c.c. of solutions,* 0·008925M-U *and* 0·05004M-Cl [i.e., 0·008925M-$U(OH)_{0\cdot40}Cl_{5\cdot60}$] *with* 0·0965N-NaOH.

NaOH c.c.	NaOH equivs.	p_H obs.	*x*.	$\kappa \times 10^3$ obs.	$\kappa_{HCl} \times 10^3$.	$\kappa_{NaCl} \times 10^3$.	$\kappa_B \times 10^3$.
0·97	0·5	1·52	3·92	13·10	12·79	0·12	0·19
5·60	1·0	1·60	3·97	11·40	10·64	0·62	0·14
10·23	1·5	1·70	3·96	9·85	8·45	1·08	0·32
14·85	2·0	1·80	4·04	8·40	6·71	1·48	0·21
19·48	2·5	1·94	4·04	7·02	4·86	1·85	0·31
24·10	3·0	2·16	3·96	5·80	2·93	2·19	0·68
28·73	3·5	2·57	3·89	4·61	1·14	2·50	0·97
33·35	4·0	3·78	4·02	4·00	0·07	2·79	0·14
37·98	4·5	4·23	4·51	3·88	0·02	3·02	0·84
42·60	5·0	4·78	5·00	3·81	0·006	3·27	0·53
47·23	5·5	5·88	5·50	3·75	0·001	3·50	0·25
51·85	6·0	—	—	3·72	—	3·72	—

FIG. 1.



slightly before the solute acquired the composition UO_2Cl_2. Much of the rapid diminution in specific conductivity can be accounted for by the removal of HCl and the substitution of an equiv. quantity of NaCl. Thus the values of κ_{HCl} given in col. 6 of the table were calc. from the observed p_H values (it being considered that no appreciable error would be introduced by the fact that the p_H values were determined at 18° while the conductometric titration was performed at 25°), Λ_∞ of HCl being taken as 423·6 (Jeffrey and Vogel, this vol., p. 400), and the values of κ_{NaCl} were calc. on the basis of the measurements of Walden (*Z. physikal. Chem.*, 1888, **2**, 49). These spec. conductivities are plotted in Fig. 1, and so also are the sum of κ_{HCl} and κ_{NaCl} for each titre, which curve lies only just below the exptl. curve. If the assumptions involved in these calculations are valid, then only very little conductivity (κ_B) remains to be attributed to the basic uranium chloride, the precise amounts being given by the broken line at the bottom of the diagram. During the neutralisation of the acid, the solution remained pale yellow, but afterwards it became intensely yellow until the solute had acquired the composition, $U(OH)_{5\cdot4}Cl_{0\cdot6}$, whereupon $U(OH)_6$ began to be pptd., and not sodium diuranate, as is often stated, for the conductivity of the alk. solution was very nearly that which would have been produced by an excess of alkali over 6 equivs. That the diuranate was not pptd. was also proved by a glass-electrode titration.

An attempt was made to ascertain from the p_H values the exact amount of HCl present in the solution at each titre, in order to find whether the $U(OH)_6$ had actually combined with more than the 2 equivs. required to form UO_2Cl_2. In this way, it was possible to compute the composition of the basic $U(OH)_xCl_{6-x}$ at any stage of the reaction. From the values of x so obtained and recorded in col. 4, it follows that comparatively little HCl had combined beyond the uranyl stage, for until that stage had been reached the values of x did not deviate greatly from 4. It is significant, however, that the value of x corresponding to 3·5 equivs. is 3·9, which seems to indicate that a trifling amount of HCl had combined beyond that required to form UO_2Cl_2. Other potentiometric curves have led to the same conclusion; in general, however, they show that UO_2Cl_2 chiefly exists as such in solutions containing an excess of acid.

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