400. *The Heat of Solution of Uranium Tetrachloride and the Hydrolysis of the Uranium*(IV) *Ion.*

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Measurements have been made of the heat of solution of anhydrous uranium tetrachloride in aqueous hydrochloric acid–lithium chloride mixtures at constant ionic strength. The variation of the heat of solution with hydrochloric acid concentration is in apparent disagreement with current views on the hydrolysis of uranium(IV) and an explanation is offered in terms of the effect of the electrolyte in the solvent on the solvation energy of uranium tetrachloride.

THE hydrolysis of quadrivalent uranium in aqueous solution has received little attention. Kraus and Nelson,[1] using a spectrophotometric method, have shown that in acid solutions it is adequately represented by the reaction (*A*), at least down to hydrogen-ion concen-

$$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+ \quad . \; . \; . \; . \; . \; . \; . \quad (A)$$

trations of the order of 0·01 M. From the variation of the hydrolysis constant, K_H, with temperature these authors calculate a value of 11·7 kcal./mole for the heat-content change, ΔH_H, accompanying reaction (*A*) at infinite dilution. Recently Hietanen [2] has shown that at lower acid concentrations polymeric uranium(IV) species also make an important contribution to the hydrolytic process. The value which she has obtained for K_H is in reasonable agreement with that of the earlier workers.

A direct thermochemical determination of ΔH_H is desirable and, in principle, could be derived from measurements of the heat of solution of anhydrous uranium tetrachloride in aqueous hydrochloric acid–lithium chloride mixtures at constant ionic strength. In such conditions the observed heat of solution $\Delta H_{\text{obs.}}$ would be given by eqn. 1, where ΔH_S

$$\Delta H_{\text{obs.}} = \Delta H_S + \phi(\Delta H_H) + \psi(\Delta H_C) \quad . \; . \; . \; . \; . \; . \quad (1)$$

is the true heat of solution and the functions ϕ and ψ can be derived from the mechanism of the hydrolytic and chloride-ion complex-forming reactions respectively. The inclusion of a term involving ΔH_C, the heat of formation of a chloride-ion complex, is necessary as it has previously been shown [1a, 3] that the reaction (*B*) also takes place in aqueous systems.

$$U^4 + Cl^- \rightleftharpoons UCl^{3-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (B)$$

Fontana [4] has made a few measurements of the heat of solution of UCl_4 in perchloric acid but these are not sufficiently extensive to yield any reliable conclusions. This paper presents the results of a more systematic series of observations.

EXPERIMENTAL

Uranium tetrachloride was prepared from the pentachloride (kindly provided by Dr. J. K. Dawson of this Division) by heating it in a stream of nitrogen at 500°. The nitrogen was purified by passage over copper heated to 450° and dried by passing through silica gel, magnesium perchlorate, and finally a trap cooled with liquid nitrogen. Thorough drying of the gas stream and apparatus is important and to achieve the latter the preparation vessel was baked out at

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[1] Kraus and Nelson, *J. Amer. Chem. Soc.*, (*a*) 1950, **72**, 3901; (*b*) 1955, **77**, 3721.
[2] Hietanen, *Rec. Trav. chim.*, 1956, **75**, 711.
[3] Ahrland and Larsson, *Acta Chem. Scand.*, 1954, **8**, 137.
[4] Fontana, U.S. Atomic Energy Commission Report MDDC 1452 (1947).

500°, with the dry nitrogen stream flowing, for several hours before loading with UCl_5. The uranium tetrachloride (Found: U, 62·5; Cl, 37·3. Calc. for UCl_4: U, 62·7; Cl, 37·3%; unchanged on vacuum sublimation) was concluded to be not less than 99·6% pure.

All operations with both the pentachloride and tetrachloride were carried out with standard "dry box" techniques. Owing to the extremely hygroscopic nature of these compounds it was found necessary to circulate the air in the dry box slowly through a large trap cooled with liquid oxygen in order to obtain a sufficiently low partial pressure of water in the box.

The calorimetric samples (approx. 20 mg.) were contained in thin-walled glass bulbs, 1 cm. in diameter, which had a small constriction in the neck. The bulbs were weighed in thoroughly dried weighing bottles, which had carefully ground and lightly greased stoppers, returned to the dry box for introduction of the sample, by means of a stainless steel microfunnel, and then reweighed. On return to the box the bulbs were sealed by inserting a glass bead, which rested on the constriction in the neck, placing a small piece of Apiezon W wax above the bead and then melting this, to form a seal around the bead, by means of an electrically heated wire shaped to fit the neck of the bulb. Before use the Apiezon W wax was melted *in vacuo* and maintained at 250—300° for several hours, volatile products being trapped out, in order to prevent any reaction of the sample with volatile materials released when the wax was melted. The efficacy of the bulb-sealing technique was tested by sealing small quantities of P_2O_5 in a number of bulbs and immersing then in water. No change in appearance of the P_2O_5 occurred during 1 yr. All the sample bulbs and microfunnels used were baked *in vacuo* at 350—400° for 6—8 hr. and then transferred to the dry box in an evacuated container. These precautions were necessary to ensure the absence of any appreciable amount of water, for with 20 mg. samples of UCl_4 only 1 mg. of water provides a 1 : 1 molar ratio so that quantities of water of even 100 µg. would greatly affect the heat of solution.

TABLE 1. *Heat of solution of anhydrous* UCl_4 *at* 25·0° *in aqueous* HCl–LiCl *solutions at constant ionic strength,* $\mu = 2{\cdot}0$. *Final uranium*(IV) *concentration* $\sim 5 \times 10^{-4}$M.

$[H^+]$	Heat evolved (kcal./mole)	Mean $\Delta H_{obs.}$ (kcal./mole) *
2·0	51·31, 51·75	−51·53
1·6	54·40	−54·40
1·2	56·10	−56·10
1·0	57·00, 56·78	−56·89
0·6	57·40, 56·90	−57·15
0·4	58·42, 58·35, 57·93, 58·03, 57·59, 57·54, 57·52, 58·31, 57·97	−57·96 (0·9, ± 0·33)
0·2	58·65, 58·22, 58·18, 58·06, 58·25, 58·62, 58·18	−58·31 (0·6, ±0·21)
0·1	58·39, 58·22, 58·69	−58·43
0·04	58·50	−58·50
0·02	58·26, 58·55, 58·57	−58·46

* Numerals in parentheses are the range in ΔH followed by the standard deviation, σ.

The calorimetric equipment used was a modification of that previously described.[5] The volume of the calorimeter was 130 ml., and 100 ml. quantities of solvent were used for each run. The stirrer and glass tubes containing the thermistor and heater were replaced by components made from platinum and the sample-carrying and -breaking mechanism was replaced by a tungsten rod which ended a little above the calorimeter and carried on its lower end a short section of Perspex rod (to prevent rapid heat conduction) followed by a length of platinum rod the end of which fitted into the neck of the sample bulb. The sample bulbs were fixed to the platinum rod with Apiezon W wax and were broken by depressing them on a small platinum platform carrying three stout spikes. The platform was suspended from the Polythene plug closing the calorimeter by platinum tubing.

The solvent was prepared by mixing appropriate amounts of 2M stock solutions of hydrochloric acid and lithium chloride.

Results.—The values obtained for the heat of solution of uranium tetrachloride are presented in Table 1 and the mean values of $\Delta H_{obs.}$ are plotted as a function of $\log_{10}[H^+]$ in Fig. 1. The two series of measurements at $[H^+] = 0{\cdot}4$ and 0·2 were carried out to determine the overall reproducibility of the results and from these it would seem reasonable to assign a standard deviation of ±0·33 kcal./mole to the values of $\Delta H_{obs.}$.

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[5] Hutchinson and White, *J. Sci. Instr.*, 1955, **32**, 309.

DISCUSSION

If current views on the mechanism of hydrolysis of uranium(IV) in acid solutions and of the formation of a chloride-ion complex [1,2,3] are accepted then the functions ϕ and ψ of eqn. 1 are

$$\phi = \frac{[\mathrm{UOH^{3+}}]}{[\mathrm{U^{IV}}]}\,\Delta H_H \text{ and } \psi = \frac{[\mathrm{UCl^{3+}}]}{[\mathrm{U^{IV}}]}\,\Delta H_C$$

where $[\mathrm{U^{IV}}]$ is the total analytical concentration of uranium(IV).

Now $$[\mathrm{UOH^{3+}}] = \frac{K_H[\mathrm{U^{4+}}]}{[\mathrm{H^+}]} \quad ; \quad [\mathrm{UCl^{3+}}] = K_c[\mathrm{U^{4+}}][\mathrm{Cl^-}]$$

where K_c is the equilibrium constant for the formation of the $\mathrm{UCl^{3+}}$ ion, and

$$[\mathrm{U^{IV}}] = [\mathrm{U^{4+}}] + [\mathrm{UOH^{3+}}] + [\mathrm{UCl^{3+}}]$$

from which $$[\mathrm{U^{4+}}] = [\mathrm{U^{IV}}]/(1 + K_H/[\mathrm{H^+}] + K_c[\mathrm{Cl^-}])$$

When the appropriate substitutions are made for ϕ and ψ, equation 1 becomes

$$\Delta H_{\mathrm{obs.}} = \Delta H_S + \frac{K_H}{K_H + [\mathrm{H^+}](1 + K_c[\mathrm{Cl^-}])}\,\Delta H_H + \frac{K_c[\mathrm{Cl^-}]}{1 + K_c[\mathrm{Cl^-}] + K_H/[\mathrm{H^+}]}\,\Delta H_c \quad (2)$$

In order to make use of eqn. (2) it is necessary to know ΔH_S, ΔH_C, K_H, and K_c in addition to the hydrogen-ion and chloride-ion concentrations. Of these quantities ΔH_H and K_H are given by Kraus and Nelson [1] and K_c can also be calculated from these authors' data. A value of K_c, at ionic strength $\mu = 1{\cdot}0$, is also given by Ahrland and Larsson [3] but in view of their technique, which depends upon an accurate knowledge of complex-formation between chloride ion and the uranyl ion, the value is probably less reliable than those obtained from the former workers' results. Fontana [4] has measured the heat of solution of $\mathrm{UCl_4}$ in 2M-$\mathrm{HClO_4}$ and finds $\Delta H_{\mathrm{obs.}} = -53{\cdot}62$ kcal./mole. This value, together with that given in our Experimental section for 2M-HCl, can be used with the known constants to derive ΔH_c from eqn. 2. With $K_c = 0{\cdot}27$ at $\mu = 2{\cdot}0$ (estimated from the data of Kraus and Nelson [1]), $\Delta H_H = 11{\cdot}0$ kcal./mole, and $K_H = 0{\cdot}0236$ at $\mu = 2{\cdot}0$, the value obtained for ΔH_c is 6·2 kcal./mole.

The second and the third term of eqn. 2 have been computed, this set of values being used for the constants, and ΔH_S has been chosen to make eqn. (2) coincide with the experimental $\Delta H_{\mathrm{obs.}}$ at $[\mathrm{H^+}] = 2{\cdot}0$M. The values of $\Delta H_{\mathrm{obs.}}$ which result are plotted against $\log_{10}[\mathrm{H^+}]$ in the Figure, from which it is evident that a considerable divergence exists between the experimental and calculated curves. The calculated values of $\Delta H_{\mathrm{obs.}}$ are almost unchanged from hydrogen-ion concentrations of 2·0—0·5M and below this steadily become more positive, while from 2·0 to 0·5M the experimental results become rapidly more negative and thereafter are almost constant.

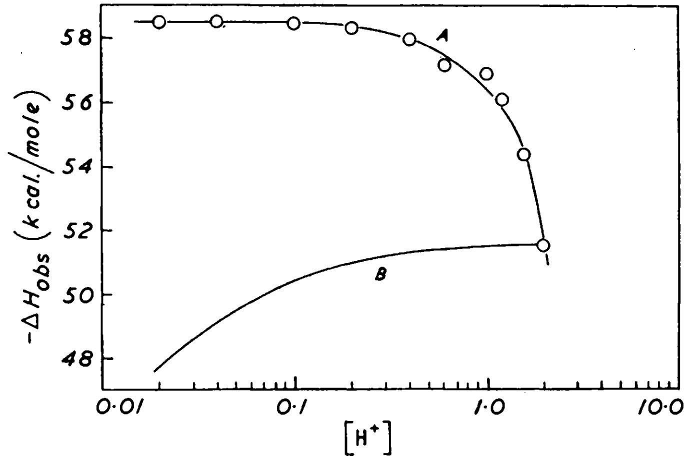
In seeking an explanation of this anomaly two major possibilities must be considered, namely, (1) that (*A*) does not correctly represent the course of hydrolysis, and (2) that eqn. (2) does not express the observed heat of solution accurately. The weight of evidence available is such as to leave no doubt that the first of these possibilities can be excluded. In particular it is certain [1b] that ΔH_H must be positive and not, as the experimental values of $\Delta H_{\mathrm{obs.}}$ seem to imply, negative. Further, to obtain even approximate agreement between calculated and experimental values of $\Delta H_{\mathrm{obs.}}$ not only would a negative value of ΔH_H be required, but it would be necessary to postulate the occurrence of a hydrolytic reaction (*C*)

$$\mathrm{U^{4+}} + n\mathrm{H_2O} \rightleftharpoons \mathrm{U(OH)}_n^{(4-n)+} + n\mathrm{H^+} \quad . \quad . \quad . \quad . \quad . \quad (C)$$

with values of n between 2 and 3; Kraus and Nelson[1a] have confirmed that when anhydrous UCl_4 is dissolved in aqueous acid solutions n is always less than unity. The good agreement between the values of K_H determined by these authors and by Hietanen,[2] who used an entirely different experimental technique, is also very strong support for the correctness of their views.

These considerations suggest that an explanation must be sought in the second possibility. Equation (2) can be inadequate for only two reasons: there may be other reactions occurring which have not been considered in its derivation, and the true heat of solution ΔH_S may be a function of the composition of the solvent medium and not, as was tacitly assumed, a constant. In the system under consideration the only additional reactions which could occur are the polymerisation of the hydrolysed uranium ions and the oxidation of U^{IV} to U^{VI} by dissolved oxygen. Polymerisation is unlikely to be important under these conditions as it is markedly retarded by hydrogen ions and the temperature–time plots of the calorimetric measurements showed no abnormalities which could be attributed to a slow thermal process. To determine the extent of oxidation experiments were carried out in which 20 mg. of UCl_4 were dissolved in 100 ml. of HCl–LiCl mixtures and then stirred, in air, for 15—20 min. (*i.e.*, for approximately the same length of time as a calorimetric measurement required) after which the U^{IV} content of the solution was determined. The results obtained were ratios of U^{IV} to total uranium of 0·996 and 1·002 at hydrogen-ion concentrations 2·0 and 0·2 respectively, and it is clear that no oxidation can have occurred. The only remaining explanation of the discrepancy is that ΔH_S is markedly dependent on the composition of the solvent.

Heat of solution of uranium tetrachloride in hydrochloric acid–lithium chloride mixtures at 25° (μ = 2·0).



A, Experimental. *B*, Calc. from eqn. (2).

A number of factors contribute to ΔH_S; the lattice energy of the crystal, the heats of solvation of the positive and negative ions and the heat of dilution of the solution. Of these the heat of dilution will certainly depend on the nature of the medium, but its contribution to ΔH_S is a minor one (20% variations in the weight of UCl_4 used have no detectable effect on $\Delta H_{obs.}$) and in a medium of constant ionic strength it would be expected to be almost constant. The lattice energy is a function only of the solid material and will be entirely independent of the solvent; but in recent years evidence has been accumulating which shows that the heats of solvation of ions are quite markedly affected by the presence of other electrolytes in the solvent.[6, 7, 8] None of these investigations has been carried out at constant ionic strength but the work of Samoilov[8] indicates that the hydrogen ion causes a particularly large effect, one observation which has an important bearing on the present work being that at equivalent concentrations the heat of solution of NaCl is depressed more strongly by hydrochloric acid than by lithium chloride. In all the salts studied (LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$) the heat of solution becomes more endothermic on addition of hydrochloric acid to the solvent, the effect being linearly related to its concentration. Klemm[6] has examined the data available for $AlCl_3$, $GaCl_3$, $InCl_3$, $LaCl_3$, and $FeCl_3$ and has shown that in all cases the addition of a given amount of hydrochloric acid to the solvent produces approximately the same change in $\Delta H_{obs.}$. In these cases the relation between $\Delta H_{obs.}$ and HCl concentration is not linear but is roughly parallel to that found for uranium tetrachloride in the present work as are the results for $ThCl_4$[9] and $PuCl_3$.[10] To account for these results Klemm suggests that they reflect the formation of chloride ion complexes, the process being considered to be highly endothermic owing to the strong binding between chloride ion and water. This explanation however, as the present results show, can be only partly true. At a constant total chloride-ion concentration and constant ionic strength no explanation based solely on chloride-complex formation could account for the large change in $\Delta H_{obs.}$ with change in hydrogen-ion concentration and as this cannot be due to hydrolysis then it is clear that the positive ions must have a special effect on the heat of hydration, that of the hydrogen ion being much greater than that of lithium ion, in agreement with Samoilov's finding.[8]

The heat of solution of UCl_4 in 0·5M-perchloric acid (—55·6 kcal./mole) and in 0·1M-$HClO_4$ + 0·4M-$LiClO_4$ (—54·2 kcal./mole) has been measured by Fontana[4] and it will be noticed that the change in $\Delta H_{obs.}$ is in the direction predicted by eqn. (2) and opposite to that found in 2M-HCl–LiCl mixtures at these acid concentrations. This difference in behaviour is undoubtedly related to the difference in ionic strength in the two sets of measurements, a lower ionic strength leading to a smaller effect of hydrogen-ion concentration on ΔH_S. It is possible to use these results, in combination with equation (2), to calculate a value for ΔH_H and by using the constants given previously a figure of 8·3 kcal./mole is obtained. This value is less than that found by Kraus and Nelson[1b] but this is to be expected as the change from 0·1M to 0·5M acid will not only alter the second term in eqn.(2) but will also make ΔH_S more positive, thus making the overall difference in $\Delta H_{obs.}$ less than that required by the hydrolytic process alone. It is apparent that any attempt to derive heats of hydrolysis from measurements of heats of solution is liable to be seriously misleading unless adequate data are available from which the effect of the medium on the heats of solvation of the ions can be evaluated.

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[6] Klemm, *Z. anorg. Chem.*, 1942, 249, 23.

[7] Voskresenskaya and Ponomareva, *Zhur. fiz. Khim.*, 1946, **20**, 433; Samoilov, *Izvest Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1952, 627; Kaganovich and Mishchenko, *Doklady Akad. Nauk. S.S.S.R.*, 1952, **87**, 89.

[8] Samoilov, *Doklady Akad. Nauk, S.S.S.R.*, 1951, **81**, 641.

[9] Westrum and Robinson, Paper 6.50, " The Transuranium Elements," Vol. 14*B*, National Nuclear Energy Series, McGraw-Hill, New York, 1949.

[10] *Idem, ibid.*, Paper 6.54.