507. *The Heat of Solution of Plutonium Trichloride.*

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The heat of solution of anhydrous plutonium trichloride in aqueous perchloric acid and in perchloric acid–lithium perchlorate solutions at constant ionic strength has been measured. The results provide further evidence for the formation of a chloride complex by the tervalent plutonium ion and an approximate value for the change of heat content accompanying its formation has been calculated.

SOME measurements of the heat of solution of plutonium trichloride in hydrochloric acid have been reported by Westrum and Robinson.[1] The heat of solution varied markedly with the acid concentration, as is the case with uranium [2] and thorium tetrachloride,[3] but the data do not suffice to indicate whether this variation is due to increasing complex-ion formation, changing ionic strength, or a specific variation of the true heat of solvation of the ions with hydrogen-ion concentration. Therefore measurements are now reported of the heat of solution in perchloric acid and in perchloric acid–lithium perchlorate solutions. A comparison of the former with the previous results [1] should show the effect of complex-ion formation, while the latter will demonstrate the effects of ionic strength and hydrogen-ion concentration.

EXPERIMENTAL

Glove-box techniques were used throughout the work.

Anhydrous plutonium trichloride was supplied by Mr. J. H. Freeman of General Physics Division, A.E.R.E., to whom we are much indebted. It contained a small amount of insoluble matter and analysis indicated 96·5% of $PuCl_3$. Chloride was determined volumetrically with silver nitrate, and plutonium by alpha-particle counting with a low-geometry counter, the two methods giving excellent agreement.

As plutonium trichloride is very hygroscopic it was handled under dry conditions and the calorimetric samples (approx. 40 mg.) were weighed out and sealed into the thin glass sample-bulbs (5 mm. in diameter) as described for uranium tetrachloride.[2]

The general arrangement of the calorimeter closely resembled that described by Westrum and Eyring.[4] The calorimeter vessel was of stainless steel, 2 inches in diameter and 2⅜ inches deep. It was suspended from a Perspex support (cf. ref. 4) inside a brass " submarine " and the dead-air gap was 1·2 cm. The normal charge was 70 ml. of solution. In place of the quartz shaft used by Westrum and Eyring a thin-walled stainless-steel tube carrying a stainless-steel rod at the end passed axially through a polytetrafluoroethylene bush in the calorimeter lid and carried the sample-bulb which was waxed to the end of the rod. This tube was spring-loaded and the sample-bulb could be broken against a projection on the floor of the vessel by removing a pin which released the spring. Stirring was carried out by oscillating the entire assembly through approx. 120° at a rate of 117 strokes per min. Tests with permanganate and a glass vessel showed this to be satisfactory.

Temperature measurements were made with two 1000 ohm nickel resistance thermometers, in opposite arms of a bridge network, which were wound on the outside of the calorimeter vessel. This vessel also carried a further winding, of 50 ohms of manganin, for the calibration heater. The output from the thermometer bridge was taken to a D.C. amplifier and from thence to a Brown potentiometer-recorder to give a continuous time–temperature record. The heat-input and timing arrangements for the calibration heater were as described previously.[5]

The entire calorimeter was immersed in water in a large Dewar vessel (15 cm. in diameter and 28·5 cm. deep) suspended in a water-bath ($\pm 0{\cdot}001°$). The working temperature was 25·0°.

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[1] Westrum and Robinson, Paper 6.54, " The Transuranium Elements," Vol. 14B, National Nuclear Energy Series, McGraw Hill, New York, 1949.

[2] Hearne and White, *J.*, 1957, 2081.

[3] Westrum and Robinson, ref. 1, Paper 6.50.

[4] Westrum and Eyring, *J. Amer. Chem. Soc.*, 1952, **74**, 2045.

[5] Salman and White, *J.*, 1957, 3197.

RESULTS AND DISCUSSION

The heats of solution of plutonium trichloride in perchloric acid–lithium perchlorate solutions at a constant ionic strength (μ) 2·0 and in perchloric acid at various values of μ were measured and are presented in Table 1. For comparison Table 2 contains the results obtained by Westrum and Robinson [1] for the heat of solution in hydrochloric acid. At acid concentrations of 0·1M and 1·5M the heat of solution is markedly lower in hydrochloric than in perchloric acid. This confirms the belief that tervalent plutonium is appreciably involved in complex-formation in chloride solutions (this conclusion would not be valid if replacement of chloride ion by perchlorate affected the solvation energies of the ions). Ward and Welch [6] used an ion-exchange method to determine equilibrium constants for reaction (*A*) at 21° ± 1°, and at ionic strengths of 0·2, 0·5, and 1·0 the values of the equilibrium constant, *K*, obtained were 0·44, 0·57, and 1·1 g.-ion l.$^{-1}$ respectively. Extrapolation of Ward and Welch's data to ionic strengths of 0·1 and 1·5 would enable the heat content change, ΔH, associated with reaction (*A*) to be calculated from the values given in Tables 1 and 2 as follows.

TABLE 1. *Heat of solution of plutonium trichloride in aqueous perchlorate solutions at* 25·0°.

Final plutonium concn. 1·5 × 10^{-3}M.

$[HClO_4]$ (M)	$[LiClO_4]$ (M)	μ	Heat evolved (kcal./mole of $PuCl_3$)
0·1	1·9	2·0	31·67; 31·25
0·5	1·5	2·0	30·23; 30·31
1·0	1·0	2·0	30·58; 30·18
1·5	0·5	2·0	30·44; 30·56; 30·73
2·0	0	2·0	28·29; 28·55
1·5	0	1·5	31·49; 31·02
0·1	0	0·1	33·15; 32·90

TABLE 2. *Heat of solution of plutonium trichloride in hydrochloric acid at* 25°.

[HCl]	0·1	1·5	6·0	9·0	11·38
Heat evolved (kcal./mole of $PuCl_3$)	31·76	29·43; 29·57	22·14; 22·20; 22·15	14·54	(9·8—10·2)

$$\mathrm{PuCl^{2+} \rightleftharpoons Pu^{3+} + Cl^-} \qquad (A)$$

Let the equilibrium constant of (*A*) be *K*:

$$K = [\mathrm{Pu^{3+}}][\mathrm{Cl^-}]/[\mathrm{PuCl^{2+}}] \qquad (1)$$

and assume that the concentration of free chloride ion in the hydrochloric acid solutions is the analytical HCl concentration and that the extent of chloride-complex formation in the perchloric acid solutions is negligible (in view of the very low Pu^{3+} concentrations these assumptions should be valid). The difference between the heat of solution in HCl, $\Delta H_S{}^1$, and the heat of solution in perchloric acid at the same concentration, $\Delta H_S{}^2$, will be due to the heat effect produced by the dissociation of that fraction of the total plutonium which is present as $PuCl^{2+}$ in the hydrochloric acid solution, so that:

$$\Delta H_S{}^2 - \Delta H_S{}^1 = (1 - [\mathrm{Pu^{3+}}]/[\mathrm{Pu}]_T)\Delta H \qquad (2)$$

where

$$[\mathrm{Pu}]_T = [\mathrm{Pu^{3+}}] + [\mathrm{PuCl^{2+}}] \qquad (3)$$

From (1) and (3), $(1 - [\mathrm{Pu^{3+}}]/[\mathrm{Pu}]_T) = [\mathrm{Cl^-}]/(K + [\mathrm{Cl^-}])$

Hence

$$\Delta H = (\Delta H_S{}^2 - \Delta H_S{}^1)(K + [\mathrm{Cl^-}])/[\mathrm{Cl^-}] \qquad (4)$$

Ward and Welch used Davies's empirical equation [7] to extrapolate their values of *K* to zero ionic strength. They state, however, that their value of *K* at $\mu = 1{\cdot}0$ is of doubtful validity as there is an indication in their experimental results that at the chloride-ion

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[6] Ward and Welch, *J. Inorg. Nucl. Chem.*, 1956, **2**, 395; personal communication.

[7] Davies, *J.*, 1938, 2093.

concentration used, 1·0M, dichloro-complex formation also occurred to a considerable extent. Thus it would be pointless to attempt an extrapolation to $\mu = 1{\cdot}5$ where in hydrochloric acid even more dichloro-complex formation would be expected. We have, therefore, carried out the extrapolation (by means of the Davies equation) only for $\mu = 0{\cdot}1$ at which value we find $K = 0{\cdot}299$ at Ward and Welch's temperature of 21°. As this temperature is rather far from our experimental temperature of 25° we have calculated ΔH by successive approximations, the value of $K = 0{\cdot}299$ first being used in equation (4) to give an approximate value of ΔH which was then used to correct K to 25°, the corrected value of K then being used to give a more accurate value of ΔH, and the whole process repeated until the value of ΔH obtained no longer varied.

By this means we have obtained values of $\Delta H = -4{\cdot}6$ kcal./mole and $K = 0{\cdot}269$ at 25° and $\mu = 0{\cdot}1$. From these values the free-energy and entropy changes associated with reaction (A) at $\mu = 0{\cdot}1$ can be calculated and are $\Delta F = +0{\cdot}78$ kcal./mole and $\Delta S = -18$ entropy units. The entropy change may be correlated with the changes in charge of the reactants which will produce a fairly large change in the extent of solvation, the dissociation of the $PuCl^{2+}$ ion to give the Pu^{3+} ion being accompanied by an increase in the ordering of the solvent and hence a marked decrease in entropy.

The series of results at $\mu = 2{\cdot}0$, given in Table 1, show that in contrast to results with uranium tetrachloride [2] there is no marked specific effect of the hydrogen ion on the heat of solvation until the concentration of this species exceeds 1·5M (we are unable to explain the rise at 0·1M). With uranium tetrachloride there is a rapid decrease in the heat of solution, at constant ionic strength, from hydrogen-ion concentrations of 0·5M onwards. If, as suggested by Samoilov,[8] the effect is largely electrostatic in origin and due to the statistical spreading of the hydrogen-ion charge over all available water molecules, then this difference in behaviour is qualitatively understandable. The lower charge on the Pu^{3+} ion than on the U^{4+} ion would require a higher concentration of hydrogen ion to produce a given repulsive effect.

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