Thermodynamics of the Actinide Elements. Part IV.[1] Heats and Free Energies of Formation of the Tetrachlorides, Tetrabromides, and Tetraiodides of Thorium, Uranium, and Neptunium

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Heats of solution measured at 298·15 ± 0·05 K for $ThCl_4$(s), $ThBr_4$(s), ThI_4(s), UBr_4(s), UI_4(s), and $NpBr_4$(s) in 1M-HCl are −241·8 ± 0·7, −283·5 ± 1·3, −322·0 ± 0·6, −264·6 ± 0·5, −289·9 ± 1·3, and −258·8 ± 0·5 kJ mol^{-1} respectively, and in 6M-HCl, −188·3 ± 0·4, −233·9 ± 0·8, −276·0 ± 1·2, −205·7 ± 0·9, −240·2 ± 1·3, and −199·2 ± 0·4 kJ mol^{-1} respectively. Combination of these values with other thermodynamic data yields the following standard heats of formation: $ThCl_4$(s), −1184·4 ± 1·0 kJ mol^{-1}; $ThBr_4$(s), −963·4 ± 1·4 kJ mol^{-1}; ThI_4(s), −662·0 ± 1·8 kJ mol^{-1}; UBr_4(s), −802·5 ± 3·4 kJ mol^{-1}; UI_4(s), −511·5 ± 4·0 kJ mol^{-1}; and $NpBr_4$(s), −773·2 ± 1·7 kJ mol^{-1}. By use of suitable entropy and heat capacity data, the thermodynamic functions associated with the formation of these compounds, and of UCl_4(s) and $NpCl_4$(s), have been calculated as a function of temperature from 298 K to the m.p. of the halide.

EXPERIMENTAL data on the heats of formation of actinide(IV) chlorides, bromides, and iodides are fragmentary and, in some cases, the existing values appear to be inconsistent. Eyring and Westrum[2] have measured the heat of solution of $ThCl_4$(s) and of Th metal in 6·004M-HCl–0·005M-Na_2SiF_6; combination of their results with the most recent value[3] for the partial molal heat of formation of hydrochloric acid in this medium yields for the heat of formation † of $ThCl_4$(s) the value[4] −1187·4 ± 1·7 kJ mol^{-1}. Earlier values reported by Von Wartenberg[5] and by Chauvenet[6] are incorrect, apparently as a result of lack of proper characterisation of starting materials or the observed calorimetric reactions. The available values[4] for the heat of formation of $ThBr_4$(s) and ThI_4(s), −962·3 ± 4 kJ mol^{-1} and −670·7 ± 4 kJ mol^{-1} respectively, are based on heats of solution of the appropriate compounds in either water ($ThBr_4$[6]) or 1M-HCl (ThI_4[7]).

Although heats of solution have been measured for the corresponding protactinium tetrahalides[8] reliable values for their heats of formation cannot be calculated until experimental data on the enthalpy of formation of the Pa^{IV} ion in solution are available.

The heat of formation of UCl_4(s) has recently been redetermined by Fitzgibbon *et al.*[9] who employed two independent reaction schemes involving respectively the heat of solution of the metal and of the tetrachloride in oxygen-free hydrochloric acid solutions containing 0·009M-Na_2SiF_6, and of the dioxide and the tetrachloride in sulphuric acid solutions. The latter scheme is, of course, based on the enthalpy of formation of UO_2(s) (−1084·9 ± 0·8 kJ mol^{-1}) obtained by combustion calorimetry.[10] The weighted average of the two sets of determinations, which are remarkably consistent, leads to a value of 1019·2 ± 2·5 kJ mol^{-1} for the standard heat of formation of UCl_4(s), which differs greatly from all the previously reported results which were −1051·4,[11] −1050·6,[12] −1051·0,[13] and, more recently, −1052·3 kJ mol^{-1}.[14] Such good agreement between the earlier data could appear convincing. However the fact that the value of Fitzgibbon *et al.*[9] is obtained from two independent reaction schemes and that only one of them depends on the heat of solution of the metal in acid solution (for which, as pointed out by Fitzgibbon *et al.* themselves,[9] difficulties may arise unless oxygen is totally excluded) implies that their value is at present the most reliable. In addition, this value substantiates the opinion of Rand and Kubaschewski[15] that previously accepted values for the enthalpy of formation of the uranium ions were *ca.* 25 kJ mol^{-1} too negative. The recently reported value for the heat of formation of UCl_5[16] (−1036·4 ± 2·1 kJ mol^{-1}) also supports the above choice of the value of ΔH_f° (UCl_4, s).

In their evaluation of the existing experimental data on the heat of formation of UBr_4, Rand and Kubaschewski give −826·3 ± 4 kJ mol^{-1} from the data of Barkelew[12,17] on the heat of solution of uranium metal and UBr_4(s) in 12M-HCl–10% $FeCl_3$ solution and

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† Unless otherwise specified the heats of formation given in this paper are standard values; *i.e.*, for the compounds and elements in their stable forms at 298 K and 1 atm = 101,325 Pa.

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−843·1 kJ mol^{-1} from the results of Shchukarev *et al.*[18] on the heat of solution of UBr_4(s) and UCl_4(s) in an aqueous solution of $FeCl_3$. Although there is no apparent reason to prefer one value rather than the other it is worth noting that the use of the new value for the heat of formation of UCl_4(s) with the results of Shchukarev *et al.* brings their value to −811·3 kJ mol^{-1} for $\Delta H_f°(UBr_4,s)$.

Barkelew has also determined the heat of formation of UI_4(s) by comparing its heat of solution in 12M-HCl saturated with iodine with those of UCl_3(s) and UI_3(s) in the same medium, the result, therefore, being based on the heat of formation of UCl_3(s). On the basis of these results Rand and Kubaschewski[15] have recommended the value −529·3 ± 4 kJ mol^{-1} for the heat of formation of UI_4(s).

The heats of formation calculated for UBr_4(s) and UI_4(s) from Barkelew's data are, like that originally reported for UCl_4(s) by the same author, based on his value for the heat of solution of uranium metal. If, as appears likely, this is the source of error in the older values for the heat of formation of UCl_4(s) a similar correction (31·4 kJ mol^{-1}) will yield −794·9 ± 4 kJ mol^{-1} and −497·9 ± 4 kJ mol^{-1} for the respective heats of formation of UBr_4(s) and UI_4(s).

We have reported[19] the value of −987·4 ± 1·3 kJ mol^{-1} for the heat of formation of $NpCl_4$(s); with the more recently available figure for the partial molal heat of formation of hydrochloric acid in 1M-HCl this becomes 986·2 ± 1·3 kJ mol^{-1}. No experimental value is available for the heat of formation of $NpBr_4$(s) which is estimated[20] as −766 kJ mol^{-1}.

We now report the heat of solution of $ThCl_4$(s), $ThBr_4$(s), ThI_4(s), UBr_4(s), UI_4(s), and $NpBr_4$(s) in both 1M- and 6M-HCl together with their heats of formation. In addition, using either experimentally determined values or suitably extrapolated data for entropies and heat capacities we have calculated, as a function of temperature, expressions for the thermodynamic functions associated with the formation of these compounds and of UCl_4(s) and $NpCl_4$(s).

EXPERIMENTAL

Instruments and Operating Procedure.—The microcalorimeter has been described[21] and details of calibration runs have been published.[19,22] All compounds were handled in dry, oxygen-free nitrogen. The atmosphere of the boxes used for the filling and weighing of the samples contained less than 10 p.p.m. water vapour as detected with an Alnor Dew-point meter (Casella, London) and less than 10 p.p.m. oxygen as measured from the potential drop across a heated ZrO_2 membrane.[23] Samples were weighed with a Cahn (Paramount, California) electric microbalance with an ultimate sensitivity of 0·1 μg. Sample weights were reduced to weights *in vacuo*. Except for the thorium compounds, the visible spectra of the calorimetric solutions were recorded on a Cary 14H spectrophotometer in order to confirm that only quadrivalent actinide ions were present.

Units and Limits of Errors.—In order to comply with the International System of Units, we have used the joule (J) as energy unit. All previous literature data used in this paper and originally reported in calories, or its multiples, have been recalculated by use of the conversion factor 1 calorie = 4·184 J. The ^{12}C scale of atomic weights was used to calculate the molecular weights; thus for thorium, uranium, and neptunium the atomic weights have been taken as 232·04, 238·03, and 237·07 respectively.

Heat measurements are reported for 298·15 ± 0·05 K. Errors on the mean of several identical measurements are reported for the 95% confidence interval, standard statistical methods being used[24] but we have not attempted to retain this limit when combining our data with those from other sources for which we take the error to be that stated by the author. The errors given on the calculated heats of formation have been obtained from the error on the individual terms of the thermodynamic cycle used, according to a standard procedure.[25] Unless otherwise specified, auxiliary thermodynamic data used in the calculations are taken from those of Wagman *et al.*[3]

Materials and Reagents.—The tetrahalides were prepared in duplicate according to published methods[26–30] and purified by repeated vacuum sublimation in evacuated silica vessels, an excess of iodine being present in the case of UI_4. Analytical procedures have been described;[28–30] results are in Table 1. *X*-Ray powder photographs were recorded for each compound and the absence of extraneous lines confirmed. This procedure also showed that the thorium tetrabromide used was pure β, *i.e.*, isostructural with the other tetragonal actinide tetrahalides ($ThCl_4$, $NpCl_4$, and $PaBr_4$). However, contrary to the results

TABLE 1

Analytical results

	Found (%)		Required (%)	
	M	X	M	X
$ThCl_4$ (I)	62·1	38·0	62·05	37·95
$ThCl_4$ (II)	62·0	38·0		
$ThBr_4$ (I)	42·1	57·9	42·05	57·95
ThI_4 (I)	31·4	68·5	31·35	68·65
ThI_4 (II)	31·3	68·6		
UBr_4 (I)	42·6	51·3	42·7	51·3
UI_4 (I)	31·8	68·0	31·9	68·1
UI_4 (II)	31·9	68·0		
$NpBr_4$ (I)	42·7	57·4	42·6	57·4

M = metal, X = halogen.

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TABLE 2

Heat of solution of various tetrahalides at 298·15 ± 0·05 K

Prep. no.	Expt. no.	Wt. of sample/mg	$10^3 \times$ Molarity of compound in soln.	Heat effect / J	ΔH_1 / kJ mol^{-1}
$ThCl_4$					
In 1M-HCl					
I	1	8·148	2·564	5·2898	−242·7
I	2	6·256	1·969	4·0201	−240·3
I	3	7·286	2·293	4·7320	−242·8
I	4	5·167	1·626	3·3435	−241·9
I	5	6·533	2·056	4·2298	−242·0
II	6	9·212	2·899	5·9544	−241·7
II	7	4·744	1·485	3·0696	−243·0
II	8	6·404	2·015	4·1212	−240·6
II	9	7·510	2·363	4·8679	−242·3
II	10	5·730	1·803	3·6942	−241·0
				Average:	−241·8 ± 0·7
In 6M-HCl					
I	1	4·898	1·542	2·4593	−187·7
I	2	7·444	2·343	3·7457	−188·1
I	3	8·466	2·664	4·2765	−188·8
I	4	8·704	2·739	4·3906	−188·6
I	5	8·279	2·605	4·1671	−188·1
I	6	7·670	2·414	3·8656	−188·4
				Average:	−188·3 ± 0·4
$ThBr_4$					
In 1M-HCl					
I	1	4·703	1·003	2·4129	−283·0
I	2	7·737	1·650	3·9807	−283·0
I	3	6·119	1·305	3·1459	−283·6
				Average:	−283·2 ± 1·3
In 6M-HCl					
I	1	8·601	1·834	3·6480	−234·0
I	2	5·824	1·242	2·4656	−233·5
I	3	4·260	0·909	1·8087	−234·2
				Average:	−233·9 ± 0·8
ThI_4					
In 1M-HCl					
I	1	8·974	1·427	3·9137	−322·6
I	2	4·840	0·770	2·1071	−322·0
I	3	7·132	1·134	3·1075	−322·3
II	4	9·067	1·442	3·9489	−322·1
II	5	7·641	1·215	3·3196	−321·3
				Average:	−322·0 ± 0·6
In 6M-HCl					
I	1	5·691	0·905	2·1313	−277·0
I	2	7·984	1·270	2·9606	−274·0
I	3	8·625	1·372	3·2292	−276·9
II	4	7·269	1·156	2·7020	−274·9
II	5	7·720	1·228	2·8865	−276·6
II	6	7·599	1·209	2·8401	−276·4
				Average:	−276·0 ± 1·2
UBr_4					
In 1M-HCl					
I	1	4·203	0·886	1·9966	−265·1
I	2	6·605	1·393	3·1355	−264·7
I	3	5·775	1·218	2·7351	−264·1
I	4	5·631	1·188	2·6706	−264·5
I	5	7·808	1·660	3·7321	−264·5
				Average:	−264·6 ± 0·5
In 6M-HCl					
I	1	6·205	1·309	2·2899	−205·8
I	2	5·143	1·085	1·8903	−205·0
I	3	6·709	1·415	2·4757	−205·8
I	4	6·474	1·366	2·3966	−206·4
				Average:	−205·7 ± 0·9

TABLE 2 (*Continued*)

Prep. no.	Expt. no.	Wt. of sample/mg	10^3 × Molarity of compound in soln.	Heat effect / J	ΔH / kJ mol^{-1}
UI_4					
In 1M-HCl					
I	1	4·667	0·736	1·8146	−289·9
I	2	8·699	1·373	3·3715	−289·0
I	3	6·216	0·981	2·4146	−289·7
II	4	9·247	1·459	3·6104	−291·1
II	5	6·559	1·035	2·5589	−290·9
				Average:	−289·9 ± 1·3 [a]
In 6M-HCl					
I	1	7·563	1·193	2·4259	−239·2
I	2	6·843	1·080	2·1999	−239·7
I	3	8·152	1·286	2·6264	−240·1
I	4	7·155	1·129	2·2979	−239·4
II	5	7·874	1·242	2·5468	−241·2
II	6	6·108	0·964	1·9694	−240·4
				Average:	−240·2 ± 1·3 [a]
$NpBr_4$					
In 1M-HCl					
I	1	6·754	1·427	3·1380	−258·7
I	2	4·328	0·915	2·0092	−258·4
I	3	6·155	1·307	2·8644	−259·1
I	4	4·184	0·884	1·9481	−259·1
				Average:	−258·8 ± 0·5
In 6M-HCl					
I	1	5·065	1·070	1·8158	−199·6
I	2	7·155	1·520	2·5573	−199·0
I	3	5·686	1·202	2·0301	−198·7
I	4	5·308	1·122	1·9004	−199·3
I	5	1·536	0·325	0·5448	−199·2
				Average:	−199·2 ± 0·4

[a] Error limit set to include an approximate discrepancy of about 1 kJ mol^{-1} between the two UI_4 preparations.

reported by Scaife,[31] we found no line which could not be accurately indexed in the space group —$I4_1/amd$. We have been unable to repeat the preparation of α-$ThBr_4$.

Other reagents were of analytical grade. The concentrations of the hydrochloric acid solutions were established by titration as 1·00 ± 0·01 and 6·00 ± 0·05M, respectively.

RESULTS AND DISCUSSION

Table 2 shows the results for the solution of the various compounds in 1M- and 6M-HCl, according to reaction (1), with $a = ca.$ 400 for $ThCl_4 = ca.$ 800 for the bromides

$$MX_4(s) + [a\mathrm{HCl}, b\mathrm{H_2O}] \longrightarrow [MX_4, a\mathrm{HCl}, b\mathrm{H_2O}];\ \Delta H_1 \quad (1)$$

and iodides, and $b/a = 54{\cdot}4$ in 1M-HCl, and $a = ca.$ 2500 for $ThCl_4 = ca.$ 5000 for the bromides and iodides, and $b/a = 8{\cdot}16$ in 6M-HCl. As observed for the tetrachlorides,[8] the heats of solution of the tetrabromides and tetraiodides decrease with increasing atomic number (decreasing ionic radius) of the actinide. It is important to recall, however, that unlike the tetrachlorides, the tetrabromides are not isomorphous, and neither are the tetraiodides, which necessarily limits comparisons on the basis of the heats of solution.

The $ThBr_4$ used for the present determinations possessed tetragonal symmetry, isomorphous with $PaBr_4$,[32] while UBr_4 and $NpBr_4$ are monoclinic.[30,33] Scaife [31] has reported that the tetragonal form of $ThBr_4$ is in fact metastable at room temperature and slowly transforms during 6 months into an orthorhombic form (α-$ThBr_4$) which would be the thermodynamically stable form at room temperature. The transformation is stated to be more rapid at 600 K. Scaife also reports from differential thermal analysis data that the α ⟶ β transformation occurs at 693 K with a heat effect of *ca.* 4 kJ mol^{-1}. As part of another investigation concerning the structural properties of the actinide tetrahalides [34] numerous attempts have been made to repeat the preparation of α-$ThBr_4$ but all have been unsuccessful. In addition no β ⟶ α transformation has been observed for samples stored for 18 months. However, we prefer to retain the ' β ' nomenclature for the tetragonal phase at this stage. On the basis of *X*-ray powder results neither PaI_4 nor UI_4 appear to be isostructural with ThI_4,[35] or for that matter with each other.

The standard heats of formation of the various tetrahalides MX_4(s) according to equation (2) can be calculated by the use of the relationships (1), (3), and (4),

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which, upon combination, yield equation (A). $\frac{1}{4}\Delta H_3$

$$\mathrm{M(s,\ \alpha) + 2X_2(g,\ l,\ or\ s) \longrightarrow MX_4(s)};\ \Delta H_2 = \Delta H_f^\circ(\mathrm{MX_4,\ s}) \quad (2)$$

$$\mathrm{2X_2(g,\ l,\ or\ s) + 2H_2(g) + [MCl_4,}(a-4)\mathrm{HCl,}b\mathrm{H_2O]} \longrightarrow [\mathrm{MX_4,}a\mathrm{HCl,}b\mathrm{H_2O}];\ \Delta H_3 \quad (3)$$

$$\mathrm{M(s,\alpha)} + [a\mathrm{HCl,}b\mathrm{H_2O}] \longrightarrow [\mathrm{MCl_4,}(a-4)\mathrm{HCl,}b\mathrm{H_2O}] + \mathrm{2H_2(g)};\ \Delta H_4 \quad (4)$$

$$\Delta H_f^\circ(\mathrm{MX_4,\ s}) = -\Delta H_1 + \Delta H_3 + \Delta H_4 \quad \text{(A)}$$

thus represents the partial molal heat of formation of hydrochloric, hydrobromic, or hydroiodic acid, respectively, in 1M- or 6M-HCl from the elements in their standard states at 298 K. As usual, this value is obtained from the heat of formation of the infinitely dilute acid and the relative apparent molal heat content of the 1M and 6M acids. As customary, we have assumed in these calculations that the apparent heat of formation of hydrobromic and hydroiodic acids, respectively, are the same in hydrochloric acid as in hydrobromic or hydroiodic acid of the same molality. We have also neglected in these calculations, the influence of the low actinide ion concentrations ($<3 \times 10^{-3}$M). Thus we take for $\frac{1}{4}\Delta H_3$, $\Delta\bar{H}_f$(HCl, 1M-HCl) = −164·43 ± 0·08 kJ mol^{-1}, $\Delta\bar{H}_f$(HCl, 6M-HCl) = −153·43 ± 0·21 kJ mol^{-1}, $\Delta\bar{H}_f$(HBr, 1M-HCl) = −119·54 ± 0·08 kJ mol^{-1}, $\Delta\bar{H}_f$(HBr, 6M-HCl) = −109·62 ± 0·21 kJ mol^{-1}, $\Delta\bar{H}_f$ (HI, 1M-HCl) = −53·81 ± 0·08 kJ mol^{-1}, and $\Delta\bar{H}_f$ (HI, 6M-HCl) = −44·81 ± 0·21 kJ mol^{-1}.

For the heat of formation of the actinide(IV) ions (ΔH_4) we have used various literature values. That for $\mathrm{Th^{4+}}$ in 6M-HCl, −759·0 ± 0·8 kJ mol^{-1}, is from Eyring and Westrum [2] after correction for the influence (1·2 kJ mol^{-1}) of the $\mathrm{SiF_6^{2-}}$ ion (0·005M) which ensured complete dissolution of the thorium metal. For the heat of formation of $\mathrm{U^{4+}}$ in 6M-HCl we have used the value of Fitzgibbon *et al.*,[9] −569·9 ± 4·2 kJ mol^{-1}. No accurate correction could be made for the presence of the $\mathrm{SiF_6^{2-}}$ ion (0·009M) in the absence of appropriate experimental data but it is almost certain that this correction would be well within the above accepted error limits. The heat of formation of $\mathrm{U^{4+}}$ in 1M-HCl has been deduced from the value obtained by Fitzgibbon *et al.*[9] for the heat of formation of $\mathrm{UCl_4(s)}$, −1018·4 ± 2·9 kJ mol^{-1} (from the solution of the metal and $\mathrm{UCl_4}$ in 4M- and 6M-HCl), and our value [8] for the heat of solution of $\mathrm{UCl_4(s)}$ in 1M-HCl, −227·9 ± 1·0 kJ mol^{-1}, yielding −588·7 ± 3·3 kJ mol^{-1}. For the heat of formation of $\mathrm{Np^{4+}}$ in 1M-HCl we have used [19] −553·5 ± 1·3 kJ mol^{-1}.

In order to make full use of all our heats of solution values, we need also the heat of formation of $\mathrm{Th^{4+}}$ in 1M-HCl and of $\mathrm{Np^{4+}}$ in 6M-HCl. From the accumulation of heats of solution data on other quadrivalent actinide compounds, especially the caesium chloro-complexes [36] and oxydihalides,[37] a fairly accurate relationship between the heats of formation in 1M- and 6M-HCl, for each of the quadrivalent actinide ions (thorium to plutonium) has been obtained, as shown in equation (5)

$$\Delta H_f(\mathrm{M^{4+}},\ 1\mathrm{M\text{-}HCl}) - \Delta H_f(\mathrm{M^{4+}},\ 6\mathrm{M\text{-}HCl}) = -(9{\cdot}6 \pm 0{\cdot}8) - (3{\cdot}14 \pm 0{\cdot}4)(Z - 90)\ \mathrm{kJ\ mol^{-1}} \quad (5)$$

in which Z is the atomic number of the actinide. Using this relation, we obtain ΔH_f($\mathrm{Th^{4+}}$, 1M-HCl) = −768·6 ± 1·7 kJ mol^{-1} and ΔH_f($\mathrm{Np^{4+}}$, 6M-HCl) = −534·3 ± 2·1 kJ mol^{-1}.

This procedure yields −585·8 ± 4·6 kJ mol^{-1} for the heat of formation of $\mathrm{U^{4+}}$ in 1M-HCl which compares well with the value of −588·7 ± 3·3 kJ mol^{-1} accepted above.

The standard heat of formation data obtained from the heats of solution in 1M-HCl and 6M-HCl are listed in Table 3 together with the weighted average of these values and literature values for $\mathrm{UCl_4}$ and $\mathrm{NpCl_4}$.

TABLE 3

Heats of formation of various quadrivalent halides at 298·15 K

	$-\Delta H_f^\circ$/kJ mol^{-1}		
Compound	From 1M-HCl soln.	From 6M-HCl soln.	Average
$\mathrm{ThCl_4}$	1184·5 ± 1·9	1184·4 ± 1·0	1184·4 ± 1·0
$\mathrm{ThBr_4}$(β)	963·2 ± 2·1	963·5 ± 1·4	963·4 ± 1·4
$\mathrm{ThI_4}$	661·8 ± 1·8	662·2 ± 1·9	662·0 ± 1·8
$\mathrm{UCl_4}$ [a]	—	—	1019·2 ± 0·8
$\mathrm{UBr_4}$	802·3 ± 3·4	802·7 ± 4·4	802·5 ± 3·4
$\mathrm{UI_4}$	514·0 ± 3·6	508·9 ± 4·5	511·5 ± 4·0
$\mathrm{NpCl_4}$ [b]	—	—	986·2 ± 1·3
$\mathrm{NpBr_4}$	772·9 ± 1·7	773·6 ± 2·4	773·2 ± 1·7

[a] Ref. 9. [b] Ref. 19 (see also text).

Our value for the heat of formation of $\mathrm{ThCl_4(s)}$ is 3 kJ mol^{-1} less negative than the ' best ' value deduced by Rand [4] during an assessment of the previously available data.[2,38] The difference is essentially due to our slightly more negative values for the heats of solution, −241·8 ± 0·7 and −188·3 ± 0·4 kJ cal^{-1} for 1M- and 6M-HCl, respectively, compared with −240·2 ± 0·4 and −185·2 ± 0·4 kJ mol^{-1}. The value we obtain for ΔH_f° (ThBr, s), −963·4 ± 1·4 kJ mol^{-1}, is very close to that based [4] on the heat of solution of this compound in water, −962·3 ± 4 kJ mol^{-1}, indicating the relatively small hydrolysis of thorium(IV) ions in water. However, our value for $\mathrm{ThI_4(s)}$, −662·0 ± 1·8 kJ mol^{-1}, is in only moderate agreement with that based [4] on the preliminary results of Scaife *et al.*,[7] −670·7 ± 4 kJ mol^{-1}.

Our values for the heats of formation of $\mathrm{UBr_4(s)}$ and $\mathrm{UI_4(s)}$, −802·5 ± 3·4 and −511·5 ± 4·0 kJ mol^{-1}, respectively, are appreciably different from the values recommended by Rand and Kubaschewski [15] from the data of Barkelew,[12,17] −826·3 ± 4 and −529·3 ± 4 kJ mol^{-1}, respectively. However, as mentioned in the Introduction section, correction of the $\mathrm{UBr_4(s)}$ results on the basis of an error in the earlier value for the heat of solution of uranium metal yields the value −794·9 ±

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[36] J. Fuger and D. Brown, *J. Chem. Soc.* (*A*), 1971, 841.

[37] J. Fuger and D. Brown, unpublished results.

[38] H. P. Robinson and E. F. Westrum, jun., NNES Plutonium Project Record, Vol. 14B, Paper 6.54, McGraw-Hill, New York, 1949.

4 kJ mol^{-1} which is very much closer to our new value which lies, in fact, between this value and the corrected value of Shchukarev *et al.*,[18] $-811{\cdot}3 \pm 4$ kJ mol^{-1}. Correction of Barkelew's value for UI_4(s) yields, as mentioned earlier, $-497{\cdot}9 \pm 4$ kJ mol^{-1}, a value which is appreciably less negative than the one we have obtained.

Our value for the heat of formation of $NpBr_4$(s), $-773{\cdot}2 \pm 1{\cdot}7$ kJ mol^{-1}, is close to the previously estimated[20] value, -766 kJ mol^{-1}.

By use of the heats of formation listed in Table 3 and either experimental or suitably extrapolated values for entropies and heat capacities, thermodynamic functions associated with the formation of the compounds in Table 3 have been calculated as a function of temperature from 298 K to the m.p.s of the compounds. In order to allow immediate comparison of the results the formation reactions from *gaseous* halides are considered according to equation (6). The fundamental

$$M(s) + 2X_2(g) \longrightarrow MX_4(s) \qquad (6)$$

(7)—(9) equations are well known. In these relations

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p \, dT \qquad (7)$$

$$\Delta S_T = \Delta S_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} \, dT \qquad (8)$$

$$\Delta G_T = \Delta H_T - T\Delta S_T \qquad (9)$$

the subscripts indicate the temperature and ΔH, ΔS, ΔG, and ΔC_p are, respectively, the molal heat, entropy, Gibbs free energy, and heat-capacity change for reaction (6). An accurate calculation would require the variation of C_p as a function of temperature for each of the substances involved in the reaction. However, the ΔC_p values vary little as a function of temperature. Therefore, as is customary,[4,15] we have considered these ΔC_p values as constant over the temperature range considered and in practice have evaluated the C_p values at 600 K. This procedure usually introduces an error which is negligible compared with the error affecting the final ΔG_T values. The equations are, of course, only valid if there is no phase change in any of the substances considered.

Equations (7)—(9) now reduce to (10)—(12). Table 4

$$\Delta H_T = A + \Delta C_p T, \text{ with } A = \Delta H_{298} - 298\Delta C_p \qquad (10)$$

$$\Delta S_T = B + C \log_{10} T, \text{ with } B = \Delta S_{298} - 2{\cdot}3026\, \Delta C_p \log_{10} 298 \text{ and } C = 2{\cdot}3026 \Delta C_p \qquad (11)$$

$$\Delta G_T = A - (B - \Delta C_p)T - CT \log_{10} T \qquad (12)$$

summarises the various thermodynamic data[39,40] used in the calculations of these thermodynamic functions. A few data in this Table require comment. The heat capacity of neptunium metal at 600 K, 36·78 J mol^{-1} K^{-1}, has been obtained by taking the experimental[39] C_p value at 298 K, 29·63 J mol^{-1} K^{-1}, and assuming the same temperature dependence as for uranium metal[15] between 298 and 600 K. In fact neptunium metal undergoes a phase change[41] at 553 K (orthorhombic to tetragonal) with an associated heat of $+5{\cdot}61 \pm 0{\cdot}54$ kJ mol^{-1} and entropy change of $+10{\cdot}13$ J mol^{-1} K^{-1}. We have taken these data into account in the calculations of the thermodynamic functions for the formation of the neptunium halides, but in the absence of experimental data on C_p of the metal as a function of temperature, we have used throughout the whole temperature range the above value for C_p estimated for 600 K. The same remark applies to the calculations for $ThCl_4$(s) for which a phase change at 679 K with a heat effect of $+5{\cdot}0 \pm 0{\cdot}5$ kJ mol^{-1} has been reported.[33,42] On the other hand the thermodynamic functions for $ThBr_4$(s) have been calculated for the tetragonal form (β) used in our experiments in view of the uncertainty in the reported heat effect (*ca.* 4 kJ mol^{-1}) associated with the α to β transformation.[31] The heat capacities

TABLE 4

Data used in the calculation of the various thermodynamic functions associated with the formation of the tetrahalides

$$M(s) + X_2(g) \longrightarrow MX_4(s)$$

Compound	S_{298} / J mol^{-1} K^{-1}	Ref.	$\Delta H_{f\,298}$ / J mol^{-1}	Ref.	$C_{p\,600}$ / J mol^{-1} K^{-1}	Ref.
Th(s, α)	53·39	4	0		30·04	4
U(s, α)	50·21	15	0		34·75	15
Np(s, α)	50·45	39	0		36·78	*a*
Cl_2(g)	222·96	3	0		36·61	40
Br_2(g)	245·35	3	30 907	40	37·28	40
I_2(g)	260·58	3	62 438	40	37·66	40
$ThCl_4$(s)	190·4	4	−1 184 400	*b*	132·54	4
$ThBr_4$(s)	228·0	4	−1 025 200	*b*	138·21	*a*
ThI_4(s)	265·7	4	−786 900	*b*	144·23	*a*
UCl_4(s)	198·3	15	−1 019 200	9	134·40	15
UBr_4(s)	234·3	15	−864 300	*b*	140·07	15
UI_4(s)	280·3	15	−636 400	*b*	146·09	15
$NpCl_4$(s)	207·1	*a*	−986 200	19	135·33	*a*
$NpBr_4$(s)	238·9	*a*	−835 000	*b*	141·00	*a*

[a] See text. [b] This work.

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[39] J. A. Lee, K. Mendelssohn, and P. W. Sutcliffe, *Proc. Roy. Soc.*, 1970, *A*, **317**, 303.

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at 600 K of $ThBr_4$(s) and ThI_4(s) have been estimated by assuming that the changes in heat capacity along the UCl_4–UBr_4–UI_4 series are the same for the corresponding thorium compounds, using the heat capacity of $ThCl_4$(s) as starting value. The entropies of $NpCl_4$(s) and $NpBr_4$(s) have been obtained by Latimer's method [43] with use of 71·5 J mol^{-1} K^{-1} for the contribution of the neptunium atom to the entropy of the compound, with 33·9 and 41·8 J mol^{-1} K^{-1} for the contribution of each of the chlorine and bromine atoms, respectively. The choice of 71·5 J mol^{-1} K^{-1} for the entropy of the neptunium atom in these compounds arises from the following considerations. The entropy of NpO_2(s) has been given [44] as 80·3 ± 0·4 J mol^{-1} K^{-1}; with a value of 4·2 J mol^{-1} K^{-1} for the contribution of each oxygen atom, one obtains 71·9 J mol^{-1} K^{-1} for the contribution of the neptunium to the entropy of the oxide. On the other hand, the contribution to the entropy of thorium in simple quadrivalent compounds is [4] 57·7 J mol^{-1} K^{-1} and that of uranium [15] is 66·9 J mol^{-1} K^{-1}. From the entropy of PuO_2(s),[45,46] 82·4 J mol^{-1} K^{-1}, a contribution of 74·1 J mol^{-1} K^{-1} can be deduced for the contribution of the plutonium atom. From the entropy of PuF_4(s),[45,46] 161·9 J mol^{-1} K^{-1}, one obtains 78·2 J mol^{-1} K^{-1} for the contribution of the plutonium atom to the entropy, after subtraction of 83·7 J mol^{-1} K^{-1} for the contribution of the four fluorine atoms. An average value 76·2 J mol^{-1} K^{-1} can thus be taken for the contribution of plutonium to the entropy of simple quadrivalent compounds. A linear interpolation between thorium and plutonium then gives 71·5 J mol^{-1} K^{-1} for the entropy of the neptunium atom in a quadrivalent compound; this value, in agreement with the entropy of NpO_2(s), has been employed in our calculations. The heat capacities at 600 K of $NpCl_4$(s) and $NpBr_4$(s) have been estimated by adding to the C_p value of the corresponding uranium compound half the difference between the uranium and the thorium compound.

Table 5 shows the coefficients of the equations (10), (11), and (12) for the enthalpy, entropy, and free energy of formation of the various halides, according to equation (6). In these calculations we have used 298 K instead of 298·15 K. The upper values for the temperature range of validity of the various equations is either a phase change reported above or the m.p. [47] of the tetrahalide.

TABLE 5

Coefficients for the calculation of the thermodynamic functions associated with the formation of the tetrahalides

$$M(s) + 2X_2(g) \longrightarrow MX_4(s)$$
$$\Delta H_T = A + \Delta C_p\, T$$
$$\Delta S_T = B + C \log_{10} T$$
$$\Delta G_T = A - (B - \Delta C_p)\, T - CT \log_{10} T \text{ (joules, mol, K)}$$

Compd.	A	B	ΔC_p	C	Range/K
$ThCl_4$(s)	−1 193 100	−475·7	29·28	67·42	298—679
$ThCl_4$(s)	−1 188 100	−468·3	29·28	67·42	679—1043
$ThBr_4$(s)	−1 035 200	−507·6	33·61	77·39	298—952
ThI_4(s)	−798 500	−530·3	38·87	89·50	298—839
UCl_4(s)	−1 027 100	−448·4	26·43	60·86	298—863
UBr_4(s)	−873 500	−481·8	30·76	70·83	298—792
UI_4(s)	−647 100	−496·3	36·02	82·94	298—779
$NpCl_4$(s)	−993 700	−433·6	25·33	58·32	298—553
$NpCl_4$(s)	−999 300	−443·7	25·33	58·32	553—811
$NpBr_4$(s)	−843 800	−471·2	29·66	68·30	298—553
$NpBr_4$(s)	−849 400	−481·3	29·66	68·30	553—737

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