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Standard enthalpies of formation of uranium compounds VIII. UCl₃, UCl₅, and UCl₆

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Enthalpies of solution of UCl₃ in $H_2SO_4(aq)$ have been measured calorimetrically. In the same way enthalpies of solution of UCl₅ and UCl₆ have been measured in (HCl+FeCl₃)(aq) and HCl(aq), respectively. Together with data for the auxiliary reactions, the standard enthalpies of formation of UCl₃(s), UCl₅(s), and UCl₆(s) have been derived. The results obtained are as follows:

	$\Delta H_{\rm f}^{\circ}({\rm s}, 298.15 \ {\rm K})/({\rm kJ} \cdot {\rm mol}^{-1})$
UCI,	$-(862.1\pm3.2)$
UCl ₅	$-(1041.6\pm1.9)$
UCL	$-(1066.5\pm1.9)$

1. Introduction

In a previous paper in this series we reported on the enthalpy of formation of $UCl_4(s)$.⁽¹⁾ Since that time an evaluation of the thermochemical properties of the uranium halides by Parker⁽²⁾ appeared in which the unsatisfactory situation with respect to the enthalpy of formation of the other uranium chlorides is emphasized.

As part of our work to provide accurate thermodynamic quantities for important uranium compounds, we here present enthalpy-of-solution measurements from which the enthalpies of formation of UCl_3 , UCl_5 , and UCl_6 have been derived.

2. Experimental

Uranium trichloride, UCl₃, was prepared by heating uranium hydride with hydrogen chloride at 623 to 673 K. The X-ray powder diagram of the product obtained showed that besides UCl₃ a small amount of UCl₄ was present. The UCl₄ impurity was converted into UCl₃ by treatment of the sample with purified hydrogen at 600 to 793 K. Reaction of the reduced product with dilute sulphuric acid left a small residue which by X-ray analysis proved to be UO₂.

The uranium hydride used was prepared as described before.⁽³⁾

Uranium pentachloride, UCl_5 , can be prepared by treatment of UCl_3 or UCl_4 with chlorine at 773 to 823 K, but by this method UCl_5 is obtained as an extremely fine dust which is difficult to handle. Besides, the n(Cl)/n(U) ratio may be as high as 5.5.⁽⁴⁾ A second method, which we followed, is the liquid-phase chlorination of UO_3 by tetrachloromethane in a sealed ampoule.^(4, 5) Preliminary experiments showed that the reaction temperature of 523 K as stated in the literature^(4, 5) is too high; according to the X-ray diagram the product obtained proved to be a mixture of UCl_5 and UCl_4 . It is assumed that the primary product of the reaction of UO_3 with CCl_4 is UCl_6 and that UCl_5 and UCl_4 arise by thermal decomposition of UCl_6 .⁽⁶⁾ Heating of the ampoules at 388 K for 4 h yielded a product that besides UCl_5 contained only a small amount of UCl_6 .

In contradiction with results of other investigators ⁽⁷⁾ we found that loss of chlorine from UCl₅ at room temperature is negligible. A short note on this subject (also including UCl₆) will be published elsewhere.⁽⁸⁾

Uranium hexachloride, UCl₆, was prepared by disproportionation of UCl₅ into UCl₄ and UCl₆ at 353 to 398 K *in vacuo*. The apparatus used was essentially identical to that described by Johnson *et al.*;⁽⁹⁾ however, electrical heating was applied instead of using a sulphuric-acid heating bath. The volatilized UCl₆ was collected on a cold finger filled with (acetone + solid carbon dioxide). Since the starting material, UCl₅, is also notably volatile at the temperatures mentioned, the UCl₆ contained a small amount of UCl₅. According to the literature⁽¹⁰⁾ it is difficult if not impossible to separate UCl₅ and UCl₆ by sublimation: therefore a further purification of the UCl₆ sample was not attempted.

The various chlorides were characterized by X-ray diffraction and chemical analysis. The X-ray diagrams showed that some UO₂ was present in UCl₃, UCl₆ in UCl₅, and UCl₅ in UCl₆; other impurities such as oxychlorides could not be detected. The total uranium content was determined by a computer-controlled titration according to the procedure described by Lingerak *et al.*⁽¹¹⁾ The U(VI) content was found by titration with Fe(II) in phosphoric acid solution⁽¹²⁾ and the U(IV) content by oxidation with potassium dichromate solution and back titration with Fe(II). Chloride was determined by potentiometric titration with standard silver nitrate solution. The results of the analyses are given in table 1.

	М		10 ² w	v(U)	10 ² w(Cl)	
Compound	g·mol ^{−1}		obs.	calc.	obs.	calc.
UCl ₃	344.388	UO ₂ :	$ \begin{array}{r} 69.10 \pm 0.05 \\ 0.81 \pm 0.02 \end{array} $	69.12	30.87±0.03	30.88
UCl5	415.294	U(VI) :	$56.90 \pm 0.02 \\ 30.16 \pm 0.03$	57.32 28.66	42.85 ± 0.01	42.68
UCl ₆	450.747	U(IV):	$52.80 \pm 0.04 \\ 0.934 \pm 0.006$	52.81	$\textbf{46.95} \pm 0.04$	47.19

TABLE 1. Analytical results; molar mass M and mass fraction w

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TABLE 2. Enthalpy of solution of a mass m of a specified solute in 200 cm ³	of a specified aqueous solvent at
298.15 K	

m(solute)/g	20/J	$\Delta \theta / \theta$	~ 2	$M/(KJ \cdot mol^{-1})$	$ \delta \Delta H /(kJ \cdot mol)$
(a) Solute: $UCl_3 + 2.960$	07NaCl	Solvent: 1.51	1 mol·dm ³	H ₂ SO ₄ solution	
			UCl ₃	+	
UCI ₃ NaCl			2.9607N	aCl UCl ₃	UCl ₃
0.35477 + 0.17825	92.353	2.1491	192.6	7 209.79	2.37
0.35538+0.17856	94.528	2.0604	188.7	4 205.86	1.56
0.33660+0.16912	93.361	1.9818	189.3	0 206.42	1.00
0.37355+0.18768	94.214	2.1932	190.5	0 207.62	0.20
				average: 207.42	1.28
			twi	ce standard error	of mean: 1.74
(b) Solute: NaCl		Solvent: 1.5	11 mol·dm	³ H ₂ SO ₄ solution	
0.17974	93.340	-0.1900		- 5.766	0.018
0.17919	93.583	-0.1901		-5.802	0.018
			average:	- 5.784	0.018
			twic	e standard error o	of mean : 0.036
(c) Solute: UCl ₅		Solvent: HO	Cl · 0.0419Fe	Cl ₃ ·70.66H ₂ O	
0.47289	92.618	3.4667		281.97	1.11
0.47301	91.584	3.5208		283.10	0.02
0.48873	93.323	3.5807		283.95	0.87
0.47004	93.205	3.4539		284.43	1.35
0.47315	92.135	3.4866		281.96	1.12
			average:	283.08	0.89
			twi	ce standard error	of mean: 1.01
		corrected for	or impurity:	278.32	1.21
(d) Solute: UCl ₆		Solvent: HO	Cl · 0.0419Fe	Cl ₃ ·70.66H ₂ O	
0.49870	91.281	4,4235		364.96	0.70
0.48478	92.515	4.2590		366.36	0.70
			average	365 66	0.70
			twi	ce standard error	of mean: 1.40
(e) Solute: UCL		Solvent · H(CI+0.0419Fe	Cl. 70.66H.O	
0 44727	92 466	2 3922		187.85	0.27
0.43482	93 104	2.3922		186.98	0.27
0.43338	92.660	2.3138		187.91	0.33
			average	187 58	0.40
			twi	ce standard error	of mean: 0.60
(f) Solute: UO-Cl-		Solvent · H(CI-0.0419Fe	CL . 70 66H .O	
0 66928	92 625	2 1646	2. 0.011210	102.13	0.55
0.66057	92.025	2.1040		102.1.5	0.55
0.67123	92.488	2.1859		102.69	0.01
			avera ce ·	102.68	0.37
			average.	102.00	0.3/

m(solute)/g	$arepsilon heta / {f J}$	$\Delta \theta / \theta$	- 2	$M/(kJ \cdot mol^{-1})$	$ \delta\Delta H /(kJ\cdot mol^{-1})$
(g) Solute: UCl ₆		Solvent	: HC1 · 54	7H ₂ O	
0.39924	93.715	3.5778		378.55	0.68
0.39967	94.693	3.5337		377.38	0.49
0.41289	93.984	3.6937		378.98	1.11
0.39291	95.109	3.4694		378.54	0.67
0.40302	94.403	3.5603		375.91	1.96
		a	verage:	377.87	0.98
			twic	e standard error o	of mean: 1.12
		Corrected for in	npurity:	378.72	1.31
(h) Solute: UCl ₅		Solvent	: HCl · 54	7H2O	
0.35571	93 403	2 8041		305 78	1.48
0.37522	93.891	2.9710		308.74	1.48
		a	verage :	307.26	1.48
			twic	e standard error o	of mean: 2.96
(i) Solute: UO_2Cl_2		Solvent:	HCl · 54	7H ₂ O	
0.40064	94.174	1.3573		108.77	0.48
0.37632	95.226	1.2605		108.75	0.46
0.38703	93.237	1.3124		107.79	0.50
0.40541	94.105	1.3649		108.02	0.27
0.39778	93.351	1.3516		108.14	0.15
		a	verage:	108.29	0.37
			twic	e standard error o	of mean: 0.40

TABLE 2-continued

All handlings of the very hygroscopic compounds were performed in a glove box filled with dry recirculating argon.

The enthalpies of solution were measured in a calorimeter which has been described previously, together with the calorimetric procedure and calibration method.⁽¹³⁾ Corrections to the temperature rise in the calorimeter were based on a complete calculation of the pre- and post-period according to Newton's cooling law.

The H_2SO_4 , $HCl + FeCl_3$, and HCl solutions were prepared from reagent-grade acids and iron(III) chloride. They were analysed by potentiometric titration with standard NaOH solution; Fe(III) was determined by reduction with excess standard Sn(II) solution and back-titration of Sn(II) with standard Hg(II) solution.

3. Results

Details of the measurements are given in table 2, where *m* is mass of the sample dissolved, ε is the energy equivalent of the calorimeter, $\Delta\theta$ is the temperature change, ΔH is the molar enthalpy of solution, and $|\delta\Delta H|$ is the deviation of the measured ΔH from the average value; θ is an arbitrary unit of temperature.

ENTHALPY OF FORMATION OF UCl₃

The reaction scheme to derive $\Delta H_{f}^{\circ}(UCl_{3})$ is given in table 3. Preliminary calorimetric experiments showed that UCl₃ reacted vigorously with the sulphuric acid solution, so that part of the sample was ejected from the solvent. To avoid this, a mixture of UCl₃ and NaCl was pressed into pellets; the enthalpy of solution of these pellets could be measured smoothly. Likewise the enthalpy of solution of NaCl in the solvent was determined. From the two series of measurements the enthalpy of solution of UCl₃ was calculated. Details of the experiments are given in table 2, (a) and (b). The masses of UCl₃ listed in table 2 are the values obtained after correction of the UO₂ impurity mentioned in table 1 (UO₂ does not dissolve in the sulphuric acid solution).

TABLE 3. Reaction scheme for the enthalpy of formation of UCl₃; (sln) refers to 1.511 mol \cdot dm⁻³ H₂SO₄ in water;

Reaction	$\Delta H/(kJ \cdot mol^{-1})$
1. $UCl_1(s) + 2H_2SO_4(sln) = \{U(SO_4)_2 + 3HCl\}(sln) + \frac{1}{2}H_2(g)$	-207.90 ± 1.75
2. $UCl_{4}(s) + 2H_{2}SO_{4}(sln) = \{U(SO_{4})_{2} + 4HCl\}(sln)$	-213.13 ± 0.84
3. $U(s) + 2Cl_2(g) = UCl_4(s)$	-1018.8 ± 2.5
4. $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) + (sln) = HCl(sln)$	-161.98 ± 0.23
5. $U(s) + \frac{3}{2}Cl_2(g) = UCl_3(s)$	-862.1 ± 3.2

 $\Delta H_5 = -\Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$

The enthalpy of solution of UCl₃, $-(207.42 \pm 1.74)$ kJ·mol⁻¹, has to be corrected for the vaporization of water by the evolved hydrogen. Assuming the hydrogen to be (75 ± 25) per cent saturated and taking the vapour pressure over the solution at 298.15 K as 2.96 kPa,⁽¹⁴⁾ and the enthalpy of vaporization of water as (44.016 ± 0.059) kJ·mol⁻¹,⁽¹⁵⁾ the correction for the evolution of $\frac{1}{2}$ H₂ is (0.48 ± 0.16) kJ·mol⁻¹, resulting in $-(207.90\pm1.75)$ kJ·mol⁻¹ for the enthalpy of solution of UCl₃ in 1.511 mol·dm⁻³ H₂SO₄ solution. This value has to be combined with the enthalpy of solution of UCl₄ in the same solvent, $-(213.13\pm0.84)$ kJ·mol⁻¹,⁽¹⁾ with the enthalpy of formation of UCl₄(s),⁽²⁾ and with the enthalpy of formation of HCl(sln). The latter quantity was calculated from the reaction scheme given in table 4 of reference 1. The small difference in composition of the H₂SO₄ solutions: 1.505 mol·dm⁻³ in reference 1 and 1.511 mol·dm⁻³ in the present investigation is neglected. Thus we obtain the enthalpy of formation of UCl₃(s). $\Delta H_{0}^{c}(298.15 \text{ K}) = -(862.1\pm3.2)$ kJ·mol⁻¹.

ENTHALPY OF FORMATION OF UCI,

The reaction scheme to derive $\Delta H_{f}^{\circ}(UCl_{5})$ is given in table 4. The sample of UCl₅, which contains UCl₆ as an impurity, has the composition UCl₅ \cdot (0.080±0.020)UCl₆. as has been calculated from the content of total U and U(VI) (the chemical analysis of the chlorine content is considered to be less reliable). The enthalpy of solution of

TABLE 4. Reaction scheme for the enthalpy of formation of UCl_5 ; (sln) refers to $HCl \cdot 0.0419 FeCl_3 \cdot 70.66 H_2O$;

	Reaction	$\Delta H/(kJ \cdot mol^{-1})$
1.	$UCl_{s}(s) + \{FeCl_{3} + 2H_{2}O\}(sln) = \{UO_{2}Cl_{2} + FeCl_{2} + 4HCl\}(sln)$	-278.32 +1.21
2.	$\frac{1}{2}UCl_4(s) + \{FeCl_3 + H_2O\}(sln) = \{\frac{1}{2}UO_2Cl_2 + FeCl_2 + 2HCl\}(sln)$	-93.79 + 0.30
3.	$\frac{1}{2}UO_2Cl_2(s) + (sln) = \frac{1}{2}UO_2Cl_2(sln)$	-51.34 + 0.32
4.	$\frac{1}{2}U(s) + \frac{1}{2}O_2(g) + \frac{1}{2}Cl_2(g) = \frac{1}{2}UO_2Cl_2(s)$	-621.7 ± 0.6
5.	$\frac{1}{2}U(s) + Cl_2(g) = \frac{1}{2}UCl_4(s)$	-509.4 + 1.3
6.	$H_2(g) + \frac{1}{2}O_2(g) = H_2O(1)$	-285.830 ± 0.042
7.	$H_2O(l) + (sln) = H_2O(sln)$	-0.01
8.	$H_2(g) + Cl_2(g) + (sln) = 2HCl(sln)$	-329.56 ± 0.18
9.	$U(s) + \frac{5}{2}Cl_2(g) = UCl_5(s)$	-1041.6 ±1.9

 $\Delta H_9 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - \Delta H_6 - \Delta H_7 + \Delta H_8$

UCl₅ must be corrected for this UCl₆ impurity, using the enthalpy of solution of UCl₆ in the same solvent. The UCl₆ sample contains UCl₅ as an impurity and has the composition UCl₆ \cdot (0.019 \pm 0.019)UCl₅, calculated from the content of total U and U(IV). The enthalpies of solution of "impure" UCl₅ and UCl₆ with compositions UCl₅, (0.080 \pm 0.020)UCl₆ and UCl₆ \cdot (0.019 \pm 0.019)UCl₅, respectively, are measured and the enthalpy of solution of pure UCl₅ is calculated from the two calorimetric results and the two compositions. Details of the experiments are given in table 2, (c) and (d).

The enthalpy of solution of UCl₅ in HCl·0.0419FeCl₃·70.66H₂O, $-(278.32 \pm 1.21)$ kJ·mol⁻¹, has to be combined with the enthalpies of solution of UCl₄ and UO₂Cl₂ in the same solvent [table 2, (e) and (f)], with the enthalpies of formation of UO₂Cl₂,^(1,2) UCl₄,⁽²⁾ and H₂O,⁽¹⁵⁾ and with the partial molar enthalpies of dilution and formation of the solution. The latter two quantities have been calculated from the tabulated enthalpies of formation of HCl solutions,⁽¹⁵⁻¹⁷⁾ neglecting the presence of FeCl₃. Thus the enthalpy of formation of UCl₅ is found to be $\Delta H_f^{\circ}(298.15 \text{ K}) = -(1041.6 \pm 1.9)$ kJ·mol⁻¹.

TABLE 5 Reaction scheme for	the enthalow of formation	of UCL (alm) refere to	101 64711 0
TABLE 5. Reaction scheme for	the enthalpy of formation	$1 \text{ of } U C I_6$; (sin) refers to	$HC1.54/H_2O$;

$$\Delta H_7 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6$$

$\Delta H/(kJ \cdot mol^{-1})$
-378.72 ± 1.31
-108.29 ± 0.40
-1243.5 + 1.3
-665.06 + 0.35
-571.660 ± 0.084
0.00
-1066.5 ± 1.9

ENTHALPY OF FORMATION OF UCl₆

The reaction scheme to derive $\Delta H_f^{\circ}(UCl_6)$ is given in table 5. The enthalpy of solution of UCl_6 has to be corrected for the UCl_5 impurity of the sample. This is done in the same way as described in the preceding section. Details of the experiments are given in table 2, (g) and (h).

The enthalpy of solution of UCl₆ in HCl \cdot 547H₂O, $-(378.72 \pm 1.31)$ kJ·mol⁻¹, is combined with the enthalpy of solution of UO₂Cl₂ in the same solvent [table 2 (i)] and with the auxiliary values for UO₂Cl₂, HCl, and H₂O as mentioned in the preceding section to give the enthalpy of formation of UCl₆(s): $\Delta H_f^{\circ}(298.15 \text{ K}) = -(1066.5 \pm 1.9)$ kJ·mol⁻¹.

4. Discussion

The enthalpy of formation of $UCl_3(s)$ has been discussed by Parker.⁽²⁾ From a number of independent measurements along different routes, *via* both enthalpy-of-solution measurements and a determination of the equilibrium:

$$UCl_4(s) + \frac{1}{2}H_2(g) = UCl_3(s) + HCl(g)$$
.

she selected the value $-(866.1 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1}$ for the enthalpy of formation of UCl₃(s). This value is in agreement with the present value of $-(862.1 \pm 3.2) \text{ kJ} \cdot \text{mol}^{-1}$.

The enthalpies of formation of UCl₅(s) and UCl₆(s) have also been discussed by Parker.⁽²⁾ From measurements by Barkelew, cited by MacWood,⁽¹⁸⁾ of the enthalpies of solution of UCl₄(s), UCl₅(s), and UCl₆(s) in (HCl+FeCl₃) solution, Parker calculates $\Delta H_{\rm f}^{\circ}({\rm UCl}_5, {\rm s}, 298.15 {\rm K}) = -1062 {\rm kJ} \cdot {\rm mol}^{-1}$ and $\Delta H_{\rm f}^{\circ}({\rm UCl}_6, {\rm s}, 298.15 {\rm K}) = -1102 {\rm kJ} \cdot {\rm mol}^{-1}$.

However, Gross *et al.*⁽¹⁹⁾ measured by direct chlorination of U(s) with Cl₂(l): $\Delta H_f^{\circ}(UCl_5, s, 298.15 \text{ K}) = -(1036.4 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$. Parker concludes that, since $\Delta H_f^{\circ}(UCl_4, s, 298.15 \text{ K}) = -(1018.8) \text{ kJ} \cdot \text{mol}^{-1}$, and $\{\Delta H_f^{\circ}(UCl_4) - \Delta H_f^{\circ}(UCl_5)\}$ $\approx \{\Delta H_f^{\circ}(UCl_5) - \Delta H_f^{\circ}(UCl_6)\}$, one would expect for the enthalpy of formation of $UCl_6(s)$: $\Delta H_f^{\circ}(298.15 \text{ K}) \approx -1054 \text{ kJ} \cdot \text{mol}^{-1}$ if the results of Gross *et al.* are accepted. Parker disregarded Gross *et al.*'s results because "the overall picture they present appears unreasonable, as compared to the other halides". However, our result for the enthalpy of formation of $UCl_5(s)$ is in good agreement with the value of Gross *et al.*; likewise our result for $UCl_6(s)$ is in good agreement with the value that can be predicted from the enthalpies of formation of $UCl_4(s)$ and $UCl_5(s)$. Obviously, the results of Barkelew are in error, as is known to be so also for ΔH of oxidation of U(s) in the same medium.

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