UCRL--21055

DE88 010715

Thermochemistry of Uranium Compounds. XVI. Calorimetric Determination of the Standard Molar Enthalpy of Formation at 298.15 K, Low-Temperature Heat Capacity, and High-Temperature Enthalpy Increments of $UO_2(OH)_2 \cdot H_2O$ (Schoepite)

I.R. Tasker
P.A.G. O'Hare
B.M. Lewis
G.K. Johnson
E.H.P. Cordfunke

Work Performed at
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

August 1987

Lawrence Livermore National Laboratory

DISCLAIMER

Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under *contract number* W-7405-ENG-48.

Prepared by Nevada Nuclear Waste Storage Investigations (NNWSI)) Project participants as part of the Civilian Radioactive Waste Management Program. The NNWSI Project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. NNWSI Project work is sponsored by the DOE Office of Civilian Radioactive Waste Management.

Thermochemistry of uranium compounds. XVI. Calorimetric determination of the standard molar enthalpy of formation at 298.15 K, low-temperature heat capacity, and high-temperature enthalpy increments of $UO_2(OH)_2 \cdot H_2O$ (schoepite)

I. R. TASKER, P. A. G. O'HARE, BRETT M. LEWIS, G. K. JOHNSON
Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

and

E. H. P. CORDFUNKE
Netherlands Energy Research Foundation ECN, Petten, The Netherlands

This paper is dedicated to Professor James A. Morrison
on the occasion of his 70th birthday.

(The Canadian Journal of Chemistry, in press)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Three precise calorimetric methods, viz., low-temperature adiabatic, high-temperature drop, and solution-reaction, have been used to determine as a function of temperature the key chemical thermodynamic properties of a pure sample of schoepite, $UO_2(OH)_2 \cdot H_2O$. The following results have been obtained at the standard reference temperature $T = 298.15$ K: standard molar enthalpy of formation $\Delta_f H^\circ_m(T) = -1825.4 \pm 2.1$ kJ mol^{-1}; molar heat capacity $C^\circ_{p,m}(T) = 172.07 \pm 0.34$ JK^{-1} mol^{-1}; and the standard molar entropy $S^\circ_m(T) = 188.54 \pm 0.38$ JK^{-1} mol^{-1}. The molar enthalpy increments relative to 298.15 K and the molar heat capacity are given by the polynomials: $\{H^\circ_m(T) - H^\circ_m(298.15\ K)\}/(J\ mol^{-1}) = -38209.0 + 84.2375\ (T/K) + 0.1472958\ (T/K)^2$ and $C^\circ_{p,m}(T)/(JK^{-1}\ mol^{-1}) = 84.238 + 0.294592\ (T/K)$, where $298.15\ K < T < 400\ K$. The present result for $\Delta_f H^\circ_m$ at 298.15 K has been combined with three other closely-agreeing values from the literature to give a recommended weighted mean $\Delta_f H^\circ_m = -1826.4 \pm 1.7$ kJ mol^{-1}, from which is calculated the standard Gibbs energy of formation $\Delta_f G^\circ_m = -1637.0 \pm 1.7$ kJ mol^{-1} at 298.15 K. Complete thermodynamic properties of schoepite are tabulated from 298.15 to 423.15 K.

Introduction

Schoepite, $UO_3{\cdot}2H_2O$, is, on the basis of X-ray diffraction and infrared spectroscopic evidence (1), more accurately depicted as $UO_2(OH)_2{\cdot}H_2O$. However, the more compact formula will be used for convenience in the present paper. The hydrate has an orthorhombic unit cell (Pbna) with a = 1.3977 nm, b = 1.6696 nm, and c = 1.4672 nm, and there are 32 molecules in the cell. Uranium exhibits eight-fold octahedral coordination; the structure is layered with the hydrate water situated between the layers (2).

Our current technical interest in schoepite arises from modelling studies connected with the burial of nuclear waste. Specifically, the question being addressed is the fate of dissolved uranium in contact with concrete at 298.15 K. Under such conditions, and on the basis of existing thermodynamic values, schoepite is calculated to be the phase that limits the uranium activity in solution (3).

The objective of the present research was to obtain by high-precision calorimetry the following molar thermodynamic properties of a single specimen of pure schoepite: the standard enthalpy of formation $\Delta_f H^{\circ}_{m}$ at 298.15 K; the low-temperature heat capacity $C^{\circ}_{p,m}$ and, thence, the standard entropy S°_{m}; and the enthalpy increments relative to 298.15 K, up to the limit of stability of the material.

Experimental

Schoepite was prepared at ECN by hydration of anhydrous, amorphous UO_3 which had been obtained by thermal decomposition at 625 K of ammonium diuranate $(NH_4)_2U_2O_7$. The UO_3 was hydrated by equilibration with water which was stirred in a round-bottom flask equipped with a reflux condenser. The hydration was performed initially for 5 d at 315 K, and then for 14 d at 345 K, after which the sample was cooled slowly, filtered, washed with water, and dried in the air at room temperature. The X-ray diffraction patterns were identical to those in the literature for schoepite (2). By ignition to U_3O_8, the uranium content of the preparation was determined to be (73.89±0.01) mass per cent, very close to the theoretical value of 73.91 per cent. The schoepite was boiled with deionized H_2O and the supernatant aqueous extract was analyzed by ion chromatography. Only $F^-(aq)$, $NO_3^-(aq)$, $SO_4^{2-}(aq)$, $NH_4^+(aq)$, and $Na^+(aq)$ were detected, but all were at or below the 1×10^{-6} mass fraction level. All the analytical results, therefore, indicate that our sample of schoepite was very pure.

For the low-temperature heat-capacity measurements, 7.6699 g of schoepite was loaded into the calorimeter (laboratory designation 6-GS-1) with gentle tamping. The calorimeter was constructed from oxygen-free high-thermal-conductivity copper, had an internal volume of 5.976 cm^3 at 298.15 K, and was sealed by means of a gold gasket. Prior tests had shown, as expected, that intimate contact between copper and schoepite produced no reaction. The calorimeter was cooled to 195 K, evacuated, and 2.317×10^{-5} mol of He was introduced to act as an exchange gas and promote rapid thermal equilibration. For buoyancy and volume corrections, the density of schoepite was taken as 4.65 g cm^{-3} (2). Descriptions of the cryostat, peripheral equipment, the calorimetric procedure, and other relevant details are available in the literature (4).

Our determination of the standard molar enthalpy of formation was based on solution-calorimetric measurements of the enthalpy of the reaction:

$$[1] \qquad UO_3 \cdot 2H_2O(cr) + 2HF(aq) = UO_2F_2(aq) + 3H_2O(aq).$$

The calorimeter, an LKB-8700 model (LKB Produkter, Bromma, Sweden) was equipped with a stirrer and a 100-cm^3 reaction vessel made of 18-ct gold. Calorimetric specimens of schoepite, each of mass $\approx$0.56 g, were weighed in air and encapsulated in Teflon as described in an earlier publication (5). The calorimeter was calibrated electrically immediately before and after each enthalpy of reaction measurement, and the arithmetic mean of the values was used for the energy equivalent of the calorimetric system $<\epsilon(\text{calor})>$. The reaction of schoepite with HF(aq), prepared by dilution of reagent-grade acid, was quite rapid and the calorimeter reached equilibrium about 600 s after the sample came into contact with the solution. Temperatures were recorded automatically with a quartz-crystal thermometer (Hewlett-Packard, Model 2804-A) interfaced with a computer which calculated the corrected temperature rise for each experiment and calibration. In order to check the performance of the calorimetric system, we measured the specific enthalpy of protonation in 0.1 $\text{mol}\cdot\text{kg}^{-1}$ HCl(aq) of tris (hydroxymethyl) aminomethane, National Bureau of Standards Reference Material 724a. Our result, $-(246.09\pm0.11)\ \text{J}\cdot\text{g}^{-1}$, overlapped the certified value of $-(245.76\pm0.26)\ \text{J}\cdot\text{g}^{-1}$, and indicated that the calorimeter was operating properly.

The drop-calorimetric system (6) used for the enthalpy measurements consisted of a resistance-heated molybdenum-core furnace and a copper-block calorimeter. Furnace-temperature measurements were made with platinum-to-(platinum + mass fraction 0.1 of rhodium) thermocouples. Calorimetric temperatures were determined with a quartz-crystal thermometer (Hewlett-Packard Model 2804-A). The energy equivalent ϵ(calor) of the empty copper-block calorimeter was determined by electrical calibration.

The schoepite (mass 8.7960 g) was loaded into a (platinum + mass fraction 0.1 of rhodium) capsule (mass 19.1948 g and internal volume 6.42 cm^3), which was then welded shut. The capsule also contained 1.85×10^{-4} mol of air. Enthalpy measurements were also conducted on an empty capsule of similar mass and dimensions in order to correct for the enthalpy of the capsule. Experiments were performed at temperatures between 350 and 500 K. However, the enthalpy values at $T \geq 425$ K, when plotted against temperature, lay on a different line than those at lower temperatures. This suggested that the sample had decomposed or undergone a transition. Upon completion of the experiments, the capsule was opened and the schoepite examined. The material was visibly wet and readily lost mass when exposed to the air. It was concluded that the schoepite had undergone decomposition to some form of dehydrated schoepite and water. Hence, only the enthalpy values at approximately 350, 375, and 400 K are valid for pure schoepite.

Results

The molar heat capacities $C^{\circ}_{p,m}(T)$ of schoepite given in Table 1 were calculated as the difference, with some minor corrections, between the values obtained with the loaded calorimeter and the results of a prior set of experiments with the empty calorimeter.

Such a correction had to be made to allow for decomposition of the schoepite. There is convincing evidence from the studies of Dawson et al. (7), Lindval' and Kuznetsova (8), and Perez-Bustamante et al. (9) that schoepite undergoes dehydration upon heating. Thus, in the low-temperature heat-capacity measurements made at $T \geq 273.5$ K, a small part of the electrical energy input contributed to dehydration of the schoepite, and not heating of the sample, as would have occurred in the absence of the decomposition. There is, unfortunately, no experimental vapor-pressure equation for the decomposition of schoepite which would enable us to make a precise correction for the thermal effect of dehydration. We have, however, constructed an approximate equation on the basis of our present $\Delta_f H^{\circ}_m$ value for schoepite and that for dehydrated schoepite (10) and $H_2O(g)$ (11), along with an estimated standard entropy change for the dehydration. That equation is as follows:

$$[2] \qquad \log_{10}(p/p^{\circ}) = -2523.8(K/T) + 6.722.$$

Because of the vaporization correction, the original (uncorrected) heat-capacity values have been <u>reduced</u> in Table 1 by (JK^{-1} mol^{-1}): 0.08 at 273.50 K; 0.15 at 283.59 K; 0.28 at 293.67 K; 0.50 at 303.69 K; 0.81 at 313.23 K; 1.32 at 323.62 K; 2.07 at 333.70 K; and 3.17 at 343.88 K. Thus, above 330 K, the correction exceeds one per cent of the calculated heat capacity. Although the uncertainty increases above this temperature, the correction is only 0.25 per cent at 298.15 K and the corresponding errors are not significant here. Other minor corrections were made for differences in the amounts of helium, Apiezon-T grease (Metropolitan-Vickers, U.K.), copper, and gold between the results for the empty and filled calorimeters. A small curvature correction equal to $-(d^2C_{p,m}/dT^2)(\Delta T)^2/24$ was applied to each heat-capacity determination.

At 5 K, the heat capacity of the sample was 35 per cent of the total, at 20 K it was 34 per cent, at 100 K it was 19 per cent, and from 200 to 350 K it was about 25 per cent. The values given in Table 1 are estimated to be uncertain by ±5 per cent near 6 K, ±1 per cent near 14 K, and by ±0.2 per cent above 25 K. A plot of $C^{\circ}_{p,m}(T)$ against $<T>$ showed the normal sigmoidal shape and exhibited no anomalies.

The experimental heat capacities in Table 1 were fitted by means of a weighted least-squares procedure using two polynomials in T, one for the region below 40 K, the other for the region above 20 K. The standard deviations from the fits were ±0.14 per cent and ±0.15 per cent, respectively, with the polynomials merging smoothly at 23.5 K. In the region below the lowest experimental determination, it was assumed that $C^{\circ}_{p,m} = AT^3$. At $T = 6$ K, $C^{\circ}_{p,m}(T) = 0.3955$ JK^{-1} mol^{-1}, $\{S^{\circ}_m(T) - S^{\circ}_m(0)\} = 0.1318$ JK^{-1} mol^{-1}, and $\{H^{\circ}_m(T) - H^{\circ}_m(0)\} = 0.5933$ J mol^{-1}. Above 6 K, the thermodynamic properties were obtained by appropriate integrations of the two polynomials over their respective temperature ranges, and values at selected temperatures are given in Table 2.

Calorimetric results for the reaction of schoepite with HF(aq) are given in Table 3 and the column headings are explained in a footnote. The $\Delta_{vap}H$ term was calculated based upon the assumption that the internal volume of each ampoule was 1 cm^3 and the molar enthalpy of vaporization of water was taken as 44016 J mol^{-1} (11). The apparent sample masses were converted to mass based on a density of 4.65 g cm^{-3} for schoepite (2). The thermochemical cycle for the derivation of $\Delta_f H^{\circ}_m$ of schoepite is shown in Table 4. The enthalpies of reaction of γ-UO_3 and of schoepite with HF(aq) are taken from an earlier study (12) at this laboratory and from Table 3, respectively. Standard molar enthalpies of formation of γ-UO_3 and $H_2O(l)$ are CODATA-selected values (11).

The drop-calorimetric results are presented in Table 5. The entries in the table have their usual meanings (13). The correction for the water-vapor pressure over the schoepite sample was calculated from equation (2) except for the experiment at 400.55 K, where the equilibrium vapor pressure was taken to be that of water at the same temperature. These enthalpy values, as well as those between 298.15 and 350 K obtained by low-temperature calorimetry, were fitted by the method of least squares to various polynomials. The following fit was satisfactory:

$$[3] \qquad \{H^{\circ}_{m}(T) - H^{\circ}_{m}(298.15\ \mathrm{K})\}/(\mathrm{J\ mol^{-1}}) = -38209.0 + 84.2375(T/\mathrm{K}) + 0.1472958(T/\mathrm{K})^2 \qquad (298.15\ \mathrm{K} < T < 400\ \mathrm{K}).$$

The fit was constrained to give $\{H^{\circ}_{m}(T) - H^{\circ}_{m}(298.15\ \mathrm{K})\} = 0$ and $C^{\circ}_{p,m}(T) = 172.07\ \mathrm{J\ K^{-1}\ mol^{-1}}$ at $T = 298.15$ K. The heat capacity of $UO_3{\cdot}2H_2O$ between 298.15 and 400 K is given by the first derivative of equation (3):

$$[4] \qquad C^{\circ}_{p,m}(T)/(\mathrm{JK^{-1}\ mol^{-1}}) = 84.238 + 0.294592(T/\mathrm{K}).$$

Discussion

There have been no previous determinations of the low-temperature heat capacity or high-temperature enthalpy increments of schoepite. An earlier estimate (14) of the standard entropy at 298.15 K, 176±8 $\mathrm{JK^{-1}\ mol^{-1}}$, is somewhat lower than the experimental result, 188.5±0.4 $\mathrm{JK^{-1}\ mol^{-1}}$.

The standard molar enthalpy of formation has previously been reported by Santalova et al. (15), Drobnič and Kolar (16), and Cordfunke (17). Santalova et al. measured the enthalpy of reaction of schoepite with $HF{\cdot}267H_2O$. In their experiments, the HF was more dilute than ours, and $n(UO_2^{2+})/n(HF)$ was also quite different. It is not surprising, therefore, that the enthalpy of reaction of schoepite given by Santalova et al., −72.7±0.9 kJ $\mathrm{mol^{-1}}$, differs from our value, −76.25±0.35 kJ $\mathrm{mol^{-1}}$. The magnitude of the difference is, perhaps, unexpected. When the Santalova et al. result is combined with their enthalpy of hydrolysis of UF_6(cr) and the best modern $\Delta_f H^{\circ}_{m}$ values for UF_6(cr) (18), H_2O(l) (11), F^-(aq) (11), and the enthalpy of dilution of HF(aq) (19), $\Delta_f H^{\circ}_{m}(UO_3{\cdot}2H_2O,\ \mathrm{cr}) = -1831.1 \pm 4.4$ kJ $\mathrm{mol^{-1}}$ is obtained, in fair agreement with the present result.

Drobnič and Kolar measured directly the enthalpy of hydration of a highly-reactive specimen of $UO_3(am)$:

$$[5] \qquad UO_3(am) + 2H_2O(l) = UO_3 \cdot 2H_2O(cr).$$

Their corrected results give $\Delta_r H^\circ_m = -45.9 \pm 0.4$ kJ mol^{-1} for reaction (5). Combination of this value with selected $\Delta_f H^\circ_m$s for $UO_3(am)$ (18) and $H_2O(l)$ (11) yields $\Delta_f H^\circ_m = -1825.9 \pm 2.0$ kJ mol^{-1} for schoepite, in excellent agreement with the present determination.

Cordfunke has measured the enthalpies of reaction of γ-UO_3 and schoepite with $\approx$6 mol dm^{-3} HNO_3. His reported values yield $\Delta_r H^\circ_m = -30.2 \pm 0.3$ kJ mol^{-1} for the reaction:

$$[6] \qquad UO_3(cr, \gamma) + 2H_2O(aq) = UO_3 \cdot 2H_2O(cr),$$

where $H_2O(aq)$ is for a medium of $\approx$6 mol dm^{-3} HNO_3. We have taken $\Delta_f H^\circ_m$ (H_2O, aq) = -286.44 ± 0.04 kJ mol^{-1} (11,18) and calculate $\Delta_f H^\circ_m$ ($UO_3 \cdot 2H_2O$) = $-(1826.9 \pm 2.0)$ kJ mol^{-1}; this result also agrees very well with the present determination.

The weighed mean value of $\Delta_f H^\circ_m$ from the four studies just discussed yields $\Delta_f H^\circ_m$ ($UO_3 \cdot 2H_2O$, cr, 298.15 K) = -1826.4 ± 1.7 kJ mol^{-1}, which is our recommended value for the formation reaction:

$$[7] \qquad U(cr) + 2H_2(g) + \frac{5}{2}O_2(g) = UO_3 \cdot 2H_2O(cr),$$

The thermodynamic quantities determined in the present study have been combined with auxiliary quantities from the literature for U(18), H_2(11), and O_2(11) to compute the complete set of properties given in table 6.

It is believed that the thermodynamic properties of schoepite determined and reviewed in the present study may be used with a high degree of confidence in thermodynamic calculations and modelling studies such as those referred to at the beginning of this paper.

Acknowledgement

The authors thank Florence Williams for the ion-chromatographic analyses.

TABLE 1. Experimental low-temperature molar heat capacities of schoepite ($p^{\circ} = 0.1013$ MPa)

$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$
7.59	0.7220	27.24	12.72	87.15	65.33	197.07	131.78
7.68	0.7498	28.00	13.39	89.69	67.62	202.22	134.42
11.68	2.117	29.16	14.34	93.50	70.76	207.06	136.88
12.23	2.362	29.98	15.07	97.21	73.42	212.48	139.60
12.99	2.741	31.65	16.51	102.13	76.82	217.06	142.19
13.66	3.095	34.77	19.23	107.70	81.01	222.73	145.02
14.26	3.424	35.87	20.14	112.21	84.29	227.08	147.02
14.97	3.830	39.43	23.29	118.23	88.64	232.72	149.13
15.30	4.026	41.97	25.55	122.22	91.30	237.10	151.32
15.62	4.231	43.40	26.86	126.82	94.53	242.70	154.44
17.00	5.099	46.21	29.37	128.62	95.62	247.11	155.67
17.21	5.245	47.79	30.76	132.23	97.86	252.68	158.20
17.59	5.501	50.91	33.60	136.91	100.56	257.13	159.55
17.94	5.724	52.65	35.16	142.23	103.78	262.68	161.54
18.30	5.969	55.09	37.34	146.94	106.43	263.44	162.09
19.02	6.467	57.49	39.54	152.24	109.20	266.91	163.24
19.19	6.609	59.74	41.51	156.98	111.59	273.50	165.15
19.92	7.103	63.56	44.85	162.24	114.55	283.59	167.02
21.13	7.950	66.72	47.69	167.03	116.96	293.67	170.65
21.93	8.551	70.45	51.05	172.23	119.55	303.69	174.50
23.41	9.659	73.71	53.86	177.04	121.89	313.23	176.53
23.95	10.08	78.17	57.68	182.26	124.32	323.62	180.57
25.32	11.15	81.62	60.60	187.06	126.56	333.70	183.77
25.99	11.71	86.87	65.07	192.22	129.32	343.88	186.91

TABLE 2. Standard molar low-temperature thermodynamic properties of schoepite ($p^\circ = 0.1013$ MPa)

$\langle T \rangle / \mathrm{K}$	$C^\circ_{p,m} / \mathrm{J\,K^{-1}\,mol^{-1}}$	$S^\circ_m(T) / \mathrm{J\,K^{-1}\,mol^{-1}}$	$\{H^\circ_m(T) - H^\circ_m(0)\} / \mathrm{J\,mol^{-1}}$	$-\{G^\circ_m(T) - H^\circ_m(0)\}/T / \mathrm{J\,K^{-1}\,mol^{-1}}$
10	1.445	0.535	3.97	1.383
20	7.157	3.083	44.0	8.829
30	15.07	7.428	153.8	2.300
40	23.82	12.95	348.0	4.253
50	32.76	19.23	630.8	6.611
60	41.73	25.99	1003	9.272
70	50.62	33.10	1465	12.16
80	59.27	40.42	2015	15.24
90	67.57	47.89	2649	18.45
100	75.45	55.42	3365	21.77
110	82.88	62.96	4157	25.17
120	89.85	70.48	5021	28.63
130	96.36	77.93	5953	32.14
140	102.43	85.30	6947	35.67
150	108.07	92.56	8000	39.23
160	113.36	99.70	9107	42.78
170	118.39	106.73	10266	46.34
180	123.33	113.63	11475	49.88
190	128.23	120.43	12732	53.42

TABLE 2. *continued*

$\frac{\langle T \rangle}{K}$	$\frac{C^{\circ}_{p,m}}{J\ K^{-1}\ mol^{-1}}$	$\frac{S^{\circ}_{m}(T)}{J\ K^{-1}\ mol^{-1}}$	$\frac{H^{\circ}_{m}(T) - H^{\circ}_{m}(0)}{J\ mol^{-1}}$	$\frac{-\{G^{\circ}_{m}(T) - H^{\circ}_{m}(0)\}/T}{J\ K^{-1}\ mol^{-1}}$
200	133.23	127.14	14039	56.94
210	138.32	133.76	15397	60.44
220	143.42	140.31	16806	63.92
230	148.36	146.80	18265	67.38
240	152.96	153.21	19772	70.83
250	157.09	159.54	21322	74.25
260	160.69	165.77	22912	77.65
270	163.83	171.90	24535	81.03
280	166.73	177.91	26188	84.38
290	169.60	183.81	27869	87.71
300	172.65	189.61	29580	91.01
310	175.92	195.32	31323	94.28
320	179.29	200.96	33099	97.53
330	182.56	206.53	34908	100.74
340	185.68	212.02	36750	103.94
350	188.86	217.45	38622	107.10
360	191.99	222.82	40527	110.24
273.15	164.76±0.33	173.80±0.35	25052±50	82.08±0.16
298.15	172.07±0.34	188.54±0.38	29261±59	90.40±0.18

TABLE 3. Calorimetric results for the reaction of $UO_3{\cdot}2H_2O$ with HF(aq); T = 298.15 K, p^0 = 0.1013 MPa[a]

Expt. no.	$\frac{<\epsilon(\text{calor})>}{\text{J K}^{-1}}$	$\frac{\Delta\theta_c}{\text{K}}$	$\frac{<\epsilon(\text{calor})>(-\Delta\theta_c)}{\text{J}}$	$\frac{\Delta_{\text{vap}}H}{\text{J}}$	$\frac{m}{\text{g}}$	$\frac{\Delta_r H_m/M}{\text{J g}^{-1}}$
1	439.30	0.30143	−132.418	−0.052	0.56048	−236.35
2	439.43	0.30211	−132.756	−0.052	0.56299	−235.90
3	439.65	0.30118	−132.414	−0.052	0.56142	−235.95
5	439.51	0.30190	−132.688	−0.052	0.56352	−235.56
6	440.55	0.30471	−134.240	−0.052	0.56191	−238.99
7	439.31	0.30398	−133.541	−0.052	0.56189	−237.76

$$<\Delta_r H_m/M> = -(236.75 \pm 0.55)\ \text{J g}^{-1}$$ [b]

---

[a] The headings in the table are as follows: $<\epsilon(\text{calor})>$, the mean energy equivalent of the calorimetric system; $\Delta\theta_c$, the corrected calorimetric temperature increase; $\Delta_{\text{vap}}H$, the correction for saturation of the air in the ampoule with water vapor; m, the mass of schoepite reacted; and $\Delta_r H_m/M$, the specific enthalpy of reaction of schoepite with HF(aq).

[b] Mean and standard deviation of the specific enthalpy of reaction.

TABLE 4. Thermochemical cycle for calculation of standard molar enthalpy of formation of schoepite ($T = 298.15$ K, $p^0 = 0.1013$ MPa).

Reaction	$\frac{\Delta_r H_m}{\text{kJ mol}^{-1}}$
1. $UO_3(cr,\gamma) + 27.540(HF \cdot 115.30H_2O) = UO_2^{2+} \cdot 27.540F^- \cdot 25.540H^+ \cdot 3176.362H_2O$	-106.18 ± 0.38 [a]
2. $UO_2^{2+} \cdot 27.540F^- \cdot 25.540H^+ \cdot 3176.362H_2O = UO_3 \cdot 2H_2O(cr) + 27.540(HF \cdot 115.227H_2O)$	76.25 ± 0.35 [b]
3. $27.540(HF \cdot 115.227H_2O) + 2H_2O(l) = 27.540(HF \cdot 115.30H_2O)$	0.00 [c]
4. $U(cr) + \frac{3}{2}O_2(g) = UO_3(cr,\gamma)$	-1223.8 ± 2.0 [d]
5. $2H_2(g) + O_2(g) = 2H_2O(l)$	-571.66 ± 0.08 [d]
6. $U(cr) + \frac{5}{2}O_2(g) + 2H_2(g) = UO_3 \cdot 2H_2O(cr)$	-1825.4 ± 2.1 [e]

---

[a] Taken from earlier work (12) at this laboratory.

[b] Based on $< \Delta H_r/M >$ from Table 3 and the molar mass of schoepite $M = 322.057$ g mol^{-1}.

[c] Based on a previous study (19) at this laboratory.

[d] CODATA selected value (11).

[e] Standard molar enthalpy of formation $\Delta_f H_m^\circ$ of schoepite, the sum of reactions 1 through 5. The uncertainty is the square root of the sum of the squares of the uncertainties (standard deviations) of the reactions.

TABLE 5. Drop-calorimetric results for schoepite ($p^\circ = 0.1013$ MPa)

$\frac{T}{K}$	$\frac{\Delta\theta_c}{K}$	$\frac{\epsilon(\text{calor})(-\Delta\theta_c)}{J}$	$\frac{\Delta H(\text{capsule})}{J}$	$\frac{\Delta H(H_2O)}{J}$	$\frac{\Delta H(\text{corr})}{J}$	$\frac{H^\circ_m(T) - H^\circ_m(298.15\ K)}{J\ mol^{-1}}$[a]
350.57	0.09174	-401.54	142.25	2.10[b]	0.11	9411.7
376.43	0.13963	-611.14	213.12	5.99[b]	0.22	14344.1
400.55	0.18685	-817.81	279.62	13.96[c]	0.40	19177.4

[a] $\{H^\circ_m(T) - H^\circ_m(298.15\ K)\} = -\{\epsilon(\text{calor})(-\Delta\theta) + \Delta H(\text{capsule}) + \Delta H(H_2O) + \Delta H(\text{corr})\}/$ (0.027315 mol). The capsule contained 0.027315 mol of $UO_3 \cdot 2H_2O$.

[b] Correction for the vaporization of H_2O is based on equation (2).

[c] Correction made on the basis of the enthalpy of vaporization of $H_2O(l)$.

TABLE 6. Thermodynamic values for schoepite ($R = 8.31451\ J{\cdot}K^{-1}{\cdot}mol^{-1}$; $p^{\circ} = 101.325$ kPa; $T' = 298.15$ K)

$\frac{T}{K}$	$\frac{C^{\circ}_{p,m}}{R}$	$\frac{\Delta^{T}_{T'}H^{\circ}_{m}}{R\cdot K}$ [a]	$\frac{\Phi^{\circ}_{m}}{R}$ [b]	$\frac{\Delta^{T}_{0}S^{\circ}_{m}}{R}$ [c]	$\frac{\Delta_f H^{\circ}_{m}}{R\cdot kK}$	$\frac{\Delta_f G^{\circ}_{m}}{R\cdot kK}$
298.15	20.695	0.00	22.676	22.676	−219.66	−196.86
300	20.760	38.49	22.805	22.676	−219.66	−196.73
320	21.470	460.6	24.166	22.728	−219.63	−195.30
340	22.178	897.2	25.489	22.850	−219.58	−193.85
360	22.886	1348	26.777	23.033	−219.51	−192.40
380	23.595	1218	28.034	23.264	−219.44	−190.94
400	24.303	2291	29.262	23.534	−219.34	−189.45
423.15	25.124	2864	23.885	30.652	−219.23	−187.82

---

[a] $\Delta^{T}_{T'}H^{\circ}_{m} = H^{\circ}_{m}(T) - H^{\circ}_{m}(T')$.

[b] $\Phi^{\circ}_{m} = -\{G^{\circ}_{m}(T) - H^{\circ}_{m}(T')\}/T$.

[c] $\Delta^{T}_{0}S^{\circ}_{m} = S^{\circ}_{m}(T) - S^{\circ}_{m}(0)$.

1. E. H. P. CORDFUNKE. The Chemistry of Uranium. Elsevier, Amsterdam. 1969. pp. 109-112.
2. P. C. DEBETS and B. O. LOOPSTRA. J. Inorg. Nucl. Chem. **25**, 945 (1963).
3. T. J. WOLERY, D. J. ISHERWOOD, K. J. JACKSON, J. M. DELANY, and I. PUIG-DOMENECH. Report no. UCRL-91884. 1984.
4. D. W. OSBORNE, F. SCHREINER, H. E. FLOTOW, and J. G. MALM. J. Chem. Phys. **57**, 3401 (1972); E. F. WESTRUM, JR., J. B. HATCHER, and D. W. OSBORNE. J. Chem. Phys. **21**, 419 (1953); G. K. JOHNSON, H. FLOTOW, P. A. G. O'HARE, and W. S. WISE. Am. Mineral. **67**, 736 (1982); J. S. PRICE, I. R. TASKER, E. H. APPELMAN, and P. A. G. O'HARE. J. Chem. Thermodyn. **18**, 923 (1986); P. A. G. O'HARE, G. K. JOHNSON, I. R. TASKER, and H. E. FLOTOW. J. Chem. Thermodyn. **19**, 77 (1987).
5. G. K. JOHNSON, H. E. FLOTOW, P. A. G. O'HARE, and W. S. WISE. Am. Mineral. **68**, 1134 (1983).
6. D. R. FREDRICKSON, R. D. BARNES, M. G. CHASANOV, R. L. NUTTALL, R. KLEB, and W. N. HUBBARD. High Temp. Sci. **1**, 373 (1969).
7. J. K. DAWSON, E. WAIT, K. ALCOCK, and D. R. CHILTON. J. Chem. Soc. 3531 (1956).
8. R. V. LINDVAL' and V. V. KUZNETSOVA. Tr. Kazan. Khim. Tekhnol. Inst. **(54)**, 145 (1974).
9. J. A. PEREZ-BUSTAMANTE, J. B. POLONIO, and R. F. CELLINI. Anal. Real Soc. Españ. Fis. Quim. **B58**, 677 (1962).
10. P. A. G. O'HARE, B. M. LEWIS, and S. NGUYEN. To be published.
11. CODATA recommended key values for thermodynamics, 1977. J. Chem. Thermodyn. **10**, 903 (1978).
12. G. K. JOHNSON and P. A. G. O'HARE. J. Chem. Thermodyn. **10**, 577 (1978).

13. P. A. G. O'HARE, W. N. HUBBARD, G. K. JOHNSON, and H. E. FLOTOW. J. Chem. Thermodyn. **16**, 45 (1984).

14. E. H. P. CORDFUNKE and P. A. G. O'HARE. The Chemical Thermodynamics of Actinide Elements and Compounds. Part 3. Miscellaneous Actinide Compounds. International Atomic Energy Agency. Vienna (1978).

15. N. A. SANTALOVA, L. M. VIDAVSKII, K. M. DUNAEVA, and E. A. IPPOLITOVA. Radiokhim. **13**, 592 (1971).

16. M. DROBNIČ and D. KOLAR. J. Inorg. Nucl. Chem. **28**, 2833 (1966).

17. E. H. P. CORDFUNKE. J. Phys. Chem. **68**, 3353 (1964).

18. D. D. WAGMAN, W. H. EVANS, V. B. PARKER, R. H. SCHUMM, I. HALOW, S. M. BAILEY, K. L. CHURNEY, and R. L. NUTTALL. J. Phys. Chem. Ref. Data. **11** (1982), Supplement no. 2.

19. G. K. JOHNSON, P. N. SMITH, and W. N. HUBBARD. J. Chem. Thermodyn. **5**, 793 (1973).