

## Thermodynamics of the Actinoid Elements. Part 6.<sup>1</sup> The Preparation and Heats of Formation of Some Sodium Uranates(vi)

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The preparation of sodium uranates(vi) has been investigated by heating together appropriate amounts of  $\text{Na}_2\text{O}_2$  and  $\text{UO}_2$  and also by the thermal decomposition of complexes such as  $\text{Na}_4\text{U}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ ,  $\text{Na}_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ . The enthalpies of solution in  $1.00 \text{ mol dm}^{-3}$  HCl of high-purity samples of  $\beta\text{-Na}_4\text{UO}_5$ ,  $\alpha\text{-}$  and  $\beta\text{-Na}_2\text{UO}_4$ , and  $\text{Na}_2\text{U}_2\text{O}_7$ , prepared by the latter method, are  $-386.6 \pm 0.6$ ,  $-171.9 \pm 0.4$ ,  $-184.2 \pm 0.4$  and  $-171.8 \pm 1.0 \text{ kJ mol}^{-1}$ , respectively. The resulting enthalpies of formation,  $-2457.3 \pm 2.8$ ,  $-1901.3 \pm 2.3$ ,  $-1889.0 \pm 2.3$ , and  $-3203.8 \pm 2.8 \text{ kJ mol}^{-1}$ , are discussed in relationship to published values. X-Ray powder diffraction studies appear to confirm the existence of  $\alpha\text{-Na}_4\text{UO}_5$ .

Alkali-metal and alkaline-earth-metal uranates(vi) have been extensively investigated, see for example ref. 2 and 3, but relatively little is known about the properties of analogous transuranium-element compounds. This is particularly true for thermodynamic properties where the first data on neptunium-(vi) and plutonium(vi) alkaline-earth-metal oxides have appeared recently<sup>4,5</sup> or have just been determined.<sup>6</sup> As a preliminary to work on alkali-metal neptunates(vi) and plutonates(vi) the preparation of selected high-purity sodium uranates(vi) has been explored with the dual aims of establishing reliable preparative methods which yield stoichiometric oxides, and providing additional thermodynamic data in those instances where either only a single value was available or a discrepancy existed.

Investigations of the  $\text{Na}_2\text{O}_2\text{-UO}_2$  reaction under a variety of conditions are described together with results on the thermal decomposition of the uranium-(iv) and -(vi) complexes  $\text{Na}_4\text{U}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ ,  $\text{Na}_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ . Using the latter technique high-purity samples of  $\beta\text{-Na}_4\text{UO}_5$ ,  $\alpha\text{-Na}_2\text{UO}_4$ ,  $\beta\text{-Na}_2\text{UO}_4$ , and  $\text{Na}_2\text{U}_2\text{O}_7$  have been prepared and their enthalpies of solution in  $1 \text{ mol dm}^{-3}$  HCl determined. The resulting enthalpies of formation are compared with available literature values.

### Experimental

**Reagents.**—Sodium peroxide,  $\text{Na}_2\text{O}_2$  (Alpha chemicals) (>99% purity), was used as purchased. Stoichiometric uranium dioxide was provided by M. Mignanelli (Chemistry Division, A.E.R.E., Harwell). Sodium acetate, oxalate, and carbonate (AnalaR grade materials) were used without further purification. The compounds  $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{UO}_2 \cdot (\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$  were precipitated from aqueous oxalic acid solutions on addition of  $\text{UCl}_4$  and  $\text{UO}_2\text{Cl}_2$ , respectively;  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was crystallised from a solution of  $\text{UO}_3$  in hot, glacial acetic acid.

**Uranium Complexes.**—The compound  $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.29 g) was added to an aqueous solution of sodium oxalate (0.69 g). Complete dissolution was achieved by heating at  $80^\circ\text{C}$ . After cooling the addition of methanol resulted in a precipitate of  $\text{Na}_4\text{U}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$  which was isolated by centrifugation,

washed with methanol, and vacuum dried at room temperature. Typical product analysis: Found, Na 12.6, U 32.3, 32.4;  $\text{Na}_4\text{U}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$  requires Na 12.5, U 32.3%.

The compound  $\text{UO}_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$  (2.25 g) was dissolved in a hot ( $80^\circ\text{C}$ ) aqueous solution containing a 1:3 stoichiometric molar excess of sodium oxalate. The solution was filtered and cooled; crystals of  $\text{Na}_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  formed after several days. Typical product analysis: Found, Na 8.1, U 42.1;  $\text{Na}_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  requires Na 8.15, U 42.2%.

Sodium acetate (0.82 g) was added to a hot solution of uranyl(vi) acetate (3.85 g) in glacial acetic acid containing ammonium acetate to assist dissolution. On cooling crystals of  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  separated: these were isolated by filtration, washed with a mixture of diethyl ether and ethanol, and vacuum dried. Typical product analysis: Found, Na 4.8, U 50.45, 50.2;  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  requires Na 4.9, U 50.65%.

Addition of an aqueous, saturated solution of  $\text{Na}_2\text{CO}_3$  to uranyl(vi) nitrate (5.2 g) in water initially gave a yellow precipitate. This was redissolved by addition of just sufficient of the saturated  $\text{Na}_2\text{CO}_3$  solution to give a clear solution, from which crystals of  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$  ( $1.5 < n < 3.5$ ) were obtained on addition of methanol. The product was washed with small volumes of 50% aqueous methanol, methanol, and finally ether and air-dried at room temperature. The variable uranium analyses were attributed to different water contents of different preparations since U:Na mol ratios of 1:4 were found (e.g. Na 16.05, U 41.2%) and, as described later, uranium analyses showed that  $\beta\text{-Na}_4\text{UO}_5$  was obtained on thermal decomposition of the products. This is supported by the absence of impurity reflections on the high-quality X-ray powder photographs of the various preparations of this sodium uranate(vi).

Samples of  $\beta\text{-Na}_4\text{UO}_5$ ,  $\alpha\text{-}$  and  $\beta\text{-Na}_2\text{UO}_4$ , and  $\text{Na}_2\text{U}_2\text{O}_7$  used for calorimetric studies were prepared on the 100–300 mg scale by thermal decomposition of uranium-(iv) and -(vi) complexes in gold crucibles using the conditions given in Table 1. Reactions involving stoichiometric amounts of  $\text{Na}_2\text{O}_2$  and  $\text{UO}_2$  (100–200 mg scale) for the formation of  $\text{Na}_4\text{UO}_5$  and  $\text{Na}_2\text{UO}_4$  were also done in gold crucibles *in vacuo* or in an argon, argon-oxygen, or oxygen atmosphere. Alternatively, evacuated, sealed silica ampoules were used to contain the reactants.

**Table 1.** Preparative conditions and analyses of the various sodium uranates(vi)

Compound	Preparation	Method	Analysis (%) <sup>a</sup>	
			U	Na
$\beta$ -Na <sub>4</sub> UO <sub>5</sub>	I	Na <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ·nH <sub>2</sub> O at 800 °C in O <sub>2</sub> for 21.5 h	58.0, 57.9 (58.0)	57.9 (22.4)
	II	Na <sub>4</sub> U(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O at 800 °C in O <sub>2</sub> for 19 h	58.0	22.4
$\alpha$ -Na <sub>2</sub> UO <sub>4</sub>	I	Na <sub>2</sub> UO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O at 760 °C in O <sub>2</sub> for 19.5 h	68.5, 68.2 (68.4)	13.2 (13.2)
	II	Na <sub>2</sub> UO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O at 720 °C in O <sub>2</sub> for 22 h	68.3, 68.4	13.2
	III	Na <sub>2</sub> UO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O at 760 °C in O <sub>2</sub> for 21 h	68.4, 68.2	13.2
$\beta$ -Na <sub>2</sub> UO <sub>4</sub>	I	Na <sub>2</sub> UO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O at 880 °C in O <sub>2</sub> for 22.5 h	68.3, 68.4	13.2
	II	Na <sub>2</sub> UO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O at 900 °C in O <sub>2</sub> for 20 h	68.4, 68.4	13.2
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	I	NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub> at 650 °C in O <sub>2</sub> for 22.5 h	75.0, 75.1 (75.1)	7.1, 7.3 (7.3)
	II	NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub> at 700 °C in O <sub>2</sub> for 19 h	74.9, 75.1	7.1, 7.2
	III	NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub> at 800 °C in O <sub>2</sub> for 19 h	74.9, 75.1	7.1, 7.1
	IV	NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub> at 800 °C in O <sub>2</sub> for 22 h	75.0, 75.1	7.2, 7.2
	V	NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub> at 750 °C in O <sub>2</sub> for 16 h	<i>b</i>	<i>b</i>
	VI	NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub> at 750 °C in O <sub>2</sub> for 2 h	74.1	7.3
	VII	NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub> at 750 °C in O <sub>2</sub> for 2.5 h	75.1	7.4

<sup>a</sup>Theoretical values in parentheses. <sup>b</sup>Identified by X-ray powder diffraction analysis which showed the absence of impurity reflections.

Products were removed from the reaction vessels in a nitrogen glove-box (water and oxygen <20 p.p.m.) and all subsequent handling was done in nitrogen atmospheres.

**Analyses.**—Uranium was determined gravimetrically by heating precipitated hydrated oxides at >700 °C in air and weighing as U<sub>3</sub>O<sub>8</sub>. Sodium was determined by atomic absorption spectroscopy. Results are given in Table 1.

**X-Ray Measurements.**—X-Ray powder photographs were recorded as described previously.<sup>7</sup> Unit-cell dimensions were refined using the program COHEN.<sup>8</sup>

**Enthalpies of Solution.**—Measurements were made using two calorimeters: a vacuum-jacketed isoperibol microcalorimeter with a tantalum chamber, which has been described elsewhere,<sup>9,\*</sup> and an air-jacketed isoperibol calorimeter (model 8700-1; LKB, Bromma, Sweden) with a glass vessel, and equipped with a Hewlett-Packard (San Diego, California) model 7131 A/B strip chart recorder. Details of calibration runs have been published.<sup>10-12</sup>

Samples were weighed, in the appropriate calorimetric ampoules, on a model GRAM electric balance (Cahn, Paramount, California); weights were reduced to weights *in vacuo*. The sodium uranates(vi) were handled in a dry, oxygen-free nitrogen atmosphere, which contained less than 10 p.p.m. water vapour (Alnor Dewpoint meter, Casella, London) and

\* Although the calorimeter chamber has remained unchanged, many modifications to the circuitry (timer, power source, etc.) have been made throughout the years.

less than 10 p.p.m. oxygen (potential drop across a ZrO<sub>2</sub> membrane<sup>13</sup>).

Merck-titrated 1.000 mol dm<sup>-3</sup> hydrochloric acid solutions were used for sample dissolution.

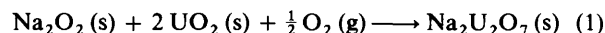
**Units and Limits of Error.**—The joule (J) is used throughout as the energy unit. All literature data originally reported in calories were recalculated using the conversion factor 1 cal (thermochemical) = 4.184 J. The <sup>12</sup>C scale of atomic weights<sup>14</sup> was used to calculate molecular weights. All the calorimetric measurements are reported for 298.15 ± 0.05 K.

Uncertainty limits on the mean of several identical measurements and representing the consistency of the measurements are based on the 95% confidence interval<sup>15</sup> except where stated (*cf.*, Table 2). When combining the new results with data from other sources no attempt has been made to retain this limit; the error stated by the author has been accepted. The errors quoted for the calculated enthalpies of formation were obtained from the errors on the individual terms of the thermodynamic cycle used, according to a standard procedure.<sup>16</sup> Unless otherwise specified, auxiliary data recommended by CODATA or values consistent with the CODATA selection were employed.<sup>17</sup>

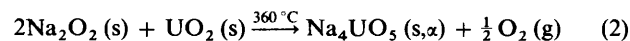
## Results and Discussion

**Preparation of Sodium Uranates(vi).**—The compounds chosen for investigation were Na<sub>4</sub>UO<sub>5</sub>,  $\alpha$ - and  $\beta$ -Na<sub>2</sub>UO<sub>4</sub>, and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>.

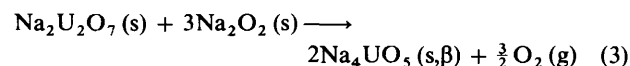
Initial studies of the preparation of Na<sub>4</sub>UO<sub>5</sub> involved the interaction of UO<sub>2</sub> and Na<sub>2</sub>O<sub>2</sub>, stoichiometric amounts (1:2) of which were intimately mixed by grinding prior to being heated in gold crucibles either *in vacuo*, or in argon, argon-oxygen mixtures, or oxygen at temperatures in the range 360–800 °C. At temperatures below 400 °C the deep red products were shown by X-ray powder diffraction analysis to be mixtures of sodium uranates(vi). Thus, for 36-h reactions (2 × 18 h with intermediate regrinding) done *in vacuo* or under argon the major phase could be indexed on the basis of a face-centred cubic (f.c.c.) unit cell, whilst the additional very weak reflections could be attributed to Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>. For reactions done in oxygen-argon mixtures and in oxygen the changes in relative intensities of the reflections indicated that increasing amounts of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub> were being formed, presumably *via* reaction (1).



The unit-cell dimension of the f.c.c. phase [ $a = 4.764(1) \text{ \AA}$ ] is very close to that reported by Keller<sup>18</sup> for a  $\alpha$ -Na<sub>4</sub>UO<sub>5</sub> ( $a = 4.766 \text{ \AA}$ ), which he obtained by reaction of UO<sub>3</sub> with Na<sub>2</sub>O at 400–450 °C. Although the existence of this phase has been queried by Cordfunke and Loopstra,<sup>19</sup> who obtained only  $\beta$ -Na<sub>4</sub>UO<sub>5</sub> under the same conditions, the present crystallographic results appear to confirm that a low-temperature modification does exist and can also be obtained by reaction (2).



For reaction periods of 100–120 h in an oxygen atmosphere the  $\alpha$ -Na<sub>4</sub>UO<sub>5</sub> was contaminated with  $\beta$ -Na<sub>4</sub>UO<sub>5</sub> and larger amounts of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub> than in 36-h reactions, presumably due to reaction (3).



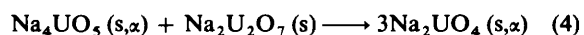
Additional studies at 360 °C in evacuated, sealed silica ampoules yielded  $\alpha$ -Na<sub>4</sub>UO<sub>5</sub> mixed with Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub> after 36 h,

**Table 2.** Enthalpies of solution of various sodium uranates(vi) in 1 mol dm<sup>-3</sup> hydrochloric acid at 298.15 ± 0.10 K

Compound	Preparation	Experiment	Calorimeter <sup>a</sup>	Sample weight (mg)	Concentration of compound in solution (10 <sup>-3</sup> mol dm <sup>-3</sup> )	Enthalpy effect (J)	$\Delta H^b$ /kJ mol <sup>-1</sup>
$\beta$ -Na <sub>4</sub> UO <sub>5</sub>	I	1	A	4.024	1.155	3.8053	-387.7
		2		3.284	0.942	3.1005	-387.1
		3		3.952	1.134	3.7387	-387.9
		4		3.399	0.975	3.2074	-386.9
		5		5.048	1.449	4.7457	-385.4
		6		5.203	1.493	4.9084	-386.8
	II	1	B	11.930	1.164	11.253	-386.7
		2		13.630	1.330	12.827	-385.8
		3		16.430	1.603	15.464	-385.9
		4		16.425	1.602	15.464	-386.0
	Average: -386.6 ± 0.6						
	$\alpha$ -Na <sub>2</sub> UO <sub>4</sub>	I	1	A	8.457	2.850	4.1692
2			9.406		3.180	4.6605	-172.4
3			7.642		2.583	3.8022	-173.1
4			6.556		2.216	3.2538	-172.7
5			7.594		2.567	3.7595	-172.3
II		1	A	5.767	1.950	2.8412	-171.5
		2		9.011	3.046	4.4512	-171.9
		3		5.971	2.019	2.9470	-171.8
		4		6.076	2.054	3.0220	-172.0
		5		5.744	1.942	2.8227	-171.0
III		1	B(1)	37.175	1.068	18.322	-171.5
		2		34.600	0.994	17.118	-172.2
		3		29.600	0.880	14.514	-170.6
Average: -171.9 ± 0.4							
$\beta$ -Na <sub>2</sub> UO <sub>4</sub>		I	1	A	7.005	2.385	3.7290
	2		5.508		1.862	2.9097	-183.8
	3		7.909		2.674	4.1853	-184.2
	II	1	B(1)	33.120	0.952	17.529	-184.2
		2		24.980	0.718	13.254	-184.6
		3		38.795	1.115	20.575	-184.6
Average: -184.2 ± 0.4							
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	I	1	B	10.650	0.672	2.866	-170.6
		2		19.910	1.256	5.372	-171.1
		3		20.905	1.319	5.612	-170.2
		4		18.215	1.149	4.896	-170.4
	II	1	B(1)	28.025	0.442	7.549	-170.8
		4		47.83	0.754	13.053	-173.0
	IV	1	B(1)	53.16	0.838	14.434	-172.2
		2		56.76	0.895	15.491	-173.0
		3		52.42	0.827	14.326	-173.3
		4		47.83	0.754	13.053	-173.0
		5		72.22	1.139	19.679	-172.8
	V	1	B(1)	41.61	0.656	11.194	-170.6
		2		48.84	0.770	13.329	-173.0
		3		39.16	0.618	10.571	-171.2
	VI	1	B(1)	46.53	0.734	12.585	-171.5
		2		40.14	0.633	10.923	-172.5
	VII	1	B(1)	49.57	0.782	13.504	-172.7
		2		53.63	0.846	14.519	-171.6
3		60.87		0.960	16.480	-171.7	
Average: -171.8 ± 1.0 <sup>c</sup>							

<sup>a</sup> A, microcalorimeter; B, LKB, 25 cm<sup>3</sup>; B(1), LKB, 100 cm<sup>3</sup>. <sup>b</sup> Represents  $\Delta H_5$ ,  $\Delta H_6$ ,  $\Delta H_6$ , and  $\Delta H_7$ , respectively, for the dissolution of  $\beta$ -Na<sub>4</sub>UO<sub>5</sub>,  $\alpha$ -Na<sub>2</sub>UO<sub>4</sub>,  $\beta$ -Na<sub>2</sub>UO<sub>4</sub>, and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>. <sup>c</sup> Uncertainty limits increased to account for a slight discrepancy between the solution data for preparation I and for the others.

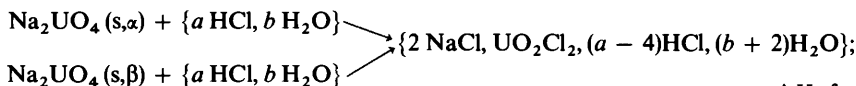
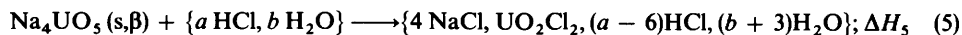
but with reaction periods of 94 h  $\alpha$ -Na<sub>2</sub>UO<sub>4</sub> was also present, probably due to the interaction of  $\alpha$ -Na<sub>4</sub>UO<sub>5</sub> and the diuranate, according to reaction (4).



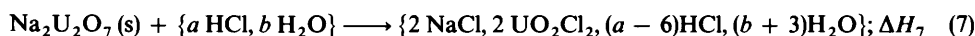
The interaction of Na<sub>2</sub>O<sub>2</sub> and UO<sub>2</sub> at 800 °C in oxygen gave salmon coloured  $\beta$ -Na<sub>4</sub>UO<sub>5</sub> but according to X-ray powder diffraction analysis the product was always contaminated with a small amount of  $\beta$ -Na<sub>2</sub>UO<sub>4</sub>. The reaction of 630 °C *in vacuo* gave a mixture of  $\beta$ -Na<sub>4</sub>UO<sub>5</sub>, Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>, and  $\alpha$ -Na<sub>2</sub>UO<sub>4</sub>.

Although  $\beta$ - $\text{Na}_4\text{UO}_5$  appears to be stable up to  $950^\circ\text{C}$  in oxygen, it decomposes in argon at temperatures as low as  $750^\circ\text{C}$ , with the formation of  $\alpha$ - $\text{Na}_2\text{UO}_4$ .

The direct preparation of  $\text{Na}_2\text{UO}_4$  has been examined *via* the interaction of equimolar amounts of  $\text{Na}_2\text{O}_2$  and  $\text{UO}_2$ . At temperatures between  $600$  and  $760^\circ\text{C}$   $\alpha$ - $\text{Na}_2\text{UO}_4$  was formed in both argon and oxygen but the products were contaminated



$\Delta H_6$  for the  $\alpha$  phase,  $\Delta H_6'$  for the  $\beta$  phase (6), (6')



with  $\text{Na}_2\text{U}_2\text{O}_7$ , the amount of impurity being less in an oxygen atmosphere. The compound  $\beta$ - $\text{Na}_2\text{UO}_4$ , which is formed at *ca.*  $860^\circ\text{C}$  in oxygen, was essentially pure according to the *X*-ray powder pattern of the product. An alternative reaction involving 1:1 mol ratios of  $\beta$ - $\text{Na}_4\text{UO}_5$  and  $\text{UO}_2$  at  $700^\circ\text{C}$  in oxygen resulted in the formation of almost pure  $\alpha$ - $\text{Na}_2\text{UO}_4$  after 63 h, only traces of unreacted  $\beta$ - $\text{Na}_4\text{UO}_5$  being indicated by *X*-ray powder diffraction analysis;  $\beta$ - $\text{Na}_2\text{UO}_4$  of similar purity was obtained at *ca.*  $800^\circ\text{C}$ .

The somewhat lower temperature observed for the formation of  $\beta$ - $\text{Na}_2\text{UO}_4$  (*ca.*  $800^\circ\text{C}$ ) than reported previously<sup>19-21</sup> (*ca.*  $900^\circ\text{C}$ ) may be attributed to the prolonged heating periods during the present study during which the  $\alpha \rightarrow \beta$  conversion was found to be complete only after  $>40$  h.

Attempts to repeat the reported preparation<sup>19,22</sup> of  $\text{Na}_2\text{UO}_4$  by heating together  $\text{UO}_3$  and  $\text{Na}_2\text{CO}_3$  in dry air have been unsuccessful. Thus, even after  $>120$  h at temperatures in the range  $760$ – $800^\circ\text{C}$  the product was still contaminated with  $\text{Na}_2\text{U}_2\text{O}_7$  and  $\text{Na}_2\text{CO}_3$ .

Although 'almost pure' phases have been obtained in certain instances, it is apparent from the foregoing discussion that oxide interactions and, in the case of  $\text{Na}_2\text{UO}_4$ , uranium oxide-sodium carbonate reactions, are not completely satisfactory for the preparation of sodium uranates(vi) of the high purity required for thermodynamic studies. This may be attributed to factors such as difficulties in ensuring intimate mixing of the reagents, the relative ease with which  $\text{Na}_2\text{U}_2\text{O}_7$  is formed, and the side reactions it may undergo with, for example,  $\text{Na}_2\text{O}_2$  and  $\text{Na}_4\text{UO}_5$ . In addition, the various  $\text{UO}_2$ - $\text{Na}_2\text{O}_2$  reactions all involve prolonged reaction periods, often at elevated temperatures, and require frequent regrinding of the mixture.

In view of the difficulties encountered in obtaining pure sodium uranates(vi) from the above reactions, and since in subsequent studies it is intended to extend the scope of the investigations to include other alkali metals as well as the actinide elements neptunium and plutonium, alternative preparative routes have been explored. These involved the preparation of uranium-(iv) and -(vi) complexes with different Na:U ratios followed by thermal decomposition in oxygen.

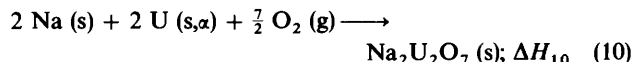
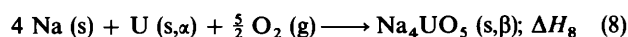
The complexes studied, all of which were prepared by crystallisation as opposed to precipitation as fine powders, were  $\text{Na}_4\text{U}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$  ( $n$  varied between 1.5 and 3.5 depending on the extent of drying),  $\text{Na}_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ . Preliminary d.t.a. and t.g.a. studies indicated that these compounds decomposed in the temperature range  $300$ – $400^\circ\text{C}$ . In order to obtain highly crystalline sodium uranates(vi) the temperatures chosen for decomposition in oxygen were somewhat higher than these as indicated in Table 1, which also gives the heating periods employed. The products,  $\beta$ - $\text{Na}_4\text{UO}_5$ ,  $\alpha$ - and  $\beta$ - $\text{Na}_2\text{UO}_4$ , and  $\text{Na}_2\text{U}_2\text{O}_7$ , were all single phases according to *X*-ray powder

diffraction analysis and, as shown in Table 1, the analytical results were in good agreement with theoretical values.

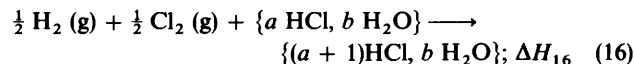
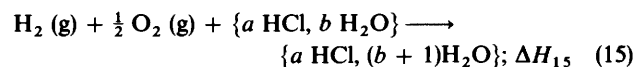
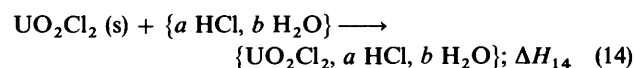
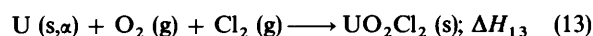
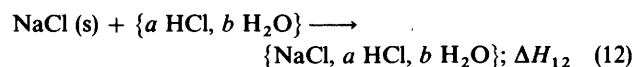
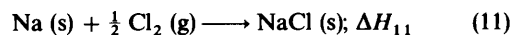
*Enthalpies of Solution and Formation.*—Table 2 shows the results obtained for dissolution of the various sodium uranates(vi) in  $1 \text{ mol dm}^{-3}$  hydrochloric acid. The dissolution reactions can be represented by equations (5), (6), (6') and (7),

respectively, with  $b/a = 54.4$  and  $a$  ranging from *ca.* 400 to 2500.

The enthalpy of formation at 298 K of the various uranates(vi), according to reactions (8), (9), (9'), and (10),



respectively, are calculated from the enthalpies of solution and the relationships (11)–(16). In these calculations,  $\Delta H_{11}$ , the



standard enthalpy of formation of  $\text{NaCl}(\text{s})$ ,<sup>23</sup>  $-411.26 \pm 0.11 \text{ kJ mol}^{-1}$ , and  $\Delta H_{13}$ , the standard enthalpy of formation of  $\text{UO}_2\text{Cl}_2(\text{s})$ ,<sup>24</sup>  $-1243.6 \pm 1.2 \text{ kJ mol}^{-1}$ , are taken from the literature;  $\Delta H_{15}$  and  $\Delta H_{16}$  represent the partial molar enthalpy of formation of water and hydrochloric acid in  $1 \text{ mol dm}^{-3}$  HCl, respectively,  $-285.85 \pm 0.04$  and  $-164.36 \pm 0.10 \text{ kJ mol}^{-1}$ .<sup>24</sup> All these data are compatible with the CODATA selections.<sup>17</sup>

For  $\Delta H_{12}$ , the enthalpy of solution of  $\text{NaCl}(\text{s})$  in  $1 \text{ mol dm}^{-3}$  HCl, the average of  $4.60 \pm 0.40 \text{ kJ mol}^{-1}$  (for a final solution *ca.*  $10^{-2} \text{ mol dm}^{-3}$  in NaCl), as given by O'Hare *et al.*<sup>25</sup> and  $4.31 \pm 0.40 \text{ kJ mol}^{-1}$  (for a final solution *ca.*  $3 \times 10^{-3} \text{ mol dm}^{-3}$  in NaCl), as obtained in the present study from three concordant measurements, has been used; thus  $\Delta H_{12} = 4.46 \pm 0.40 \text{ kJ mol}^{-1}$ . The enthalpy of solution of  $\text{UO}_2\text{Cl}_2(\text{s})$  in  $1 \text{ mol dm}^{-3}$  HCl,  $\Delta H_{14}$ , is taken as  $-101.7 \pm 1.7 \text{ kJ mol}^{-1}$  as recommended by Parker<sup>24</sup> for a solution  $<10^{-3} \text{ mol dm}^{-3}$  in  $\text{UO}_2\text{Cl}_2$ .

**Table 3.** Crystallographic data for sodium uranates(vi)

Compound	Preparation <sup>a</sup>	Symmetry <sup>b</sup>	Unit-cell dimensions			
			a/Å	b/Å	c/Å	β/°
α-Na <sub>4</sub> UO <sub>5</sub>		C	4.764(1)			
β-Na <sub>4</sub> UO <sub>5</sub>	I	T	7.556(1)		4.639(1)	
	II		7.557(1)		4.638(1)	
α-Na <sub>2</sub> UO <sub>4</sub>	I	O	9.767(1)	5.731(1)	3.498(1)	
β-Na <sub>2</sub> UO <sub>4</sub>	II	O	5.979(1)	5.813(1)	11.726(1)	
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	IV	M	12.794(3)	7.828(2)	6.888(3)	111.44(3)

<sup>a</sup> Preparation number refers to Table 1. <sup>b</sup> C = Cubic, T = tetragonal, O = orthorhombic, and M = monoclinic.

In combining equations (11)–(16) with (5), (6), (6'), and (7) to obtain the standard enthalpies of formation of the various uranates, the small dilution effects due to the water and HCl formation or depletion in 1 mol dm<sup>-3</sup> HCl have been assumed to be negligible: this customary practice is quite acceptable in view of the fact that in all instances the uranium concentration in the solutes remains quite low (<3 × 10<sup>-3</sup> mol dm<sup>-3</sup>). The influence of the presence of these small uranium concentrations on the various terms (ΔH<sub>12</sub>, ΔH<sub>15</sub>, and ΔH<sub>16</sub>) of the thermodynamic cycle used to obtain the enthalpies of formation of the uranates has also been neglected. These are obtained according to relations (A)–(D).

$$\Delta H_f^\circ(\text{Na}_4\text{UO}_5, \text{s}, \beta) = \Delta H_8 = 4 \Delta H_{11} + 4 \Delta H_{12} + \Delta H_{13} + \Delta H_{14} + 3 \Delta H_{15} - 6 \Delta H_{16} - \Delta H_5 = -2457.3 \pm 2.8 \text{ kJ mol}^{-1} \quad (\text{A})$$

$$\Delta H_f^\circ(\text{Na}_2\text{UO}_4, \text{s}, \alpha) = \Delta H_9 = 2 \Delta H_{11} + 2 \Delta H_{12} + \Delta H_{13} + \Delta H_{14} + 2 \Delta H_{15} - 4 \Delta H_{16} - \Delta H_6 = -1901.3 \pm 2.3 \text{ kJ mol}^{-1} \quad (\text{B})$$

$$\Delta H_f^\circ(\text{Na}_2\text{UO}_4, \text{s}, \beta) = \Delta H_{9'} = 2 \Delta H_{11} + 2 \Delta H_{12} + \Delta H_{13} + \Delta H_{14} + 2 \Delta H_{15} - 4 \Delta H_{16} - \Delta H_{6'} = -1889.0 \pm 2.3 \text{ kJ mol}^{-1} \quad (\text{C})$$

$$\Delta H_f^\circ(\text{Na}_2\text{U}_2\text{O}_7, \text{s}) = \Delta H_{10} = 2 \Delta H_{11} + 2 \Delta H_{12} + 2 \Delta H_{13} + 2 \Delta H_{14} + 3 \Delta H_{15} - 6 \Delta H_{16} - \Delta H_7 = -3203.8 \pm 2.8 \text{ kJ mol}^{-1} \quad (\text{D})$$

The present result for ΔH<sub>f</sub><sup>°</sup>(Na<sub>4</sub>UO<sub>5</sub>, s, β), -2457.3 ± 2.8 kJ mol<sup>-1</sup>, is in very moderate agreement with the value of -2450.6 ± 2.1 kJ mol<sup>-1</sup> based on the enthalpy of solution of this compound in 6 mol dm<sup>-3</sup> HNO<sub>3</sub> obtained by Cordfunke and Loopstra<sup>19</sup> and recalculated by Cordfunke and O'Hare<sup>26</sup> using CODATA-compatible auxiliary values. Our value for ΔH<sub>f</sub><sup>°</sup>(Na<sub>2</sub>UO<sub>4</sub>, s, α), -1901.3 ± 2.3 kJ mol<sup>-1</sup>, compares with the value -1897.3 ± 1.1 kJ mol<sup>-1</sup> recently reported by Cordfunke *et al.*<sup>22</sup> based on measurements in 1.505 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The latter result superseded two earlier literature values, obtained by the same group of authors, which, after recalculation using CODATA compatible auxiliary values yielded -1889.9 ± 2.1 kJ mol<sup>-1</sup> (based on a cycle involving 6 mol dm<sup>-3</sup> HNO<sub>3</sub>)<sup>19</sup> and -1887.8 ± 2.1 kJ mol<sup>-1</sup> (based on a cycle involving 0.1 mol dm<sup>-3</sup> HCl).<sup>27</sup> According to Cordfunke *et al.*<sup>22</sup> the less negative value obtained for the data in 0.1 mol dm<sup>-3</sup> HCl is due to the fact that the UO<sub>2</sub>Cl<sub>2</sub> sample used in that cycle was hydrated.

The difference between the enthalpies of solution of α- and β-Na<sub>2</sub>UO<sub>4</sub>, obtained in this study, +12.3 ± 0.6 kJ mol<sup>-1</sup>, which reflects the difference in the enthalpies of formation of the two

crystallographic forms of this compound, is in marginal agreement with the value of 13.85 ± 0.04 reported by O'Hare *et al.*<sup>25</sup> In view of the use of the same media by these authors and ourselves, it appears obvious that the small difference in the two sets of data may be due to small variations in the sample nature. The present data and the result of O'Hare *et al.*<sup>25</sup> establish with a reasonable accuracy the enthalpy difference between β- and α-Na<sub>2</sub>UO<sub>4</sub>, a question which required resolution<sup>26</sup> in view of the early value given by Cordfunke and Loopstra,<sup>19</sup> +6.2 ± 0.4 kJ mol<sup>-1</sup>.

Our value for ΔH<sub>f</sub><sup>°</sup>(Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>, s), -3203.8 ± 2.8 kJ mol<sup>-1</sup>, diverges somewhat from the values published earlier by Cordfunke and Loopstra<sup>19</sup> and Cordfunke *et al.*<sup>22</sup> Those investigations, using CODATA-compatible auxiliary data, yield -3194.5 ± 2.1 kJ mol<sup>-1</sup> (based on a cycle<sup>19</sup> involving 6 mol dm<sup>-3</sup> HNO<sub>3</sub>) and -3194.8 ± 1.8 kJ mol<sup>-1</sup> (based on cycle<sup>22</sup> involving 1.505 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>). In view of the care taken to characterise the samples used in the various studies and in our case to report data based on multiple (six) preparations, we believe that the difference between our results and the previous data may be due to unidentified inconsistencies in the auxiliary data used in the various thermodynamic cycles. This opinion is supported by the fact that recently O'Hare<sup>28</sup> obtained a value of -172.4 ± 2.0 kJ mol<sup>-1</sup> for the enthalpy of solution in 1 mol dm<sup>-3</sup> HCl, of part of the Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub> sample employed by Cordfunke *et al.*<sup>22</sup> for their determination in 1.505 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. This value in 1 mol dm<sup>-3</sup> HCl is in excellent agreement with our own result of -171.8 ± 1.0 kJ mol<sup>-1</sup> for the same medium.

**Crystallographic Results.**—Unit-cell dimensions obtained for 'α-Na<sub>4</sub>UO<sub>5</sub>' prepared by the interaction of UO<sub>2</sub> and Na<sub>2</sub>O<sub>2</sub> at ca. 360 °C and for α-Na<sub>2</sub>UO<sub>4</sub>, β-Na<sub>2</sub>UO<sub>4</sub>, and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub> samples prepared by this method and by thermal decomposition of the complexes are in good agreement with published values.<sup>3</sup> The results listed in Table 3 for samples used for determination of enthalpies of solution are typical of those obtained.

## Conclusions

Thermal decomposition of uranium-(iv) and -(vi) complexes such as Na<sub>4</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O (1.5 < n < 3.5), Na<sub>4</sub>U(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>·3H<sub>2</sub>O, Na<sub>2</sub>UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, and NaUO<sub>2</sub>(CH<sub>3</sub>COO)<sub>3</sub> in oxygen provides convenient routes to the high-purity sodium uranates(vi), β-Na<sub>4</sub>UO<sub>5</sub>, α- and β-Na<sub>2</sub>UO<sub>4</sub>, and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>. This method appears to be more convenient and more reliable than Na<sub>2</sub>O<sub>2</sub>-UO<sub>2</sub> interactions.

The enthalpies of formation reported, based on enthalpies of solution of compounds prepared by thermal decomposition methods, reveal small differences compared with literature data either as assessed by Cordfunke and O'Hare<sup>26</sup> or published

more recently;<sup>22</sup> it is unlikely, however, in view of the efforts to characterise the samples fully, that in all instances sample variation is the major cause for these differences.

The results for  $\alpha$ - and  $\beta$ -Na<sub>2</sub>UO<sub>4</sub> agree reasonably well with those recalculated<sup>26</sup> on the basis of the results of O'Hare *et al.*<sup>25</sup> and therefore provide confirmation of the enthalpy of the  $\alpha \rightarrow \beta$  transition for this compound.

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### References

- 1 Part 5, J. Fuger and D. Brown, *J. Chem. Soc., Dalton Trans.*, 1975, 2256.
- 2 C. Keller, *Int. Rev. Sci., Inorg. Chem. Ser. 1*, 1972, 7, 47.
- 3 C. Keller, *Gmelin Handbuch der Anorg. Chemie, Uran.*, 1979, vol. 3C.
- 4 L. R. Morss, J. Fuger, and H. D. B. Jenkins, *J. Chem. Thermodyn.*, 1982, 14, 377.
- 5 L. R. Morss, C. W. Williams, I. K. Choi, R. Gens, and J. Fuger, *J. Chem. Thermodyn.*, 1983, 15, 1093.
- 6 R. Gens, J. Fuger, L. R. Morss, and C. W. Williams, *J. Chem. Thermodyn.*, in the press.
- 7 D. Brown, B. Whittaker, and P. E. Lidster, Report AERE-R-8035, A.E.R.E., Harwell, 1975.
- 8 J. A. C. Marples, and J. L. Shaw, Report AERE-R-5210, A.E.R.E., Harwell, 1966.
- 9 J. Fuger, Annual Reports Euratom-University of Liège Research Contract 011-64 TPUB, 1965, 1966.
- 10 J. Fuger, D. Brown, and J. F. Easey, *J. Chem. Soc. A*, 1969, 2995.
- 11 J. Fuger, J. C. Spirlet, and W. Müller, *Inorg. Nucl. Chem. Lett.*, 1972, 8, 709.
- 12 J. Fuger and D. Brown, *J. Chem. Soc., Dalton Trans.*, 1980, 1076.
- 13 H. Sunderman and H. Wagner, Report KFK-819, Kernforschungszentrum Karlsruhe, 1968.
- 14 'Atomic Weights of the Elements 1979,' ed. N. E. Holden, *Pure Appl. Chem.*, 1980, 52, 2349.
- 15 W. J. Youden, 'Statistical Methods for Chemists,' Wiley, New York, 1967, pp. 18—20.
- 16 J. W. Mellor, 'Higher Mathematics,' Dover, New York, 1946, pp. 527—531.
- 17 'CODATA Recommended Key Values for Thermodynamics 1977,' *J. Chem. Thermodyn.*, 1978, 10, 903.
- 18 C. Keller, Report KFK-225, Kernforschungszentrum Karlsruhe, 1964.
- 19 E. H. P. Cordfunke and B. O. Loopstra, *J. Inorg. Nucl. Chem.*, 1971, 33, 2427.
- 20 S. F. Bartram and R. E. Fryxell, *J. Inorg. Nucl. Chem.*, 1970, 32, 3701.
- 21 E. A. Ippolitova, Yu. P. Simonov, K. M. Efremova, and V. M. Shatskii, English Translation of *Issledovaniya V. Oblasti Khimii Urana*, Moscow University (1964), ANL Trans-33-34, 1964.
- 22 E. H. P. Cordfunke, R. P. Muis, W. Ouweltjes, H. P. Flotow, and P. A. G. O'Hare, *J. Chem. Thermodyn.*, 1982, 14, 313.
- 23 V. B. Parker, D. D. Wagman, and D. Garvin, U.S. National Bureau of Standards, Report NBSIR75-968, 1976.
- 24 V. B. Parker, U.S. National Bureau of Standards, Report NBSIR80-2029, 1980.
- 25 P. A. G. O'Hare, H. R. Hoekstra, and D. K. Fredrickson, *J. Chem. Thermodyn.*, 1976, 8, 255.
- 26 E. H. P. Cordfunke and P. A. G. O'Hare, 'The Chemical Thermodynamics of Actinide Elements and Compounds,' eds. E. F. Westrum, jun., and V. A. Medvedev, IAEA, Vienna, 1978, part 3.
- 27 P. A. G. O'Hare and H. R. Hoekstra, *J. Chem. Thermodyn.*, 1973, 5, 769.
- 28 P. A. G. O'Hare, personal communication, 1984.

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