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# The standard molar enthalpy of formation of UNCl

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The enthalpies of solution of UNCl(s) and a mixture of UCl<sub>4</sub> and NH<sub>4</sub>Cl in  $(0.76\,\text{mol}\cdot\text{dm}^{-3}~\text{HCl}+0.03\,\text{mol}\cdot\text{dm}^{-3}~\text{FeCl}_3)$  have been measured. From these values the standard molar enthalpy of formation of UNCl(s) has been derived:  $\Delta_f H^{\rm o}_m(\text{UNCl},s,298.15\,\text{K}) = -(559\pm4)\,\text{kJ}\cdot\text{mol}^{-1}.$  © 2002 Elsevier Science Ltd. All rights reserved.

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# **1. Introduction**

A molten-salt electrorefining process has been proposed for application to the reprocessing of nitride fuels and targets for transmutation of minor actinide elements.<sup>(1,2)</sup> This pyrochemical reprocessing with electrorefining has advantages over the conventional wet processes. The suggested process is very compact and very simple, where the actinide nitrides are anodically dissolved in the molten salt and the actinide metals are deposited on the cathode. In addition, <sup>15</sup>N-enriched N<sub>2</sub> can be easily recycled in this process.

Kobayashi *et al.*<sup>(3)</sup> found that UNCl(s) was formed and deposited at the bottom of the reaction cell during the electrolytic decomposition of UN in (uranium trichloride + lithium chloride + potassium chloride) molten salts at T = 773 K. The formation of by-products in the process would result in an undesirable lower recovery of actinides. Therefore, it is important to clarify the thermodynamic properties and stability of UNCl for development of pyrochemical reprocessing.

In the ternary system (U, N, Cl), there are few data on the UNCl compound.<sup>(4-6)</sup> Juza and Meyer<sup>(5)</sup> prepared UNCl and determined the crystal structure to be tetragonal with

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space group P4/nmm. Mitamura *et al.*<sup>(7)</sup> showed that UNCI decomposed above T = 1273 K at low pressure into U<sub>2</sub>N<sub>3</sub> and UCl<sub>3</sub>. Ogawa *et al.*<sup>(8)</sup> discussed the thermodynamic stability of UNCI during the electrochemical dissolution of UN in (lithium chloride + potassium chloride) eutectic melt. The stability diagram of (U, N, Cl) at T = 773 K was derived from e.m.f. measurements<sup>(3)</sup> and was compared with the stabilities of UNF and PuNCI in the (U, N, F) and (Pu, N, Cl) systems, respectively.

In this study, the standard molar enthalpy of formation of solid UNCl was determined by isoperibol solution calorimetry and its thermochemistry is discussed.

#### 2. Experimental

The compound uranium nitride chloride UNCl(s) was synthesized by reacting powdered uranium sesquinitride (U<sub>2</sub>N<sub>3</sub>) and uranium trichloride (UCl<sub>3</sub>). The details of the preparation have been reported previously.<sup>(3)</sup> In the first step, U<sub>2</sub>N<sub>3+x</sub>(s) and UCl<sub>3</sub>(s) powders were prepared from pure uranium metal by direct nitridation at T = 1073 K in flowing purified nitrogen and reaction with purified chlorine gas at T = 523 K, respectively. Next, the stoichiometric amounts of the U<sub>2</sub>N<sub>3+x</sub>(s) and UCl<sub>3</sub>(s) powders are well mixed in an agate mortar and then heated for 24 h at T = 923 K in a closed system with over  $4 \text{ dm}^3$  of free volume to contain the nitrogen gas released during the reaction: U<sub>2</sub>N<sub>3+x</sub> + UCl<sub>3</sub> = 3UNCl + (x/2)N<sub>2</sub>. The UNCl with unreacted UCl<sub>3</sub> and U<sub>2</sub>N<sub>3</sub> was subsequently heated for 24 h at T = 1023 K and for 5 h at T = 1073 K in order to eliminate the residual UCl<sub>3</sub>. A small amount of U<sub>2</sub>N<sub>3</sub> fragments remained in the product. The UNCl(s) powder obtained was then screened with a sieve of 50 µm in size in order to enhance the dissolution rate in the solvent and remove unreacted residuals such as U<sub>2</sub>N<sub>3</sub>(s).

Chemical analysis of uranium in UNCl was performed gravimetrically by oxidizing it to  $U_3O_8(s)$ . The amount of chlorine in the UNCl was measured by liquid-chromatography with potassium hydrogen phthalate as eluent. The analytical results are given in table 1. No nitrogen content is indicated, because we were unable to analyse for nitrogen.

The final UNCl(s) powder was examined by X-ray diffraction (Guiner de Wolff camera, Cu–K $\alpha_{1,2}$ ) which confirmed the earlier results by Jazu and Meyer<sup>(5)</sup> that UNCl(s) had a tetragonal structure with a P4/nmm symmetry (JCPDS card number 25-0995, reference 6). Also, some trace amounts of UO<sub>2</sub>(s) and U<sub>2</sub> N<sub>3</sub>(s) were found. The impurities in the UNCl(s) were mainly due to oxidation during heat treatments and unreacted starting material.

	$M/(g \cdot mol^{-1})$	$10^2 \cdot w(U)$		$10^2 \cdot w(N)$		$10^2 \cdot w(Cl)$	
		Found	Calculated	Found	Calculated	Found	Calculated
UNCI	287.488	$82.6\pm1.65$	82.80		4.87	$12.3\pm0.50$	12.33
UC <sub>14</sub>	379.840	$62.70\pm0.05$	62.67			$37.55\pm0.03$	37.33

TABLE 1. Analytical results of UNCl(s) as mass fraction w

Uranium tetrachloride (UCl<sub>4</sub>) and ammonium chloride (NH<sub>4</sub>Cl) were used as auxiliary compounds to obtain the standard molar enthalpy of formation of UNCl in the thermodynamic cycle. The compound UCl<sub>4</sub> was prepared by the reaction of chlorine gas with an intimate mixture of UO<sub>2</sub> and C at temperatures varying from 675 K to 775 K, as reported earlier.<sup>(9)</sup> During the preparation, much UCl<sub>5</sub> was formed, which is very volatile, whereas some unreacted UO<sub>2</sub> remained behind. In order to purify the UCl<sub>4</sub>, it was well pulverized and sublimed in a mixture of argon and chlorine with  $_V(Ar)/_V(Cl_2) = 20$  at T = 1075 K, followed by a treatment at low pressure and the same temperature. The compound NH<sub>4</sub>Cl was obtained from the Aldrich Chemical Co. and had a mass fraction of 0.99998. The phase purities of UCl<sub>4</sub> and NH<sub>4</sub>Cl have been confirmed by X-ray diffraction.

The enthalpies of solution were measured with an isoperibol solution calorimeter that has been described together with the calorimetric procedure and the calibration method.<sup>(10)</sup> In this method, the temperature of a reaction vessel in a constant-temperature environment was monitored as a function of time. The calorimeter includes a Dewar vessel as a reaction cell, a rapid-responding temperature-measuring thermistor, and an electrical heater for temperature equilibration and calibration. The enthalpy of solution measurements were performed in 250 cm<sup>3</sup> of solvent, and the reaction vessel was immersed in a water bath controlled at  $T = (298.150 \pm 0.001)$  K. Calorimetric energy equivalents were determined during each run by electrical energy inputs. Correction to the temperature rise in the calorimeter was based on Newton's cooling law. Calorimetric specimens were loaded in well-dried sample holders constructed of glass and KEL-F plastic for UNCl(s) and the mixtures of  $UCl_4(s)$  and  $NH_4Cl(s)$ , respectively. The uncertainties are given as twice the standard deviation of the mean. The weighing, loading, and the previously mentioned preparative handlings were done in a glovebox filled with recirculating purified argon with an average mass fraction of water and oxygen of less than  $2 \cdot 10^{-6}$ . The molar mass of UNCl was taken as  $287.488 \text{ g} \cdot \text{mol}^{-1}$ ,<sup>(11)</sup> the isotope abunancy of the sample being that of natural uranium.

Based on preliminary tests on the dissolution behaviour of UNCl in water and some other diluted solvents, it was established that a mixture of hydrochloric acid and a FeCl<sub>3</sub>-solution gave best results. This solvent containing  $0.76 \text{ mol} \cdot \text{dm}^{-3}$  HCl and  $0.0304 \text{ mol} \cdot \text{dm}^{-3}$  FeCl<sub>3</sub> will be called hereafter solution "A". Although UNCl(s) usually dissolved completely in this solution, occasionally a small black precipitate was found after the experiments. Since the amount never exceeded a few µg, no attempts have been made to correct for this material.

The use of other solvents such as water and hydrochloric acid resulted in the precipitation of a large amount of a black substance that was identified by X-ray diffraction analysis as  $U_2N_3$ . To ascertain the valence state of uranium in solution, the absorption spectra of solution "A" and pure HCl solutions after dissolution of UNCl(s) were taken with a conventional absorption spectrometer. The hydrochloric acid to prepare solution "A" was prepared from reagent grade HCl (Merck) and boiled demineralized water. The solvent was titrated potentiometrically with a calibrated standard NaOH solution prior to use.

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## 3. Results and discussion

The results of the enthalpy-of-solution measurements are given in table 2, where *m* is the mass of the sample dissolved,  $\varepsilon$  the energy equivalent of the calorimeter,  $\Theta$  an arbitrary temperature,  $\Delta\Theta$  the temperature change, and  $\Delta_{sol}H_m$  the experimental molar enthalpy of solution.

The formation of only  $U^{4+}(aq)$  after dissolution of UNCl in 0.76 mol  $\cdot$  dm<sup>-3</sup> HCl without FeCl<sub>3</sub> was clearly confirmed from the absorption spectroscopic measurement. In addition, NH<sub>4</sub><sup>+</sup>(aq) was observed by ion chromatography. Therefore, the reaction of the dissolution of UNCl in 0.76 mol  $\cdot$  dm<sup>-3</sup> HCl is given by the following:

$$UNCl(s) + 4HCl(aq) = (UCl_4 + NH_4Cl)(aq).$$
(1)

In solution "A", uranium is expected to be oxidized to its hexavalent state due to the presence of the  $(Fe^{3+}, Fe^{2+})$  couple. Therefore the formation of UO<sub>2</sub>Cl<sub>2</sub> is expected by the following mechanism starting from reaction (1):

$$(UCl_4 + 2FeCl_3 + 2H_2O)(aq) = (UO_2Cl_2 + 2FeCl_2 + 4HCl)(aq).$$
(2)

TABLE 2. The molar enthalpy of solution of a mass *m* of a specified solute in 250 cm<sup>3</sup> of solvent "A" at T = 298.15 K;  $\varepsilon$  denotes the energy equivalent of the calorimeter,  $\Theta$  an arbitrary temperature, and  $\Delta \Theta$  the temperature change<sup>*a*</sup>

m/g	m/g	$\mathbf{\epsilon}\cdot\mathbf{\Theta}/\mathbf{J}$	$\Delta \Theta / \Theta$	$\Delta_{ m sol} H_{ m m}/( m kJ\cdot m mol^{-1})$		
UNCl						
0.05891		118.570	0.4780	-276.587		
0.05783		119.050	0.4706	-278.516		
0.05465		119.082	0.4443	-278.326		
0.05465		118.894	0.4412	-275.946		
0.05201		119.889	0.4128	-273.560		
0.05489		118.380	0.4421	-274.111		
0.05286		118.899	0.4246	-274.569		
			$\langle \Delta_{ m sol} H_{ m m}  angle : -$	$\langle \Delta_{ m sol} H_{ m m}  angle : -(275.95 \pm 1.50)$		
UCl <sub>4</sub>	NH <sub>4</sub> Cl					
0.04991	0.02481	117.088	0.1304	-32.919		
0.06374	0.01176	118.068	0.2057	-110.469		
0.06705	0.00897	117.515	0.2428	-170.150		
0.06949	0.00741	119.790	0.2597	-224.567		
0.05992	0.01562	121.586	0.1876	-78.112		
For $n(\text{UCl}_4)/n(\text{NH}_4\text{Cl}) = 1$ , $\langle \Delta_{\text{sol}}/H_{\text{m}} \rangle = -(161.55 \pm 2.75)\text{kJ} \cdot \text{mol}^{-1}$						

<sup>*a*</sup> Mean values are denoted by  $\langle \Delta_{sol}H_m \rangle$ . Solution "A" refers to  $(0.76 \text{ mol} \cdot dm^{-3}\text{HCl} + 0.03 \text{ mol} \cdot dm^{-3} \text{FeCl}_3)(aq)$ .

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As a result, the total reaction is given by:

$$UNCl(s) + (2FeCl_3 + 2H_2O)(aq) = (UO_2Cl_2 + 2FeCl_2 + NH_4Cl)(aq).$$
(3)

However, due to the interference of  $Fe^{3+}(aq)$  in the absorption spectrum, the existence of  $UO_2^{2+}(aq)$  could not be confirmed in solution "A". Based on the previous reactions, the dissolution process of UCl<sub>4</sub> and NH<sub>4</sub>Cl in solution "A" can be represented by:

$$UCl_4(s) + NH_4Cl(s) + (2FeCl_3 + 2H_2O)(aq)$$
  
= (UO<sub>2</sub>Cl<sub>2</sub> + NH<sub>4</sub>Cl + 2FeCl<sub>2</sub>)(aq) + 4HCl. (4)

The reaction scheme to derive the standard molar enthalpy of formation of UNCl(s) is given in table 3. The enthalpy of solution of UNCl(s) in solution "A" is  $-(275.95 \pm 1.50) \text{ kJ} \cdot \text{mol}^{-1}$  (top of table 2). The enthalpy of solution of the auxiliary chlorides, UCl<sub>4</sub> and NH<sub>4</sub>Cl, were not measured at their stoichiometric ratios. Instead, the enthalpies of solution of various mixtures of these compounds were measured (bottom of table 2). The enthalpy of solution corresponding to the desired stoichiometric composition was interpolated to  $r = n\{\text{UCl}_4(s)\}/n\{\text{NH}_4\text{Cl}(s)\} = 1$  by means of a least-squares procedure, a linear dependence of  $\Delta_{sol}H_m^o$  (298.15 K) on *r* being assumed, to yield a value of:  $-(161.55 \pm 2.75) \text{ kJ} \cdot \text{mol}^{-1}$ .

Combining these results with the standard molar enthalpies of formation of  $UCl_4(s)$ ,<sup>(12)</sup>  $NH_4Cl(s)$ ,<sup>(13)</sup> and the partial molar enthalpy of formation of HCl in solution "A", by using reference 14 corrected for the CODATA-value at infinite dilution,<sup>(15)</sup> the standard molar enthalpy of formation of UNCl(s) is:  $\Delta_f H^o_m(298.15 \text{ K}) = -(559.42 \pm 4.14) \text{ kJ} \cdot \text{mol}^{-1}$ . Therefore we recommend the value:  $\Delta_f H^o_m(UNCl, s, 298.15 \text{ K}) = -(559 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$ .

Recently, Ogawa<sup>(16)</sup> also determined the standard molar enthalpy of formation of UNCl(s) from e.m.f measurements.<sup>(2,3)</sup> From the cell reaction he calculated  $\Delta_f H_m^o$  (UNCl, s, 298.15 K) to be approximately  $-554 \text{ kJ} \cdot \text{mol}^{-1}$ , by using  $\Delta_f S_m^o$  (UNCl, s,

Reaction	$\Delta_{\rm r} H_{\rm m}^{\rm o}/({\rm kJ}\cdot{\rm mol}^{-1})$	
$1. \text{ UNCl}(s) + (2\text{FeCl}_3 + 2\text{H}_2\text{O})(\text{slnin "A"})$	$-275.95 \pm 1.50$	
$= (UO_2Cl_2 + NH_4Cl + 2FeCl_2)(aq) + sol ~``A"$		
2. $UCl_4(s) + NH_4Cl(s) + (2FeCl_3 + 2H_2O)(slnin "A")$	$-161.55 \pm 2.75$	
$= (UO_2Cl_2 + NH_4Cl + 2FeCl_2)(aq) + 4HCl(sln in "A")$		
$3. \ U(s) + 2Cl_2(g) = UCl_4(s)$	$-1017.80 \pm 2.50$	
$4. \ 1/2N_2(g) + 2H_2(g) + 1/2Cl_2(g) = NH_4Cl(s)$	$-314.55 \pm 0.84$	
5. $2H_2(g) + 2Cl_2(g) + sol$ "A" = 4HCl(sln in "A")	$-659.53 \pm 0.40$	
6. $U(s) + 1/2N_2(g) + 1/2Cl_2(g) = UNCl(s)$	$-559.42 \pm 4.14^{b}$	

TABLE 3. Reaction scheme for the standard molar enthalpy of formation of UNCl(s) in solution "A" at  $T = 298.15 \text{ K}^a$ 

<sup>*a*</sup> Solution "A" refers to  $(0.76 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl} + 0.03 \text{ mol} \cdot \text{dm}^{-3} \text{ FeCl}_3)(\text{aq})$ .

 ${}^{b}\Delta_{\mathbf{r}}H^{\mathbf{o}}_{\mathbf{m}}(6) = -\Delta_{\mathbf{r}}H^{\mathbf{o}}_{\mathbf{m}}(1) + \Delta_{\mathbf{r}}H^{\mathbf{o}}_{\mathbf{m}}(2) + \Delta_{\mathbf{r}}H^{\mathbf{o}}_{\mathbf{m}}(3) + \Delta_{\mathbf{r}}H^{\mathbf{o}}_{\mathbf{m}}(4) - \Delta_{\mathbf{r}}H^{\mathbf{o}}_{\mathbf{m}}(5).$ 

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298.15 K) =  $-164 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  estimated with Latimer's empirical relation.<sup>(17)</sup> This result is, considering the approximation used, in good agreement with the value obtained in the present work.

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