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The accurate determination of the thermochemical properties of uranyl halides

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1. INTRODUCTION

The various measurements of enthalpies of formation and high-temperature enthalpy increments of uranyl halides, mentioned in the present report, were carried out as part of a research programme of our laboratory to provide accurate thermodynamic data for uranium compounds that are of interest in nuclear technology. The data obtained, together with low-temperature heat capacities from the literature, may permit to draw conclusions regarding the (relative) stabilities of these compounds.

Before the signing of the Agency Research Contract the following part of the work on the halides had already been accomplished and was published shortly before or in the Contract period: the enthalpy of formation of uranyl chloride, UO_2Cl_2 |1|, uranyl fluoride, UO_2F_2 |2|, and uranium (V, VI) oxide chloride, $(UO_2)_2Cl_3$ |3|.

In the course of the Contract period the following investigations were carried out:

- preparation and determination of the enthalpy of formation of uranyl bromide, UO_2Br_2, its two hydrates, and a basic salt;
- determination of the high-temperature enthalpy increments of uranyl fluoride, UO_2F_2, uranyl chloride, UO_2Cl_2, and uranyl bromide, UO_2Br_2;
- attempt to prepare a hydrate of uranyl iodide, UO_2I_2.

These investigations are mentioned in the present report.

After the expiration of the Contract, work on another oxide halide, uranium (IV) oxide chloride, $UOCl_2$, was not quite finished. The determination of its enthalpy of formation and high-temperature enthalpy increments will take place in the near future. If the results will prove of sufficient quality to be published, the financial support of the Agency will be mentioned in the paper.

2. EXPERIMENTAL

2.1. Preparation of compounds

Since the uranyl halides are difficult to prepare in a pure form, and most of them are extremely hygroscopic, special attention was given to the preparative details of the work and also to the chemical analyses of the compounds obtained |1,2,3|. Especially the synthesis of anhydrous uranyl bromide, UO_2Br_2, took much time, because none of the few published methods for the preparation of this salt gives a pure product, so that we had to develop a procedure of our own. The latter investigation has been described in the progress report sent to the Agency in April 1977 |4|. The method for the preparation of UO_2Br_2 will also be reported in a forthcoming paper on the enthalpy of formation of this compound |5|. Likewise the preparation of uranyl fluoride, UO_2F_2, entailed difficulties. It was necessary first to discover the various conditions that give a pure and crystalline product |2|.

In the past various workers attempted to prepare uranyl iodide, UO_2I_2, but without success. We have tried to synthesize the monohydrate, $UO_2I_2.H_2O$, likewise without result. This attempt has been described in a previous progress report sent to the Agency in November 1977 |6| and also in reference 5 together with an evaluation of the stability of UO_2I_2.

2.2. Calorimetric measurements

The various enthalpies of formation were calculated from enthalpies of solution, combined with auxiliary thermodynamic data from the literature. These enthalpies of solution (in a solution of a suitable acid) were measured in a calorimeter of the isoperibol type. This calorimeter has been described in reference 7 and a modification of it for the use of hydrofluoric acid in reference 2.

The high-temperature enthalpy measurements were made in an isothermal diphenyl ether drop calorimeter of the type described by Giguère et al. |8|. In this type of calorimeter heat from the sample melts a quantity of diphenyl ether; the resulting volume change of the ether is determined by displaced mercury.

A description of the calorimeter used is given in reference 9.

3. RESULTS

Values for the enthalpy of formation, ΔH_f^0 (298.15 K), of the uranyl bromides UO_2Br_2, $UO_2Br_2.H_2O$, $UO_2Br_2.3H_2O$, and $UO_2(OH)Br.2H_2O$ have been determined (table 1). A paper describing the results has been accepted by the Journal of Chemical Thermodynamics and will appear before the end of 1978 |5|.

The high-temperature enthalpy increments, H(T)-H(298.15 K), of uranyl fluoride, UO_2F_2, uranyl chloride, UO_2Cl_2, and uranyl bromide, UO_2Br_2, have also been determined (table 2). In contradiction with the statement in the previous progress report |6|, enthalpy values for UO_2Br_2 could be obtained, though for a very limited temperature range (298 to 454 K), because of the low thermal stability of the compound.

A paper on the enthalpy measurements is nearly finished and will be submitted to the Journal of Chemical Thermodynamics |9|.

The main results of the investigations mentioned are given in table 1 and 2.

Table 1 Enthalpies of formation [5]
(cal = 4.184 J)

Compound	$\{ \Delta H_f^0 (298.15 K) \}$/kcal mol^{-1}
$UO_2Br_2(s)$	- (271.8 ± 0.2)
$UO_2Br_2.H_2O(s)$	- (347.9 ± 0.2)
$UO_2Br_2.3H_2O(s)$	- (491.8 ± 0.2)
$UO_2(OH)Br.2H_2O(s)$	- (468.1 ± 0.2)

Table 2 Enthalpy functions:
$H(T) - H(298.15 K) = aT + bT^2 + cT^{-1} + d$ [9]

Compound	{H(T) - H(298.15 K)} / J mol^{-1}				(Temperature range) / K
	a	b × 10^3	c × 10^{-5}	d	
$UO_2F_2(s)$	112.066	9.6574	12.984	- 38626	298 - 811
$UO_2Cl_2(s)$	115.275	9.1116	11.418	- 39009	298 - 649
$UO_2Br_2(s)$	104.270	18.969	-	- 32774	298 - 454

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