QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS OF THE REDUCTION OF URANYL FLUORIDE

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The enthalpy of the reduction of UO_2F_2 with hydrogen was obtained from quantitative DTA measurements with a linear heating rate and under isothermal conditions, and the thermodynamic data on UO_2F, formed as a stable intermediate in the reduction of UO_2F_2 to UO_2, are also presented. The advantages of isothermal DTA in the reduction of U_3O_8 to UO_2 could be demonstrated.

Examinations of the reaction $UO_2F_2 + H_2 \rightarrow UO_2 + 2\,HF$ by means of kinetic, thermal and X-ray methods showed that this reaction consists of the partial steps

$$UO_2F_2 + \frac{1}{2}H_2 \rightarrow UO_2F + HF$$

and

$$UO_2F + \frac{1}{2}H_2 \rightarrow UO_2 + HF$$
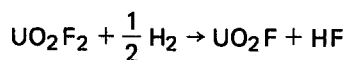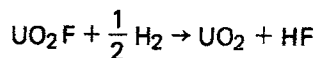
the latter reaction being superimposed by a change in the structure of UO_2F at temperature above 973 K [1]. From X-ray studies it follows that the structure of the UO_2F lattice is similar to that of α-U_3O_8 and then changes into a real α-U_3O_8 structure during tempering in hydrogen.

Simultaneously, fluoride is partially released and UO_2 is formed. In hydrogen, this compound is converted to the lattice of UO_2 in a fast and exothermic reaction. The share of the phases UO_2 and UO_2F in the intermediates was determined by chemical, kinetic and X-ray methods.

The present paper reports the reaction enthalpies of the partial steps in the reduction of UO_2F_2 to UO_2 by means of quantitative DTA, and the calculated thermodynamic data on UO_2F.

Experimental

Anhydrous uranyl fluoride was prepared by the hydrolysis of uranium hexafluoride in water and evaporation of the solution in a platinum boat. The evaporation residue (UO_2F_2) was tempered at 473 K in air for several days and at 870 K in hydrogen for several minutes. The resulting solid is yellow; its X-ray diagram and chemical analysis are presented in [1].

Quantitative measurements were carried out in a home-made DTA apparatus described in [1], and qualitative measurements in a Mettler TA-1 thermoanalyzer.

The home-made DTA apparatus was constructed from nickel and the thermocouples were of NiCr/Ni. The DTA apparatus was calibrated by means of various substances ($AgNO_3$, $CuSO_4 \cdot 5\ H_2O$, $PbCO_3$, $BaCO_3$, and the reaction $3\ UO_2 + O_2 \rightleftharpoons U_3O_8$) up to 1080 K. The apparatus constant K (J/cm^2) varied between $0.1139 \pm 6.1\%$ at 433 K and $0.5317 \pm 8.6\%$ at 1080 K. The sample weight was 50–60 mg UO_2F_2. The simultaneous DTA–TG measurements in the TA-1 thermoanalyzer were carried out in PtRh10 plate-crucibles and with a PtRh–Pt specimen holder assembly. The sample weight was 65 mg.

Results and discussion

For quantitative analysis, DTA curves of the reduction of UO_2F_2 were used; these were obtained with a linear heating rate (3–10 deg./min) and under isothermal conditions. Examples are given in Figs 1 and 2. UO_2F_2 is stable up to 920 K in hydrogen if it is well crystallized. The DTA curve at a linear heating rate (Fig. 1) shows an endothermic drift up to about 1050 K, after which there is a sharp exothermic peak. At this temperature all the UO_2F_2 is reduced to UO_2F, which is partially reduced to UO_2 without change into the pure α-U_3O_8 structure. 30% of the UO_2F is changed into the pure α-U_3O_8 structure, which is converted in hydrogen to the lattice of UO_2 in a fast and exothermic reaction. With poorly-crystallized samples of UO_2F_2, which are highly reactive, the endothermic effect of the reduction to UO_2 (at temperature lower than 860 K) could be measured without the occurrence of the exothermic peak.
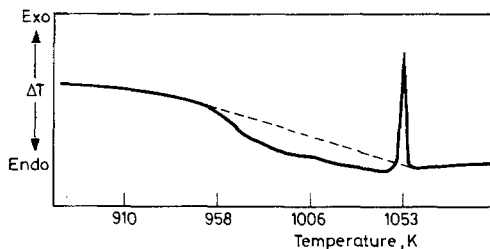

Fig. 1 DTA curve of reduction of UO_2F_2 at linear heating rate 6 deg/min

The advantages of isothermal DTA are shown in Fig. 2. By variation of the temperature, it was possible to separate the endothermic and exothermic peaks completely and to obtain a sharp endothermic peak. The share of the phases UO_2 and UO_2F_2 in the intermediates was determined by chemical, kinetic (TG curves) and X-ray methods.
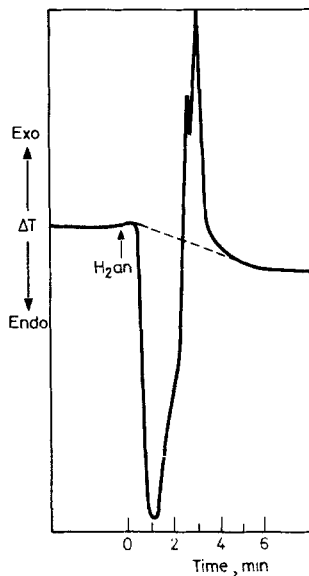

Fig. 2 DTA curve of reduction of UO_2F_2 at constant temperature 1053 K

The majority of the quantitative DTA measurements were carried out under isothermal conditions. The advantages of isothermal DTA could also be demonstrated in the reduction of U_3O_8 to UO_2 (Fig. 3).
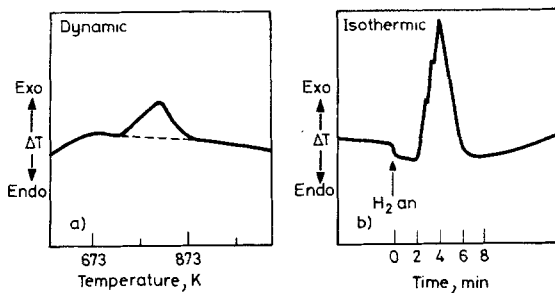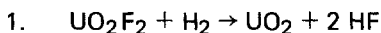

Fig. 3 DTA curve of reduction of U_3O_8 at linear heating rate 6 deg/min (a) and at constant temperature 973 K (b)
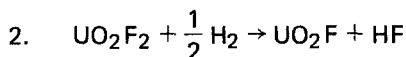
From DTA measurements, by means of the equation

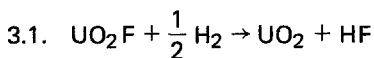$$\Delta H_T^0 = \frac{K \cdot F \cdot M}{m}$$

where K (J/cm^2) = apparatus constant, F (cm^2) = peak area, M (g/mol) = molar weight of the substance, m (g) = weight of the sample, and ΔH_T^0 (J/mol) = reaction enthalpy, the following reaction enthalpies were determined:

1. $UO_2F_2 + H_2 \rightarrow UO_2 + 2\,HF$

$\Delta H_{850\,K}^0 = 21.3 \pm 2.9$ kJ/mol UO_2F_2

2. $UO_2F_2 + \dfrac{1}{2}\,H_2 \rightarrow UO_2F + HF$

$\Delta H_{1000\,K}^0 = 18.4 \pm 2.3$ kJ/mol UO_2F_2

3.1. $UO_2F + \dfrac{1}{2}\,H_2 \rightarrow UO_2 + HF$

$\Delta H_{950\,K}^0 = 3.2 \pm 1.7$ kJ/mol UO_2F

which is reduced to UO_2 without change into the pure α-U_3C structure.

3.2. $UO_2F + \dfrac{1}{2}\,H_2 \rightarrow UO_2 + HF$
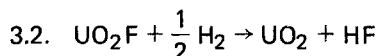
$\Delta H_{1000\,K}^0 = -13.1 \pm 3.0$ kJ/mol UO_2F

with the pure α-U_3O_8 structure.

From thermodynamic data (ΔH_f^0 UO_2F_2 from [2] and the other data from [3]), a $\Delta H_{850\,K}^0$ value of 19.8 kJ was calculated for the first reaction. From the measured reaction enthalpy of the second reaction and the formation enthalpies of the compounds taking part in the reaction, the formation enthalpy of UO_2F at 1000 K was found to be — 1290 kJ/mol, with an estimated standard deviation of $\pm$5 kJ/mol.

When the formation enthalpies of uranium oxides and uranium oxyfluorides are plotted against the number of anions in these compounds, a linear dependence is found, into which the determined formation enthalpy of UO_2F fits well (Fig. 4). From this diagram the standard formation enthalpy of UO_2F was determined. Further thermodynamic data on UO_2F are compiled in Table 1. The standard entropy of UO_2F was calculated according to the additive system for the calculation of the entropy of inorganic compounds in the solid state [4]. A linear curve was also found for the dependence of the entropy on the number of anions for the following compounds: UO_2, UO_2F and UO_2F_2. The entropy value of UO_2F at 1000 K, derived from this relation, allows calculation of free formation enthalpy of the UO_2F at 1000 K.
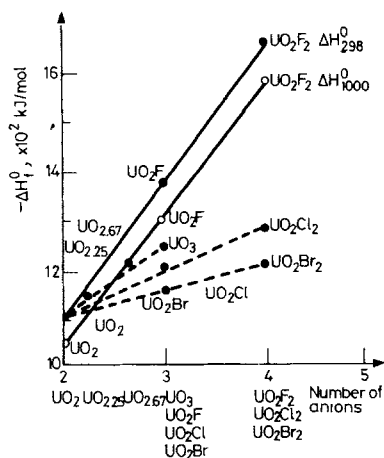
Fig. 4 Dependence of ΔH_f^0 for oxides and oxyhalogenides of uranium on number of anions per uranium atom

Table 1 Thermodynamic data of UO_2F

ΔH_f^0, kJ mol^{-1} 298 K	ΔH_f^0, kJ mol^{-1} 1000 K	ΔG_f^0, kJ mol^{-1} 298 K	ΔG_f^0, kJ mol^{-1} 1000 K	S^0, J mol^{-1} K^{-1} 298 K	S^0, J mol^{-1} K^{-1} 1000 K
− 1351	− 1290	− 1278	− 1056	111.4	226.1

References

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Zusammenfassung — Die Reaktionsenthalpie der Reduktion des UO_2F_2 mit Wasserstoff wurde mittels quantitativer DTA bei linearer Aufheizung und bei isothermen Bedingungen gemessen und die thermodynamischen Daten des UO_2F bestimmt, das als stabiles Zwischenprodukt bei der Reduktion des UO_2F_2 zum UO_2 entsteht. Die Vorteile der isothermen DTA würden auch bei der Reduktion des U_3O_8 zum UO_2 demonstriert.

Резюме — Энтальпия реакции восстановления UO_2F_2 водородом была определена, исходя из количественных ДТА измерений при линейной скорости нагрева в изотермических условиях. Представлены термодинамические данные для UO_2F, образующегося в качестве стабильного промежуточного продукта в реакции восстановления UO_2F_2 до UO_2. Показаны преимущества изотермического метода ДТА в реакции восстановления U_3O_8 до UO_2.