*Thermochimica Acta,* 118 (1987) 107–110
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# CHEMICAL STABILITY OF ARSENATES OF URANIUM WITH A VALENCY LOWER THAN SIX, WITH EMPHASIS ON URANIUM(V) ARSENIC OXIDE $UAsO_5$

H. BARTEN *

*Netherlands Energy Research Foundation ECN, Petten (The Netherlands)*

(Received 29 January 1987)

## ABSTRACT

Three new U–As–O compounds, $UAsO_5$ and probably $U_3As_2O_{12}$ and $U_3As_4O_{18}$, have been prepared by selected syntheses. The thermochemistry of $UAsO_5$ was studied in more detail. As a result, its high temperature thermodynamic data can be calculated.

## INTRODUCTION

In the course of a study on uranyl phosphates various compounds have been met in which the uranium has a valency lower than six [1]. The compounds $UP_2O_7$, $U_2O_3P_2O_7$, $(UO)_2P_2O_7$ and $U_3O_5P_2O_7$ are formed when oxygen is evolved as a result of thermal decomposition. In contrast to this behaviour, the uranyl arsenates [2,3] evolve arsenic oxide vapour at elevated temperatures to form either uranyl arsenates, containing less $As_2O_5$, or $U_3O_8$. No reduced uranium arsenates have been found in which uranium has a lower valency than six under the experimental conditions.

Nevertheless, it can be expected that these kinds of arsenate, comparable with the phosphates, exist. This paper gives results of selected experiments which were performed to prepare arsenates containing uranium with lower valencies. The thermochemistry of one of the compounds met, $UAsO_5$, is studied in more detail.

## RESULTS AND DISCUSSION OF THE SYNTHESES

To prepare uranium arsenates with lower uranium valencies, mixtures of $UO_2$, $U_3O_8$, $As_2O_5$ and/or $As_2O_3$ were heated in evacuated silica ampoules

---

* Present address: KEMA Laboratories, Arnhem, The Netherlands.

0040-6031/87/$03.50

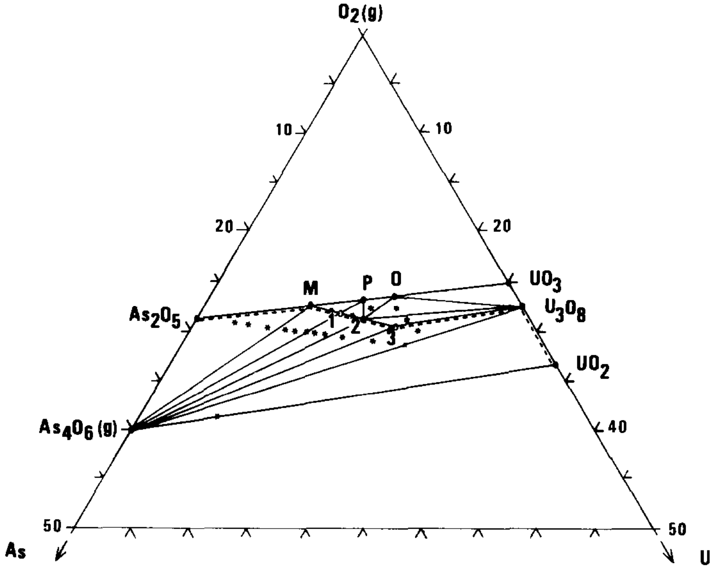

Fig. 1. Composition diagram indicating initial compositions (*) and the proposed new compounds (O, see text).

at 873 K for 48 h. To exclude water and gaseous oxygen the powders were kept in an argon-filled drybox. X-ray diffraction patterns of the samples were recorded (Nonius-Guinier camera, Cu $K_\alpha$ radiation) and compared with each other and relevant known patterns.

The results of the preparations are depicted in Fig. 1. The initial compositions (marked *) consist of mixtures of the compounds indicated along the axis of the distorted arsenic–uranium–oxides diagram. In this respect, it must be noted that in this diagram the oxygen pressure is not defined.

One of the observed products is $As_2O_3$, which is shown on the diagram as $As_4O_6(g)$ because it is in its gaseous state at 873 K. From the X-ray diagrams, three new compounds (marked O in Fig. 1) have been found, probably having the composition $U_3As_2O_{12}$, $UAsO_5$ and $U_3As_4O_{18}$ respectively. It is remarkable that tetravalent uranium arsenates have not been found although an extended series of tetravalent uranium phosphates is known. Instead, the compositions of $UO_2$ and $As_2O_5$ give $As_2O_3$ and mixtures of compounds along the indicated broken line in Fig. 1.

Of the three new compounds the first and third compounds have not been investigated. The formation of the second compound, the green-coloured $UAsO_5$, has been confirmed after more detailed study.

Initially it was formed from mixtures of $UO_2$ and $As_2O_5$ according to the reaction

$$2UO_2(s) + 1\tfrac{1}{2}As_2O_5(s) \rightleftarrows 2UAsO_5(s) + \tfrac{1}{4}As_4O_6(g) \qquad (1)$$

Further evidence for its formation comes from the fact that this compound is also formed, free of $As_2O_3$, from a mixture of $UO_2$ and the meta arsenate $UO_2(AsO_3)_2$ in the molar ratio of 1 : 1 under the cited conditions. The formation reaction in this case is

$$UO_2(s) + UO_2(AsO_3)_2(s) \rightleftarrows 2UAsO_5(s) \quad (2)$$

In this way, well-crystallized $As_2O_3$-free samples have been obtained. These samples appeared suitable for an X-ray diffraction study, which is described elsewhere [4] and for determinations of thermodynamic quantities. These results are reported below.

## THERMOCHEMISTRY OF $UAsO_5$

As determined previously for the uranyl arsenates [5], Cordfunke et al. [6] determined the enthalpy of formation of $UAsO_5$ by using solution calorimetry, and the high temperature enthalpy increment function by using drop calorimetry. They found

$$\Delta H_f^\circ(UAsO_5, c, 298.15\ K) = -1678.6 \pm 2.7\ kJ\ mol^{-1}$$

and the parameters of the enthalpy increment function

$$H^\circ(T) - H^\circ(298.15\ K) = AT + BT^2 + CT^{-1} + D$$

TABLE 1

Thermodynamic functions of solid $UAsO_5$

| $T$ (K) | $C_p^\circ(T)$ (J $K^{-1}$ $mol^{-1}$) | $S^\circ(T)$ (J $K^{-1}$ $mol^{-1}$) | −GEF [a] (J $K^{-1}$ $mol^{-1}$) | $H^\circ(T)-H^\circ(298\ K)$ (kJ $mol^{-1}$) | $\Delta H_f^\circ(T)$ (kJ $mol^{-1}$) | $\Delta G_f^\circ(T)$ (kJ $mol^{-1}$) | log $K_p^\circ$ |
|---|---|---|---|---|---|---|---|
| 298.15 | 138.00 | 136.40 | 136.40 | 0.00 | −1678.60 | −1540.82 | 269.94 |
| 300 | 138.27 | 137.25 | 136.38 | 0.26 | −1678.54 | −1539.97 | 268.13 |
| 400 | 149.82 | 178.72 | 141.97 | 14.70 | −1675.07 | −1494.28 | 195.13 |
| 500 | 158.61 | 213.12 | 152.86 | 30.13 | −1671.08 | −1449.53 | 151.43 |
| 600 | 166.33 | 242.73 | 165.43 | 46.38 | −1666.72 | −1405.63 | 122.37 |
| 700 | 173.53 | 268.92 | 178.38 | 63.38 | −1662.06 | −1362.48 | 101.67 |
| 800 | 180.46 | 292.55 | 191.20 | 81.08 | −1657.20 | −1320.01 | 86.19 |
| 876 | 185.62 | 309.15 | 200.71 | 94.99 | −1653.41 | −1288.15 | 76.81 |
| 876 | 185.62 | 309.15 | 200.71 | 94.99 | −1661.16 | −1288.15 | 76.81 |
| 900 | 187.23 | 314.19 | 203.67 | 99.47 | −1660.28 | −1277.94 | 74.17 |
| 942 | 190.04 | 322.80 | 208.80 | 107.39 | −1658.72 | −1260.14 | 69.87 |
| 942 | 190.04 | 322.80 | 208.80 | 107.39 | −1661.51 | −1260.14 | 69.87 |
| 1000 | 193.90 | 334.27 | 215.75 | 118.52 | −1658.96 | −1235.50 | 64.35 |

[a] The −GEF denotes $-[G^\circ(T) - H^\circ(298.15\ K)]/T$, which equals $S^\circ - [H^\circ(T) - H^\circ(298.15\ K)]/T$.

where $A = 130.701$, $B = 32.129 \times 10^{-3}$ and $C = 10.542 \times 10^{-5}$; thus, $D = -45360.4$ J K$^{-1}$ mol$^{-1}$.

The standard entropy of $UAsO_5$ is not known; low temperature enthalpy measurements have not been carried out. Furthermore, its value cannot be derived, in a way similar to that for the uranyl arsenates [7], as no vapour pressure measurements are available. Thus, the entropy value is estimated. To do this, use is made of the derived entropy values of the related phosphates [8] and arsenates [7]. For the estimation, the assumption is made that the entropy differences between $(UO_2)_2(X_2O_7)$ and $UXO_5$ are equal for X = P or As. Thus, we find

$$S^\circ(UAsO_5, s, 298.15 \text{ K}) = 136.4 \pm 6.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

As a result, high temperature molar thermodynamic data of $UAsO_5$ can be calculated. Table 1 gives these data at several temperatures.

## REFERENCES

1 H. Barten and E.H.P. Cordfunke, Thermochim. Acta, 40 (1980) 357.
2 H. Barten and E.H.P. Cordfunke, Thermochim. Acta, 40 (1980) 367.
3 H. Barten and E.H.P. Cordfunke, Thermochim. Acta, 90 (1985) 177.
4 H. Barten, J. Appl. Crystallogr., 19 (1986) 486.
5 E.H.P. Cordfunke, W. Ouweltjes and H. Barten, J. Chem. Thermodyn., 14 (1982) 883.
6 E.H.P. Cordfunke et al., Private communication.
7 H. Barten, Thermochim. Acta, in press.
8 H. Barten, Thermochim. Acta, in press.