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# THE FORMATION AND STABILITY OF HYDRATED AND ANHYDROUS URANYL ARSENATES

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## ABSTRACT

Three hydrated uranyl arsenates, $(UO_2)_3(AsO_4)_2 \cdot 11\ H_2O$, $UO_2HAsO_4 \cdot 4\ H_2O$, and $UO_2(H_2AsO_4)_2 \cdot 1\ H_2O$, have been prepared. The dehydration of these compounds has been studied by thermal analysis. Three crystalline anhydrous uranyl arsenates, $(UO_2)_3(AsO_4)_2$, $(UO_2)_2As_2O_7$ and $UO_2(AsO_3)_2$, have been found. These show melting phenomena and lose arsenic oxide vapour at high temperatures to result, finally, in $U_3O_8$ at 1500°C in air. The anhydrous compounds have been prepared under isothermal conditions and the strongest X-ray reflections are given. A tentative phase diagram in the composition range $UO_3$ to $As_2O_5$ has been constructed.

## INTRODUCTION

Phosphates and arsenates generally have similar chemical properties. Having recently studied the uranyl phosphates [1], we were interested in comparing them with the uranyl arsenates. So far, very little information is available about the latter compounds.

Three uranyl arsenate hydrates are known: $(UO_2)_3(AsO_4)_2 \cdot 10\text{—}12\ H_2O$, which is the mineral troegerit, $UO_2HAsO_4 \cdot 4\ H_2O$ or "hydrogen spinit" and $UO_2(H_2AsO_4)_2 \cdot 3\ H_2O$. The dehydration properties of the second compound have been studied previously by Weiss et al. [2] and Weigel et al. [3].

To the present, $(UO_2)_2As_2O_7$ is the only anhydrous uranyl arsenate which has been reported. Puller [4] prepared the compound by heating $UO_2NH_4AsO_4 \cdot x\ H_2O$. The formation of the pyroarsenate was later confirmed by Yoshida [5] and by Korenev et al. [6].

This paper presents the results of a systematic investigation of the formation and thermal stability of compounds in the system $UO_3\text{—}As_2O_5$, including its hydrates. The results have been obtained by both differential thermal analysis (DTA) and thermogravimetric analysis (TGA), by high-temperature X-ray diffraction and by isothermal experiments. The chemical properties of the uranyl phosphates and arsenates are compared.

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## EXPERIMENTAL

### *Samples*

$(UO_2)_3(AsO_4)_2 \cdot 11\ H_2O$ was prepared by adding a solution of $UO_2(NO_3)_2$ in an excess of 5% to a solution of $H_3AsO_4$. The very insoluble, pale yellow precipitate was repeatedly washed with large volumes of water and filtered. In contact with water, the compound has an X-ray pattern which differs from that of the undecahydrate. There is probably a uranyl arsenate with a higher water content.

$UO_2HAsO_4 \cdot 4\ H_2O$ was made by the method described by Weiss et al. [2]. $UO_2(NO_3)_2 \cdot 6\ H_2O$ was used as the uranium source instead of $UO_2(C_2H_3O_2)_2$.

Attempts to prepare the arsenic compound analogous to $UO_2(H_2PO_4)_2 \cdot 3\ H_2O$ [1,7,8] were unsuccessful, although Werther [9] reported its preparation in 1848. Instead, we were able to prepare a monohydrate, not previously described, by adding 1 mole of amorphous $UO_3$ (from $UO_4 \cdot 2\ H_2O$ at 400°C in air for 90 min) to a solution of 7.5 mole $H_3AsO_4$ in 30 moles of water. The slurry was heated at 80°C for 20 h and then the amount of water that had evaporated was added. The precipitate was recovered after a period of 24 h at ambient temperature with the help of a glass filter (filter paper was attacked by the solution). The washing procedure could not be carried out thoroughly because the compound easily dissolves in water or water—acetone mixtures. It is hygroscopic at ambient temperature (±60% relative humidity). Under these circumstances we expected the trihydrate to be formed, but instead the monohydrate dissolved. Furthermore, only the monohydrate was present in the slurry under the preparation conditions described. These findings deny the existence of the trihydrate.

The anhydrous uranyl arsenates were prepared by dehydration of the hydrates by heating in oxygen.

The $As_2O_5$ was made from $As_2O_5 \cdot \frac{5}{3}\ H_2O$ after a heat treatment at 600°C in a stream of dry oxygen. The $As_2O_3$ content was $0.34 \pm 0.01$ wt.% (as determined iodometrically). The anhydrous compounds were stored and handled in an argon-filled dry box.

### *Chemical analysis*

The analytical procedure was essentially the same as described for the uranyl phosphates [1]. Arsenic could be determined in the same way as phosphorus, namely by acid—base titration. The results are shown in Table 1.

### *Physical measurements*

The thermal stability of the samples was studied in dry nitrogen, air, and oxygen up to 1500°C. The Netzsch, STA-429, equipment was used under conditions identical to those described previously [1].

A Nonius—Guinier III camera (Cu $K_\alpha$-radiation, $\lambda = 1.5418$ Å) was used to study phase changes and decompositions of the compounds up to 1000°C.

TABLE 1

Chemical analysis of the uranyl arsenates

| Sample | Uranium (wt. %) | | Arsenic (wt. %) | | Water (wt. %) | |
|---|---|---|---|---|---|---|
| | Found | Calcd. | Found | Calcd. | Found | Calcd. |
| $(UO_2)_3(AsO_4)_2 \cdot 11\ H_2O$ | 55.42 ± 0.09 | 55.52 | 11.81 ± 0.06 | 11.65 | 15.31 ± 0.08 | 15.41 |
| $UO_2HAsO_4 \cdot 4\ H_2O$ | 49.20 ± 0.10 | 49.38 | 15.44 ± 0.04 | 15.54 | 16.81 ± 0.09 | 16.82 |
| $UO_2(H_2AsO_4)_2 \cdot 1.2\ H_2O$ * | 40.58 ± 0.13 | 41.50 | 26.55 ± 0.03 | 26.13 | 10.09 ± 0.05 | 10.05 |

* Contains some extra water which is easily driven off at 50°C.

### *Static experiments*

In addition, samples of various compositions were isothermally heated in air for 15 h and identified by X-ray diffraction (Guinier—de Wolff camera). To prevent hydration during the exposure, the samples were wrapped in polythene foil (0.05 mm).

The new compounds found by TGA were prepared under isothermal conditions in order to characterise them.

The melting phenomena in the system $UO_3$—$As_2O_5$ were also studied by means of static experiments. After short heating periods (1—10 min), the samples were visually inspected. The weight change gave information about the degree of decomposition. The melting temperatures were also studied with a Leitz type 1750 hot-stage microscope. The atmosphere was dried oxygen.

## RESULTS AND DISCUSSION

### *Hydrates*

#### *Thermal analysis*

Since no oxygen is evolved during the dehydration, the thermal effects observed are due to dehydration only.

As can be seen from Fig. 1, the decomposition of $(UO_2)_3(AsO_4)_2 \cdot 11\ H_2O$ leads via the hexa-, tetra-, and mono-hydrates to the anhydrous compound. The last step leading to the anhydrous compound is in the same temperature range (<180—350°C) as the phosphate.

The decomposition of $UO_2 \cdot HAsO_4 \cdot 4\ H_2O$ via its monohydrate [2,3] and $UO_2HAsO_4$ [3] has been reported before. Our results agree with these findings and, in addition, reveal that the dehydration to $(UO_2)_2As_2O_7$ takes place at 260—350°C. This temperature range is considerably lower than that of the corresponding phosphate (440—600°C).

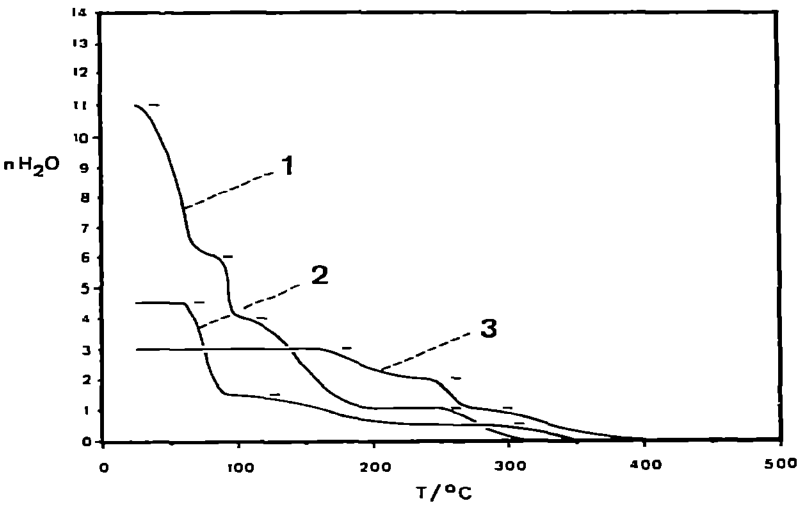

Fig. 1. Dehydration of uranyl arsenate hydrates. 1, $(UO_2)_3(AsO_4)_2 \cdot 11\ H_2O$ or $3\ UO_3 \cdot As_2O_5 \cdot 11\ H_2O$; 2, $UO_2HAsO_4 \cdot 4\ H_2O$ or $UO_3 \cdot 0.5\ As_2O_5 \cdot 4.5\ H_2O$; 3, $UO_2(H_2AsO_4)_2 \cdot 1\ H_2O$ or $UO_3 \cdot As_2O_5 \cdot 3\ H_2O$.

It has been concluded before [10,11] that during the thermal decomposition of $UO_2HPO_4 \cdot 4\ H_2O$, competition occurs between the dehydration via an ortho- and a pyro-compound, as shown by the reaction

$$2\ UO_2HPO_4 \rightleftharpoons (UO_2)_2P_2O_7 \cdot H_2O$$

proposed by Schaekers [10]. The corresponding arsenate, however, does not show this phenomenon.

From the thermogram of $UO_2(H_2AsO_4)_2 \cdot 1\ H_2O$ (Fig. 1), a decomposition via $UO_2(H_2AsO_4)_2$ and $UO_2H_2As_2O_7$ to $UO_2(AsO_3)_2$ has been found. The presence of $UO_2(H_2PO_4)_2$ has not been observed in the phosphate system. Previously, Kamo and Ohashi [8] proved that $UO_2(H_2PO_4)_2 \cdot 1\ H_2O$ directly forms pyrophosphate groups on heating.

Dehydration to $UO_2(AsO_3)_2$ is completed at 400°C. Because $UO_2(PO_3)_2$ is formed at 600°C, it can be concluded that polymerisation to the metaarsenate is more easily accomplished than polymerisation to the metaphosphate.

### *Static experiments*

With the exception of $UO_2(H_2AsO_4)_2$ and $UO_2H_2As_2O_7$, all the compounds mentioned above were prepared in crystalline form. The strongest X-ray reflections are given in Table 2.

The hygroscopic $(UO_2)_3(AsO_4)_2$ probably forms a hemihydrate when it is exposed to humid air for a short time. This has been observed before with the phosphate [1].

Only the tetrahydrates of $UO_2HAsO_4$ and $UO_2HPO_4$ (already known from the literature [2,12]), and the monohydrates of $UO_2(H_2AsO_4)_2$ and $UO_2(H_2PO_4)_2$ have similar X-ray patterns. This indicates that these compounds are isostructural.

TABLE 2

**Strongest interplanar spacings of uranyl arsenates**

**The *d* values are uncorrected and the intensities are visually estimated.**

| Compound | *d* (Å) | | | | | 100 $I/I_{max}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $(UO_2)_3(AsO_4)_2$ (Aq) | 3.46 | 4.20 | 4.73 | 6.48 | 13.0 | 100 | 80 | 80 | 80 | 60 |
| $(UO_2)_3(AsO_4)_2 \cdot$ 11 $H_2O$ | 3.52 | 11.6 | 5.77 | 3.57 | 4.63 | 100 | 80 | 80 | 70 | 50 |
| $(UO_2)_3(AsO_4)_2 \cdot$ 6 $H_2O$ | 3.50 | 3.07 | 3.59 | 5.80 | 5.95 | 100 | 70 | 70 | 50 | 40 |
| $(UO_2)_3(AsO_4)_2 \cdot$ 4 $H_2O$ | 3.58 | 3.07 | 5.80 | 5.95 | 5.40 | 100 | 70 | 30 | 30 | 30 |
| $(UO_2)_3(AsO_4)_2 \cdot$ 1 $H_2O$ * | 4.90 | 3.55 | 3.05 | 3.37 | 2.90 | 100 | 100 | 60 | 30 | 30 |
| $(UO_2)_3(AsO_4)_2 \cdot$ ~0.5 $H_2O$ | 3.58 | 2.80 | 4.90 | 7.50 | 5.00 | 100 | 80 | 80 | 60 | 40 |
| $\beta$-$(UO_2)_3(AsO_4)_2$ | 4.95 | 3.55 | 7.20 | 2.81 | 3.61 | 100 | 90 | 90 | 70 | 50 |
| $\alpha$-$(UO_2)_3(AsO_4)_2$ | 4.85 | 7.05 | 5.60 | 4.27 | 2.85 | 100 | 90 | 90 | 80 | 60 |
| $UO_2HAsO_4 \cdot$ 1 $H_2O$ | 5.82 | 10.2 | 4.40 | 2.62 | 3.05 | 100 | 60 | 60 | 50 | 40 |
| $UO_2HAsO_4$ * | 5.75 | 1.965 | 6.70 | 3.55 | 3.60 | 100 | 30 | 30 | 10 | 5 |
| $(UO_2)_2As_2O_7$ | 3.47 | 6.40 | 8.60 | 5.90 | 3.60 | 100 | 90 | 60 | 50 | 30 |
| $UO_2(H_2AsO_4)_2 \cdot$ 1 $H_2O$ | 4.48 | 6.35 | 3.35 | 4.35 | 2.85 | 100 | 90 | 80 | 60 | 60 |
| $\beta$-$UO_2(AsO_3)_2$ | 4.08 | 4.13 | 3.17 | 7.00 | 3.66 | 100 | 100 | 50 | 30 | 30 |
| $\alpha$-$UO_2(AsO_3)_2$ | 3.58 | 4.43 | 4.07 | 4.23 | 3.03 | 100 | 100 | 95 | 85 | 60 |

* Poorly crystalline sample.

## *Anhydrous compounds*

### *Thermal analysis*

The results of TGA in air are shown in Fig. 2. For comparison, the observed changes of mass are expressed as the percentage by which they exceed $U_3O_8$, which is the final product of the three uranyl arsenates when heated to 1500°C in air. Large decomposition ranges are found, which implies that the reaction steps are not fully separated. Nevertheless, it seems that at least the presently known uranyl arsenates were found. In nitrogen, the decompositions occur at lower temperatures, whereas $UO_2$ was obtained at 1500°C.

### *Static experiments*

*$(UO_2)_3(AsO_4)_2$*. Anhydrous $(UO_2)_3(AsO_4)_2$ can be prepared from the hydrate by heating it to 500°C in a stream of dry oxygen. Characteristic X-ray data of this $\beta$-phase are given in Table 2.

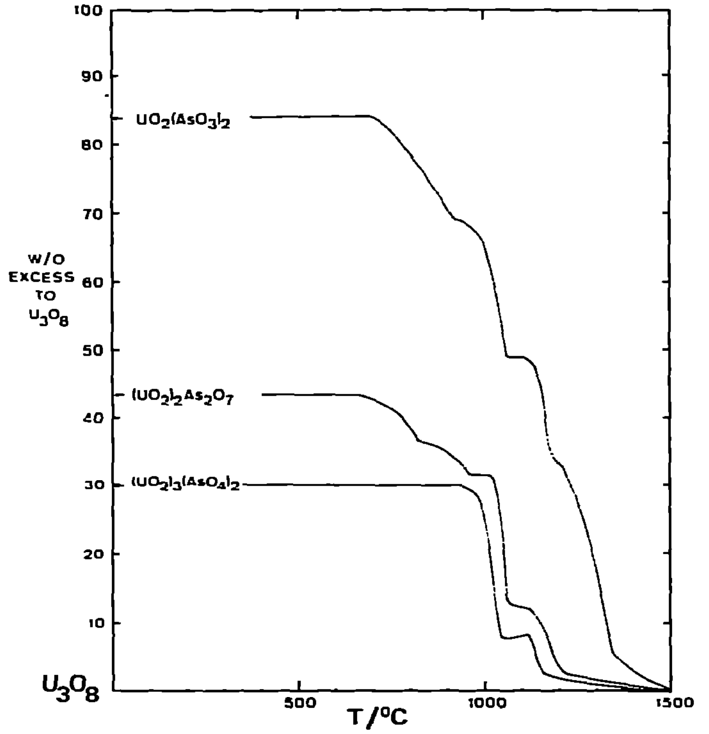

Fig. 2. Thermogravimetric analyses of uranyl arsenates in air (2.5°C $\text{min}^{-1}$). Changes of mass are referred to $U_3O_8$.

On the HTX-exposure, it is shown that a slow transition to $\alpha$-$(UO_2)_3(AsO_4)_2$ occurs at 750°C (Table 2). This phase can be obtained at ambient temperature by heating a sample at 850°C in oxygen and subsequently cooling. Only the diagram of $U_3O_8$ is visible beyond 880°C. The results are summarized in the phase diagram (Fig. 3).

*$(UO_2)_2As_2O_7$.* Crystalline anhydrous $(UO_2)_2As_2O_7$ has been prepared by heating $UO_2HAsO_4 \cdot 4\ H_2O$ at 550°C for two days in a stream of dry oxygen. $(UO_2)_2As_2O_7$ is very hygroscopic and forms orthoarsenate hydrates on exposure to humid air, although at first an unknown X-ray pattern was observed (a pyroarsenate hydrate?).

A crystalline sample of $(UO_2)_2As_2O_7$ could be brought from the dry box into the high-temperature X-ray camera, whilst the sample holder plus sample were protected from moisture with polythene foil (0.05 mm). It is seen on the exposure that $(UO_2)_2As_2O_7$ decomposes into $\alpha$-$(UO_2)_3(AsO_4)_2$ at 745°C. From 870°C, gradually more $U_3O_8$ is present, and above 940°C only $U_3O_8$ is found. This is in accordance with the findings obtained by TGA (Fig. 2). In nitrogen, increasingly crystalline $UO_2$ is observed at these temperatures.

Earlier publications report that $(UO_2)_2As_2O_7$ was formed from $UO_2NH_4AsO_4 \cdot x\ H_2O$ at temperatures ranging from 620 to 680°C [5] and above 590°C [6]. These temperatures are somewhat higher than the ones we

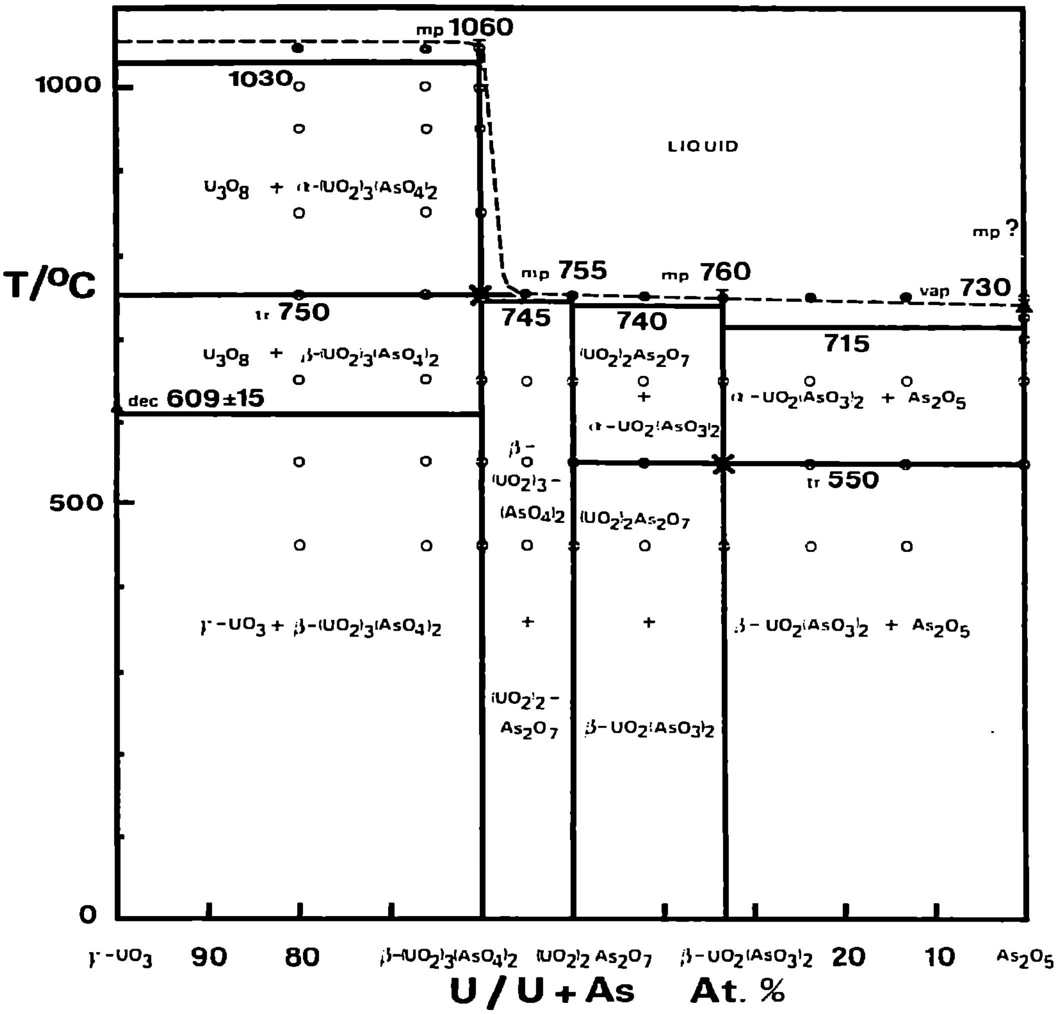

Fig. 3. Tentative subliquidus part of the phase diagram $UO_2$—$As_2O_5$ at 0.21 atm oxygen pressure. * = Phase transitions; — — — = maximum accessible temperatures under present conditions; ○ = isothermal heating; ● = quickly decomposing samples. The accuracy of the temperatures shown is about 30°C.

found for the formation of $(UO_2)_2As_2O_7$ from $UO_2HAsO_4 \cdot 4\ H_2O$ (namely <260—350°C). The decomposition temperature that we found for $(UO_2)_2As_2O_7$ is distinctly lower than the temperature of 900°C reported previously [6]. It must be concluded that these investigators did not study $(UO_2)_2As_2O_7$ but $(UO_2)_3(AsO_4)_2$, because the latter is stable up to that temperature. Arsenic oxide is probably lost during the heating process.

*$UO_2(AsO_3)_2$*. Isothermal heating of $UO_2(H_2AsO_4)_2 \cdot 1\ H_2O$ at 525°C in oxygen leads to the formation of crystalline $\beta$-$UO_2(AsO_3)_2$ (Table 2). This compound is hygroscopic.

HTX-exposures show a phase transition to $\alpha$-$UO_2(AsO_3)_2$ at 670°C (Table 2). The transition is slow and irreversible (the $\alpha$-phase can be prepared isothermally at 550°C!). At 760°C, the pattern changes into that of $\alpha$-$(UO_2)_3(AsO_4)_2$. From 880 to 925°C, the pattern of an unknown compound is present, together with an increasing amount of $U_3O_8$. Above 925°C only $U_3O_8$ is found.

By thermal analysis, it is found that $UO_2(AsO_3)_2$ decomposes in air at 680°C. The results from the HTX-experiments confirm the previously suggested decomposition path via the pyro- and ortho-arsenate to $U_3O_8$. A separate TGA run in hydrogen indicates the direct decomposition of $UO_2(AsO_3)_2$ into $UO_2$ above 420°C.

*Reductions.* Reductions of the solid arsenates have not been observed prior to the loss of arsenic oxide and melting. This contrasts with the findings for the uranyl phosphates [1,9,10,13,14].

*Melting phenomena.* It was difficult to study melting phenomena in this system because the compounds lose considerable amounts of arsenic oxide at the temperatures of interest. We were unable to use DTA because the evolution of arsenic oxide also causes enthalpy changes of the same order. By isothermal heating, the partial melting of the samples can be recognized in hot samples because the colour of the melt differs from that of the yellow compounds. It is pale yellow near $As_2O_5$ and orange at $(UO_2)_2As_2O_7$ to black near $U_3O_8$. The results are shown in Fig. 3. Only the initial melting can be seen with the hot-stage microscope. The observed temperatures agree within 30°C with the values shown. From the HTX-exposures, 755°C is found to be the melting point for $(UO_2)_2As_2O_7$.

*$As_2O_5$ and $UO_3$.* It has been reported that $As_2O_5$ decomposes prior to melting [15,16]. The qualification "at red heat" is used as a temperature indication in the old literature. From our isothermal heatings, it can be concluded that solid $As_2O_5$ evaporates quickly at temperatures higher than 730°C.

The temperature at which $\gamma$-$UO_3$ decomposes into $U_3O_8$ in air has been calculated from ref. 17. In Fig. 2, the transition to $\beta$-$U_3O_8$ and the further loss of oxygen at elevated temperatures have been neglected.

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