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COMPARISON OF THE THERMOCHEMISTRY OF URANYL/URANIUM PHOSPHATES AND ARSENATES

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ABSTRACT

Recently-derived high-temperature thermochemical data of uranyl/uranium phosphates and arsenates are used to discuss phase relations. Their interstabilities are shown in diagrams as function of the pressures of oxygen and of phosphorus oxide or arsenic oxide, $P_4O_{10}(g)$ or $As_4O_{10}(g)$, respectively. The stabilities of the two systems are compared.

INTRODUCTION

In previous papers [1–3] thermodynamic parameters were obtained to calculate the high-temperature thermochemistry of uranyl/uranium phosphates and arsenates.

The aim of this paper is to use those data to compare the stabilities of these compounds using stability diagrams. The diagrams will be expressed in terms of the pressures of oxygen and of phosphorus oxide or arsenic oxide, $P_4O_{10}(g)$ or $As_4O_{10}(g)$, respectively.

RESULTS AND DISCUSSION

An overview of the applied thermodynamic data is given in Table 1. This table also shows the data of $As_4O_{10}(g)$, which were obtained as a result of the study of the vapour pressure of As_2O_5 [4].

Uranyl phosphates

Figures 1 and 2 depict the stability diagrams of the uranyl/uranium phosphates as functions of log p_{O_2} and log $p_{P_4O_{10}}$, at 900 and 1100 K.

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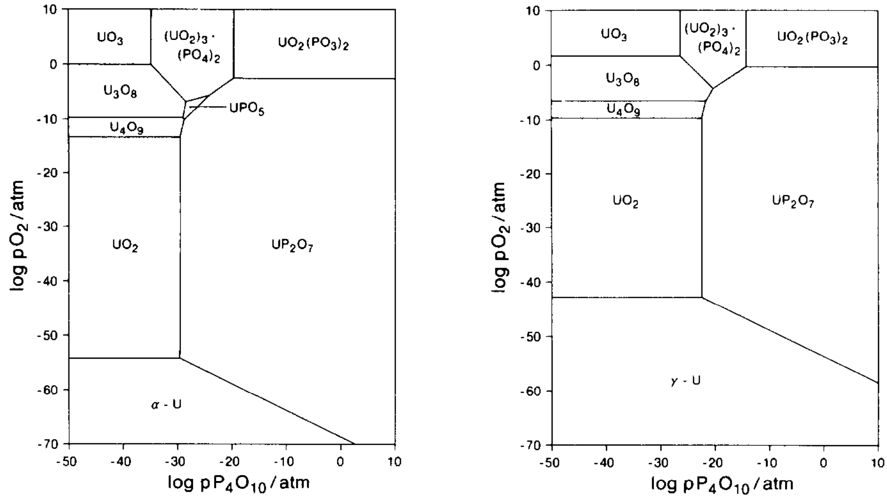
TABLE 1

Thermodynamic data of U–P–O and U–As–O compounds

Compound	$H_f^\ominus$ (298 K) (kJ mol^{-1})	$S^\ominus$ (298 K) (J K^{-1} mol^{-1})	$C_p(T) = a + bT + cT^{-2} + dT^{-3} + eT^2$ (J K^{-1} mol^{-1})				Temperature (K)	Reference
			a	b (10^{-3} T^{-1})	c (10^5 T^2)	d and/or e		
$(UO_2)_3(PO_4)_2$	−5491.3	405.8	326.375	196.438	−40.840	–	298– 771	1
$(UO_2)_2P_2O_7$	−4232.6	284.0	250.669	154.299	−34.003	–	298– 883	1
$UO_2(PO_3)_2$	−2973.0	195.6	184.304	121.287	−38.540	–	298– 900	1
UPO_5	−2064.3	135.2	110.427	85.228	−10.379	–	298– 726	1
UP_2O_7	−2852.0	197.1	198.531	60.724	−29.011	–	298– 882	1
$(UO_2)_3(AsO_4)_2$	−4710.1	366.6	331.151	211.360	−26.818	–	298– 867	2
$(UO_2)_2As_2O_7$	−3446.7	286.5	307.412	105.818	−58.513	–	398– 868	2
$UO_2(AsO_3)_2$	−2177.3	211.3	208.461	88.910	−30.346	–	298– 781	2
$UAsO_5$	−1678.6	136.4	130.701	64.258	−10.542	–	298– 800	3
$As_4O_{10}(g)$	−1565.0	456.9	344.33	−20.37	−257.56	$+45.158 \times 10^8\ T^{-3}$ $+11.91 \times 10^{-6}\ T^2$	298–1000	4



Figs. 1 and 2. Calculated stability diagrams of uranyl/uranium phosphates at 900 (left) and 1100 K.

It is noticed that no $(UO_2)_2P_2O_7$ is indicated in either figure. This indicates a metastable state for this compound. Furthermore the tendency is demonstrated in these figures for UPO_5 to become relatively less stable at increasing temperatures.

Additional calculations have been performed to find out the effects on these findings of uncertainties in the thermodynamic data, however, the above findings do not change even in the case of relative high uncertainties in the entropy values seen in some cases. A main conclusion must be that $(UO_2)_2P_2O_7$ is metastable.

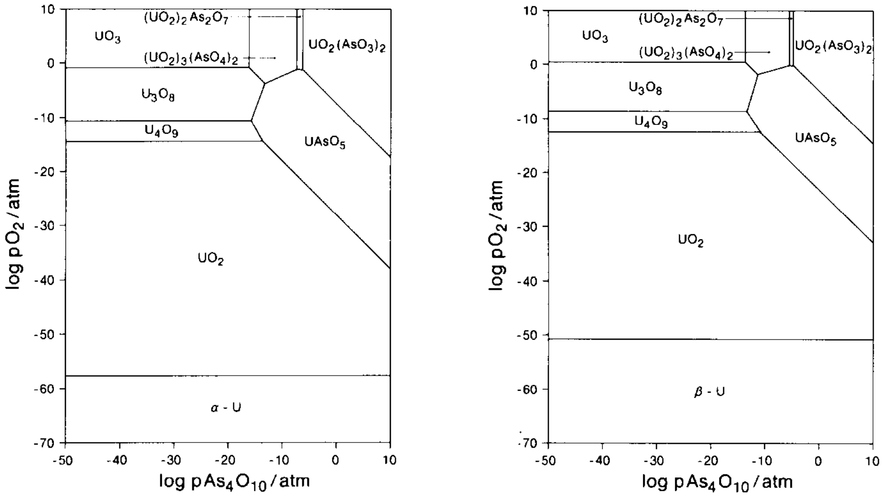
Uranyl arsenates

Similarly, the stabilities of the uranyl/uranium arsenates have been compared using calculated phase diagrams, as functions of log p_{O_2} and log $p_{As_4O_{10}}$. In this way, Figs. 3 and 4 have been constructed, giving the stability ranges at 850 and 950 K.

The diagrams indicate that the three uranyl arsenates are stable, whereas $UAsO_5$ is present at lower oxygen pressures. This appears to be the general picture at other temperatures. Notable differences between the arsenate and phosphate systems are the stable state of the pyroarsenate and the absence of tetravalent uranium arsenates, both in contrast to the phosphates.

Extension of the diagrams

The above diagrams do not depict all known uranium phosphates and arsenates. It would be of interest to extend the studies to the thermochem-



Figs. 3 and 4. Calculated stability diagrams of uranyl/uranium arsenates at 850 (left) and 950 K.

istry of the missing compounds, in order to complete the description of the thermochemistry of both systems.

To be of use for possible future studies, it was decided to indicate these compounds (assumed stable) in two additional diagrams. The relevant phosphates and arsenates are given in Table 2.

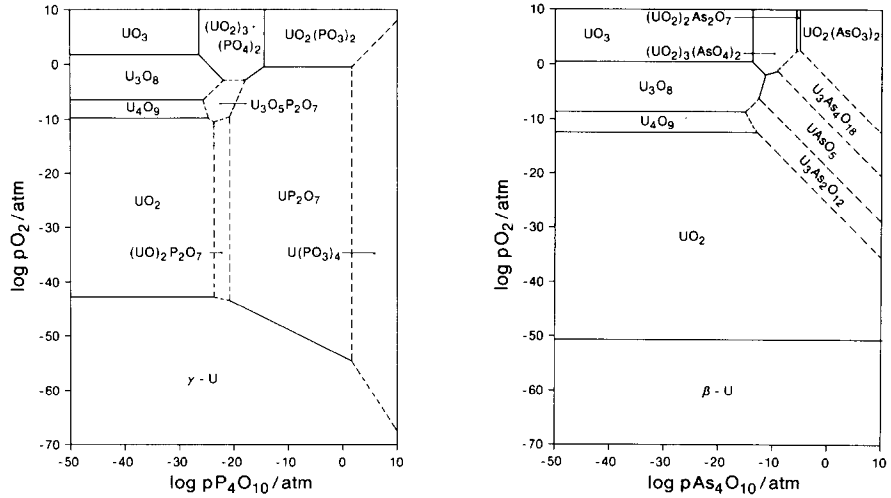
Of these compounds, three phosphates and two arsenates were not taken into account in the previous calculations of the stability diagrams; neither thermodynamic data nor useful estimation parameters were available to obtain thermodynamic data of any quality.

The existence of the compounds is a qualitative datum which may be used to insert these compounds into the diagrams. If possible metastable conditions are neglected, their places in the stability diagrams can be indicated on the basis of their composition and considerations of their decomposition. It

TABLE 2

Tabulation of the uranium phosphates and arsenates containing uranium with a valency lower than six. The reported compounds $(UO)_3(PO_4)_2$ and $U_3(PO_4)_4$ [6] have not been included as these has been rejected later [7,8]

Phosphates	Arsenates [3]
$U_3O_5P_2O_7$ ($U_3P_2O_{12}$)	$U_3As_2O_{12}$ (possibly)
unknown	$U_3As_4O_{18}$ (possibly)
UPO_5 [6] ($= \frac{1}{2}U_2O_3P_2O_7$)	$UAsO_5$
$U(PO_3)_4$ [6]	not observed
UP_2O_7	not observed
$(UO)_2P_2O_7$ [6]	not observed



Figs. 5 and 6. Extended stability diagrams of uranyl/uranium phosphates (left) and arsenates. Compounds of assumed stabilities have been projected (broken lines) onto earlier diagrams.

is stressed that the actual proportion of the indicated area has to be found from additional thermochemical studies. The results of these considerations are projected onto earlier diagrams to give the hypothetical stability diagrams, Figs. 5 and 6.

It is interesting to note in Fig. 5 that, even at oxygen pressures sufficient for the uranyl metaphosphate, the tetravalent metaphosphate is more stable, when more phosphorus oxide is absorbed at high P_4O_{10} pressures. This conclusion agrees with the observations of Baskin [5], who prepared $U(PO_3)_4$ by solid-state reactions in air, regardless of the initial oxidation state of the uranium oxide, and an excess of $P_2O_5(s)$. This phenomenon may be of importance if uranyl phosphates are prepared by a solid-state reaction, in which one of the components is $P_2O_5(s)$. Since local reduction may occur, and generally the reoxidation kinetics are poor, then the product may contain an amount of uranium with a valency lower than six. Figure 5 also shows the path of thermal decomposition under inert conditions of $U(PO_3)_4$ via UP_2O_7 into $(UO)_2P_2O_7$ and eventually into UO_2 [5–7].

The uranyl/uranium arsenate system is extended by only two compounds for which no further experimental data are available. Nevertheless, it is clearly demonstrated that this system does not contain the same series of tetravalent uranium compounds as met in the phosphate system.

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