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THERMOCHEMICAL PROPERTIES OF URANYL ARSENATES. I. ARSENIC OXIDE DISSOCIATION PRESSURES

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ABSTRACT

A transportation method has been used to measure the arsenic oxide pressure of uranyl arsenates at various oxygen pressures. It is concluded that at 1 atm oxygen the vaporization reactions lead, stepwise, from meta, pyro, and orthoarsenate to U_3O_8, whilst gaseous As_4O_{10} is evolved. The free energy functions of the evaporation reactions have been calculated from the pressure functions.

INTRODUCTION

A study of the chemistry of uranyl arsenates [1] has revealed three anhydrous compounds: $(UO_2)_3(AsO_4)_2$, $(UO_2)_2As_2O_7$ and $UO_2(AsO_3)_2$. Their stabilities have been studied by thermal analysis and static experiments. In addition, the enthalpies of solution of these compounds have been measured, from which the standard enthalpies of formation have been derived [2].

In order to describe the high-temperature stability of the uranyl arsenates, we have measured the vapour pressure of As_4O_{10}(g) in equilibrium with the solid arsenates using a transportation method. This method has been used recently to study the vapour pressure of As_2O_5(s) [3]. The present paper gives the results of similar measurements on the uranyl arsenates.

EXPERIMENTAL

Materials

The crystalline anhydrous uranyl arsenates have been made by dehydration of the hydrates; the preparation and analytical details have been published elsewhere [1]. The crystallinity after the drying procedure has been

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investigated by X-ray diffraction. During the exposures (Guinier-De Wolff camera, Cu K_α radiation, $\lambda = 1.5418$ Å), polythene foil (0.05 mm) was used to protect the very hygroscopic samples from moisture. The patterns were compared with the diagrams of the uranyl arsenates [1] and uranium oxides. The U^{6+} and U^{4+} content of the initial materials has been determined [4], and that of some samples during the course of the measurements.

Measurements and analytical procedure

The transportation apparatus and experimental conditions were described before [3]. Because of the relatively low pressures met, it was necessary to use large volumes of transport gas (usually about 20 l) and to determine the arsenic more sensitively by atomic absorption. The accuracy of the results depends on the amount of arsenic collected, and varied from 1 to 5% relatively. In some samples with a high arsenic content, the As^{3+} fraction was determined iodometrically.

RESULTS AND DISCUSSION

Uranyl ortho-arsenate

The evolution of arsenic oxide vapour causes a change in composition of the solid phase. This change does not, however, result in arsenic oxide pressures which deviate from the initial pressures. After the vapour pressure measurements a mixture of ortho-arsenate and U_3O_8 is found on the X-ray diagrams in agreement with our previous results [1]. The arsenic oxide pressures appear to depend on the oxygen pressures, as is shown in Fig. 1. From the pressures given in Table 1, the parameters A and B of the function

$$\log(p\mathrm{As_4O}_x/\mathrm{atm}\ ^*) = A/T + B$$

(x being an average, not yet specified value) have been calculated using least squares. The results are also given in Table 1.

It can be expected, based on our previous work on the vapour pressure of $As_2O_5(s)$ [3], that the vaporization occurs via the reaction

$$\mathrm{(UO_2)_3(AsO_4)_2} \rightleftarrows \mathrm{U_3O_8(s)} + \tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{As_4O_{10}(g)} \qquad (1)$$

However, since reactions in the gas phase

$$\mathrm{As_4O_{10}(g)} \rightleftarrows \mathrm{As_4O_{(10-y)}(g)} + \tfrac{1}{2}y\ \mathrm{O_2(g)} \qquad (2)$$

(in which y = integers 1 to 4) also take place, the general vaporization reaction

$$\mathrm{(UO_2)_3(AsO_4)_2(s)} \rightleftarrows \mathrm{U_3O_8(s)} + \frac{1+\frac{1}{2}y}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{As_4O_{(10-y)}(g)} \qquad (3)$$

must be considered.

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* Throughout this paper, 1 atm = 101.325 kPa, $R = 8.3143$ J K^{-1} mol^{-1}.

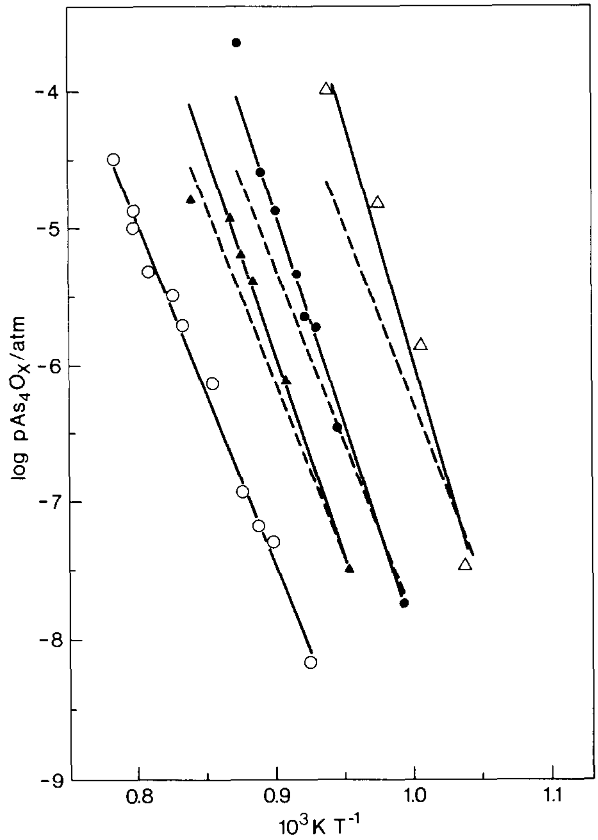

Fig. 1. The vapour pressure of $(UO_2)_3(AsO_4)_2$ at various oxygen pressures: (○) 1, (▲) 4.32×10^{-2}, (●) 7.8×10^{-3}, and (△) 1.9×10^{-4} atm. The experimental (———) and calculated (- - - - -) functions are shown for comparison.

It can be seen from this reaction that the arsenic oxide-to-oxygen pressure dependency will give information on the value of y, since

$$\log K_p = \frac{1+\frac{1}{2}y}{2}\log p\, O_2(g) + \tfrac{1}{2}\log pAs_4O_{(10-y)}(g)$$

has a constant value at constant temperature.

To discuss the results of the experiments, log pO_2 is plotted against log $pAs_4O_{(10-y)}$ in Fig. 2 at 1100 K. It is shown that the slope tends to -1 at higher oxygen pressures. At 1 atm oxygen, the value of the tangent, T, is between -1.05 and -1.00.

The conclusion is that the vaporization reaction at 1 atm oxygen can be presented by reaction (1) and, consequently, as in the case of solid As_2O_5 [3], gaseous As_4O_{10} molecules evaporate from the surface of the solid.

The free energy function of reaction (1) can now be calculated via the relation

$$\Delta G_r^0(T) = -RT \ln K_p$$

TABLE 1

Uranyl arsenates: individual arsenic oxide pressures as measured at the temperatures and oxygen pressures stated. The *A* and *B* values are the parameters of the pressure function given in the text

Exp. No.	T (K)	$p\mathrm{As}_4\mathrm{O}_x$ (atm)
$(UO_2)_3(AsO_4)_2$		
1.00 atm oxygen		
212	1273.0	3.180×10^{-5}
211	1252.1	1.316×10^{-5}
214	1252.7	9.844×10^{-6}
209	1235.1	4.809×10^{-6}
206	1209.0	3.225×10^{-6}
120	1199.3	1.980×10^{-6}
187	1169.1	7.320×10^{-7}
202	1141.1	1.174×10^{-7}
205	1125.6	6.787×10^{-8}
201	1111.9	5.146×10^{-8}
204	1080.7	6.779×10^{-9}
$A=-25040\pm800$, $B=15.12\pm0.68$		
4.32×10^{-2} atm oxygen		
112	1190.4	1.595×10^{-5}
113	1151.2	1.179×10^{-5}
190	1139.9	6.321×10^{-6}
111	1130.2	4.039×10^{-6}
114	1102.7	7.661×10^{-7}
191	1047.5	3.264×10^{-8}
$A=-29810\pm420$, $B=20.96\pm0.38$		
7.80×10^{-3} atm oxygen		
117	1143.7	2.221×10^{-4}
115	1121.7	2.535×10^{-5}
193	1107.9	1.304×10^{-5}
116	1091.1	4.533×10^{-6}
198	1084.4	2.298×10^{-6}
118	1075.3	1.905×10^{-6}
196	1057.6	3.413×10^{-7}
194	1005.9	1.868×10^{-8}
$A=-31170\pm1200$, $B=23.2\pm1.2$		
1.90×10^{-4} atm oxygen		
250 [a]	1065.3	1.030×10^{-4}
249	1025.7	1.498×10^{-5}
248	994.0	1.102×10^{-6}
251	963.3	3.450×10^{-8}
$A=-34900\pm3900$, $B=29.0\pm3.9$		

TABLE 1 (continued)

Exp. No.	T (K)	$p\mathrm{As_4O}_x$ (atm)
$(UO_2)_2As_2O_7$		
1.00 atm oxygen		
88	1026.7	2.913×10^{-4}
89	989.1	6.895×10^{-5}
274	986.9	5.343×10^{-5}
254	983.1	4.504×10^{-5}
86	978.3	3.678×10^{-5}
87	996.5	2.976×10^{-5}
272	965.6	1.257×10^{-5}
253	951.7	3.725×10^{-6}
242	899.8	1.408×10^{-7}
$A=-24500\pm1800$, $B=20.4\pm1.9$		
5.08×10^{-1} atm oxygen		
278	985.3	1.118×10^{-4}
277	964.1	2.464×10^{-5}
276	929.7	4.745×10^{-6}
241	901.8	3.896×10^{-7}
$A=-25200\pm2000$, $B=21.6\pm2.1$		
2.14×10^{-1} atm oxygen		
279	968.0	8.343×10^{-5}
281	936.7	9.647×10^{-6}
240	899.8	1.878×10^{-6}
$A=-20800\pm3100$, $B=17.4\pm3.3$		
4.32×10^{-2} atm oxygen		
283 [a]	968.6	1.866×10^{-4}
225	936.2	3.541×10^{-5}
224	896.6	9.791×10^{-6}
239	887.5	4.557×10^{-7}
227	843.7	7.581×10^{-7}
282	800.7	1.408×10^{-7}
$A=-13480\pm650$, $B=9.94\pm0.74$		
$UO_2(AsO_3)_2$		
1.00 atm oxygen		
71	985.3	7.060×10^{-5}
76	970.2	4.011×10^{-5}
130	971.6	4.051×10^{-5}
75	969.9	3.494×10^{-5}
146	960.9	2.703×10^{-5}
129	954.5	1.985×10^{-5}
74	939.4	1.047×10^{-5}
73	907.9	2.772×10^{-6}
131	892.0	9.867×10^{-7}
$A=-17020\pm350$, $B=13.13\pm0.37$		

TABLE 1 (continued)

Exp. No.	T (K)	$p\mathrm{As_4O}_x$ (atm)
4.32×10^{-2} atm oxygen		
143	976.8	2.146×10^{-4}
125	951.2	9.767×10^{-5}
126	905.2	1.099×10^{-5}
127	880.5	4.894×10^{-6}
142	870.4	2.238×10^{-6}
136	847.7	8.343×10^{-7}
$A=-15690\pm480$, $B=12.43\pm0.53$		
7.80×10^{-3} atm oxygen		
121	952.8	5.688×10^{-4}
81	925.9	1.143×10^{-4}
122	903.7	6.297×10^{-5}
123	871.0	8.905×10^{-6}
124	846.9	5.616×10^{-6}
132	830.2	1.420×10^{-6}
$A=-15900\pm1000$, $B=13.3\pm1.3$		

[a] These two experiments have not been used for the calculations of A and B.

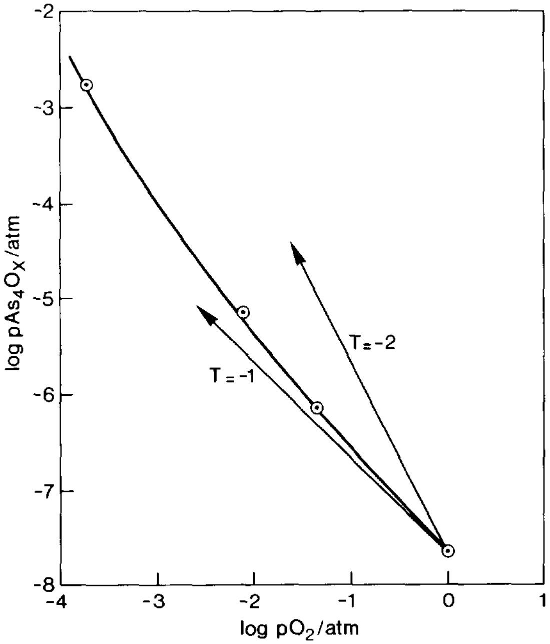

Fig. 2. The relation between the log pO_2 and $p\mathrm{As_4O}_x$ at 1100 K, as calculated with the use of the parameters of Table 1. The tangents, $T=-1$ and -2, are also shown.

to give

$$\Delta G_1^0/\text{kJ mol}^{-1} = (239.7 \pm 7.7) - (144.7 \pm 6.5) \times 10^{-3}T(963\text{–}1273 \text{ K})$$

It should be noted that the stoichiometry of U_3O_8 is influenced by the oxygen pressure at elevated temperatures. However, deviations can be neglected at 1 atm oxygen and the temperatures given [5].

The present results at 1 atm oxygen have been used to calculate the As_4O_{10} pressures at the oxygen pressures at which the other measurements have been carried out. The results have been given in Fig. 1 as the dashed lines. It appears that the difference between the measured and calculated pressures increases at lower oxygen pressures, in agreement with the preceding discussion and as demonstrated in Fig. 2.

By analogy to As_2O_5 [3] the arsenic oxide condensate also contains As_2O_3. The As^{3+} content of the condensate varies from 77 to 96% at 1 to 1.9×10^{-4} atm oxygen in the transportation gas, respectively. We have the impression that the composition of the condensate depends on the duration of the experiment. These kinetic aspects do not interfere at 1 atm oxygen, as has been shown previously for As_2O_5.

Uranyl pyro-arsenate

The results of the vapour pressure measurements have been given in Table 1, and are depicted in Fig. 3. The pressures appear to depend on the oxygen pressure. X-ray diagrams indicate that after the measurements at 1 atm oxygen the solid consists of a mixture of the pyro- and the ortho-arsenate. This is in agreement with the results from previous work [1].

The evaporation reaction at 1 atm oxygen may thus be assumed to be

$$3(UO_2)_2As_2O_7(s) \rightleftarrows 2(UO_2)_3(AsO_4)_2(s) + \tfrac{1}{2}As_4O_{10}(g) \qquad (4)$$

However, from additional thermogravimetric analyses at various oxygen pressures (Fig. 4) it appears that in nitrogen the pyro-arsenate decomposes directly into U_3O_8, probably according to the reaction

$$3(UO_2)_2As_2O_7(s) \rightleftarrows 2U_3O_8(s) + O_2(g) + 1\tfrac{1}{2}As_4O_{10}(g) \qquad (5)$$

In air or 1 atm oxygen, the ortho-arsenate is formed in accordance with reaction (4). Apparently, both reactions (4) and (5) must be considered to interpret the vapour pressure measurements.

The free energy functions of both reactions (4) and (5) can be calculated using present results to give

$$\Delta G_4^0/\text{kJ mol}^{-1} = (234.5 \pm 17.2) - (195.34 \pm 18.2) \times 10^{-3}T(900\text{–}1027 \text{ K})$$

and (at $pO_2 = 1$ atm)

$$\Delta G_5^0/\text{kJ mol}^{-1} = (713.9 \pm 32.6) - (484.7 \pm 31.2) \times 10^{-3}T(963\text{–}1027 \text{ K})$$

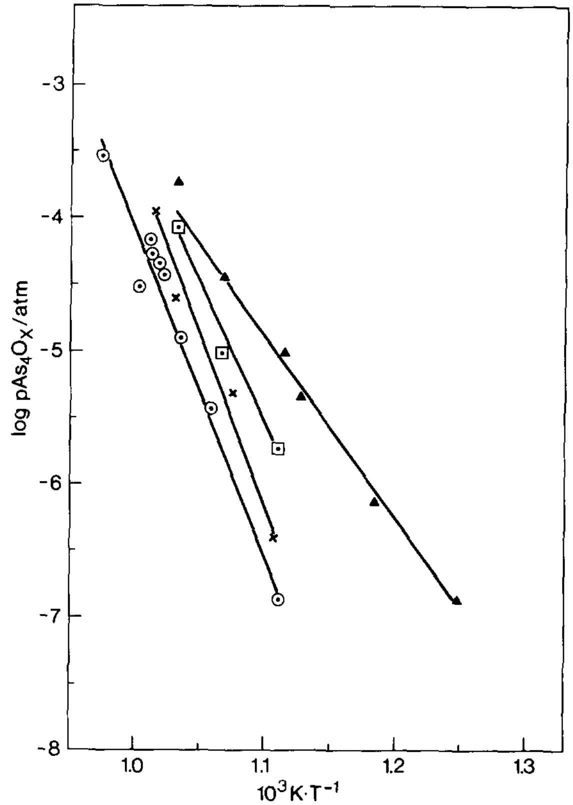

Fig. 3. The vapour pressure of $(UO_2)_2As_2O_7$ at various oxygen pressures. Symbols have the same legends as Fig. 1, (×) 5.08×10^{-1}, (□) 2.14×10^{-1} atm oxygen.

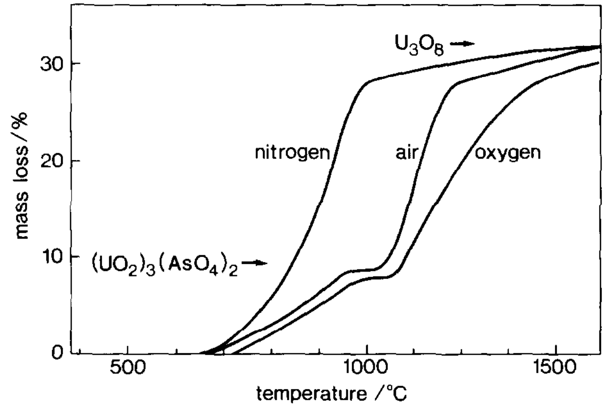

Fig. 4. Thermogravimetric analysis (Netzsch, STA-429) of uranyl pyroarsenate under various atmospheres. The expected mass losses to $(UO_2)_3(AsO_4)_2$ and to U_3O_8 are indicated.

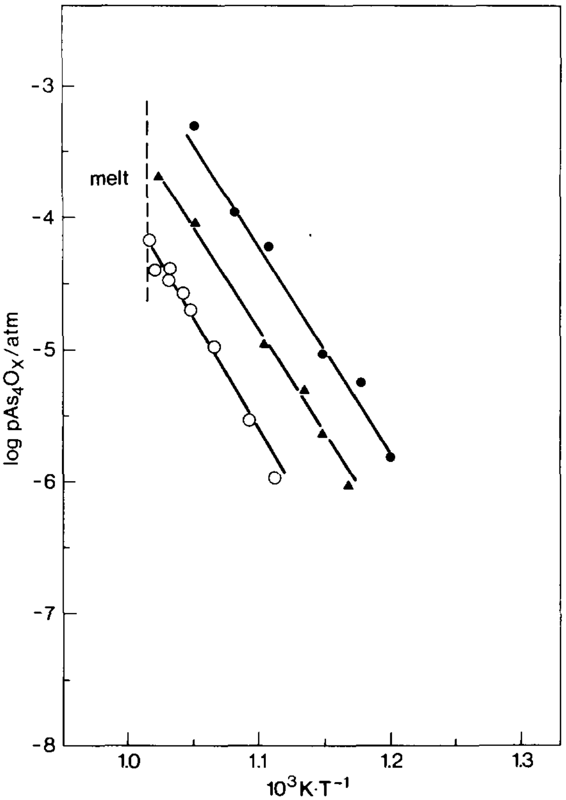

Fig. 5. The vapour pressure of $UO_2(AsO_3)_2$ at various oxygen pressures. The melting temperature of the compound is 988 K. Symbols have the same legends as Fig. 1.

From these relations it follows that (at $pO_2 = 1$ atm) reaction (5) is (up to 1650 K) metastable with respect to reaction (4). Below about 10^{-6} atm oxygen the pyro-arsenate decomposes directly into U_3O_8 (reaction 5). This conclusion is in agreement with the results of the thermogravimetric analyses.

Uranyl meta-arsenate

From X-ray diffraction it is found that this compound decomposes into $(UO_2)_2As_2O_7$, in accordance with previous results [1]. The vapour pressures measured are given in Table 1 and are shown in Fig. 5. An oxygen dependency is found which tends to decrease at higher oxygen pressures.

If it is accepted that the pressure function at 1 atm oxygen is valid for the reaction

$$2UO_2(AsO_3)_2(s) \rightleftarrows (UO_2)_2As_2O_7(s) + \tfrac{1}{2}As_4O_{10}(g) \qquad (6)$$

then, using the parameters of Table 1, the free energy function of this reaction can be described by

$$\Delta G_6^0/\text{kJ mol}^{-1} = (162.92 \pm 3.35) - (125.68 \pm 3.54) \times 10^{-3}T(892\text{–}985\ \text{K})$$

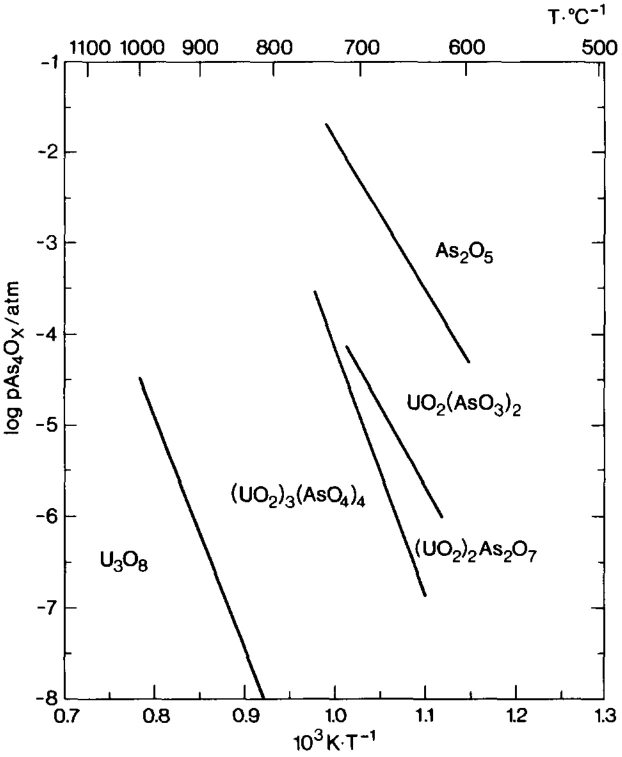

Fig. 6. The As_4O_{10} pressure of the uranyl arsenates and of As_2O_5 [3] as function of temperature at 1 atm oxygen. The regions of stability of these compounds have been indicated.

CONCLUSION

To overview the results, Fig. 6 is given in which the As_4O_{10} pressures of the uranyl arsenates and As_2O_5 [3] at 1 atm oxygen are given as a function of temperature. In this way the regions of stability are shown for the compounds considered. As will be discussed in further detail in part II of this communication, it appears that the meta-arsenate is slightly more stable than the pyro-arsenate.

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