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THE VAPOUR PRESSURE OF DI-ARSENIC PENTOXIDE (As_2O_5)

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ABSTRACT

The arsenic oxide pressure of As_2O_5 has been studied using mass spectrometry and a transportation method. Mass spectrometry revealed the presence of the species $As_4O_6^+$, $As_4O_7^+$, and $As_4O_8^+$ in the vapour. The existence of volatile species up to As_4O_{10}(g) as a result of the reaction

$$As_4O_{10}(g) \rightleftarrows As_4O_{(10-y)}(g) + 1/2yO_2(g)$$

has been assumed.

The oxygen pressure of this equilibrium builds up very slowly. The equilibrium pressure can be expressed by

$$\log(p_{O_2}/\text{atm})\ (880-952\text{ K}) = -(13940 \pm 930)/T + (14.53 \pm 1.01)$$

A stationary arsenic oxide pressure has been measured using the transportation method. Since the oxygen pressure in the transportation gas did not influence the arsenic oxide pressure, it is assumed that only the As_4O_{10}(g) pressure has been measured. The results can be expressed by the linear function

$$\log(p_{As_4O_{10}}/\text{atm})\ (865-1009\text{ K}) = -(15741 \pm 410)/T + (13.87 \pm 0.42).$$

INTRODUCTION

It is generally assumed that As_2O_5 evaporates according to

$$2\ As_2O_5(s) \rightleftarrows As_4O_6(g) + 2\ O_2(g) \tag{1}$$

Already Biltz [1] showed, in 1898, that the classical "furnace fumes", obtained from evaporation of As_2O_3, consisted of As_4O_6 molecules. In addition, it has been found that oxygen is evolved during evaporation of As_2O_5 [2]. Based on these facts, it has been concluded that reaction (1) takes place.

During our work on the high-temperature stability of the uranyl arsenates, it was evident that the evaporation of arsenic oxide from these compounds,

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and also from solid As_2O_5, is more complicated than previously assumed. This has also been shown in a recent mass spectrometric study [3] of the evaporation of As_2O_5, in which volatile species As_4O_6 up to As_4O_{10} have been found.

In connection with our work on the stability of the uranyl arsenates, this paper reports a study in which the vapour pressure of As_2O_5 above solid As_2O_5 has been measured using the transportation method.

EXPERIMENTAL

Sample characterization

The starting material was $As_2O_5 \cdot 5/3\ H_2O$ (Merck p.a. quality: 99 (mass)% purity; 0.05% As_2O_3; 0.01% total impurities) which was heated in a silica boat in air at 873 K, to prepare the anhydrous compound. Flame emission spectroscopy indicated no substantial increase of impurities after this treatment. The As_2O_3 content (0.3%) was determined iodometrically. The X-ray pattern, obtained with a Guinier-de Wolff II camera (Cu$K\alpha$ radiation, $\lambda = 1.5418$ Å), showed the presence of orthorhombic As_2O_5 only [4].

Mass spectroscopic measurements

Some preliminary mass spectroscopic experiments were carried out to obtain information on the gaseous species present. The mass spectrometer was an AEI type MS 902, ionisation energy 70 eV at 8 kV acceleration potential.

Vapour pressure measurements

The arsenic oxide pressures were measured using a transportation technique. Jellinek and Rosner [5] described this method in 1929, whereas Platteeuw [6] reported on the theoretical background and an improved experimental procedure in 1953. The principle is that the saturated vapour of the sample is condensed and determined after transportation with a carrier gas. A particular advantage of this method is the possibility of varying the partial oxygen pressure of the carrier gas. This enables us to study the equilibrium given in reaction (1).

The transportation apparatus consists of a reaction tube, sample holder, thermocouple pocket, and a condensor tube, all made of silica, and of the necessary external tubes. The temperature of the furnace is controlled to within 1 K by means of a Shinko type MIC-P proportional temperature controller. To extend the region of homogeneous temperature in the centre of the furnace, a cylindrical steel plate is fixed around the reaction tube.

The total amount of the dried carrier gas is measured by replacing water from a calibrated (water, 293 K) bottle. Corrections must be made for atmospheric pressure, over pressure in the system, the water vapour pressure, and the liberated "permanent" gas of the samples.

After reversion of the gas stream and cooling of the furnace, a chemical analysis of the condensate in the condensor tube is made. To do so, the condensed arsenic oxide was dissolved in 2–3 ml of a 1 M solution of sodium hydroxide (NaOH, Merck p.a.) and collected in 30 ml of water in polythene bottles. The arsenic trioxide was determined iodometrically (1% relative accuracy), and the arsenic pentoxide by means of ion chromatography (Dionex system 10, 5% relative accuracy). These methods were checked with As_2O_3 (NBS standard material) and As_2O_5 (Merck, p.a., 99.7% As_2O_5 by mass).

To study the experimental conditions, runs with different gas flows were carried out. Saturation of the carrier gas was found in the region from 20 to 60 ml min^{-1}. After a number of experiments the As_2O_5 surface tends to become vitreous, and then the "plateau curve" is shifted to somewhat lower gas velocities. The experiments were carried out with nitrogen gas, containing oxygen in the compositions 0.8 and 4% by volume, and with pure oxygen, in a temperature range varying from 865 to 1009 K. This range is limited by the detection limit of the analytical method used and the melting of As_2O_5, respectively.

The oxygen pressure * was measured with a static method, as previously used by Guérin and Boulitrop [2]. About 0.2–0.5 g of As_2O_5 were encapsulated in evacuated silica ampoules (volume about 4 cm^3). These were heated for 120 h in a furnace with a temperature control to within 1 K. The temperature was measured with a Pt/Pt–10%Rh thermocouple. After the heating period, the ampoules were quenched in iced-water. The ampoules were then opened in an evacuated compartment. Using helium as a carrier gas, the liberated gas is brought on molsieve 5A, which is kept at liquid nitrogen temperature. The collected gas was thermally desorbed and the oxygen was determined, using gas chromatography. The sensitivity of the apparatus was experimentally determined using standard mixtures and pure oxygen. The accuracy of the method is 5% relative. Some ampoules with As_2O_5 have been heated at 880 K for various periods of time to find the necessary equilibration time. The results are shown in Fig. 1. From this figure it is evident that the oxygen pressure is built up slowly and reaches the equilibrium pressure asymptotically. We decided to use 120 h heating time for the measurements.

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

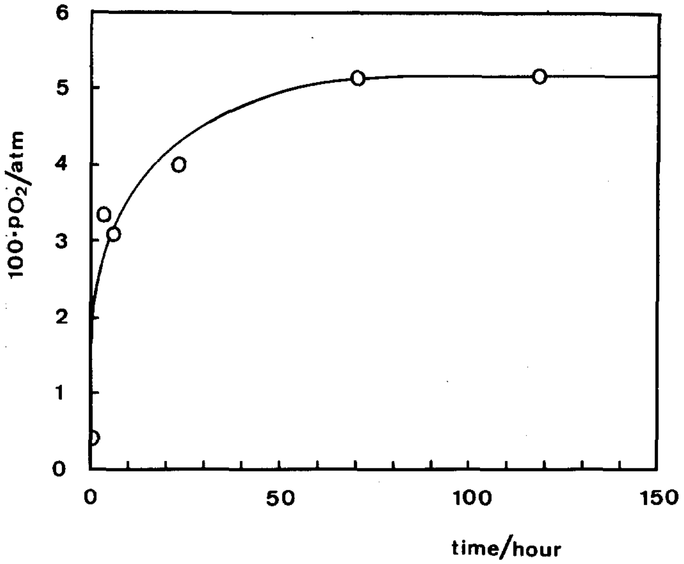

Fig. 1. The evolution of oxygen from As_2O_5 as a function of time at 880 K.

RESULTS

Arsenic oxide pressure

Preliminary mass spectrometric experiments carried out at 553 K revealed the species $As_4O_6^+$, $As_4O_7^+$, and $As_4O_8^+$ in the vapour, and we assume that the gaseous species up to As_4O_{10} can exist. This has been confirmed recently by Plies and Jansen [3]. An analogous series is known for the gaseous phosphorus oxides. We also observed high intensities of species which are probably fragments such as $As_3O_5^+$ and $As_3O_4^+$. X-ray analysis of the condensate in the condensor tube not only reveals As_2O_3, but higher oxides as well. Three distinct areas can be recognized in the condensor tube which appear to consist of As_2O_5, As_2O_4 *, and As_2O_3, respectively, at decreasing temperatures.

The results of the transportation experiments are listed in Table 1 and shown in Fig. 2. The pressures have been calculated from Table 1, taking As_4O_x as the gaseous species (x being an average value, not yet specified). From Fig. 2, it is clear that the pressures are independent of the oxygen pressures in the transportation gas.

A linear pressure function is calculated with least-squares to be

$$\log\left(p_{As_4O_x}/\text{atm}\right)\ [865-1009\ \text{K}] = -(15741 \pm 410)/T + (13.87 \pm 0.42)$$

This function is also plotted.

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* The X-ray pattern of this fraction does not agree with the known As_2O_4 [7]; its As_2O_3 content varies from 45 to 55 mass% (46.3% for As_2O_4 by formula).

TABLE 1

Numerical results of the transportation measurements [a]

Furnace temp. (K)	O_2-gas % by volume	Atm. pressure (mmHg)	Δ press. manometer (mmHg)	Volume bottle (10^{-6} m^3)	Water temp. (°C)	Lab. temp. (°C)	As_2O_5 (mg)	As_2O_3 (mg)	$p_{As_4O_x}$ in atm. (calculated)
956.0	4.0	758.70	8.13	2046.7	20.0	23.0	33.9	50.76	2.463×10^{-3}
946.9	4.0	748.45	8.06	2046.7	20.0	22.4	23.7	33.85	1.674×10^{-3}
911.1	4.0	758.99	7.75	2046.7	21.0	23.3	5.76	6.95	3.693×10^{-4}
865.5	4.0	749.34	7.99	2046.7	20.5	23.1	0.515	0.855	4.021×10^{-5}
917.5	0.8	764.39	8.03	2046.7	20.6	23.5	7.12	8.52	4.534×10^{-4}
947.9	0.8	775.81	7.97	2046.7	21.0	23.5	22.45	32.18	1.595×10^{-3}
915.9	4.0	762.65	6.73	2046.7	20.6	23.0	8.10	10.40	5.368×10^{-4}
914.5	100	757.77	7.36	2046.7	20.0	23.0	9.37	8.61	5.143×10^{-4}
912.5	0.8	736.06	7.17	2046.7	20.0	23.2	7.17	8.96	4.671×10^{-4}
896.5	4.0	759.89	7.43	2046.7	19.6	23.0	5.20	4.36	2.721×10^{-4}
881.9	100	776.89	7.27	2046.7	19.8	24.0	1.43	1.88	9.581×10^{-5}
930.7	100	752.05	7.27	2046.7	20.8	23.2	13.22	17.52	8.946×10^{-4}
974.5	100	751.11	6.96	1027.9	20.0	22.0	48.8	56.13	5.992×10^{-3}
1008.6	100	751.24	7.97	512.5	20.2	23.5	47.2	97.43	1.676×10^{-2}
1033.7 [b]	0.8	753.71	7.59	512.5	20.2	23.2	81.7	156.17	—

[a] The collected carrier gas has the mean temperature of the laboratory and the replaced water.

[b] The sample decomposed and melted.

TABLE 2

The oxygen pressures of As_2O_5 as a function of temperature. For comparison, the results of Guérin and Boulitrop [2] have been given

Temperature (K)	Oxygen pressure (atom)	Ref.
880.1	5.14×10^{-2}	this work
902.5	1.23×10^{-1}	this work
923.7	2.36×10^{-1}	this work
940.0	5.66×10^{-1}	this work
952.4	7.86×10^{-1}	this work
831	$7.5\ \times10^{-2}$	[2]
866	1.35×10^{-1}	[2]

Oxygen pressures

The results of the measurements of the equilibrium oxygen pressures are given in Table 2. From these values the pressure-to-temperature function has been calculated with least-squares to give

$$\log(p_{O_2}/\text{atm})\ [880-952\ \text{K}] = -(13940 \pm 930)/T + (14.53 \pm 1.01)$$

This function is shown in Fig. 3, together with our individual results, and, for comparison, with the data of Guérin and Boulitrop [2]. It is evident that

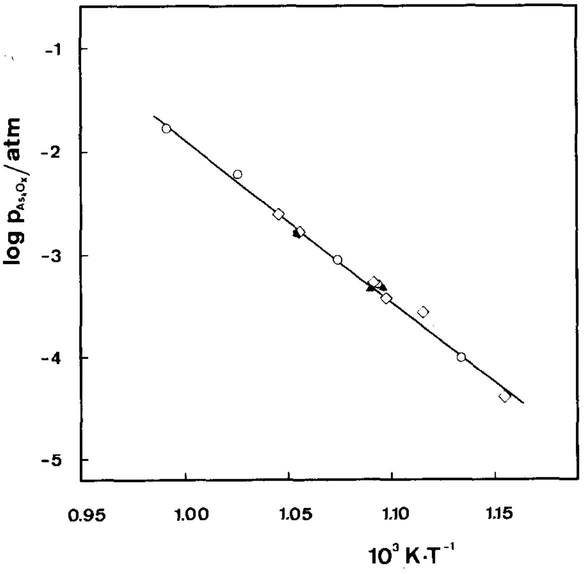

Fig. 2. The arsenic oxide pressure of As_2O_5 measured at various oxygen pressures. (▲) 0.8% O_2; (◇) 4.0% O_2; (○) 100% O_2.

the latter data do not agree with our observations. However, we are not able to recalculate these measurements, because the authors gave insufficient details of their experiments.

DISCUSSION

Apparently, the various results obtained for the vapour pressure measurements are in contradiction. If it is accepted that the species As_4O_6 up to As_4O_{10} exist [3], then a general reaction for their coexistence can be described by

$$2\ As_2O_5(s) \rightleftarrows As_4O_{(10-y)}(g) + y/2\ O_2(g) \qquad (2)$$

where y represents the integers 0 to 4. This implicates an oxygen dependency when y equals 1 to 4. The average value of y has been calculated from the composition of the condensate; the value 2.4 ± 0.3 is obtained.

However, the necessary oxygen dependency has not been observed during our transportation experiments, as is evident from the experiments shown in Fig. 2. From the oxygen pressure measurements we know that oxygen is

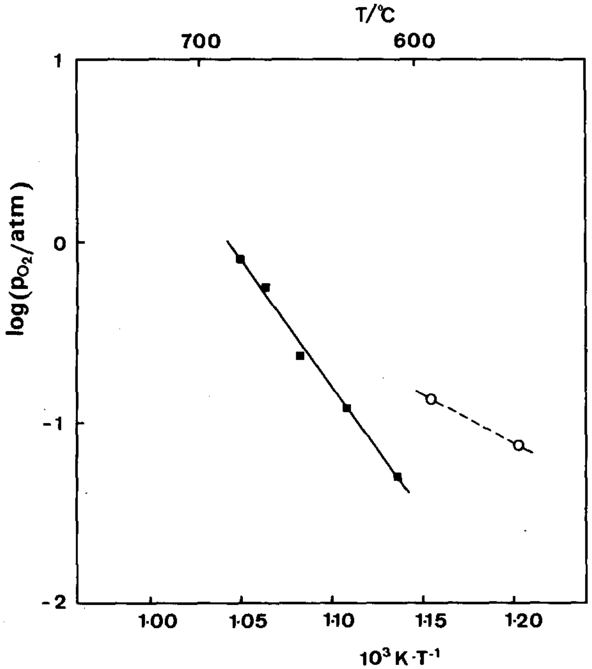

Fig. 3. The oxygen pressure of As_2O_5. (■) This work, (○) Guérin and Boulitrop [2].

evolved slowly. Obviously, the reactions in the gas phase like

$$As_4O_{(10-y)}(g) \rightleftarrows As_4O_{(9-y)}(g) + 1/2\ O_2(g) \tag{3}$$

are too slow to interfere with the evaporation from the $As_2O_5(s)$ surface. We must conclude, therefore, that the stationary arsenic oxide pressure measured is the equilibrium pressure of the non-dissociative evaporation

$$2\ As_2O_5(s) \rightleftarrows As_4O_{10}(g) \tag{4}$$

This means that the value for y in the $As_4O_{(10-y)}$ pressure function is 0, and that the O/As ratio in the oxide changes via reaction (3) during the transportation experiments.

From the vapour pressure equation obtained for $As_4O_{10}(g)$, the free energy change of the sublimation reaction (4) can be derived to be

$$\Delta G^0_{\text{subl}}(\text{kJ mol}^{-1}) = (301.4 \pm 7.8) - (265.5 \pm 8.0) \times 10^{-3} T_{(865-1009\ \text{K})}$$

Plies and Jansen [3] also found indications for gaseous species up to As_4O_{10}. From their measurements they derived for the enthalpy of formation of $As_4O_{10}(g)$, at 900 K, the value -1618.8 kJ mol^{-1}, and for the enthalpy of sublimation $+256.5 \pm 10.0$ kJ mol^{-1}. They then calculated the enthalpy of formation of $As_2O_5(s)$ at 298.15 K using a non-specified Cp-function, and obtained the value -1007.9 kJ mol^{-1}. This value does not agree at all with the value $\Delta H_f^0 = -918.4 \pm 4.2$ kJ mol^{-1} given by NBS [8]. When we combine the experimental data of Plies and Jansen, as given above, with our experimental values for the enthalpy increment of $As_2O_5(s)$ [9]

$$H_T - H_{298}(\text{J mol}^{-1}) = 138.307T + 24.086 \times 10^{-3}T^2 + 32.130 \times 10^5 T^{-1} - 54154$$

we obtain for the enthalpy of formation of $As_2O_5(s)$ the value -880.6 kJ mol^{-1}. This value is not only too positive compared with the NBS value, but also differs from that of Plies and Jansen mainly by an error in their calculations. Since the other values, derived by Plies and Jansen, also differ from ours, we doubt whether they have paid full attention to the consequences of the fragmentations, which disturb a proper calculation of the mutual stabilities. Besides the $As_3O_5^+$ and $As_3O_4^+$ ions, mentioned in the present paper, we recently found the fragments $As_4O_6^+$ up to $As_4O_9^+$, and metastable ions [10]. This will influence the quantitative interpretation of the mass spectrometric measurements considerably. Our conclusion is that further mass spectroscopic measurements are necessary.

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