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Note

ON THE HIGH TEMPERATURE STABILITY OF DIARSENIC TETROXIDE (As_2O_4)

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Preceding a mass-spectroscopic investigation of arsenic oxide vapours the thermal stability of diarsenic tetroxide (As_2O_4) was studied both by thermal analysis and static experiments.

EXPERIMENTAL

As_2O_4 was prepared according to the procedure described by Long and Sackman [1]. The heating period at 350 °C was shortened from 4 to 1.5 h.

The As^{3+} content was determined iodometrically to give $33.84 \pm 0.04\%$ (35.04% by formula weight). With the use of X-ray exposures some diarsenic pentoxide (As_2O_5) was found in addition to the As_2O_4 [2]. Thus, the sample was considered to be a mixture of 96.6% As_2O_4 and 3.4% As_2O_5.

The thermal analyses were carried out with a Netzsch type STA 429 equipment. The samples were heated in an oxygen or nitrogen (plus 100 ppm oxygen) atmosphere from ambient temperatures up to 700 °C. The heating rate was $2° \text{ min}^{-1}$.

The contents of water and oxygen were continuously measured in the effluent gas stream (Panametric hygrometer model 1000 and Teledyne analyser model 311, respectively).

RESULTS AND DISCUSSION

Thermal analysis

The thermogravimetric curve indicates that the As_2O_4 decomposes gradually after 440 °C (See Fig. 1). Finally, at 630 °C the weight loss is 56.4 or 55.8% in nitrogen or oxygen, respectively. The oxygen content of the outgas

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rises to 200 ppm during the decomposition. The water content remains at 7 ppm; this proves that the initial sample has been dried sufficiently. The decomposition temperatures have not been influenced by the atmospheres used. The rather insensitive differential thermal signal only shows thermal effects near the decomposition temperatures.

Static experiments

Some As_2O_4 was heated at 650 °C for 1 h to obtain information on the solid formed after the decomposition.

The X-ray diagram of the product agreed with that of As_2O_5 and trivalent arsenic was not found ($< 0.5\%$). Thus, it was concluded that the product formed was As_2O_5. As a result, corrections have been made for the As_2O_5 initially present to give 58.4 and 57.8% weight losses for nitrogen or oxygen atmospheres, respectively.

The As_2O_5 can be formed by several reactions, of which the incongruent evaporation may be proposed.

$$As_2O_4(s) \rightleftharpoons 0.25\ As_4O_6(g) + 0.5\ As_2O_5(s) \quad (1)$$

However, the weight loss is 46.26% for this reaction. Apparently, other evaporation reactions occur.

Since it is known that arsenic oxides higher than As_4O_6 exist in the gas phase [3,4], a reaction such as

$$1.5\ As_2O_4(s) \rightleftharpoons 0.5\ As_4O_7(g) + 0.5\ As_2O_5(s) \quad (2)$$

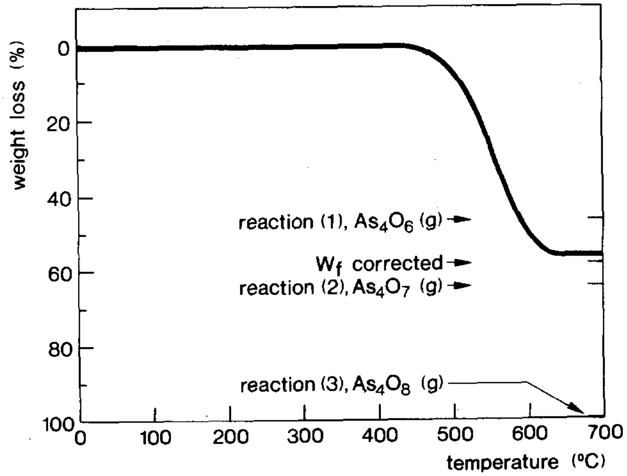

Fig. 1. Thermogravimetric analysis of As_2O_4 in oxygen or nitrogen (2° min^{-1}). W_f is the final weight loss after correction of the As_2O_5 present in the initial samples. Also, final weight losses calculated for the individual reactions in the text, are given.

may also occur. The calculated weight loss for this reaction is 64.17%. Also the congruent evaporation may occur

$$As_2O_4(s) \rightleftharpoons 0.5\ As_4O_8(g) \qquad (3)$$

This reaction fully evaporates the sample and can, therefore, only be of minor importance. It was therefore concluded that the As_2O_5 is formed via the simultaneous reactions (1) and (2), and possibly reaction (3). Reactions like

$$As_2O_4(s) \rightleftharpoons 0.5\ As_4O_6(g) + 0.5\ O_2(g) \qquad (4)$$

have quantitatively no significance, since only a small amount of oxygen is evolved.

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