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ATOMIC ENERGY

RESEARCH ESTABLISHMENT

PREPARATION OF ANHYDROUS TUNGSTEN HEXACHLORIDE

AN A. E. R. E. MEMORANDUM

by

C E.C. RICHARDS

M. L. SMITH

DEPARTMENT OF ATOMIC ENERGY,
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ABSTRACT

A method is described for preparing 500 gram batches of anhydrous tungsten hexachloride suitable as source material in ion arcs. The process involves the direct chlorination of tungsten freshly reduced from tungsten trioxide, and the collection of the product in such a way as to minimise hydrolysis by atmospheric water vapour. The material obtained by this process was 100% volatile in vacuo at 150°C.

A.E.R.E.
HARWELL.

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1. INTRODUCTION

In the course of the large electromagnetic separator programme it became necessary to prepare several kilograms of anhydrous tungsten hexachloride suitable for use as a source material for the ion arc. This material spoils extremely rapidly in air, therefore the whole process had to be carried out in a closed apparatus, and the product sublimed into a container from which it could easily be removed for transfer to airtight storage bottles.

Two methods are given in the literature for preparing anhydrous tungsten hexachloride. The first, using the reaction between tungsten trioxide and phosphorus pentachloride[1,2] involves the subsequent somewhat difficult separation of the phosphorus compounds from the tungsten hexachloride, and is unsuitable for large quantities. The second method is that of direct chlorination of tungsten[3,4] and this was the method used as a basis for the present work. Practical details have been worked out for the small scale (8 gram) preparation by Lietzke and Holt[5], but their apparatus is unsuitable for scaling up. Consequently a completely new apparatus had to be designed.

Since powdered tungsten commercially available contains considerable quantities of molybdenum, the chloride of which being more volatile than tungsten hexachloride, would adversely affect the ion arc, the tungsten is manufactured in situ by the reduction of tungsten trioxide, which may be obtained fairly pure.

Nitrogen is used to flush the apparatus out before each stage, and Lietzke and Holt recommend that this be purified with heated copper; however, the author's experience is that "white spot" oxygen-free nitrogen is sufficiently pure without further treatment.

2. APPARATUS

The apparatus used is shown in Fig. 1. The reaction chamber consists of a silica envelope inside which are a number of separable graphite trays or boats, details of which are given in Fig. 2. The gas can easily flow all round these trays, thus presenting a large surface area of material to the gas. The whole is surrounded by a furnace which is controlled through a thermocouple by a potentiometric controller. The lip of the silica envelope, two or three inches outside the lower end of the furnace, is cemented with thermal cement "K" into the groove in a brass plate, which is bolted with a "sulfesto" gasket to a length of 3" bore pyrex pipe fitted near the top with a 1" bore side arm. During the first (reduction) stage of the preparation this is fitted with a water cooled condenser, and also during this stage the larger pyrex pipe is wound with twelve feet of "electro-thermal" tape to prevent water produced in the reduction from condensing in the receiver. Originally a suitably drilled glass plate was bolted to the bottom of the pyrex pipe with an "O" section rubber ring, but later a plate made of "Tufnol" was used and proved quite satisfactory. The part of the brass plate exposed to the chlorine is smeared with silicone grease, and in addition the plate is water cooled. The gas, hydrogen, nitrogen, or chlorine, enters at the top of the apparatus after being washed with concentrated sulphuric acid.

3. DETAILED PROCEDURE

Fifty grams of tungsten trioxide are placed in each of the carbon trays, the apparatus is assembled and flushed out with "white spot" nitrogen. The pyrex receiving chamber is heated to 100°C by means of the "electro-thermal" tape, and hydrogen is passed through the

apparatus while the temperature is brought up to 1000°C. When no more water is produced (3-4 hours) the reduction is complete; nitrogen is used to flush out the apparatus, the furnace temperature is dropped to 600°C, the condenser is removed and the heating tape removed from the receiver, which is allowed to cool to room temperature. A magnesium perchlorate drying tube is attached to the receiver side-arm, and chlorine is passed through the apparatus at about 2 litres/min. The tungsten hexachloride falls into the receiver as dark red crystals. The product is light, and needs to be packed down by occasionally tapping the side of the receiver lightly. When no more reaction occurs (2-3 hrs.) the apparatus is allowed to cool down in a slow stream of chlorine, after which the bolts and gasket are removed, and the chloride transferred immediately to dry airtight storage bottles.

4. REMARKS

The efficiency of the process in different runs varied from 90-97%; low figures may only be apparent due to slight dampness of the original tungsten oxide.

In the course of a few weeks the bottles of tungsten hexachloride were found to contain a moderate pressure of hydrogen chloride, presumably due to hydrolysis by traces of moisture in the bottles. Subsequently the bottles were much more rigourously dried, and this trouble was not experienced again.

When heated to 150°C in vacuo, all samples have been 100% volatile.

REFERENCES

(1) Teclu, Ann. 187, 255, (1887).

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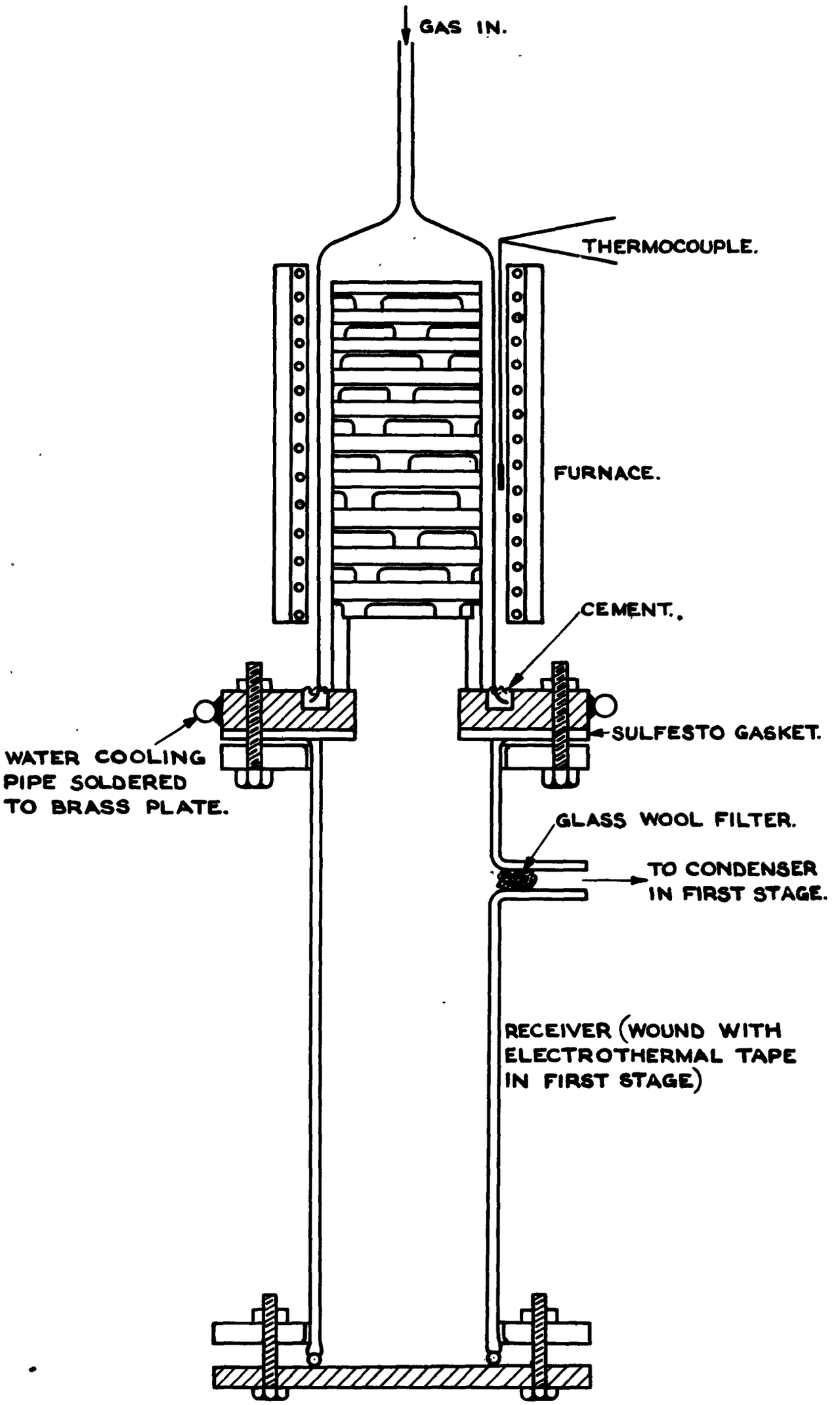
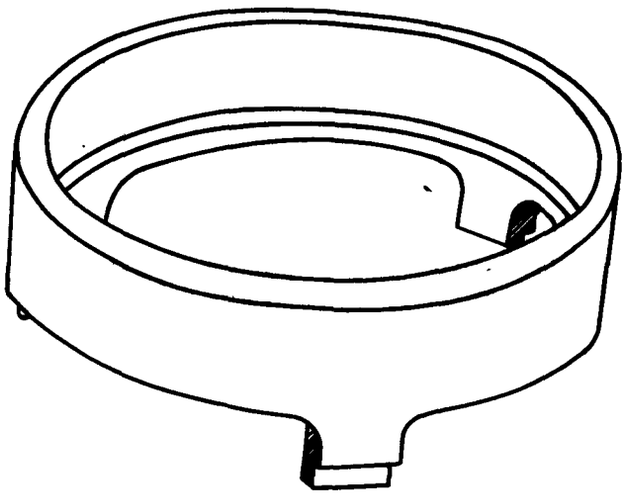
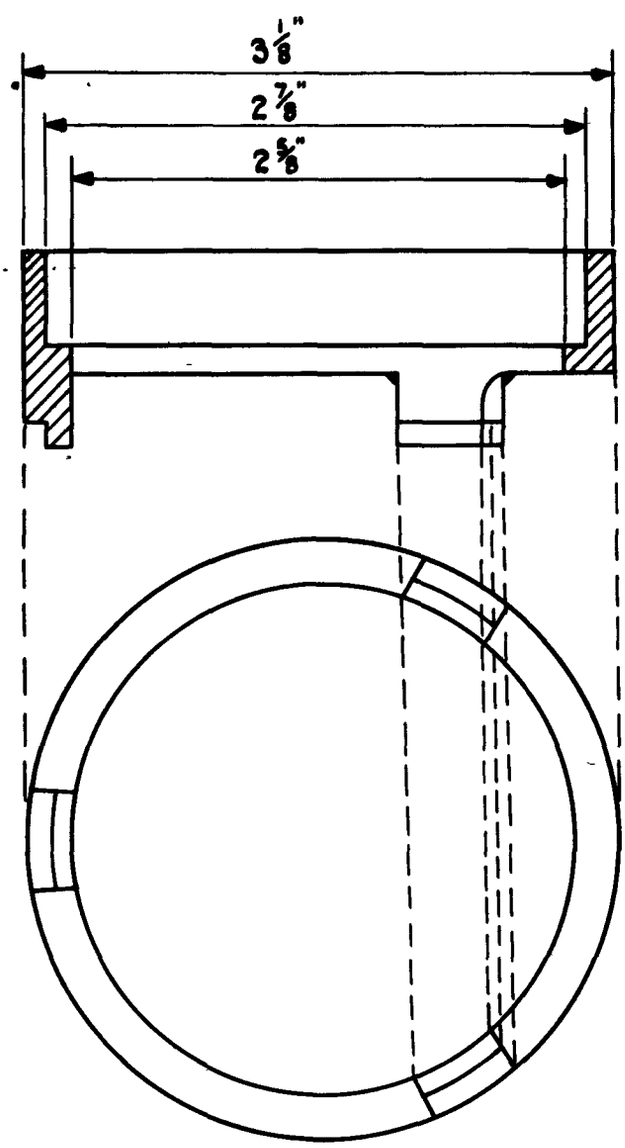
(4) Smith and Exner: Chem. News, 90, 66, (1904).

(5) Lietzke and Holt: Inorganic Syntheses, Vol.III (edited by L. F. Audrieth) p. 163.



A.E.R.E. GP/M167. FIG. 1. APPARATUS FOR PREPARING ANHYDROUS TUNGSTEN HEXACHLORIDE.





A GRAPHITE PLATE 2 7/8" DIA. RESTS ON THE SHELF.

THREE LEGS EQUALLY SPACED ON 2·860" p.c.d.

A.E.R.E. GP/M 167. FIG. 2. DETAIL OF GRAPHITE BOAT.