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Mr. G. H. Clewett, Head

PURIFICATION OF URANIUM TETRACHLORIDE

BY FRACTIONAL CONDENSATION

The effect of a single vacuum sublimation of contaminated uranium tetrachloride, with fractional condensation of the vapors, was investigated to determine whether a high degree of purity would result. It was found that this procedure was an excellent and simple method for obtaining exceedingly pure uranium tetrachloride.

Oak Ridge, Tennessee
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H. S. Young

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PURIFICATION OF URANIUM TETRACHLORIDE BY FRACTIONAL CONDENSATION

By H. S. Young

INTRODUCTION

The separation of pure uranium tetrachloride from other volatile chlorides is a tedious operation, which usually must be repeated many times to obtain even a fairly pure product. In an effort to provide a simple method and a product with a high degree of purity, the effect of a single vacuum sublimation of the contaminated material with fractional condensation of the vapors was investigated.

DISCUSSION

After considerable initial experimentation, the apparatus shown in Figures 1 and 2 was constructed for heating materials in vacuum under controlled conditions, and condensing the vapors along a closely controlled temperature gradient from 35° to 475°C. A series of pure inorganic anhydrous chlorides were then sublimed and fractionally condensed, and their behavior compared with that of uranium tetrachloride.

The observed temperature range over which condensation occurred for the chlorides investigated are shown in Figure 3. Most of the chlorides deposit in the middle of the indicated range, with only small amounts at the ends. The form of the deposited chloride varies considerably. For example, uranium tetrachloride deposits as black crystals, some as large as a cubic centimeter, while cuprous chloride

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deposits as a white glass-like material. Uranium oxychloride, UOCl_2 , is non-volatile, but tends to be blown from the charge compartment because of its low density. A baffle prevents this material from contaminating the condenser. The more volatile substances pass completely through the condenser into the trap cooled by liquid nitrogen.

Although many of the chlorides have condensation ranges well separated from that of uranium tetrachloride the chlorides of iron, chromium, and nickel, FeCl_2 , CrCl_3 , and NiCl_2 , condense in very nearly the same range. It is probable that uranium tetrachloride can be separated from them to a fair degree in the fractional condensation apparatus, if only material from the center of the uranium range, containing about 90 percent of the tetrachloride volatilized, is taken.

To test the degree of purification obtained on an actual sample, contaminated charges of tetrachloride for the fractional condenser were prepared by decomposing uranium pentachloride in a stainless steel apparatus. This procedure introduced nickel chloride, chromium chloride, and both ferrous and ferric chlorides. Before fractional condensation one charge contained 0.3 percent iron, and somewhat smaller amounts of chromium and nickel. After the sublimation the deposit in the center of the uranium tetrachloride range in the fractional condenser was contaminated with only 0.001 percent iron and spectrographic traces of chromium and nickel⁽¹⁾. Another charge initially containing 0.8 percent iron, 0.14 percent nickel, and 0.06 percent chromium was found to contain 0.2 percent iron and spectrographic traces of chromium and nickel after fractional condensation⁽²⁾. The extent of the removal of iron

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evidently depended upon the relative amounts of ferrous and ferric chlorides in the charge.

EXPERIMENTAL SECTION

Fractional Condenser⁽³⁾

The apparatus, shown in detail in Figures 1 and 2, consisted in part of a 57-inch condensing tube, made of 13 separate sections. This tube could be taken apart in a dry box after a run, and the individual fractions of condensate removed for analysis. Twelve of the sections were each 5-5/8 inches in over-all length with a 40/50 standard taper male joint on one end, a female joint of the same size on the other, and a constriction to an inside diameter of 13 mm between the joints. Behind each constriction was placed a baffle, consisting of a 25-mm test tube two-inches long. The closed end of the baffle pointed toward the hot end of the tube, so that condensing vapors often built up a "cap" on the baffle. To one end of this group of 12 sections was attached the thirteenth section, a foot long and 35-mm in diameter, forming the cold end of the condensing tube.

The charge section, also of 35-mm tubing, was sealed at one end, constricted to 13-mm six inches from this end, and connected to the other sections by a male 40/50 standard taper joint. As shown in the drawing, a baffle with its open end pointing toward the charge was placed behind the constriction in the charge section. When a charge of tetrachloride was run in the apparatus, this baffle was usually

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found to contain a green powder, uranium oxychloride, of a very low density which had been blown from the charge compartment.

The entire condensing tube and charge section fitted into a Pyrex vacuum jacket 60-mm in diameter and 6-feet long, with one end sealed off and the other closed by a 102/75 sealed ball joint. Near the ball joint was a 25-mm outlet connected to a trap, which in turn was connected to the vacuum system. One vacuum pump was used, a Cenco Hypervac-20. The pressure was measured by a wide range Kipp gauge.

Around the 60-mm Pyrex vacuum jacket, on asbestos paper, were wrapped two nichrome wire heating coils connected to Powerstats. One of these coils heated only the section of the tube containing the charge section. The second coil followed immediately, and continued for two-thirds the length of the jacket with increasing space between the successive turns, so that the heat imparted to the condensing tube gradually became less as the open end was approached. Twelve thermocouples were placed along the jacket under the heating coils, so that temperature measurements could be made. The entire jacket was covered with a two-inch layer of 85 percent magnesia pipe covering, the upper half of which could be removed at the end of a run for rapid cooling of the jacket.

This apparatus was mounted in such a way that the end containing the charge section was slightly lower than the exit end, so if a chloride melted and boiled, the liquid would not run down the tube. There was no proof that some chlorides did not boil, rather than sublime.

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Experimental Procedure⁽³⁾

A uniform procedure was established involving time of heating to a standard temperature gradient, time of maintaining this temperature, time of cooling, pressure of operation, and method of handling the charge material and the fractions from the condenser.

About 40 grams of metal chloride were placed in the charge section in an atmosphere of dry nitrogen. The condensing tube was filled with dry nitrogen, attached to the charge section, and placed in the vacuum jacket. The vacuum pump was started, and when the pressure reached three microns the Powerstats were turned on. In two hours the charge section reached 475°C , and the condenser attained the desired temperature gradient. The Powerstats were then adjusted so that the temperatures ranging from 475°C at the charge section to 35°C at the cold end of the condensing tube were maintained. The temperature at any point on the jacket did not vary more than 8°C for 18 hours. At the end of this 18-hour period the Powerstats were turned off, and the system cooled, under vacuum, to room temperature in two hours. The pressure was maintained at one to three microns during the entire experiment.

The condensing tube was removed after the apparatus had been flushed with dry nitrogen, and its open end immediately sealed. Although no lubricant was ever used on the joints it was easily disassembled for analysis. The sections adhered seriously only once, when a sample of an alkali salt was fractionally condensed.

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FRACTIONAL CONDENSER BALL JOINT - CASE 16

FIGURE 1

① CONDENSING SECTION	⑥ THERMOCOUPLE
② CONDENSING SECTION BAFFLE	⑦ 85% MAGNETIA PIPE COVERING
③ 6 MM VACUUM JACKET	⑧ COLD END OF 5.5 FT CONDENSING TUBE
④ ASBESTOS PAPER	⑨ CHARGE SECTION
⑤ NICHROME WIRE HEATING COIL	⑩ 102/75 SEALED BALL JOINT
⑪ CONNECTIONS TO POWER TAP	

FRACTIONAL CONDENSER
CUTAWAY SECTION - SCALE 1:2

FIGURE 2

① CONDENSING SECTION	④ ASBESTOS PAPER
② CONDENSING SECTION BAFFLE	⑤ NICHROME WIRE HEATING COIL
③ 60 MM VACUUM JACKET	⑥ THERMOCOUPLE
⑦ 85% MAGNESIA PIPE COVERING	

FIGURE 3

CONCENTRATION RANGE: TEMPERATURES FOR
ANHYDROUS CHLORIDES *

* PRESSURE OF 1 TO 3 MICRONS.

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SUMMARY

It was found that an excellent method for the simple preparation of exceedingly pure uranium tetrachloride, free from gases, organic matter, oxychlorides of uranium, and many metal chlorides consists of a single vacuum sublimation in an all glass apparatus, with fractional condensation of the vapors along a tube with a controlled temperature gradient. A fractional condensing apparatus for utilizing the method is described, and the separations obtained with it are tabulated.

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