[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

Preparation of Uranium Trioxide

BY IRVING SHEFT, SHERMAN FRIED AND NORMAN DAVIDSON[1]

The usual methods of preparation of UO_3 are thermal decomposition of uranyl peroxide and ignition of uranyl salt or uranates. Neither of these methods gives pure anhydrous UO_3 unless the temperature of decomposition is very closely controlled. Preparation of anhydrous UO_3 from aqueous UO_4 first requires decomposing the UO_4 in oxygen at 200° to give hydrates of UO_3. These hydrates are further decomposed by heating in vacuum to 325°. Above 400°, U_3O_8 is slowly formed. Difficulties are encountered in the preparation of UO_3 by ignition of $UO_2(NO_3)_2 \cdot 6H_2O$ because of the closeness of the limits on temperature required to remove the nitrogen completely without decomposing the UO_3 to U_3O_8. Low temperature decomposition of $(NH_4)_2U_2O_7$ gives UO_3 containing ammonia which is not easily removed by heating without decomposition to U_3O_8. Hydrolysis of uranyl salts of mineral acids yields hydrates of UO_3 with the accompanying problem of dehydration without further decomposition.[2]

This paper describes the preparation of pure anhydrous UO_3. The reaction involved, first reported by Fried and Davidson,[3] is the high pressure oxidation of U_3O_8 using oxygen which has been distilled from liquid oxygen to insure dryness. When U_3O_8 or amorphous UO_3 is heated in sealed glass bomb-tubes at 450–750° in oxygen pressures of 30–150 atmospheres, it is converted to one of three crystalline phases of UO_3. The most stable of these is yellow and is isomorphous with UO_3 made from ignited uranyl nitrate. The least stable is red, hexagonal UO_3 with a crystal structure similar to that of U_3O_8. The intermediate phase has never been prepared free from the other two phases. The yellow phase is prepared at temperatures above 550°, whereas the red, hexagonal phase results when the reaction is carried out at 450–500°.

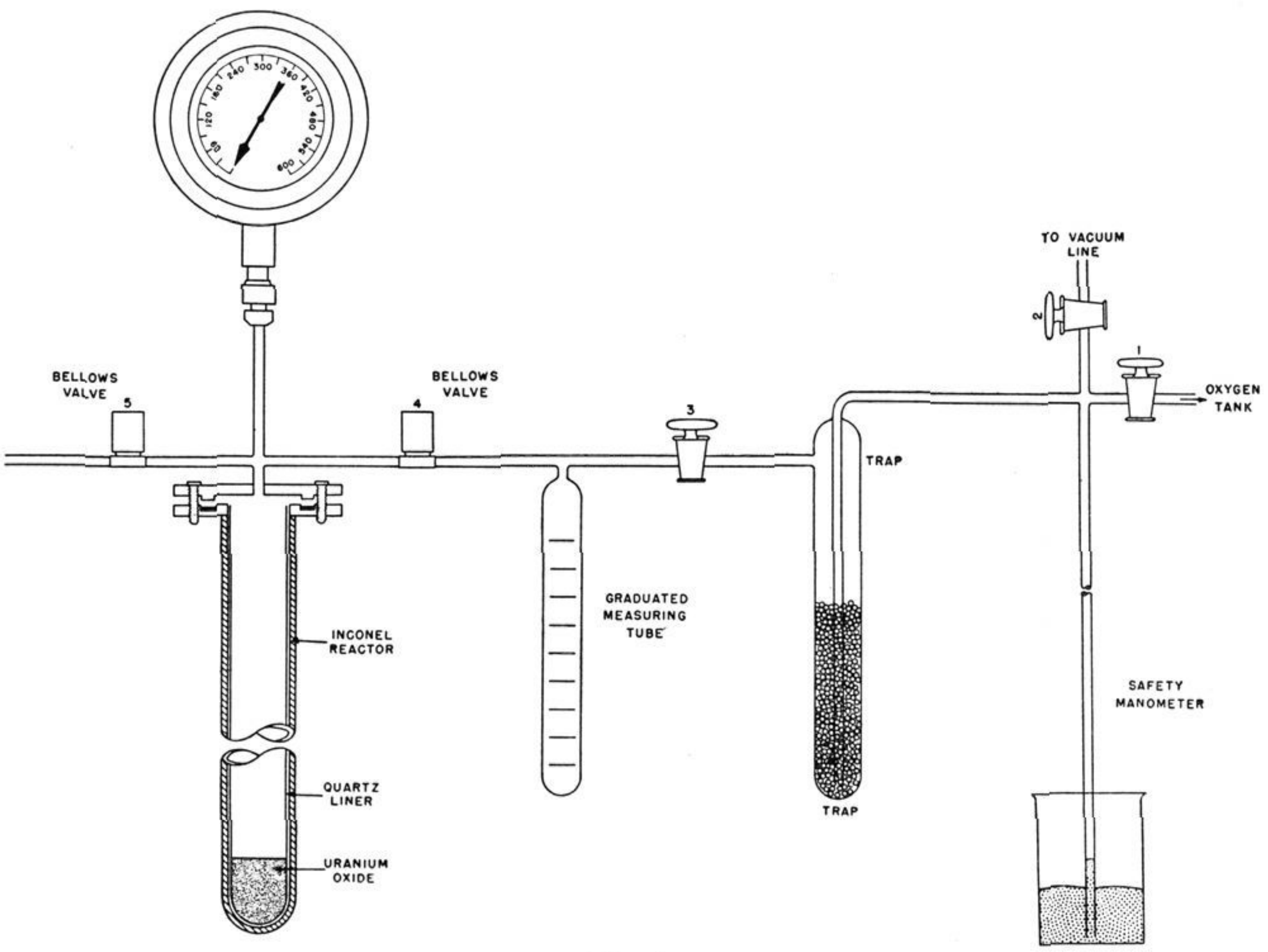

Fig. 1.

Experimental

An apparatus in which U_3O_8 can be treated with oxygen at high pressures, shown in Fig. 1, has been constructed which permits the handling of large amounts of U_3O_8, and which eliminates the necessity of using sealed glass bomb-tubes. The reactor consists of an Inconel tube affixed to a grooved brass plate with a neoprene washer. The brass top plate is connected to two Crane bellows valves and a pressure gage through a brass crosspiece. A removable quartz liner is used to prevent scale from falling into the reaction mixture and to facilitate removal of the product.

---

(1) Present address: California Institute of Technology, Pasadena, California.

(2) Plutonium Project Record of the National Nuclear Energy Series, Chemistry of Uranium (A), Chapter 11, pp. 108, *et seq.*

(3) S. Fried and N. Davidson, Plutonium Project Record of the National Nuclear Energy Series, Chemistry of Uranium (B).

The manometer is desirable both to indicate the pressure and to act as a vent if the pressure becomes too great while the oxygen is being distilled. The measuring tube is made of sufficiently large capacity to hold enough liquid oxygen to give the desired pressure in the reactor.

In the procedure for preparing UO_3, pure U_3O_8 is placed in the quartz liner of the reactor which is then bolted shut. The tubing connected to the oxygen tank is flushed with oxygen by opening stopcock 1 and bubbling oxygen through the manometer. Stopcock 1 is then shut and the system evacuated by opening stopcocks 2 and 3. Valve 4 is open and valve 5 is kept shut. The U_3O_8 is thoroughly dried during the evacuation by heating at 850° for about one hour. When the apparatus is evacuated, as determined by a McLeod gage on the vacuum system, the vacuum line is shut off at stopcock 2. Stopcock 3 and valve 4 are also shut.

To collect liquid oxygen in the trap, the trap is immersed in liquid nitrogen and stopcock 1 is opened. About 10% more oxygen than is needed to fill the reactor to 400 p. s. i. is condensed in the trap. The amount required for the reactor is dependent on its volume and is determined from the gas laws. After the apparatus has once been used, the necessary volume of liquid oxygen can be determined more accurately.

After sufficient liquid oxygen has been condensed in the trap, stopcock 1 is shut. A dewar containing liquid nitrogen is placed around the measuring tube and stopcock 3 opened. The dewar of liquid nitrogen around the trap is replaced by a dewar containing liquid oxygen. The proper amount of oxygen, calculated to produce the proper pressure, is measured into the graduated tube and stopcock 3 closed. The reactor is cooled with a bath of liquid nitrogen. Valve 4 is then opened and the measuring tube placed in a dewar of liquid oxygen to maintain the liquid oxygen in the measuring tube at approximately 1 atmosphere while it distills into the reactor. Valve 4 is then shut and the reactor warmed to room temperature slowly[4] to prevent scattering of the U_3O_8 by the evaporating oxygen. A furnace placed around the reactor is maintained at 600–700° for forty hours. Should too much oxygen have been collected in the reactor, the excess can be vented through valve 5. The residual liquid oxygen in the trap can be removed through the pumps or can be slowly evaporated through the manometer by keeping the trap in a dewar containing liquid nitrogen and permitting the latter to evaporate by itself. Examination of X-ray diffraction patterns of the yellow product by Dr. W. H. Zachariasen of the Physics Division of this Laboratory and ignition to U_3O_8 have shown the product to be pure UO_3 of the type obtained by ignition of uranyl nitrate.

Summary

The method for the preparation of UO_3 described here is considered to be superior to those commonly used because the purity of the product is dependent only on the purity of the original U_3O_8, which should be high for good results, and the product is obtained in 100% yield. The oxygen is dried and purified during the liquefaction so that this presents no problem, while U_3O_8 is generally obtained sufficiently pure.

Within wide limits the temperature at which the reaction is run is not critical. The upper temperature limit, however, is important. Experiments run at 750° yielded oxides intermediate between U_3O_8 and UO_3. Even at 750°, however, UO_3 can be prepared by going to pressures over 400 p. s. i. Preparations made at temperatures as low as 550° also yielded UO_3, but required somewhat longer time for complete reaction.

CHICAGO, ILLINOIS RECEIVED AUGUST 29, 1949

---

(4) Replacing the dewar containing the liquid nitrogen by an empty one is adequate.

[CONTRIBUTION FROM SCHOOL OF CHEMISTRY, INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Reaction of Ferrous and Ferric Iron with 1,10-Phenanthroline. III. The Ferrous Monophenanthroline Complex and the Colorimetric Determination of Phenanthroline

BY I. M. KOLTHOFF, D. L. LEUSSING AND T. S. LEE

One of the most important methods for the determination of iron is the colorimetric method based on the formation of the red ferrous triphenanthroline complex ion. In addition to this well-known complex there appear to be two other complex ions of ferrous iron and phenanthroline, the pale yellow ferrous monophenanthroline and ferrous diphenanthroline.[1] The latter is relatively unstable with respect to the other ferrous phenanthroline complex ions and for most purposes its existence may be neglected. In the investigation described below the dissociation constant of ferrous monophenanthroline was determined and the visible spectrum recorded.

The knowledge of this constant is of importance in the determination of complex constants of other metals with *o*-phenanthroline when the excess of phenanthroline is being determined colorimetrically. In the present work an excess of iron was added to the phenanthroline solution and the intensity of the red ferrous triphenanthroline color was measured with a spectrophotometer. The formation of ferrous monophenanthroline causes low results unless a correction is made. A systematic study of the effect of ferrous ion concentration, acidity, and phenanthroline concentration on the equilibria and the accuracy of the determination has been made.

Experimental

Materials Used.—The preparation of most of the reagents used was described in previous papers. The purity of the *o*-phenanthroline monohydrate was determined by conductometric titration with acid. Experience has shown that the product obtained from the G. Frederick Smith Chemical Company can probably be depended upon to be more than 99% pure. This cannot be said for "phenanthroline dihydrochloride" from the same source.

The *p*H of the acetic acid–acetate buffer used in the determination of *o*-phenanthroline was measured with a *p*H meter equipped with glass electrode.

---

(1) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, 70, 2348, 3596 (1948).