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PREPARATION OF URANIUM TRIFLUORIDE AND STUDIES ON ITS DISPROPORTIONATION

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ABSTRACT

The reduction of UF_4 to UF_3 by molecular hydrogen has been studied. At hydrogen flow rates which yield a constant H_2/HF ratio in the outlet gas stream, the optimum conversion temperature range is 1070—1125 K. Disproportionation studies on UF_3 have also been carried out in the temperature range 1169—1360 K. The variation of specific disproportionation rate (k) with temperature can be represented by

$$\log_{10}k(\mathrm{h}^{-1}) = (5.07 \pm 0.17) - (5842 \pm 211)/T(\mathrm{K})$$

INTRODUCTION

Uranium trifluoride is prepared mainly as a reduction product of uranium tetrafluoride. The reductants used have been molecular [1—3] or atomic [4] hydrogen, finely divided uranium metal [4—7], aluminium [3,8], silicon [9] and zinc amalgam [10]. The use of metallic reductants is likely to introduce metallic impurities and for this reason use of hydrogen as reductant is preferable. However, the product is likely to be contaminated with UF_4 and U, as UF_3 is known to disproportionate on heating according to the reaction

$$4\,\langle UF_3\rangle \rightleftharpoons 3\,\langle UF_4\rangle + \langle U\rangle$$

The disproportionation reaction has been reported to begin at 973 K [11], to be appreciable at 1273 K [8], and to be of the order of 20 mole % h^{-1} at 1773 K [12]. However, no systematic study of the disproportionation reaction has been made. In the present work preparation of pure UF_3 by H_2 reduction of UF_4 in the temperature range 1070—1180 K and disproportionation studies in the temperature range 1169—1360 K have been carried out.

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EXPERIMENTAL

Materials

Uranium tetrafluoride used in the present work was prepared from nuclear grade reactive uranium dioxide (>99.95 mass %) by the action of anhydrous hydrogen fluoride at 800 K. Its purity was checked by X-ray diffraction technique and pyrohydrolysis (estimated F = 24.1 mass %, theoretical 24.2 mass %).

Hydrogen and argon gases used in all the experiments were purified by passing separately through towers of molecular sieves and hot titanium sponge (1170 K) to remove moisture and oxygen, respectively. The moisture and oxygen levels in purified gases were less than 1 ppm. Purification of gases was essential for preventing the following reactions

$$\langle UF_4 \rangle + 2\,(H_2O) \rightarrow \langle UO_2 \rangle + 4\,(HF)$$

$$2\,\langle UF_4 \rangle + (O_2) \rightarrow \langle UO_2F_2 \rangle + (UF_6)$$

Apparatus

The reaction vessel for UF_3 preparation was made from a 75 mm inner diameter nickel-200 pipe and the sample was contained in a 75 X 50 X 20 mm nickel boat. For disproportionation studies, a 10 mm i.d. nickel tube was used as reaction vessel, as shown in Fig. 1. A chromel—alumel thermocouple placed inside a 6 mm i.d. nickel thermowell was used to measure the sample temperature. The thermocouple was calibrated at the melting temperature [13] of bismuth (544.5 K), antimony (904 K), and silver (1234 K). A Kanthal wire wound furnace with a flat zone of 130 mm (±1.0 K) was used for the work. The temperature of the furnace was controlled to ±0.5 K using a proportional temperature controller.

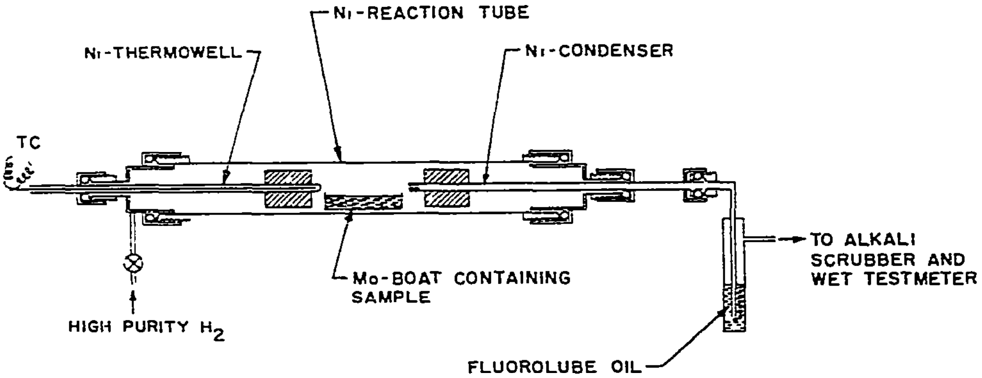

Fig. 1 Apparatus for the disproportionation studies on UF_3.

Procedure for UF_3 preparation

A weighed amount of UF_4 (~20 g) was taken in a nickel boat and placed inside the reaction vessel. The assembly was then evacuated to 10^{-3} Torr and the sample gradually heated to 550 K, when purified argon was introduced and the sample further heated to reaction temperature (1070—1125 K). When the temperature became constant, argon was replaced by purified hydrogen. The hydrogen flow rate was controlled using a calibrated differential oil manometer. The flow rates ranged between 600 and 700 ml min^{-1}. The unreacted hydrogen and the HF formed were passed through a fluorolube oil bubbler (to avoid back diffusion of moisture) and through a bubbler having a known quantity of standard NaOH. The progress of the reaction was followed by measuring the time required for the neutralisation of known quantities of alkali by HF in the effluent gas. When the quantity of HF in the effluent gas became insignificant, H_2 flow was replaced by argon and the furnace was cooled. The product consisted of shining black crystals. Several batches of UF_4 have been converted to UF_3 in this manner.

Analysis

X-Ray diffraction studies on the product revealed peaks for UF_3 alone and none for UF_4 or UO_2. Pyrohydrolysis of the product at 1073 K yielded a fluorine value of ($F = 19.2 \pm 0.2$) mass % as compared to the theoretical value of 19.3 mass %. The product of pyrohydrolysis (U_3O_8) was weighed which gave $U = (80.4 \pm 0.2)$ mass % in UF_3 as compared to the theoretical value of 80.68 mass %.

Procedure for measuring disproportionation of UF_3

A weighed amount of UF_3 in a molybdenum boat was placed inside the nickel reaction vessel and rapidly heated to the desired temperature in a current of high purity hydrogen passing at a constant flow rate (100—120 ml min^{-1}). This flow rate range was obtained by determining the flow rate 'plateau' for HF where the mole ratio of HF/H_2 remains constant irrespective of hydrogen flow rate. The UF_4 produced as a result of disproportionation of UF_3 was reconverted to UF_3 by the hydrogen stream and the quantity of HF gave the extent of disproportionation. The outgoing gas mixture (H_2 + HF) was bubbled through fluorolube oil and the quantity of HF was determined as described earlier.

RESULTS AND DISCUSSION

All preparations of UF_3 carried out previously by this method have been performed at 1273 K with little success. The failures were attributed mainly to insufficiently purified hydrogen or to the use of porcelain or quartz apparatus [4]. Even in cases where purified hydrogen and monel apparatus were used, the poor yields can be attributed to the sintering of UF_4 at this tem-

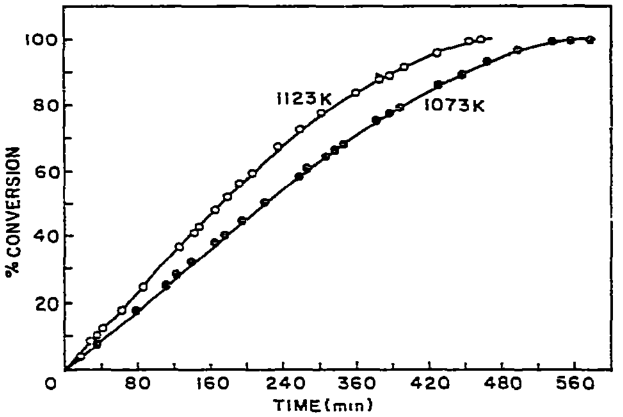

Fig. 2. Plot of percentage UF_4 converted against time.

perature which is close to the melting temperature of UF_4 [14]. Also when this reduction reaction was carried out at a lower temperature (1180 K) during the course of this work, some interesting observations were made. With a UF_4 charge of 40 g having a bed depth of 5 mm the reaction proceeded at a constant rate up to 60 mole % conversion. Thereafter HF evolution became negligible. Examination of the charge showed that it had fused. The fused mass was powdered and reloaded into the reaction vessel. The reaction was then continued to completion at a lower temperature (1120 K). However, the total quantity of HF determined was more than the theoretical value, due to the disproportionation of UF_3. The phase diagram for the UF_3—UF_4 [15] system indicates the formation of a eutectic at 33 mole % UF_3 at 1152 K. Thus any attempt to prepare UF_3 above 1152 K will lead to extremely slow reaction rates, because of the appearance of the liquid phase. Another reason to consider 1273 K to be unsuitable for reduction is the appreciable disproportionation rate of UF_3 at this temperature. Hence, in this work reduction studies were carried out only in the temperature range 1075—1125 K using H_2 flow rates in the range where the number of moles of HF evolved per litre of H_2 passed were constant. These limiting flow rates were found to be 600—700 ml min^{-1}. It was necessary to work within these limits in order to carry out kinetic studies.

TABLE 1

Disproportionation of solid uranium trifluoride

T (K)	k (mole % h^{-1})
1169.0	1.17
1191.5	1.58
1229.5	2.07
1239.5	2.13
1263.0	2.64
1291.0	3.48
1333.0	5.20
1360.0	5.86

The progress of the reaction during typical runs at 1073 and 1123 K using approximately 9 g of UF_4 spread out in a thin layer (~1 mm) is depicted in Fig. 2. From Fig. 2 it is evident that the reaction rate is constant up to 65 mole % UF_3. Thereafter the rate is no longer linear, indicating that diffusion effects predominate. Thus this reaction represents a typical gas—solid reaction in which the rate of HF removal from the reaction site is the rate controlling step.

Disproportionation studies on UF_3 have been carried out in the temperature range 1169—1360 K. The rate of disproportionation reaction was measured at each temperature by determining the quantity of HF evolved over a known period of time. The number of moles of UF_3 disproportionated can be evaluated using the following reaction

$$4\,\langle UF_3\rangle + 3/2\,(H_2) \rightleftharpoons 3\,\langle UF_3\rangle + 3\,(HF) + \langle U\rangle$$

Thus for each mole of HF evolved 4/3 moles of UF_3 will disproportionate. Knowing the initial mass of UF_3 taken and the quantity of HF evolved over a definite period of time, the disproportionation rate in mole % UF_3 h^{-1} was calculated. These data at various temperatures are given in Table 1. The relation between the rate and temperature is given by

$$\log_{10}k(h^{-1}) = (5.07 \pm 0.17) - \frac{(5842 \pm 211)}{T(K)}$$

Enthalpy of activation is thus determined as 26.7 kcal $mole^{-1}$ and the entropy of activation is —54.5 cal K^{-1} $mole^{-1}$. This large negative value for the entropy term is responsible for the slow rate of disproportionation even at high temperatures.

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