J. inorg. nucl. Chem., 1975, Vol. 37, pp. 731-733. Pergamon Press. Printed in Great Britain

THE REACTION OF URANIUM TETRAFLUORIDE WITH URANIUM MONONITRIDE

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(*First received* 1 *May* 1974; *in final form* 8 *July* 1974)

Abstract—The reaction of UF_4 with UN at 950°C yields UF_3 or UNF depending on the mixing ratio; the product is UF_3 for the UF_4:UN ratio of 3:1, and UNF for 1:3. The reaction is generally expressed as

$$x\ UF_4(s) + y\ UN(s) \rightarrow \frac{3x-y}{2}\,UF_3(s) + \frac{3y-x}{2}\,UNF(s) + \frac{x-y}{4}\,N_2(g).$$

The free energy change for the formation of UF_3 is discussed on the basis of the experimental results.

INTRODUCTION

In the course of studies of the high-temperature reactions with uranium nitride, it was found that UF_4 was readily converted to UF_3 or UNF. The typical reactions are represented by the equations:

$$3\ UF_4(s) + UN(s) \rightarrow 4\ UF_3(s) + \frac{1}{2}N_2(g) \qquad (1)$$

and

$$UF_4(s) + 3\ UN(s) + \frac{1}{2}N_2(g) \rightarrow 4\ UNF(s). \qquad (2)$$

In the present paper, the reaction of UF_4 with UN has been investigated, with the different mixing ratios of starting materials in a nitrogen atmosphere or in a vacuum at temperatures below 1000°C.

EXPERIMENTAL

Materials

UF_4 was provided from Sumitomo Metal and Mining Co., with the composition: UF_4, >99·0%; UO_2F_2, 0·8%; and UO_2, 0·05%.

UN, prepared by arc-melting of uranium metal in a nitrogen atmosphere, was provided from Mitsubishi Metal Co. The composition is as follows: total U, 94·73%; nitrogen 5·53%; and oxygen, 0·01%; the N/U atom ratio is 1·00.

Procedure

Both the compounds were ground in a dry box filled with high-purity argon gas and were mixed at different mole ratios (UF_4:UN = 3:1, 1:1 and 1:3) and compacted at 3 ton/cm^2 into cylindrical pellets, 7 mm in diameter and 5 mm in height. The resulting pellets of about 2 gm, placed in a nickel crucible, were heated in a quartz tube. The reactions were carried out in a closed system of an atmosphere of nitrogen or of a vacuum. The volume of the reaction system, consisting of the quartz tube, a liquid nitrogen trap, an oil manometer and a mercury manometer, was about 400 ml. The temperature was raised at the rate of 3°C/min.

Analysis

The fluorine was separated as hydrogen fluoride by pyrohydrolysis at 850°C for 20 min. Its content was determined photometrically using lanthanum-alizarine complexone[1]. The uranium content was determined as U_3O_8 from the residual oxide of pyrohydrolysis. The amount of nitrogen was determined photometrically with thymol[2].

RESULTS

The conditions of experiments and the results are given in Table 1.

Reactions in mole ratio UF_4:UN = 3:1

The reaction *in vacuo* was followed with the pressure change in nitrogen evolved with time. The reaction took place at about 700°C, became rapid at temperatures above 840°C, and terminated before the temperature attained 900°C. The nitrogen pressures at temperatures between 1103 and 1148K are given by the equation:

$$\log p_{N_2}(\mathrm{atm}) = 39{\cdot}57 - 4{\cdot}695 \times 10^4/T. \qquad (3)$$

X-ray diffraction pattern showed that the product was the single phase of UF_3. The pattern of UF_3 was consistent with that of the ASTM file[3]. The reaction therefore is expressed as Eqn (1).

On the inside surface of the quartz tube slightly above the crucible, grayish-brown film was formed. This compound was found to be UO_2 by chemical and X-ray analyses. It is probably produced by the reaction of the evaporated UF_4 with the quartz tube. The reaction product $SiF_4(g)$ was trapped by the liquid nitrogen, so that the nitrogen pressure in the system was not affected by it.

When heated in 1 atm nitrogen to 950°C, the mixture was also converted to UF_3. The formation of a UO_2 film was not observed.

Reaction in mole ratio UF_4:UN = 1:1

In the reaction in vacuo, nitrogen was not evolved by heating up to 950°C. Gray-brown film was deposited on

Table 1. The reaction of UF_4 with UN

Experimental conditions				Products				
					Chemical analysis			
Mixing ratio (mole) UF_4:UN	p_{N^2} (atm)	Max. temp.* (°C)	Retention time (min)	X-ray analysis	(wt%) U	N	F	(atom ratio) U:N:F
3:1	0	900	20	UF_3	80·70	0·10	20·32	1·00:0·02:3·15
3:1	1	950	10	UF_3	80·11	0·04	20·20	1·00:0·01:3·16
1:1	0	900	30	UF_3, UNF	83·69	2·56	12·63	1·92:1·00:3·64
1:1	1	950	0	UF_3, UNF	83·76	2·66	11·83	1·85:1·00:3·28
1:3	0	950	0	UF_3, UNF, UN	86·87	3·86	9·20	1·33:1·00:1·76
1:3	1	950	20	UNF	86·86	4·73	5·87	1·08:1·00:0·92

*The heating rate was 3°C/min.

the inner wall of the quartz tube, similarily to the case of the reaction (UF_4 : UN = 3 : 1) *in vacuo*. The product was a mixture of UF_3 and UNF. The compound UNF was identified by X-ray diffraction to have a tetragonal structure with lattice parameters of a_0 = 5·61 Å and c_0 = 5·71 Å; its pattern was consistent with that reported by Yoshihara *et al.*[4]. The reaction thus proceeds as

$$UF_4(s) + UN(s) \rightarrow UF_3(s) + UNF(s). \qquad (4)$$

When heated in a nitrogen atmosphere, the product also consisted of UF_3 and UNF. There was no change in the nitrogen pressure before and after heating. The formation of UO_2 was hardly observed on the wall of the tube.

Reaction in mole ratio UF_4 : UN = 1 : 3

In the reaction *in vacuo*, no evolution of nitrogen was observed. A gray-brown film of UO_2 was also found on the inner wall of the tube. X-ray diffraction showed the product to be a mixture of UF_3, UNF and UN. It is considered that the reaction occurs in equimolar ratio of UF_4 and UN as shown in Eqn (4), and UN remains as the unreacted starting material.

When heated in a nitrogen atmosphere, the reaction could be followed by the pressure change. The reaction occured above 740°C and was terminated at about 900°C. The product was only UNF; U_2N_3 was not formed. The reaction is given as Eqn (2). The gain in weight during the heating process is in agreement with Eqn (2). The formation of UO_2 on the inner wall of the quartz tube was not observed.

DISCUSSION

UF_3 can not be prepared directly by the reaction of uranium with fluorine. The attempts to synthesize UF_3 have been reviewed by Katz and Rabinowitch[5]. Two successful methods are described:

(A) UF_4 is reduced with purified hydrogen at 1000°C. The reaction proceeds according to

$$UF_4(s) + \frac{1}{2}H_2(g) \rightarrow UF_3(s) + HF(g). \qquad (5)$$

(B) UF_4 is reduced with finely divided uranium metal at 1050°C:

$$3UF_4(s) + U(s) \rightarrow 4UF_3(s). \qquad (6)$$

Subsequently, another method was reported by Runnals[6]:

$$UF_4(s) + Al(l) \xrightarrow{900°C} UF_3(s) + AlF(g). \qquad (7)$$

In these reactions, UF_4 is partially reduced by hydrogen, uranium or aluminium. The reaction (1), observed in the present work, is considered a modification of Eqn (6); UN acts as the reducing agent.

Uranium nitride–fluoride UNF was found by Yoshihara *et al.*[4] as an intermediate in the nitride formation from UF_4 using the reducing agent Si. Before that, Juza *et al.*[7–9] prepared the similar compounds UNX (X = Cl, Br and I) by the reactions: $UX_4(s) + 3\,UN(s) + \frac{1}{2}N_2(g) \rightarrow 4\,UNX(s)$; and $UX_4(s) + NH_3(g) \rightarrow UNX(s) + 3HX(g)$. In the present experiments, however, UNF is readily formed in the reaction of UF_4 with UN at the UF_4/UN mole ratio smaller than three. When an equimolar mixture of UF_4 and UN is heated, the product is then the equimolar mixture of UF_3 and UNF, regardless of the presence of nitrogen. In the case of UF_4 : UN = 1 : 3, UNF is obtained as the single phase. Therefore, the reaction of UF_4 with UN can be generally described as

$$xUF_4(s) + y\,UN(s) = \frac{3x - y}{2}UF_3(s) + \frac{3y - x}{2}UNF(s) + \frac{x - y}{4}N_2(g). \qquad (8)$$

By using the free energies for the formation of UF_3 and UF_4[10], it cannot be shown thermochemically that the reaction of UF_4 with UN yields UF_3 even at temperatures as high as 1000°C. Actually, however, the reaction takes place at temperatures above 700°C *in vacuo*, and proceeds at a sufficient velocity at temperatures between 800 and 900°C. Therefore, the thermochemical data for UF_3 and UF_4 should be reexamined.

The reaction (1) is composed of two equations (a) and (b):

$$UN \rightarrow U + \frac{1}{2}N_2, \qquad (a)$$

$$3\,UF_4 + U \rightarrow 4\,UF_3. \qquad (b)$$

$$3\,UF_4 + UN \rightarrow 4\,UF_3 + \frac{1}{2}N_2. \qquad (1)$$

The nitrogen pressures in Eqn(1) around 1120K were already given as Eqn (3). Using this equation, the temperature where the nitrogen pressure becomes 1 atm is taken to be 913°C. This temperature agrees well with the result that the reaction in the mole ratio $UF_4 : UN = 3:1$ yields only UF_3 at 950°C even at 1 atm nitrogen. Assuming that the reaction system is in equilibrium and the activities of UF_3 and UF_4 are unity, the Gibbs free energy change of the reaction (1) is shown as

$$\Delta G^\circ_T = 107{\cdot}4 - 90{\cdot}5(T/1000)\ \text{(kcal/mole, 1100–1150K)}, \qquad (9)$$

and the value at 1100K becomes $\Delta G^\circ_{1100}(1) = 7{\cdot}9$ kcal/mole. The reaction (a) is the decomposition of UN. Its free energy change at 1100K evaluated from the data in the literature is $\Delta G^\circ_{1100}(a) = 49{\cdot}4$ kcal/mole[11]. The free energy change of the reaction (b), obtained from Eqn (1) and (a), is thus $\Delta G^\circ_{1100}(b) = -41{\cdot}5$ kcal/mole. On the other hand, the free energies for the formation of UF_3 and UF_4 at 1100K estimated by Rand and Kubaschewski[10] are $-285{\cdot}0$ and $-376{\cdot}1$ kcal/mole, respectively, so that the free energy change in Eqn (b) is $\Delta G^\circ_{1100}(b) = -11{\cdot}9$ kcal/mole. The difference in $\Delta G^\circ_{1100}(b)$ values between the present result and Rand and Kubaschewski's result[10] is about 30 kcal/mole. If calculation is based on the free energy for the formation of UF_4, the value for UF_3, obtained from the present results, is $\Delta G^\circ_{1100} = -292{\cdot}5$ kcal/mole; which is in agreement with that determined by Long and Blankenship[12], $\Delta G^\circ_{1100} = -295 \pm 5$ kcal/mole.

Acknowledgments—The author wishes to express his appreciation to Dr. H. Hashitani and Mr. H. Yoshida for chemical analysis and to Drs. T. Ishimori and K. Ueno for their encouragements.

REFERENCES

1. H. Hashitani and H. Yoshida, *Bunseki Kagaku* **16**, 44 (1967).
2. H. Hashitani and H. Yoshida, *Bunseki Kagaku* **19**, 1081 (1970).
3. ASTM card No. 9–339; see also E. Staritzky and R. M. Douglass, *Analyt. Chem.* **28**, 1056 (1956).
4. K. Yoshihara, M. Kanno and T. Mukaibo, *J. inorg. nucl. Chem.* **31**, 985 (1969).
5. J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium*, p. 349. McGraw-Hill, New York (1951).
6. O. J. C. Runnalls, *Can. J. Chem.* **31**, 694 (1953).
7. R. Juza und R. Sievers, *Naturwissenschaften* **52**, 538 (1965).
8. R. Juza und W. Meyer, *Naturwissenschaften* **53**, 552 (1966).
9. R. Juza und W. Meyer, *Z. anorg. allg. Chem.* **366**, 43 (1969).
10. M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, Oliver and Boyd, London (1963); see also AERE-R 3487 (1960).
11. H. Tagawa, *J. nucl. Mater.* **51**, 78 (1974).
12. G. Long and F. F. Blankenship, ORNL-TM-2065, Part I, 1969.