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THE FEASIBILITY OF DIRECT GAS-PHASE CONVERSION OF UF_6 TO UC

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ABSTRACT

It is shown thermodynamically that the gas phase reaction of UF_6 with CH_4 and H_2 to form UC solid is approximately 80% complete at 2000°K and 0.01 atmosphere equilibrium pressure. UC formation is shown to be strongly favored by decreased pressure and increased temperature.

Thirteen pertinent reactions and their equilibrium constants as a function of temperature are tabulated.

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1. SUMMARY

Calculations from thermodynamic data (1,2,3) suggest the possibility of the direct gas-phase conversion of UF_6 to UC by reaction with a mixture of methane and hydrogen at temperatures of 2000°K and above, and equilibrium pressures of 0.01 atmosphere and below. Competing reaction paths considered are summarized in the following three reactions with corresponding equilibrium constant-temperature equations (see Appendix A):

$$UF_{6(g)} + CH_{4(g)} + H_{2(g)} \rightleftharpoons UC_{(s)} + 6HF_{(g)}, \qquad (8)$$

$$\log K_8 = -3.26 \times 10^4 \ (1/T) + 22.0;$$

$$UF_{6(g)} + 1/4CH_{4(g)} \rightleftharpoons UF_{4(s,l,g)} + 1/4CF_{4(g)} + HF_{(g)}, \qquad (11')$$

$$\log K_{11'} = -0.46 \times 10^4 \ (1/T) + 7.2 \ (1309\text{-}1723^\circ K)$$

$$\log K_{11'} = -1.37 \times 10^4 \ (1/T) + 12.0 \ (1723\text{-}2000^\circ K);$$

$$UF_{6(g)} + 2CH_{4(g)} \rightleftharpoons UC_{(s)} + CF_{4(g)} + 2HF_{(g)} + 3H_{2(g)}, \qquad (13)$$

$$\log K_{13} = -4.1 \times 10^4 \ (1/T) + 25.1.$$

Plots of the equations are shown in Fig. 1. The primary reactions and the secondary reactions derived therefrom which were used to arrive at the three reactions above are summarized in Appendix A along with their equilibrium constant-temperature equations.

2. EFFECTS OF TEMPERATURE AND PRESSURE

Under the assumption of equal initial reactant partial pressure, it is easy to calculate reaction yields of interest for the reactions independently. The effects of deviating from this assumption may be qualitatively predicted from the law of mass action, and in special cases may be easily calculated quantitatively.

The equilibrium expression for reaction 8 under the condition of equal initial reactant partial pressures may be written

$$K_8 = \frac{1728\ x^6\ P^3}{(A^2 - x^2)^3},$$

where x = moles of UC at equilibrium,

P = total pressure at equilibrium, and

A = moles of UF_6, CH_4, and H_2 initially present.

This equation may be solved for x/A at various temperatures, since K_8 is known as a function of temperature. The quantity 100 (x/A) is the percent conversion of UF_6 to UC. Figure 2 is a plot of 100 (x/A) vs T for the conditions P = 1 and P = 0.1 atmosphere, with a single point calculated for x/A = 0.90 at 0.01 atmosphere. The large influence of the change in equilibrium pressure is apparent. The points plotted in Fig. 2 were calculated assuming no reaction to occur other than reaction 8. In the actual case, reaction 11' occurs in competition with 8. Reaction 13 has been neglected since it also forms UC and its effect is beneficial. In addition, it does not contribute much to the overall reaction, as is apparent from Fig. 1. If reaction 11' is taken into account, the temperatures and pressures which must be employed to achieve specified conversions of UF_6 to UC may be estimated by making several approximations (Appendix B). The table below summarizes the results of several such estimations. (The values of temperature recorded in the table are not meant to reflect a knowledge of them

UC Formation at Several Temperatures and Pressures

(See Appendix B)

% UF_6 Converted to UC	Pressure, Atmos.	Temp., °K
90	0.01	>2000
80	0.01	~2000
70	0.01	1920
50	0.01	1810

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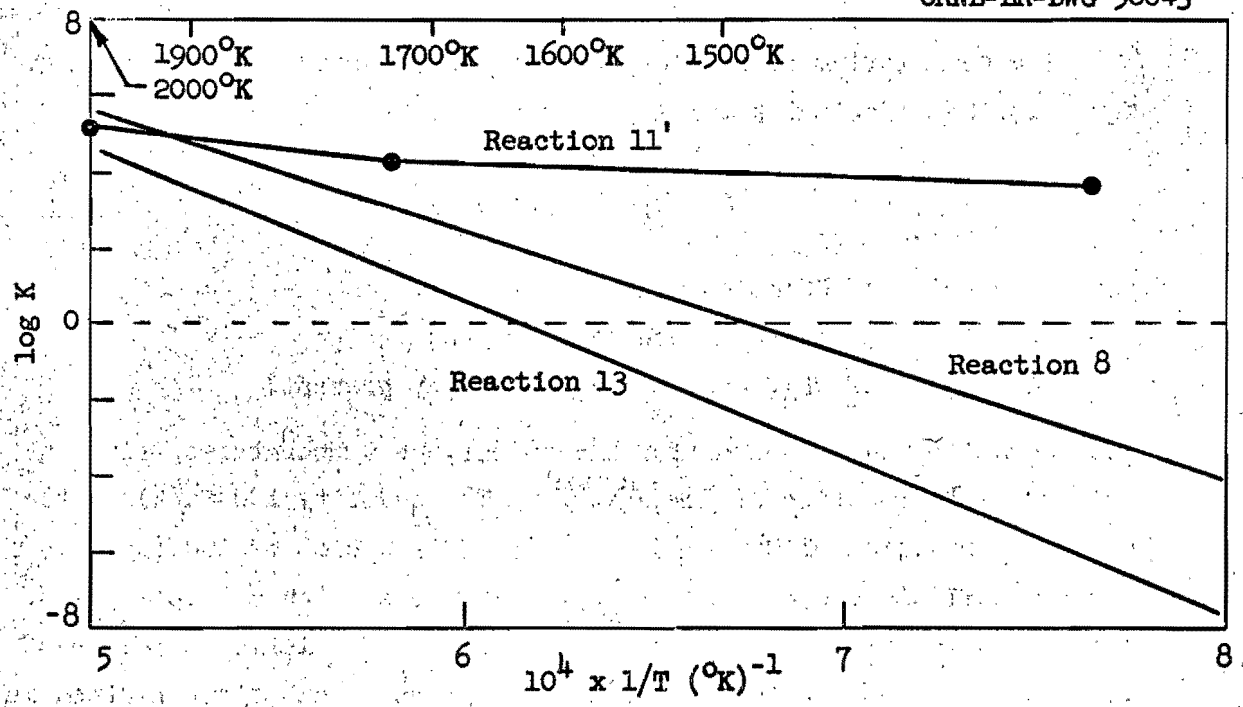

Fig. 1. Effect of Temperature on Equilibrium Constants for Reactions 8, 11' and 13.

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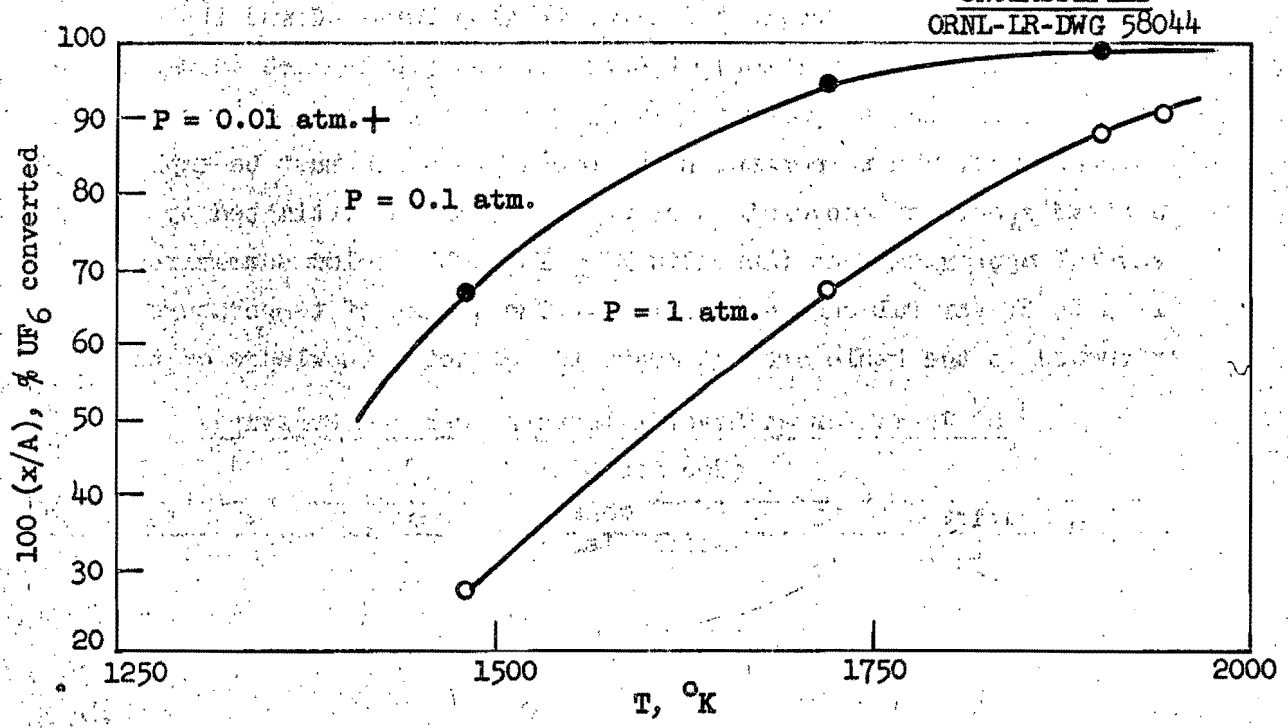

Fig. 2. Effect of Temperature on UC Yield Calculated for Reaction 8 at P = 1 and P = 0.1 and Equal Initial Reactant Partial Pressures.

to 5 or 10°K, but are merely recorded as they come out of the estimation procedure. If desired, the magnitude of error in the estimations may be evaluated from a consideration of the approximations made in the calculations involved in the estimation.) It is seen that the presence of the competing reaction 11' necessitates a large increase in temperature to obtain a 90% yield of UC at 0.01 atmosphere equilibrium pressure over that required for reaction 8 alone (see Fig. 2). It should be noted that the lower percentage conversions listed in the table do not meet the conditions of the approximations made in Appendix B, and should therefore be considered as highly tentative.

3. GENERAL CONSIDERATIONS

It is clear that excessively high temperatures and low pressures are required to achieve UC in good yield free of UF_4. However, UF_4 in the products would not be particularly deleterious, except insofar as it represents a parasitic consumption of UF_6. At the temperature needed to get good UC yields (~2000°K) nothing other than UC would be present as a solid. All other constituents of the equilibrium mixture would be gases, including UF_4, and these could be removed by an inert gas sparge. To avoid reaction of UC with UF_4 to form less volatile fluorides such as UF_3, it would be necessary to sparge at or above the principal reaction temperature. To avoid carbon deposition and possible formation of higher uranium carbides than UC, it seems that a slight deficiency of CH_4 under that required by reaction stoichiometry should be maintained.

It seems certain that the UC product would be extremely finely divided under most methods of carrying out the reactions, so its consolidation would pose a problem. Present technology would suggest arc melting at around 2800°K as a feasible approach to UC consolidation. The probable extremely high reactivity of the finely divided UC also suggests handling difficulties if high product purity is to be achieved.

The nature of the reactants and the indicated required temperatures make the problem of proper selection of materials of construction for process equipment difficult. Besides the obvious corrosive nature of

the UF_6, it must be recognized that the possibilities exist for hydrogen embrittlement as well as for carburization to occur.

It does not seem unreasonable to suggest the possibility of the use of a plasma jet for this synthesis of UC from UF_6, since the necessary temperatures are readily obtained, as are the pressures. Use of a plasma jet would obviate many of the materials of construction problems, and on the whole would quite likely solve more problems than it created. A possible bonus is that the UC product might be obtained in a consolidated form rather than finely divided, as suggested above. This possibility is apparent from the melting point shown in the table of properties of UC given below:

Physical Properties of UC

Melting point, ^{o}K (not well known)	2520-2910
Density, g/cm^3 at $25^{o}C$ (theoretical)	13.63
Thermal conductivity, $cal/sec \cdot cm \cdot {}^{o}C$	0.045 (393-509°K)

4. REFERENCES

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5. APPENDIX A

Summary of Reactions and Equilibrium Constant-Temperature Equations

Primary Reactions (T in ^{o}K; equilibrium concentrations in partial pressures)

1. $U_{(s,l)} + 3F_{2(g)} \rightleftharpoons UF_{6(g)}$ $\quad \log K_1 = 11.8 \times 10^4 (1/T) - 16.5$

2. $U_{(s,l)} + C_{(s)} \rightleftharpoons UC_{(s)}$ $\quad \log K_2 = 0.498 \times 10^4 (1/T) - 1.05$

3. $CH_{4(g)} \rightleftharpoons 2H_{2(g)} + C_{(s)}$ $\quad \log K_3 = -0.507 \times 10^4 (1/T) + 6.08$

4. $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$ $\quad \log K_4 = 2.85 \times 10^4 (1/T) + 0.13$

5. $C_{(s)} + 2F_{2(g)} \rightleftharpoons CF_{4(g)}$ $\quad \log K_5 = 4.74 \times 10^4 (1/T) - 7.83$

6. $U_{(s,l)} + 2F_{2(g)} \rightleftharpoons UF_{4(l,g)}$ $\quad \log K_6 = 8.86 \times 10^4 (1/T) - 8.9$ (1309-1723°K)
   $\log K_6 = 8.00 \times 10^4 (1/T) - 4.1$ (1723-2000°K)

Secondary Reactions

7. $UF_{6(g)} + 3H_{2(g)} \rightleftharpoons U_{(s,l)} + 6HF_{(g)}$ $\quad \log K_7 = -3.25 \times 10^4 (1/T) + 16.9$

8.* $UF_{6(g)} + CH_{4(g)} + H_{2(g)} \rightleftharpoons UC_{(s)} + 6HF_{(g)}$ $\quad \log K_8 = -2.63 \times 10^4 (1/T) + 27.1$

9. $4UF_{6(g)} + 4H_{2(g)} \rightleftharpoons 4UF_{4(l,g)} + 8HF_{(g)}$ $\quad \log K_9 = -0.36 \times 10^4 (1/T) + 30.9$ (1309-1723°K)
   $\log K_9 = -4.0 \times 10^4 (1/T) + 50.0$ (1723-2000°K)

10. $CH_{4(g)} + 2F_{2(g)} \rightleftharpoons CF_{4(g)} + 2H_{2(g)}$ $\quad \log K_{10} = 4.23 \times 10^4 (1/T) - 1.75$

11.* $4UF_{6(g)} + CH_{4(g)} \rightleftharpoons 4UF_{4(l,g)} + CF_{4(g)} + 4HF_{(g)}$ $\log K_{11} = -1.83 \times 10^4 (1/T) + 28.9$ (1309-1723°K)

$\log K_{11} = -5.47 \times 10^4 (1/T) + 47.9$ (1723-2000°K)

12. $CF_{4(g)} + 2H_{2(g)} \rightleftharpoons 4HF_{(g)} + C_{(s)}$ $\log K_{12} = 0.96 \times 10^4 (1/T) + 8.09$

13.* $UF_{6(g)} + 2CH_{4(g)} \rightleftharpoons UC_{(s)} + CF_{4(g)} + 2HF_{(g)} + 3H_{2(g)}$ $\log K_{13} = -4.10 \times 10^4 (1/T) = 25.1$

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*Equations 8, 11, and 13 are the three reactions considered as representative of those likely to occur between UF_6 and hydrocarbons. Equation 11 has been divided by 4 and the resulting equation called 11' in the body of this memo.

6. APPENDIX B

The effect on UF_6 conversion to UC of the simultaneous occurrence of reactions 8 and 11' may be estimated at various temperatures and pressures with the use of several approximations, as shown below.

A sum reaction of reactions 8 and 11' may be written in the form

$$\overset{(A-x-y)}{2UF_6} + \overset{(B-x-y/4)}{5/4\ CH_4} + \overset{(C-x)}{H_2} \rightleftharpoons \overset{(x)}{UC} + \overset{(y)}{UF_4} + \overset{(y/4)}{1/4\ CF_4} + \overset{(6x+y)}{7HF},$$

where the quantities in parentheses above the reactants and products are the moles of the respective substances present at equilibrium. Partial pressures of the gaseous substances may be expressed in terms of the moles present at equilibrium and the total equilibrium pressure, P. The partial pressure of UF_6 at equilibrium, p_{UF_6}, given as an example, is

$$p_{UF_6} = \frac{(A-x-y)\ P}{(A+B+C+4x+y)} .$$

The fractional conversion of UF_6 to UC, viz. x/A, under the condition of equal initial reactant partial pressures, is of primary concern here, so the above example is more convenient in the form

$$p_{UF_6} = \frac{(1-x/A-y/A)\ P}{(3+4\ x/A + y/A)} \ .$$

The equilibrium expression for reaction 8 is given in its most general form by

$$K_8 = \frac{p_{HF}^{\ 6}}{p_{UF_6} \cdot p_{CH_4} \cdot p_{H_2}} \ .$$

Substituting for the p's their corresponding equilibrium values in terms of x/A and y/A leads to the expression

$$K_8 = \frac{(6x/A+y/A)^6\ P^3}{(1-x/A-y/A)(1-x/A-y/4A)(1-x/A)(3+4x/A+y/A)^3} \ .$$

The equilibrium expression for reaction 11' is, similarly,

$$K_{11'} = \frac{(y/4A)^{1/4}(6x/A+y/A)(y/A)\ P}{(1-x/A-y/A)(1-x/A-y/4A)^{1/4}(3+4x/A+y/A)} \ .$$

The ratio $K_8/K_{11'}$ may be taken to give the expression

$$K_8/K_{11'} = \frac{(6x/A+y/A)^5\ P^2}{(1-x/A-y/4A)^{3/4}(1-x/A)(3+4x/A+y/A)^2(y/4A)^{1/4}(y/A)} \ .$$

From Figs. 1 and 2 and the reactions involved, it is apparent that the conversion of UF_6 to products, whether it be UC or UF_4, may be made essentially 100% complete by proper selection of temperature and pressure. Therefore, $x/A+y/A \approx 1$ to a very good approximation under conditions of low pressure and high temperature. Using this approximation, and letting the symbol F equal x/A, the above ratio may be written

$$K_8/K_{11'} \approx \frac{(5F + 1)^5\ P^2}{(3/4-3/4F)^{3/4}(1-F)^2(4+3F)^2(1/4-1/4F)^{1/4}} \ .$$

If it is specified that the reaction shall be carried out under conditions such that UC is the principal product, then the ratio may be simplified to

$$K_8/K_{11'} \approx \frac{278.5\ P^2}{(1-F)^3} \ , \quad x/A \gg y/A.$$

The assignment of numerical values to F and P permits calculation of $K_8/K_{11'}$, and the ratio $K_8/K_{11'}$ uniquely defines a temperature, as is apparent from Fig. 1. This is the procedure which was used to estimate the temperature values given in the table on page 3.

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