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URANIUM ISOTOPE SEPARATION BY CHEMICAL EXCHANGE REACTIONS BETWEEN UF_6 AND DERIVATIVES OF UF_6-NITROGEN OXIDE COMPLEXES

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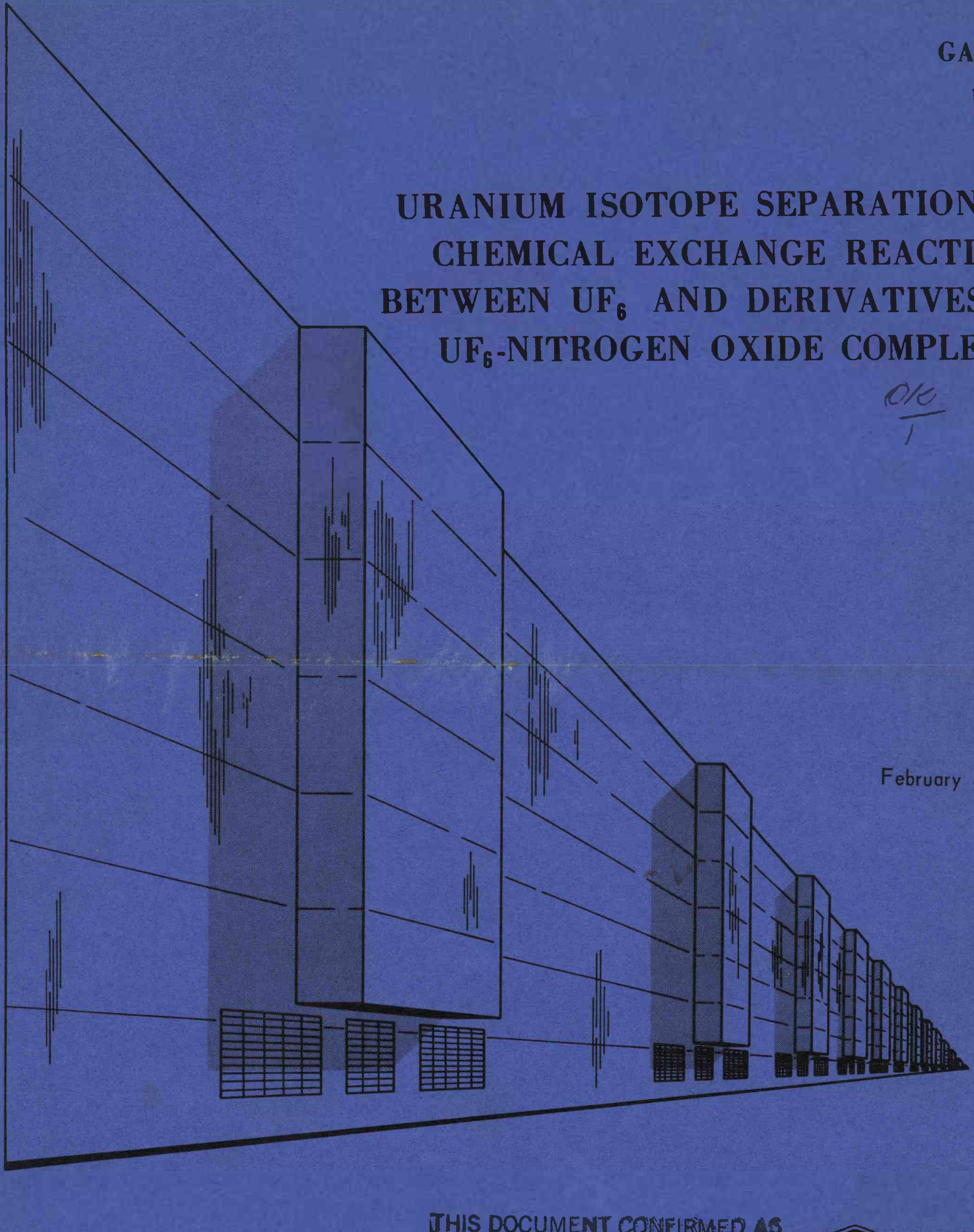

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Isotope Separation

URANIUM ISOTOPE SEPARATION BY CHEMICAL EXCHANGE REACTIONS BETWEEN UF_6 AND DERIVATIVES OF UF_6-NITROGEN OXIDE COMPLEXES

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February 4, 1972

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ABSTRACT

Chemical exchange reactions for the separation of the principal uranium isotopes have been investigated for systems consisting of uranium hexafluoride and nitrogen oxide-derived complexes of uranium hexafluoride. The equation representing the chemical equilibrium is:

$$^{238}UF_6 + NO^{235}UF_6 \rightleftharpoons {}^{235}UF_6 + NO^{238}UF_6$$

with the ^{235}U enrichment occurring in the UF_6 phase when UF_6 gas was contacted with solid $NOUF_6$. Single stage separation factors of 1.0016 at 25°C and 1.0011 at 70°C were observed. Similar results were obtained using $NOUF_7$ and NO_2UF_7 in place of $NOUF_6$. These exchange reactions were found to be impractically slow, but when they were catalyzed by HF, equilibrium time was reduced from about 100 hours to less than 2 hours. This led to an approach based on contacting two-phase immiscible solvent systems. The most promising system consisted of $NOUF_6$ dissolved in HF, a polar ionizing solvent that catalyzes the exchange, and UF_6 dissolved in Freon-114 ($C_2F_4Cl_2$). This system yielded a $^{235}U/^{238}U$ single stage separation factor of 1.0016 at 25°C after one hour of contact time. ^{235}U enrichment was always observed in the heavier (Freon-114) UF_6-containing phase. The system was investigated further in a column-type operation to determine how well it might operate in a large scale operation. This work was discontinued when difficulties were encountered in adapting the system to multi-stage operation or cascading. No efficient economic means could be found for interconverting $NOUF_6$ and UF_6 in their respective solvents and the work was discontinued.

This report summarizes the progress reports of P. R. Ogle, who performed the work during the period of October 1961 to December 1964.

INTRODUCTION

Successful development of methods of separating the ^{235}U and ^{238}U isotopes by chemical exchange reactions has never been realized even though exchange reactions are commonly used for the separation of the isotopes of boron, hydrogen, nitrogen, and other light elements. Principal reasons for this failure are the lack of suitable chemical systems for uranium and the fact that the separation factors for chemical processes, although quite large in the case of light atoms and molecules, rapidly become smaller as the atomic number increases[1]. On the other hand, since they are reversible, chemical separation processes require much less energy input than irreversible physical separation processes[1] such as gaseous diffusion or centrifugation. The equipment they require is much smaller since one of the phases is condensed. The advantages with respect to energy requirements and equipment size could combine to offset a lower separation factor and make chemical separation of the uranium isotopes economically competitive with, or superior to, the gaseous diffusion or centrifuge processes. Several potentially attractive applications of a chemical process for enriching uranium in the ^{235}U isotope can be visualized: (1) more economical production of partially enriched uranium for reactor fuel, (2) replacement of the bottom sections of the present diffusion cascades with equipment which would be cheaper to operate and maintain, (3) reduction of the ^{235}U content of tails material below the level which is economically feasible using gaseous diffusion.

The possibility of separating the uranium isotopes by chemical methods was investigated by H.C. Urey and co-workers at Columbia University in the period 1942-45. Theoretical considerations indicated that the separation factors for certain chemical processes would be sufficiently high to be competitive with gaseous diffusion provided other requirements were met. However, attempts to find a two-phase system suitable for countercurrent fractionation of the uranium isotopes were unsuccessful.

None of the systems tested could satisfy the combined requirements of chemical stability, rapidity of exchange, and degree of separative effect. In many cases, failure to find compounds having the desired chemical properties prevented further investigation. Undoubtedly, investigation also was hampered by the state of the art at that time with respect to making the isotope ratio analyses required to establish the degree of separation attained in each system tested. These requirements are now met by modern mass spectrometers.

In studies of reactions between nitrogen oxides and uranium hexafluoride,[2,3,4] several new solid compounds ($NOUF_6$, $NOUF_7$, and NO_2UF_7) have been prepared. In comparison with uranium hexafluoride (UF_6) these compounds affort sufficient differences in chemical uranium binding to suggest their application for isotopic separation in systems with UF_6. Exchange equilibria were examined in two basic systems: (1) gaseous UF_6 in contact with solid $NOUF_6$, $NOUF_7$, or NO_2UF_7; and (2) UF_6 in a suitable solvent such as Freon-114 in contact with $NOUF_6$ in a solvent such as liquid HF.

BRIEF EXPERIMENTAL SUMMARY

MATERIALS, APPARATUS AND PROCEDURE

The compounds, $NOUF_7$, NO_2UF_7, and $NOUF_6$ were prepared as required according to methods already described.[2,4] The formulas $NOF\cdot UF_6$ and $NO_2F\cdot UF_6$ are used interchangeably throughout for $NOUF_7$ and NO_2UF_7, respectively.

General chemical laboratory apparatus for safe handling of fluorine-containing compounds was employed. Where possible, all systems were constructed of Monel or nickel and the usual precautions for transfer and manipulation of such chemicals were followed. Details concerning the countercurrent column operation, employing a two-phase liquid system, are covered elsewhere.[5]

$^{235}U/^{238}U$ ratios were determined by electron bombardment mass spectrometry. All analyses were performed on UF_6--samples being converted from other forms to UF_6 when it was required. The separation factor (a) was calculated according to the definition:[6]

$$a = \frac{^{235}U/^{238}U \text{ (in } UF_6 \text{ phase)}}{^{235}U/^{238}U \text{ (in } NOUF_6 \text{ phase)}}$$

RESULTS AND DISCUSSION

Physical Properties of the Nitrogen Oxide Addition Compounds of Uranium Hexafluoride: $NOUF_7$, NO_2UF_7, and $NOUF_6$

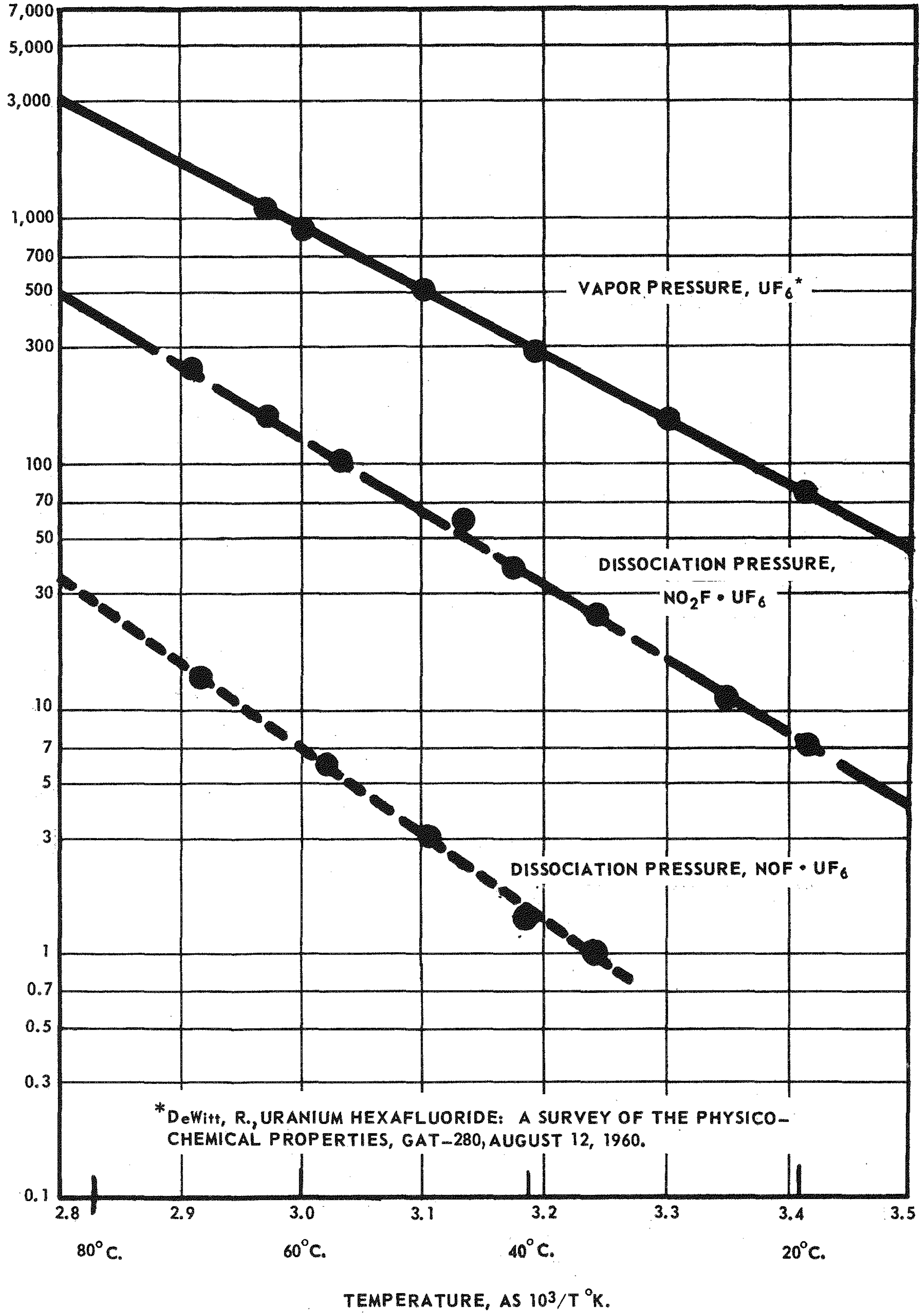
The dissociation pressures of $NO_2F\cdot UF_6(NO_2UF_7)$ and $NOF\cdot UF_6$ ($NOUF_7$) have been determined over the approximate temperature range 20-75°C and are compared in Figure 1 with the vapor pressure of uranium hexafluoride. (The vapor pressure of $NOUF_6$ is negligible in the same temperature range.) The compounds $NO_2F\cdot UF_6$ and $NOF\cdot UF_6$ are solids over the temperature range of the measurements. The dissociation pressure of $NO_2F\cdot UF_6$ from 20 to 70°C conforms to the equation,

$$\text{Log P} = 11.194 - \frac{3018}{T},$$

while the dissociation pressure of $NOF\cdot UF_6$ is represented by the equation,

$$\text{Log P} = 11.759 - \frac{3633}{T},$$

where P and T are in mm Hg, and T is in degrees Kelvin. Based upon the temperature dependence of the dissociation pressures as represented by these equations, the calculated heats of dissociation of $NO_2F\cdot UF_6$ and $NOF\cdot UF_6$ are 13.8 and 16.6 kcal/mole respectively. The larger value for $NOF\cdot UF_6$ suggests a greater contribution of an ionic form to the structure of the solid than in the case of $NO_2F\cdot UF_6$.



*DeWitt, R., URANIUM HEXAFLUORIDE: A SURVEY OF THE PHYSICO-CHEMICAL PROPERTIES, GAT-280, AUGUST 12, 1960.

Figure 1.

DISSOCIATION PRESSURE OF $NO_2F \cdot UF_6$ AND $NOF \cdot UF_6$ COMPARED TO VAPOR PRESSURE OF UF_6.

While $NOUF_6$ is completely ionic, a progressive loss of ionic character is exhibited by $NOF \cdot UF_6$ and $NO_2F \cdot UF_6$. Therefore, these three compounds afford a spectrum of structural types for investigation with regards to exchange reactions with uranium hexafluoride. Actual exchange experiments were attempted between each of the compounds and the hexafluoride, and, as described below in detail, the data indicate these systems favor enrichment of the lighter isotope, ^{235}U, in the UF_6 phase.

Isotope Exchange Equilibria Studies (Gas-Solid System)

The exchange reaction involving uranium atoms in UF_6 and the uranium-containing nitrogen oxide complexes was initially examined for systems consisting only of pure components, namely, gaseous UF_6 and one of the solid complexes, $NOUF_6$, $NOUF_7$ or NO_2UF_7. The UF_6 (gas)-$NOUF_6$ (solid) reaction resulted in enrichment of the ^{235}U content of the UF_6 gas phase. Accordingly, the exchange reaction for this system may be written with ^{235}U enrichment proceeding to the right side of the equation:

$$NO^{235}UF_{6(s)} + {}^{238}UF_{6(g)} \rightleftarrows NO^{238}UF_{6(s)} + {}^{235}UF_{6(g)}.$$

Data on the effect of time and temperature are graphically presented in Figures 2 and 3. The results show that (1) at 85°C equilibrium is not reached at well over 64 hours and possibly is not attained at 200 hours of contact time; (2) at the higher temperatures of 153° and 190°C, equilibrium is apparently attained at contact times of less than 100 hours; (3) the greatest degree of gas phase enrichment was achieved at the lowest temperatures (85°C) and contact times in excess of 100 hours; (4) at contact times of 200 hours, the degree of gas phase enrichment is inversely dependent upon temperature reflecting a shift to the left position in the exchange process; (5) at short contact times (64 and 16 hours), a maximum is observed in the temperature effect on the ^{235}U enrichment suggesting the combined effects of increased rate of exchange (predominating at lower temperatures) and the decrease in equilibrium constant (becoming the more important factor at the higher temperature). Corroborating the initial observations, increasing the $NOUF_6$-to-UF_6 mole ratio from 0.8-1.4 to 10-14 was found to increase, markedly, the apparent degree of $^{235}UF_6$ enrichment in the gas phase at 153°C (Figure 3). The equilibrium separation factor, α, is estimated from experimental data to be in the order of 1.002 at 85°C. However, the contact time required to reach equilibrium is much too long for a practical process. Several runs were made at 25°C and little if any enrichment of the gas phase was observed after 13 days. Thus, while increasing the temperature decreases the time required to reach equilibrium, the equilibrium constant shifts unfavorably, decreasing the separation factor.

Systems in which UF_6 gas is paired with solid $NOUF_7$ and NO_2UF_7 also yielded separation factors of significant magnitude; however, the equilibrium time was again observed to be impractically long. Although the highest separation factor was observed with the $NOUF_6$-UF_6 pair, the results obtained for the $NOUF_7$-UF_6 and NO_2UF_7-UF_6 systems suggest that further work could be done here.

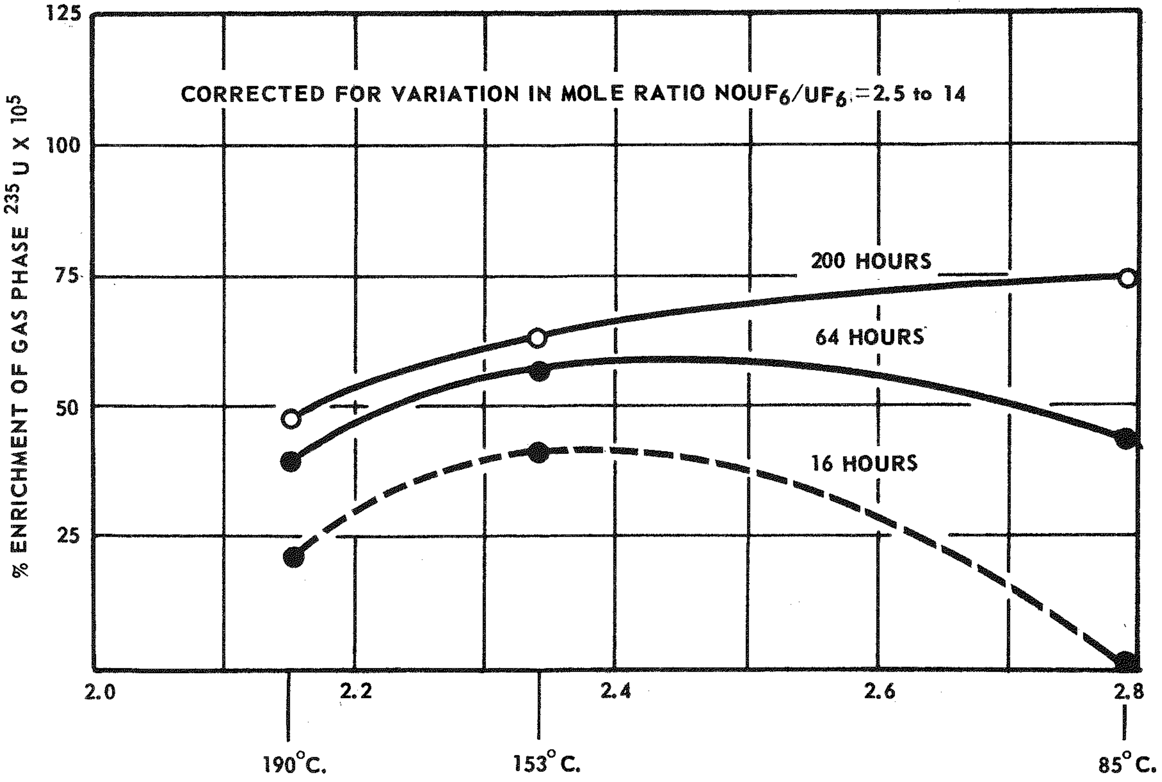


Figure 2.

EFFECT OF TEMPERATURE ON DEGREE OF GAS PHASE ENRICHMENT IN THE $NOUF_6$ SOLID–UF_6 GAS SYSTEM AT VARIOUS CONTACT TIMES

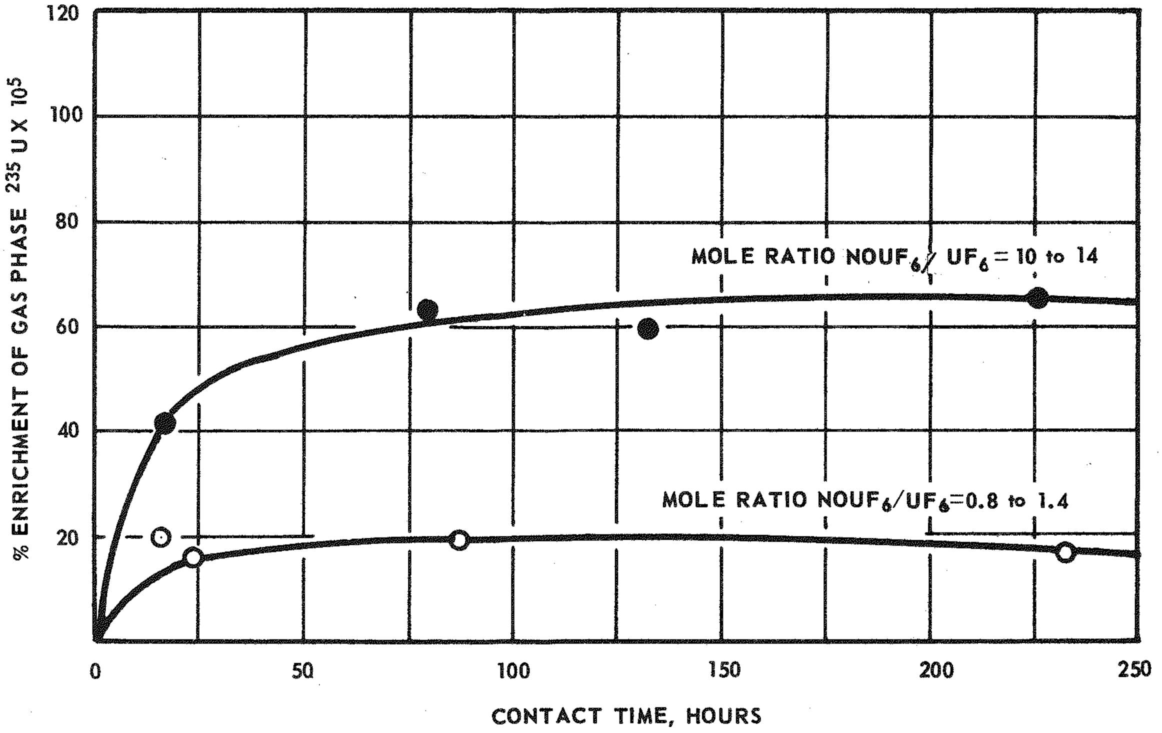


Figure 3.

EFFECT OF SOLID–GAS RATIO ON DEGREE OF GAS PHASE ENRICHMENT IN THE $NOUF_6$ SOLID–UF_6 GAS SYSTEM AT 153° C.

Several variations of the exchange reaction were attempted with the objective of decreasing the time required to reach equilibrium. These are summarized as follows:

1. Conducting the exchange by in situ preparation of the solid complexes: In these experiments excess UF_6 was reacted with NO, NO_2, NOF and NO_2F at 25°C, and the ^{235}U enrichment in the excess UF_6 was determined. No enrichment was observed when NO_2F or NOF was reacted with UF_6, but significant separation factors were measured when UF_6 was reacted with NO_2 or NO.

2. Use of solid or liquid UF_6: Little or no separation occurred when UF_6 was present in either liquid or solid phase in contact with $NOUF_6$, $NOUF_7$ or NO_2UF_7. Thus, under conditions investigated thus far, separation of appreciable enrichments had been observed only for systems containing UF_6 gas.

3. Use of HF: Hydrogen fluoride gas added to the UF_6-$NOUF_6$ system was found to have a beneficial effect upon the exchange. Significant enrichment of the uranium hexafluoride gas occurred even at 25°C after only 2 hours contact. Separation factors of 1.0016 at 25°C and 1.0011 at 70°C were measured.

Liquid HF System

Experiments were performed to determine the temperature dependence of uranium isotope enrichment, taking advantage of the ability of HF to promote the attainment of equilibrium, according to the following equation:

$$NO^{235}UF_6 \text{ (in HF solvent)} + {}^{238}UF_6 \rightleftarrows NO^{238}UF_6 \text{ (in HF solvent)} + {}^{235}UF_6$$

Solutions of $NOUF_6$ and UF_6 of the same uranium isotope composition in anhydrous HF were equilibrated at 0, 20, and 61°C. The UF_6 and HF were volatized rapidly from the $NOUF_6$, and the equilibrium constant for the reaction was determined from the uranium isotopic composition of the UF_6. The results presented in Table I show the temperature dependence of the reaction and verify the necessity of chemical exchange between two separated uranium compounds rather than a mere solvent partition to achieve any isotope separation.

TABLE I
TEMPERATURE VARIATION OF EQUILIBRIUM CONSTANT
FOR THE SYSTEM $NOUF_6/HF - UF_6$

Temperature (°C)	Equilibrium Constant Single Stage or Separation Factor, *a*
0	1.00157
20	1.00136
61	1.00108

Liquid-Liquid System

A more convenient approach to achieving the same exchange reaction is one based on the countercurrent flow of two immiscible solvent systems. Systems consisting of $NOUF_6$ dissolved in anhydrous HF and UF_6 dissolved in perfluorotributyl-amine (PFTBA) were tested. At 25°C single stage enrichment factors (α) of 1.0012 and 1.0016 were obtained with PFTBA and Freon-114, respectively. Further runs were made using the Freon-114 - HF solvent systems. Based on a total of 14 values of changes in isotopic ratios in both phases of the system, the average α was calculated to be 1.00142 ± 0.00061 at the 95 percent confidence interval. Data taken at various time intervals suggest that equilibrium is reached in one to two hours.

The ability of HF to promote the attainment of equilibrium in a short time suggested the possibility of a UF_6-HF-Freon-114 system (without the presence of $NOUF_6$) since UF_6 may form complex ions such as UF_7^- or $UF_8^=$ in liquid HF, but not in Freon-114. Experiments based on this approach were attempted but no isotopic separation was observed.

To characterize the Freon-114/HF immiscible solvent system, the distribution coefficient of UF_6 between the two immiscible solvents, Freon-114 and liquid HF, was measured at varying total UF_6 content and a fixed $NOUF_6$/HF ratio. The results shown in Table II indicate the distribution coefficient is reasonably constant up to a concentration of 0.48 gUF_6/g in Freon-114. This suggests the presence of similar species occurring in both phases under these conditions. Similar data on the distribution coefficient for $NOUF_6$ in the two solvents were not obtained.

TABLE II
DISTRIBUTION COEFFICIENT OF UF_6* BETWEEN FREON-114
(HEAVY PHASE) AND LIQUID HF (LIGHT PHASE)

Conc. UF_6 (g/g) in Freon-114	Conc. UF_6 (g/g) in Liquid HF	Distribution Coefficient $= \frac{g\ UF_6/g\ \text{Freon-114}}{g\ UF_6/g\ \text{Liquid HF}}$
0.2488	0.0583	4.268
0.4400	0.997	4.413
0.4550	0.1109	4.103
0.4827	0.1147	4.208
0.4903	0.1574	3.115

---

*The weight ratios of $NOUF_6$/HF in the 5 tests were between 0.70 and 0.77.

Extensive liquid-liquid separation tests on the Freon-114-UF_6/liquid HF-$NOUF_6$ system were made on both a batch system and on a 17-foot column. Some success was achieved operating the column initially without refluxing. Difficulties were encountered, however, when attempts were made to achieve reflux of even one phase of the system, i.e., the UF_6-Freon phase that was converted to $NOUF_6$. In view of the difficulties, and of the fact that the $NOUF_6$ conversion to UF_6 is even more difficult chemically, work on isotope separation by this system was discontinued. A detailed report of the work on uranium isotope separation using $NOUF_6$ and UF_6 in a two-phase liquid system has been prepared by Nugent and Ogle.~~[8]~~[5]

Miscellaneous Compounds Also Prepared and Evaluated

1. $C_5H_5NUF_6$ - A solid of this approximate composition is formed by the reaction of pyridine with either UF_6 or NOF_6. Data have been obtained indicating that recovery of UF_6 from the solid would be too difficult.

2. $C_5H_5NUO_2F_2$ - Precipitated from an aqueous solution of uranyl fluoride by the addition of pyridine. It is a yellow, non-volatile solid infusible as high as 300°C. It has a density of 3.04 g/cm^3 at 0°C. No solvents could be found for the solid, and it is, therefore, not amenable to chemical exchange systems of the type described in this report.

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