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K-790(Del.)

Date of Issue: July 13, 1951

[redacted]

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EXCHANGE OF URANIUM BETWEEN BETA URANIUM PENTAFLUORIDE AND GASEOUS URANIUM HEXAFLUORIDE

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Report Number: K-790

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Subject Category: CHEMISTRY-GENERAL

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Author: W. Davis, Jr. and G. P. Rutledge

ABSTRACT

Exchange of uranium between beta uranium pentafluoride and gaseous uranium hexafluoride has been studied in the temperature range 80 to 140°C. Series experiments, consisting of exposure of a sample of enriched (17.98 wt. % U-235) uranium pentafluoride to several successive samples of normal uranium hexafluoride, as well as one-exposure experiments have been performed. The decrease in first order rate constants for successive exposures, as well as the absolute values of these constants, indicates that neither chemical reaction at the gas-solid interface nor diffusion of uranium hexafluoride through an adsorbed gas layer controls the rate of exchange of uranium between gas and solid. Exchange rates are compatible with a process controlled by diffusion of uranium in and through the solid. Estimates of the diffusion coefficient vary from 0.3 to 11 x 10^{-14} sq. cm./hr. (on the basis of nitrogen surface areas and the assumption of uniform particle size). The effect of temperature is poorly defined by the present data, being equivalent to an activation energy for diffusion of 7.3 ± 12.5 kcal./mole. Over the temperature range 80 to 140°C. the average value of the diffusion coefficient is 2.6 x 10^{-14} sq. cm./hr.

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EXCHANGE OF URANIUM BETWEEN BETA URANIUM PENTAFLUORIDE AND GASEOUS URANIUM HEXAFLUORIDE

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The earliest exchange experiments performed in connection with the Manhattan Project were those of Grosse (7) involving the system liquid uranium hexafluoride-uranium tetrafluoride. At low temperatures, in the order of 100°C., Grosse found that exchange of uranium between these two compounds proceeded through formation of the intermediate uranium pentafluoride. A half-time of 360 hours was obtained for the "non-catalytic" reaction at 97 to 99°C. These studies established exchange of uranium between uranium hexafluoride and both uranium tetrafluoride and uranium pentafluoride. Further, they indicated that exchange of uranium between uranium hexafluoride and the intermediate uranium fluorides (UF_5, U_2F_9, U_4F_{17}) could proceed through partial decomposition of the latter, according, for example, to equation 1.

$$\left.\begin{aligned} &2\ UF_5 \longrightarrow UF_6 + UF_4 \\ &U^*F_6 + UF_4 \longrightarrow U^*F_5 + UF_5 \end{aligned}\right\} \qquad (1)$$

Two important questions remained unanswered by Grosse's data: 1) the nature of the process(es) controlling the rate of exchange; 2) the rate of exchange in gas-solid systems. There are three limiting processes that may be involved in exchange in heterogeneous systems: 1) diffusion of gas (or liquid) through a film of adsorbed gas (or liquid); 2) chemical reaction within the solid; 3) diffusion in and through the solid. A major purpose of the present work has been to establish whether one of these controls the rate of exchange of uranium between gaseous uranium hexafluoride and beta uranium pentafluoride. The second objective of the present work has been to determine exchange rate constants in gas-solid systems at several temperatures, thereby providing an estimate of the activation energy for this reaction.

EXPERIMENTAL

Materials

The beta form of uranium pentafluoride was prepared according to the method of Grosse (8) (see appendix B). Normal (0.7115 wt. per cent U-235) uranium tetrafluoride was reacted with excess enriched (28.89 wt. per cent U-235) uranium hexafluoride in a nickel container at 100°C. for 744 hours. X-ray diffraction and chemical methods were used to analyze the resulting uranium pentafluoride. Isotopic analysis (by the fission counting technique) of this material indicated an assay of 17.98 weight per cent U-235. Chemical analysis of the compound is given in table I. Surface area measurements were run on two portions of the uranium pentafluoride before exchange and on one sample (from Run No. VIII) after exchange. These gave values of specific surface of 0.87 and 0.66 square meters per gram before exchange and 0.57 square meters per gram after exchange.

TABLE I

ANALYSIS OF BETA URANIUM PENTAFLUORIDE

	Composition, weight per cent			
Material	U	F	U^{+4}	U^{+6}
Sample	71.5	28.0	37.7	36.1
Theoretical for UF_5	71.5	28.5	35.7	35.7

Uranium hexafluoride used in this work contained less than 0.015 weight per cent impurity. When vapor pressures at room temperature or 0°C. were higher than reported values (6) this material was pumped at room temperature or 0°C. until correct pressures were obtained.

Apparatus

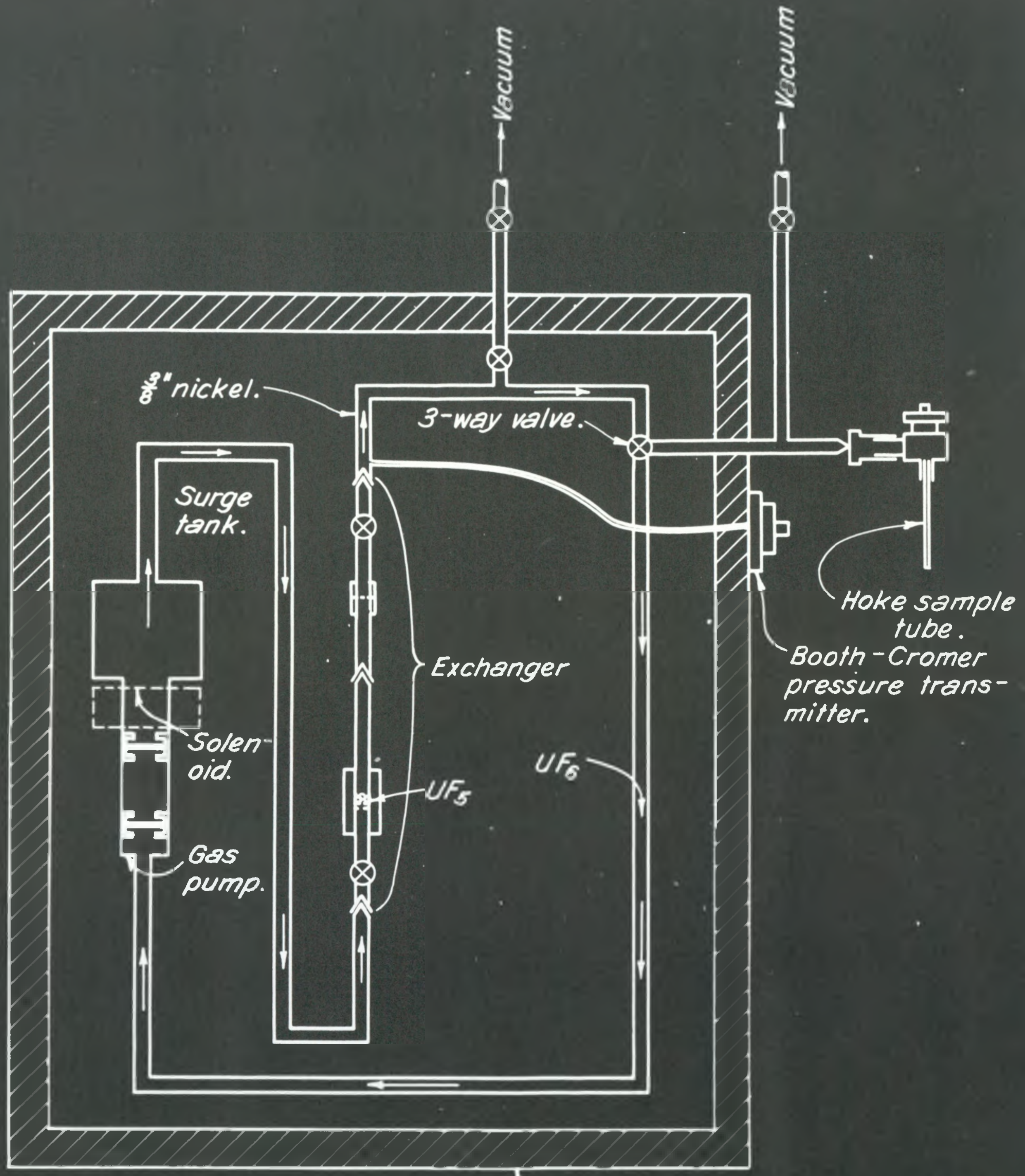
Diagrams of the system, exchanger, and pump are given in figures 1, 2, and 3. The pump shell was made from 3/4 inch diameter monel tubing; 3/8 inch Hoke, monel body, diaphragm valves were used throughout. All other components were made of nickel. The total volume of the system was 433 cc. in five experiments and 409 in the other three.

A pump modeled after that of Porter, Bardwell, and Lind (12) was used to circulate uranium hexafluoride through the system. Details of this pump are shown in figure 3. Flows of uranium hexafluoride at operating pressures were not determined; however, at atmospheric pressure and at piston frequencies of about 70 per minute (the same as those used in the exchange experiments) the pumping capacity was about 2 to 10 liters of air per hour, during direct discharge into a wet test meter. Current used to operate the pump solenoid was controlled by a thyratron which, in turn, was triggered by a neon bulb relaxation oscillator.

The exchanger, shown in detail in figure 2, was designed to permit loading with uranium pentafluoride in a dry box.

Procedure

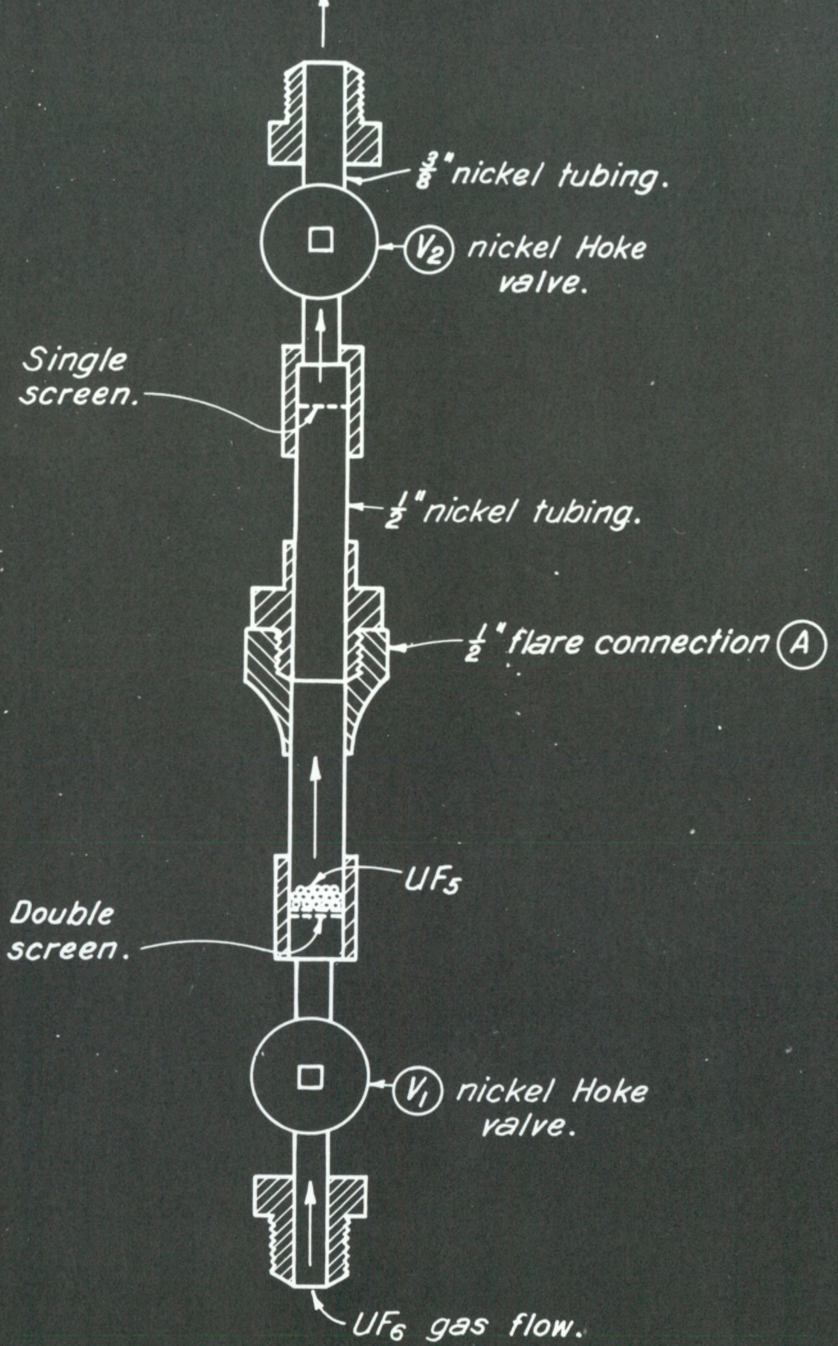
Transfer of uranium pentafluoride from a closed container to the reactor was performed in a dry box, maintained with nitrogen at a dew point of -30°C. or lower. The solid charge, always as close to 1.47 g. as possible, was weighed in the dry box with an accuracy of 0.01 g. and then loaded into the exchanger (figures 1 and 2). Flare connection A (figure 2), and both Hoke valves (V_1, V_2) were closed tightly before the unit was removed from the dry box. Following further tightening of the flare in a vice the exchanger was inserted into the system. The latter, with the exception of the exchanger, was evacuated and treated with fluorine at about 1 atmosphere pressure and 100°C. for 2 days. Fluorine was then exhausted to a soda-lime trap, following which the entire system, including exchanger, was pumped until the leak rate was less than 1 x 10^{-5} mm./min.



LEGEND:
○ ---- Ni Hoke valves.
← ---- Direction of UF$_6$ gas flow.

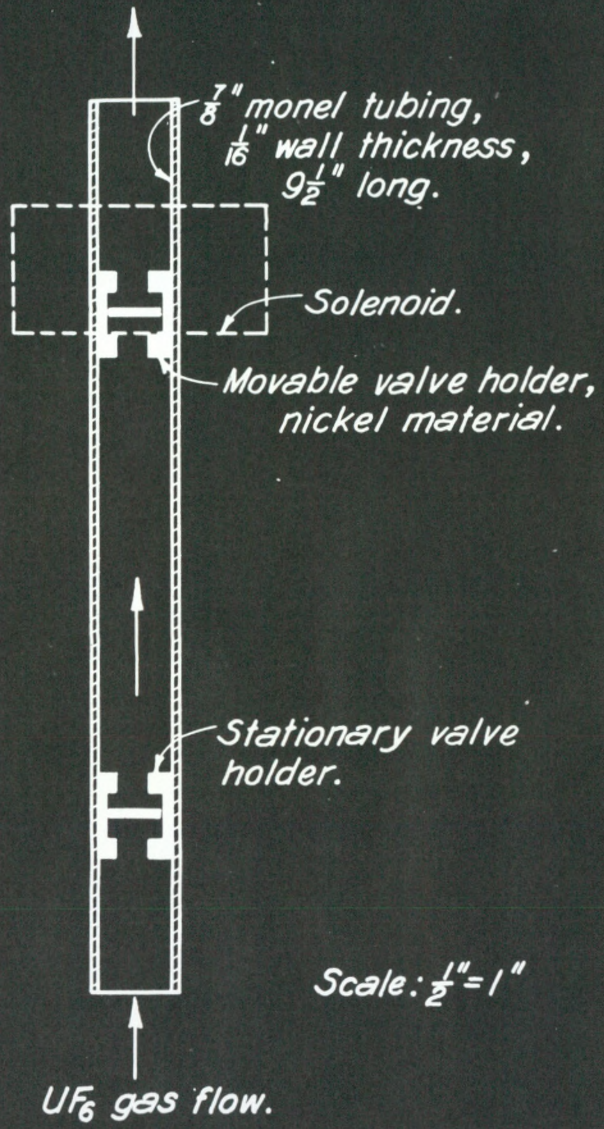
EXCHANGE SYSTEM

FIGURE I



EXCHANGER

FIGURE 2



GAS PUMP

FIGURE 3

Uranium hexafluoride was admitted to the system after the exchanger had been closed (V_1 and V_2). The latter was placed on-stream only after the circulation pump had been started and the air thermostat was maintaining the desired temperature.

About a week after an exchange experiment had been started, all uranium hexafluoride was condensed into a Hoke sample tube. This material was then submitted for isotopic (mass spectrometer) analysis. Without changing the uranium pentafluoride sample, the system was recharged with normal uranium hexafluoride and a second run at the same temperature was initiated.

New charges of uranium pentafluoride were used to start experiments at different temperatures; in some cases only a single test was performed on a sample of solid.

RESULTS

Exchange experiments were performed at 80, 100, 120, and 140°C. Some of these consisted of consecutive exposures, designated by 1, 2, etc., of a sample of uranium pentafluoride to three or four charges of normal uranium hexafluoride; others consisted of reacting a solid sample with uranium hexa- only once. Results, based on mass spectrometer assay of the gas phase, as well as other experimental data, are summarized in table II.

Average uranium pentafluoride assays listed in table II were calculated by means of the U-235 material balance equation 2.

$$n^s A_o^s + n^g A_o^g = n^s A^s + n^g A^g \qquad (2)$$

A_o^s = initial assay of solid.

A_o^g = initial assay of gas (always 0.7115 wt. % U-235).

A^s = assay of solid at the sampling time, t.

A^g = assay of gas at the sampling time, t.

n^s = quantity (moles) of exchanging material in the solid phase.

n^g = quantity (moles) of exchanging material in the gas phase.

The extent of exchange was calculated according to equation 3 and the assumption that, at equilibrium, gas and solid would have the same assay.

$$F = \frac{A_o^g - A^g}{A_o^g - A_\infty} \qquad (3)$$

F = the fractional exchange toward equilibrium.

$$A_\infty = \frac{n^s A_o^s + n^g A_o^g}{n^s + n^g} = \text{equilibrium assay of gas and solid.}$$

TABLE II

ISOTOPIC EXCHANGE DATA FOR THE SYSTEM URANIUM PENTAFLUORIDE-GASEOUS URANIUM HEXAFLUORIDE*

Run No.	Exposure No.	Temp., °C.	Contact Time, hr.	UF_6 Charge, g.	Mole Ratio UF_5/UF_6, n^s/n^g	Final UF_6 Assay, wt. % U-235	Calculated Final Average UF_5 Assay, wt. % U-235	Extent of Exchange, %
I	1	80	143	1.414	1.091	1.691	17.08	10.87
	2	80	143	1.785	0.865	0.897	16.87	2.44
	3	80	167	1.845	0.837	0.851	16.70	1.90
II	1	80	142	1.801	0.857	1.021	17.62	3.88
	2	80	142	2.060	0.749	0.791	17.51	1.10
	3	80	142	1.972	0.783	0.761	17.45	0.67
III	1	100	142	2.082	0.741	1.347	17.12	8.65
	2	100	142	1.725	0.895	1.060	16.73	4.50
	3	100	145	1.651	0.934	0.982	16.44	3.49
IV	1	120	149	1.716	0.899	3.324	15.07	31.95
	2	120	161	1.725	0.895	1.266	14.45	8.18
	3	120	162	1.933	0.798	0.912	14.20	3.29
V	1	120	142	1.776	0.869	1.341	17.26	7.84
VI	1	120	142	2.180	0.708	1.057	17.49	4.83
VII	1	140	142	1.810	0.853	2.318	16.10	20.21
	2	140	142	2.018	0.765	1.226	15.42	7.72
	3	140	142	1.982	0.779	1.121	14.90	6.36
	4	140	574	2.051	0.752	2.185	12.95	24.19
VIII	1	140	142	2.057	0.750	1.586	16.81	11.81

*All UF_5 charges were 1.47 ± 0.01 g.; original assay of solid was 17.98 wt. % U-235
All UF_6 charges were of 0.7115 wt. % U-235

Photomicrographs, with a magnification of 6,000X, of uranium pentafluoride used in this work are shown in figure 4.

DISCUSSION

Gas-solid exchange reactions can be controlled by one or more of three processes. These are: 1) diffusional transfer of the exchanging species through a film of adsorbed gas; 2) chemical reaction at the gas-solid interface; 3) diffusion of the exchanging components within the solid. Each of these has been discussed by Zimens (15) in considerable detail. Isotopic exchange of uranium between uranium hexafluoride and beta uranium pentafluoride will be controlled by but one of the three processes only if the other two are relatively fast. Using the notation of Zimens, the rate laws governing these for spherical particles of constant diameter are given in equations 4, 5, and 6.

Diffusion through a surface film is the rate controlling process:

$$\frac{A^g - A_\infty}{A_o^g - A_\infty} = e^{-t/\tau_z} \tag{4}$$

$$\tau_z = \frac{n^s \delta}{q\, D^g c^g}(1-s) = \frac{1-s}{K_z} \tag{4a}$$

$$\left.\begin{aligned} \frac{D^g}{\delta} &= \frac{1}{\tau_z} \cdot \frac{n^s(1-s)}{q\, c^g} = \frac{1}{\tau_z}\,\frac{n^s}{q}\left(\frac{n^g}{n^s + n^g}\right)\frac{V}{n^g} \\ \frac{D^g}{\delta} &= \frac{sV}{q\tau_z} \end{aligned}\right\} \tag{4b}$$

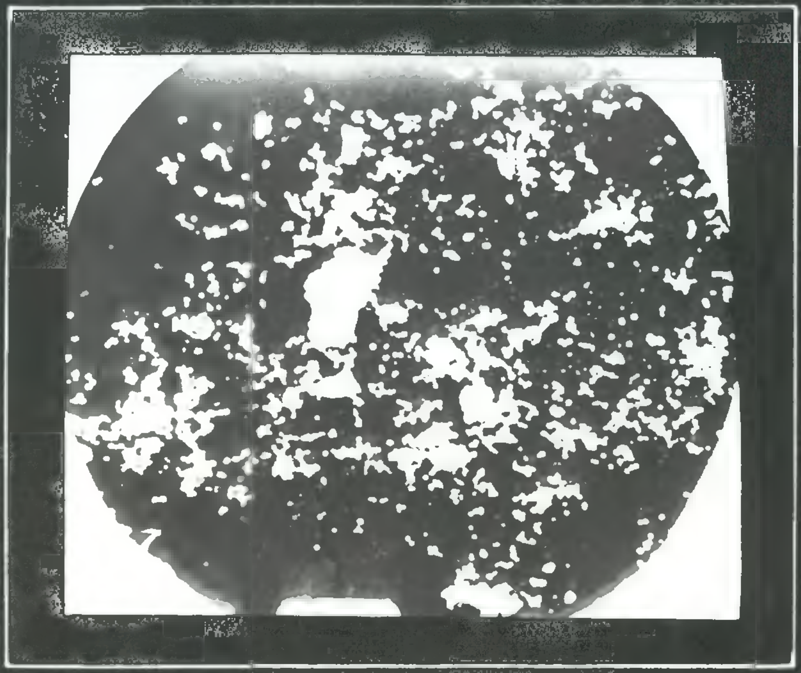
Chemical reaction within the solid is the rate controlling process:

$$\frac{A^g - A_\infty}{A_o^g - A_\infty} = e^{-t/\tau_R} \tag{5}$$

$$\tau_R = \frac{n^s}{\dot{n}}\,(1-s) = \frac{(1-s)}{K_R} \tag{5a}$$

$$\dot{n} = \frac{n^s(1-s)}{\tau_R} \tag{5b}$$

Diffusion within the solid is the rate controlling process:

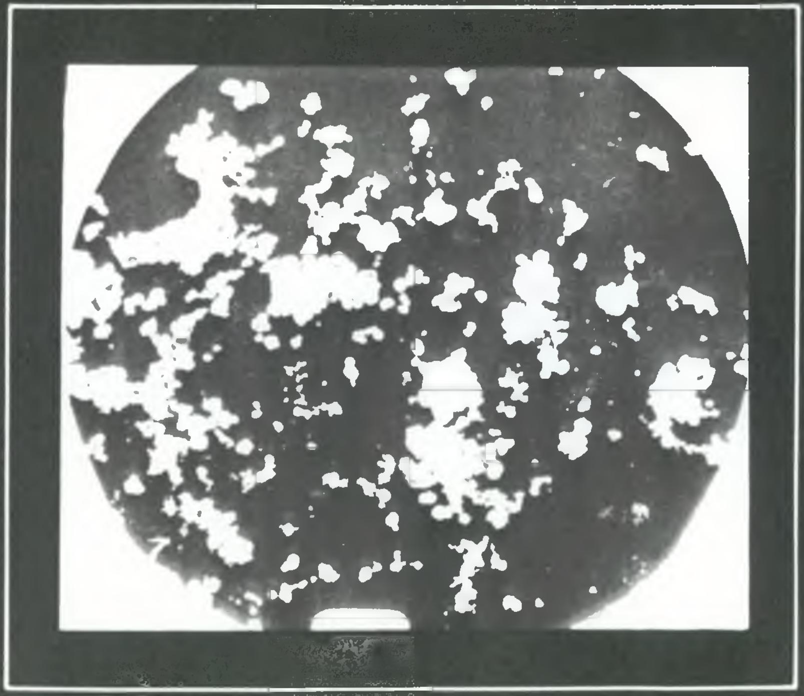


a. Sample not exchanged but used in Nitrogen Surface Area detemination.

6000 Diameters

Scale

1μ



b. Sample exchanged in run VIII at 140°C.

6000 Diameters

Electron Micrograph of Beta Uranium Pentafluoride

Figure 4

$$\frac{A^g - A_\infty}{A_o^g - A_\infty} = \sum_{m=1}^{\infty} \frac{2\left[1 + \frac{n^s}{n^g}\right] e^{-t/\tau_m}}{\frac{R^2}{3D\tau_m} + 3\left(\frac{n^s}{n^g}\right) + 3\left(\frac{n^s}{n^g}\right)^2} \tag{6}$$

$$\text{cot.}\ \frac{R}{\sqrt{D\tau_m}} = \frac{\sqrt{D\tau_m}}{R} + \frac{R}{3\frac{n^s}{n^g}\sqrt{D\tau_m}} \tag{6a}$$

V = volume of the system, in cc.

δ = thickness of surface (gas) film.

q = area of solid.

D^g = coefficient of diffusion of gaseous species (UF_6) through the surface (gas) film.

c^g = concentration (moles/cc.) of gas.

s = $n^s/(n^s + n^g)$

$\dot{n}$ = the total quantity of material (in moles) that migrates from one phase to the other through the exchange cross section (surface area) per unit time.

D = coefficient of diffusion of uranium through solid uranium pentafluoride.

R = radius of a spherical particle of solid (here assumed to be constant).

m = running number (1,2,3, etc.).

τ_z = time constant for exchange controlled by diffusion through a surface film.

τ_R = time constant for exchange controlled by chemical reaction.

τ_m = time constants for exchange controlled by diffusion within the solid.

Values of rate constants calculated according to equations 4 through 6a are listed in table III. First order rate constants ($\frac{1}{\tau}$ or K) are applicable to calculations involving diffusion through a surface gas film or chemical reaction as the rate controlling process, all other reactions being assumed relatively fast. From estimates of $\frac{1}{\tau}$ the quantities D^g/δ (diffusion through a surface gas film) and $\dot{n}$ (chemical reaction) have been calculated. These are given in table III. If either one of these processes is the controlling factor in the rate of exchange, then diffusion of uranium within the solid must be rapid. Hence, essentially no assay gradient should exist in the solid. Each successive experiment within a series should then represent exchange of a homogeneous solid uranium pentafluoride with normal uranium hexafluoride, in which case the first order rate constants ($\frac{1}{\tau}$) should be constant except for small variations resulting from minor changes in the quantity of gas. Correction for these changes have been made to obtain the quantities D^s/δ and $\dot{n}$ in table III. It is quite obvious that these are not constant; rather, they decrease from experiment to experiment within a series. Thus, exchange of uranium between beta uranium pentafluoride and uranium hexafluoride appears not to be controlled by diffusion of uranium hexafluoride through a surface (gas) film or by chemical reaction at the gas-solid interface.

Qualitatively, other observations support the validity of the last statement. Thus, diffusion coefficients in many aqueous and organic liquids (11) are in the order of 10^{-5} sq. cm./sec. From table III it may be seen that the quantity D^g/δ is in the order of 10^{-5} cm./hr. The thickness, δ, of uranium hexafluoride adsorbed on uranium pentafluoride is not known exactly, but its value within a factor of 100 can be estimated. Pressures in the present experiments were in the order of 30 to 50 cm. of uranium hexafluoride, corresponding to a range in relative pressures (P/P_0) at 80 to 140°C. of 0.27 to 0.04 (6). Measurements of adsorption of uranium hexafluoride on calcium fluoride (1) [redacted] have shown that at such relative pressures, no more than a monolayer (about 4 Å. thick) of uranium hexafluoride would be adsorbed. Thus, if uranium hexafluoride is adsorbed about as strongly on beta uranium pentafluoride as it is on calcium fluoride [redacted] δ would have a value of about 4×10^{-8} cm.

Estimates of the amount of uranium hexafluoride charged into the reactor were made on the basis of PVT measurements. These agreed so closely (0.1 to 0.2 g. out of 1.5 to 2 g.) with estimates obtained by weighing the hexafluoride source can that extensive adsorption under experimental conditions can be precluded. Hence, the value of δ is certainly no larger than 100×10^{-8} cm., in which case D^g (i.e., the value that would be calculated for the coefficient of self diffusion of uranium hexafluoride through a thick surface film, having the properties of liquid uranium hexafluoride) would be in the order of 10^{-11} sq. cm./hr., or 10^{-14} sq. cm./sec. If this number were valid it would indicate that the diffusion of uranium hexafluoride molecules through liquid hexafluoride is slower by a factor of 10^9 than is diffusion of molecules in aqueous and organic liquids. Such a discrepancy is much too large to be reasonable, and furnishes additional evidence that diffusion of uranium hexafluoride molecules through a surface film is not the rate controlling process.

A second qualitative observation provides further evidence that chemical reaction at the gas-solid interface is not the rate controlling process in the exchange of uranium between uranium hexafluoride and beta uranium pentafluoride. Thus, Agron (2) and others who have reported the vapor pressures of uranium hexafluoride over beta uranium pentafluoride have found that equilibrium pressure is obtained within a few hours. First order time constants (τ) calculated from results in table III indicate "half-exchange times" in the order 10^3 to 10^4 hours.

Diffusion of uranium within the uranium pentafluoride has been indicated as the exchange-rate controlling factor by elimination of the other two possibilities. Coefficients of diffusion, calculated on the basis of an average particle radius from surface area measurements, are summarized in table III. Details of calculation are indicated in appendix A.

TABLE III

RATE CONSTANTS IN THE EXCHANGE OF URANIUM BETWEEN URANIUM HEXAFLUORIDE AND URANIUM PENTAFLUORIDE

			First Order Rate Constants			
Run No.	Exposure No.	Temp., °C.	Time Constant, $\frac{1}{\tau} \times 10^{4}$, per hr.	Diffusion through Surface Film $(D^{g}/\delta) \times 10^{6}$, cm./hr.	Chemical Reaction $\dot{n} \times 10^{6}$, moles/hr.	Apparent Diffusion Coefficient*,**, $D \times 10^{14}$, sq. cm./hr.
I	1	80	8.05	16.	1.7	1.0
	2	80	1.73	3.1	0.41	(0.36)
	3	80	1.15	2.0	0.27	(0.31)
II	1	80	2.79	5.0	0.66	0.31
	2	80	0.782	1.3	0.20	(0.12)
	3	80	0.472	0.81	0.12	(0.074)
III	1	100	6.37	11.	1.6	1.1
	2	100	3.24	6.0	0.75	(0.74)
	3	100	2.45	4.6	0.56	(0.79)
IV	1	120	25.8	48.	6.0	11.
	2	120	5.30	9.8	1.2	(4.2)
	3	120	2.07	3.6	0.50	(2.0)
V	1	120	5.75	10.	1.3	0.74
VI	1	120	3.49	5.3	0.90	0.55
VII	1	140	15.9	29.	3.8	4.2
	2	140	5.66	9.6	1.4	(3.3)
	3	140	4.63	7.9	1.1	(3.6)
	4	140	4.82	8.1	1.2	(5.5)
VIII	1	140	8.85	14.	2.2	1.6

*Based on nitrogen adsorption value of average particle radius (0.68×10^{-4} cm. before exchange).
**Values in parentheses are not considered reliable.

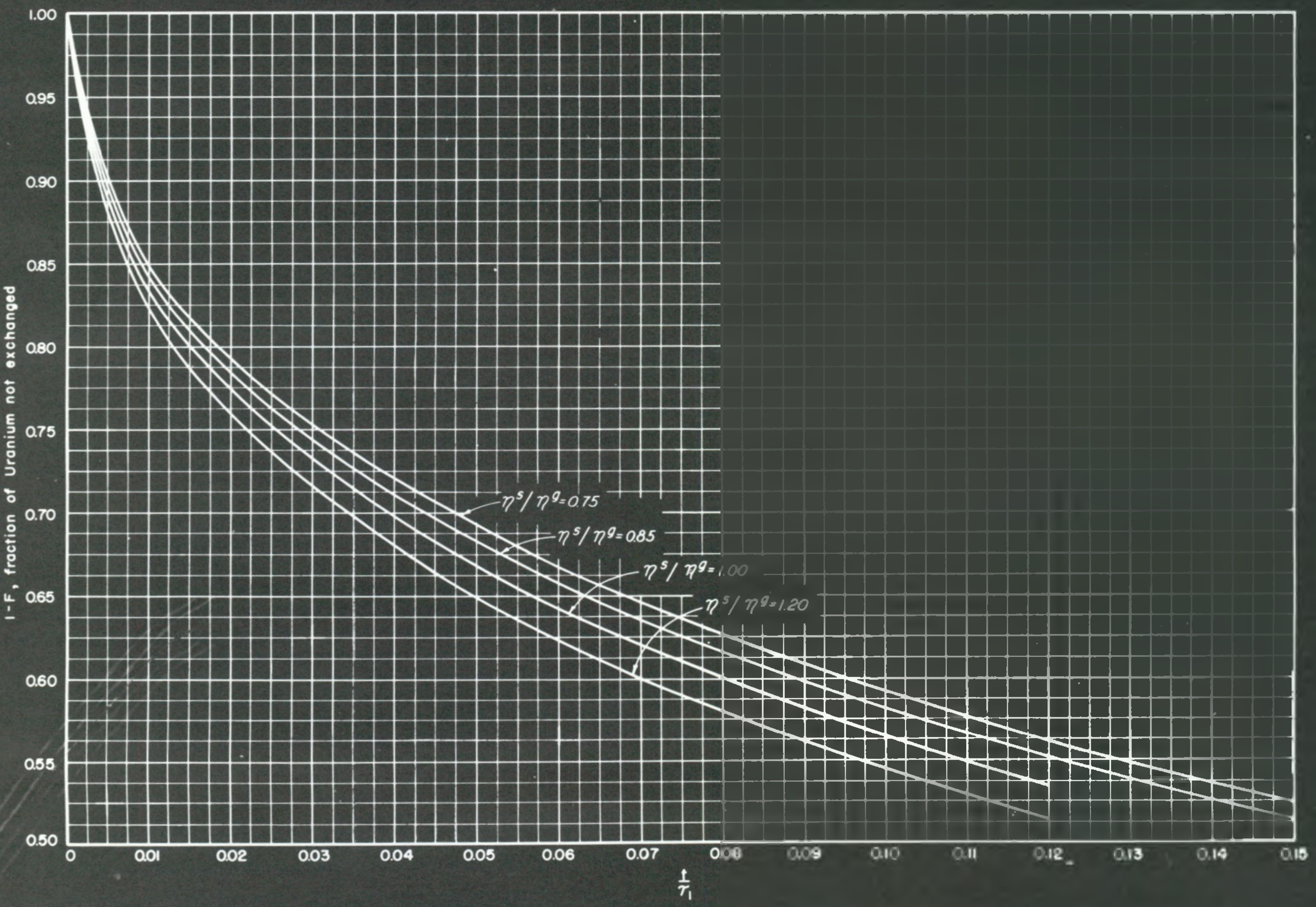
Exchange data obtained after the first exposure in series experiments, i.e., successive exposures of a sample of solid to three or four charges of normal uranium hexafluoride, are not amenable to exact mathematical treatment with the diffusion equation; therefore, diffusion coefficients calculated from all but the first member of such series have been listed in parentheses. The reason for this is readily understandable, since during an experiment a radial U-235 gradient is established in the solid uranium pentafluoride. One of the boundary conditions in the solution of the differential diffusion equation (4,15) is the maintenance of equality of assay of gas and of solid surface. When enriched gas is withdrawn after an exchange experiment and the reactor recharged with normal uranium hexafluoride, the solid assay gradient must change to accomodate the change in gas assay. Parenthetic values of diffusion coefficients listed in table III were obtained by assuming that such recharging with lower assay material did not affect the solid assay gradient. This assumption becomes more valid as the difference between final and recharge (0.7115 wt. % U-235) gas assays diminishes.

Diffusion coefficients were obtained from estimates of the following quantities: 1) τ_1, determined from graphical evaluation of t/τ_1, according to figure 5, and the relation $\tau_1 = (\frac{t}{t/\tau_1})$; 2) $R^2/D\tau_1$, calculated according to equation 6a, and $R^2/D = (R^2/D\tau_1)\tau_1$; 3) and D, estimated from the relation $D = (D/R^2)R^2$. The last calculation is subject to considerable uncertainty because all particles of uranium pentafluoride probably were not of the same radius. Nitrogen surface area measurements indicated an average particle radius of 0.68×10^{-4} cm.; the photomicrographs (figure 4) indicate a range of particle radii of 0.01 to 1.1×10^{-4} cm. To obtain these micrographs a sample of the solid was dispersed by working the powder into Parlodion moistened with Cellosolve acetate, on a polished stone plate, using a fairly stiff spatula (10). If there is no reduction of uranium pentafluoride by Parlodion during this rubdown process, loosely bound aggregates of the ultimate particles are broken up, to some extent. Values of the diffusion coefficient listed in table III were calculated on a basis of nitrogen surface area measurements.

Agreement from run to run of estimates of the diffusion coefficient are within a factor of 3 at a given temperature, with the exception of that from run IV, exposure 1. Results from this run, although in disagreement with those from other experiments, have not been discarded because no known differences in experimental procedure existed.

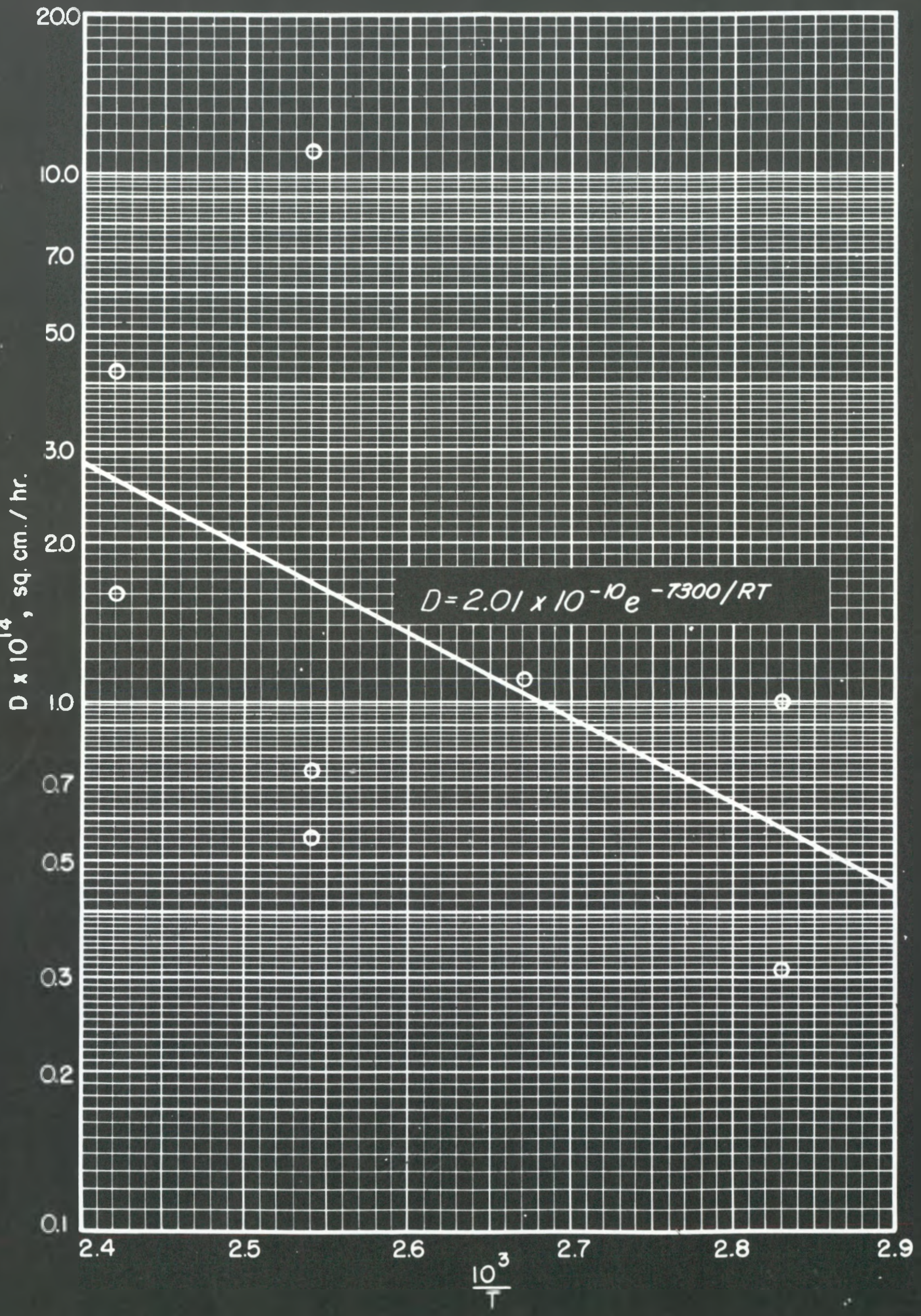
Exchange experiments were performed at different temperatures so that some estimate of the energy of activation for the rate controlling process could be obtained. It is evident from the data in table III that the scatter in values of D is large. Thus, although it is possible to calculate an activation energy, according to equation 7, of 7.3 kcal./mole, the uncertainty in this value is about 12.5 kcal./mole. With this uncertainty an average of all values, namely $D = 2.6 \times 10^{-14}$ sq. cm./hr., probably provides as good an estimate of the coefficient of diffusion of uranium in beta uranium pentafluoride as is available for the temperature range 80 to 140°C.

$$D = fe^{-\Delta E/RT} \tag{7}$$



PLOT OF FRACTION OF URANIUM NOT EXCHANGED (1-F) Vs t/τ_1

FIGURE 5



SUMMARY OF ISOTOPIC EXCHANGE DATA IN TERMS OF THE PLOT LOG D Vs. $10^3/T$.

FIGURE 6

Calculations of the activation energy were made by assuming that temperatures were accurately known and that measured diffusion coefficients were subject to a constant percentage error. Thus, equation 7 was solved by minimizing around ln D_i, in which case the constant f has a value of 2.01 x 10^{-10} sq. cm./hr. Figure 6, in which the diffusion coefficient, D, is plotted on a logarithmic scale against the reciprocal temperature, summarizes the data and indicates the scatter thereof. The straight line represents equation 7.

CONCLUSIONS AND SUMMARY

Exchange of uranium between beta uranium pentafluoride and gaseous uranium hexafluoride has been studied by means of series and single experiments in the temperature range 80 to 140°C. Data have been examined by use of equations for the three limiting, rate-controlling mechanisms. These are: 1) chemical reaction at the gas-solid interface; 2) diffusion of uranium hexafluoride through an adsorbed surface film; 3) diffusion of uranium in and through the solid. Variations of first order rate constants, as well as absolute magnitudes of the latter, have shown that exchange is not controlled by either of the first two processes. Results obtained in the present experiments can be explained fairly well on the basis of exchange controlled by diffusion of uranium in and through the solid after adsorption or uranium hexafluoride on the surface of uranium pentafluoride. Diffusion coefficients, with one exception, have been reproduced within a factor of 3. An activation energy for diffusion of 7.3 kcal./mole has been calculated from the variation of exchange rate with temperature in the range 80 to 140°C.; however, the scatter in the data is so large that no estimate of the diffusion coefficient, D, in this temperature range can be considered appreciably better than the overall average, namely 2.6 x 10^{-14} sq. cm./hr.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to W. W. Harris of the Analytical Chemistry Department for electron photomicrographs of the uranium pentafluoride, to F. D. Rosen of this laboratory for help in design of the circulation pump, to R. L. Jarry of this laboratory for help in taking some of the data, and to the Works Laboratory for chemical, isotopic, and surface area analyses. Special acknowledgement is given to O. S. Carpenter of the Engineering Division for helpful discussions and for calculations of mathematical tables necessary for interpretation of the data.

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Experimental work was completed June 1, 1951

APPENDIX A

Calculation of Diffusion Coefficients

The quantity $R/\sqrt{D\tau_m}$ can be calculated by means of equation 6a for specified values of n^s/n^g. In the present experiments all particles have been assumed to have the same radius, R, namely that obtained from nitrogen surface area measurements and Zachariasen's (14) value of the density of β-UF_5 (5.81 g./cc.). Selected values of the quantity $R^2/D\tau_1$, where τ_1 is the "principal time constant" of Wagner (13), at various ratios of n^s/n^g are listed in table A-I. In practice $R^2/D\tau_1$ at the experimental value of n^s/n^g was obtained by interpolation.

TABLE A-I

SELECTED VALUES OF $R^2/D\tau_1$

$\frac{n^s}{n^g}$	$\frac{R^2}{D\tau_1}$
0.75	13.17
0.85	13.47
0.90	13.63
0.95	13.76
1.00	13.90
1.05	14.03
1.10	14.15
1.15	14.27
1.20	14.41

The diffusion equation 6 has been evaluated at 4 ratios n^s/n^g, 0.75, 0.85, 1.00, and 1.20, and plotted in terms of 1-F (the fraction not exchanged) against t/τ_1 in figure 5. Hence, for any experimental value of 1-F and molecular ratio n^s/n^g the quantity t/τ_1 may be obtained. The simple relation $\tau_1 = t/\frac{t}{\tau_1}$ is used to calculate the "principal time constant". From table A-I the quantity $R^2/D\tau_1$ is obtained, whence $R^2/D = (R^2/D\tau_1)\tau_1$. Finally $D = (D/R^2)R^2$. These procedures have been used to calculate the diffusion coefficient for all first exposure experiments.

Methods used to estimate diffusion coefficients from successive exposures of a sample of enriched uranium pentafluoride to normal uranium hexafluoride are based on the assumption that the extent of exchange measured is the same as that which would have been observed if the recharge gas had been at the same assay as the material just removed. The amount of exchange measured is given by equation A-1.

$$F_{i-1 \longrightarrow i} = \frac{A^g_o - A^g}{A^g_o - A_\infty} \qquad \text{(A-1)}$$

$F_{i-1 \longrightarrow i}$ is the fractional exchange during the i^{th} exposure.

The fractional exchange that would have been observed if recharge material assay had been the same as that removed (namely A^g_{i-1}) is given by equation A-2. The assumption mentioned above may be expressed by $F_{i-1 \rightarrow i} = F'_{i-1 \rightarrow i}$.

$$F'_{i-1 \rightarrow i} = \frac{A^g_{i-1} - A^g_i}{A^g_{i-1} - A_{i,\infty}} \qquad \text{(A-2)}$$

Equation A-2 may be readily shown to convert to equation A-3. Use of this and the defining equation 3 leads to equation A-4.

$$1-F'_{i-1 \rightarrow i} = \frac{(A^g_i - A_{i,\infty})/(A^g_o - A_{i,\infty})}{(A^g_{i-1} - A_{i,\infty})/(A^g_o - A_{i,\infty})} \qquad \text{(A-3)}$$

$$1-F'_{i-1 \rightarrow i} = \frac{1-F'_i}{1-F'_{i-1}} = 1-F_{i-1 \rightarrow i} \qquad \text{(A-4)}$$

According to equations A-3 and A-4, $1-F'_i$ is the fraction not exchanged at time t_i and mole ratio $(n^s/n^g)_i$ and $1-F'_{i-1}$ the fraction not exchanged at time t_{i-1} and mole ratio $(n^s/n^g)_i$, rather than $(n^s/n^g)_{i-1}$.

Gas assays are used to calculate $1-F_{i-1 \rightarrow i}$. The quantity $(1-F'_{i-1})$ is calculated by means of equation A-5, following which $(1-F'_i)$ is obtained from equation A-4.

$$1-F'_{i-1} = \frac{A^g_{i-1} - A_{i,\infty}}{A^g_o - A_{i,\infty}} \qquad \text{(A-5)}$$

From the curves of figure 5 the quantities t'_i/τ_1 and t'_{i-1}/τ_1, corresponding to $(1-F'_i)$ and $(1-F'_{i-1})$, can be calculated. Times t'_i and t'_{i-1} are unknown but are related by equation A-6, where t_i and t_{i-1} are measured, elapsed times from the beginning of an exchange series to withdrawal of samples i and i-1; i.e., $(t_i - t_{i-1})$ is the contact time of an experiment. Finally, τ_1 is obtained from equation A-7.

$$t'_i - t'_{i-1} = t_i - t_{i-1} \qquad \text{(A-6)}$$

$$t_i - t_{i-1} = \left(\frac{t'_i}{\tau_1} - \frac{t'_{i-1}}{\tau_1}\right)\tau_1$$

or

$$\tau_1 = \frac{t_i - t_{i-1}}{\left(\dfrac{t'_i}{\tau_1} - \dfrac{t'_{i-1}}{\tau_1}\right)} \qquad \text{(A-7)}$$

After τ_1 has been determined, D is calculated in a manner similar to that described in the first portion of the appendix.

APPENDIX B

Preparation of Enriched Beta Uranium Pentafluoride

Enriched beta uranium pentafluoride was prepared by reaction between uranium tetrafluoride and uranium hexafluoride as follows. High temperature electrolytic (3) uranium tetrafluoride ($UF_4 \cdot 3/4\ H_2O$) of normal assay was dehydrated at elevated temperatures in a stream of nitrogen. Some of this material was placed in a nickel tube reactor and then pumped at 100°C. for 2 days to remove water adsorbed after dehydration. The charge of 17.671 g. of uranium tetrafluoride lost 0.106 g. in weight, leaving 17.565 g. of anhydrous uranium tetrafluoride. To this was added 60.764 g. of enriched uranium hexafluoride (28.89 wt. % U-235). The reactor, of about 50 cc. volume, was placed in an oven at 100°C. for 31 days, after which excess uranium hexafluoride was removed from the reactor (at room temperature) by vacuum transfer. On the basis of weights and assays of reactants, a product of 37.201 g. of uranium pentafluoride, with an assay of 21.28 wt. % U-235, was expected. Weights and assays of the product gave 35.84 g. with an assay of 17.98 wt. % U-235. Thus, during 31.00 days, exchange of uranium between uranium tetrafluoride and uranium hexafluoride was at least 81.16 % complete under the experimental conditions.

According to nitrogen surface area measurements the dehydrated uranium tetrafluoride had a specific surface of 2.1 sq. m./g. (3); uranium pentafluoride formed during the reaction had a specific surface of 0.76 sq. m./g.