RADIATION EFFECTS OF ALPHA PARTICLES ON URANIUM HEXAFLUORIDE^a

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It is well known that the separation of uranium isotopes in gaseous diffusion plants is performed with uranium hexafluoride. Uranium of natural isotopic composition has a very low disintegration rate, about 25 α -particles per milligram of element per second. Self irradiation would not produce any large chemical effects in normal uranium compounds. However, as the uranium-235 isotope is enriched in a diffusion cascade, so also is the uranium-234 isotope, to an even greater extent. When both isotopes are enriched 100 fold, the resulting uranium emits about 1230 α -particles per milligram per second, based on decay constants (1) of 4.87×10^{-18} sec.⁻¹, 3.09×10^{-17} sec.⁻¹, and 8.8×10^{-14} sec.⁻¹ for uranium-238, uranium-235, and uranium-234, respectively. A single α -particle from uranium-234 produces approximately 1.37×10^7 ion pairs over its entire path (2). Thus, one gram of uranium enriched 100 fold will produce about 5.3×10^{18} ion pairs per year. Assuming all α -particles are able to complete their paths within the uranium compound, about 0.2% of the molecules present would have become ionized in the course of a year by self α -irradiation. The amount of chemical reaction as a result of this over any extended period of time might become quite appreciable.

In addition to the interest in the α -particle decomposition of uranium hexafluoride as it applies to the gaseous diffusion process, there is an additional interest in the more general effects of radiation on this compound. This interest is based on the possibilities of a uranium hexafluoride nuclear reactor. Such a pile, although presenting many new problems, would have a very simple spent uranium recovery process.

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EXPERIMENTAL

Apparatus

The reaction chamber in most of the experiments was constructed of a nickel cylinder connected by means of small bore nickel tubing to a Booth-Cromer nickel-diaphragm pressure transmitter (3). The transmitter chamber had an internal diameter of 3 inches and a depth of 0.01 inch, giving it a volume of approximately 1.2 cc. The volume of the connecting tubing was about 0.5 cc.; total volume varied from about 7 to 36 cc.

In a few of the early experiments the reaction chamber was a Pyrex glass bulb connected by a Kovar seal to the pressure transmitter. Figure 1 shows the arrangement of the various components of a reactor used in most of these experiments.

Figure 1

Materials

Radon, used for the source of alpha particles, was obtained from 230 mg. of radium on loan from the United States Bureau of Mines. The gas was collected and purified in a system previously described (4).

Uranium hexafluoride contained less than 0.015 weight per cent impurity; further purification was accomplished by pumping the hexafluoride while it was maintained at -78°C . Fluorine was taken from standard fluorine cells (5), and had an estimated purity greater than 95%.

A lead box with three-inch thick walls was used as a shield against the gamma radiation emitted from the reaction systems. A second box constructed of 1/2-in. asbestos board was contained within this box. Heaters and a thermal regulator in this air thermostat permitted heating the reactor and maintaining its temperature constant to $\pm 3^{\circ}\text{C}$.

Procedure

In preparing the system for an experimental run, the apparatus described above was pumped, flamed, and the zero point of the Booth-Cromer transmitter then determined. The system was purged a number of times with fluorine and again pumped and flamed. Finally, fluorine was admitted at just under atmospheric pressure and the system maintained at 80 to 100°C. for at least 24 hours in order to fluorinate the metal surfaces. When the temperature at which a decomposition experiment was to be run exceeded 45°C., the time of fluorination was increased to several days.

Radon was admitted to the evacuated reactor by direct transfer from the radon purification plant (4). The reactor was then connected to a manifold through which the various gases to be studied were admitted. After the experiment had proceeded for a few hours and the rate of pressure change well established manometrically, the reactor was immersed in a water-ice (0°C.) or a dry-ice (-78°C.) bath; in later experiments a liquid nitrogen bath (-196°C.) was also used. Pressures at the lower temperatures were observed until thermal equilibrium had apparently been attained. The low temperature bath was then removed and the reaction allowed to proceed at the experimental temperature.

Radon charges used in the individual experiments were measured by gamma ray comparison with radium standards on loan from the Bureau of Mines. A Lind electrometer was used for the measurements.

PRESSURE MEASUREMENTS

Most of the experiments presented here involve the effects of α -particles on uranium hexafluoride alone or in the presence of fluorine. Pressures recorded in Figures 2, 3, 4, and 8 were obtained by correcting observed pressures to their equivalents at 0°C. These corrections were made by use of the ideal gas laws and may be summarized as follows. Let total pressures measured at a reaction temperature T and at a lower temperature, say 0°C., be represented by P_T and P_0 , and the values corrected to 0°C. represented by P_T° and P_0° . The conversion from P_0 to P_0° includes a correction for that portion of the reactor volume (mainly the pressure transmitter) that is not immersed in the 0°C. (low temperature) bath. It has been assumed that uranium hexafluoride exhibits its vapor pressure (6) of 17.3 mm. at 0°C. in the presence of fluorine. Thus, $P_0^\circ - 17.3 = P_{F_2}^\circ$ is the pressure of fluorine in the system, corrected to 0°C.; $P_T^\circ - P_{F_2}^\circ = P_{UF_6}^\circ$ is, by difference, the pressure of uranium hexafluoride, also corrected to 0°C.

In experiments involving the addition of nitrogen, oxygen, or helium to the uranium hexafluoride-radon system, pressures were measured after cooling the reactor to -196°C. as well as to 0°C. and to -78°C. From these data, pressures of permanent gases were calculated by use of calibration factors. The latter were obtained by cooling known mixtures of nitrogen and uranium hexafluoride, or of pure uranium hexafluoride, to these same temperatures.

In all cases a rigorous time schedule was followed in making pressure measurements at low temperatures so that the calibration factors would apply as accurately as possible.

RESULTS

Under alpha particle irradiation there is a depletion of uranium hexafluoride from the gas phase accompanied by an evolution of fluorine. Figure 2 contains a summary of three typical experiments performed in a vessel originally containing no uranium fluoride deposit.

Figure 2

On addition of fluorine to uranium hexafluoride in a reactor containing solid uranium fluorides deposited from the gas phase, there is an initial increase followed by a decrease in the uranium hexafluoride pressure, as seen in Figure 3.

It has not been possible to establish the exact identity of the solid uranium fluoride product, although some information is obtained from the ratio of fluorine produced to uranium hexafluoride decomposed. Such ratios for 7 experiments are summarized in Table I.

TABLE I

RATIO OF FLUORINE PRESSURE
INCREASE TO URANIUM HEXA-
FLUORIDE PRESSURE DECREASE

Experiment Number	$\Delta P_{F_2} / \Delta P_{UF_6}$
3	0.625
4	0.585
5	0.240
7	0.290
15	0.770
16	0.860
24	1.250

Ratios that would be obtained
for several possible uranium
fluoride products are listed
in Table II.

TABLE II

RATIO OF FLUORINE PRESSURE
INCREASE TO URANIUM HEXA-
FLUORIDE PRESSURE DECREASE
FOR KNOWN URANIUM FLUORIDES

Compound	$\Delta P_{F_2} / \Delta P_{UF_6}$
UF_6	0.0
UF_5	0.5
UF_4	1.0
UF_3	1.5

TIME VARIATION OF UF_6 PRESSURE,
CORRECTED TO $0^\circ C$.
EXPERIMENT 9. VESSEL INITIALLY
CONTAINED UF_x DEPOSIT

Figure 3

In the presence of solid fluorides and added fluorine, the change in fluorine pressure with uranium hexafluoride decomposition exhibits different values before and after the time of maximum uranium hexafluoride pressure, Figure 3. These values are illustrated in Table III.

A number of experiments were performed with nitrogen, oxygen, or helium added at various pressures to reactors containing uranium hexafluoride. With nitrogen or helium as the diluent gas, results were similar to those obtained without the diluent gas. For example, permanent gas pressures were similar to the fluorine formation curves of Figure 2 but displaced by an amount equal to the initial nitrogen or helium pressure. Results of experiments with oxygen as a diluent gas were somewhat erratic and indicated large quantities of oxygen being permanently removed from the system.

TABLE III

COMPARISON OF THE CHANGE IN FLUORINE PRESSURE TO THE CHANGE IN URANIUM
HEXAFLUORIDE PRESSURE IN THE PRESENCE OF THE SOLID FLUORIDES

Experiment No.	$\left \frac{\Delta P_{F_2}}{\Delta P_{UF_6}} \right $	
	Before Max. UF_6 Press.	After Max. UF_6 Press.
8	0.88	0.13
9	0.67	0.28

DISCUSSION

From the data obtained, it is obvious that the uranium hexafluoride is ionized by alpha particles and dissociated to produce solid uranium fluorides. Chemical analyses have failed to aid in the identification of this material because the quantities available are so small (1 to 2 mg.). X-ray diffraction patterns of the compound are not very clear due to the radiation background level and to small particle size, estimated to be less than 100 Å. However, halos have appeared in the region where beta uranium pentafluoride exhibits strong lines (7). Such evidence is indicative but certainly not conclusive of the presence of some pentafluoride. As shown by the ratios of fluorine pressure change to uranium hexafluoride pressure change (Tables I, II, and III) the solid compound may have a composition intermediate between uranium trifluoride and uranium hexafluoride. Because further identification is not possible, the solid products are designated as UF_x .

If the reaction of uranium hexafluoride under α -particle irradiation were to be dependent on the gas pressure and the radiation intensity alone, equation 1 could be used to represent the whole course of the decomposition.

The rate expression corresponding to equation 1 is

$$-\frac{d(UF_6)}{dt} = k_1 (UF_6) E_0 e^{-\lambda t}, \quad (2)$$

where E_0 is the initial radon disintegration rate, in curies, and λ is the decay constant of radon. When $\log P_{UF_6}$ is plotted against $e^{-\lambda t} = E/E_0$, the data should follow a straight line with an intercept of $\log (P_{UF_6})_0$ if equation 2 describes the radiation reaction. Instead of a straight line there is obtained a curve of decreasing slope in each experiment.

In view of the decreasing slope, a back reaction of the solid product with fluorine has been assumed. This reaction has been indicated to be dependent

upon radiation since, at the reaction temperatures employed, it is doubtful that measurable thermal reaction would occur (8). Further, when fluorine was placed and maintained at room temperature in a vessel that had previously been used in a radiation experiment, uranium hexafluoride was not formed in measurable quantities.

The rate equation for the over-all reaction of equations 1 and 3 may be written as

$$-\frac{d(\text{UF}_6)}{dt} = k_1 E_0 (\text{UF}_6) e^{-\lambda t} - k_2 E_0 (\text{F}_2) (S) e^{-\lambda t}, \quad (4)$$

where (S) is some function of the surface of solid UF_6 . The fluorine concentration has been found experimentally to be approximately a linear function of the uranium hexafluoride pressure, which is expressed by equation 5.

$$P_{\text{F}_2} = a - b P_{\text{UF}_6} \quad (5)$$

Typical correlations indicated by equation 5 may be seen in Figure 4. Values of the constant b have been summarized in Tables I and III. Following substitution of equation 5 into 4, the integrated rate equation 6 is obtained.

$$\ln \left[(\text{UF}_6) - \frac{k_2 (S)a}{k_1 + k_2 (S)b} \right] = \left\{ k_1 + k_2 (S)b \right\} \frac{E_0}{\lambda} e^{-\lambda t} + C \quad (6)$$

When values of k_1 and $k_2(S)$ are determined and the results plotted according to Figure 5, a straight line results. Calculated values of k_1 and $k_2(S)$, determined by least squares procedures, are listed in Table IV.

As indicated previously, experiments have also been performed with nitrogen, oxygen, and helium as diluent gases. Of these, only experiments with nitrogen are presented here. Data from these experiments are summarized in Table V and Figure 6.

Calculation of E_a and G

Uranium hexafluoride can be ionized and decomposed to non-volatile uranium fluorides. These ionization processes are readily observable in a mass spectrometer; appearance potentials of the various ions, UF_5^+ , UF_4^+ , etc., have been reported by Cameron (9). The extent of a second decomposition process, namely electronic excitation of uranium hexafluoride molecules and their subsequent decomposition to free radicals (such as UF_5 and F) or molecules (such as UF_4 and F_2) is unknown.

Terms used in calculating G, dN/dt , the number of molecules of uranium hexafluoride decomposed per second, and dE_a/dt , the quantity of energy absorbed

VARIATION OF F_2 PRESSURE WITH UF_6 PRESSURE,
CORRECTED TO $0^\circ C$.

Figure 4

CORRELATION OF EXPERIMENTAL DATA
ACCORDING TO EQUATION 6

Figure 5

TABLE IV

RATE CONSTANTS FOR URANIUM HEXAFLUORIDE DECOMPOSITION

Expt. No.	Temp., °C.	Radon Charge, curies	Initial UF ₆ Press. ^a , mm. Hg	UF ₆ Decomposition		UF ₆ Formation k ₂ (S) × 10 ⁵ , curie ⁻¹ sec. ⁻¹	G _U , Molecules 100 e.v.
				k ₁ × 10 ⁵ , curie ⁻¹ sec. ⁻¹			
3 ^{b,c}	30	(0.1)	120	(3.95)		(23.05)	-
4 ^{b,c}	30	(0.1)	123	(2.04)		(13.49)	-
5 ^c	30	0.042	105	1.06		23.08	0.76
24	26	0.078	78.0	4.15		6.83	1.40
16	30	0.105	90.5	2.68		9.09	0.96
15	33	0.099	125.0	3.26		11.37	1.13
7	48	0.042	185.0	3.02		16.13	1.04
31	52	0.091	51.5	2.10		1.59	0.59
33	84	0.112	62.7	4.03		3.11	1.14
36	85	0.036	71.8	2.08		1.43	0.59
34	87	0.034	70.0	1.64		3.70	0.47

Average and standard deviation

0.90 ± 0.31

^aCorrected to 0°C.^bThe radon charge was not measured. The activity was estimated to be 100 millicuries.^cExperiments 3, 4, and 5 were carried out in spherical glass bulbs of radii 1.94, 1.96, and 1.98 cm., respectively.

are as follows.

e₁, e₂, e₃ = energies of α-particles from Rn-222, Po-218, and Po-214, 5.486, 5.998, and 7.680 mev., respectively,e = average α-particle energy, (e₁ + e₂ + e₃)/3 = 6.388 mev.;S₁, S₂, S₃ = stopping powers of uranium hexafluoride for the Rn-222, Po-218, and Po-214 α-particles, respectively, cm.⁻¹ at STP;S = average stopping power, (S₁ + S₂ + S₃)/3;R₁, R₂, R₃ = ranges of Rn-222, Po-218, and Po-214 α-particles in uranium hexafluoride, cm. at STP;R = average α-particle range, (R₁ + R₂ + R₃)/3;B = the number of α-particles emitted in one second from a system containing one curie of Rn-222 in equilibrium with its decay products, 3 × 3.72 × 10¹⁰ α/sec. curie;

I.P. = the average amount of energy required to produce one ion pair, ev.;

L₁ = average path of an α-particle emitted from gaseous Rn-222 that is homogeneously distributed in a sphere of internal radius r;L₂ = L₃ = average path of an α-particle emitted from solid Po-218 or solid Po-214 that is uniformly distributed on the inner surface of a sphere of internal radius r;

TABLE V

DECOMPOSITION OF UF_6 BY ALPHA PARTICLES IN THE PRESENCE OF N_2

Expt. No.	Initial UF_6 Press., mm.	Initial N_2 Press., mm.	Radon Charge, curie	Initial Decomposition Rate Constant, $k_1 \times 10^5$ $\text{curie}^{-1} \text{sec.}^{-1}$	Contribution of UF_6 to Total Energy Absorbed, %	Decomposition Yield, UF_6 Molecules/100 ev.,	
						G_T^*	G_U^{**}
1	84.0	47.8	0.0904	4.6	93.9	1.46	1.55
2	67.5	75.4	0.1352	8.2	88.7	2.45	2.77
3	79.2	183.6	0.1205	9.6	79.1	2.56	3.24
4	65.6	200.0	0.1100	16.1	74.2	4.03	5.43
5	78.0	59.4	0.1298	1.5	92.0	0.47	0.51

*Number of UF_6 molecules decomposed per 100 ev. of total energy absorbed.**Number of UF_6 molecules decomposed per 100 ev. of energy absorbed by the UF_6 alone.

EFFECT OF N_2 PRESSURE ON INITIAL UF_6
DECOMPOSITION RATE CONSTANT

Figure 6

A = Loschmidt number, 2.69×10^{19} molecules/cc. at STP;
 λ = decay constant of Rn-222, 2.10×10^{-6} /sec.;
 n_i = number of α -particles per sec. from nucleus i (i = Rn-222, Po-218, Po-214);
 P_j = pressure of gas j , atm.;
 V_j^r = principal volume of reactor (Figure 1), cc.;
 V_s^r = total reactor volume, cc.;

Lind (10) has shown that the average paths of α -particles are related to the radius, r , of a spherical container by equation 7.

$$\left. \begin{aligned} L_1 &= 0.75 r \\ L_2 &= L_3 = 0.5 r \end{aligned} \right\} \quad (7)$$

An accurate calculation of the rate of absorption of energy by a mixture of gases in a spherical container of volume V , radius r , at pressure P , containing initially E_0 curies of radon can be made only if the ionization curve of each α -particle from the radon decay scheme in each pure gas is known. Such ionization curves, schematically shown in Figure 7, have not been measured for uranium hexafluoride. Thus, estimates of G are based on an estimate of the average range, R , of the radon scheme α -particles in this gas, or on the number of ion pairs produced per centimeter of α -particle path.

Figure 7

If the only assumption involved in calculating the energy absorption rate, dE_a/dt , were that ionization be constant over the path, then equation 8 could be written if the path length is less than the range (i.e., every α -particle reaches the wall).

$$\frac{d(E_a)_{ij}}{dt} = \frac{L_{ij}}{R_{ij}} e_i P_j n_i \quad (8)$$

Subscript i refers to the α -particle, j to the gas. The quantity n_i may be expressed as

$$n_i = \frac{B}{3} E_o e^{-\lambda t}. \quad (9)$$

By inserting equations 7 and 9 into 8 we obtain equation 10.

$$\frac{d E_a}{dt} = \frac{B}{3} E_o e^{-\lambda t} \sum_j \left\{ \frac{0.75 r}{R_{1j}} e_1 + 0.5 r \left(\frac{e_2}{R_{2j}} + \frac{e_3}{R_{3j}} \right) \right\} P_j \quad (10)$$

Quantities R_{ij} have not been determined experimentally, but have been calculated as described below. The necessity of estimating R makes the use of specific values of e_i superfluous; hence, e_i has been replaced by the average value e in equation 11.

$$\frac{d E_a}{dt} = 0.5833 B e E_o e^{-\lambda t} r \sum_j \frac{P_j}{R_j} \quad (11)$$

The quantity $0.5833 r$ is the calculated average path of α -particles from the three nuclei; however, Lind and Bardwell (11) experimentally determined a value of $0.61 r$, which is used in subsequent discussion and calculation in this report.

Reactors used in the present work, with the exception of the first few, were not spherical; instead they were composed (Figure 1) of a cylindrical section that constituted the main volume, a section of small bore tubing, and the Booth-Cromer pressure transmitter. Lind (10) has quoted Lunn to the effect that the average path in a cylinder of diameter nearly equal to its length is about the same as that in a sphere of the same volume. Thus, designating as V_r the main reaction volume, the effective radius of this unit is

$$r = \left[\frac{3V_r}{4\pi} \right]^{1/3}, \quad (12)$$

and the average path of an α -particle may be written as

$$L = 0.61 r = 0.379 \left[V_r \right]^{1/3}. \quad (13)$$

Dissociation of uranium hexafluoride also occurs in the small bore lines and in the pressure transmitter. However, the α -particle paths in these sections are considerably smaller than the paths in the volume V_r . A reasonable estimate is given by assuming α -particle utilization in these short path sections

to be only 15% as efficient as it is in the volume V_r . The effective value of the radon charge, E'_t , is then given by equation 14.

$$E'_t = E_t \left[\frac{V_r}{V_s} + 0.15 \frac{V_s - V_r}{V_s} \right] = \left[0.15 + 0.85 \frac{V_r}{V_s} \right] E_t \quad (14)$$

By inserting the right hand term of equation 14 and equation 13 into 11, we obtain the rate of energy absorption for the reactors actually used.

$$\frac{d E_a}{dt} = (0.379 V_r^{1/3}) e B (0.15 + 0.85 \frac{V_r}{V_s}) E_o e^{-\lambda t} \sum_j \frac{P_j}{R_j} \quad (15)$$

As described previously, the effects of α -particles on uranium hexafluoride can be described in terms of reactions 1 and 3, the first of these summarizing decomposition, the second, reformation of the hexafluoride. It is apparent that k_1 of equation 2 actually contains the efficiency factor of equation 14, i.e.,

$$k_1 = k'_1 (0.15 + 0.85 \frac{V_r}{V_s}). \quad (16)$$

The number rate of decomposition of uranium hexafluoride by reaction 1 is

$$\frac{dN}{dt} = AV_s \frac{dP_{UF_6}}{dt} = AV_s k_1 P_{UF_6} E_o e^{-\lambda t}. \quad (17)$$

Then G_T , given by 100 times the ratio of quantities in equations 15 and 17 is as follows:

$$G_T = \frac{100 AV_s k_1 P_{UF_6}}{0.379 V_r^{1/3} e B (0.15 + 0.85 \frac{V_r}{V_s}) \sum_j \frac{P_j}{R_j}}, \quad (18)$$

or

$$G_T = \frac{100 AV_s k'_1 P_{UF_6}}{0.379 V_r^{1/3} e B \sum_j \frac{P_j}{R_j}}. \quad (19)$$

It should be noted that G_T is the number of molecules of uranium hexafluoride decomposed per 100 e.v. of energy absorbed by all components present. The number of molecules of uranium hexafluoride decomposed per 100 e.v. of energy absorbed by this gas alone is G_U , which is given by equation 20.

$$G_U = \frac{100 \text{ AV}_s k_1 R_{\text{UF}_6}}{0.379 V_r^{1/3} \text{ eB} (0.15 + 0.85 \frac{V_r}{V_s})} \quad (20)$$

Since experimental data on the ranges of α -particles in uranium hexafluoride are not available, these quantities have been estimated from the correlation of Steidlitz (2), et al., equation 21.

$$R = \delta V_o^3 / \sum_j n_j Z_j^{2/3} \quad (21)$$

$$\delta = 6.75 \times 10^{-26} \text{ mm. } (\frac{\text{sec.}}{\text{cm.}})^3$$

V_o = initial velocity of α -particle

n_j = number of atoms of atomic number Z_j

From equation 21 the average range of the three α -particles in uranium hexafluoride is 0.572 cm., 4.254 cm. in fluorine, 5.030 cm. in nitrogen, 4.602 cm. in oxygen, and 23.20 cm. in helium. Values of G_U or G_T listed in Tables IV and V have been calculated by use of equations 18 and 20 and the above-stated ranges.

Reformation of Uranium Hexafluoride

In order to facilitate an understanding of the back reaction, two of the reactors which had been used in studies of the decomposition of uranium hexafluoride were reused with a mixture of fluorine and uranium hexafluoride, experiments 8 and 9. Under these conditions the pressure of uranium hexafluoride increased, and later decreased, as shown in Figure 3. While the uranium hexafluoride pressure passed through a maximum, the fluorine pressure went through a minimum. It is noteworthy that the maximum uranium hexafluoride pressure occurred when the solid fluoride had been converted almost 100% to uranium hexafluoride. Data of experiments 8 and 9 were divided as follows: Group 1, taken before the maximum uranium hexafluoride pressure was attained; Group 2, taken after this maximum. Values of the constants so calculated are listed in Table VI. It is apparent from this table that, within experimental error, k_1 is constant throughout the course of reaction. However, the Group 1 value of $k_2(S)$ is larger in both experiments than the Group 2 value. The data thus suggest that during the interim between the completion of a decomposition experiment and subsequent reuse of a vessel, the UF_6^x deposit becomes more reactive toward α -particle induced fluorination to UF_6 . Among the factors that may be involved in this activation are crystal modifications and evacuation of the reactor.

TABLE VI

RATE CONSTANTS OF EXPERIMENTS 8 AND 9

Run No.	Temp., °C.	UF ₆ Decomposition		UF ₆ Formation		Initial F ₂ Press., cm.
		k ₁ x 10 ⁵ , curie ⁻¹ sec. ⁻¹		k ₂ (S) x 10 ⁵ , curie ⁻¹ sec. ⁻¹		
8-Group 1	63	3.16		16.52		10.4
8-Group 2	63	2.82		10.49		
9-Group 1	65	3.96		53.94		5.1
9-Group 2	65	4.06		21.66		

Effect of Temperature

Experiments were performed at temperatures ranging from 26 to 87°C. Although there is a considerable spread in the data, Table IV, values of G_U do not show any increase with temperature. This lack of temperature dependence is expected since temperature, within limits, does not have any appreciable effects on ionization processes and, in addition, would have little effect on the efficiency of any electronic excitation process over this small temperature range. It is apparent, however, that as the temperature is increased toward 200 to 300°C., thermal reaction of fluorine and uranium fluorides would become important (8).

Effect of Diluent Gases

Experiments with diluent gases were performed, at ca. 25°C., in an effort to determine whether the uranium fluoride ions could participate in charge transfer processes. In experiments with helium, the quantity of the total energy that was absorbed by that gas was in each case less than 10%. Because this is less than the experimental error in determining G_T , these experiments were inconclusive.

Results of experiments with oxygen as a diluent gas were inconclusive with respect to charge transfer processes for a different reason. Here it was found that oxygen was permanently removed from the system, probably by reaction with the uranium fluoride ions. The extent of oxygen reaction appeared to depend on pressure.

Nitrogen was the only diluent gas that provided definite indications of the probability of a charge transfer process, although even in this case reaction of fluorine or its ions with nitrogen or its ions may have occurred to some extent. In Figure 6 it is apparent that the initial rate of decomposition of uranium hexafluoride increases as the nitrogen pressure increases. Energetically this is possible since, for example, the first ionization potential of nitrogen, 15.51 e.v., is very close to the appearance potential of the UF_5^+ ion (9), 15.5 e.v. The effect of nitrogen corresponds to a 6.4% increase in the initial rate of uranium hexafluoride decomposition per 1 mm. of nitrogen present. On the basis of the range data listed above it

is evident that at equal pressures, in a vessel small enough so that most α -particles reach the walls, only 11% as many nitrogen molecules are ionized as are uranium hexafluoride molecules. Comparison of the 6.4% effect per mm. Hg pressure of nitrogen with 11% indicates that for each two nitrogen ions formed one molecule of uranium hexafluoride is decomposed.

It is apparent from Figure 6 and from a comparison of G values in Tables IV and V that the yield of decomposition of uranium hexafluoride in the absence of added gases is between 0.5 and 1. Data in Table IV are based on measurements made at the stated temperature and at 0°C.; data in Table V are based on room temperature (ca. 25°C.) and pressures measured at -196°C. There appear to be real differences in the values of G calculated from the two sets of data, indicating a bias in one or both types of measurement. This may arise from the following possibilities: (1) when the reactor (V_r in Figure 1) plus part of the small bore tubing to the Booth-Cromer pressure transmitter are immersed in a 0°C. bath, diffusion of uranium hexafluoride from the diaphragm area to the cold area may not have been complete in the 15-minute cooling period; (2) when the reactor was immersed in liquid nitrogen (-196°C.), part of the permanent gas (fluorine) may have been entrained and trapped with the rapidly condensing uranium hexafluoride. The first factor would tend to yield high G values, Table IV; the second low G values, Table V. A comparison of the two types of data is shown in Figure 8.

THE ORIGIN OF MAJOR UNCERTAINTIES IN G VALUES

Figure 8

SUMMARY

Alpha irradiation of uranium hexafluoride results in the formation of fluorine and intermediate, solid uranium fluorides; these products react with each other, apparently by a radiation-induced process, to reform uranium hexafluoride. The number of molecules of uranium hexafluoride decomposed, excluding recombination, per 100 e.v. of energy absorbed, G_U , is approximately 1 in the temperature range 21° to 87°C. At fluorine pressures of 50 to 100 mm. Hg, there is an increase, rather than a decrease, in uranium hexafluoride pressure. Rates of both decomposition and recombination processes appear to depend only on the rates of radiation energy absorption under the conditions of these experiments.

The effects of three diluent gases, helium, nitrogen, and oxygen, were studied in an attempt to find possible electron transfer processes. Experiments with helium were inconclusive, primarily because of the low stopping power of this gas and a limitation on the maximum pressure at which it could be used. Experiments showed that nitrogen increases the rate of the alpha particle decomposition of uranium hexafluoride. In terms of the energy absorbed by nitrogen, the efficiency of this electron transfer process is about 0.5. On the basis of an electron transfer process, oxygen would be expected to inhibit the alpha particle decomposition of uranium hexafluoride. In this reaction, however, other processes control the extent of decomposition. Pressure against time data suggest that oxygen and uranium fluoride ions combine to form uranyl fluoride, when the initial oxygen pressure is less than 100 mm. Hg. The rate of uranium hexafluoride decomposition is probably increased by a factor of 2 to 4 in the presence of oxygen.

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