THE DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION*

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(Received 10 January 1964; in revised form 2 March 1964)

Abstract—Plutonium hexafluoride is decomposed by γ -radiation to produce plutonium tetrafluoride and elemental fluorine. The G value for the decomposition is 7.5 \pm 1.7. Addition of one atmosphere of helium to 80 mm Hg plutonium hexafluoride resulted in a G for the decomposition of 7.2 \pm 1.3. When two atmospheres helium were added to 80 mm Hg plutonium hexafluoride, the resulting G for the decomposition is 5.8 \pm 0.9. A study of the decomposition in the presence of various amounts of krypton revealed a pronounced enhancement of the decomposition of plutonium hexafluoride at an electron fraction of krypton of 0.73 and an exposure dose of 1 \times 10⁸ rads. Mechanisms for the decomposition are proposed.

PLUTONIUM hexafluoride has been shown to be less stable than the corresponding fluorides of uranium and neptunium.^(1,2) This instability is evidenced not only in the case of thermal decomposition of plutonium hexafluoride but also in the decomposition of plutonium hexafluoride by radiation. The decomposition of plutonium hexafluoride by its own α -radiation is well known and decomposition rates as great as two per cent per day in the solid state have been reported.⁽³⁾ A study of the decomposition of plutonium hexafluoride by γ -radiation was expected to shed light on the mechanism of the decomposition and permit a broader understanding of the decomposition of plutonium hexafluoride by its own α -radiation. In the course of this work, the effect of gases such as helium and krypton on the decomposition was also studied.

EXPERIMENTAL

Plutonium hexafluoride was prepared from plutonium tetrafluoride and fluorine at elevated temperatures.⁽⁴⁾ The product of fluorination was purified by trap-to-trap distillation in vacuum to remove hydrogen fluoride and other impurities. The vapour-pressure of plutonium hexafluoride at the ice-point^(ā) was used as a criterion of purity. The gases used in this work were obtained from commercial cylinders and were freed from water either by passage of the gas through a trap cooled by liquid nitrogen or through a bed of molecular sieves. Mass spectrometric analysis of the gases indicated that the impurity content of these gases was generally less than 50 p.p.m.

Standard Blickman hoods were converted to glove box enclosures suitable for work with plutonium.⁽⁶⁾ Air circulation was maintained in the hoods through suitable inlet and outlet filters and the hoods were connected to the laboratory ventilation system through several high-efficiency filters. Materials were transferred into and out of the hood by standard bagging techniques using polyvinyl chloride pouches sealed with a dielectric sealer. A vacuum line with associated equipment was l ocated within the hood and all manipulations of plutonium compounds were carried out using this

- * This work was performed under the auspices of the U.S.A.E.C.
- ⁽¹⁾ J. FISCHER, L. E. TREVORROW and W. SHINN, J. Phys. Chem. 65, 1843 (1961).
- ⁽²⁾ J. G. MALM, B. WEINSTOCK and E. E. WEAVER, J. Phys. Chem. 62, 1506 (1958).
- ⁽³⁾ M. J. STEINDLER, U.S.A.E.C. Report ANL-6753 (1963).
- ⁽⁴⁾ M. J. STEINDLER, D. V. STEIDL and R. K. STEUNENBERG, Nucl. Sci. Engng. 6, 333 (1959).
- ⁽⁵⁾ B. WEINSTOCK, E. E. WEAVER and J. G. MALM, J. Inorg. Nucl. Chem. 11, 104 (1959).
- ⁽⁶⁾ M. J. STEINDLER, D. V. STEIDL and R. K. STEUNENBERG, U.S.A.E.C. Report ANL-5875 (1958).

line. The portion of the apparatus which was exposed to fluorine or plutonium hexafluoride was constructed of nickel, using standard flare fittings, traps and other fixtures. Hoke No. 411 or 413 valves were used throughout. Pressure measurements were made using a Booth-Cromer pressure transmitter and self-balancing relay⁽⁷⁾ connected to a Heise precision gage or a mercury manometer located outside of the hood. The reaction vessels used for this study were cylindrical nickel containers with a wall thickness of 0.0625 in. The vessels were equipped with a $\frac{3}{4}$ in. flare fitting to which an assembly consisting of a flare plug and valve was attached. The flare connection was sealed with an annealed copper gasket.

The reaction vessels were treated with approximately one atmosphere fluorine at 100° for a minimum of 48 hr prior to the introduction of plutonium hexafluoride. The vessels were also pretreated with plutonium hexafluoride at room temperature for 17 hr prior to the introduction of samples for study of the decomposition. Careful treatment of the vessels in this manner resulted in an uptake of plutonium hexafluoride during the conditioning of the nickel vessel which was generally predictable and reproducible. Suitable corrections were made for the plutonium tetrafluoride which was formed chemically during the pretreatment of the vessels. In addition, the decomposition of plutonium hexafluoride by α -radiation, yielding plutonium tetrafluoride and fluorine, proceeds at a low rate in the gas phase. Correction for this source of fluorine and plutonium tetrafluoride, based on an observed decomposition rate of 0.22 per cent per day, was also made.

Samples of purified plutonium hexafluoride were introduced into a reaction vessel of known volume and the pressure and temperature of the system were measured. The valve on the vessel was closed and the flare fittings by which the vessel was attached to the vacuum line was tightly capped. The reaction vessel was next encased in a plastic bag which was sealed. The sealed bag was introduced into a container made of several commercial number 2 cans assembled into a vertical array. The container lid was sealed to the array with soft solder. This assembly was then irradiated to a predetermined exposure dose. After removal of the container from the irradiation facility, the container was bagged into the hood, opened, the plastic bag removed, and the irradiation vessel attached to the vacuum line. Fluorine was measured manometrically while a portion of the vessel was cooled to -78° . The fluorine was removed by evacuation through a trap filled with activated alumina. The quantity of undecomposed plutonium hexafluoride remaining in the reaction vessel was determined by warming the vessel to room temperature and measuring the pressure in a calibrated volume. In order to determine the quantity of plutonium tetrafluoride formed, the vessel was opened at the flare connection and rinsed several times with a mixture of dilute nitric acid and aluminium nitrate. A check of this procedure demonstrated that all of the plutonium tetrafluoride could be removed from the vessel by this procedure. The aqueous solutions were analysed for plutonium by solvent extraction of plutonium and α -counting or, in the case of large samples, by extraction of plutonium followed by an amperometric titration.⁽⁸⁾

All irradiations were carried out in the High Level Gamma Irradiation Facility at Argonne National Laboratory.⁽⁹⁾ This facility utilized spent reactor fuel elements from the Materials Testing Reactor as the source of γ -radiation. Calculations, based on the irradiation and cooling time of the fuel elements, indicated that the average energy of the γ -radiation was approximately 0.75 MeV. The temperature of the reaction vessel during irradiation was $60-70^{\circ}$ due to γ -heating. At these temperatures the thermal decomposition of plutonium hexafluoride contributes no significant amounts of plutonium tetrafluoride and fluorine. The dose rates available in the facility were variable owing to the decay of the fission products; dose rates utilized in the experiments varied from approximately 1×10^4 rads per min to 4×10^4 rads per min. Dosimetry was based on the Fricke dosimeter using a G value of 15.6.⁽¹⁰⁾ Owing to the fact that the irradiation vessels were constructed of nickel, dosimetry was carried out in nickel tubes plated with a thin layer of gold to avoid reaction of the dosimeter solution with nickel. Energy absorption in plutonium hexafluoride was calculated from aqueous dosimetry data and the ratio of the electron densities of liquid water and gaseous plutonium hexafluoride. Energy absorption in gaseous mixtures of plutonium hexafluoride and helium or krypton were calculated by use of the ratio of electron densities of liquid water and the gaseous mixture which was irradiated.

⁽⁷⁾ S. CROMER, U.S.A.E.C. Report MDDC 803 (1947).

⁽⁸⁾ C. A. SEILS, JR., R. J. MEYER and R. P. LARSEN, Analyt. Chem. 35, 1673 (1963).

⁽⁹⁾ H. G. SWOPE, The Argonne High Level Gamma Irradiation Facility, Atompraxis 7/8, 249 (1958). ⁽¹⁰⁾ H. G. SWOPE, U.S.A.E.C. Report ANL-5819 (1958).

RESULTS

Stoicheiometry

The decomposition of plutonium hexafluoride by heat⁽¹⁾ as well as the product of all reported chemical reductions of plutonium hexafluoride yield only plutonium tetrafluoride.⁽³⁾ In order to demonstrate that the decomposition of plutonium hexafluoride by γ -radiation yields the tetrafluoride, a sample of plutonium hexafluoride was exposed to approximately 1×10^8 rads. The solid produced by the irradiation was analyzed by X-ray diffraction and chemical techniques which established its composition as plutonium tetrafluoride. (Found: F, 23.5, Pu, 76.4; Calc. for PuF₄: F, 24.1, Pu, 75.9%.) Further evidence to support the conclusion that plutonium tetrafluoride is the only non volatile product is obtained directly from the decomposition experiments. The molar ratio of fluorine to non volatile plutonium was observed to be unity and also corresponded to the amount of plutonium hexafluoride lost. It can be concluded that the decomposition proceeds according to the equation:

$$PuF_6 \rightarrow PuF_4 + F_2$$

Since the determination of fluorine in the products of the decomposition is relatively troublesome, once the stoicheiometry for the decomposition was established, no further attempt to obtain accurate values for the fluorine produced during the decomposition were carried out.

Decomposition of plutonium hexafluoride

Irradiation of samples of pure, gaseous plutonium hexafluoride according to the procedures outlined above yielded results shown in Fig. 1. A G value for the decomposition of 7.5 ± 1.7 is calculated by fitting the indicated curve to the data. The value of the error represents one standard deviation. Although experiments were



FIG. 1.—Decomposition of plutonium hexafluoride by gamma radiation. Pressure of PuF_6 : 80–380 mm Hg (0·28–2·1 mmole); Temperature: 60–70°; Average gamma energy: 0·75 MeV; Dose rate: $1-4 \times 10^4$ rads/min.

usually carried out at approximately 80 mm Hg, several experiments carried out at greater pressures indicated no significant effect of pressure on the G value for the decomposition. Further, within the range of dose rates used, no effect of dose rate on the G value was observed.

Decomposition of plutonium hexafluoride in mixtures with helium

The decomposition of plutonium hexafluoride on irradiation of mixtures of plutonium hexafluoride and helium resulted in data shown in Figs. 2 and 3. The data shown in Fig. 2 were obtained at an added pressure of helium of 1 atm. The pressure of plutonium hexafluoride was approximately 80 mm Hg. The G value obtained from the slope of the curve is 7.3 ± 1.3 , where the uncertainty represents 1σ . While a straight line has been fitted to the data, it is also possible to fit the data



FIG. 2.—Decomposition of plutonium hexafluoride by γ -radiation in mixtures with helium. Pressure of PuF₆: ~80 mm Hg (1 mmole); Pressure of helium: ~1 atm; Temperature: 60-70°; Dose rate: $1-4 \times 10^4$ rads/min; Average γ -energy: 0.75 MeV.



FIG. 3.—Decomposition of plutonium hexafluoride by γ -radiation in mixtures with helium. Pressure of PuF₆: ~80 mm Hg (1 mmole); Pressure of helium: ~2 atm; Temperature: 60-70°; Dose rate: $1-4 \times 10^4$ rads/min; Average γ -energy: 0.75 MeV.

to a curve which would result in a lowering of the G value for the decomposition with increasing total dose. The data obtained from the decomposition of plutonium hexafluoride to which two atmospheres of helium have been added are shown in Fig. 3. The initial partial pressure of plutonium hexafluoride was again approximately 80 mm Hg. The slope of the curve permits calculation of a G value for the decomposition of 5.8 ± 0.9 which is significantly different from the G obtained from mixtures containing 1 atm of helium.[†] The uncertainty is the value of 1σ .

Decomposition of plutonium hexafluoride in mixtures with krypton

Experiments on the decomposition of plutonium hexafluoride in mixtures with krypton resulted in data shown in Figs. 4 and 5. In all cases, the initial partial pressure of plutonium hexafluoride was approximately 80 mm Hg. Different values for the electron fraction of krypton were obtained by varying the partial pressure of krypton in the mixture. The G values shown on the abscissa of Figs. 4 and 5 were obtained from individual experiments rather than being determined from the slope of a graph of absorbed energy versus the quantity decomposed. Further, the G values have



FIG. 4.—Decomposition of plutonium hexafluoride by γ -radiation in mixtures with krypton. Pressure of PuF₆: ~80 mm Hg (1 mmole); Pressure of krypton: variable; Total exposure dose: ~1 × 10⁸ rads (~15 × 10²⁰ eV absorbed in PuF₆); Dose rate: 1-4 × 10⁴ rads/min; Temperature: 60-70°; Average γ -energy: 0.75 MeV. *G* calculated only from energy absorbed in PuF₆.

[†] On the basis of a *t*-test, the probability that the G values are the same is slightly greater than 2.5 per cent.



FIG. 5.—Decomposition of plutonium hexafluoride by γ -radiation in mixtures with krypton. Pressure of PuF₆: ~80 mm Hg (1 mmole); Pressure of krypton-variable; Total exposure dose: $\bigcirc 2 \times 10^8$ rads (~30 $\times 10^{20}$ eV absorbed in PuF₆), $\triangle 1.5 \times 10^8$ rads; Dose rate: $1-4 \times 10^4$ rads/min; Temperature: 60-70°; Average γ -energy: 0.75 MeV. G calculated only from energy absorbed in PuF₆.

been calculated on the basis of only the energy absorbed in plutonium hexafluoride to permit comparison with the data obtained from the decomposition of pure plutonium hexafluoride. Fig. 4 shows the G values for the decomposition of plutonium hexafluoride in mixtures with krypton when the mixtures were irradiated to a total exposure dose of 1×10^8 rads ($\sim 15 \times 10^{20}$ eV absorbed in plutonium hexafluoride). Similar data for a total exposure dose of 2×10^8 rads ($\sim 30 \times 10^{20}$ eV absorbed in plutonium hexafluoride) are shown in Fig. 5. A pronounced increase in the G value for the decomposition is observed at an exposure dose of 1×10^8 rads and an electron fraction of krypton of approximately 0.73. Comparison of the data in Figs. 4 and 5 indicates that the G value for the decomposition of plutonium hexafluoride at 1×10^8 rads is greater than the corresponding value obtained at 2×10^8 rads for all electron fractions of krypton between 0.30 and 0.85.

DISCUSSION

It is recognized that the calculation of absorbed energy by use of the electron density ratio between liquid water and gaseous PuF_6 may result in errors in the absorbed dose. There exists insufficient information to resolve this difficulty. However, the relative values of G for the decomposition under various conditions are not affected, even though the absolute values of G may be in error.

The decomposition of pure, gaseous plutonium hexafluoride shows no dependence on total dose nor, within the limits of the present experiments, on dose rate. Experiments in which one atmosphere of helium was added to plutonium hexafluoride showed no significant difference in the G value for the decomposition of plutonium hexafluoride when compared to the G value for the decomposition of pure plutonium hexafluoride. One atmosphere helium is equivalent to an electron fraction of helium of approximately 0.1 and hence the energy absorbed in helium is relatively small. When 2 atms helium pressure are added to plutonium hexafluoride, the resulting Gvalue for the decomposition is significantly lower than that obtained either from pure plutonium hexafluoride or from mixtures of plutonium hexafluoride with one atmosphere helium. It should be emphasized that the absence of data below 15×10^{20} eV in Fig. 3 adds uncertainty to the linearity and slope of this curve. In the absence of other data, it is not possible to formulate a definite conclusion as to the mechanism responsible for this difference. It may be pointed out, however, that a decrease in G value for the decomposition can be brought about by either the deactivation of precursors of the decomposition products or an enhancement of the back reaction. The latter may be written as

$$PuF_4 - F_2 \rightarrow PuF_6$$

and has been shown⁽¹¹⁾ to proceed as written in the presence of gamma radiation. The quantities of plutonium hexafluoride produced by irradiation of mixtures of elemental fluorine and plutonium tetrafluoride⁽¹¹⁾ are greater than the small quantities anticipated from a knowledge of the usual equilibrium constant for the reaction.⁽¹²⁾ It is possible, that activated helium reacts with either fluorine or plutonium tetrafluoride which, in turn, leads to the formation of significant amounts of plutonium hexafluoride. This reaction would become important only as the amount of energy deposited in helium become larger which is in agreement with the observations. The magnitude of the drop in G for the decomposition is in qualitative agreement with the data obtained for the effect of krypton on the decomposition (see below).

The effect of krypton on the decomposition of plutonium hexafluoride is unusual. The enhancement of the G value for the decomposition has observed only at an exposure dose of 1×10^8 rads (approximately 15×10^{20} eV absorbed in plutonium hexafluoride) although a single experiment, carried out at $\frac{1}{2} \times 10^8$ rads, and an electron fraction of krypton of 0.31 also resulted in a high G value for the decomposition. It is possible to explain the shape of the curve shown in Fig. 4 by considering several competing processes, although in the absence of additional data it is not possible to suggest a definitive mechanism.

The initial drop in G for the decomposition, occurring at low concentrations of krypton and hence low electron fractions of krypton, may be due to deactivation processes such as shown in Equations (1) and (2)

$$PuF_6^* + Kr \rightarrow PuF_6 + Kr^*$$
⁽¹⁾

$$PuF_6^+ + Kr \rightarrow PuF_6^+ + Kr^+.$$
⁽²⁾

Owing to the fact that the G values were obtained from single experiments it is possible that the initial drop in G may, in fact, not be significant. Nevertheless the present discussion will assume that a significant drop in G takes place at low (0 to ~ 0.6) electron fractions of krypton. While no data are available on the energy levels of plutonium hexafluoride, the lowest excited state of krypton is 9.915 eV above the ground state.⁽¹³⁾ If it is assumed that the first ionization potential of plutonium hexafluoride is the same as that of uranium hexafluoride,⁽¹⁴⁾ the value would be 15 eV. Thus excitation energy could be transferred between krypton and plutonium hexafluoride without ionization of either species if the energy available is less than the ionization potential of krypton⁽¹³⁾ (13.99 eV). Reaction (2) represents a charge

⁽¹¹⁾ M. J. STEINDLER, U.S.A.E.C. Report ANL-6596 (1962).

⁽¹²⁾ L. E. TREVORROW, W. A. SHINN and R. K. STEUNENBERG, J. Phys. Chem. 65, 398 (1961).

⁽¹³⁾ C. E. MOORE, Atomic Energy Levels, Vol. 2. NBS Circular 467 (1952).

⁽¹⁴⁾ V. L. WARREN and J. C. HORTON, U.S.A.E.C. Report K-1429 (1959).

transfer process which is energetically possible, except that 1 eV of excitation energy must be dissipated. This probably occurs in plutonium hexafluoride. The absorption spectrum of plutonium hexafluoride⁽¹⁵⁾ shows several peaks above and below 8100 cm⁻¹ (1 eV) indicating that partition of excitation energy is at least possible. Both reactions (1) and (2) result in the deactivation of excited or ionized plutonium hexafluoride which, in turn, should result in a lowering of the G value for the decomposition.

Another process may become important as the concentration, and hence the energy absorbed by krypton, increases. This is shown by Equation (3)

$$PuF_6 + Kr^{*'} \rightarrow PuF_4 + F_2 + Kr$$
(3)

The reaction has been written to show complete decomposition although it is realized that the primary reaction product may be a precursor of the products indicated. As the energy absorbed by krypton increases, reaction (3) should become increasingly important and hence result in an increase in the G value for the decomposition.

It is necessary to mention the possible contribution of krypton fluorides to the decomposition of plutonium hexafluoride. This work was begun at a time when the rare gases were believed to be unreactive but recent data have shown the existence of rare gas fluoride compounds, particularly krypton fluorides.⁽¹⁶⁾ No direct evidence for the formation of krypton fluorides has been obtained in the present experiments. On the basis of the few data which are available on the properties and preparation of krypton fluorides, it appears unlikely that appreciable quantities of krypton fluorides would remain in the reaction vessels after irradiation, owing to the thermal instability of these fluorides.⁽¹⁶⁾ On the other hand, low concentrations of krypton fluorides could be formed during the irradiation by processes such as those shown by Equations (4) and (5)

$$2\mathrm{PuF}_{6} + \mathrm{Kr} \rightarrow 2\mathrm{PuF}_{4} + \mathrm{KrF}_{4} \tag{4}$$

$$PuF_6 + Kr \rightarrow PuF_4 + KrF_2 \tag{5}$$

In both instances, the krypton fluorides would be unstable and decompose to elemental fluorine and krypton according to the Equation (6).

$$KrF_x \rightarrow Kr + x/2F_2$$
 (6)

If, in fact, krypton fluorides are important in the decomposition of plutonium hexafluoride, then all reactions leading to the formation of krypton fluorides can be expected to enhance the G value for the decomposition of plutonium hexafluoride and thus may contribute to the rise in G value observed at an exposure dose of 1×10^8 rads. In order to account for the fact that at longer exposures to radiation, no enhancement of the G value of the decomposition is observed, it is necessary to assume that the formation of krypton fluorides proceeds either with unactivated molecules or with molecules having a very small amount of excitation energy. In view of the instability of the krypton fluorides, such an assumption is not unreasonable.

⁽¹⁵⁾ M. J. STEINDLER. Unpublished. (1963).

 ^{(16) (}a) A. V. GROSSE, A. D. KIRSHENBAUM, A. G. STRENG and L. V. STRENG, Science 139, 1047 (1963).
 (b) J. J. TURNER and G. C. PIMENTEL, Science 140, 974 (1963).

^(c) D. R. MACKENZIE and R. H. WISWALL, JR., J. Inorg. Chem. 2, 1064 (1963).

At still larger concentrations of krypton, reactions shown by Equations (7) and (8) may become important

$$PuF_6^{*'} + Kr \rightarrow PuF_6 + Kr^{*''}$$
(7)

$$PuF_4 + F_2 + Kr^* \rightarrow PuF_6 + Kr$$
(8)

Reaction (7) would represent the deactivation of a highly excited and short-lived species of plutonium hexafluoride. There exists no evidence for this reaction at this time. On the other hand, enhancement of the back reaction by a process such as shown by Equation (8) may well be possible. As mentioned earlier, the formation of plutonium hexafluoride by irradiation of mixtures of elemental fluorine and plutonium tetrafluoride has been demonstrated.⁽¹¹⁾ Although the reaction has been written as a three body process, it may be that either fluorine or plutonium tetrafluoride is first activated by krypton and then reacts with the other species to form plutonium hexafluoride.

While the series of reactions mentioned above may account for the results obtained at an exposure dose of 1×10^8 rads ($\sim 15 \times 10^{20}$ eV absorbed in plutonium hexafluoride), the same scheme is not easily applied to the data obtained at an exposure dose of 2×10^8 rads. In the latter case, the *G* value for the decomposition of plutonium hexafluoride decreases with increasing electron fraction of krypton and no rise in the *G* value is observed. This complete lack of enhancement of the *G* value is in contrast to most phenomena observed in radiation chemistry of gases where the processes generally do not vary abruptly with absorbed dose. A set of processes must be operative at longer exposures† which reduces the net extent of decomposition of plutonium hexafluoride. Thus, at longer exposures, reactions (1), (2), (7) and (8) may be operative. The formation of krypton fluorides, mentioned above in connection with the increasing *G* for the decomposition must, by inference, not be important at long exposures although it is not clear why this should be necessarily so. We are therefore led to the conclusion that the nature of the processes in action here is not clearly understood.

If the mechanism proposed for the decomposition of plutonium hexafluoride is coherent, it can be predicted that the addition of other gases incapable of forming fluorides would inhibit the decomposition of plutonium hexafluoride. Further, if the back reaction is important in reducing the net decomposition of plutonium hexafluoride, a gradual decrease in G with increasing exposure dose would be predicted. Addition of gases which form fluorides should result in an increase of the Gvalue for decomposition. Experiments carried out with elemental fluorine and elemental oxygen added to plutonium hexafluoride,⁽¹⁵⁾ show a pronounced decrease in G for the decomposition. In the case of added fluorine, it can be anticipated that the net decomposition is decreased because of enhancement of the back reaction. In the case of added oxygen, the picture is not quite as clear since it is possible that the stoicheiometry of the decomposition reaction involves species other than plutonium tetrafluoride. Experiments in which nitrogen was added to plutonium hexafluoride

† Experiments done at differing total exposure doses were carried out in identical fashion and differed only in length of exposure. The dose rates, materials of construction, methods of analysis methods of calculating results, etc. were the same in both sets of experiments. In addition, experiments were done without attention as to the sequence of either the krypton concentration or the irradiation time.

showed a marked increase in the decomposition of plutonium hexafluoride by alpha radiation⁽¹⁷⁾ together with the formation of nitrogen trifluoride.

It was pointed out earlier that over the range of absorbed energy studied, the decomposition of plutonium hexafluoride does not show dependence on total absorbed dose, except possibly in the case of added helium. It is believed that the absence of an observed decrease in G is due only to the limitations of the experiments. In experiments of long duration on the decomposition of plutonium hexafluoride by α -radiation⁽¹⁸⁾ it has been shown that the rate of decomposition decreases with increasing time. In view of the fact that increasing time is equivalent to increasing exposure dose, such a decrease in rate serves to confirm the equilibrium nature of the processes which affect the decomposition of plutonium hexafluoride by radiation.

Acknowledgement—Irradiations were carried out at the Argonne High Level Gamma Irradiation Facility under the direction of H. G. SWOPE. Chemical and radiochemical analyses were carried out by C. A. SEILS. The authors also wish to acknowledge the contributions made by Dr. L. DORFMAN and Dr. M. SAUER in several helpful discussions.

⁽¹⁷⁾ R. WAGNER. Unpublished results, Argonne National Laboratory (1963).

⁽¹⁸⁾ M. J. STEINDLER, R. P. WAGNER and J. FISCHER. Abstracts of Papers presented at the 144th ACS Meeting, Los Angeles, California, 1963, p. 41P.