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RADIOLYTIC AND THERMAL STABILITY OF  
SELECTED PLUTONIUM SALTS CONTAINING NITRATE GROUPS

By

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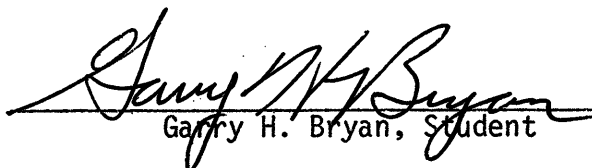
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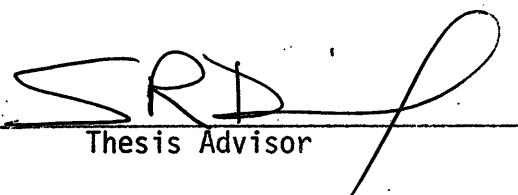
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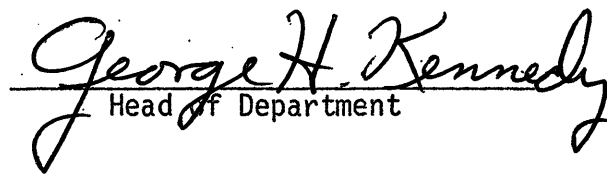
A Thesis submitted to the Faculty and the Board of Trustees  
of the Colorado School of Mines in partial fulfillment of the  
requirements for the degree of Master of Science.

  
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ABSTRACT

A solid plutonium shipping form that is easily prepared, reasonably stable, and which may be dissolved directly in nitric acid would be most desirable. Plutonium compounds that may meet these criteria are  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ ,  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ , and  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ . All of these compounds have been prepared with  $^{239}\text{Pu}$  for TGA and X-ray analysis and with  $^{238}\text{Pu}$  to accelerate radiolytic degradation studies. Oxygen is the primary radiolytic gas produced by  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  while  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  produces mostly  $\text{NO}_x$  and  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$  yields large amounts of  $\text{N}_2$ . G values have been calculated for each of the identified gases.

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ACKNOWLEDGMENTS

I would like to express by appreciation to the following people for their invaluable assistance in the completion of this thesis:

Dr. S. R. Daniel for his help, patience, advice, and constructive criticism during the course of this research.

Dr.'s D. W. Dickerhoof, G. B. Lucas, and K. W. Edwards who served on my thesis committee.

The many staff members of Battelle-Northwest who provided encouragement and inspiration.

Joanne, my wife, for her patience and perseverance throughout the course of this investigation.

The United States Energy Research and Development Administration who sponsored the research reported in this thesis.

## INTRODUCTION

It is generally recognized that the most probable situation for harm to the public from radioactive material is during the shipping mode. Thus, there is considerable emphasis at this time on increasing the safety of this portion of the nuclear fuel cycle. Current trends are for the shipment of radioactive material in the solid form as opposed to solution. The potential for release in an uncontrolled manner is considered greater for liquids as they may:

1. Steam pressurize the container if sufficient heat is available.
2. Pressurize the container due to radiolysis of the solution.
3. Produce an explosive mixture of hydrogen and oxygen.

Because solids are considered to be safer while shipping, it has been read into the Federal Register that as of June 17, 1978, all shipments of plutonium in excess of 20 curies will be in a solid form. Plutonium is considered to be an especially hazardous material as it is a bone-seeking alpha emitter with a long half-life.

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Plutonium oxide would seem to be the solid of choice. It is a stable, easily made powder that would seem an almost ideal shipping form. The oxide, however, is a compound which dissolves in nitric acid only with difficulty, and the use of hydrofluoric acid is usually necessary. Hydrofluoric acid reacts with stainless steel, thus making use of ordinary materials for glove box construction, piping and storage tanks a virtual impossibility. Purification of the plutonium, which may be necessary after long storage times, is also difficult until the fluoride ion is either complexed or removed. This requires the use of more chemicals which can only add to waste disposal problems. The presence of the fluoride also tends to increase the neutron flux, making shielding more difficult and expensive.

With the above listed difficulties in mind for the use of  $\text{PuO}_2$ , a program was funded by the Division of Waste Management and Transportation to define new chemical forms for the shipment of plutonium as a solid. The criteria for the type of material needed were as follows:

1. Solid.
2. Readily soluble in  $\text{HNO}_3$ .
3. Inexpensive to prepare.
4. Minimum amount of explosive or flammable gas produced by radiolysis.
5. Reasonable storage life without conversion to the oxide or some other insoluble form.

This form is intended to provide a more convenient form for fuel cycle utilization than the oxide. It would allow the fuel fabrication segment of the fuel cycle to store a solid that could be easily purified before

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conversion to the oxide without use of specially designed facilities that are able to withstand the use of hydrofluoric acid.

The three compounds chosen for evaluation in this study were  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ ,  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ , and  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ . The nitrates were selected as they would not add an extraneous anion to the process streams. The halides were ruled out as they would not be compatible with stainless steel, and the organics were not felt to be sufficiently radiologically stable for use. Other inorganic salts such as sulfates and phosphates were not considered, as they have limited solubility, cause impurity problems, and add to waste disposal problems.

The mechanism by which the gases are formed during the radiolysis of each compound is not fully understood. Gaseous products usually associated with the alpha-radiolysis of nitrate solutions have been studied (1,2) to some extent, and have been found to usually contain hydrogen peroxide, hydrogen, and oxygen. Several papers have been published on the decomposition of inorganic nitrates; (3,4,5,6,7) however, they deal with salts that were irradiated with gamma or X-rays and so do not necessarily correspond to experimental results found during this research.

The studies that have been made on the radiation-induced decomposition of inorganic nitrates show a very complex nature. Different nitrates show varying degrees of stability when exposed to ionizing radiation leading to numerous explanations for the different yields (G-values) that are observed.

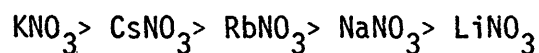
The inorganic nitrates appear to decompose when subjected to ionizing

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radiation in the following manner:

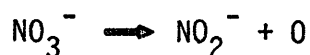


The variation in yield found when using different cations has been attributed to field strength exerted by the cation on the nitrate ion (polarizing power of the cation) (8). Henning, Lees, and Matheson (9) found large differences in yields during radiation decomposition of  $\text{NaNO}_3$  and  $\text{KNO}_3$ . They felt bonding energy differences were insufficient to account for the differences and proposed that the variation in "free space" might be a possible explanation, presumably due to the fact that in solid state decompositions the products and their rates of formation are dependent upon the immediate spatial and electronic environment. "Free space" was defined as the average volume per ion pair minus the average volume of cation and anion as calculated from standard ionic radii. Cunningham and Heal (4) made an extensive study of the radiolysis of several nitrates and their yields (G-values) plotted as a smooth function of free space. The order of decreasing G-values was as follows:

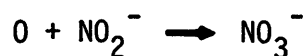


There is an anomaly in this work; however, inasmuch as  $\text{CsNO}_3$  has subsequently been found to have a higher G-value than  $\text{KNO}_3$ , but a smaller free space (5).

An ambient temperature study of inorganic nitrate decomposition by Chen and Johnson (6) has led to a proposed mechanism that would seem to agree with experimental data. It is as follows:



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The back reaction was found to occur in all the nitrate studies, and decompositions appeared to approach a steady state. The second derivative or slope of the  $NO_2^-$  yield vs. dose curve ( $d^2x/dT^2$  where  $x = NO_2^-$  concentration and  $T$  is proportional to dose), indicates  $CsNO_3$  approaches a steady state more rapidly than does  $KNO_3$  or  $NaNO_3$ . This information indicates that the back reaction for  $CsNO_3$  is much greater than it is for  $KNO_3$ , which is a more loosely packed lattice or  $NaNO_3$  which is a more tightly packed lattice. Free space, therefore, would appear to have no substantial effect on the kinetics of the reaction.

Logan and Moore (10) have indicated that G-values are affected by the relative ease of transferring energy to lattice vibrational modes of the crystal structure. The density of the vibrational states as well as any increase in the average energy of the force constants due to tightness of packing will facilitate the dissipation of energy into the lattice vibrations. The amount of electronic coupling to lattice vibrations will have some relationship to the polarizability of the cation and to the free space in the lattice, and these parameters are also responsible for a particular crystal structure.

Factors such as reactions between radiation induced reaction products, lattice damage from the radiation, stability of primary products, and impurities may also be expected to play some role--major or minor--in the

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radiation decomposition of any given inorganic nitrate. Variations in any or all of these factors may change the yields (G-values) to an appreciable extent.

The ammonium salt is somewhat different inasmuch as the cation itself may be decomposed and is sensitive to the effects of heat and radiation. The radiolytic decomposition of ammonium nitrate has been reported to be comparable to thermal decomposition at high dose rates (11). Ammonium nitrate volatilizes reversibly at moderate temperatures; irreversibly at higher temperatures giving mainly  $N_2O$  and at still higher temperatures, the  $N_2O$  decomposes into nitrogen and oxygen (12).

EXPERIMENTAL

The 84.8 wt %  $^{238}\text{Pu}$  used in this work was prepared by the neutron irradiation of  $^{237}\text{Np}$ . The 17.8 wt %  $^{238}\text{Pu}$  was prepared by the mixing of appropriate amounts of nitric acid solutions of the 84.8 wt %  $^{238}\text{Pu}$  and 91.3 wt %  $^{239}\text{Pu}$ . The results of mass spectrometric isotopic analysis of the final product in each case are shown in Tables I and II. All other chemicals were reagent grade and were used without further purification.

The simple plutonium(IV) nitrate salt  $[\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}]$  was prepared by vacuum evaporation at 1 torr and ambient temperature of an 8M nitric acid solution of plutonium nitrate that was prepared by dissolution of  $\text{PuO}_2$  with  $\text{HNO}_3$ -HF followed by anion exchange to remove fluorides and other impurities. Less than 24 hours was required to prepare a solid sample from the 84.8 wt %  $^{238}\text{Pu}$  due to self-heating. Samples prepared from 17.8 wt %  $^{238}\text{Pu}$  required from 3-5 days.

Table I

<u>Isotope</u>	<u>Weight Percent</u>
$^{238}\text{Pu}$	84.8 $\pm$ 0.06 wt %
$^{239}\text{Pu}$	11.19 $\pm$ 0.06 wt %
$^{240}\text{Pu}$	3.22 $\pm$ 0.02 wt %

Table I (cont'd)

<u>Isotope</u>	<u>Weight Percent</u>
$^{241}\text{Pu}$	$0.665 \pm 0.007 \text{ wt } \%$
$^{242}\text{Pu}$	$0.122 \pm 0.003 \text{ wt } \%$

Table II

<u>Isotope</u>	<u>Weight Percent</u>
$^{238}\text{Pu}$	$17.4 \pm 0.1 \text{ wt } \%$
$^{239}\text{Pu}$	$74.9 \pm 0.1 \text{ wt } \%$
$^{240}\text{Pu}$	$6.946 \pm 0.005 \text{ wt } \%$
$^{241}\text{Pu}$	$0.635 \pm 0.005 \text{ wt } \%$
$^{242}\text{Pu}$	$0.079 \pm 0.002 \text{ wt } \%$

The starting plutonium concentration in all cases was about 230 g Pu/liter solution.

The potassium and ammonium hexanitratoplutonate (IV) salts were prepared by the addition of a 10% stoichiometric excess of potassium or ammonium nitrate to plutonium(IV) nitrate in 8M nitric acid, followed by vacuum evaporation at ambient temperature. Once again, the 84.8 wt %  $^{238}\text{Pu}$  compounds required less than 24 hours to prepare while those samples having lesser amounts of  $^{238}\text{Pu}$  required 3-5 days of evaporation before dryness was obtained.

During the course of evaporation, the simple plutonium(IV) nitrate  $[\text{Pu}(\text{NO}_3)_4 \cdot \text{xH}_2\text{O}]$  solution became extremely viscous before becoming a solid, indicating a very high solubility. The potassium and ammonium salts are

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less soluble and crystallized during the course of evaporation. The uranium salt,  $KUO_2(NO_3)_3$ , that was used for X-ray comparison purposes, was prepared by the mixing of stoichiometric amounts of  $KNO_3$  and  $UO_2(NO_3)_2$  in nitric acid followed by filtering, washing, and drying.

The radiolytic gas measurement apparatus used is shown in Figure I. A weighed sample of the solid compound to be tested was placed in the glass sample container and held in place with a glass wool plug. The sample container was then placed in a stainless steel outer sample container with a cap containing a stainless steel frit to allow the passage of gases. The stainless steel sample container was placed in the radiolytic gas measurement apparatus and closed off. The sample was then purged with helium gas for 30 minutes with pressure pulsing to insure removal of all other gases. This arrangement was found to contain the plutonium compound under study quite well and allowed measurements to be taken in an open hood without contamination of the apparatus.

A 10 mm layer of silicon oil was placed on top of the mercury on each side of the monometer prior to use to retard reaction with any corrosive gases produced during the course of the experiment. All manometer readings were obtained by use of a cathometer.

Gas samples were taken by evacuating to less than 1 torr in the sample collector and the area between the collector and the measurement apparatus (see Figure I) with the gas then being drawn into the collector from the apparatus and placed on a Consolidated Electrodynamics Corporation 21-130 mass spectrometer to determine the gases which had been produced.

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The amount of gas generated by the solid per 100 ev ( $G_T$  value) was calculated using the ideal gas law (see Appendix B); and the dose rate of the material used as determined by the following equation:

$$\text{Dose rate} = (\text{Sp. activity } ^{239}\text{Pu})E_{\alpha} [(\%^{239}\text{Pu}) + 3.7(\%^{240}\text{Pu}) + 301(\%^{238}\text{Pu}) + 6.7(\%^{241}\text{Pu})^* + 62.2(\%^{241}\text{Pu}) (1 - e^{-0.049Y})]/100 \quad (1)$$

$E_{\alpha}$  = alpha energy of  $^{239}\text{Pu}$  in millions of electron volts (Mev)

Y = time in years since chemical separation of Am from Pu.

\* This factor assumed the  $\beta$  radiation contribution will produce about the same G-values as  $\alpha$  radiation.

The  $^{238}\text{Pu}$  contributes, by far, the largest amount of energy in the case of the 84.8 wt %  $^{238}\text{Pu}$  material allowing the energy contributions of the other isotopes to be disregarded.

Thermogravimetric analyses were obtained using an Ainsworth Semimicro Recording Balance. All analyses were made in an air atmosphere to simulate actual conditions to which the compound might be subjected in the shipping mode. This procedure also resulted in the conversion of the compounds to  $\text{PuO}_2$  which allows calculation of the original molecular weight of the material in question. A heating rate of  $20^\circ/\text{min}$  was used in all cases.

X-ray analyses were performed on a General Electric XRD-5 x-ray diffractometer. All compounds were subjected to analysis as well as any intermediates found during thermogravimetric analysis. Patterns were obtained only for those materials which were prepared from 91.3 wt %  $^{239}\text{Pu}$ . All others were found to be amorphorous.

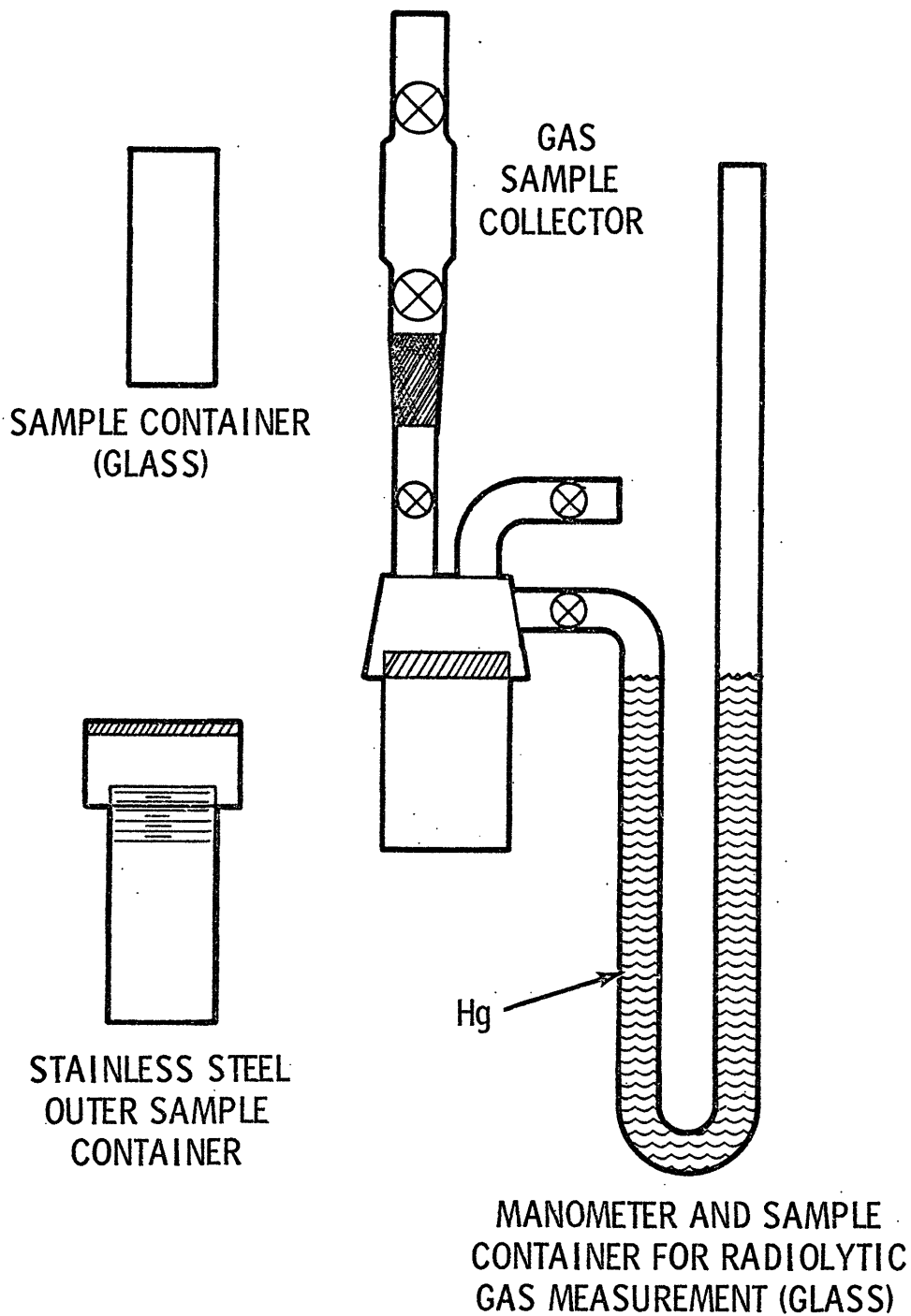


FIGURE I. RADIOLYTIC GAS MEASUREMENT APPARATUS

## RESULTS AND DISCUSSION

### A. Radiolytic Gas Generation

The  $G_T$  values (molecules per 100 ev) have been calculated as a function of dose rate for each of the three compounds under consideration [ $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ ,  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ , and  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ ], as shown in Figure II. The high  $G_T$  values found in the case of  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$  were not completely unexpected as ammonium nitrate salts are not normally stable to radiation. The  $G_T$  values of  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  and  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  were found to be much the same (each decreasing with accumulated dose and approaching a value of about 0.025) above about  $10^{18}$  Mev/g<sub>Pu</sub>.

Each of the compounds was prepared with 84.8 wt %  $^{238}\text{Pu}$  to accelerate the acquisition of data. The simple plutonium nitrate ( $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ ) was also prepared using 17.4 wt %  $^{238}\text{Pu}$  as TGA results indicated the 84.8 wt % material did not have the proper molecular weight and may have degraded to some intermediate (see TGA section for further explanation). Therefore, the figures used for Figure II were found using the 17.4 wt %  $^{238}\text{Pu}$  material which also more closely simulates actual reactor grade content.

Given the  $G_T$  values, the rate of radiolytic gas generation with a specified amount of  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  is 
$$\left( g_{\text{Pu}} \right) \left( \frac{\text{sp. activity}}{6.02 \times 10^{23}} \right) \left( E_d \right) \left( G_T \right) =$$

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$$1.67 \times 10^{-5} g_{Pu} [(\%^{239}Pu) + 3.7 (\%^{240}Pu) + 301 (\%^{238}Pu) + 6.7 (\%^{241}Pu) + 62.2 (\%^{241}Pu) (1 - e^{-0.049Y})] \text{ moles gas per day}$$

and  $G_T = G_{(H_2)} + G_{(O_2)} + G_{(N_2)} + \dots$  (2)

The rate of pressurization in a given container will be:

$$\frac{dp}{dt} = 2.01 \times 10^{-4} \frac{K}{V-W/2.90} g_{Pu} G_T [(\%^{239}Pu) + 3.7 (\%^{240}Pu) + 301 (\%^{238}Pu) + 6.7 (\%^{241}Pu) + 62.2 (\%^{241}Pu) (1 - e^{-0.049Y})]$$
 (3)

where K = degrees Kelvin

t = time in days

V = container volume in ml

W = weight of  $Pu(NO_3)_4 \cdot xH_2O$  of density  $2.90 \text{ g/cm}^3$  (ref. 5)

Y = time in years since chemical separation of Am from Pu

$E_\alpha$  = alpha energy in electron volts.

$g_{Pu}$  = grams plutonium

p = pressure in psi

Hydrogen is not a major constituent (see Table III) in any of the three cases studied, and the  $H_2/O_2$  ratio should not present an explosion hazard. Upon long term storage, the relative amount of radiolytic hydrogen does increase in the case of  $Pu(NO_3)_4 \cdot xH_2O$ , but when viewed from the standpoint of total gas produced by the solid, it remains at a low level.

Very little oxygen was found in the gaseous products of  $(NH_4)_2Pu(NO_3)_6$ ; however, a large amount of nitrogen was noted. To account for the lack of oxygen, it would be necessary to postulate the oxygen recombining with

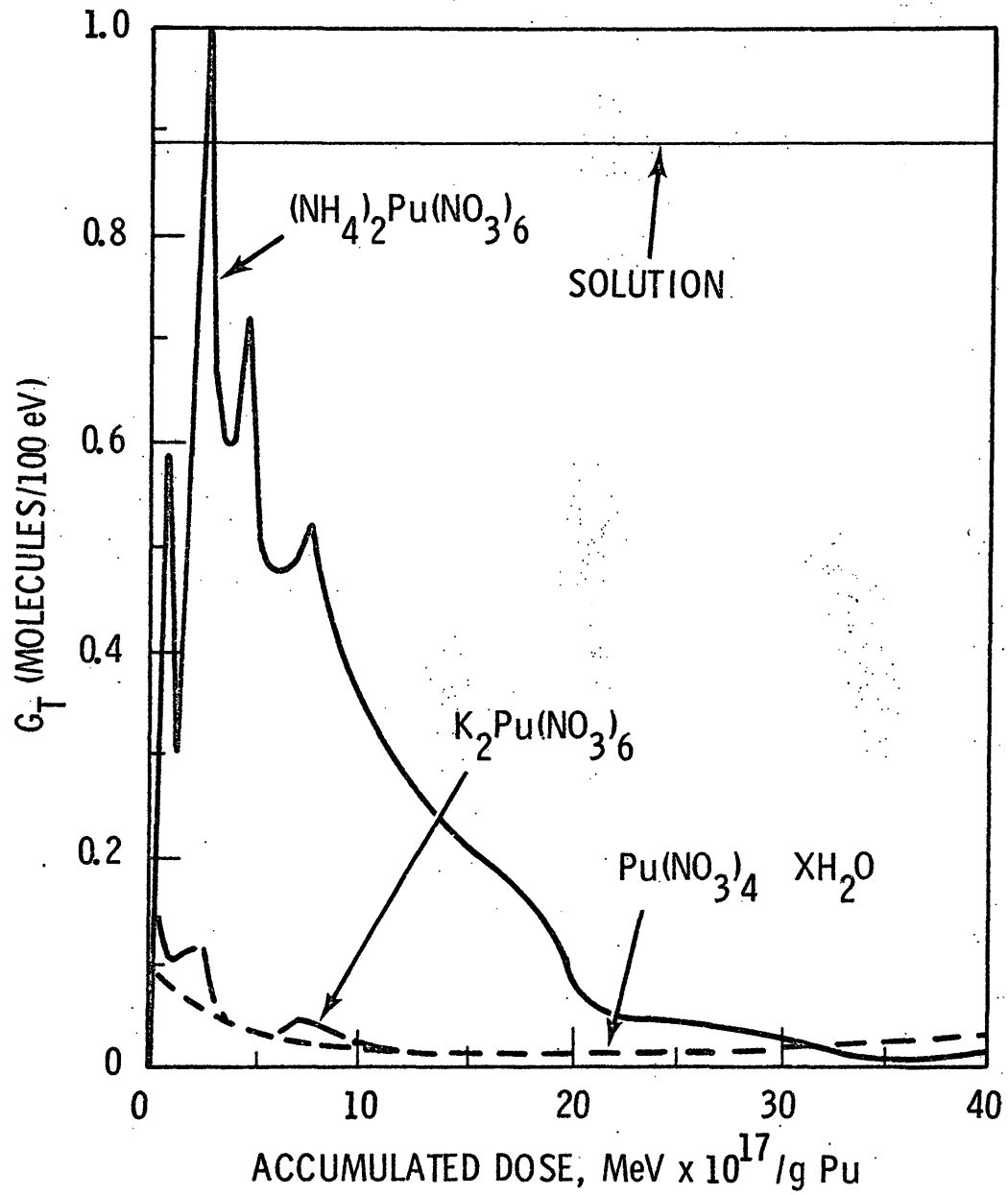
FIGURE II.  $G_T$  VALUE VS ACCUMULATED DOSE

TABLE 3. Composition of Radiolytic Gases Evolved From  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ , and  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  as a Function of Accumulated Alpha Dose\*

	1 x 10 <sup>17</sup> MeV			9 x 10 <sup>17</sup> MeV			20 x 10 <sup>17</sup> MeV		
	$\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$	$\text{K}_2\text{Pu}(\text{NO}_3)_6$	$(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$	$\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$	$\text{K}_2\text{Pu}(\text{NO}_3)_6$	$(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$	$\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$	$\text{K}_2\text{Pu}(\text{NO}_3)_6$	$(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$
O <sub>2</sub> %	57	24	0.2	71	23	0.2	49	18	0.2
N <sub>2</sub> %	18	6	55	13	20	61	27	49	56
H <sub>2</sub> %	1.4	0	0.5	2.4	0.3	0.5	6	0	0.7
NO <sub>x</sub> %	15	56	23	4	39	2.7	7	18	32
N <sub>2</sub> O%	0	14	20	6	11	8	4	8	8
CO <sub>2</sub> %	7	0	0	4	7	0	7	7	1
CO%	0	0	2	0	0	3	0	0	2

\*Typical reactor grade plutonium might undergo a dose of about  $1.3 \times 10^{17}$  MeV/g per month whereas the dose from the material used to compile this table was  $1.6 \times 10^{18}$  MeV/g per month for  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  and  $7.8 \times 10^{18}$  MeV/g per month for  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$  and  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ .

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hydrogen to form water, which would also account for the small amount of hydrogen found. The high nitrogen production could also be accounted for by the recombining of the plutonium with oxygen to form plutonium dioxide. Proof of such a mechanism might be very difficult, however. The preponderance of oxygen in the radiolytic gases of  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ , as compared to  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  is at least in part due to the waters of hydration associated with the molecule inasmuch as water may also be radiolytically decomposed. The hydrogen formed during the radiolytic decomposition of water could react with a nitrate to form nitrite and water or by a similar hydrogen "scavenging" mechanism. The other variation can probably be attributed to lattice vibrations, cation polarizability, and the other effects discussed previously. To make a measurement of the contribution of any one factor would be extremely difficult and probably cannot be done except on a theoretical basis.

#### B. Thermal Stability

Each of the compounds under study ( $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ ,  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ , and  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ ) was subjected to thermogravimetric analysis. This procedure was carried out in order to determine intermediates that may have formed and to convert the compounds to the oxides for molecular weight determinations. All runs were made in air to simulate actual conditions the compounds might be subject to as a shipping form and to convert the compounds to the oxides.

TGA curves for these compounds are shown in Figures III, IV, and V. The compound used in each case was freshly made using  $^{239}\text{Pu}$  so as to preclude excessive radiation damage. The curve found for  $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$  (Figure III) is much the same as that determined by Drummond and Welch (13) for  $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ . From molecular weight calculations the intermediate was postulated to be  $\text{PuO}_2(\text{NO}_3)_2$ . The intermediate was formed when  $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$  (MW = 541) had undergone about a 28% weight loss. The calculated molecular weight (28% weight loss of  $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ ) of the proposed intermediate ( $\text{PuO}_2(\text{NO}_3)_2$  MW = 395) is 390. Spectrophotometric analysis on freshly dissolved solid also indicated the presence of  $\text{PuO}_2^{2+}$ ; however, the intermediate formed was not identified by X-ray analysis, as it could not be isolated.

The TGA curve for  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  (Fig. IV) also indicates a somewhat unstable intermediate, probably of the formula  $\text{K}_2\text{PuO}_2(\text{NO}_3)_4$ , before decomposition to  $\text{KNO}_3$  and  $\text{PuO}_2$ . The endpoint of this TGA is not specific, however, due to formation of  $\text{K}_2\text{O}$  and evaporation of  $\text{KNO}_3$ . Because of the low temperature at which the water is evolved from the salt, it may not be a part of the crystal structure but rather sorbed. The intermediate formed with this particular compound is stable enough to permit the obtaining of an X-ray powder pattern and is apparently not a double salt as will be described in greater detail under the X-ray section.

Thermogravimetric analysis of the ammonium salt  $[(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6]$  indicated no intermediates were formed (see Fig. V). Copious amounts of gas were evolved during the course of the analyses; however, they were quite corrosive in nature.

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### C. X-ray Analysis

All X-ray patterns of  $^{238}\text{Pu}$  salts showed them to be amorphous; presumably from radiolytic breakdown of the crystal structure. Therefore, each of the three salts under study was made from  $^{239}\text{Pu}$  to obtain patterns for identification and classification (see Fig. VI). The intermediate indicated by TGA on  $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$  is unstable and powder pattern identification was not achievable; however, the intermediate found with  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  is sufficiently stable to produce an X-ray pattern as indicated in Figure VI.

Positive identification of the intermediate formed by heating of  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  (MW = 689) has not been achieved. TGA indicates the intermediate has a molecular weight of 558 (19% weight loss of  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ ) indicating it is probably  $\text{K}_2\text{PuO}_2(\text{NO}_3)_4$  (MW = 565). X-ray patterns of the uranium salt  $\text{KUO}_2(\text{NO}_3)_3$  do not compare with those found for the intermediate which probably rules out a mixture of  $\text{KNO}_3$  and  $\text{KPuO}_2(\text{NO}_3)_3$ ; however, the compound is probably  $\text{KNO}_3 \cdot \text{KPuO}_2(\text{NO}_3)_3$ . It is unlikely that it is the tetranitrato-plutonyl (VI),  $[\text{PuO}_2(\text{NO}_3)_4]^{2-}$  species. Although the tetranitratouranyl (VI) complex is known, Ryan was not able to prepare a  $\text{K}^+$  salt containing this species, (14,15) and found that the cesium salt,  $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ , contains the trinitrato complex and one ionic nitrate.

The X-ray powder pattern (see Figure VI) obtained for  $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$  is not the same as that found by Staritzky (16) for  $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ . The pentahydrate was found to be orthorhombic and isomorphous with the corresponding nitrates of thorium and cerium. It also has 8 formula units per cell, a density of 2.90 grams per cc, and is hygroscopic.

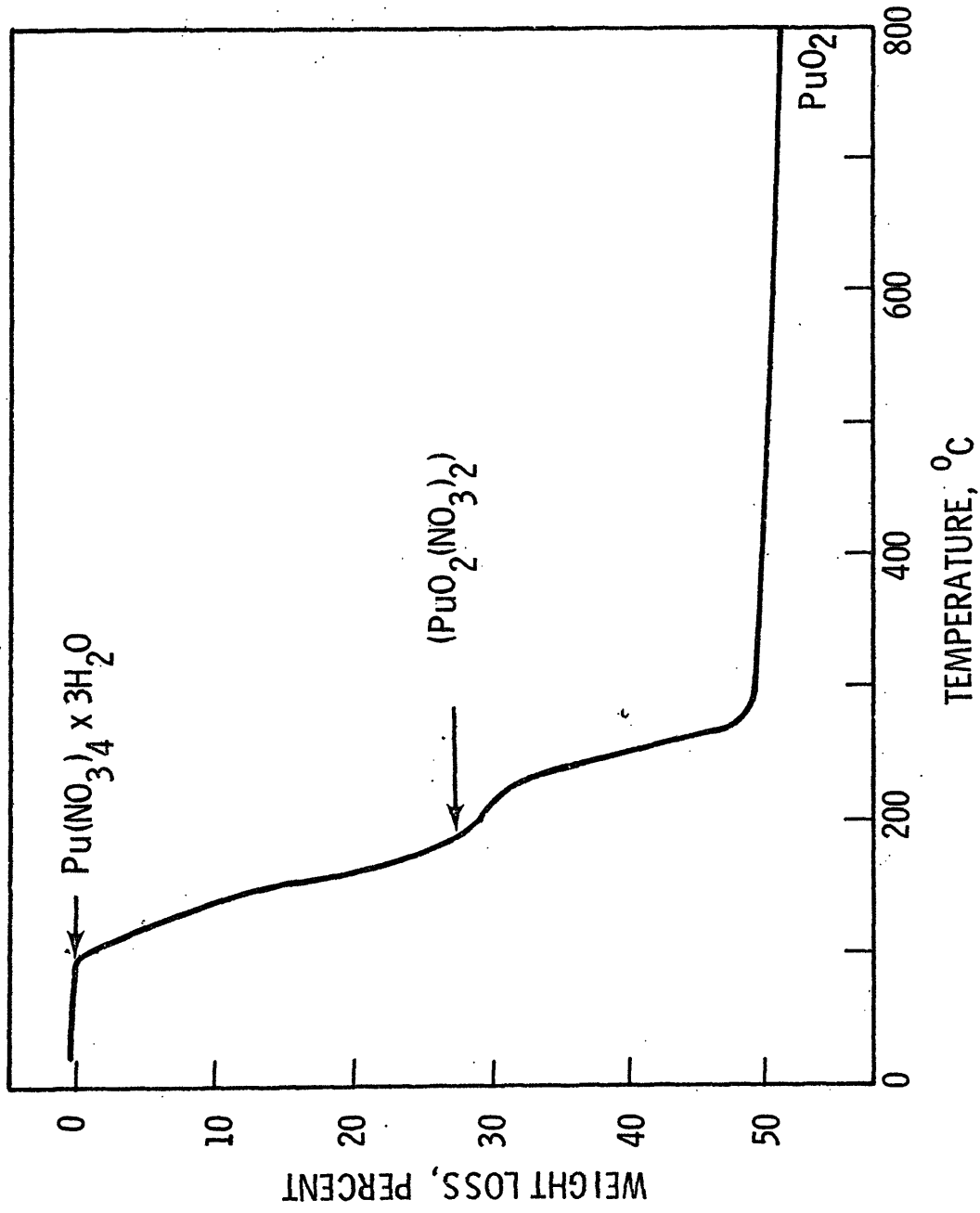


FIGURE III. THERMOGRAVIMETRIC CURVE FOR PLUTONIUM NITRATE

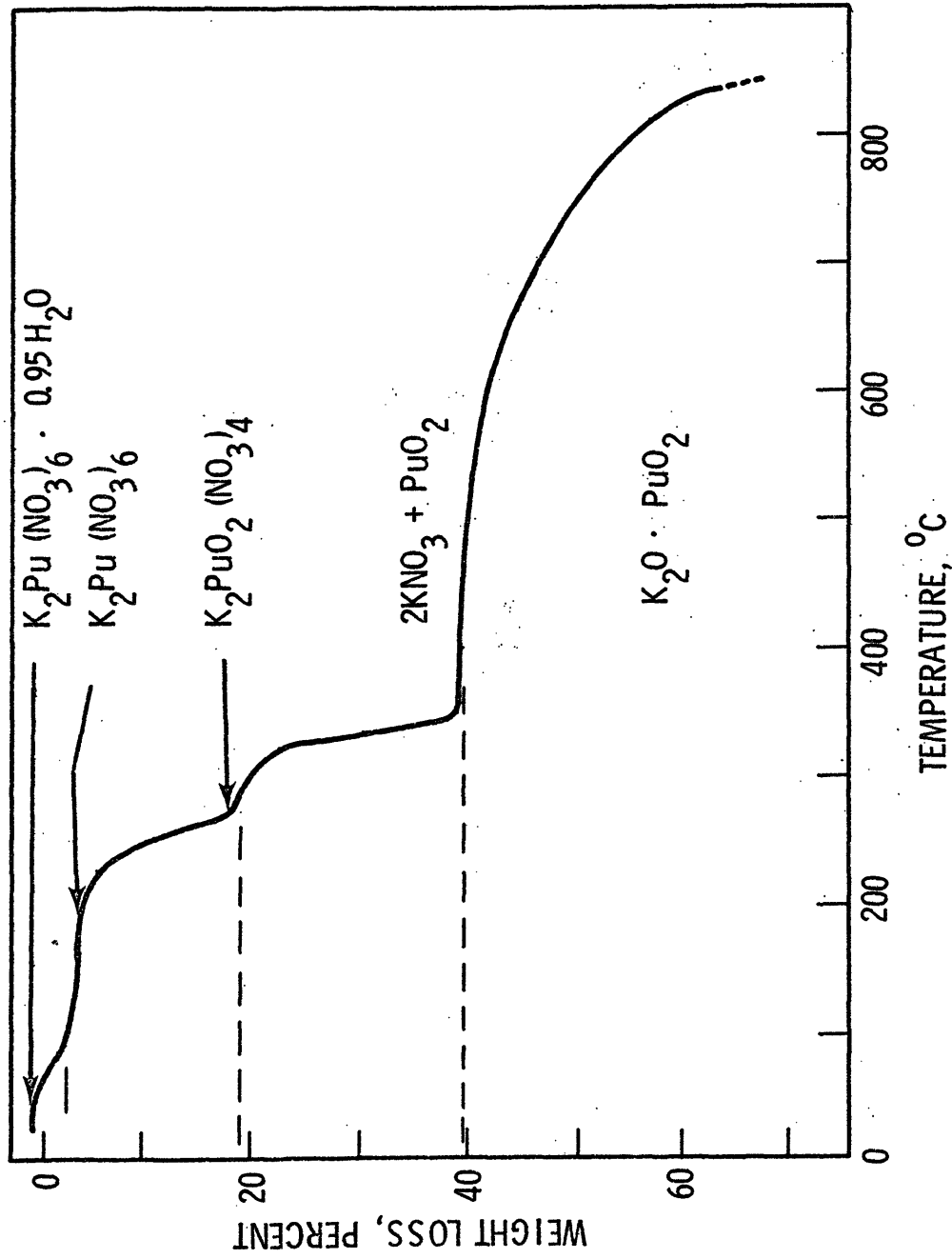


FIGURE IV. THERMOGRAVIMETRIC CURVE FOR POTASSIUM HEXANITRATOPLUTONATE

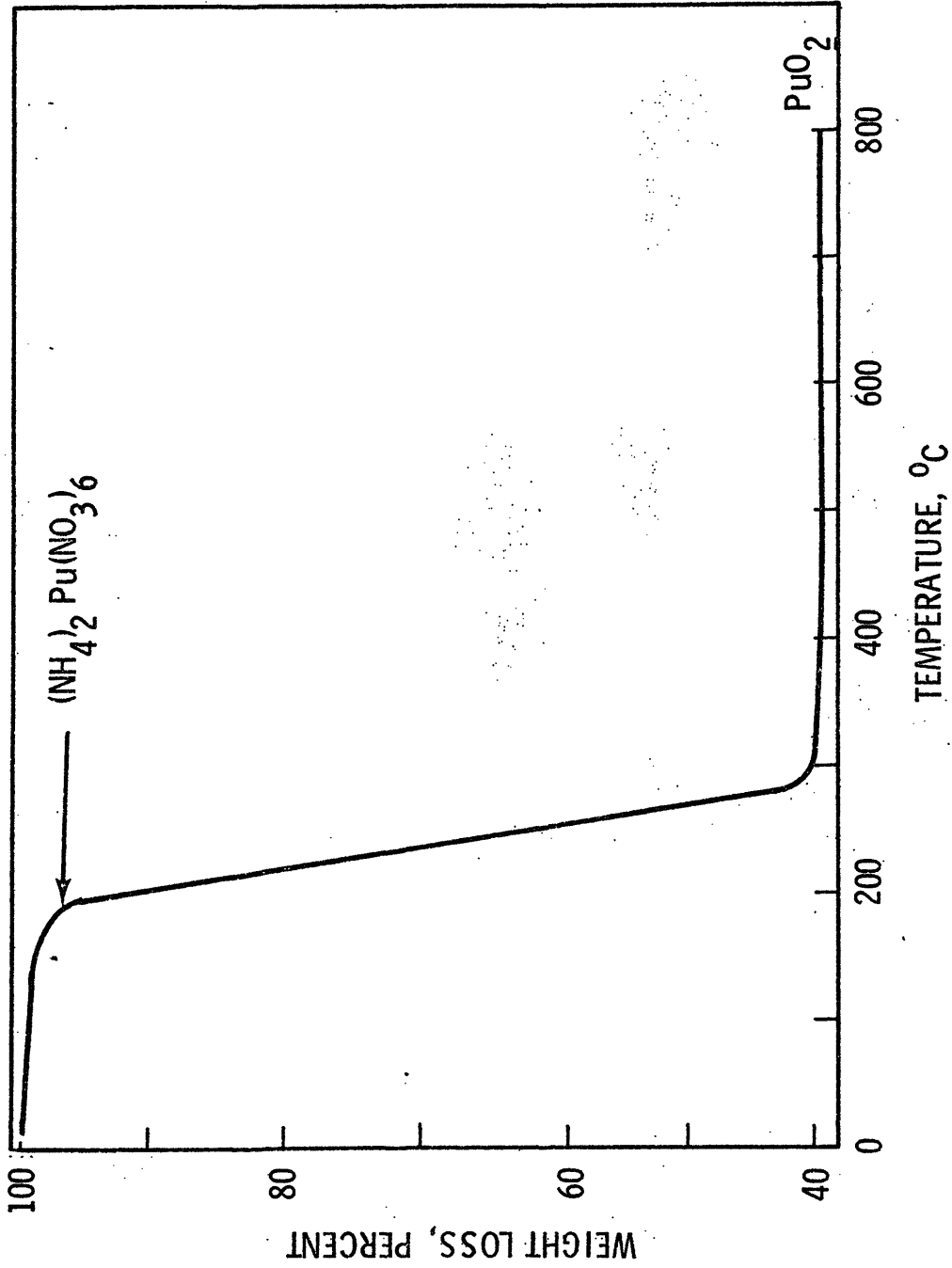


FIGURE V. THERMOGRAVIMETRIC CURVE FOR AMMONIUM HEXANITRATOPLUTONATE

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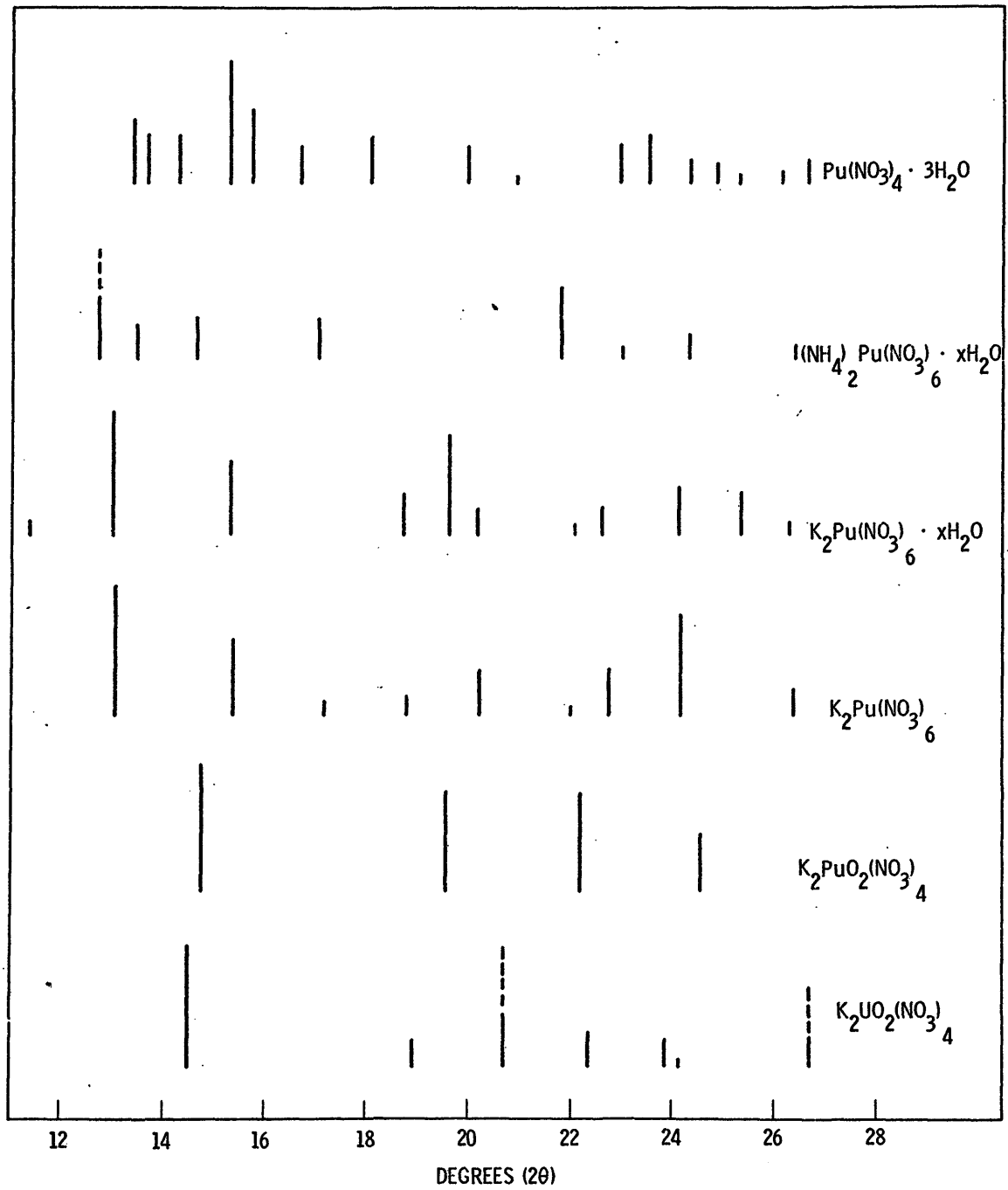


FIGURE VI. X-RAY POWDER DIFFRACTION PATTERNS

No X-ray powder patterns are known to be available for  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$  and  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ . It is interesting to note the apparent lack of correlation between the two patterns which is unusual inasmuch as they both possess the  $\text{Pu}(\text{NO}_3)_6^{2-}$  complex. (17) Complete analyses of the X-ray patterns in each case was not possible; however, further investigation could conceivably give an explanation as to the difference in radiolytic decomposition behavior.

#### D. Solubility

The solubility of each of the three compounds prepared was determined using 84.8 wt %  $^{238}\text{Pu}$  to accelerate experimental test results. The compound  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  was stored in a desiccator for 171 days and still found to be soluble in 4M  $\text{HNO}_3$  at  $28^\circ$  with 4 hours of agitation. This is equivalent to 25 or more years of radiation damage from reactor grade plutonium. The compound  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  was stored for the reactor grade plutonium radiation equivalent of about five years and  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$  for the equivalent of about three years.

Each of the compounds under study was also prepared from  $^{239}\text{Pu}$  and stored in a desiccator. The samples were all found to be completely and readily soluble in 4M  $\text{HNO}_3$  at  $25^\circ$  after the equivalent of 1.5 years storage. No further solubility tests were carried out on these compounds; however, complete solubility for several years could be expected.

### CONCLUSIONS

Three plutonium nitrate compounds ( $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ ,  $\text{K}_2\text{Pu}(\text{NO}_3)_6$ , and  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ ) have been studied to evaluate their ability to serve as shipping forms that meet the criteria as outlined in the Introduction. Each compound was subjected to a systematic study to allow the selection of the most eligible compound for further evaluation on a pilot-plant basis.

The radiolytic gas evolution study eliminated  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$  from further consideration as a shipping form due to its production of considerably more gas per gram of material than was found with either  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  or  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ , which were found to have about the same  $G_T$  value. None of the compounds produced  $\text{H}_2$  or  $\text{O}_2$  in sufficient quantity to produce a flammable mixture with the exception of  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  which produced  $\text{O}_2$  and  $\text{H}_2$  in a ratio that is above explosive limits after long storage time. However, the  $\text{H}_2/\text{O}_2$  ratio of the sum totals of these gases produced by  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  is below explosive limits.

Each compound produces differing amounts of  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NO}_x$ ,  $\text{N}_2\text{O}$ , etc., indicating somewhat different mechanisms for gaseous release. The ammonium salt decomposition appears to be about the same as that observed upon heating of  $\text{NH}_4\text{NO}_3$  to produce  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , and nitrous oxides. The potassium

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salt and simple plutonium nitrate may invoke a similar mechanism for decomposition of the nitrate; however, plutonium nitrate contains some water of hydration which will also be affected by alpha radiation and contribute to the overall gaseous release which probably accounts for its higher  $O_2$  and  $H_2$  yields.

The mechanism of radiolytic decomposition in each case may only be postulated. Although some work has been reported on the decomposition of solid nitrates by electromagnetic radiation, none has been found that deals with alpha radiation and its high specific ionization (number of ion pairs formed per millimeter of path). The mechanism of decomposition would be expected to be considerably different than is found with forms of radiation having lower specific ionization and further research is needed to specify the mechanism. The use of labeled nitrogen and oxygen may be a route by which further mechanistic evaluation could be made. This technique should allow the determination of the origin of the nitrogen products produced during the radiolysis of  $(NH_4)_2Pu(NO_3)_6$ . It should also indicate the contribution of the water in  $Pu(NO_3)_4 \cdot xH_2O$  to the gaseous oxygen yield and how yields of each gaseous product are affected by radiation dose.

Information obtained from this technique in conjunction with a detailed study of X-ray, TGA, and gaseous yield dose dependency compared against like information obtained from  $K_2Pu(NO_3)_6$  may allow the postulation of mechanisms of decomposition for each, and a comparison to that for thermal decomposition.

The water associated with  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  is of some concern due to the production of hydrogen by alpha-radiolysis. Its presence is a potential explosion hazard and must be avoided if at all possible. Two waters of hydration as determined by TGA appear to be the lower limit to which  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  may be taken before decomposition of the solid begins. The production of  $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$  as a shipping form must be carefully controlled, therefore, to insure a consistent product from the standpoint of hydrogen production, thermal stability, criticality, and accountability. The material is also somewhat hygroscopic, so care must be exercised during its handling.

X-ray data proved to be rather inconclusive as obtained powder patterns did not compare with published patterns when available. Further X-ray work to determine crystal morphology, space group, cell dimensions, formula units per cell, and density could prove to be useful in the determination of decomposition mechanisms.

TGA results indicate the simple nitrate  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  is somewhat less thermally stable than either the ammonium or potassium hexanitratoplutinate (IV) which detracts somewhat from its suitability as a shipping form. The maintaining of large quantities of this compound with a high  $^{238}\text{Pu}$  content (1%  $^{238}\text{Pu}$ ) may require specially designed containers to prevent thermal degradation and gas pressure buildup problems. These containers would undoubtedly be larger than those now in use, but in all probability would not present a problem as the controlling factor in a

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given shipment is usually the amount of plutonium and not the size or weight of its containers.

The final selection of the compound to be tested as a shipping form on a pilot-plant scale was done on the basis of the work described and on the needs of those who would ship and receive the plutonium. A meeting was held to present the information obtained to present and future plutonium processors and to solicit their input with discussion centered largely on  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  and  $\text{K}_2\text{Pu}(\text{NO}_3)_4$ . The final consensus of this group was that in spite of some thermal instability of  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  at fairly low temperatures, it was preferable to  $\text{K}_2\text{Pu}(\text{NO}_3)_6$  due to the additional waste disposal problems the potassium would present.

It is concluded that the plutonium compound  $(\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O})$  selected also has several other advantages that have not been enumerated in this report. It requires less equipment to prepare than does  $\text{PuO}_2$ , making the overall preparative procedure quite simple. The oxide may also be easily made from the nitrate if desired. The preparation of mixed oxides could be readily achieved by a precipitation step to insure uniform mixing rather than by mechanical mixing of the oxides. Also, as plutonium nitrate is a nitric acid soluble compound, purification just prior to formation of the oxide is easily accomplished if, for example, long storage times before use of the plutonium were necessary and undesirable amounts of americium from  $^{241}\text{Pu}$  decay were present.

Plutonium accountability may be a problem due to the variable weight of plutonium nitrate. However, if the plutonium content of the solution

prior to evaporation to the solid is known, the amount to be shipped is known. The receiver may then easily check the plutonium content by conversion of a weighed amount to the oxide or by dissolution of the solid in nitric acid for analysis.

Work is now in progress by another ERDA contractor to prepare kilogram quantities of plutonium nitrate. One run has been successfully made that contained 920 grams of plutonium. More pilot-plant scale work is required to optimize operating parameters and equipment design; however, the process has been successful to this point and work is continuing.

Plutonium nitrate would appear to be a viable shipping form if accepted by the nuclear industry. There are some problems, such as thermal conductivity, that need further study to completely define the material. Pilot-plant studies could easily accomplish this task. The final fate of  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  must, of course, rest with Congress and the public with regards to their acceptance of nuclear power and in particular, the plutonium recycle question. Without plutonium recycle, the use of  $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$  as a shipping form is a moot point.

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APPENDIX A

The dose rate equation (1) was derived by normalizing the sp. activities and alpha energies (Mev.) for each plutonium isotope to that of  $^{239}\text{Pu}$  in the following manner:

$$\begin{aligned} {}^{240}\text{Pu} &= \frac{t_{1/2} {}^{239}\text{Pu}^*}{t_{1/2} {}^{240}\text{Pu}} \cdot \frac{E_{\alpha} {}^{240}\text{Pu}}{E_{\alpha} {}^{239}\text{Pu}} (\% {}^{240}\text{Pu}) \\ &= \frac{24,400}{6600} \cdot \frac{5.17}{5.16} (\% {}^{240}\text{Pu}) \\ &= 3.7 (\% {}^{240}\text{Pu}) \end{aligned}$$

$$\begin{aligned} {}^{238}\text{Pu} &= \frac{t_{1/2} {}^{239}\text{Pu}}{t_{1/2} {}^{238}\text{Pu}} \cdot \frac{E_{\alpha} {}^{238}\text{Pu}}{E_{\alpha} {}^{239}\text{Pu}} (\% {}^{238}\text{Pu}) \\ &= \frac{24,400}{86.4} \cdot \frac{5.50}{5.16} (\% {}^{238}\text{Pu}) \\ &= 301 (\% {}^{238}\text{Pu}) \end{aligned}$$

$$\begin{aligned} {}^{241}\text{Pu} &= \frac{t_{1/2} {}^{239}\text{Pu}}{t_{1/2} {}^{241}\text{Pu}} \cdot \frac{E_{\beta} {}^{241}\text{Pu}}{E_{\alpha} {}^{239}\text{Pu}} (\% {}^{241}\text{Pu}) \\ &= \frac{24,400}{14.1} \cdot \frac{0.02}{5.16} (\% {}^{241}\text{Pu}) \\ &= 6.7 (\% {}^{241}\text{Pu}) \end{aligned}$$

${}^{241}\text{Am}$  from decay of  ${}^{241}\text{Pu}$

$$\begin{aligned} N_1^0 &= \text{original amount of } {}^{241}\text{Pu} \text{ at time of chemical separation from} \\ &= (\% {}^{241}\text{Pu}) \end{aligned}$$

$N_2$  = amount of  ${}^{241}\text{Am}$  produced by decay of  ${}^{241}\text{Pu}$

\*  $t_{1/2}$  = constant/sp. activity

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$Y$  = time in years

$\lambda_1$  = decay constant for  $^{241}\text{Pu}$

$\lambda_2$  = decay constant for  $^{241}\text{Am}$

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^{\circ} (e^{-\lambda_1 Y} - e^{-\lambda_2 Y}) + N_2^{\circ} e^{-\lambda_2 Y}$$

$$N_2 = \frac{0.049}{0.0016 - 0.049} N_1^{\circ} (e^{-\lambda_1 Y} - e^{-\lambda_2 Y}) + 0 \cdot e^{-\lambda_2 Y}$$

for time periods of one year or less:

$$e^{-\lambda_2 Y} = e^{-0.0016 Y} \approx e^0 = 1$$

$$N_2 = -1.04 (e^{-\lambda_1 Y} - 1) (\% \text{ } ^{241}\text{Pu})$$

$$= -1.04 (1 - e^{-0.049 Y}) (\% \text{ } ^{241}\text{Pu})$$

$$N_2 = \frac{t_{1/2} \text{ } ^{239}\text{Pu}}{t_{1/2} \text{ } ^{241}\text{Am}} \cdot \frac{E_{\alpha} \text{ } ^{241}\text{Am}}{E_{\alpha} \text{ } ^{239}\text{Pu}} (1.04 (1 - e^{-0.049 Y}) (\% \text{ } ^{241}\text{Pu}))$$

$$N_2 = \frac{24,400}{433} \cdot \frac{5.48}{5.16} (1.04) (1 - e^{-0.049 Y}) (\% \text{ } ^{241}\text{Pu})$$

$$N_2 = 62.2 (1 - e^{-0.049 Y}) (\% \text{ } ^{241}\text{Pu})$$

Equation (1) is therefore:

$$\text{Dose rate (1)} = g_{\text{Pu}} \cdot \text{sp. activity (dis/day-gm)} \cdot E_{\alpha} (\text{Mev/dis}) = \text{Mev/day}$$

$$\begin{aligned} \text{Dose rate (1)} = g_{\text{Pu}} (\text{sp. activity } ^{239}\text{Pu}) (E \text{ } ^{239}\text{Pu}) [ & (\% \text{ } ^{239}\text{Pu}) + 3.7 (\% \text{ } ^{240}\text{Pu}) \\ & + 301 (\% \text{ } ^{238}\text{Pu}) + 6.7 (\% \text{ } ^{241}\text{Pu}) \\ & + 62.2 (1 - e^{-0.049 Y}) (\% \text{ } ^{241}\text{Pu}) ] / 100. \end{aligned} \quad (1)$$

If the dose rate is known, the rate of radiolytic gas generation then becomes:

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$$\text{moles gas/day} = \text{Dose rate (Mev/day)} \cdot G_T \left( \frac{\text{molecules}}{100 \text{ ev}} \right) / 6.02 \times 10^{23} \text{ (molecules/mole)}$$

$$\text{moles gas/day} = \text{eq. (1)} \cdot G_T / 6.02 \times 10^{23}$$

$$\begin{aligned} \text{moles gas/day (2)} &= 1.68 \times 10^{-3} \cdot g_{\text{Pu}} \cdot G_T [ (\% \text{ } ^{239}\text{Pu}) + 3.7 (\% \text{ } ^{240}\text{Pu}) \\ &\quad + 301 (\% \text{ } ^{238}\text{Pu}) + 6.7 (\% \text{ } ^{241}\text{Pu}) \\ &\quad + 62.2(1 - e^{-0.049Y}) (\% \text{ } ^{241}\text{Pu}) ] \end{aligned}$$

The rate of pressurization is then:

$$\frac{dp}{dt} = \frac{RK}{V} \frac{dn}{dt} = \frac{1082K}{V-W/2.90} \quad \text{eq. (3).}$$

$$\begin{aligned} \frac{dp}{dt} (3) &= 1.68 \times 10^{-5} g_{\text{Pu}} G_T [ (\% \text{ } ^{239}\text{Pu}) + 3.7 (\% \text{ } ^{240}\text{Pu}) \\ &\quad + 301 (\% \text{ } ^{238}\text{Pu}) + 6.7 (\% \text{ } ^{241}\text{Pu}) \\ &\quad + 62.2 (1 - e^{-0.049Y}) (\% \text{ } ^{241}\text{Pu}) \end{aligned}$$

APPENDIX B

$G_T$  value calculation.

date - 8/7/74

compound -  $K_2Pu(NO_3)_6$

Sample weight - 26.705 gm

Pu content - 0.922 gm (84.8 wt %  $^{238}Pu$ )

Total elapsed experimental time - 366 hr.

Apparatus volume - 45.0 cm<sup>3</sup>

Manometer displacement - 3.95 cm of manometer has volume of 1 cm<sup>3</sup>

Manometer reading 1200 - 5.775 cm (23.0°C)

Manometer reading 1600 - 7.305 cm (27.0°C)

Sp. activity  $^{238}Pu$  -  $3.86 \times 10^{13}$  dis/min./gm

$E_{\alpha} \ ^{238}Pu$  - 5.48 Mev

At 1200 total volume of gas in apparatus is:

$$45.0 \times 10^{-3} + 5.775/3.95 \times 10^{-3} = 46.5 \times 10^{-3} \text{ liters}$$

At 1600 total volume of gas in apparatus is

$$45.0 \times 10^{-3} + 7.305/3.95 \times 10^{-3} = 46.8 \times 10^{-3} \text{ liters}$$

Total moles of gas at 1200:

$$n = \frac{PV}{RT} = \frac{(760 + 57.8)(46.5 \times 10^{-3})}{760 \times 0.082 \times (273.2 + 23.0)}$$

$$n = 2.06 \times 10^{-3}$$

Total moles of gas at 1600:

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$$n = \frac{\left(\frac{760 + 73.1}{760}\right)(46.8 \times 10^{-3})}{0.082 \times (273.2 + 27.0)}$$

$$n = 2.08 \times 10^{-3}$$

$2.08 \times 10^{-3} - 2.06 \times 10^{-3} = 2 \times 10^{-5}$  moles gas generated in 4 hours.

$$= 5 \times 10^{-6} \text{ moles gas/hr.}$$

$$\text{gms } {}^{238}\text{Pu} = 0.782$$

Other Pu isotope radiation dose contributions may be excluded as  ${}^{238}\text{Pu}$  contributes 99.9% of the total dose

$$\frac{5 \times 10^{-6}}{0.792 \times 60} = 1.1 \times 10^{-7} \text{ moles/min/gm } {}^{238}\text{Pu}$$

$$G_T = \frac{1.1 \times 10^{-7} \cdot 6.02 \times 10^{23} (\text{molecules/mole})}{3.86 \times 10^{13} (\text{sp. activity}) \times 5.48 \times 10^6 (E_\alpha)} \times 100$$

$$G_T = 0.03 \text{ moles gas/ 100 ev}$$

$$\text{Dose (366 hr)} = 0.782 \times 5.48 \times 366 \times 3.86 \times 10^{13} \times 60$$

$$\text{Dose} = 36 \times 10^{17} \text{ Mev.}$$

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