Classification reviewed and
changed to Unclassified without amendment.
Signed
for the U.K.A.E.A. Nov 26/[illegible]

UNCLASSIFIED

~~SECRET~~

A.E.R.E. C/R 1207

Copy No. ....

THE THERMOGRAVIMETRY OF SOME PLUTONIUM COMPOUNDS

by

J. K. DAWSON

(MISS) R. M. ELLIOTT

ABSTRACT

The effect of heat on some plutonium compounds has been studied by means of a silica spring thermobalance. The following are the main deductions which have been made from the thermogravimetric curves:-

(a) PuF_3 prepared by hydrofluorination of PuO_2 is stable in moist air up to ~ 300°C, the stability is reduced after the fluoride has stood in air at room temperature, however.

Sufficient water is trapped in the PuF_3 lattice when the trifluoride is precipitated from aqueous solution to give a precipitate of approximate composition "$4PuF_3.3H_2O$". The loss of this water on heating in air or in vacuum is not reversible. No oxyfluoride was detected on the air ignition of PuF_3.

(b) PuF_4 is stable in moist air up to 300°C and above this temperature is rapidly converted to PuO_2.

(c) $Pu(SO_4)_2$ is formed by fuming down plutonium nitrate solution with concentrated sulphuric acid and it appears to be a useful compound for the gravimetric estimation of plutonium. It is rapidly converted to PuO_2 by heating in air at temperatures above 650°C.

(d) $Pu(IO_3)_4$ is not precipitated from aqueous solution as the pure compound.

(e) Quadrivalent plutonium oxalate precipitates from aqueous solution as $Pu(C_2O_4)_2.6H_2O$ and heating this compound does not give a stable carbonate, although products of constant weight are achieved at temperatures below that at which PuO_2 is known to be produced.

(f) Trivalent plutonium oxalate precipitates from aqueous solution probably as $Pu_2(C_2O_4)_3.10H_2O$. The dihydrate and the anhydrous oxalate may be obtained from this by heating, preferably in vacuum. Oxides of lower valency than the dioxide did not appear to be formed on heating

A.E.R.E. Harwell

8th June, 1953

/EW

HS.6054

081 001

~~SECRET~~

UNCLASSIFIED

CONTENTS

ILLUSTRATIONS

1. INTRODUCTION

It was of interest to examine the effect of heat on various plutonium compounds. A thermobalance for continuous weighing has been described by Duval(1) but for the plutonium investigation it was necessary to devise an apparatus which would operate on much less material than the Duval balance. Consequently, we have constructed a simple silica spring balance which may be operated with as little as 10 mg. of sample, the sensitivity being about 1.3 mm./mg. The 2 cm. diameter silica spring was about 50 cm. long under a load of about 200 mg. (boat and sample) and an extension fibre extended downwards from this for 50 cm. so that the spring was not unduly heated by the furnace (see Figure 1). The lower half of this extension was made of 0.001" diameter platinum wire to reduce troubles arising from static electricity and to provide greater robustness. The sample was surrounded by a furnace controlled from a hand-operated transformer and was protected from air currents by means of a silica tube. Temperatures were measured by a thermocouple in contact with the outside of the silica tube; it was checked that this was very close to the temperature of the sample by preliminary comparison with a second thermocouple placed in the position normally occupied by the sample. For the experiments in which the change in weight with temperature was being observed, the rate of rise of temperature was kept to about 3°C per minute. Weight changes were observed by following an index fibre with a cathetometer which could be read to 0.01 mm. Sample weights were determined on a commercial microbalance.

The balance was calibrated by measuring the extension produced by lengths of platinum wire of known weight and its performance was checked by constructing a thermogravimetric curve on hydrated calcium oxalate (see Duval, loc. cit.).

The displacement of the sample due to loss of weight by decomposition on heating was usually a few millimetres and so its position relative to the furnace and the thermocouple could be considered constant. A curve for the change of apparent weight of the empty platinum boat with increasing temperature was constructed and was applied as a correction to the experiments with the plutonium compounds present (the correction was 5 - 10% of the total weight change at the highest temperatures).

The plutonium compounds were all made from a stock solution of quadrivalent plutonium in nitric acid which had been analysed spectrographically and shown to contain negligible amounts of impurities. It was necessary for health reasons to enclose the lower end of the balance in a glove box which was kept continuously under reduced pressure.

Handling the quartz tube which surrounded the sample with the rubber gloves occasionally gave rise to sufficient electrostatic charge to make the platinum boat adhere to the tube. When this happened it was necessary to place a few drops of water in the bottom of the tube to raise the water vapour content of the tube sufficiently for the charges to be dispelled. The distance of the water from the heated furnace had to be adjusted so that complete and rapid vapourisation did not occur with subsequent condensation on the quartz helix.

2. EXPERIMENTAL

2.1 Plutonium Trifluoride

(a) Anhydrous plutonium trifluoride was prepared by the reaction of plutonium dioxide (obtained by ignition of the tetraoxalate, see below) with gaseous hydrogen fluoride and hydrogen at 350°C(2). The thermogravimetric curve on a freshly prepared sample (29.63 mg.) is shown in Figure 2. There was no detectable weight change below 300°C; the total weight loss between this plateau and the final one beginning at ca. 700°C was 8.44% (theor. change for $PuF_3 \longrightarrow PuO_2$, 8.44%). The product showed the X-ray diffraction pattern of plutonium dioxide only. The weight change between 600°C and the final plateau corresponds to the possible existence of $PuO_{1.91}$ at this temperature.

(b) A second sample from the same preparation was allowed to stand in laboratory air for twelve days. A thermogravimetric curve on a 10.07 mg. sample is shown in Figure 3. The residue gave the X-ray diffraction pattern of PuO_2 and the weight change from the plateau between 100 - 200°C to the final plateau was 8.32%. The curve also shows that there was 0.61% of adsorbed moisture on the sample and that the dip in the curve at ~ 500°C might be indicative of $PuO_{1.86}$.

(c) Another sample of PuF_3 (29.53 mg.) which had been prepared the "dry way" and which had been exposed to laboratory air for several weeks showed that 0.46% of moisture had been adsorbed. This was lost on heating in air and a plateau corresponding to pure anhydrous PuF_3 was observed over the range 100 - 250°C; the weight loss between this and the final plateau (PuO_2) was 8.23%. The dip in the curve at ~ 500°C in this experiment corresponded to $PuO_{1.77}$.

2.2 Precipitated Plutonium Trifluoride

(a) Plutonium (IV) in dilute nitric acid solution was reduced to plutonium (III) by the addition of hydroxylamine hydrochloride and a precipitate was obtained on the addition of aqueous hydrofluoric acid. The precipitate was centrifuged, washed twice with water, sludged from the plastic tube in which the precipitation had taken place into a glass tube, washed with acetone and dried at room temperature in a vacuum of 10^{-5} mm. Hg. On ignition in air a 15.95 mg. sample of the dried precipitate gave the thermogravimetric curve shown in Figure 4; the total weight loss from room temperature to the final PuO_2 plateau was 12.3% (the product gave the X-ray diffraction pattern of PuO_2 and was found to have zero fluorine content by a pyrohydrolytic analysis). Some possible theoretical weight changes are:-

$PuF_3.H_2O \longrightarrow PuO_2$ 13.69%

$4PuF_3.3H_2O \longrightarrow PuO_2$ 12.44%

$2PuF_3.H_2O \longrightarrow PuO_2$ 11.15%

$PuF_3 \longrightarrow PuO_2$ 8.44%

The precipitate gave a very diffuse X-ray diffraction pattern, the main features of which seemed identical with those of anhydrous PuF_3. Small samples which were ignited to temperatures of 250, 275 and 320°C showed the gradual fading of the X-ray diffraction lines without the appearance of any other pattern (e.g. of PuOF); at 400°C the diffraction pattern was that of PuO_2.

(b) Further thermogravimetric curves on other preparations of the fluoride precipitate gave 12.25, 12.6 and 12.4% changes in weight from room temperature to the PuO_2 plateau.

(c) A 24.7 mg. sample of the fluoride precipitate was heated to 275°C while suspended on the silica spring. The weight loss observed was 5.3%. On returning to room temperature there was a weight increase of ~ 1%.

(d) Plutonium trifluoride was precipitated as in (a), but the temperature of precipitation was raised to 80°C. A thermogravimetric curve on 12.10 mg. of the dried precipitate gave a weight loss of 10.1% between room temperature and the PuO_2 plateau.

2.3 Plutonium Tetrafluoride

(a) Plutonium tetrafluoride was prepared by the reaction of the dioxide (obtained from low temperature ignition of the oxalate) at 350°C with gaseous anhydrous hydrogen fluoride containing a partial pressure of oxygen(2). A thermogravimetric curve on a freshly prepared sample (12.71 mg.) is shown in Figure 5. There was no change in weight below ~ 300°C; above that temperature the fluoride was converted directly to the dioxide the weight change observed being 14.2% (theor. for $PuF_4 \longrightarrow PuO_2$, 13.97%).

(b) A second sample (48.86 mg. from another preparation) gave the same shaped thermogravimetric curve and a weight change of 13.9%.

(c) A sample (6.98 mg.) from the same preparation as sample (a) was allowed to stand in laboratory air for two days. The thermogravimetric curve indicated an initial loss of weight of about 0.6% (adsorbed moisture) between 20 - 50°C but above this temperature the curve was the same shape as for sample (a). The weight loss from the PuF_4 plateau to the PuO_2 plateau was 13.95%. There was no trace of the trough observed at 500 - 600°C on the PuF_3 thermogravimetric curves.

2.4 Plutonium (IV) Sulphate

(a) Plutonium tetranitrate solution was pipetted into a platinum dish and concentrated sulphuric acid was added (2 - 3 times the calculated quantity for conversion to the sulphate). The sludge was fumed down under a heating lamp until almost dry and a sample was then transferred to the thermobalance. The thermogravimetric curve is shown in Figure 6. The loss of weight between A and B is attributed to evaporation of excess free sulphuric acid, the plateau BC corresponds to the existence of anhydrous plutonium sulphate ($Pu(SO_4)_2$) according to the weight change observed between it and the final PuO_2 plateau DE (weight change 58.9% with respect to PuO_2; theor. for $Pu(SO_4)_2 \longrightarrow PuO_2$, 59.1% with respect to PuO_2).

(b) A second sample of the sulphate gave a very similar thermogravimetric curve and the weight change from the plateau representing $Pu(SO_4)_2$ to that representing PuO_2 was 59.2% with respect to the PuO_2 (9.33 mg. weighed on the Sartorius microbalance).

2.5 Plutonium (IV) Iodate

Pink plutonium iodate was precipitated from tetranitrate solution by the addition of iodic acid. The precipitate was washed with ethyl alcohol and dried at room temperature in a high vacuum. The thermogravimetric curve shown in Figure 7 was obtained using 5.28 mg. of dried precipitate; the weight change from room temperature to the plateau above 540°C (which substance was shown to have the X-ray diffraction pattern of PuO_2) was 76.5% (theor. for $Pu(IO_3)_4 \longrightarrow PuO_2$, 71.1%).

2.6 Plutonium (IV) Oxalate

(a) This compound was precipitated by the addition of oxalic acid solution to the plutonium tetranitrate solution. The precipitate was washed with ethanol and dried at room temperature in a high vacuum. An 8.95 mg. sample gave the thermogravimetric curve shown in Figure 8, the total weight loss from room temperature to the final plateau (PuO_2 according to the X-ray diffraction pattern) was 48.1% (theor. for $Pu(C_2O_4)_2.6H_2O \longrightarrow PuO_2$, 48.1%).

(b) The weight change on a thermogravimetric curve observed with an 11.44 mg. sample from a second preparation was 47.9%.

(c) Isothermal degradation was observed for the following conditions:

Temperature	Wt. of sample	Loss of weight after 60 mins.
200°C	13.6 mg	29.0%
250	5.92	31.5
300	7.66	42.2
400	2.00	44.7

The results are shown in Figure 9.

2.7 Plutonium (III) Oxalate

An aliquot of the stock solution of plutonium tetranitrate was reduced with potassium iodide and a slight excess of sodium oxalate solution was added to precipitate the trivalent plutonium oxalate. The precipitate was washed with water and with ethanol and was then dried at room temperature in a high vacuum.

(a) A thermogravimetric curve obtained on 4.95 mg. of the dried oxalate is shown in Figure 10. The total weight loss between room temperature and the PuO_2 plateau beginning at 700°C was 41.5% (theor. for $Pu_2(C_2O_4)_3.9H_2O \longrightarrow PuO_2$, 40.04%; $Pu_2(C_2O_4)_3.10H_2O \longrightarrow PuO_2$, 41.2%; $Pu_2(C_2O_4)_3.11H_2O \longrightarrow PuO_2$, 42.4%). There was a plateau at 150 - 170°C corresponding to the loss of seven molecules of water from the decahydrate (observed loss 14.4%; theor. loss 13.7%) and another plateau at 172 - 192°C corresponding to the loss of eight water molecules (observed loss 15.25%; theor. loss 15.6%). At the position expected for the anhydrous oxalate there was a change of slope, but there was no plateau to indicate that it had any extensive stability region. There was no indication of the formation of any stable lower oxide before the production of PuO_2.

(b) The thermogravimetric curve for a 10.60 mg. sample of the vacuum dried oxalate on heating in a vacuum of 10^{-5} mm. Hg. is shown in Figure 11. The plateaux observed could be explained as follows:

Point on Figure 11	Temperature (°C)	Loss of weight (%)	Probable Formula	Theor. weight loss for probable formula
A	25	-	$Pu_2(C_2O_4)_3.10H_2O$	-
B-C	50-150	14.2	$Pu_2(C_2O_4)_3.3H_2O$	13.7
D-E	220-260	15.9	$Pu_2(C_2O_4)_3.2H_2O$	15.6
F-G	320-430	20.7	$Pu_2(C_2O_4)_3$	19.5
H-I	850-	40.6	PuO_2	41.2

(c) The decomposition of a 8.93 mg. sample of the vacuum dried oxalate was observed in a vacuum of 10^{-5} mm. Hg. at 400°C. Constant weight was obtained after 60 mins. and the weight loss from room temperature was 20.0% (theor. for $Pu_2(C_2O_4)_3.10H_2O \longrightarrow Pu_2(C_2O_4)_3$, 19.5%). An X-ray diffraction photograph of the product failed to show any lines.

081 006

3. DISCUSSION

3.1 Plutonium Trifluoride

Plutonium trifluoride prepared by the reaction of gaseous hydrogen fluoride with plutonium dioxide showed no detectable reaction with moist air below ~ 300°C in confirmation of the qualitative results reported previously(3). It adsorbs moisture from the atmosphere, however, and this appears to reduce its stability limit in air to ~ 250°C.

All the thermogravimetric curves on plutonium trifluoride exhibited a trough at temperatures between 500 - 600°C which was not observed with other plutonium compounds. The weight increase from the trough to the PuO_2 plateau was variable, the maximum observed was indicative of the possible existence in this temperature region of $PuO_{1.77}$.

Several attempts were made to stop experiments at the position of the trough but these were not successful, the X-ray diffraction pattern of the product in each case was similar to that of the dioxide; in one particular experiment the balance system was evacuated and the sample temperature was rapidly lowered at this point, but on raising the temperature again with the sample in air, no further weight change was observed. If a lower oxide occurs as an intermediate compound in this system it is evidently rapidly oxidising to the dioxide. No stable oxyfluoride appears to be formed by heating plutonium trifluoride in air.

3.2 Precipitated Plutonium Trifluoride

The thermogravimetric curves obtained on samples of the trifluoride precipitated from aqueous solution, washed with acetone and dried at room temperature in a high vacuum are different from those obtained from trifluoride prepared by high temperature fluorination of the dioxide (compare Figures 2 and 4). The total weight loss from room temperature to the PuO_2 plateau corresponds to the composition of the starting material being "$4\ PuF_3.3H_2O$". Heating this precipitate in vacuum to 300°C gives the anhydrous fluoride but the change is irreversible and anhydrous plutonium trifluoride kept under aqueous hydrofluoric acid for several days did not take up any water. Precipitation at a higher temperature gave a product containing less water.

The X-ray diffraction pattern of the precipitated plutonium trifluoride was very diffuse but the spacings appeared to be the same as for the anhydrous compound. It is difficult to see how the water could be accommodated in the trifluoride lattice, but it might possibly be trapped between layers of fluorine atoms at the moment of precipitation to be released on the later application of thermal energy. It would then give rise to X-ray line intensity variations which we would not have observed owing to the diffuse nature of the films. It has been observed recently that precipitated potassium thorium fluorides usually retain 1 or 2 moles of water per mole of thorium fluoride when dried in air but that this water does not play an essential part in the structure of the compounds since the X-ray diffraction patterns of the precipitated and fused fluorides are the same(4).

Westrum and Eyring have determined the heat of precipitation of plutonium trifluoride and have deduced the heat of formation on the assumption that the compound precipitates anhydrous(5). The present results indicate that a small correction may be necessary to their results to allow for the accommodation of the water in the crystal lattice.

3.3 Plutonium Tetrafluoride

In moist air, the oxidation of plutonium tetrafluoride to the dioxide proceeds rapidly above 300°C without the intermediate formation of a stable oxyfluoride. There is some absorption of atmospheric moisture at room temperature but this is removed by heating the sample to 50 - 100°C.

The thermogravimetric behaviour of the hydrated plutonium tetrafluoride which is precipitated from aqueous solution has been reported previously(3).

3.4 Plutonium (IV) Sulphate

It has been suggested that the anhydrous sulphate may be obtained by fuming down crystals of the hydrate with concentrated sulphuric acid and that the anhydrous salt is sufficiently stable in air to be used for the gravimetric estimation of plutonium(6). We have confirmed that the pure anhydrous sulphate is obtained by a fuming down procedure and Figure 6 shows that it is stable in air up to 650°C, above this temperature it is converted rapidly to yellow plutonium dioxide. In some respects it is superior to the dioxide for gravimetric estimations since it may be dissolved in aqueous solutions.

3.5 Plutonium (IV) Iodate

Like the sulphate, this compound has also been proposed for the gravimetric estimation of plutonium (Harvey et al. loc. cit.). The present study shows, however, that the iodate is not as reliable as the sulphate since the molecular weight of the precipitate is greater than that of $Pu(IO_3)_4$, possibly there is some HIO_3 also in the precipitate. There appears to be no temperature at which pure $Pu(IO_3)_4$ may be obtained by heating (see Figure 7 for lack of a corresponding plateau). A plateau on the thermogravimetric curve at 360 - 425°C remains unexplained; at 500°C there was rapid decomposition to plutonium dioxide.

3.6 Plutonium (IV) Oxalate

Westrum has stated that $Pu(C_2O_4)_2 \cdot xH_2O$ is a convenient intermediate in the preparation of a "reactive" oxide for subsequent conversion to the plutonium halides(7). The present experiments show that the oxalate precipitated from aqueous solution has six molecules of water of crystallisation per atom of plutonium. Decomposition does not form a stable carbonate (no corresponding plateau on Figure 8); this is in agreement with Duval's experiments (loc. cit.) which showed that none of the metal oxalates gave stable carbonates by loss of carbon monoxide except those of calcium, strontium and barium. On the other hand, heating the oxalate at a constant temperature below that of the final dioxide plateau does lead to products of approximately constant weight. At 200°C, the weight change is close to that expected for the formation of carbonate but this seems to be fortuitous (the product did not liberate any gas when stirred with mineral acid).

The nature of the intermediates remains unknown, X-ray diffraction photographs did not show any reflections and the plutonium dioxide pattern did not appear below about 400°C. If the dioxide is weighed before conversion to the fluoride in the finishing process at Windscale, as an analytical check, the present results show that errors are likely to be introduced if the formula of the oxide is taken as exactly PuO_2 when the decomposition temperature of the oxalate has not been taken up to > 600°C.

081 008

3. DISCUSSION

3.1 Plutonium Trifluoride

Plutonium trifluoride prepared by the reaction of gaseous hydrogen fluoride with plutonium dioxide showed no detectable reaction with moist air below ~ 300°C in confirmation of the qualitative results reported previously(3). It adsorbs moisture from the atmosphere, however, and this appears to reduce its stability limit in air to ~ 250°C.

All the thermogravimetric curves on plutonium trifluoride exhibited a trough at temperatures between 500 - 600°C which was not observed with other plutonium compounds. The weight increase from the trough to the PuO_2 plateau was variable, the maximum observed was indicative of the possible existence in this temperature region of $PuO_{1.77}$.

Several attempts were made to stop experiments at the position of the trough but these were not successful, the X-ray diffraction pattern of the product in each case was similar to that of the dioxide; in one particular experiment the balance system was evacuated and the sample temperature was rapidly lowered at this point, but on raising the temperature again with the sample in air, no further weight change was observed. If a lower oxide occurs as an intermediate compound in this system it is evidently rapidly oxidising to the dioxide. No stable oxyfluoride appears to be formed by heating plutonium trifluoride in air.

3.2 Precipitated Plutonium Trifluoride

The thermogravimetric curves obtained on samples of the trifluoride precipitated from aqueous solution, washed with acetone and dried at room temperature in a high vacuum are different from those obtained from trifluoride prepared by high temperature fluorination of the dioxide (compare Figures 2 and 4). The total weight loss from room temperature to the PuO_2 plateau corresponds to the composition of the starting material being "$4\ PuF_3.3H_2O$". Heating this precipitate in vacuum to 300°C gives the anhydrous fluoride but the change is irreversible and anhydrous plutonium trifluoride kept under aqueous hydrofluoric acid for several days did not take up any water. Precipitation at a higher temperature gave a product containing less water.

The X-ray diffraction pattern of the precipitated plutonium trifluoride was very diffuse but the spacings appeared to be the same as for the anhydrous compound. It is difficult to see how the water could be accommodated in the trifluoride lattice, but it might possibly be trapped between layers of fluorine atoms at the moment of precipitation to be released on the later application of thermal energy. It would then give rise to X-ray line intensity variations which we would not have observed owing to the diffuse nature of the films. It has been observed recently that precipitated potassium thorium fluorides usually retain 1 or 2 moles of water per mole of thorium fluoride when dried in air but that this water does not play an essential part in the structure of the compounds since the X-ray diffraction patterns of the precipitated and fused fluorides are the same(4).

Westrum and Eyring have determined the heat of precipitation of plutonium trifluoride and have deduced the heat of formation on the assumption that the compound precipitates anhydrous(5). The present results indicate that a small correction may be necessary to their results to allow for the accommodation of the water in the crystal lattice.

3.3 Plutonium Tetrafluoride

In moist air, the oxidation of plutonium tetrafluoride to the dioxide proceeds rapidly above 300°C without the intermediate formation of a stable oxyfluoride. There is some absorption of atmospheric moisture at room temperature but this is removed by heating the sample to 50 - 100°C.

The thermogravimetric behaviour of the hydrated plutonium tetrafluoride which is precipitated from aqueous solution has been reported previously(3).

3.4 Plutonium (IV) Sulphate

It has been suggested that the anhydrous sulphate may be obtained by fuming down crystals of the hydrate with concentrated sulphuric acid and that the anhydrous salt is sufficiently stable in air to be used for the gravimetric estimation of plutonium(6). We have confirmed that the pure anhydrous sulphate is obtained by a fuming down procedure and Figure 6 shows that it is stable in air up to 650°C, above this temperature it is converted rapidly to yellow plutonium dioxide. In some respects it is superior to the dioxide for gravimetric estimations since it may be dissolved in aqueous solutions.

3.5 Plutonium (IV) Iodate

Like the sulphate, this compound has also been proposed for the gravimetric estimation of plutonium (Harvey et al. loc. cit.). The present study shows, however, that the iodate is not as reliable as the sulphate since the molecular weight of the precipitate is greater than that of $Pu(IO_3)_4$, possibly there is some HIO_3 also in the precipitate. There appears to be no temperature at which pure $Pu(IO_3)_4$ may be obtained by heating (see Figure 7 for lack of a corresponding plateau). A plateau on the thermogravimetric curve at 360 - 425°C remains unexplained; at 500°C there was rapid decomposition to plutonium dioxide.

3.6 Plutonium (IV) Oxalate

Westrum has stated that $Pu(C_2O_4)_2 \cdot xH_2O$ is a convenient intermediate in the preparation of a "reactive" oxide for subsequent conversion to the plutonium halides(7). The present experiments show that the oxalate precipitated from aqueous solution has six molecules of water of crystallisation per atom of plutonium. Decomposition does not form a stable carbonate (no corresponding plateau on Figure 8); this is in agreement with Duval's experiments (loc. cit.) which showed that none of the metal oxalates gave stable carbonates by loss of carbon monoxide except those of calcium, strontium and barium. On the other hand, heating the oxalate at a constant temperature below that of the final dioxide plateau does lead to products of approximately constant weight. At 200°C, the weight change is close to that expected for the formation of carbonate but this seems to be fortuitous (the product did not liberate any gas when stirred with mineral acid).

The nature of the intermediates remains unknown, X-ray diffraction photographs did not show any reflections and the plutonium dioxide pattern did not appear below about 400°C. If the dioxide is weighed before conversion to the fluoride in the finishing process at Windscale, as an analytical check, the present results show that errors are likely to be introduced if the formula of the oxide is taken as exactly PuO_2 when the decomposition temperature of the oxalate has not been taken up to > 600°C.

3.7 Plutonium (III) Oxalate

The ignition in air or in vacuum of hydrated plutonium (III) oxalate did not show evidence of the production of any stable intermediate oxide of lower valency than the dioxide. The weight changes observed indicate that the oxalate precipitated from aqueous solution in the manner described in the experimental section has the formula $Pu_2(C_2O_4)_3.10H_2O$.

Heating this compound in air at 180°C or in vacuum at 230°C produces the dihydrate and there is evidence of the formation of anhydrous oxalate at about 200°C in air or 350°C in vacuum. This is not in agreement with Westrum's observation that $Pu_2(C_2O_4)_3$ ignited to 300°C in vacuum gave plutonium dioxide[7].

ACKNOWLEDGEMENTS

The silica springs were made by the Quartz Fibre Section of Electronics Division under the supervision of Mr. R. P. Henderson.

REFERENCES

(1) C. Duval, Analyt. Chem., 1951, 23, 1271.

(2) J. K. Dawson, A. E. Truswell, A.E.R.E. C/R 662.

(3) J. K. Dawson, A. E. Truswell, R. Hurst, (Miss) R. M. Elliott, A.E.R.E. C/R 1042.

(4) W. J. Asker, E. R. Segnit and A. W. Wylie, J.C.S., 1952, 4470.

(5) E. F. Westrum and L. Eyring, "The Transuranium Elements", N.N.E.S., 14B, paper 6.52.

(6) B. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rowley, J.C.S., 1947, 1010.

(7) E. F. Westrum, "The Transuranium Elements", N.N.E.S., 14B, paper 6.57.

DISTRIBUTION

Dr. R. Spence	A.E.R.E.
Dr. J. S. Anderson	"
Dr. J. M. Fletcher	"
Dr. R. Hurst	"
Dr. J. Milsted	"
Dr. A. G. White	"
Mr. C. J. Mandleberg	"
Mr. G. R. Hall	"
Dr. H. K. Rae	"
Dr. J. K. Dawson	"
Mr. A. E. Truswell	"
Mr. E. Furby	"
Mr. H. A. C. McKay	"
Mr. L. Airey	"
Mr. A. A. Smales	"
Dr. C. B. Amphlett	"
Mr. R. W. M. D'Eye	"
Mr. A. S. White	"
Mr. C. M. Nicholls	"
Mr. H. J. Hedger	"
Mr. K. Saddington	Windscale
Mr. G. S. Towler	C.I. "
Mr. E. F. Kemp	" "
Dr. E. Lofthouse	I.C.I. Widnes
C.I. Kidbrooke	
Prof. H. J. Emeleus	Cambridge University
Dr. W. B. Lewis	Chalk River
Dr. L. G. Cook	" "
Mr. B. G. Harvey	" "

+ Standard Distribution

1.7 [illegible]

[illegible]

[illegible]

ACKNOWLEDGEMENTS

[illegible]

REFERENCES

[illegible]

DISTRIBUTION

[illegible]

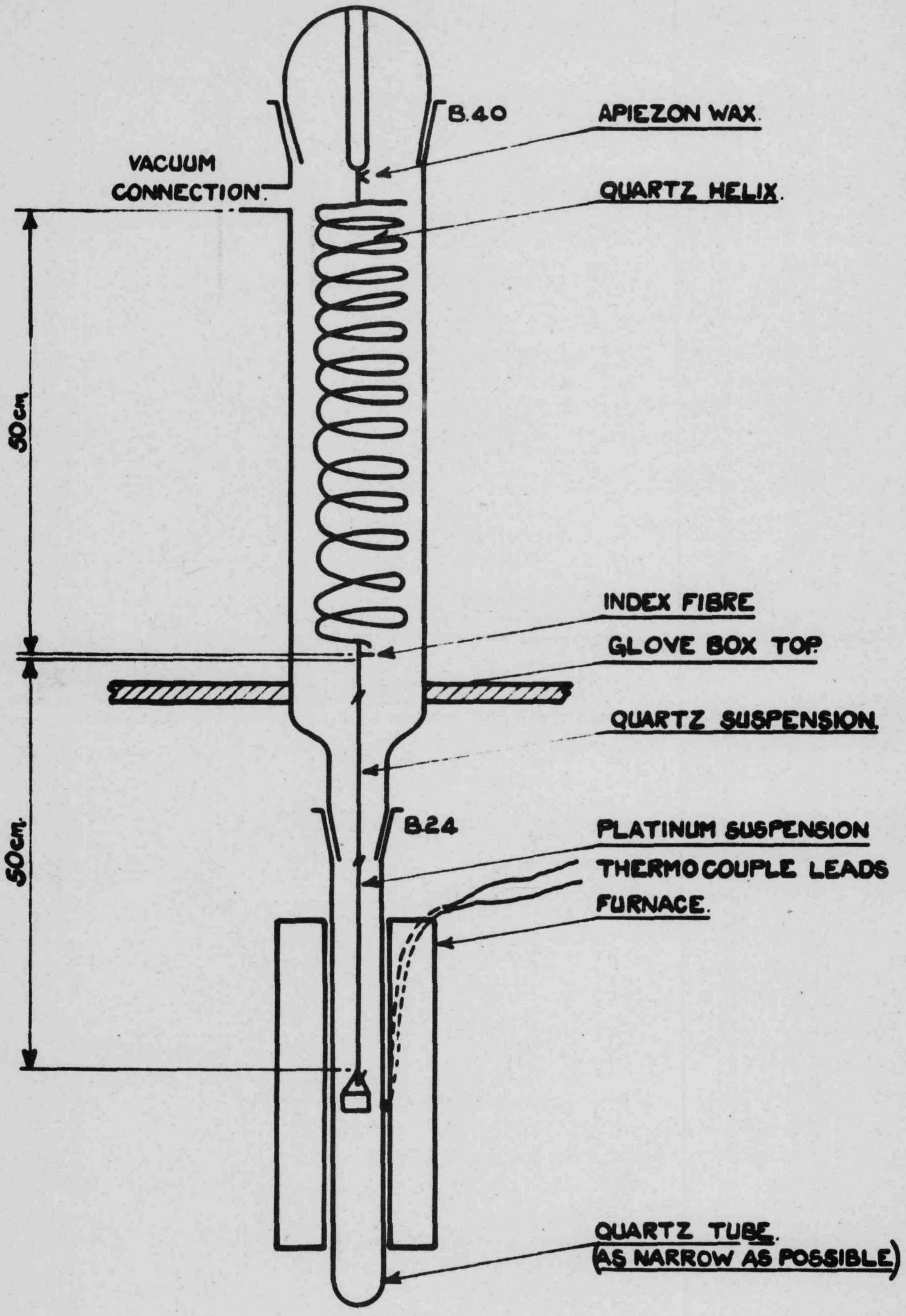

FIG. 1. THE SILICA SPRING BALANCE

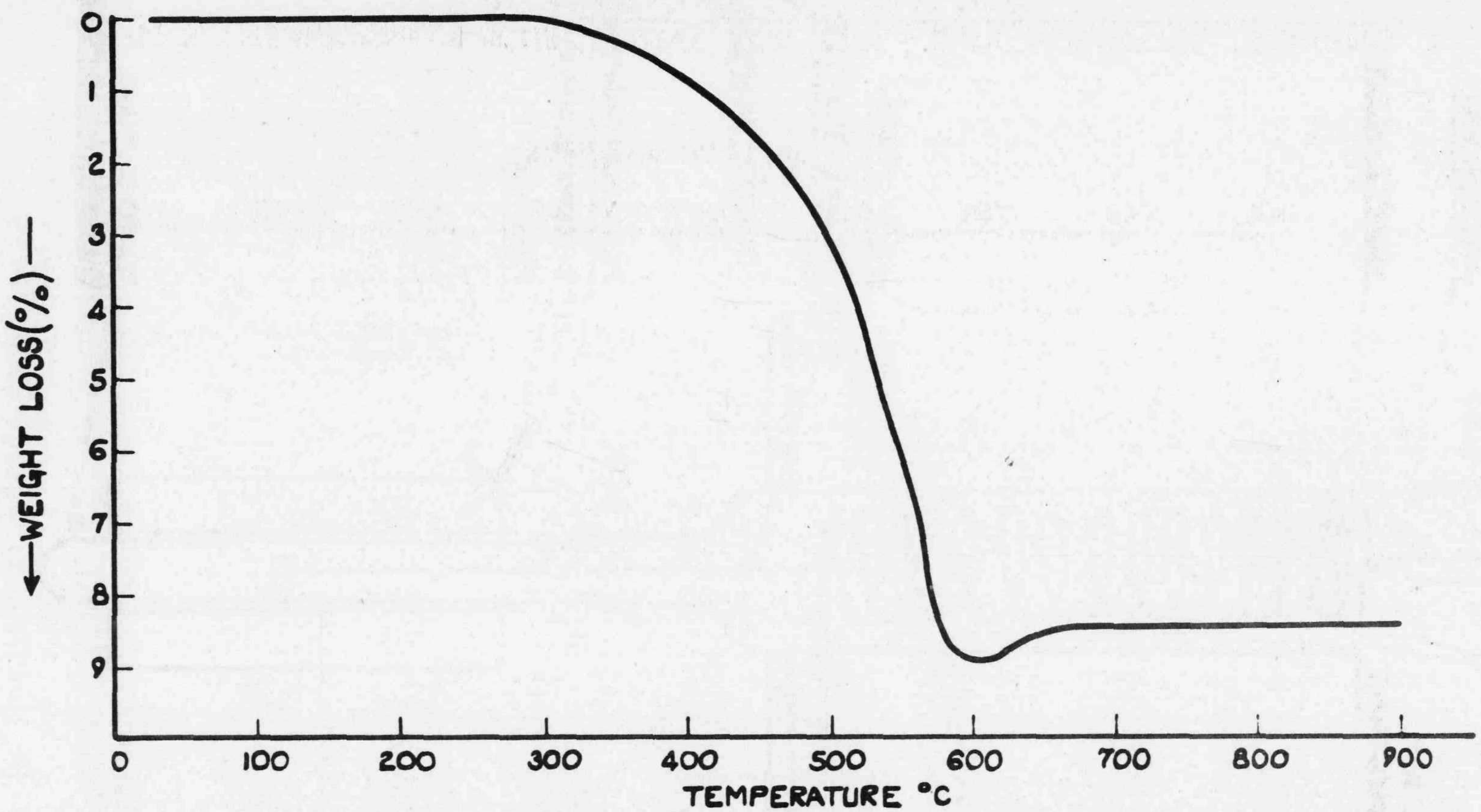

FIG. 2. THERMOGRAVIMETRIC CURVE FOR FRESHLY PREPARED 'DRY-WAY' PuF_3.

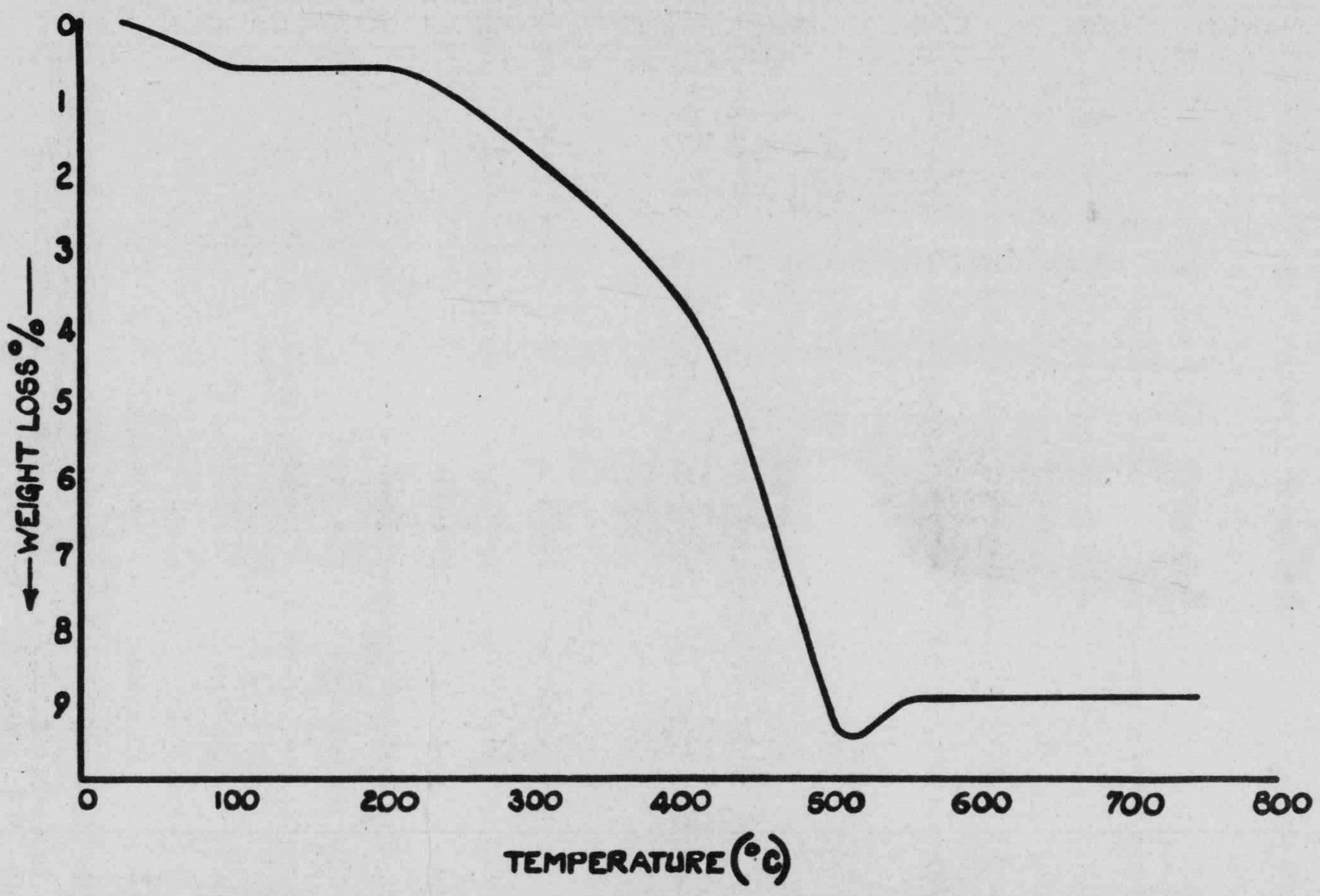

FIG. 3. THERMOGRAVIMETRIC CURVE FOR "DRY - WAY" PuF_3 AFTER STANDING IN LABORATORY AIR FOR 12 DAYS.

081 015

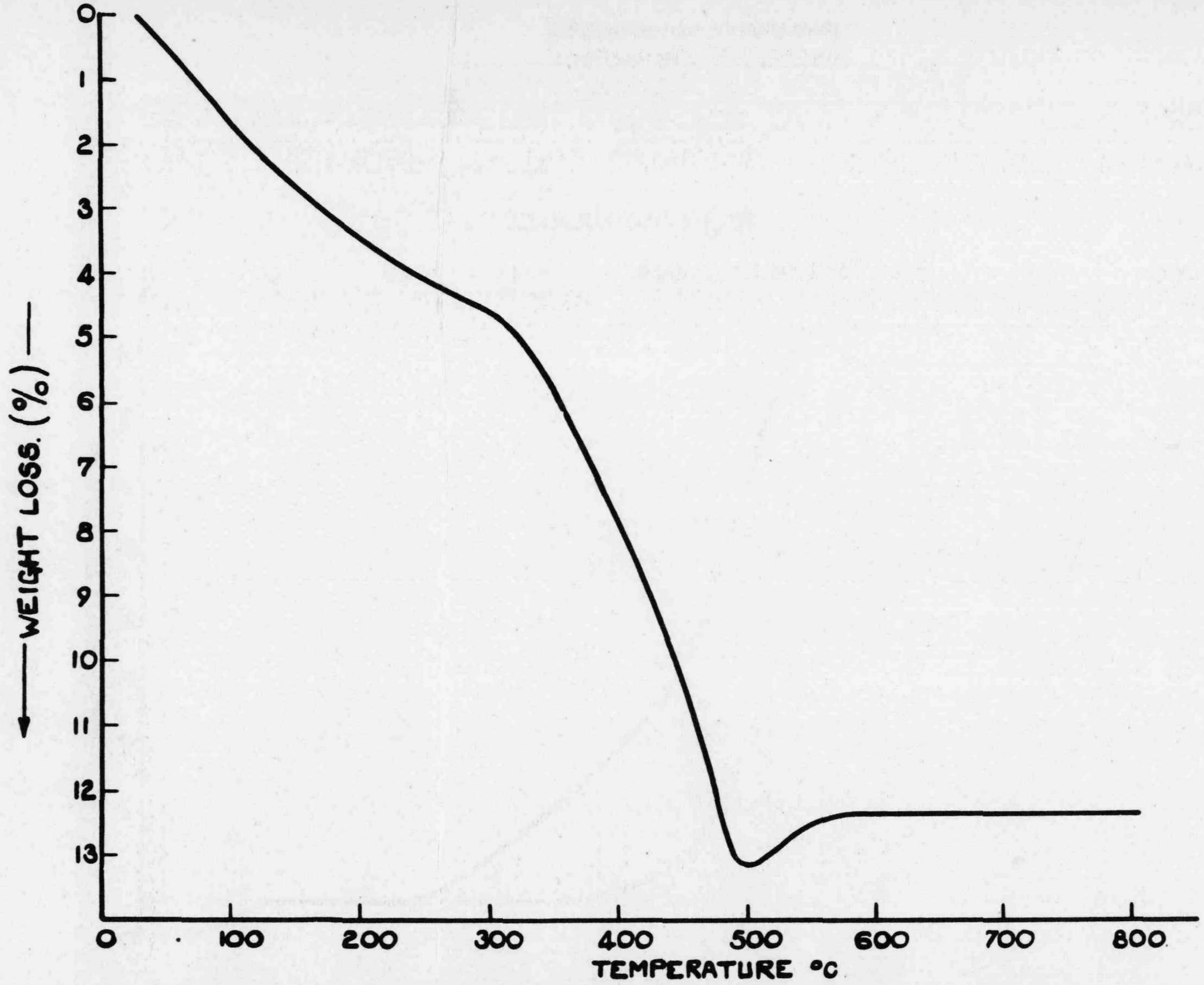

FIG.4. THERMOGRAVIMETRIC CURVE ON PRECIPITATED PLUTONIUM TRIFLOURIDE.

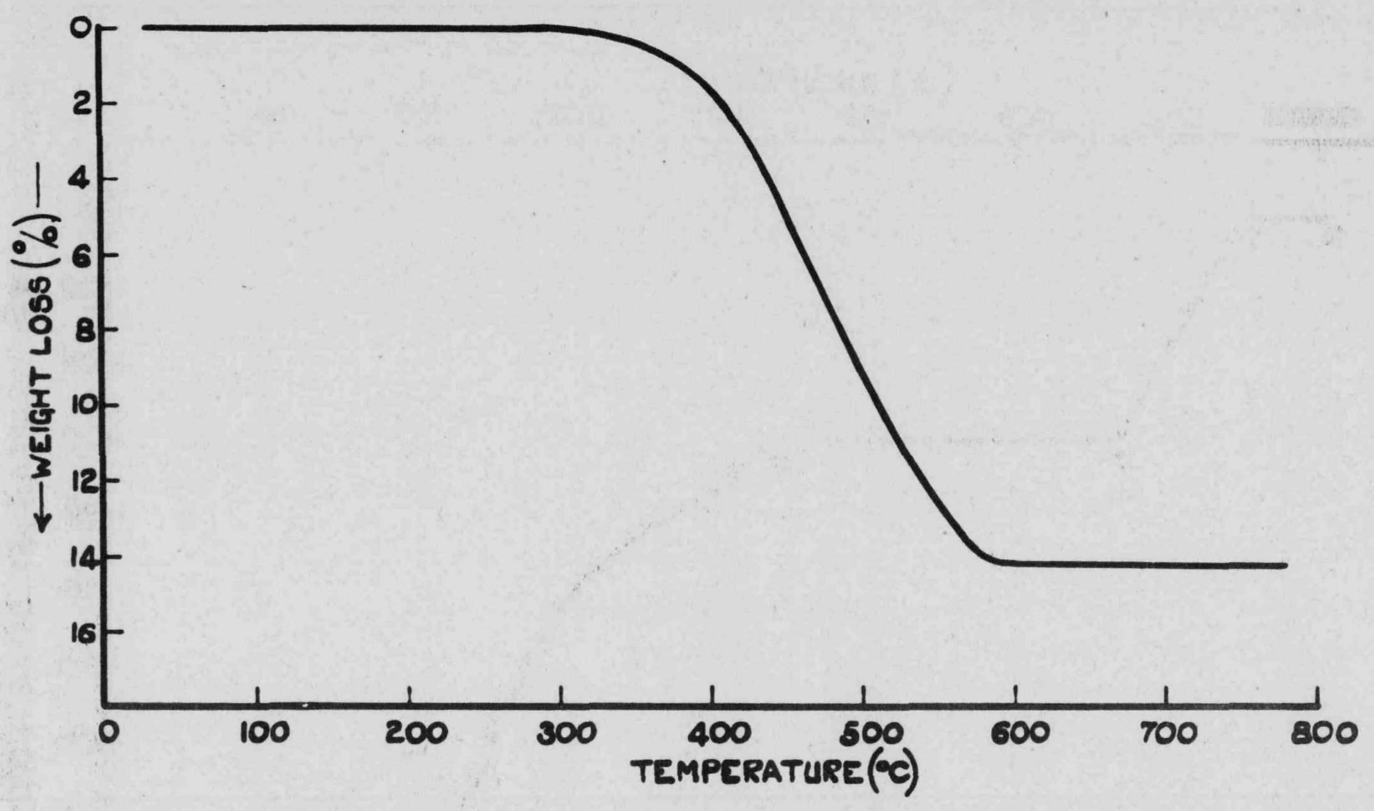

FIG. 5. THERMOGRAVIMETRIC CURVE ON FRESHLY PREPARED 'DRY-WAY' PuF_4.

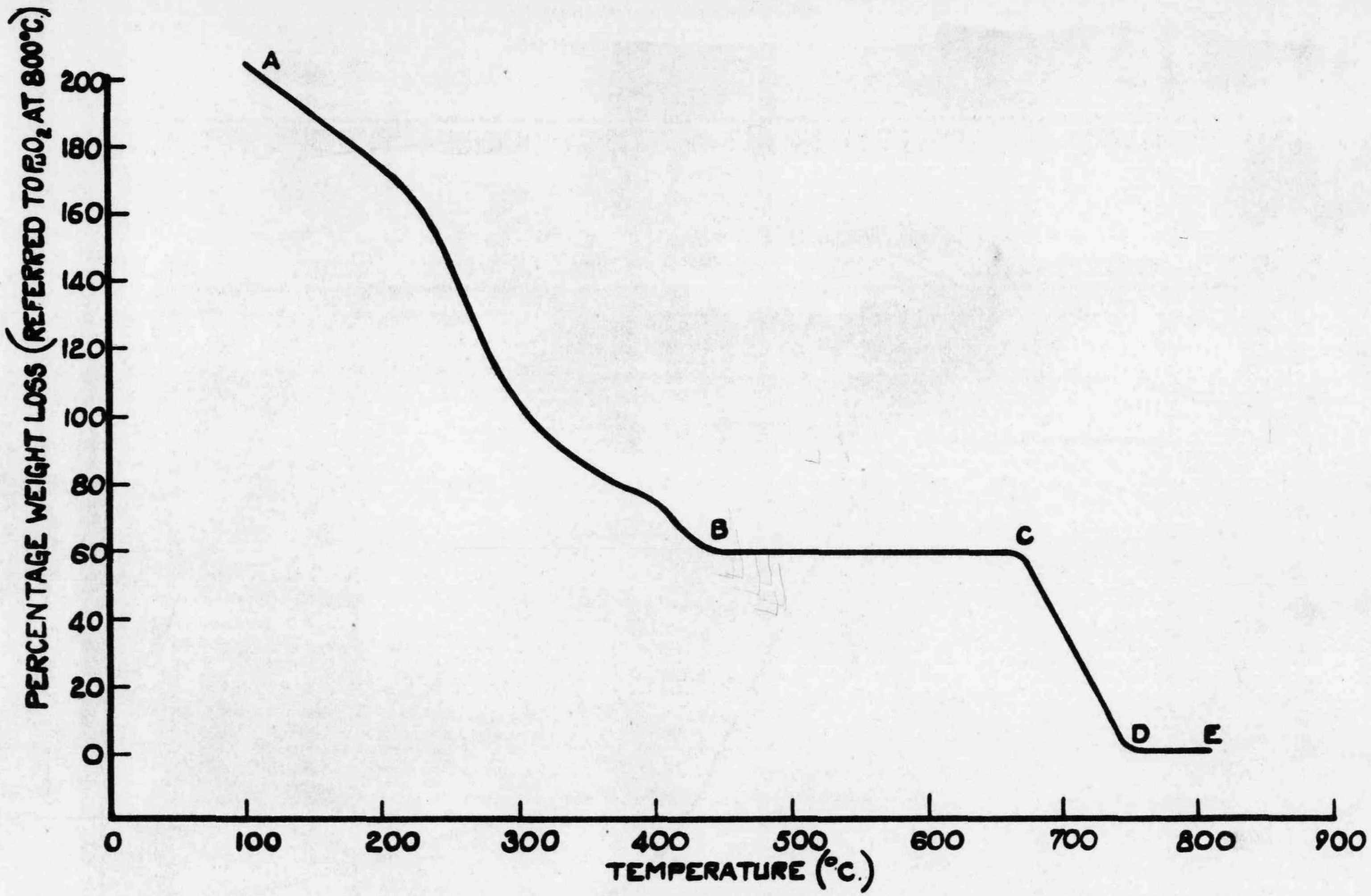

FIG. 6. AIR IGNITION OF PLUTONIUM SULPHATE ORIGINALLY CONTAINING EXCESS CONC. SULPHURIC ACID.

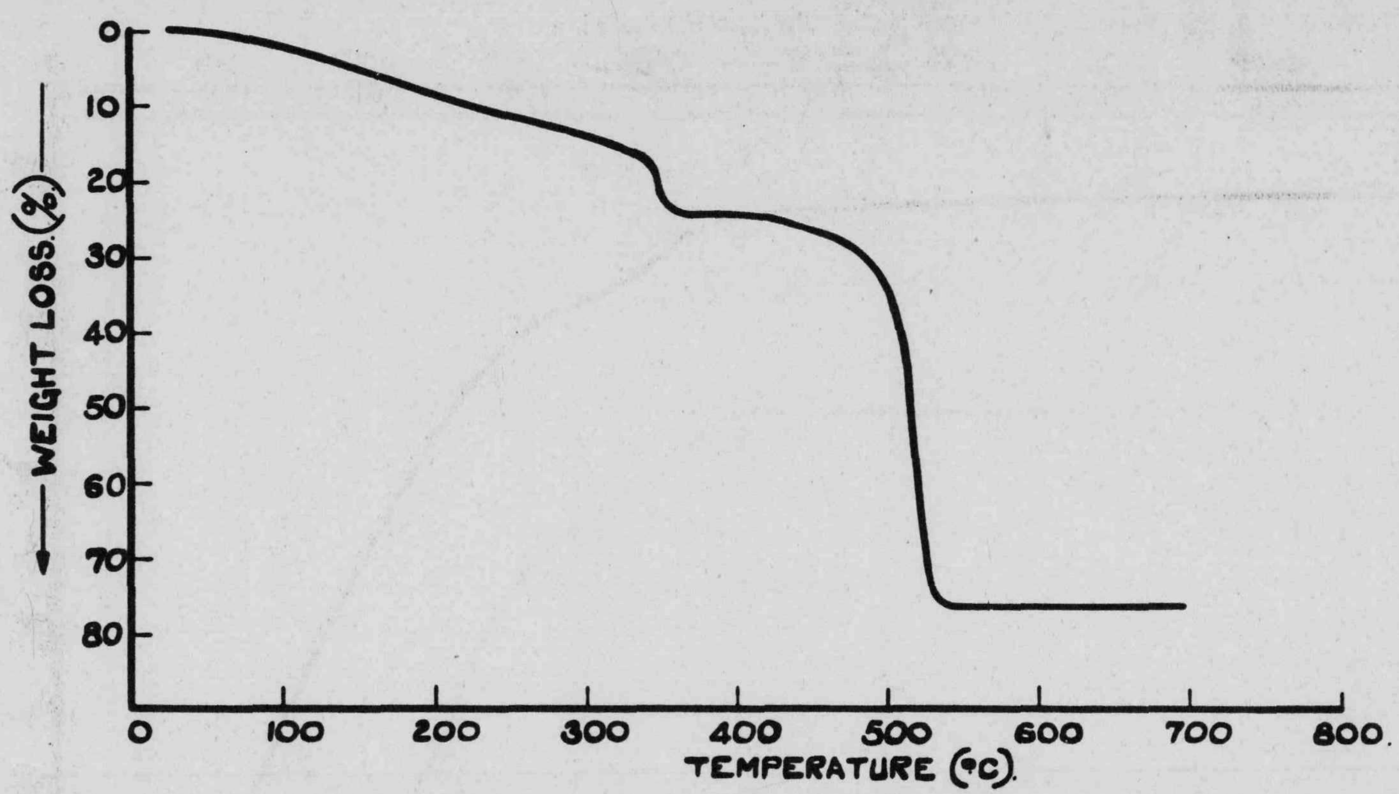

FIG.7. THERMAL DECOMPOSITION OF PLUTONIUM (IV) IODATE IN AIR.

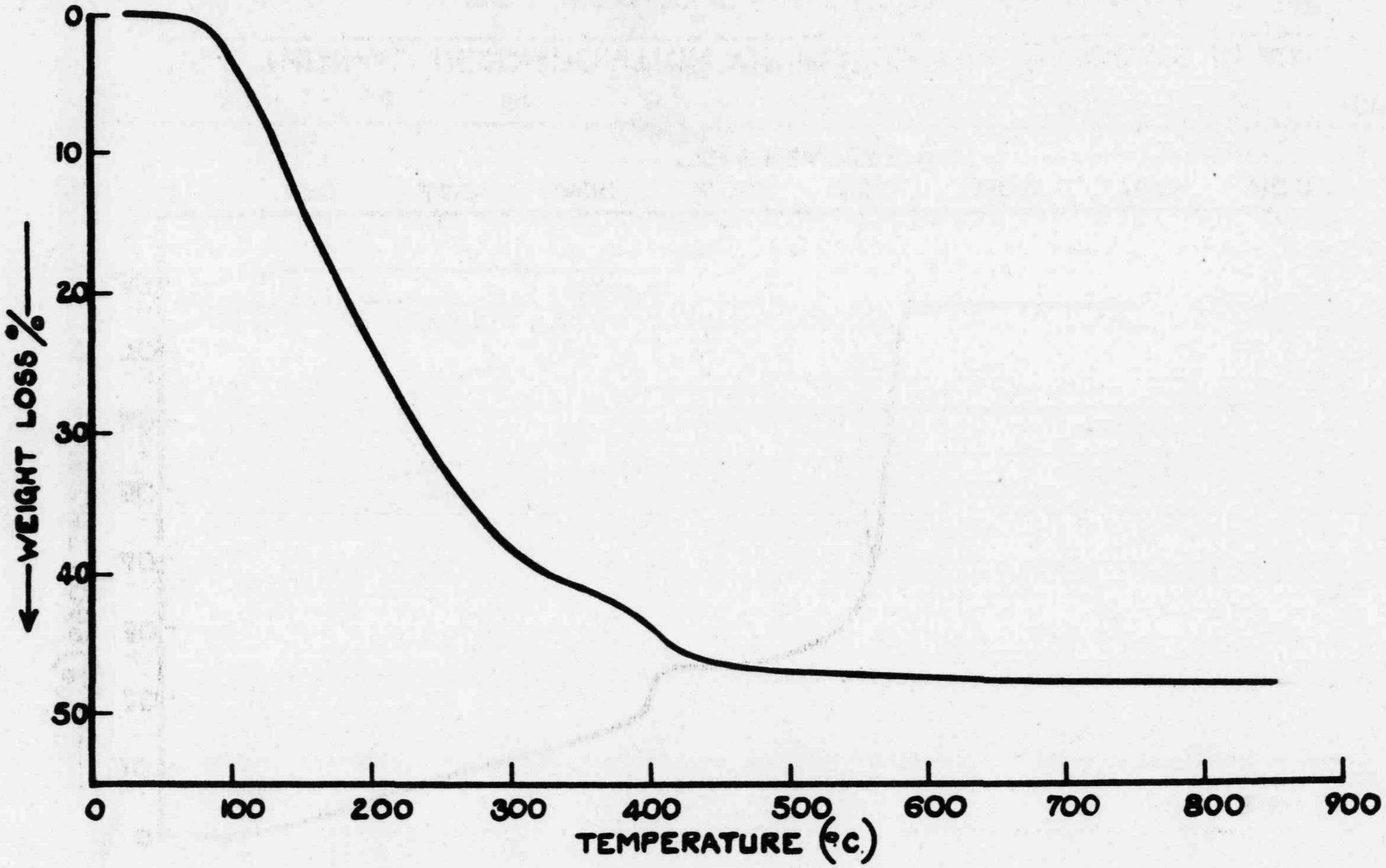

FIG. 8. THERMAL DECOMPOSITION OF Pu $(C_2O_4)_2 \cdot 6H_2O$ IN AIR.

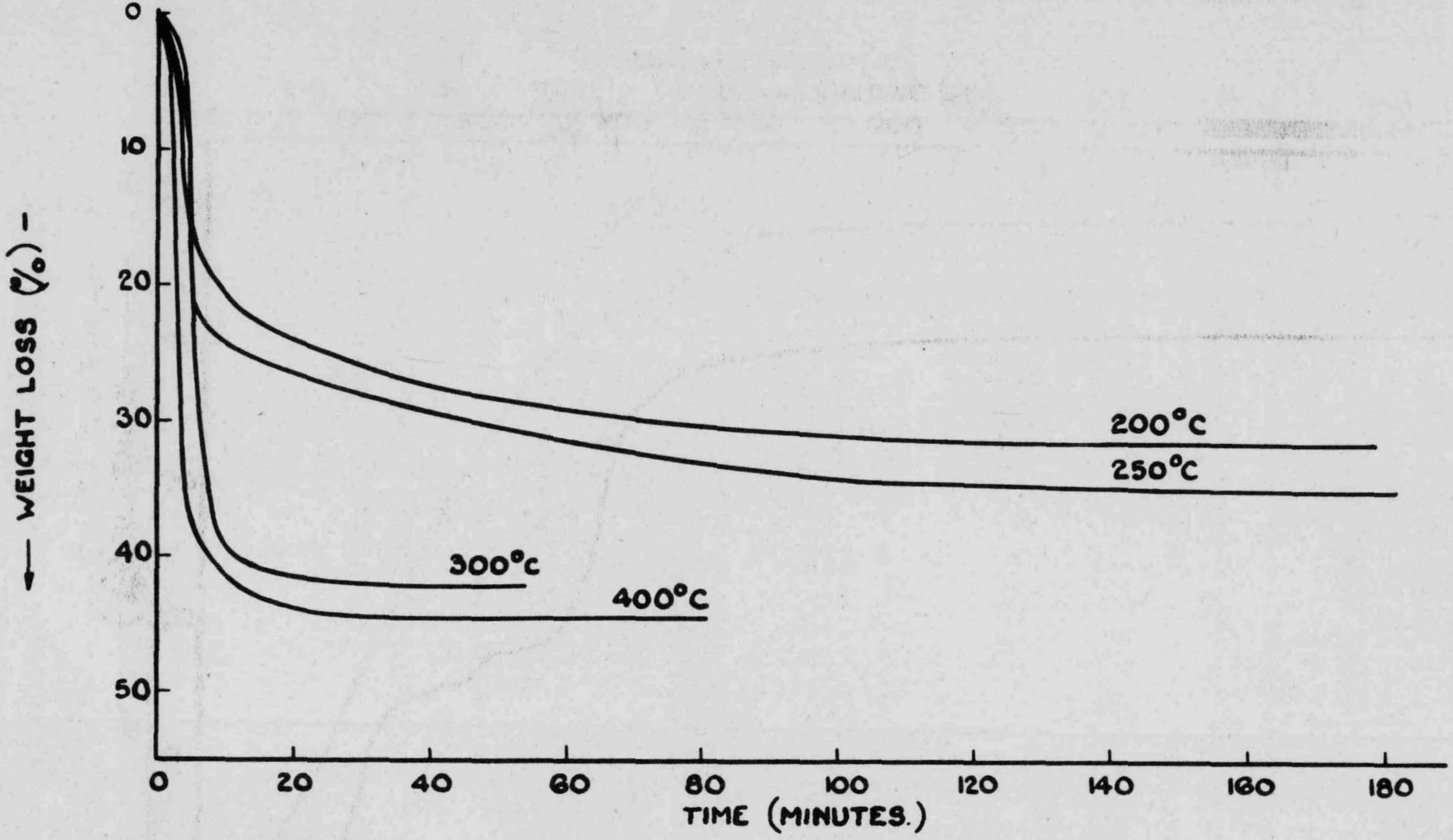

FIG. 9. ISOTHERMS FOR $Pu(C_2O_4)_2 . 6H_2O$ IN AIR.

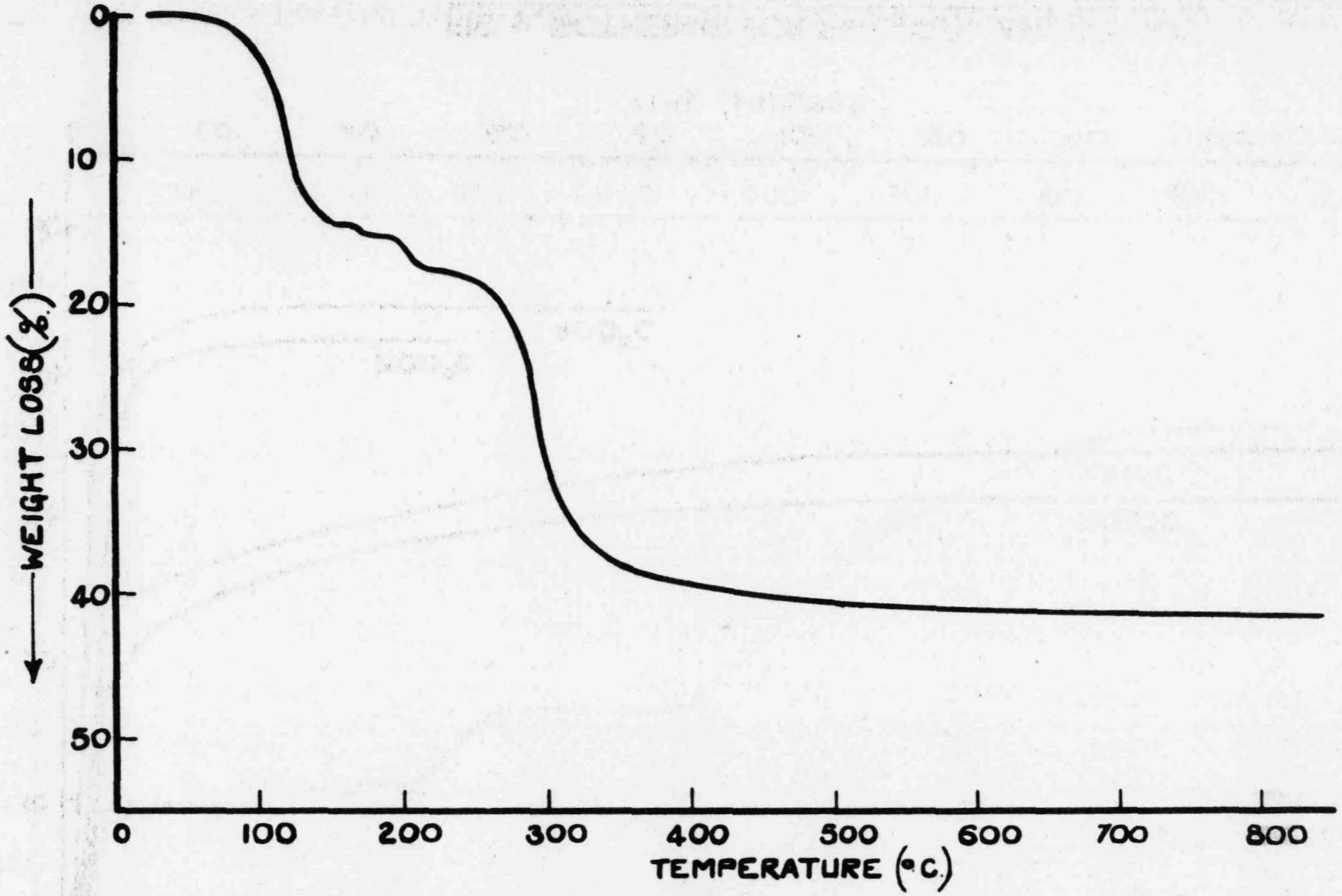

FIG. 10. THERMOGRAVIMETRIC CURVE FOR HYDRATED PLUTONIUM III OXALATE IN AIR.

081 021

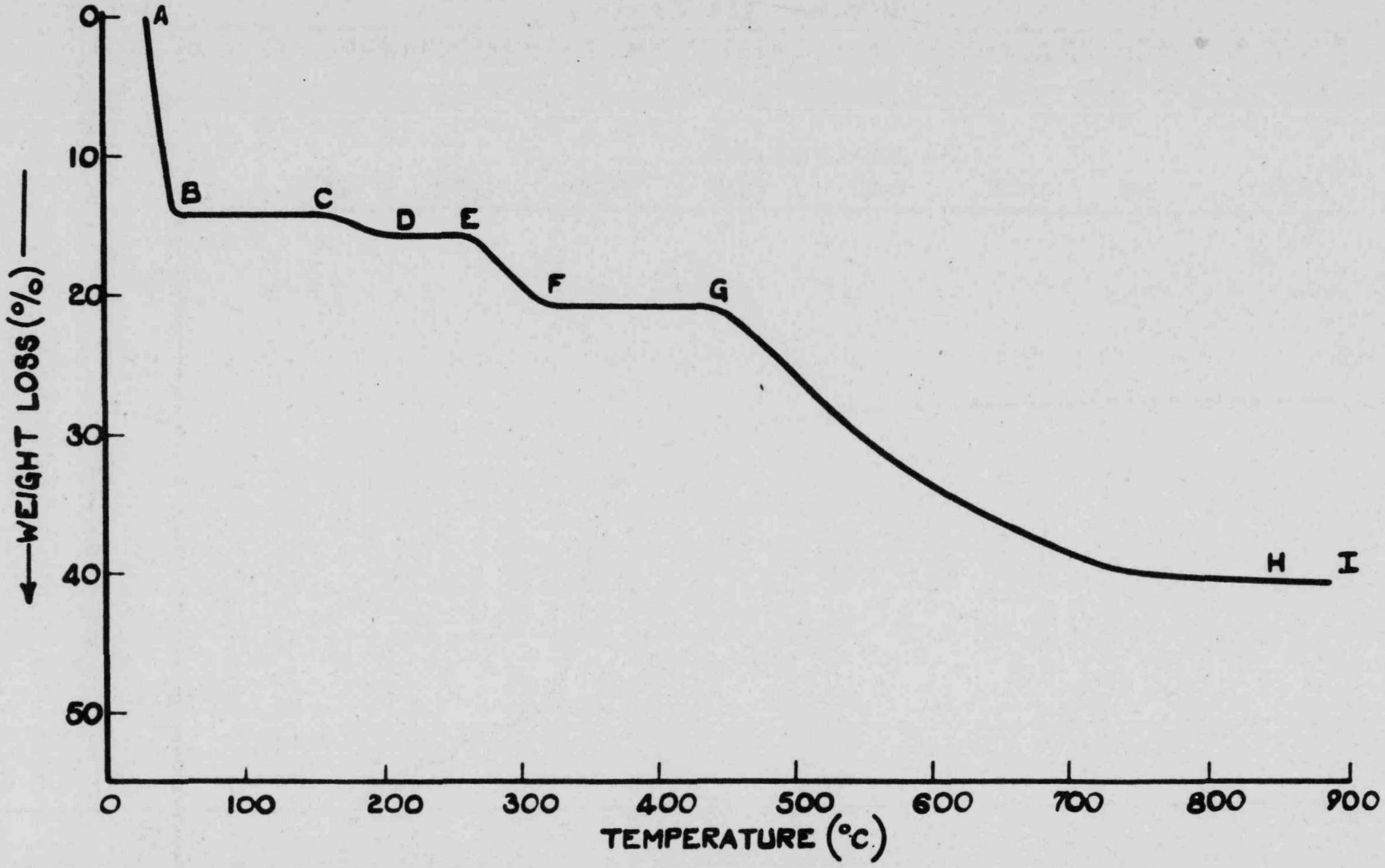

FIG. II. THERMOGRAVIMETRIC CURVE FOR HYDRATED PLUTONIUM III OXALATE AT 10^{-5} mm. Hg PRESSURE.

081 022