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RESEARCH GROUP

# THE PREPARATION OF URANIUM TRIOXIDE BY THERMAL DECOMPOSITION OF URANYL NITRATE

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## ABSTRACT

A comparison has been made between the uranium trioxides prepared by thermal decomposition of uranyl nitrate and of ammonium diuranate. An attempt has been made to follow the course of the denitration reaction, and physical properties of the material at various stages in the decomposition have been measured. Good decontamination from ruthenium has been obtained during decomposition of the nitrate.

A.E.R.E. Harwell

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## ILLUSTRATIONS

## 1. INTRODUCTION

The literature on the thermal decomposition of uranyl nitrate hexahydrate is somewhat confused. It is clear that the hexahydrate can be dehydrated to the trihydrate and then to the dihydrate, but on the course of decomposition of the dihydrate there is little agreement. It has been variously reported that

(a) a monohydrate is produced in carbon dioxide at 120-125° with little loss of nitrogen(1),

(b) nitrous fumes are lost as low as 100°C,

(c) the dihydrate is stable up to 180°C(2),

(d) the anhydrous nitrate is produced from the trihydrate in a dry nitric acid stream at 170-180°C(3),

(e) an oxide-free anhydrous salt cannot be prepared in a dry nitric acid stream at 130°C(1).

The most recent work, by Wendolkowski and Kirslis(4), has confirmed the presence of hexahydrate, trihydrate and dihydrate as stable phases, but has given no indication of the course of the final stages of decomposition to trioxide.

## 2. DECOMPOSITION EXPERIMENTS

The initial approach was the decomposition of large (300 g) batches of hexahydrate. The reaction was carried out in a round-bottomed cylindrical glass vessel fitted with a glass stirrer and immersed in a Wood's metal bath seated in an 'Electrothermal' mantle. This arrangement permitted good temperature control.

The reaction generally went through the following stages:-

(a) Solution of nitrate in its water of crystallisztion (melting starts at ca.60°C).

(b) Recrystallisation. (This stage is sometimes omitted when heating is rapid).

(c) Mass becomes pasty and darkens to an orange colour.

(d) Nitrous fumes appear, the mass is dark orange and very viscous.

(e) A further colour change to a light orange occurs together with a decrease in viscosity and the evolution of copious nitrous fumes.

(f) Slow solidification with temperature kept at 300°C.

The temperatures at which the above stages occur, vary according to the rate of heating and stages may, under some conditions, overlap or even disappear.

The product was in each case ground to pass 40 mesh and the tap density (i.e. the weight of unit volume of powder in a cylinder after a standard tapping process) determined. Fig. 1 shows the relationship between tap density and the time taken from the start of recrystallisation to the point at which solidification caused the stirrer to stop. It is seen that rapid heating (i.e. a small reaction time) gives products of the highest tap density (3.6-4.0 g/ml.). In every case, however, the tap density is considerably higher than that of trioxide prepared by decomposition of ammonium diuranate (ca. 1.6 g/ml.).

Microscopic examination of the trioxide showed that it was very different in nature from that prepared by decomposition of diuranate (Fig. 2). The aggregate size of the latter (A) material varied from 1-250μ with a mean of over 100μ, whereas the denitrated (N) material had a much smaller aggregate size distribution (1-50μ) with a mean of ca. 20μ. Determination of surface area by low temperature nitrogen adsorption showed that the individual particle size of 'A' $UO_3$ was < 0.1μ whereas that of the 'N' material was about tenfold greater. These figures assume that all available surface area is on the surface of uniform spheres and does not take into account internal surface area and fissures. However, the large difference between the two types of material is apparent.

## 3. THERMOGRAVIMETRIC EXPERIMENTS

### (i) Decomposition of hexahydrate

In order to try to determine some of the intermediate stages in the decomposition of hexahydrate, measurements were made of the weight loss (a) with continuously increasing temperature and (b) after 24 hours at a constant temperature. The experiments were carried out on a quartz spiral spring having a sensitivity of about 14 mg./mm., the sample of about 400 mg. of hexahydrate being contained in a small platinum crucible.

(a) The results are shown in Fig. 3; the general trend of the curves is the same as those determined, with smaller loads and a more sensitive balance, by Dawson and Alcock(6). In both curves (A and B) breaks are seen corresponding to the compositions $UO_2(NO_3)_2$. 5½ $H_2O$ and $UO_2(NO_3)_2.2H_2O$. No clear indication is given of a trihydrate, but in curve B there is a break corresponding to the anhydrous nitrate. The evolution of nitrous fumes were first noticed at the points marked X and Y. In curve B (with slower heating) sharp breaks are obvious at 28.5 and 35% loss in weight but they cannot be assigned to any particular composition.

(b) The loss in weight after 24 hours at a constant temperature is shown in Fig. 4, the curve indicating the composition of material stable at any given temperature. The very marked flat portion between 125° and 165°C cannot be correlated with any simple stoichiometric composition. Determinations of nitrogen content showed that nitrate starts to be lost at a temperature less than 125°, i.e. before all the water has been expelled. Thus the composition of intermediate stages is almost certainly not sharply defined and may be continuously variable between dihydrate and trioxide.

(ii) Decomposition of trioxide

The thermal instability (i.e. the ease of conversion to $U_3O_8$) of 'A' and 'N' $UO_3$ was examined on the thermogravimetric balance by slowly and regularly raising the temperature and measuring the decrease in weight. The results are shown in Fig. 5. It should be noted that the materials although previously heated at 300°C for some hours, are not true $UO_3$. With 'A' material some 7.5% is presumably water or ammonia and with 'N' material 2% is probably mainly water (analysis shows 450 ppm. nitrogen).

Decomposition of $UO_3$ to $U_3O_8$ seems to start with both types of oxide at about 560-570° but with slower heating rates this temperature could be lower. The different rates of decomposition are probably a function of particle size. The steps in the 'N' curve may not be real since the weight loss is very small and the spiral of low sensitivity. The break in the 'A' curve seems real but cannot be attributed to any definite hydrate.

Further experiments were carried out to measure the loss in weight (i.e. the percentage conversion to $U_3O_8$) after heating 1 g. samples of 'A' and 'N' $UO_3$ respectively for 2 hours at constant temperature. The results, (Fig. 6) show that the 'N' material does not decompose to $U_3O_8$ until a temperature of over 650° whereas the 'A' material starts to decompose at a lower temperature. This variation in behaviour is in general agreement with the literature which can be summarised by saying that "unstable" forms of $UO_3$ e.g. the amorphous form, begin to decompose in air at 400-500°C and can be fully converted to $U_3O_8$ at about 650°, which the "stable" forms, e.g. Mallinckrodt oxide, only begin to decompose in air at 600° and may have to be heated to 800° for complete conversion to $U_3O_8$.

## 4. PHYSICAL PROPERTIES DURING DECOMPOSITION

Rough measurements were made of the melting points and boiling points of material at stages in the decomposition of hexahydrate. The results, shown in Fig. 7, were obtained respectively by observing cooling rates of the melt and vapour temperatures above the boiling liquid. Determinations of density using a hydrometer (Fig. 8) were made up to the point where the melt became opaque but the values obtained will vary with the rate of heating.

## 5. X-RAY EXAMINATION

Samples of trioxide from decomposition of ammonium diuranate and nitrate were examined by X-ray powder diffraction methods. The samples prepared by decomposition of nitrate were found to take up atmospheric water to form an orthorhombic monohydrate. The very small particle size of those prepared from diuranate did not allow of good patterns, but the indications are that it is of different structure from the denitrated preparation. The X-ray work was carried out by Wait and D'Eye of the Heavy Elements Group and will be reported separately.

## 6. DECONTAMINATION FROM RUTHENIUM

Since ruthenium tetroxide is known to be volatile from boiling concentrated nitric acid it was thought that some decontamination from ruthenium might accompany thermal decomposition of uranyl nitrate.

To 500 ml. of a 1.2M aqueous solution of uranyl nitrate was added a solution of $RuO_4$ in nitric acid, the ruthenium having been separated from irradiated uranium by solution in nitric acid and distillation with periodic acid. The solution was evaporated and the decomposition carried out in the normal way. A decontamination factor of not less than 150 was obtained.

## 7. SUMMARY

The trioxide prepared by thermal decomposition of the nitrate is very different in character from that prepared by decomposition of ammonium diuranate. It has a larger individual particle size (although a smaller aggregate size distribution), a different crystalline form and is very much more stable to heat treatment.

The exact nature of the trioxide, i.e. its particle size, tap density etc., varies somewhat with the rate of decomposition. Confirmatory evidence has been obtained for the existence of the nitrate dihydrate, but no other simple stoichiometric compounds have been found to exist during the decomposition.

## ACKNOWLEDGEMENT

We wish to thank Miss P. M. Bartlett for the particle size determinations and for the results given in Fig. 6.

## REFERENCES

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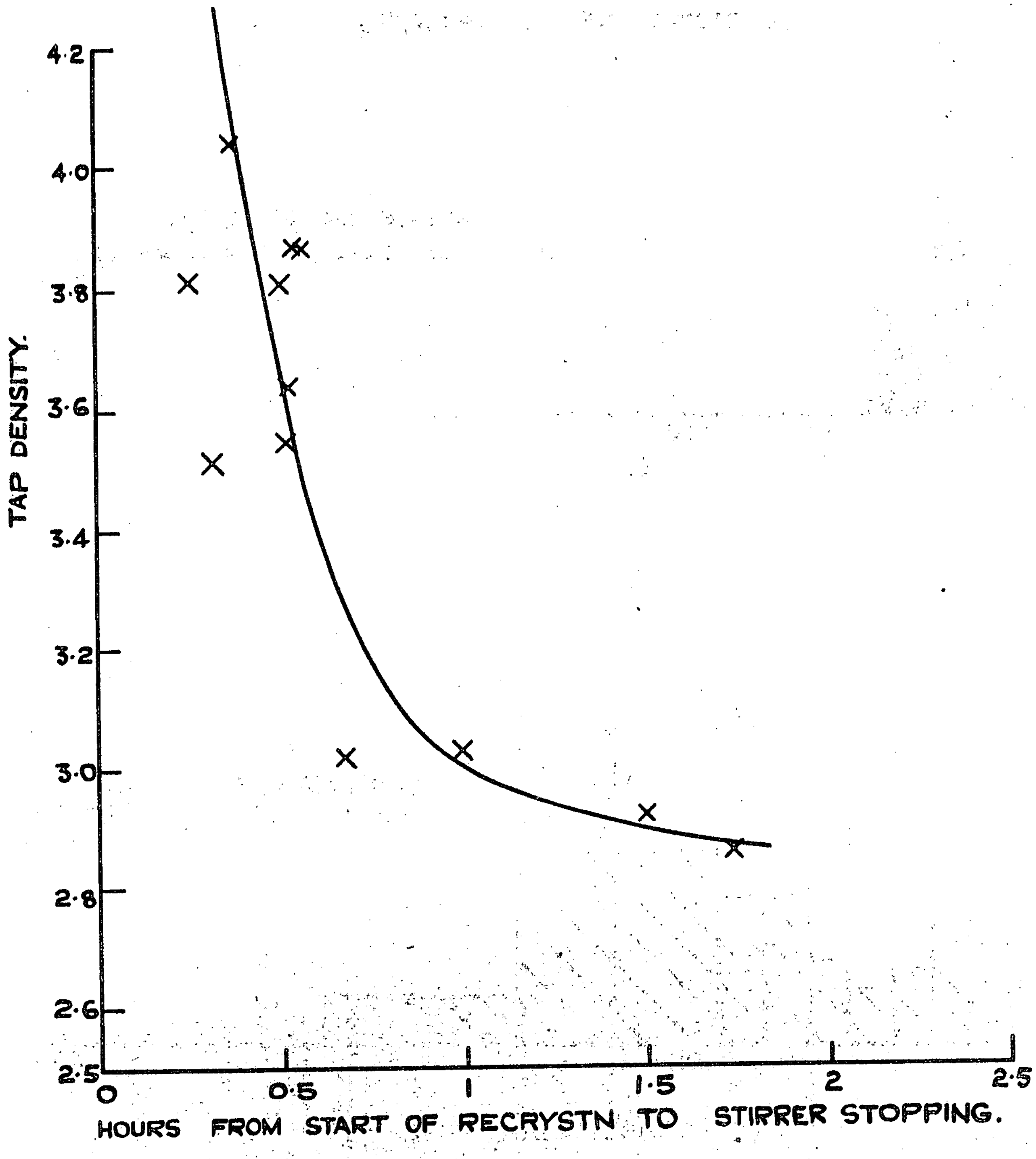
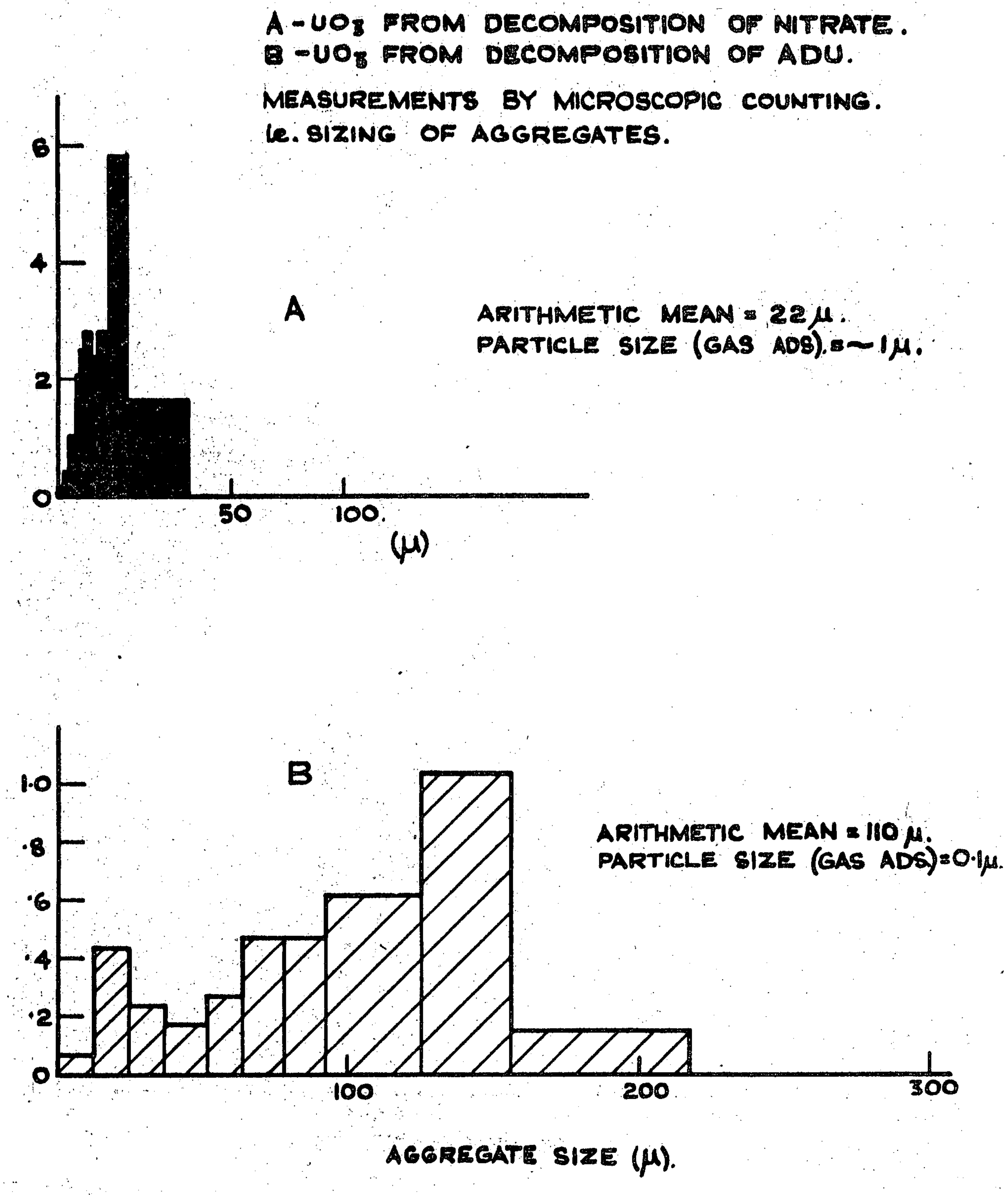
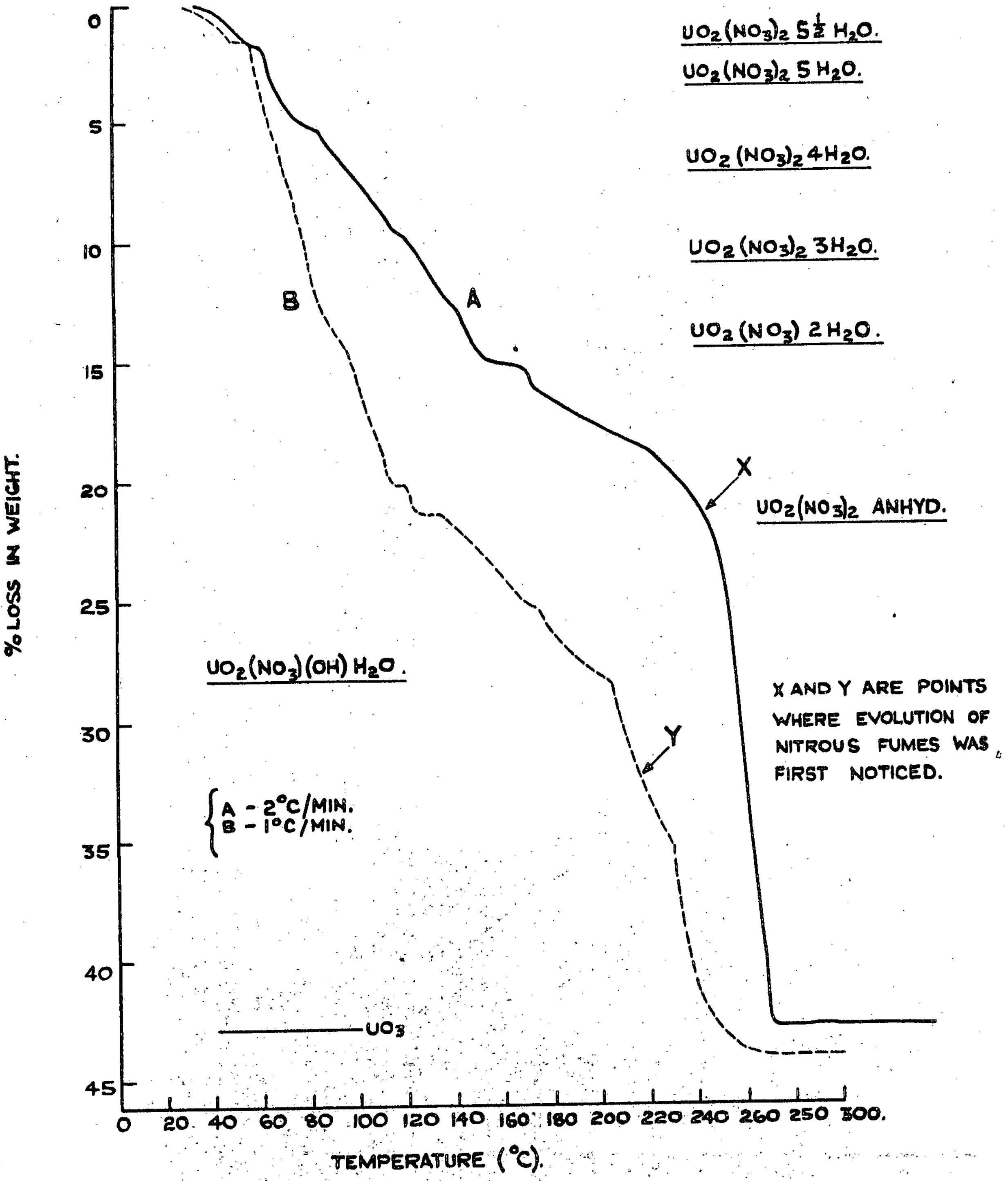
2. Marshall, Gill and Secoy. J. Am. Chem. Soc. 73, 1867 (1951).
3. Marketos, Compt. rend. 155, 210 (1912).
4. Wendolkowski and Kirslis, K-1086 (Feb. 22 1954).
5. See also Lister, RCTC/P.20 (May 1954).
6. Dawson and Alcock. Unpublished work.



A.E.R.E. C/R.2276.FIG. I. RELATION BETWEEN TAP DENSITY AND RATE OF HEATING.

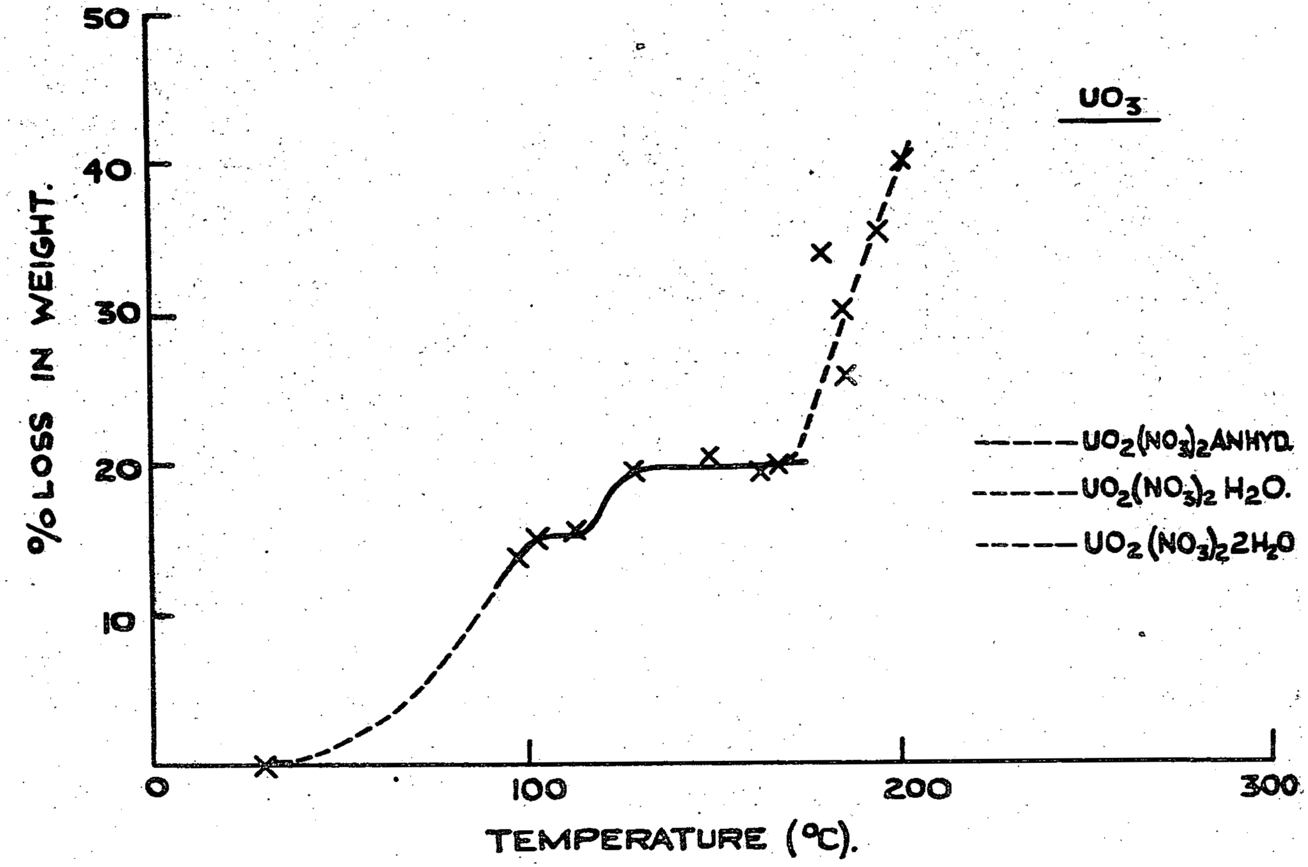


A.E.R.E. C/R.2276. FIG. 2. AGGREGATE SIZE DISTRIBUTIONS (BY WEIGHT) OF $UO_3$.

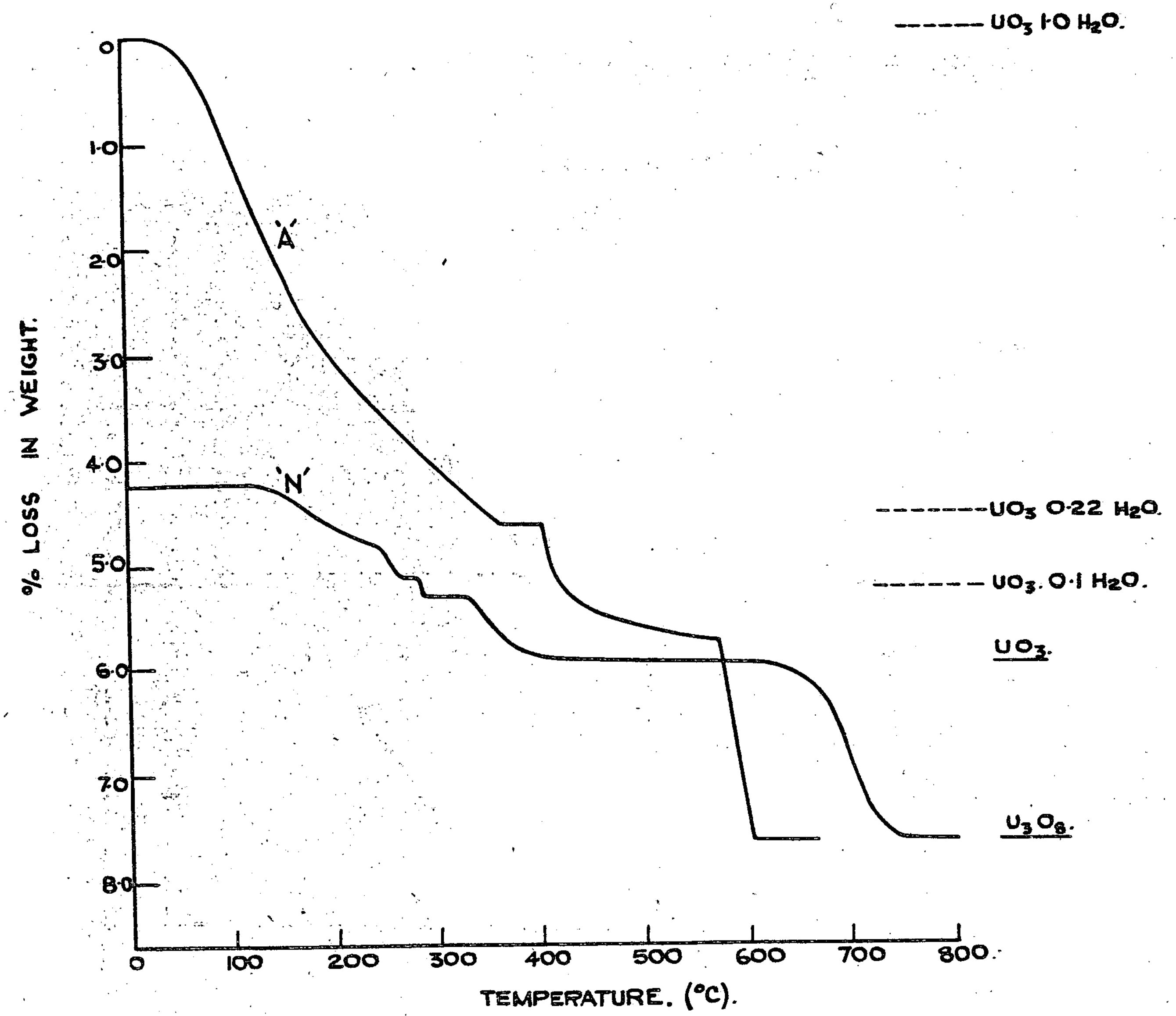


X AND Y ARE POINTS WHERE EVOLUTION OF NITROUS FUMES WAS FIRST NOTICED.

AERE. C/R.2276 FIG. 3. THERMOGRAVIMETRIC CURVES FOR DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE.

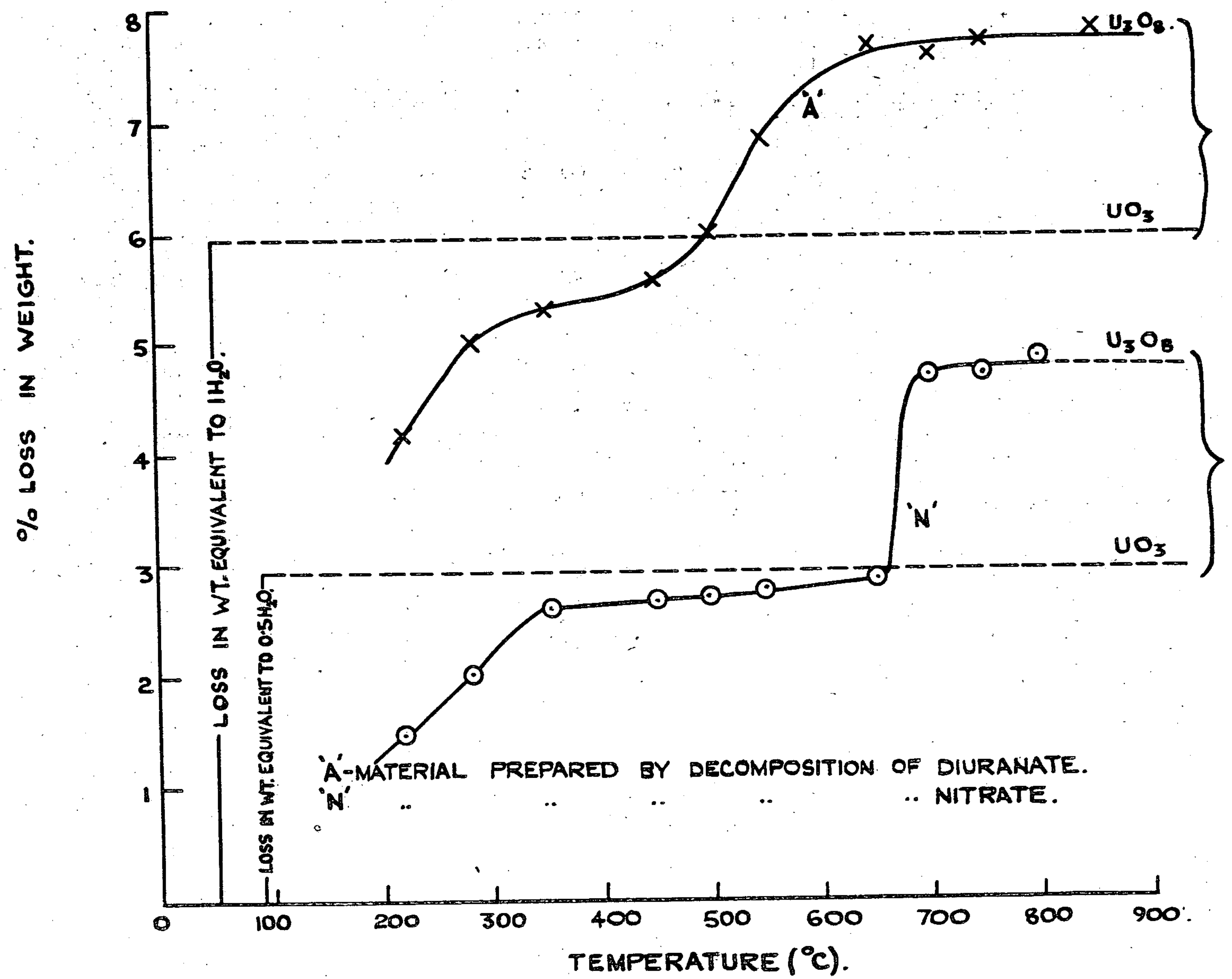


A.E.R.E. C/R. 2276. FIG. 4. DECOMPOSITION OF NITRATE (24 HOURS AT CONSTANT TEMPERATURE)

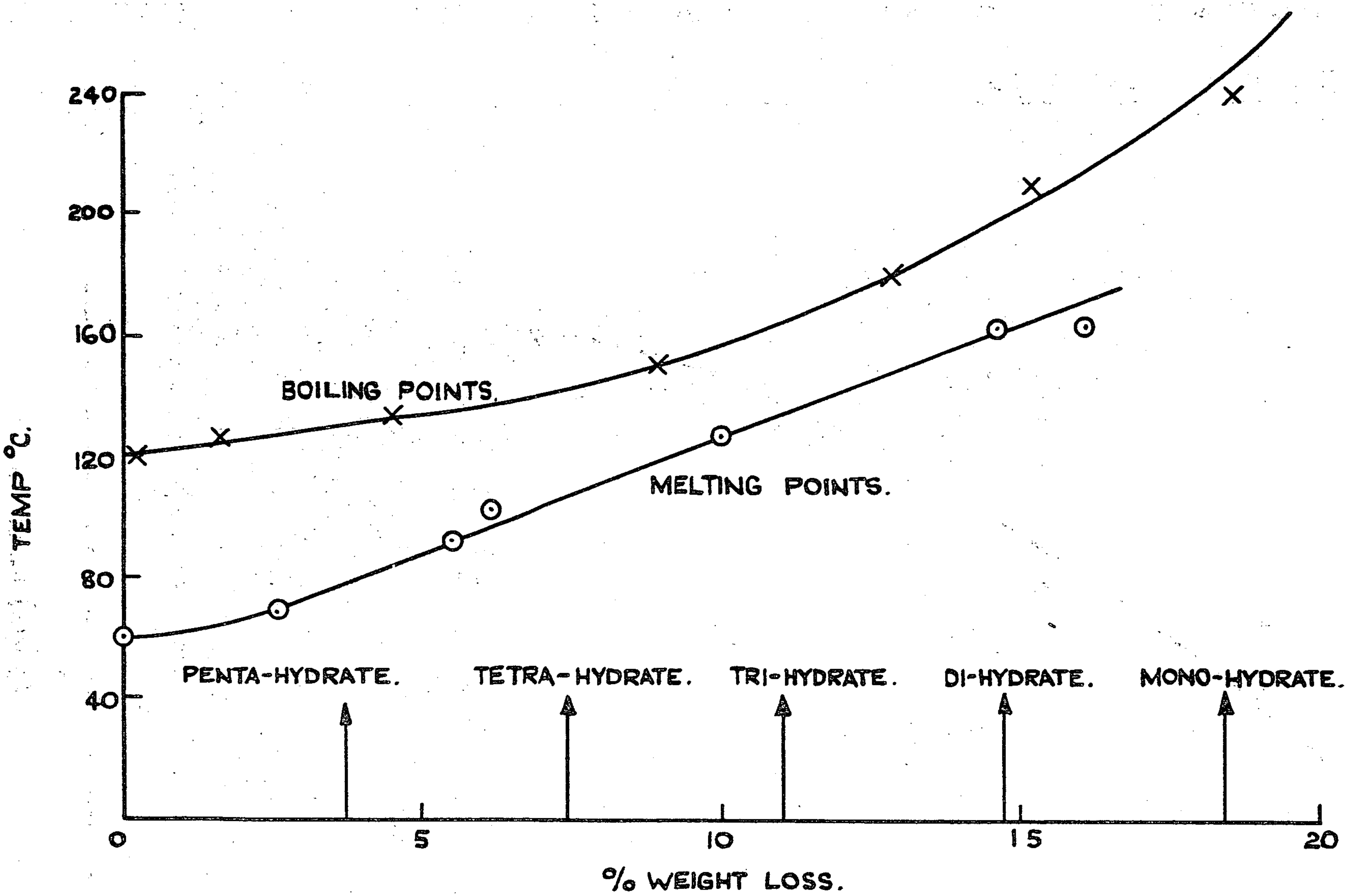


A.E.R.E. C/R.2276 FIG. 5. THERMOGRAVIMETRIC CURVES FOR DECOMPOSITION OF URANIUM TRIOXIDE.

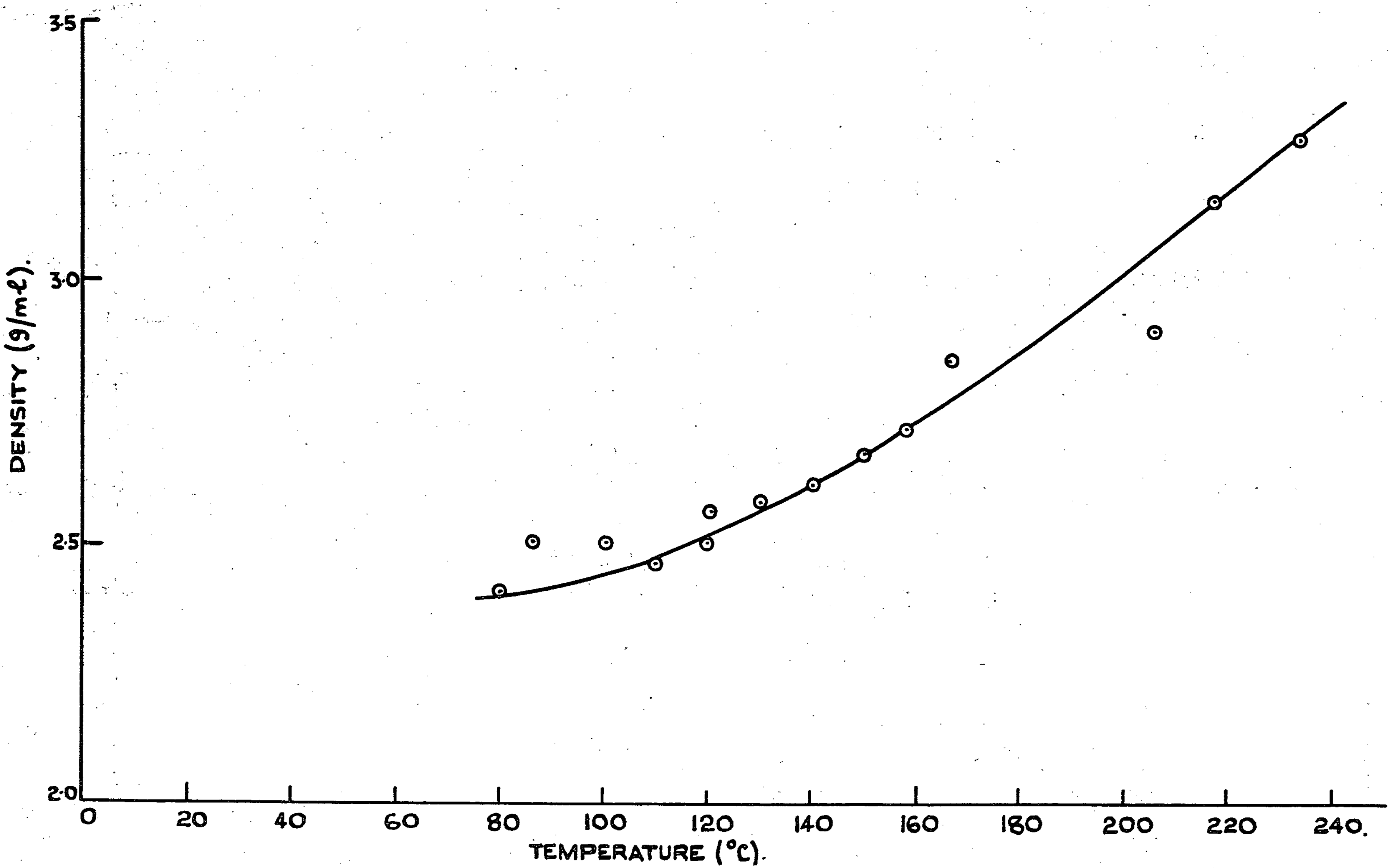
'A'. FROM THERMAL DECOMPOSITION OF ADU.
'N' FROM THERMAL DECOMPOSITION OF NITRATE.



A.E.R.E. C/R.2276.FIG.6. DECOMPOSITION OF URANIUM TRIOXIDE. (2 HOURS AT CONSTANT TEMPERATURE).



A.E.R.E. C/R.2276. FIG. 7. MELTING POINTS & BOILING POINTS DURING DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE AS FUNCTION OF WEIGHT LOSS.



A.E.R.E. C/R. 2276. FIG. 8. DENSITY OF MELT AS FUNCTION OF TEMPERATURE.