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The Reaction of UF_4 with UF_6.

by

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ABSTRACT As part of an investigation into the corrosion of metals by UF_6 the system $UF_4(s) - UF_6(g)$ has been studied under closely defined experimental conditions. The formation of the intermediate fluorides U_4F_{17}, U_2F_9 and βUF_5 was found to be stepwise, each stage proceeding at a well defined reaction-initiation temperature. The properties of the intermediate fluorides obtained were compared with previous findings, and were identified by X-ray diffraction analysis.

For the Attention of The Diffusion Plant Development Committee.

Passed for Distribution by A. B. McIntosh

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1. Introduction

Experimental work on the corrosion of metals in gaseous UF_6 has shown that the corrosion product is usually an intermediate fluoride of uranium, together with the fluoride of the metal. The particular intermediate fluoride of uranium formed is dependent on the temperature and pressure conditions under which the metal is exposed and usually bears little relation to the nature of the metal. This is due to the narrow stability ranges of these intermediate fluorides in the presence of UF_6. The mechanism of corrosion of metals in UF_6 cannot be elucidated until the phase system between UF_4 and UF_6 has been experimentally investigated over temperature and pressure ranges not previously studied. The results obtained are presented in this note.

2. Previous Work

The reaction (1) between UF_4 and UF_6 has been shown experimentally to be complex, (2) and to occur in a stepwise manner, yielding a range of intermediate uranium fluorides, namely U_4F_{17} U_2F_9, and α and β modifications of UF_5. The study of these compounds has not been widely pursued, and considerable gaps exist in the knowledge of the conditions under which they are formed.

An early and isolated experiment was the preparation of UF_5 from UCl_5 and anhydrous HF by Ruff and Heizelmann. (3) Interest in the uranium fluorides was revived when what was thought to be a crystal modification of green monoclinic UF_4 - "Black UF_4" (4 - 10) was discovered. In the subsequent investigations (4), (11 - 17) this was shown to be U_2F_9, and the other intermediate fluorides were discovered and investigated as a consequent development.

The structures of α (18), (19) and β (19) UF_5 and of U_2F_9 (20), (21) were determined by W. H. Zachariasen (22) who also suggested a structural configuration for U_4F_{17} (12). Both α and β UF_5 were shown to be tetragonal with $a_0 = 6.152 \pm .001Å$ $a_3 = 4.463 \pm .001Å.$, and $a_1 = 11.450 \pm .002Å$, $a_3 = 5.196 \pm .001Å$ respectively. U_2F_9 was found to have a cubic system with $a_0 = 8.5384 \pm .0019$. The U_4F_{17} lattice was designated as distorted UF_4, in view of the X-ray diffraction pattern resembling that of UF_4.

In all these compounds there was no X-ray evidence (12) to indicate the formation of solid solutions, and on the basis of resonance - colour considerations, equivalence of the uranium atoms, and ionic crystals radii such structures as $UF_4 . UF_6 = 2 UF_5$; $UF_4 . UF_5$ or $3 UF_4 . UF_6 = U_2F_9$; $3 UF_4 . UF_5$ or $7 UF_4 . UF_6 = 2 U_4F_{17}$ were untenable. The intermediate fluorides must be regarded as compounds in which resonance renders all the uranium atoms equivalent (1).

The field of experimental work from 1941 to 1952 was confined to the following range of conditions,

(a) Temperature 100 - 350°C.

(b) Pressures 17 mm - several atmospheres, with a great bias towards pressures in excess of 120 mm.

(c) UF_4 - (1) precipitated, with surface area 6 - 7 m^2g^{-1}.

(2) produced by high temperature fluorination, [illegible] surface area 0.2 m^2g^{-1}.

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There was considerable divergence in the results obtained, in part due to the differences in the nature of the UF$_4$ and, at first, t relatively insensitive methods of assessing results, viz, visual observation, measurement of weight increases and chemical analysis.

The kinetics of the reaction were not studied but it was apparent that the rate of attainment of equilibrium was dependent on the nature and origin of the UF$_4$, and that the rate of diffusion of UF$_6$ into the UF$_4$ was the governing step in the reactions (2).

With respect to the chemical and physical properties of the compounds the general trend was found to be of increasing stability with respect to hydrolysis and thermal disproportionation in the direction α UF$_5$ - β UF$_5$ - U$_2$F$_9$ - U$_4$F$_{17}$.

A graph (23) showing the disproportionation pressure of UF$_6$ with temperature clearly indicates the phase change between α and β UF$_5$. The temperature at which this occurs has been shown experimentally to be within the range 100 - 185°C, and theoretically 125° at 1.76 mm pressure. The modification being stable at the lower temperature.

In subsequent work attention has been given to further methods of preparation, (23 - 26), more detailed analysis of crystal structure, (27 - 35), the vapour pressures (36) and thermodynamic properties (37) of the compounds.

3. Experimental Procedure

The apparatus shown in Fig. 1 was used to determine the amount of gaseous UF6 which would completely react with a weighed quantity of UF$_4$ under known conditions of temperature and pressure. The two chambers of known volume V$_1$ and V$_2$ are interconnected by valve A. Known volume V$_1$ contains UF6 gas at a measured pressure and known volume V$_2$ contains the reactant UF$_4$ and is evacuated. On opening valve A the theoretical pressure drop can be calculated assuming no reaction, while the actual pressure drop is measured. The difference between the observed and calculated pressure changes therefore gives a direct measure of the amount of UF6 converted to N.T.P. which reacts with 1 gm of UF$_4$ using the equation (assuming UF6 to behave ideally).

$$V_A = \frac{\Delta P \times (V_1 + V_2) \times 273}{W \times 760 \times T}$$

where V_A = volume of UF$_6$ (ccs at N.T.P.)

W = weight of UF$_4$ (gms)

T = absolute temperature

ΔP = pressure drop due to chemical reaction (mm.Hg)

In practice V$_2$ was accurately measured with a burette and V$_1$ determined by a series of expansions from V$_1$ into V$_2$. Corrections were applied for the volume of the reactant UF$_4$ [illegible] tube.

The change of UF$_6$ pressure [illegible] would obviously give a measure of the rate of the reaction, but because of the difficulty of measuring the surface area of the UF$_4$ [illegible] to investigate the kinetics of the process. During [illegible] UF6 pressure was not constant but varied between 10- [illegible] Hg.

4. Experimental Results

The quantity of UF$_6$ absorbed by solid UF$_4$ was found to vary discontinuously with temperature in the range 25° – 100°C. Fig. 2. shows graphically the rate of absorption of UF$_6$ measured at various temperatures. At each temperature the absorption came to completion when the stoichiometric amount of UF$_6$ had been taken up to satisfy one of the following three equations:-

1\. --- $7UF_4 + UF_6 \longrightarrow 2U_4F_{17}$ at temperatures below 40°

2\. --- $3UF_4 + UF_6 \longrightarrow 2U_2F_9$ " " " 60° and above 40°

3\. --- $UF_4 + UF_6 \longrightarrow 2UF_5$ " " " 90° and above 60°

From this data it was obvious that there were well defined initiation temperatures in this range for the series of reactions,

$$UF_4 \xrightarrow{UF_6} U_4F_{17} \xrightarrow{UF_6} U_2F_9 \xrightarrow{UF_6} UF_5$$

To determine these initiation temperatures accurately use was made of Charles' Law. Consider a known weight of U$_4$F$_{17}$ in contact with UF$_6$ vapour, the system being below any reaction initiation temperature and consequently in equilibrium. As the temperature is raised so will the pressure increase linearly, until the reaction initiation temperature is reached when a pressure decrease will occur in the system. When equilibrium has again been obtained the pressure increase is again linear with increasing temperature.

Figs. 3 and 4 show the changes in pressure with temperature in a system containing U$_4$F$_{17}$ UF$_6$ and U$_2$F$_9$ + UF$_6$ respectively. In each case a distinct reaction initiation temperature was found and the amount of UF$_6$ absorbed corresponded stoichiometrically to the following equations:-

(1) --- $3U_4F_{17} + 2UF_6 \longrightarrow 7U_2F_9$ at 320°K. (47°C)

(2) --- $U_2F_9 + UF_6 \longrightarrow 3UF_5$ at 357°K. (84°C)

The reactions studied can now be represented by the following stepwise series of equations. The [illegible] figures [illegible] to the volume of UF$_6$(V$_A$) c.c.s. at N.T.P. found [illegible] to completely react with 1 gram of UF$_4$ or intermediate fluoride.

(1) --- $7UF_4 + \underset{10.2}{UF_6} \longrightarrow 2U_4F_{17}$ [illegible] 47°C.

Between 47° – 84°C $3U_4F_{17} + \underset{15.6}{2UF_6} \longrightarrow 7U_2F_9$

(2) --- $3UF_4 + \underset{23.6}{UF_6} \longrightarrow 2U_2F_9$ [illegible] 47° – 84°C.

Above 84°C. $U_2F_9 + \underset{[illegible]}{UF_6} \longrightarrow 3UF_5$

(3) --- $UF_4 + \underset{71.3}{UF_6} \longrightarrow 2UF_5$ [illegible] 84°C.

Each of the intermediate fluorides was isolated and identified by X-ray diffraction analysis. The U$_4$F$_{17}$ was [illegible] and hydrolysed instantly (order of seconds) to give UF$_4$ and UO$_2$F$_2$ on exposure to the atmosphere. It was stable under vacuum or in sealed tubes at temperatures up to 45°C which was the maximum [illegible].

[illegible] was [illegible] than U$_4$F$_{17}$ and presented great difficulty in obtaining X-ray diffraction patterns. It was instantly

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[illegible] moist air and was stable under vacuum at temperatures up [illegible] which was the maximum employed.

UF_5 was white or very pale green and it was shown by X-ray diffraction to be the β modification. This product again instantly hydrolysed in moist air.

5. Accuracy

The limiting factor was the accuracy with which the pressure changes could be measured. This was ± 0.05 mm Hg, giving an overall accuracy of ± 3%. V_A could thus be measured to ± 0.1 ccs. with a sample size of UF_4 chosen to give a pressure drop conveniently measurable on the manometer system. From the theoretical V_A values quoted with the relevant equations it will be seen that the experimental accuracy was well within the limits of the effect being measured and that the respective V_A values for the formation of the different compounds are sufficiently spaced apart for experimental identification of the reaction product.

6. Discussion

U_4F_{17} and U_2F_9 are both claimed to be black by previous workers, whereas all samples produced by the present method have been brown. Previous workers have also said that U_2F_9 is stable in water for one hour and for the order of days in air. U_4F_{17} was presumed to be even more resistant. The present work has shown the immediate hydrolysis within a few seconds of both U_4F_{17} and U_2F_9 when exposed to the atmosphere. The rapid hydrolysis of UF_5 is in agreement with previous findings.

Previous work (23) has shown the stability with temperature to follow the series.

$$\alpha UF_5 \longrightarrow U_2F_9 \longrightarrow U_4F_{17} \quad \text{(at known } UF_6 \text{ pressure)}$$

~100° ~[illegible] ~350°

whilst the present work shows the series

$$UF_4 \longrightarrow U_4F_{17} \longrightarrow U_2F_9 \longrightarrow \beta UF_5 \quad \text{(at } UF_6 \text{ pressures between 10-64 mm).}$$

~20 ~60° ~[illegible]

In the lo[illegible] te[illegible] [illegible] the stepwise reaction [illegible] pl[illegible] as shown in this work, [illegible] te[illegible] temperatures [illegible] of th[illegible] [illegible] pre[illegible] [illegible] decomposition occurs.

[illegible] temperatures [illegible] since the actual temperatures [illegible] UF[illegible] pressure in the [illegible]. Previous workers [illegible] temperatures (100° - [illegible]) [illegible] been st[illegible] in the present work. [illegible] temperature trans[illegible] in Figs. [illegible] 4.

7. Conclusions

By combining the [illegible] sequence of stabil[illegible] rising temperature [illegible] the [illegible] confidence t[illegible] be

$$UF_4 \longrightarrow U_4F_{17} \longrightarrow \text{[illegible]} \longrightarrow \text{[illegible]} \longrightarrow \alpha \text{ [illegible]} \longrightarrow \text{[illegible]} \longrightarrow U_4F_{17}$$

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The temperature at which these phase changes takes place will be dependent on the UF6 pressure in the system. The effect of this has not been investigated in this present work.

No evidence was found of solubility ranges between the discrete phases in this system, although this aspect of the system was not specifically investigated.

The reason for the complex nature of the [illegible] of uranium metals which have been exposed to gaseous UF6 is now [illegible]. The intermediate fluoride formed by the reaction between metal and UF6 depends on the temperature and pressure [illegible] and not on the nature of the metal, provided that UF6 is in excess.

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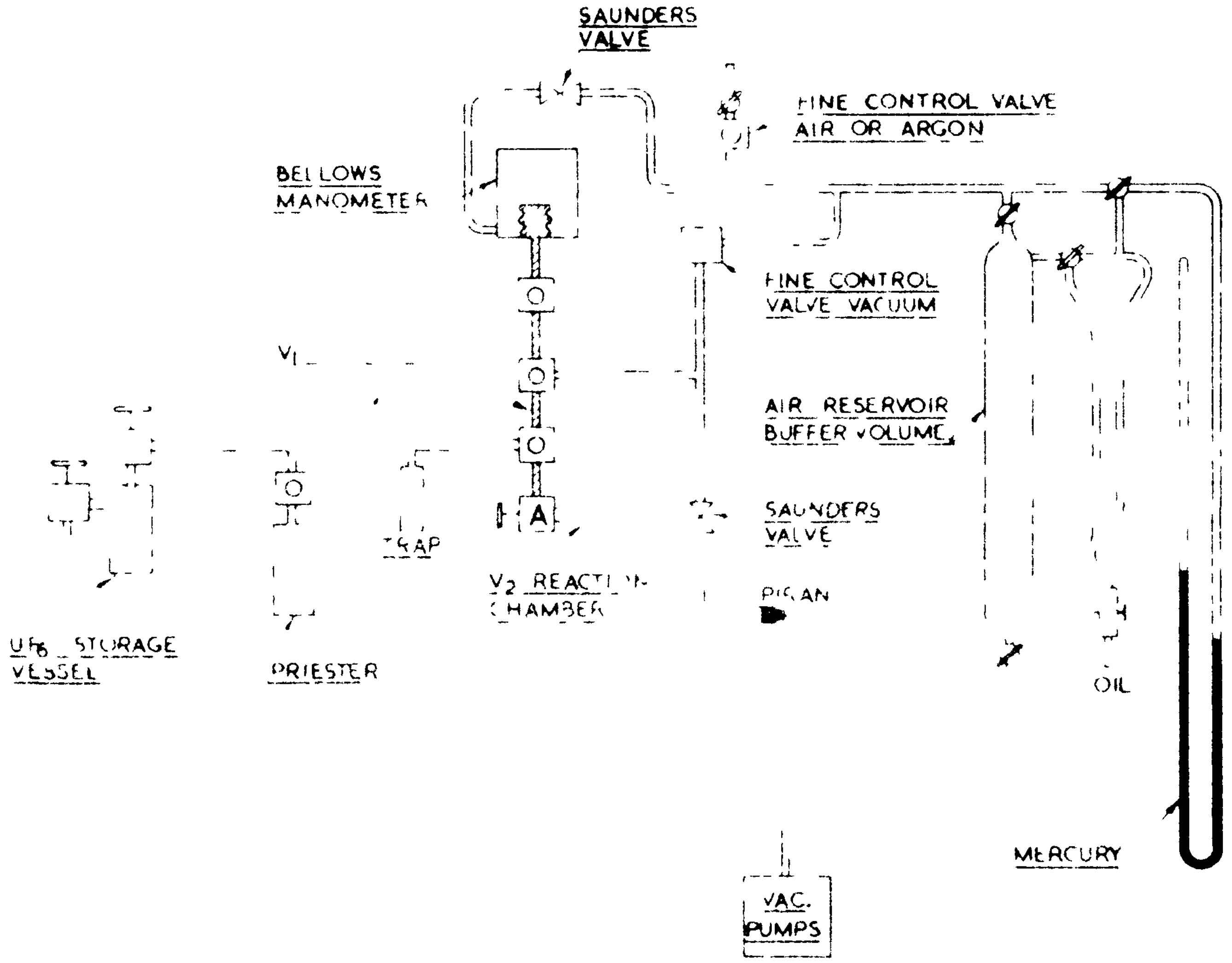

APPARATUS FOR INVESTIGATING THE REACTION OF UF_6 WITH UF_4.

FIG 1

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R.& D. B.(C) TN 60

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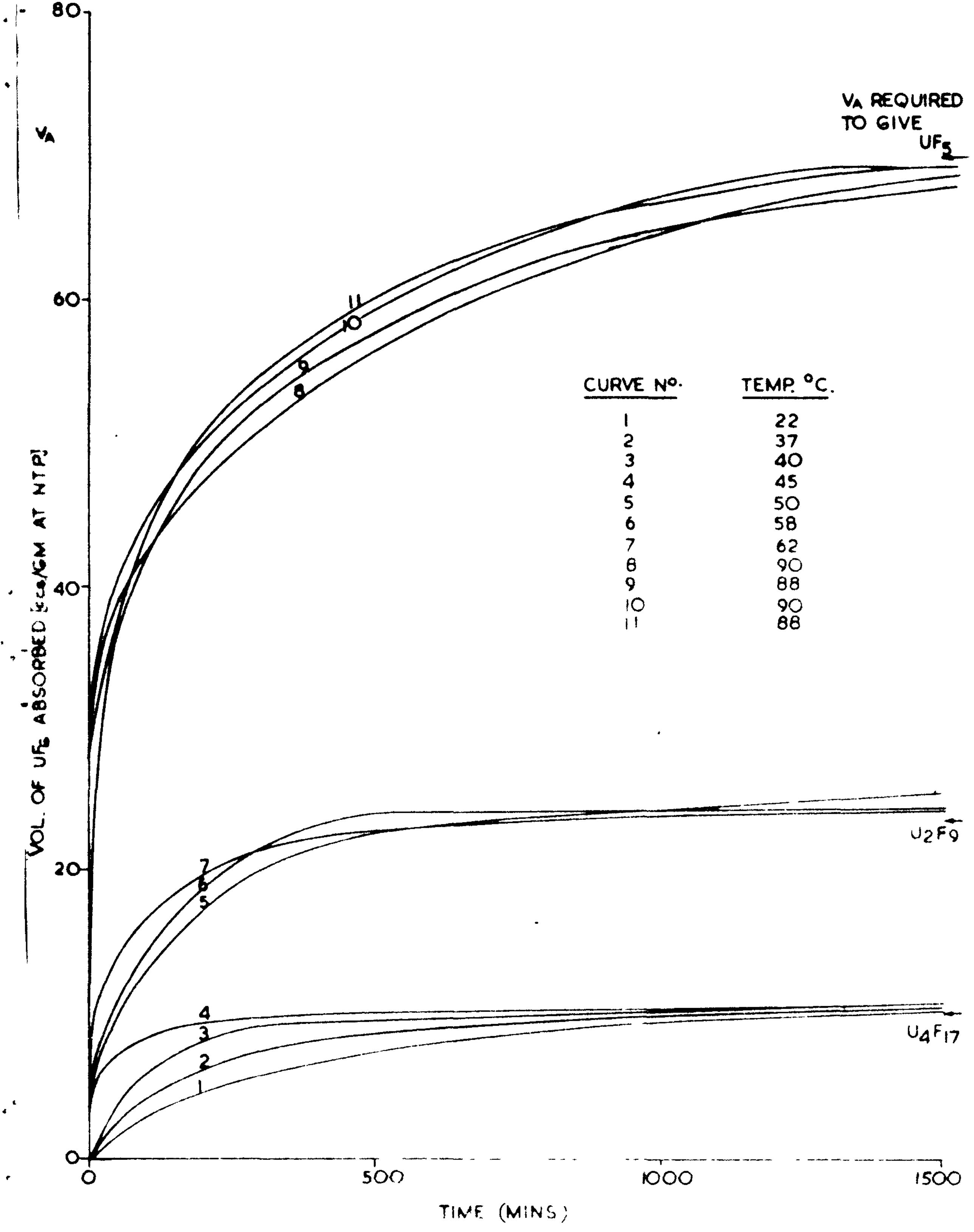

UPTAKE OF UF_6 [ccs/GM AT N.T.P.] BY UF_4
AT VARIOUS TEMPERATURES.

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FIG. 2.

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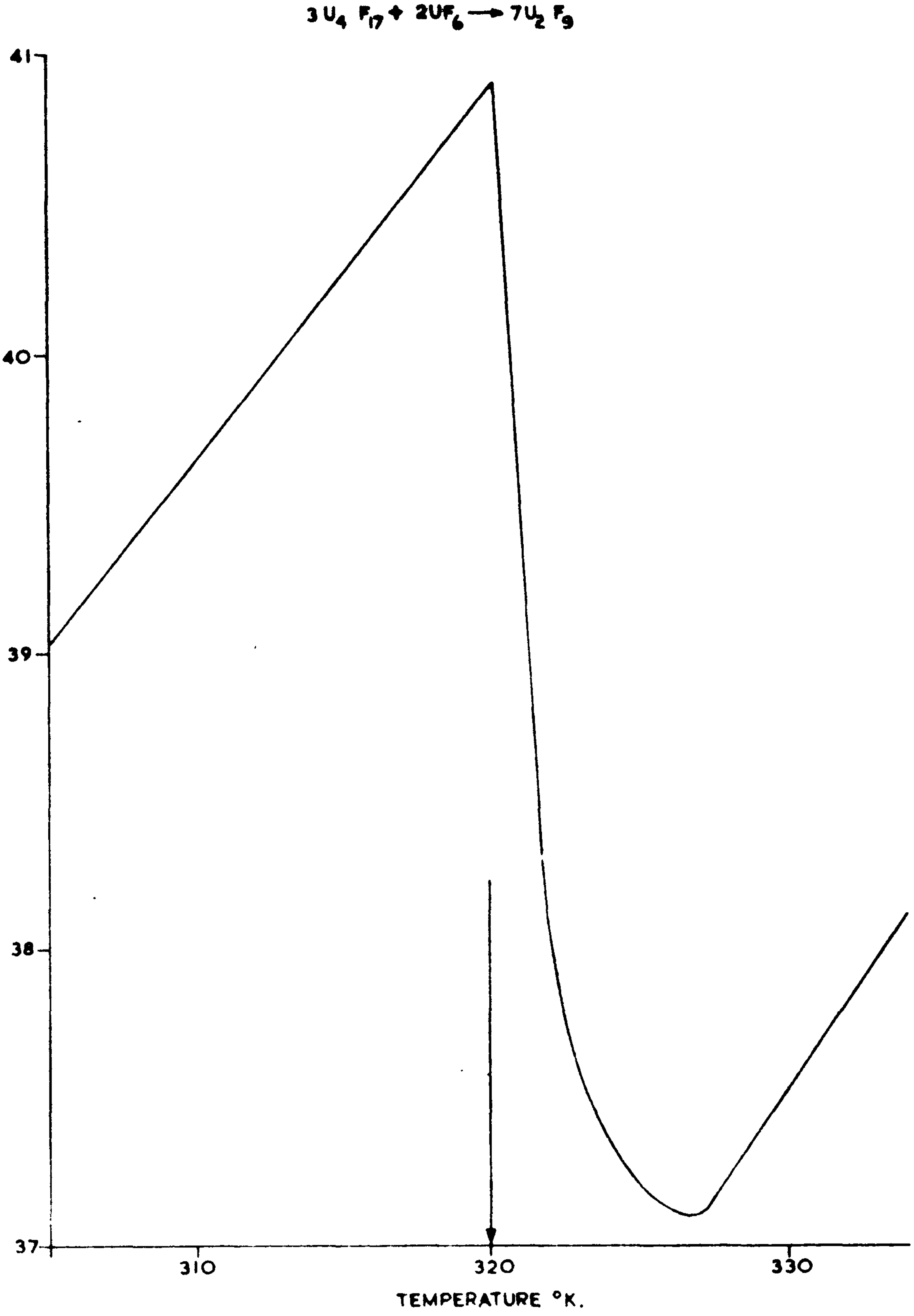

DETERMINATION OF REACTION INITIATION TEMPERATURE FOR $U_4F_{17} \rightarrow U_2F_9$

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FIG. 3.

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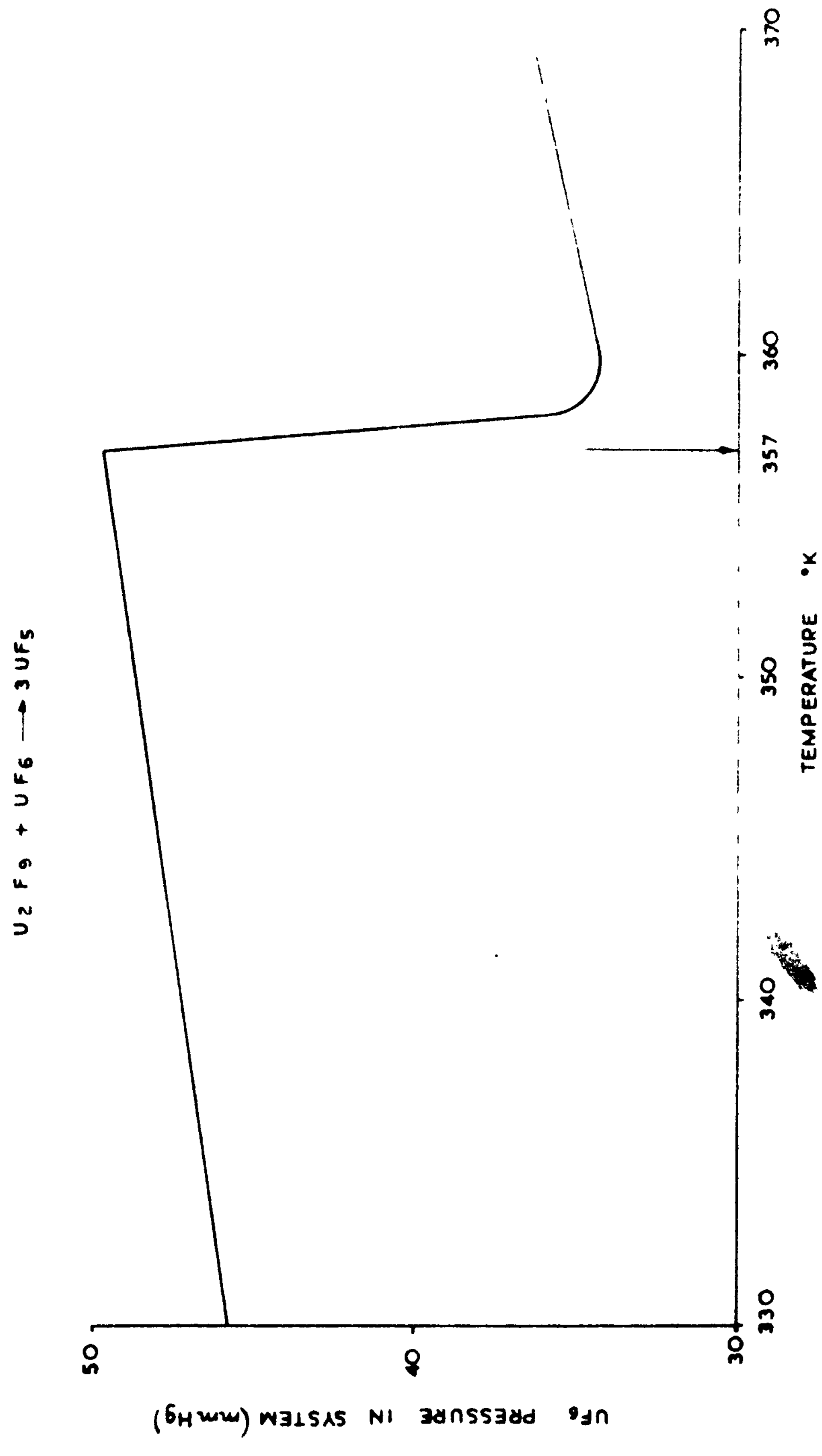

DETERMINATION OF REACTION INITIATION TEMPERATURE FOR $U_2F_9 \rightarrow UF_5$.

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FIG. 4.

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