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RESEARCH AND DEVELOPMENT

DETERMINATION OF THE DIFFUSION CONSTANT OF FISSION XENON  
IN  $\text{UO}_2$  CRYSTALS AND SINTERED COMPACTS

CRDC-720

BY

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ABSTRACT

The diffusion of fission product xenon from  $\text{UO}_2$  crystals and from compacted and sintered  $\text{UO}_2$  pellets has been measured under a variety of conditions using  $\text{Xe-133}$  as a tracer isotope. The  $\text{UO}_2$  specimens, containing  $\text{Xe-133}$  formed as a fission product, were heated at constant temperature in a furnace. The diffusion constant was calculated from the fraction of the total xenon that diffused out in a definite time interval.

With fused  $\text{UO}_2$ , i.e. well-crystallized  $\text{UO}_2$  obtained by cooling a melt, the fraction evolved at any temperature was directly proportional to the square root of the time of heating and to the reciprocal of the radius of the crystals. This behavior is that anticipated from the simplest diffusion model. In contrast, with specimens consisting of fragments of pellets of sintered  $\text{UO}_2$ , the fraction evolved was independent of the dimensions of the fragments. Apparently, evolution of the xenon from the ceramic material is a two-stage process. The rate controlling step is an activated diffusion out of the oxide lattice to an interior surface in the porous material. The second step is a rapid permeation through the pore structure to the outside.

The diffusion constant was found to vary greatly among pellets prepared by different techniques. A standard laboratory test is proposed to characterize the gas release property of a given batch. The method consists of representing the pellet as an aggregation of uniform spherical particles, and evaluating a parameter,  $D'$ , equal to  $D/a^2$ , where  $D$  is the diffusion constant in the oxide lattice and " $a$ " is the radius of the sphere. The value so obtained can be used to calculate the fraction of xenon fission gas evolved from a fuel element in an operating reactor over a given time interval.

## 1. INTRODUCTION

The rare-gases, krypton and xenon, are the most abundant elements among the fission products. The combined fission yields of all the stable and long-lived isotopes of these elements is about 25 percent; i.e., 25 atoms formed per 100 atoms of U-235 fissioned. In a long irradiation the yield is even higher because some additional Xe-136 is continuously produced by neutron capture in Xe-135. For example, in irradiations to about 4000 MWD/Tonne, the additional amount so formed raises the combined fission yields to about 29 percent.

The volume, at NTP, of the stable and long-lived rare-gas isotopes formed in the above example, would be greater than the volume of the fuel, and could generate a pressure of several thousand p.s.i. on the fuel sheath - if the sheath were tight-fitting, and if the gas were freely released from the fuel. It is apparent that a knowledge of the rate of gas release from the fuel is of importance in reactor design and fuel fabrication considerations.

The object of the present investigation was to determine the diffusion constant of xenon in various types of  $\text{UO}_2$  fuel material. The general procedure was to irradiate small specimens of  $\text{UO}_2$  in the reactor in order to generate sufficient Xe-133 in them to serve as a tracer. The specimen was then heated at constant temperature in a furnace, and the evolution of the xenon followed by radioactive counting methods. The diffusion constant at a given temperature was calculated from the fraction of the total xenon originally present that was evolved in the period of heating.

## 2. EXPERIMENTAL METHODS

### 2.1 Apparatus

The apparatus used is shown in Figures 1 and 2. It consists of a high temperature furnace in which the  $\text{UO}_2$  sample is placed, and through which helium is passed to sweep out the evolved Xe-133. The xenon is trapped out of the helium flow by means of a charcoal trap cooled with liquid nitrogen.

The furnace element consists of a tungsten wire coil cemented between two alundum crucibles with alundum cement. The assembly is supported by the tungsten wire itself, the ends of which are set into the power leads in the base plate. The sample is placed in a platinum dish which rests on an alundum spacer inside the furnace crucible to bring it near to the centre of the heating zone. The thermocouple, (platinum-platinum with 10 percent rhodium) passes through a hole in the bottom of the crucibles to a point contacting the platinum dish.

The crucible is enclosed in a chamber which is bolted on to the base plate through a flange. An O-ring seal in the flange makes the connection gas-tight. The chamber is made of brass, and is double walled, so that water can be passed through the annular space for cooling. A double quartz window in the top of the chamber permits observation of the furnace contents. The base plate is connected to an oil diffusion and a mechanical vacuum pump.

Inlet and outlet ports for the helium flow are provided through the double wall of the chamber. Before entering, the helium is purified by passing it through a furnace containing calcium metal which is heated to 700°C. The gas train on the outlet side consists of a KOH trap, used to remove fission product halogens, and charcoal traps for removing the xenon. The outlet line diverges into two parallel trains; one carries the helium flow from the furnace chamber, the other from a helium line that bypasses the furnace. A stopcock arrangement permits crossing the two flows into opposite gas trains.

The temperature of the furnace is recorded on a Speedomax recorder, which was modified to serve also as a control on the current input to the furnace, by means of a connection to a motor-driven Variac.

## 2.2 Preparation of the UO<sub>2</sub> Specimens

The UO<sub>2</sub> specimens studied can be classified as follows:

- A. A sample of crystalline UO<sub>2</sub> formed by solidification of a melt. It was supplied by the Norton Co. of Canada Ltd.
- B. Sintered pellets made at the Bureau of Mines laboratories in Ottawa.
- C. Pellets made by a number of different companies on a production basis, for use in reactor loop tests.

A list of all the samples referred to in this report is given in Table III of Section 3.10, along with the source, fabrication method, and properties (as far as these are known).

Usually only small samples of the various oxide pellets were irradiated, to avoid the necessity of remote-control handling. Commonly the specimens were in the range of 20-50 mg; the largest were about 300 mg. They were irradiated in a flux of about  $2 \times 10^{13}$  neutrons/cm.<sup>2</sup>/sec. for a period of from one to ten hours and then set aside for about 3 days to allow short-lived activities to die out. The only radioactive rare-gas isotope remaining in appreciable quantity after this time is Xe-133.

In preliminary work some samples were sealed under vacuum in quartz capsules for irradiation in the reactor. However, no difference was noted between these samples and those merely wrapped in aluminum foil and irradiated in air, so that the latter technique was used subsequently. On the other hand it was found that traces of oxygen present during the heating of the sample in the furnace gave a marked increase in the amount of xenon released. Traces of oxygen in the helium flow had to be removed completely.

## 2.3 Procedure

The irradiated specimen was placed in a platinum dish and the dish inserted in the furnace. The brass water jacket was bolted into position and the chamber evacuated. Helium gas was then passed through at a rate of about 0.5 ml./sec. The furnace was then switched on and brought up to temperature as rapidly as possible (about 10 min. for a temperature of 1400°C.). After 1 hour, the helium flow from the furnace was diverted to the parallel gas train, but a helium flow through the first train was continued by simultaneously switching in the furnace bypass line. The dewar on the first trap was then removed

and the trap warmed to about 250°C. The xenon thus removed was re-collected in the smaller downstream trap, which was taken off the line for counting. This was done by fusing off constrictions in the shoulders of the glass U-tube. At the end of the second hour the procedure was repeated on the parallel line. The experiment thus continued, alternating between the two parallel lines, for a period of 3 to 6 hours. In later work only a single sample was taken off - the total collected in 3 hours.

At the end of the collection period the furnace was cooled and the  $\text{UO}_2$  removed. It was placed in a quartz tube in a separate gas train (not shown) together with a small quantity of potassium pyrosulphate. Helium was passed through the system and the pyrosulphate was melted to dissolve the  $\text{UO}_2$ . The gases released were collected in a charcoal trap in the same manner as that used for the gases evolved on heating.

#### 2.4 Counting the Xenon Specimens

During the course of this work two methods were used to determine the activity of the fission xenon. The earlier method consisted of inserting the trap containing the activity in the well of an ionization chamber. In later work the trap was placed in a fixed geometry over the crystal of a gamma scintillation spectrometer. In both methods only relative counts were made; the activity of the gas evolved on heating was compared with the activity of the gas in the residue. The amount evolved was expressed as the fraction of the total gas originally in the sample.

In most experiments the activity measured was that of the 80 kv. gamma ray of Xe-133. The usual procedure was to allow 3 days for short-lived activities to die out before starting the experiment. However, in some cases the decay period was shortened so that Xe-135 was still a prominent activity in the gas samples. By means of the scintillation spectrometer the amount of each isotope could be determined independently in the same sample. From the spectrometer record, as illustrated in Figure 3, the fraction of the Xe-135 evolved was found to be the same as the fraction of the Xe-133 evolved.

At first sight this appears surprising, for the diffusion experiment based on Xe-135 as the tracer isotope is subject to the error that some xenon is formed from its precursor, I-135, during the course of the experiment. The error would be large if iodine diffused much faster than xenon, because the extra, newly-formed Xe-135 would be added to the small amount that is evolved on heating. In contrast, if iodine diffused more slowly, the error would be small (and in the opposite sense) because the Xe-135 would be added to the amount in the residue, which is normally large compared with the amount evolved on heating. The experiment tends to suggest, therefore, that iodine diffuses at the same rate or more slowly than xenon.

Some attempts were made to determine whether or not xenon and krypton have dissimilar diffusion rates. The krypton isotopes examined were Kr-85 and Kr-88. No significant difference was observed between these and the xenon isotopes.

#### 2.5 Precision of the Experimental Measurements

The probable error of the counting measurements on the tracer gas was approximately  $\pm 1\%$ . The precision of the diffusion experiment as a whole was

less and depended on the nature of the material tested. With the fused material (type A), moderately good reproducibility was achieved, repeated tests indicating a probable error of about  $\pm 5\%$ ; but with the sintered materials types (B and C) the probable error was often as high as  $\pm 20\%$ , especially with low density pellets. This was attributed to a variation in the properties of the material from point to point in the pellet. With careful sampling of the material throughout the pellet the precision was increased appreciably, but still remained much lower than had been hoped.

### 3. RESULTS AND DISCUSSION

For convenience, the results of the diffusion studies are discussed separately for the three classes of  $\text{UO}_2$  specimens listed in Section 2.2.

#### 3.1 Type A, Fused $\text{UO}_2$

With this material the fraction of the total Xe-133 released was small, even at  $1600^\circ\text{C}$ ., the upper working limit of the furnace. Consequently, most of the determinations were made on samples that had been reduced to a very fine powder in order to achieve sufficiently high counting rates in the gas evolved. The original material was a lump consisting of very large crystals. When the material was powdered, each particle could be considered as a fragment of a single crystal. Most work was done on a powder of 200-325 mesh size, equivalent to a particle radius of about 0.0028 cm.

#### 3.1 (a) Variation of the Diffusion Constant with Time and with Powder Radius

The fraction,  $f$ , of the Xe-133 that was evolved from the material at constant temperature was studied as a function of time of heating, of powder radius, and of temperature. As shown in the Appendix to this report, when only a small fraction of the initial amount diffuses out of a spherical particle the fraction evolved should obey an equation,

$$f \approx \frac{6}{a} \sqrt{Dt/\pi} \quad \dots\dots\dots (1)$$

Therefore  $f$  should vary directly as  $1/a$ , where "a" is the radius of the particle and as the square root of the time,  $t$ , (at constant temperature). The data obtained are shown plotted in this way in Figures 4 and 5. The theoretical relations were confirmed within the accuracy of the experiment, and the diffusion constant,  $D$ , was readily determined.

In Figure 5 it will be noted that there is a small deviation from the theoretical relation, in that the backward projection of the straight line to zero time does not go through the origin. The intercept is small, however, and the discrepancy could reasonably be accounted for as resulting from the actual powder particles not being spherical as in the theoretical model.

#### 3.1 (b) Variation of $D$ with Temperature

Values of the diffusion constant at different temperatures are shown in Table I. For an activated diffusion, the diffusion constant is expected to vary with temperature according to an equation of the form,

$$D = D_0 \exp(-E/RT) \quad \dots\dots\dots (2)$$

where  $E$  is the activation energy for diffusion, i.e. the energy barrier crossed as a xenon atom moves from one equilibrium position in the oxide lattice to an equivalent neighboring position. In Figure 6,  $\log D$  is shown plotted against  $1/T$ , and the straight line obtained confirms this general relation. From the data, the constants in the equation are evaluated as:

$$D_0 = 1.5 \times 10^{-8} \text{ cm}^2/\text{sec.}$$

$$E = 46 \text{ kilocalories/mole}$$

### 3.2 Sintered Pellets, Type B

The oxide pellets considered in this section were prepared at the Bureau of Mines laboratories in Ottawa during the course of their experiments to develop a suitable production process (1). Essentially, the method consists of forming a very fine "reactive"  $\text{UO}_2$  powder by precipitation and reduction of ammonium diuranate, followed by cold pressing at high pressure and then sintering in hydrogen at  $1700^\circ\text{C}$ . Details are given in the reference quoted.

It is evident that diffusion from pellets made by compacting and sintering a fine powder will be a much more complicated process than diffusion from single crystals. The process will involve an inter-relation of diffusion in the oxide lattice, possibly diffusion along grain boundaries, and diffusion in capillary channels. A further complication is introduced if the possibility of "trapping" in closed internal voids is considered. It is generally assumed that a rare gas atom cannot pass from a gas phase to a solid phase by diffusion, since the atom cannot be chemisorbed and will not remain on the surface long enough to make the initial diffusion step. Consequently xenon atoms diffusing to a closed void in the oxide would be trapped. The analytical description of the gas release process must therefore take account of the relative probability of a xenon atom diffusing to a closed void and to a channel leading to the surface of the pellet, i.e. the ratio of the "closed" internal surface to the "open" internal surface.

In view of these considerations the diffusion process in sintered pellets was thought to be too complex for exact analysis. An idealized model was therefore sought that would serve as an approximate representation, useful in making calculations and in rendering the results of the diffusion experiments intelligible.

#### 3.2 (a) Variation of $f$ with the Dimensions of the Sintered Pellet

The fraction,  $f$ , of the Xe-133 evolved from sintered material heated at  $1400^\circ\text{C}$ . for 3 hours was studied as a function of the size of the specimens. It was found that there was no appreciable change over the range of radii from 0.002 cm. to 0.2 cm. A powder, produced by grinding and sieving a sintered pellet, evolved no more xenon than the largest pellet fragments tested. This is illustrated in Figure 7. Actually, the fraction evolved appeared somewhat lower, rather than higher, in the case of very fine powders, but it is uncertain whether any significance can be attached to this.

On the basis of this result it appeared reasonable to adopt, as a useful approximation, a diffusion model of the simplest kind; i.e. to regard the sintered material as an aggregation of uniform spherical particles. Diffusion out of the particles would then be the rate-controlling step; permeation through



the aggregate would be relatively rapid. The particles are, of course, not spherical, but the assumption that they are should make only a small difference in the result. The fact that they are not uniform, but have a range of sizes, is probably a more serious defect of the model. It can be partially compensated for if the diffusion "constant" is established empirically on material of a given type, and applied in subsequent calculations only to material of the same type.

Trapping in closed voids can be represented in the model by cavities in the interior of the spheres, but so far this has not been done. It seemed likely that the effect would be small until a substantial fraction of the xenon had diffused out of the sphere. It would then become increasingly important. An estimate of the effect cannot be made until further experimental data has been obtained.

### 3.2 (b) Variation of $f$ with Time of Heating

Using the diffusion model discussed in Section 3.2 (a), above, the dependence of the fraction evolved on the time of heating would be the same as for crystalline material. Accordingly, the values of  $f$  obtained were plotted against the square root of the time of heating, as before. It is seen in the example in Figure 8 that the procedure is not quite satisfactory. The points do fall on a straight line, but the extrapolation to zero time does not go through the origin. The discrepancy is more serious than in the case of the crystalline  $\text{UO}_2$ , noted earlier, and it is doubtful if it can be explained in the same manner.

The height of the  $f$ -intercept of the curve when extrapolated to zero time was found to be related to the total fraction evolved during the heating. It amounts to about 20-30% of the total gas collected in three hours. No satisfactory explanation of the anomaly has been found and a special study of the question is planned.

### 3.2 (c) Determination of a Special Diffusion Constant

From the value of  $f$  determined on sintered material, it is not possible to evaluate the diffusion constant inside the hypothetical spheres composing the aggregate, because the radius,  $a$ , of the spheres is not known. However, it is possible to determine a single value for the combined constants  $D/a^2$ . This constant is henceforth written  $D'$ , following a notation used by Cubicciotti (2) in a somewhat similar case.

In determining the value of this constant from equation 1, a standard time of 3 hours was used, and a standard temperature of  $1400^\circ\text{C}$ . For reasons given later it seemed better to subtract the value of the anomalous intercept from the 3 hour total, and to ignore it in subsequent calculations.

### 3.2 (d) Variation of the Diffusion Constant with the Density of the Sintered Pellet

The constant  $D'$ , since it depends on the parameter " $a$ ", can be expected to vary with the properties of the sintered material - chiefly the grain size and the relative proportions of open and closed porosity. However, for a given method of fabrication it seemed likely that both these properties would be related to the density of the sintered oxide. In Figure 9 values of  $D'$  are shown plotted against density, for pellets prepared by the standard Bureau of Mines technique.

It is seen that the diffusion constant is independent of density up to about 10 g./ml. and then falls off steeply. However, some values of  $D'$  obtained with pellets prepared by other methods are also shown in Figure 9, and they do not fall on the curve. This point is discussed in Section 3.3, below.

Another method of considering the data is to assume that the diffusion constant in sintered material is the same as in crystalline material. Then the values of " $a$ " can be calculated. The results are shown plotted in Figure 10. For the Bureau of Mines specimens the values obtained are in agreement, at least as to order of magnitude, with the observed grain sizes observed microscopically; but with material from some other sources the  $a$ -values are larger than the apparent grain size.

There is some doubt as to whether it is possible to use the approximate diffusion model at very high pellet densities. It may well be that it becomes invalid as the theoretical maximum density is approached. The statement made in Section 3.2 (a) about the independence of the fraction evolved with respect to the dimensions of the sinter pellet would then not apply. With Bureau of Mines material it appears to be valid at least up to a density of about 10.5 g./ml.

### 3.2 (e) Variation with Temperature

The variation of the diffusion constant with temperature in low density Bureau of Mines pellets was studied and the data obtained are given in Table II. For the purpose of determining the activation energy the special constant  $D'$  can be used quite as well as the true diffusion constant. Figure 11 shows a plot of  $\log D'$  vs.  $1/T$  for some of the samples examined. As nearly as can be judged, the slope of the curves, and hence the activation energy, is the same as for fused  $UO_2$ .

### 3.3 Sintered Pellets from Other Sources, Type C

Only a few tests have been made on  $UO_2$  sintered pellets obtained from sources other than the Bureau of Mines, and they are grouped together in this section. The pellets obtained from the Canadian General Electric Co. were samples from a batch made for fuel testing in the NRX reactor. They were made by a process developed at A.E.C.L. and the Bureau of Mines. However, the details of the fabrication process and sintering treatment were not precisely the same, for the pellets were made on a production basis rather than an experimental one. The process used by the Westinghouse Atomic Power Development and the Battelle Memorial Institute differs considerably from the A.E.C.L. method, both in the preparation of the oxide powder and in the sintering treatment. For details, the references should be consulted.

It was found that pellets from these sources had  $D'$  values that were quite different from those obtained on Bureau of Mines pellets of the same density. This is illustrated in Table III, where the  $D'$  values of pellets of similar density but from different sources can be compared.

The variation is not unexpected. The constant  $D'$  depends upon the value of " $a$ ", and this parameter is not directly linked with the density. In a sense it is a measure of the mean rectilinear distance that a xenon atom diffuses to reach a channel that is part of the inter-connected pore structure. This depends upon the radius of the grains and the dimensions of the channels,

and these variables are only indirectly associated with the density.

In view of these results it is seen that the relation shown in Figure 9 is valid only for pellets made in a particular way. The constant  $D'$ , must be evaluated separately for each process by which the pellets are made. Since it appears to be difficult to obtain a highly uniform type of material in successive batches, even when the same fabrication process is used, it would appear to be better to establish  $D'$  values by routine testing of each batch of pellets processed.

#### 4. Application of the Results in Reactor Fuel Calculations

The model discussed in the foregoing sections is sufficiently simple that it can be used to calculate the rate of diffusion of fission xenon from a fuel element during irradiation in a reactor. The appropriate equations are given in the Appendix and in CRDC-721.

In making such calculations it must be remembered that the times, dimensions and heating conditions in the laboratory experiments are so far removed from those applying to reactor fuel elements that the extrapolation is not very well justified. This is particularly so in dealing with fuel pellets larger than about 1/4 in. diameter. There is a need for diffusion experiments with pellets of larger diameter than those that have been used so far.

The anomaly in the time dependence, discussed in Section 3.2 (b) should not cause much error in such calculations. The amount of xenon formed during irradiation can be analyzed into differential elements,  $R dt$ , where  $R$  is the production rate. Each element,  $R dt$ , diffuses out independently of the concentration of xenon present at any point. Hence, the amount of each such element diffusing out in time,  $t$ , is  $R \cdot f(t) dt$ , where the function  $f$  has the same meaning as in equation 1, i.e. the fraction of any initial amount that has diffused out at time,  $t$ . The total amount of gas diffusing out is the sum of these elements, or

$$R \int_0^t f(t) dt.$$

The amount represented by the height of the anomalous intercept at zero time is small compared with the amount evolved in a few hours; for an irradiation of several days, its contribution to the total gas release is negligible. Hence, over most of the interval of integration the variable  $t$  is so large that the intercept can be neglected. It will affect appreciably only those elements formed in the last few hours of the irradiation.

A more disturbing consideration would be the probability that the diffusion geometry changes during the period of irradiation, due to grain growth, and to the closing of some of the open porosity. This will be especially likely to happen at temperatures above about 1700°C. when sintering becomes appreciable.

Nevertheless, calculations of the kind indicated above have been made in reactor fuel testing experiments, and are discussed in detail in the report CRDC-721.

APPENDIXMathematical Derivations1. The Laboratory Experiment

For the laboratory experiment the diffusion model is taken as a sphere, of radius,  $a$ , with an initially uniform concentration of xenon. The concentration of xenon at the surface is taken as zero for all time. Then the fraction,  $f$ , that has diffused out in time,  $t$ , at a given temperature, is given by

$$f = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp.(-n^2 \pi^2 Dt/a^2) \quad \dots\dots\dots(1)$$

This result is well known; it is given, for example by Barrer (7). However, a note on its numerical use seems necessary.

When  $Dt/a^2$  is  $\geq 1$ , (or what is equivalent, when  $f \geq 0.77$ ), the first term in the series is a good approximation; i.e.,

$$f = 1 - \frac{6}{\pi^2} \exp.(-\pi^2 Dt/a^2), \quad \dots\dots\dots(2)$$

When  $\pi^2 Dt/a^2$  becomes  $< 1$  ( $f < 0.77$ ), this approximation rapidly becomes invalid. In this case, a very good approximation is obtained (\*) by noting that for small  $x$  the sum

$$1 + 2 \sum_{n=1}^{\infty} e^{-n^2 x} \equiv \sum_{n=-\infty}^{+\infty} e^{-n^2 x}$$

is essentially the integral,

$$\int_{-\infty}^{+\infty} e^{-xu^2} du = \sqrt{\frac{\pi}{x}}$$

Thus, 
$$\sum_{n=1}^{\infty} e^{-n^2 x} \approx \frac{1}{2} \left( \sqrt{\frac{\pi}{x}} - 1 \right)$$

Now, integrating both sides with respect to  $x$  from 0 to  $K$  gives

$$\sum_{n=1}^{\infty} \left( \frac{1 - e^{-n^2 K}}{n^2} \right) \approx \sqrt{\pi K} - \frac{K}{2}$$

\* We are indebted to Dr. J.M. Kennedy for this derivation.

from which,

$$1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp.(-n^2 K) \approx \frac{6}{\pi^2} \left( \sqrt{\pi K} - \frac{K}{2} \right)$$

Substituting  $K = \pi^2 Dt/a^2$ ,

$$f = \frac{6}{a} \sqrt{\frac{Dt}{\pi}} - \frac{3}{a^2} Dt \left[ \frac{\pi^2 Dt}{a^2} \leq 1 \right] \dots\dots\dots(3)$$

The second term on the right is negligible for values of  $\pi^2 Dt/a^2$  up to about 0.01, ( $f = 0.105$ ). It was dropped in the discussion in Section 3.1 (a).

## 2. Application to the Reactor Condition

For diffusion out of reactor fuel during irradiation, the following assumptions may be made. Xenon is generated in the fuel at a constant rate,  $R$ . The concentration at time, zero, is zero. The concentration at the surface of the sphere is zero for all time. This is equivalent to the assumption that there is no back migration of the xenon into the solid from the gas phase.

From the considerations in Section 4 it is apparent that the fraction,  $F$ , of the total amount formed to time,  $t$ , that has diffused out at time,  $t$ , is

$$F = \frac{\int_0^t R f dt}{Rt} \dots\dots\dots(4)$$

This gives, substituting  $f$  from equation 1,

$$F = 1 - \frac{6}{90} \frac{a^2}{Dt} + \frac{6}{\pi^4} \frac{a^2}{Dt} \sum_{n=1}^{\infty} \frac{1}{n^4} \exp.(-n^2 \pi^2 Dt/a^2) \dots\dots\dots(5)$$

Exactly the same result is obtained, more laboriously, if one solves the appropriate non-homogeneous partial differential equation with the prescribed boundary conditions, as indicated in CRDC-721 (1).

However, for numerical use it is more convenient to substitute into equation 4 the closed form approximations of  $f$ , equations 2 and 3. Thus, when  $\pi^2 Dt/a^2 \leq 1$ , ( $t \leq a^2/\pi^2 D$ ), all the differential elements,  $Rdt$ , obey equation 3, so that

$$F = \frac{\int_0^t R f(\text{equ.3}) dt}{Rt} = \frac{4}{3} \sqrt{Dt/\pi} a^2 - 3 Dt/2a^2 \dots\dots\dots(6)$$

When  $t$  is greater than  $a^2/\pi^2 D$ , a fraction,  $\frac{t - a^2/\pi^2 D}{t} = 1 - a^2/\pi^2 Dt$ , of the elements obey equation 2, and a fraction,  $\frac{a^2/\pi^2 D}{t} = a^2/\pi^2 Dt$ , obey equation 3.

So that (\*)

$$\begin{aligned}
 F &= \frac{a^2}{\pi^2 Dt} \cdot \frac{\int_0^{\frac{a^2}{\pi^2 D}} R f(\text{equ.3}) dt}{Rt} + \left(1 - \frac{a^2}{\pi^2 Dt}\right) \cdot \frac{\int_0^t R f(\text{equ.2}) dt}{Rt} \\
 &= \frac{0.57 a^2}{\pi^2 Dt} + 1 - \frac{a^2}{\pi^2 Dt} + \frac{6 a^2 \exp.(-\pi^2 Dt/a^2)}{\pi^4 Dt} - \frac{6 a^2}{\pi^4 Dt} + \text{negligible second order terms} \\
 &\quad \dots\dots\dots(7)
 \end{aligned}$$

It is to be noted that the experimentally determined constant,  $D'$ , ( $=D/a^2$ ), can be employed directly to evaluate equations 5, 6 and 7.

\* This derivation is written incorrectly in CRDC-721. The resulting error is negligible as it involves only the final term in equation 7; i.e.,

$$\frac{6 e^{-1} a^2}{\pi^4 Dt} \quad \text{instead of} \quad \frac{6 a^2}{\pi^4 Dt} .$$

TABLE IDiffusion Constants for Fused UO<sub>2</sub>

<u>Radius of Particles (cm.)</u>	<u>Temp. (Degrees C.)</u>	<u>Per Cent Xe Diffused Out in 3 Hours</u>	<u>D (per cm<sup>2</sup>/sec.)</u>
0.0028	1,000	0.20	$2.3 \times 10^{-16}$
0.0028	1,100	0.40	$9.3 \times 10^{-16}$
0.0028	1,200	0.75	$3.25 \times 10^{-15}$
0.0028	1,400	2.1	$2.6 \times 10^{-14}$
0.0028	1,500	2.6	$3.9 \times 10^{-14}$

TABLE II

Diffusion Constants of Xenon in Low Density Pellets of Sintered  $\text{UO}_2$ 

<u>Sample Identification</u>	<u>Density</u>	<u>Temp. (degrees C.)</u>	<u>Per Cent Xenon Evolved in 3 hrs.</u>	<u><math>D/a^2</math> (cm<sup>-1</sup>)</u>
M.Br. # IV	9.35	800	1.1	$1.0 \times 10^{-9}$
			6.2	$3.4 \times 10^{-8}$
		1000	4.5	$1.7 \times 10^{-8}$
		1200	22	$4.4 \times 10^{-7}$
			23	$5.0 \times 10^{-7}$
		1400	31	$9.4 \times 10^{-7}$
			33	$1.0 \times 10^{-6}$
M.Br. (X-2-f)	approx. 9.4	800	0.8	$5.1 \times 10^{-10}$
		1000	4.0	$1.3 \times 10^{-8}$
			5.0	$2.0 \times 10^{-8}$
			1.3	$1.4 \times 10^{-9}$
		1200	7.5	$4.5 \times 10^{-8}$
		1400	23	$4.8 \times 10^{-7}$
			15	$2.0 \times 10^{-7}$
			27	$7.0 \times 10^{-7}$



TABLE III

Diffusion Data for Various Types of  $\text{UO}_2$  Sintered Pellets at  $1400^\circ\text{C}$ .

Identif. No. This Report	Source	Identif. by Supplier, or Reactor Use	Fabrication Method	Density (gm/ml)	Per Cent Xe-133 Evolved in 3 hr.		Mean Value of $D'$ ( $1400^\circ\text{C}$ . ( $\text{sec}^{-1}$ )	Radius, $a$ , of Sphere (microns)*
					Range of Values (uncorr.)	Mean. (Corr. for anomalous intercept)		
1.	M.Br.	No. 2	Standard Mines Branch Method, Ref.(1), [1/2 hr. at sintering temp., $1700^\circ\text{C}$ ]	8.0	30 - 35	26	$6.2 \times 10^{-7}$	1.8
2.	M.Br.	No. 10		8.3	23	18	$3.0 \times 10^{-7}$	2.6
3.	M.Br.	No. 14		8.8	26	21	$4.0 \times 10^{-7}$	2.3
4.	Chalk River Fuel Dev.	T'-1		9.03	23	18	$3.0 \times 10^{-7}$	2.6
5.	M.Br.	IV		9.35	25 - 35	25	$6.0 \times 10^{-7}$	1.8
6.	M.Br.	X-2-f Loop Test		9.3-9.5	15 - 27	20	$3.5 \times 10^{-7}$	2.5
7.	Chalk River Fuel Dev.	T'-10	Same, except 8 hr. sintering.	9.53	10	8	$5.5 \times 10^{-8}$	6.2
8.	M.Br.	P-43-26	Standard Mines Branch Method.	9.85	16 - 23	16	$2.0 \times 10^{-7}$	2.9
9.	M.Br.	No. 65		10.05	10 - 17	11	$1.0 \times 10^{-7}$	4.6
10.	M.Br.	Pellet Rod MK-I		10.15	17	13	$1.4 \times 10^{-7}$	3.9
11.	M.Br.	Pellet Rod MK-I		10.25	7.5	6	$3.0 \times 10^{-8}$	8.4
12.	M.Br.	-		10.40	2.5	2	$3.5 \times 10^{-9}$	24
13.	M.Br.	L - 4		10.50	2 - 2.5	1.8	$3.0 \times 10^{-9}$	26
14.	M.Br.	L - 12	Same, except 2 hr. sintering.	10.55	0.6 - 1.2	0.8	$5.0 \times 10^{-10}$	63
15.	M.Br.	L - 18	Same, except 10 hr. sintering.	10.55	0.75	0.6	$3.0 \times 10^{-10}$	84

(Continued on next page)

(Continued)

TABLE III

Diffusion Data for Various Types of UO<sub>2</sub> Sintered Pellets at 1400°C.

Identif. No. This Report	Source	Identif. by Supplier, or Reactor Use	Fabrication Method	Density (gm/ml)	Per Cent Xe-133 Evolved in 3 hr.		Mean Value of D' (1400°C.) (sec <sup>-1</sup> )	Radius, a, of Sphere (microns)
					Range of Values (uncorr.)	Mean. (Corr. for anomalous intercept)		
16.	M.Br.	No. 82	Standard Mines Branch Method.	10.5	2 - 4	2.2	$4 \times 10^{-9}$	23
17.	M.Br.	High Density No. 13		10.5	3 - 6	3.0	$8 \times 10^{-9}$	16
18.	M.Br.	High Density No. 244		10.55	1.8 - 3.0	2.0	$3.5 \times 10^{-9}$	25
19.	M.Br.	High Density No. 29		10.60	0.6 - 1.7	0.8	$5 \times 10^{-10}$	63
20.	M.Br.	Slug No. 2	Modified Mines Branch.	10.63	0.4 - 1.3	0.6	$3 \times 10^{-10}$	84
21.	C.G.E.	X-2-g Loop Test		9.8	2.5	2.0	$3.5 \times 10^{-9}$	26
22.	C.G.E.	X-2-g Loop Test		10.2	1.3	1.0	$8 \times 10^{-10}$	51
23.	W.A.P.D.	Regular Production		10.3	0.4 - 1.0	0.5	$2 \times 10^{-10}$	100
24.	Battelle	X-2-f Loop Test	See Ref. (5).	9.3-9.5	0.8 - 1.3	0.8	$5 \times 10^{-10}$	63

\* Calculated from  $D' = D/a^2$ , where D at 1400°C. is taken as  $2.1 \times 10^{-14}$ , as found from Figure 6.

\*\* Density quoted is that determined by the authors. It differs from that given by Mines Branch for the samples 17, 18 and 19.

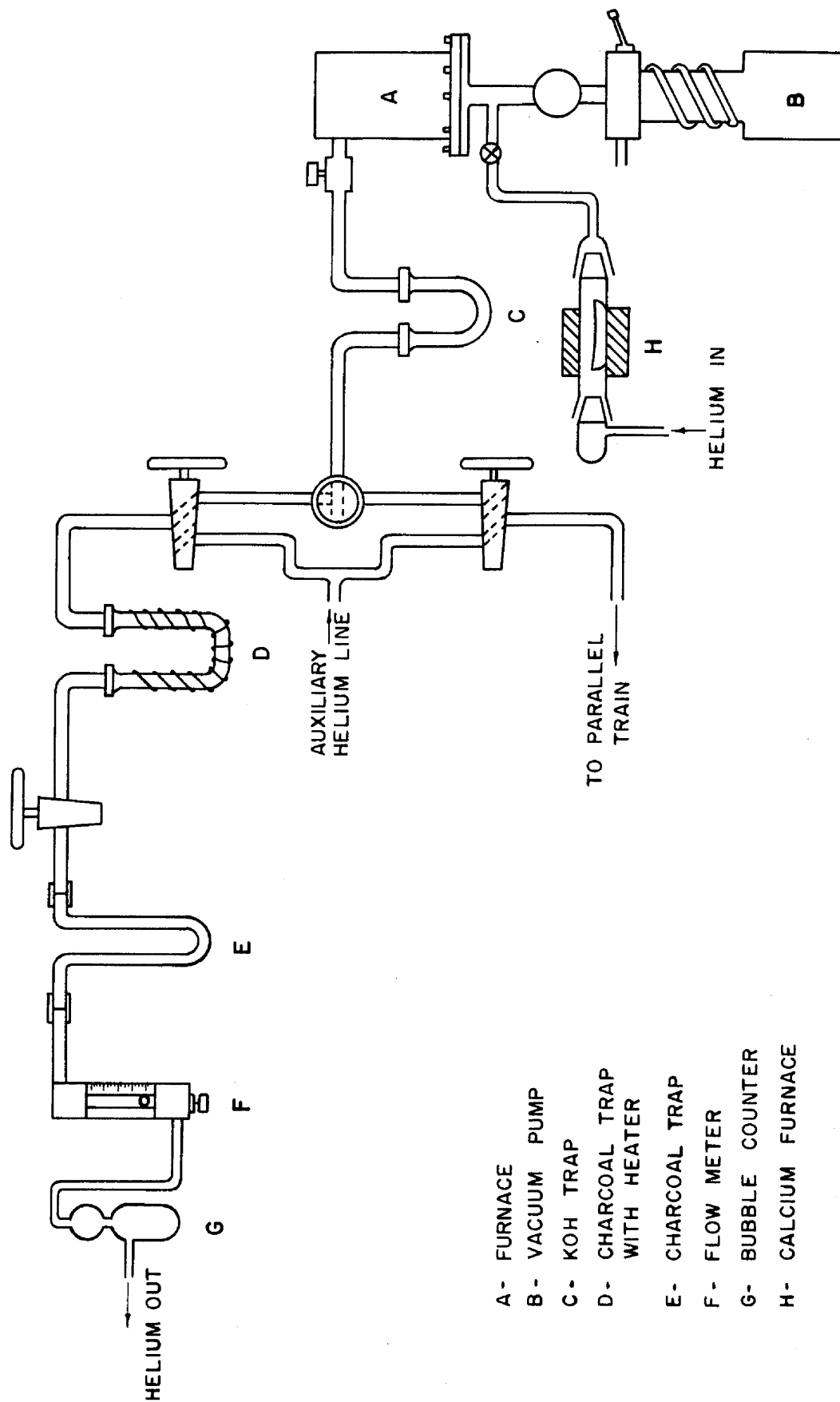


FIG. 1

## THE XENON DIFFUSION APPARATUS

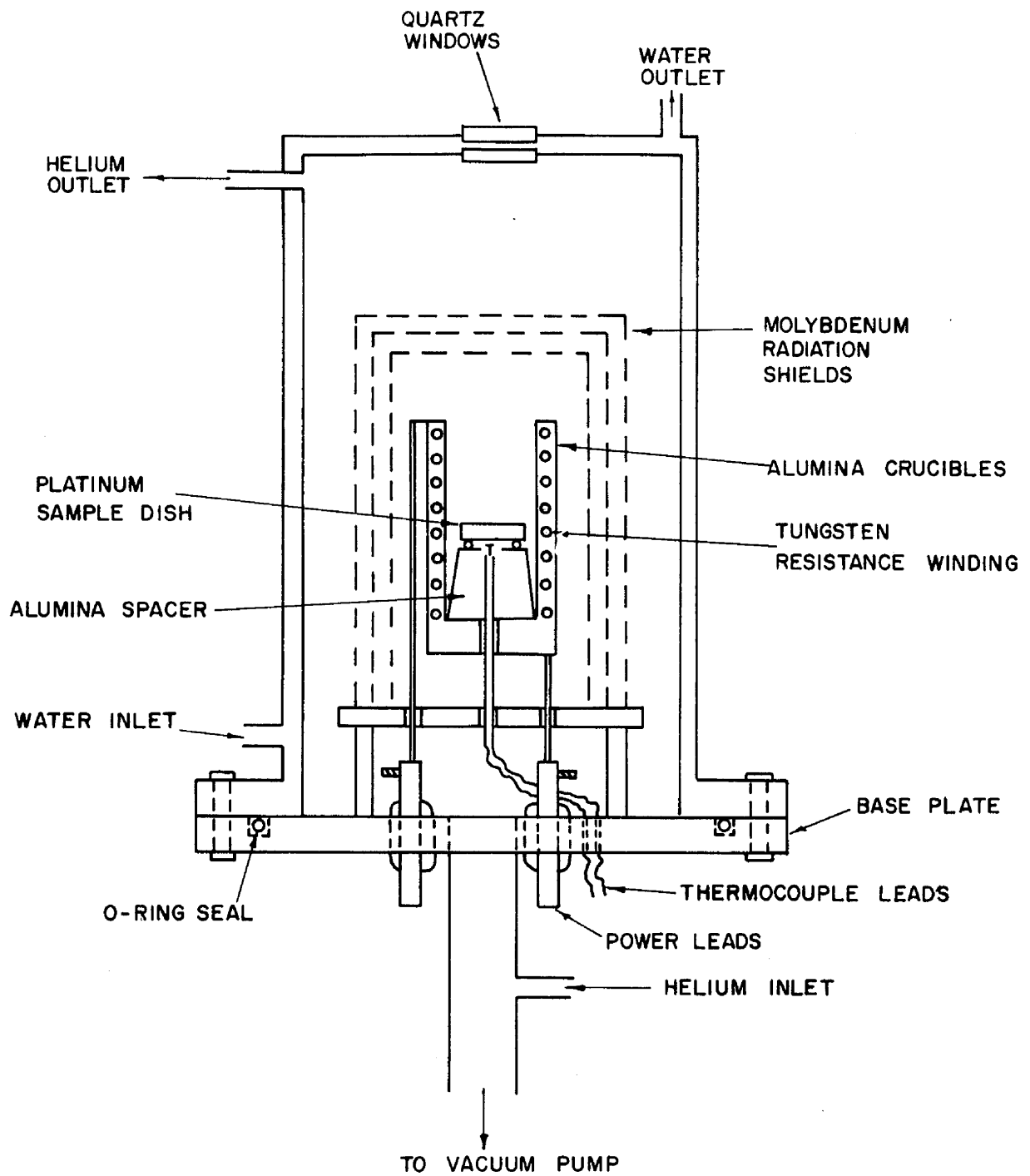


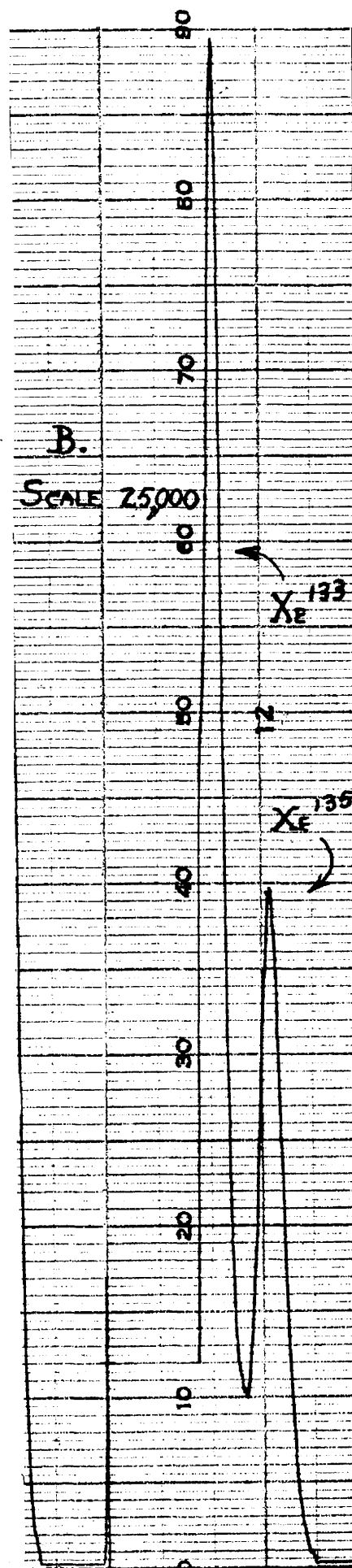
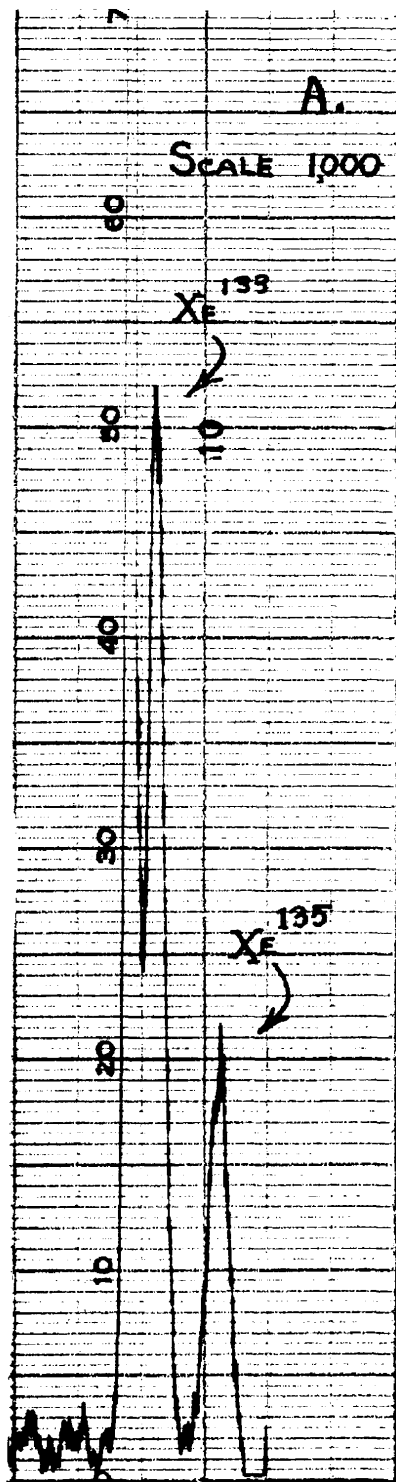
FIG. 2

## THE FURNACE OF THE DIFFUSION APPARATUS

FIG. 3. GAMMA SPECTROMETER RECORD  
OF FISSION XENON.

A. IN GAS EVOLVED ON HEATING  $\text{UO}_2$ .

B. IN GAS RELEASED ON DISSOLVING  
 $\text{UO}_2$  RESIDUE.



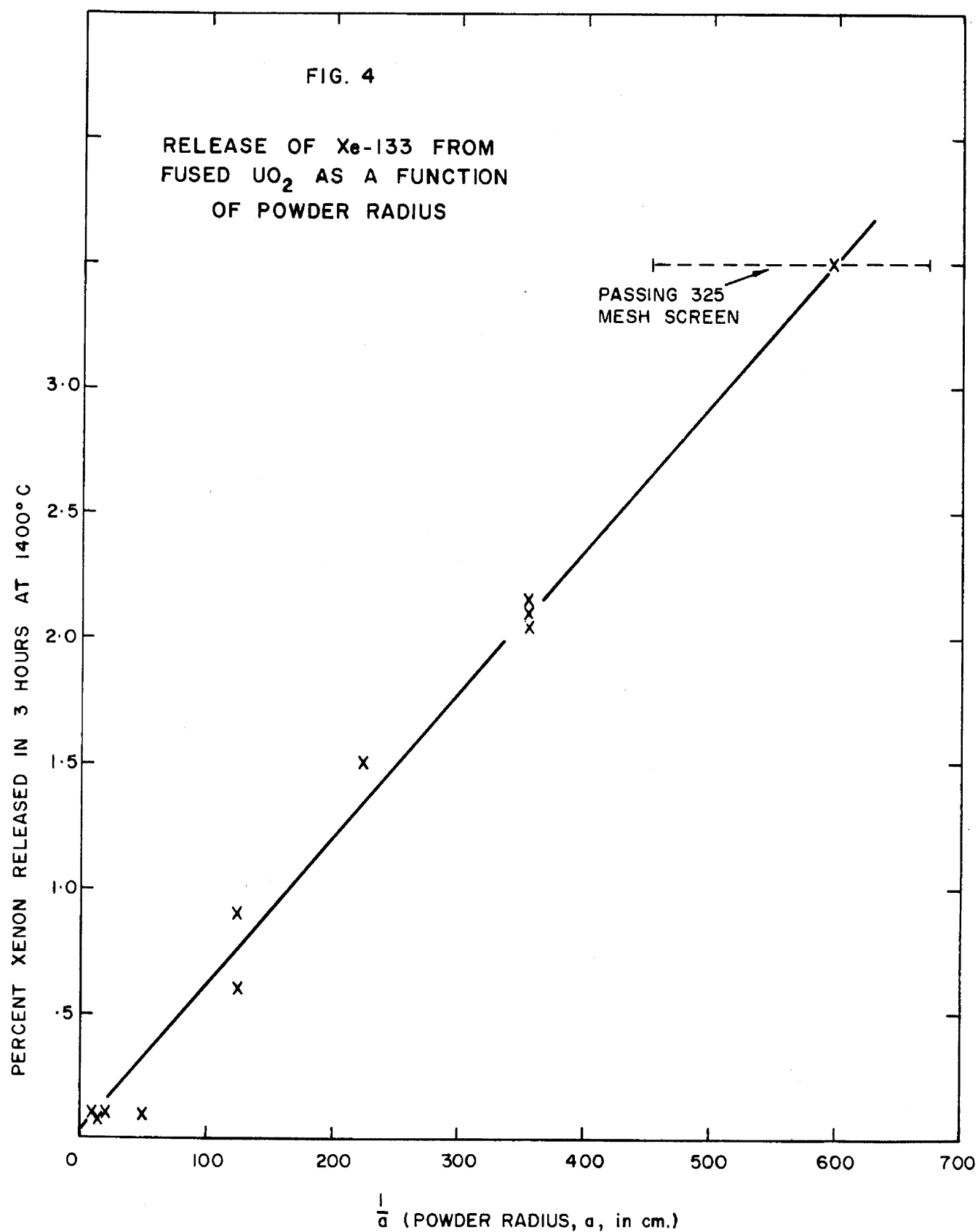


FIG. 5

RELEASE OF Xe-133 FROM  
FUSED  $\text{UO}_2$  (POWDER RADIUS, .0028 cm.)  
AS A FUNCTION OF TIME  
OF HEATING AT  $1400^\circ\text{C}$

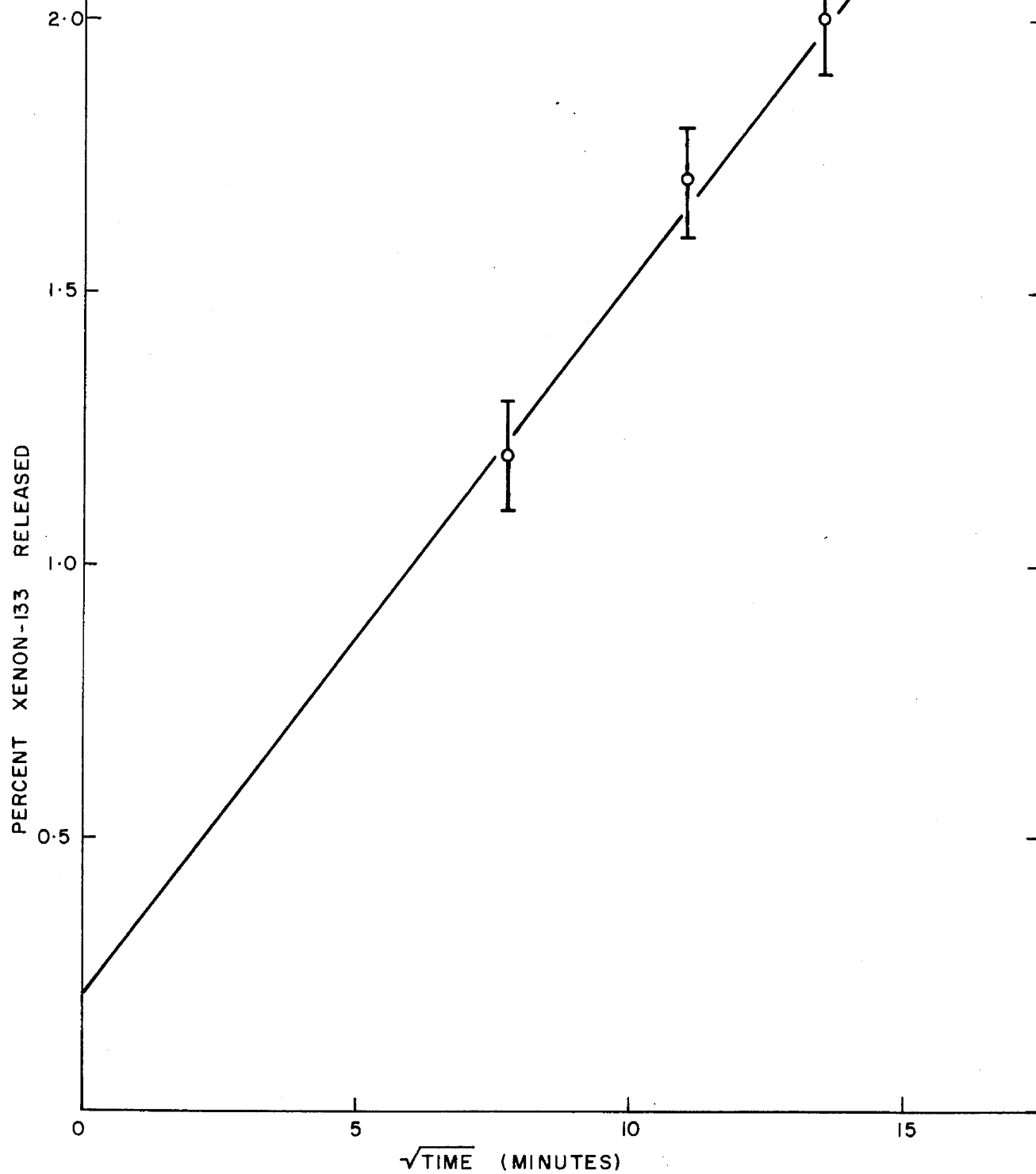
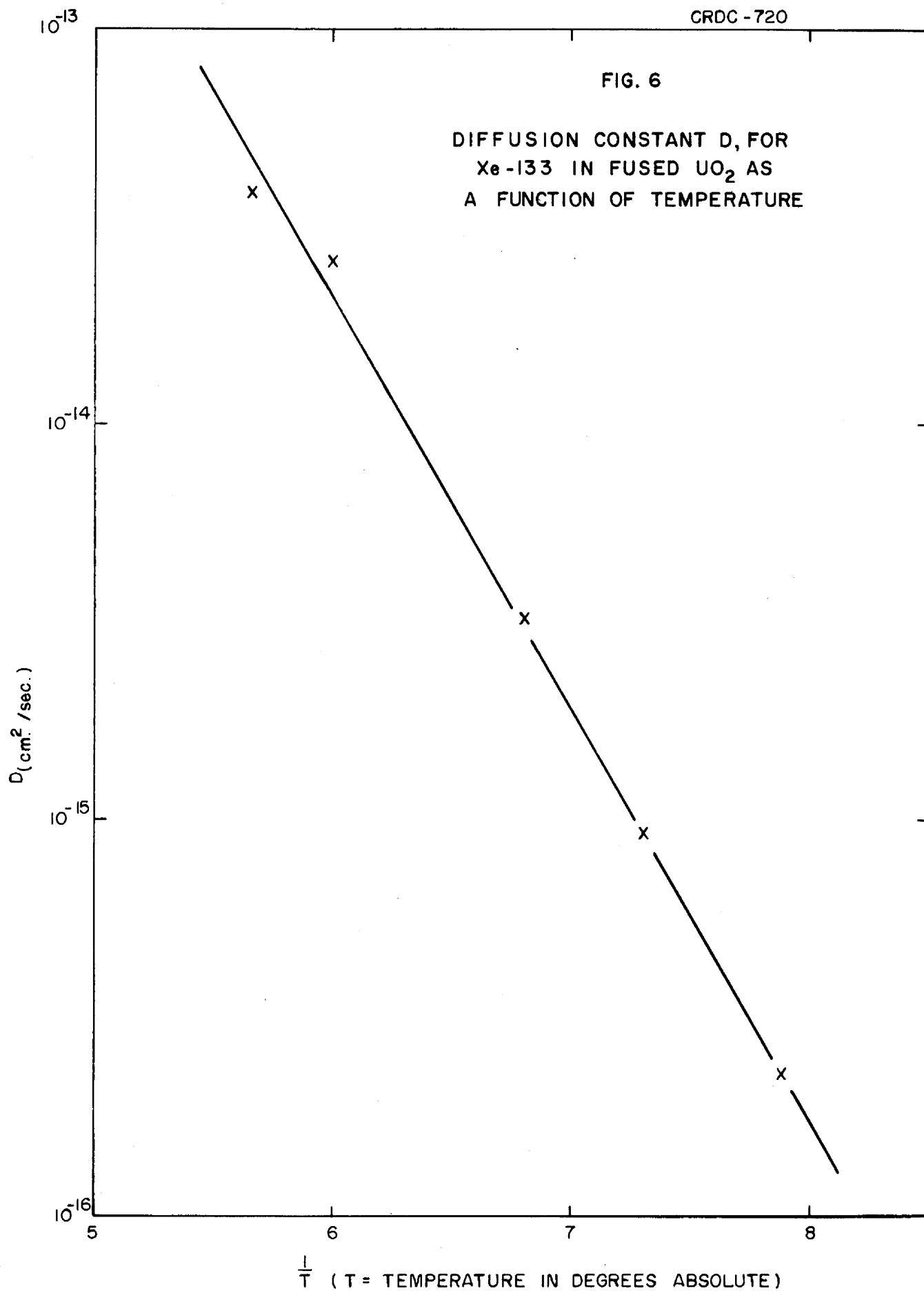


FIG. 6

DIFFUSION CONSTANT D, FOR  
Xe-133 IN FUSED  $\text{UO}_2$  AS  
A FUNCTION OF TEMPERATURE





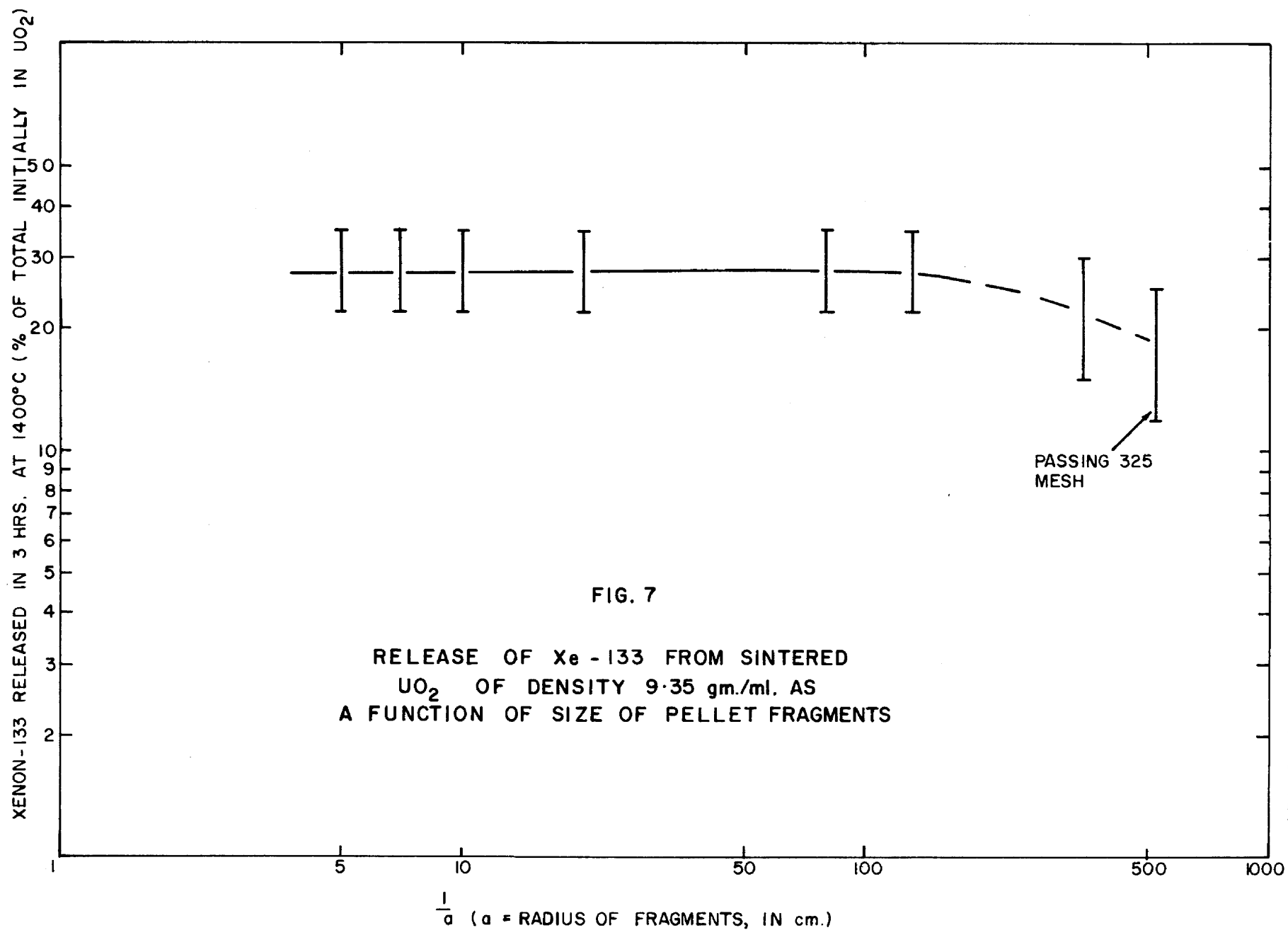
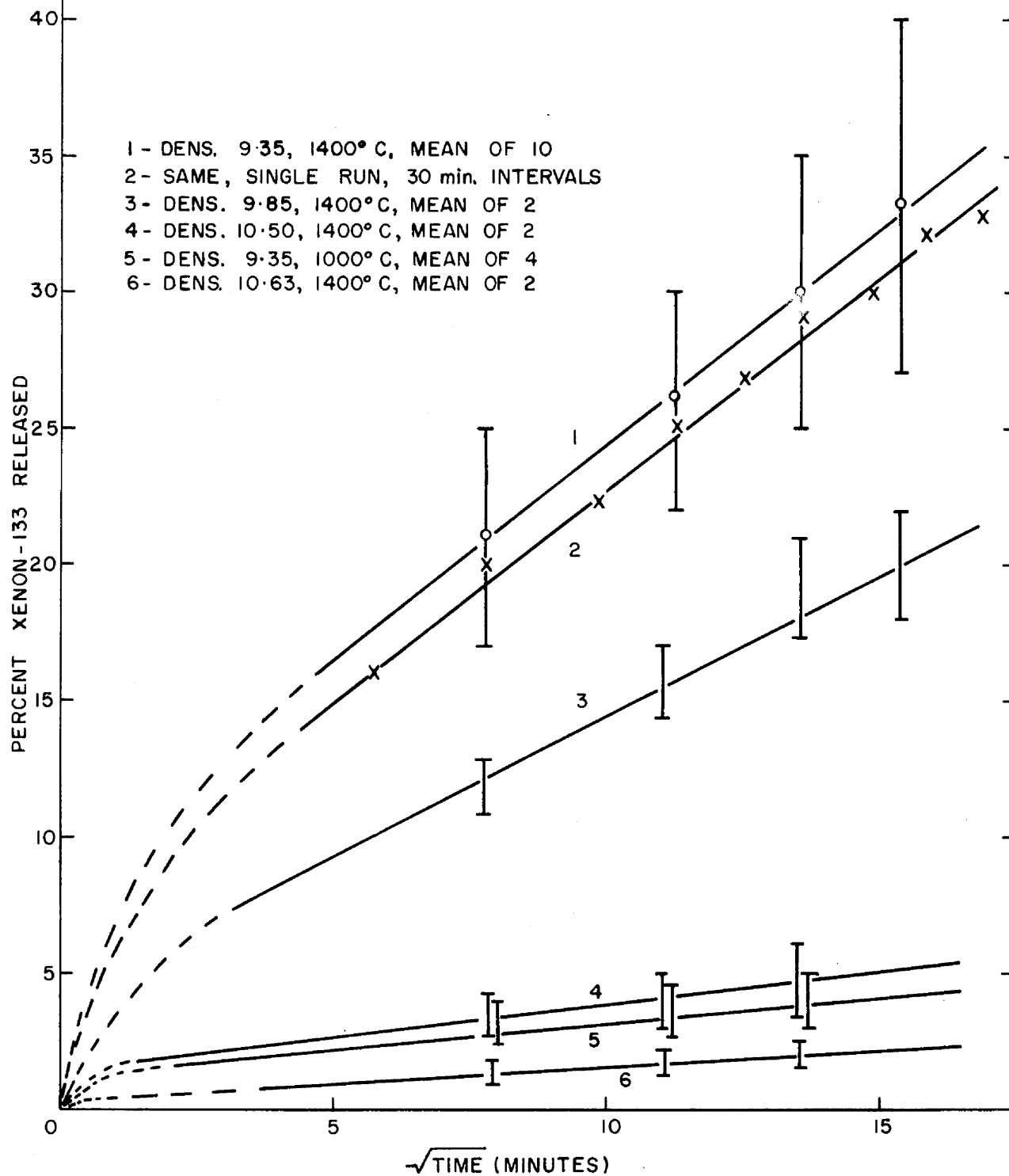
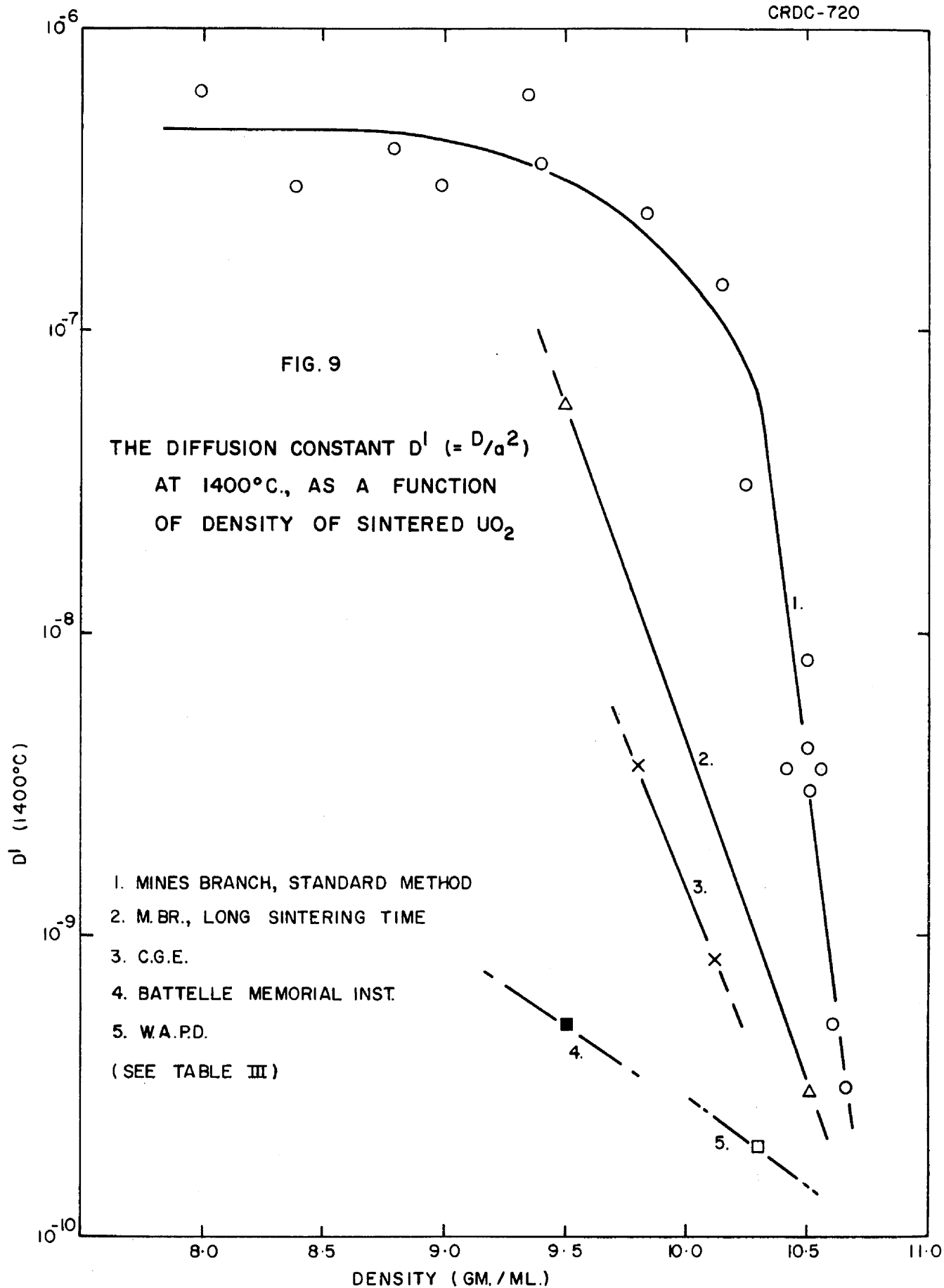


FIG. 8

RELEASE OF Xe-133 FROM SINTERED  $\text{UO}_2$   
AS A FUNCTION OF TIME OF HEATING AT  $1400^\circ\text{C}$ .





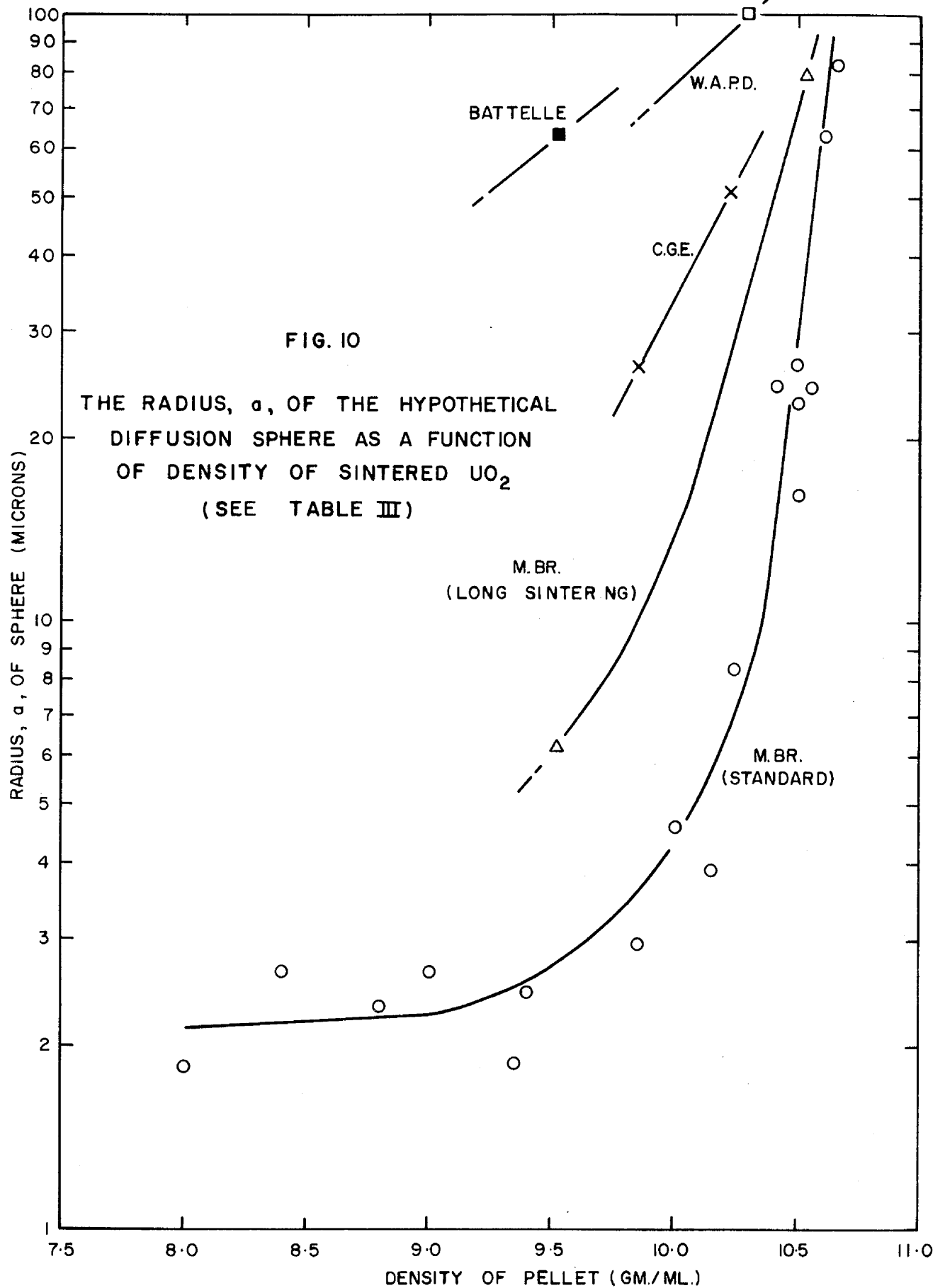
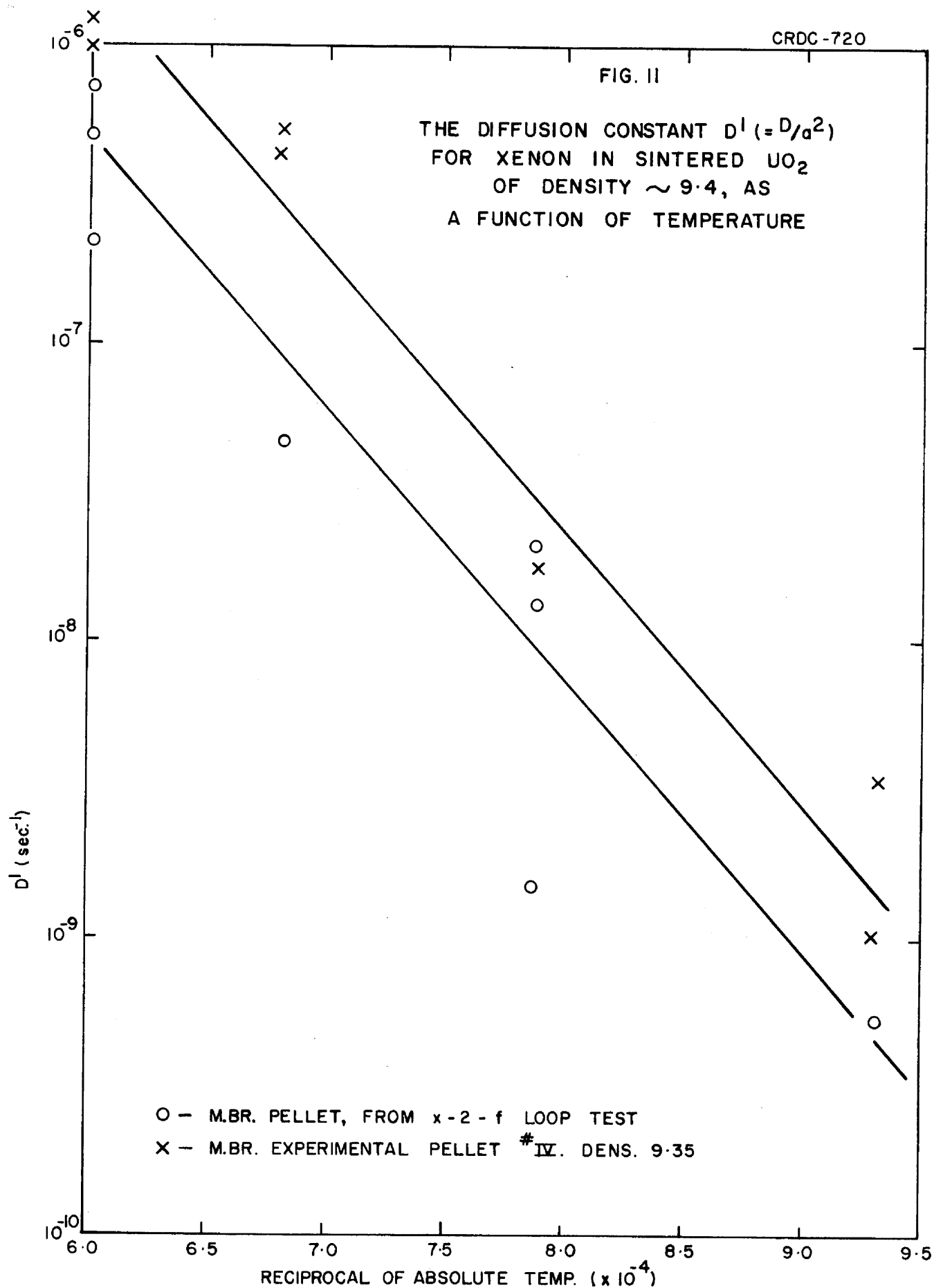


FIG. 11

THE DIFFUSION CONSTANT  $D^I (= D/a^2)$   
FOR XENON IN SINTERED  $UO_2$   
OF DENSITY  $\sim 9.4$ , AS  
A FUNCTION OF TEMPERATURE



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