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DIFFUSION OF FISSION FRAGMENTS FROM URANIUM IMPREGNATED GRAPHITE

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WRITTEN BY:
C. A. SMITH
C. T. YOUNG

WORK DONE BY:
J. D. McCLELLAND
C. A. SMITH
D. R. WESTERVELT
C. T. YOUNG

W. E. PARKINS – GROUP LEADER – EXPERIMENTAL PHYSICS

H. PEARLMAN – GROUP LEADER – CHEMISTRY

S. SIEGEL – ASSOCIATE TECHNICAL DIRECTOR

C. STARR – TECHNICAL DIRECTOR

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ABSTRACT

Measurements have been made to establish the rates of diffusion processes in graphite. Pore diffusion has been determined from flow rates of various gases through graphite samples. The gross diffusion of fission fragments from neutron-irradiated, uranium impregnated graphite has been measured at various temperatures up to 1760° C. In addition, the diffusion of the particular fragments, Ba^{140} and Sr^{89} were measured. Activation energies for the fission fragment diffusion were determined. The fraction of fission fragments penetrating the graphite crystals as a result of the neutron irradiation was measured as a function of the density of uranium impregnation. By leaching the graphite subsequent to irradiation, the uranium fuel particles were removed and diffusion studies were carried out on the residue of the graphite crystals containing fission fragments. Data obtained in this way made it possible to separate the effect of diffusion from the fuel particles and from the graphite crystals as measured in the earlier gross diffusion studies

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I. INTRODUCTION

A study of diffusion processes in uranium impregnated graphite has been undertaken to answer various questions arising in instances where this material is used in reactor construction. Radiation damage effects are known to be produced as a result of the high energy neutron flux in such a reactor. In addition, if uranium fuel particles are located in the close vicinity of the graphite crystals, radiation damage rates will be increased due to the effect of fission fragments. The present studies have given some estimate of the amount of fission fragment penetration within the graphite crystals which might be expected during operation of an actual reactor utilizing uranium impregnated graphite. Another question pertinent to the use of such a reactor is the ability of the fission fragments to diffuse out of the graphite-uranium matrix. The effect of this on an operating reactor depends upon the type of construction employed. In a unit where the fission fragments can diffuse into the coolant stream and be carried off, several points must be considered. The radioactivity level of the coolant stream would be increased by this process. The fission fragments acting as reactor poisons would be removed to a degree, depending upon the frequency of coolant recirculation, if recirculation is employed at all. Also, if the diffusion to the coolant stream is sufficiently rapid, the fission fragments releasing delayed neutrons will be swept from the active core and consequently produce a pronounced effect upon the reactor control. It is expected that such effects can only be significant in uranium-impregnated reactors operating at relatively high temperatures. Such units have been suggested[1] and have many attractive features from the standpoint of power production.

If we could examine the structure of uranium-impregnated AGOT type graphite in detail we would expect to find an agglomeration of irregular particles, each having a "deck of cards" type of structure with each layer (or crystallite) of the "stack" composed of several planes of atoms having a well ordered arrangement. Ref. 2 gives the height of the "stack" to be of the order of 150 Å and each layer to be about 50 Å thick. In directions parallel to the planes of the crystallites the stack is approximately 1000 Å in extent. Voids or pores amounting to 25 to 30 per cent of the total volume are distributed through the mass of graphite particles. For AGOT type graphites the average size of the pores is about 5 microns. Many pores are much

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larger than 5 microns and may even appear as cracks and pits in the surface. In the experiments described in this report, the pores are partially filled with uranium oxide particles having average dimensions of the order of 1 micron.[3]

Graphite is impregnated[3] with uranium by forcing an aqueous uranyl nitrate solution into the graphite under pressure. The uranyl nitrate is converted to UO_3 by heating gradually to 250° C. The UO_3 is then converted to UO_2 by heating to 900° C in an inert atmosphere. If heating is continued to higher temperatures, the carbide UC_2 is eventually formed. AGOT types can be impregnated with as much as perhaps 0.6 gram of uranium per cm^3 of graphite. A reactor might require about 0.01 gram per cm^3.

When fission occurs, the uranium atoms divide into energetic fragments, 98 per cent of which have masses between 84 and 150,[16] and which have energies from 60 to 100 Mev. Such particles should have ranges of about 10 to 17 microns in graphite[4] and about 5 microns in uranium oxide. It appears that a large fraction of the fission fragments will have sufficient energy to leave the uranium oxide and enter the graphite to depths up to 17 microns. The fraction of fission fragments which enter the graphite might be expected to vary with the density of impregnation.

If the impregnated graphite is at a high temperature we might expect to observe three distinct processes of diffusion: diffusion of fission fragments to the surface of the fuel particles (uranium oxide or uranium carbide); diffusion of fission fragments from the graphite particles; and gaseous diffusion through the pores following evaporation from the surfaces of the fuel or graphite particles. One might expect that gaseous diffusion would be extremely rapid compared to diffusion through solids, and as a result, the size of the block of graphite would have only a small effect on the rate of diffusion.

With these ideas in mind, we planned a program of small-scale experiments on diffusion of fission fragments through AGOT-KC graphite, impregnated with normal uranium. Without employing extremely large scale operations (constructing an impregnated reactor, etc.) the quantity of fission products which could be produced for these experiments was so small (perhaps 10^{13} atoms) that it could be measured only by its radioactivity. Therefore, we are concerned only with those fission fragments which have sufficient activity to be readily detected. The experiments fall into five groups, to determine:

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1. The rate of diffusion of gases through pores of graphite.
2. The diffusion of total activity (activity of all fission fragments as a group) from U-impregnated graphite as a function of temperature and heating time.
3. The diffusion of individual elements from U-impregnated graphite as a function of temperature and heating time.
4. The diffusion of activity from the graphite crystallites as a function of temperature and heating time.
5. The fraction of fission fragments in the graphite as a function of the density of impregnation.

II. DIFFUSION OF GASES THROUGH GRAPHITE PORES

We have supposed that gaseous diffusion through the pores of graphite at high temperatures would be very rapid compared to diffusion through the lattice or along grain boundries. We conducted a few simple experiments to establish the order of magnitude of this pore diffusion.

The theory of gaseous diffusion through porous media has been the subject of numerous investigations and appears to be well in hand. A brief discussion of pore diffusion is given by Schwertz,[5] whose notation we use. The quantity, Q, of gas in volume units at standard temperature and pressure, which flows through a porous plug in time, t, with a pressure drop, $\Delta P = P_1 - P_2$ across the plug is given by

$$Q = \dot{F} \Delta Pt$$

or

$$\dot{Q} = \frac{dQ}{dt} = \dot{F} \Delta P.$$

where $\dot{F}$ is the specific flow rate, measured in volume units at standard conditions.

Schwertz shows that $\dot{F}$ is a linear function of the mean pressure, $P_m = \frac{P_1+P_2}{2}$:

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$$\dot{F} = \frac{\epsilon^3 A T_o}{5(1-\epsilon)^2 S^2 \mu L T P_o} P_m + \frac{\epsilon^2 \pi A Z R T_o}{(1-\epsilon) S L P_o (2\pi M R T)^{1/2}} = \alpha P_m + \beta \qquad \ldots(1)$$

where ϵ	is the porosity, the ratio of the volume of pores to the volume of the porous object
A	is the cross sectional area of the body
T_o and P_o	are standard temperature and pressure
S	is the surface area per unit volume
μ	is the viscosity
L	is the length of the porous body
T	is the absolute temperature of the gas
Z	is a funtion of pore shape and of the fraction of gas molecules which are diffusively reflected from the pore walls
M	is the molecular weight of the gas

If the mean free path of the gas molecules is small compared to the average pore diameter, the second term in the above equation may be neglected, that is

$$\dot{F} = \alpha P_m$$

The apparatus shown in Fig. 1 was set up for measuring the rate of flow of gases through graphite. The porous plug was a graphite cylinder sealed into a pyrex tube by heating the tube and paddling the hot glass against the graphite with a carbon tool while the assembly rotated in a glass lathe. This procedure produced an excellent mechanical seal; the glass appeared to wet the graphite. A mercury manometer was attached at each side of the graphite plug. Gas from a tank was admitted at one end of the plug through a stopcock. A vacuum pump was used to remove the gas at the other end of the plug and make P_2 approximately zero for ease of computation. The exhaust from the vacuum pump was trapped over water in a volumetric flask.

The gas was collected in each measurement until the water level was the same inside and outside the flask. At that point the total pressure in the flask was the sum of the partial pressure of the gas plus the partial pressure of the water vapor and was equal to the barometric pressure P_a. The partial pressure of the water vapor should be about equal to the vapor pressure P_w

of water at the water temperature, in this case approximately 20° C.

$$P_g = P_a - P_w$$

Since P_a is very nearly 76 centimeters of Hg and P_w is 1.7 centimeters of Hg (at 20° C)[6], P_g is equal to P_a within 2.5 per cent. Since the collecting flask has a slender neck a small error in the height of the water column will result in only a very small error in volume. For this reason, we could neglect the water vapor pressure.

$\dot{F}$ is found from the relation

$$\dot{F} = \frac{Q}{t\Delta P} ,$$

where Q is corrected to standard conditions.

With this equipment a series of measurements of $\dot{F}$ as a function of P_m were made for helium, nitrogen and hydrogen diffusion through AGOT-KC graphite parallel to the direction of extrusion. The data from these measurements is plotted in Fig. 2. Table I gives values of α and β from Fig. 2.

TABLE I

Gas	α	β
N_2	1.46×10^{-2} cm^3/min x (cm of Hg)^2	0.75×10^{-1} cm^3/min x cm of Hg
He	1.35×10^{-2} cm^3/min x (cm of Hg)^2	1.76×10^{-1} cm^3/min x cm of Hg
H_2	2.97×10^{-2} cm^3/min x (cm of Hg)^2	2.11×10^{-1} cm^3/min x cm of Hg

According to Eq. (1) the values of α for different gases should be inversly proportional to their viscosities; that is

$$\alpha_2 = \frac{\mu_1}{\mu_2} \alpha_1 \qquad \text{...(2)}$$

If we use the value of α for He from our data we can compute α for H_2 and N_2.

Utilizing the following values for viscosity[6]

$\mu = 198$ micropoises for He at 20° C
$\mu = 90.0$ micropoises for H_2 at 20° C
$\mu = 176$ micropoises for N_2 at 20° C

Substituting these values in Eq. (2) we find

$$H_2 = 2.97 \times 10^{-2} \text{ cm}^3/\text{min} \times (\text{cm of Hg})^2$$

$$N_2 = 1.52 \times 10^{-2} \text{ cm}^3/\text{min} \times (\text{cm of Hg})^2$$

The agreement of the above values of α for H_2 and N_2 with the value measured directly is encouraging.

This data can be used to compute α for other gases, provided that the viscosity of the gas is known. If the viscosity is not known it can be computed from the following well known relations:[7,8]

$$\mu = \frac{\rho \bar{v} \lambda}{3}$$

$$\bar{v} = \sqrt{\frac{2.1\,T}{M}} \times 10^4$$

$$\lambda = \frac{1}{\pi n \sigma^2 \sqrt{2}}$$

$$\rho = n\,m$$

where
$\bar{v}$ = average velocity of the molecules, cm/sec
λ = mean free path, cm
n = number of molecules per unit volume, cm^{-3}
σ = molecular diameter, cm
m = mass of molecule, gm

Combining these relations, we find

$$\mu = \frac{1.087\,m}{\sigma^2} \sqrt{\frac{T}{M}} \times 10^3 \text{ poises} \qquad \ldots(3)$$

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for the particular piece of graphite which we used to measure $\dot{F}$. Since we have extrapolated ourselves by our bootstraps this far, we might as well assume that Z is a constant in Eq. (1), although this is probably not a very good approximation over a wide range of temperatures. Then we can calculate β since

$$\beta_{Ba} = \frac{C}{\sqrt{M_1 T_1}}$$

C can be found from

$$\beta_{He} = \frac{C}{\sqrt{M_2 T_2}}$$

and so

$$\beta_{Ba} = \beta_{He} \sqrt{\frac{M_2 T_2}{M_1 T_1}}$$

Then

$$\beta_{Ba} = 1.76 \times 10^{-1} \sqrt{\frac{4 \times 293}{137 \times 1773}} = 1.22 \times 10^{-2} \text{ cm}^3/\text{min} \times \text{cm of Hg.}$$

We are now in a position to estimate the specific flow rate of barium vapor through our graphite sample. Suppose $P_1 = 1$ mm, as it might for a short time, if a graphite sample containing barium were suddenly heated to 1500° C in a vacuum, and suppose that $P_2 = 0$, then $P_m = 0.5$ mm and $P_1 = 1$ mm. The rate of gas flow is

$$\begin{aligned}\dot{Q} &= (\alpha \text{ Pm} + \beta) \ \Delta P \\ &= (8.8 \times 10^{-4} \times 5 \times 10^{-2} + 1.22 \times 10^{-2}) \ 10^{-1} \\ &= 1.22 \times 10^{-3} \text{ cm}^3/\text{min,}\end{aligned}$$

the volume of gas being measured at standard temperature and pressure. This volume corresponds to 7.5×10^{-6} grams per minute or 3.3×10^{16} atoms per minute. This number is very approximate, but it represents a rate which is at least 10^6 times as great as we might expect for diffusion of barium through graphite. Therefore, it seems safe to assume that the pore diffusion time is very small and can be neglected compared to the time for diffusion through solids.

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III. DIFFUSION OF TOTAL ACTIVITY

To provide material for parts 1, 2 and 3 of the program outlined in the introduction, a block of AGOT-KC graphite approximately 2 inches by 2 inches by 1-1/8 inches with the extrusion axis parallel to the 1-1/8 inch edge was impregnated with uranium oxide to an average density of 0.3 grams of uranium per cubic centimeter of graphite. The density of impregnation was made large so that a short irradiation would produce enough fissions for easy measurement. The density of impregnation was found to vary considerably from one part of the block to another.

Cylindrical samples 1/4 inch in diameter by 1-1/8 inches long with the axis of the cylinder parallel to the extrusion axis were cut from the impregnated block. These samples were packed in an aluminum holder and sent to Los Alamos where they received 400 kilowatt hours of irradiation in the thermal column of the Fast Reactor, after which they were returned to us.

A simple vacuum furnace was constructed which consisted of a crucible supported on three tungsten rods and surrounded by a water cooled induction heating coil, the whole assembly being in a bell jar with copper to glass seals in one end for the RF leads. Radio frequency power was supplied to the heating coil by a 450 kilocycle, 3/4 kilowatt induction heater.

Two samples were heated in this furnace, the first for 17 minutes at 1200° C, the second for one hour at 1170° C. An optical pyrometer was used for temperature measurements. It was difficult to adjust the induction heater to a desired temperature, although the temperature was stable within ± 5° C at any particular adjustment.

The activity of the two heated samples was compared with two unheated samples in the following manner. The graphite was broken up electrolytically in hot concentrated nitric acid. It was then separated from the solution by filtering, after which it was dried in an oven at 120° C. The dried graphite was spread on a 1-inch watch glass and counted with a geiger counter. An aliquot of the solution was evaporated on a 1-inch watch glass and counted. The data from this counting were correlated with the weights of the samples before heating and the aliquot used, etc. The resulting data were disappointing in that the solution from the heated samples had more activity than that from the unheated ones. It was decided to cut the next sample in two and keep one half

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unheated to try to get reasonable agreement between the heated and unheated samples, with the idea that the discrepancy was due to differences in the density of impregnation from sample to sample.

Due to the difficulty in setting the induction heater to the desired temperature, we decided to seal the samples in evacuated vycor tubes and use a tube furnace for the 1200° C measurements. Accordingly, a sample was cut into halves, of which one was kept as a control and the other was placed in a vycor capsule which was evacuated and sealed. The capsule was placed in a tube furnace and heated for 34 hours at 1200° C. When the capsule was removed from the furnace it was found to have swelled to approximately twice its original volume. Evidently the uranium oxide in the sample was converted to uranium carbide and the liberated oxygen combined with the graphite to form carbon monoxide (carbon dioxide would be unlikely at 1200° C), at high pressure.

The pressure of the liberated carbon monoxide can be estimated as follows. The volume of the sample was approximately 0.5 cm^3, that of the vycor tube was about 20 cm^3, and the density of impregnation was 0.3 gram of uranium per cubic centimeter of graphite. Assuming that the uranium was present as UO_2 we have $\frac{0.3 \times 0.5}{270} = 0.55 \times 10^{-3}$ mole of $UO_2 = 1.1 \times 10^{-3}$ mole of CO. Then if n is the number of moles, R the gas constant; T the temperature; and V the volume of the vycor tube, the pressure of CO, P_{CO}, at 1200° C is $P_{CO} = \frac{nRT}{V} = \frac{1.1 \times 10^{-3} \times 82.1 \times 1473}{20} = 7$ atmospheres.

After heating, this sample was treated and counted in the same manner as before. The data from the residues and solutions of the heated half compared to those of the unheated half indicated that 27.5 per cent of the original total activity had diffused out of the heated sample.

The next sample was cut in several pieces, four of which were sealed in evacuated vycor capsules and heated in the tube furnace at 1200° C for 7-1/2 hours 17 hours, 24-1/2 hours, and 46 hours. After heating, the samples were placed in platinum boats and burned in oxygen in a tube furnace at 800° C to remove the graphite and eliminate the need for making a correction for self-absorption when measuring the activity of the samples. The unburned residue was then dissolved in concentrated nitric acid and evaporated on a watchglass for counting. This technique had been tested previously with known quantities of material and found to be very reliable. These samples gave the following data:

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TABLE II

Heading Time hours	Per Cent of Activity Lost
7-1/2	21.5
17	7.5
24-1/2	32.2
46	15.5

The above data show more scatter than one would like.

It was realized that the high carbon monoxide pressure in the vycor capsules might have a profound effect on the rate of gaseous diffusion from the graphite and that the heating should be done in a vacuum furnace. The tube furnace has the further disadvantage that its highest temperature is about 1500° C, which it reaches with difficulty. For these reasons we decided to construct a small vacuum furnace employing a helical graphite heating element surrounded by tantalum shields. This furnace is shown in Fig. 3 and is described in detail in Ref. 9.

The furnace proved to be very successful, having none of the disadvantages of the radio frequency induction furnace or the tube furnace.

Another sample was cut into eight pieces, five of which were placed in the new vacuum furnace. The temperature was held at 1200° C. The pyrometer was arranged to look through holes in the furnace shields, directly at the sample, through the helical heater. One piece was removed after 11 hours and 15 minutes; another at 14 hours and 10 minutes; the next at 16 hours and 12 minutes; the next at 18 hours and 19 minutes; and the last at 20 hours and 19 minutes. These samples were treated in the same manner as the previous sample and yielded the following data.

TABLE III

Heating Time	Per Cent of Activity Lost
11 hr 15 min	9.9
14 hr 10 min	more activity than unheated samples
16 hr 12 min	34.4
18 hr 19 min	25.6
20 hr 19 min	3.0

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It was known that formation of uranium carbide is appreciable at 1200° C and it was felt that such a chemical reaction might upset the rate of diffusion. We decided, therefore, to make the next measurements at 1500° C. At this temperature, carbide formation would proceed to completion more rapidly. In any case, it was desirable to make the rate of diffusion much larger, which would improve the accuracy of the measurements and tend to mask other disturbances.

Another irradiated sample was cut into six pieces, five of which were placed in the vacuum furnace and heated at 1560° C. A piece was removed from the furnace each hour. The samples were treated for counting as before (burned in oxygen at 800° C, dissolved in HNO_3, evaporated on a watchglass, etc.). Fig. 4 presents a flow chart for the procedures used with these samples. These samples were sufficiently active to count in an ionization chamber with a vibrating reed electrometer. This was advantageous, since it eliminated the need for coincidence corrections, etc., which were necessary with the Geiger counter.

The data were correlated by dividing the ion chamber current by the weight of the sample. The 1560° C run yielded reasonably good data (Fig. 5). The per cent of the activity lost as a function of heating time was computed using the relation

$$\text{per cent lost} = \frac{\text{unheated sample activity-heated sample activity}}{\text{unheated sample activity}} \times 100$$

These data are plotted in Fig. 6.

Another sample was cut into eight pieces and the heating and counting procedure was repeated at 1760° C. These data were correlated with sample weights and are plotted in Fig. 7. The data have considerable scatter and the curve of Fig. 7 is quite uncertain. At this point it was decided to try correlating the data with the weight of the burned residue. The weight of the burned residue is proportional to the uranium content of the samples so that correlating the data with this weight should give more consistent data if the density of impregnation varies from sample to sample. This was done and the results are plotted in Fig. 8. The data look considerably better in Fig. 8 than in Fig. 7. The agreement of the two unheated samples is especially gratifying. The per cent of the activity lost as a function of heating time was computed in the same manner as before and is plotted in Fig. 6. The manner in which the curve approaches zero is not well established and therefore is drawn with a dashed line. The experiment was repeated again at 1660° C with good results when the uranium content of each piece was taken into consideration. The loss of activity as a function of heating time is plotted in Fig. 9. The per cent of the activity lost as a function of heating time was computed as before and is plotted in Fig. 6. Again the lower end of the curve is dashed in for lack of data in this region.

IV. DIFFUSION OF BARIUM AND STRONTIUM

After the samples were counted to determine diffusion of total activity, the activity was washed off the watch glasses with nitric acid and chemical separations for barium and strontium were performed. Barium and strontium were chosen because of their high fission yield, convenient half-lives (Ba^{140} - 12.8 days, Sr^{89} - 54 days), easy chemical separation, and because barium is representative of the heavy group and strontium is representative of the light group of fission fragments. It is possible that much of the Ba and Sr present in the graphite is in the form of carbides. While barium and strontium are known to form the carbides, BaC_2 and SrC_2, these carbides are also known to be volatile in high vacuum below 1500° C.[10]

The separations were carried out in accordance with standard procedures,[11] using the carrier technique of the addition of a known amount of the desired element. The active elements precipitate along with the inactive elements. The precipitate is then mounted and counted.

The per cent of the activity lost as a function of heating time was computed using the Ba and Sr activity of the unheated sample as a basis for comparison and is shown in Fig. 10 for barium and in Fig. 11 for strontium. Data for diffusion of strontium at 1200° C is also shown in Fig. 11. No separations for barium were done on samples heated at 1200° C.

V. DIFFUSION FROM THE GRAPHITE CRYSTALLITES

Referring to Fig. 6, each of the three curves for diffusion of total activity has three parts: an initial part in which the slope is large and the curve is fairly linear, a transition region from one slope to another, and the last part which is quite linear and has a small slope. This suggests that two processes of diffusion are occurring which have quite different rates. One might suspect that the initial steep part of the curves represents diffusion from the fuel particles and that the last part may be due to diffusion from the graphite.

We performed an experiment to test this hypothesis. In order to determine the rate of diffusion of fission fragments from the graphite alone, the uranium was removed from the graphite with nitric acid and then the graphite residue was heated to a high temperature to drive off fission products. In leaching the uranium with nitric acid, we assumed that since the uranium was in the pores, it would be attacked by the nitric acid, along with any fission fragments that were also in the pores, but that the nitric acid could not leach out fission fragments driven into the crystallites during fission, present there interstitially.

The first part of this experiment required that we determine the degree to which the uranium could be removed by nitric acid leaching. Several impregnated samples were ground to dust in concentrated nitric acid in a stainless steel mortar and pestle. The stainless steel mortar and pestle were used because it was found that with porcelain mortars and pestles the graphite smeared in streaks which could not be removed without abrasives. In the stainless steel mortar, the nitric acid etches the steel slightly and any adherent graphite particles are dislodged. The mixture of graphite and nitric acid was poured into a beaker, heated to boiling and separated by filtration after standing for several hours. The uranium was plated out of the filtrate onto a copper disc by the following procedure. The solution was evaporated almost to dryness to get rid of excess HNO_3. Five milliliters of saturated ammonium oxalate and 5 milliliters of ferric ammonium sulfate (0.1 mg/cc) were added. The sample was then neutralized by addition of NH_4OH. The uranium was plated on a copper disc in the plating cell previously used in this laboratory[12] at a temperature 80 to 100° C with a current of 1 to 2 ma.[13] The powdered graphite was placed in a platinum boat, dried in an oven at 100° C and then burned in oxygen in a tube furnace at 800° C. After the graphite was completely burned, the platinum boat was throughly washed out with nitric acid and the uranium was plated out of the nitric acid wash onto a copper disc by the same method as was used with the filtrate. The relative amounts of uranium on the copper discs were determined with an alpha counter. Since no fission fragments have alpha activities, the total count was an indication of the uranium content. The burning and plating procedures were tested using known quantities and found to be reliable. The efficiency of nitric acid in removing uranium from graphite was determined with unheated and heated samples and with samples which had been irradiated with neutrons and with unirradiated samples. The results are tabulated below:

TABLE IV

Per Cent of Uranium Removed from Sample by HNO_3

Unheated Unirradiated	99.85% 99.87% 99.82% 99.80%	Unheated Irradiated	99.81% 99.79% 99.87% 99.84%
Heated (1200° C - 1/2 hr) Unirradiated	99.37% 99.32% 99.85%	Heated (1500° C - 3 hr 15 min) Irradiated	99.65% 99.71% 99.57%

The last decimal place is uncertain in the above table. Evidently, the nitric acid leach removes impregnated uranium to an extent of at least 99 per cent.

By grinding in nitric acid, the uranium was removed from two previously untreated, irradiated samples. The powdered graphite was placed in a crucible and heated in a vacuum furnace at 1660° C. A portion of the graphite was removed each hour for 8 hours. Each portion of heated graphite was placed in a platinum boat and burned in oxygen in a tube furnace. The burned residue was washed out of the boat with concentrated nitric acid and evaporated on a watchglass for counting. The samples obtained in this manner were counted with a thin-window Geiger counter. The data was correlated with sample weights and is plotted in Fig. 12.

Assuming that the data should represent a straight line a least squares treatment yields the line which is shown, with slope, -0.297 and ordinate intercept, 5.814. This line was used to compute the fraction of activity lost as a function of heating time, which we then plotted in Fig. 6, for comparison with the diffusion of activity from impregnated graphite at 1660° C. It is encouraging that the two curves approach the same slope which lends some support to the hypothesis that the last part of the curves for diffusion from impregnated graphite is due to diffusion from the graphite only.

VI. THE FRACTION OF THE FISSION ACTIVITY IN THE GRAPHITE AS A FUNCTION OF THE DENSITY OF IMPREGNATION

To determine what fraction of the fission fragments penetrates the graphite crystallites and whether this fraction varies with the density of impregnation, samples of AGOT-KC graphite were impregnated with 3.7, 10.9, and 138 milligrams of uranium per cubic centimeter of graphite and were sent to Los Alamos for neutron irradiation. We also sent some samples of EBP graphite impregnated with 0.8, 5.8, and 65.4 milligrams of uranium per cubic centimeter of graphite.

After the samples were irradiated, they were ground to dust in nitric acid with the stainless steel mortar and pestle. The powdered graphite and acid were poured into a beaker, heated to the boiling point and allowed to stand for a few hours. The solution was separated from the graphite by filtering. The filtrate was diluted to 50 milliliters and aliquots were evaporated on watch glasses and counted to determine the fission activity. Aliquots were also taken to determine the uranium content of the sample by the alpha counting method as described in Section V. The powdered graphite was dried and burned in oxygen at 800° C. The burned residue was dissolved in nitric acid, evaporated on watch glasses and counted to determine the fission activity. The per cent of the fission fragments in the graphite was computed from the formula

per cent in graphite =

$$100 \times \frac{\text{counting rate of graphite}}{\text{counting rate of graphite + counting rate of solution}}$$

These data are plotted in Fig. 13. Points were also obtained at 325, 334, and 351 milligrams of uranium per cubic centimeter of graphite from data from the control samples of the first group of experiments on diffusion of total activity. From Fig. 13, it appears that the fraction of fission fragments which enter the graphite is independent of the density of impregnation, certainly within the range of impregnation densities used.

It is of interest to calculate the activation energies associated with the diffusion of fission fragments since it may shed some light on the nature of the processes involved and will establish whether or not the diffusion is due to a single process.

If one takes several identical samples and anneals them at different temperatures for times required to change some physical property of each sample to a new fixed value, it can be shown[14, 15] that the following relation holds:

$$t\ e^{-E/kT} = \text{a constant} \qquad \ldots(4)$$

Eq. (4) applies to the isothermal time curves of any physical property, the only restrictions being that one must start with identical values of the property for each sample used, and that the relation applies only if the physical property change is due to a single process of fixed activation energy, E. This equation represents a powerful method since it allows us to compute an activation energy without having to know the physical processes involved.

If we take the logarithm of each side of Eq. (4) we have

$$\log_e t = E/kT + \log c \qquad \ldots(5)$$

which is linear in 1/T with a slope of E/k. Therefore,

$$E = k\,\frac{\Delta \log_e t}{\Delta \frac{1}{T}}, \qquad \ldots(6)$$

where t is the time and k is the Boltzmann constant.

We have supposed that the final slopes of the curves of Fig. 6 are due to diffusion from the graphite crystallites, and the data obtained from leached graphite tends to confirm this. A further confirmation is obtained by computing the activation energy from this part of the curves by means of Eq. (6).

In order to satisfy the first restriction on Eq. (4) we must have the same initial conditions for the diffusion of total activity through graphite at each of the three temperatures. We can accomplish this by drawing straight lines through the origin with the same slopes as the final slopes in Fig. 6. We have done this in Fig. 14. The times required to reach 12.5 per cent, 20 per cent and 30 per cent were determined from Fig. 14 and a semilogarithmic plot of these times versus 1/T was made in Fig. 15. From Fig. 15, we find by means of Eq. (6), an activation energy for the diffusion of total activity of 20,700 cal/mole.

In Fig. 6 the data is too meager during the initial rise to permit a computation of the activation energy in this region where we have supposed that the diffusion is predominantly from the fuel particles.

In the case of the diffusion of barium and strontium, however, we have sufficient data to compute activation energies during the initial rise but not during the later phases of diffusion. From Fig. 10 the times required for 20 per cent, 40 per cent, and 60 per cent of the barium activity to be lost were determined and plotted in Fig. 15. The strontium data of Fig. 11 was treated in a similar manner by determining the times for 20 per cent, 30 per cent, and 40 per cent to diffuse. From Fig. 15 we find an activation energy of 68,300 cal/mole for barium and 26,400 cal/mole for strontium.

The three sets of points in Fig. 15 approximate straight lines quite well, indicating that each case is due to an essentially single process.

VII. SUMMARY

A. Pore Diffusion

We have found that the gaseous diffusion of fission fragments through the pores of graphite at high temperatures should be extremely rapid compared to diffusion through a solid lattice or along grain boundaries.

B. Diffusion of Total Activity from Uranium Impregnated Graphite

This case is conveniently divided into two parts: the diffusion of total activity through the uranium oxide or carbide fuel particles and diffusion through the graphite. The diffusion was found to be strongly temperature dependent. Sufficient data was available to compute the activation energy for diffusion of total activity from the graphite but not for diffusion from the fuel particles. An effective activation energy for diffusion of total activity through graphite of 20,700 cal/mole was found. This energy is unusually low for a diffusion process. The diffusion of total activity through graphite behaves quite like a single process.

C. Diffusion of Ba^{140} and Sr^{89}

The diffusion of barium and strontium from impregnated graphite also appears to divide into two parts, not necessarily for the same reasons as in the case of total activity. In this case we had data from which to compute the activation energies of the first process but not the second. Activation energies of 68,300 cal/mole for barium and 26,400 cal/mole for strontium were found. The data available at this time does not permit speculation as to the nature of the diffusion processes involved, for instance, grain boundary, interstitial or whatever.

D. Fraction of the Activity in the Graphite as a Function of Density of Impregnation

It was found that approximately 65 per cent of the fission activity was in the graphite crystals and that this fraction was independent of the density of impregnation within the accuracy of the experiment for AGOT-KC and EBP type graphites in the range from 3.7 to 350 milligrams of uranium per cubic centimeter for AGOT-KC and 0.8 to 65.4 milligrams of uranium per cubic centimeter for EBP.

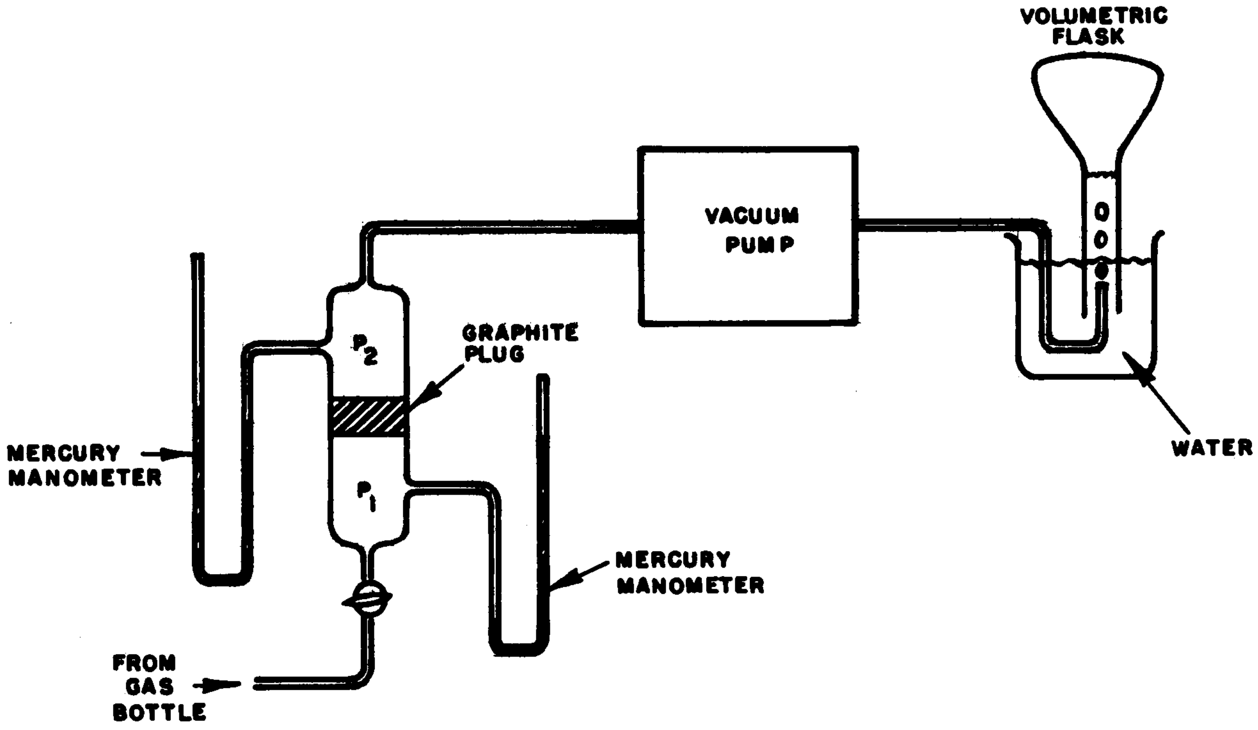

Figure 1. Apparatus for Measuring Pore Diffusion.

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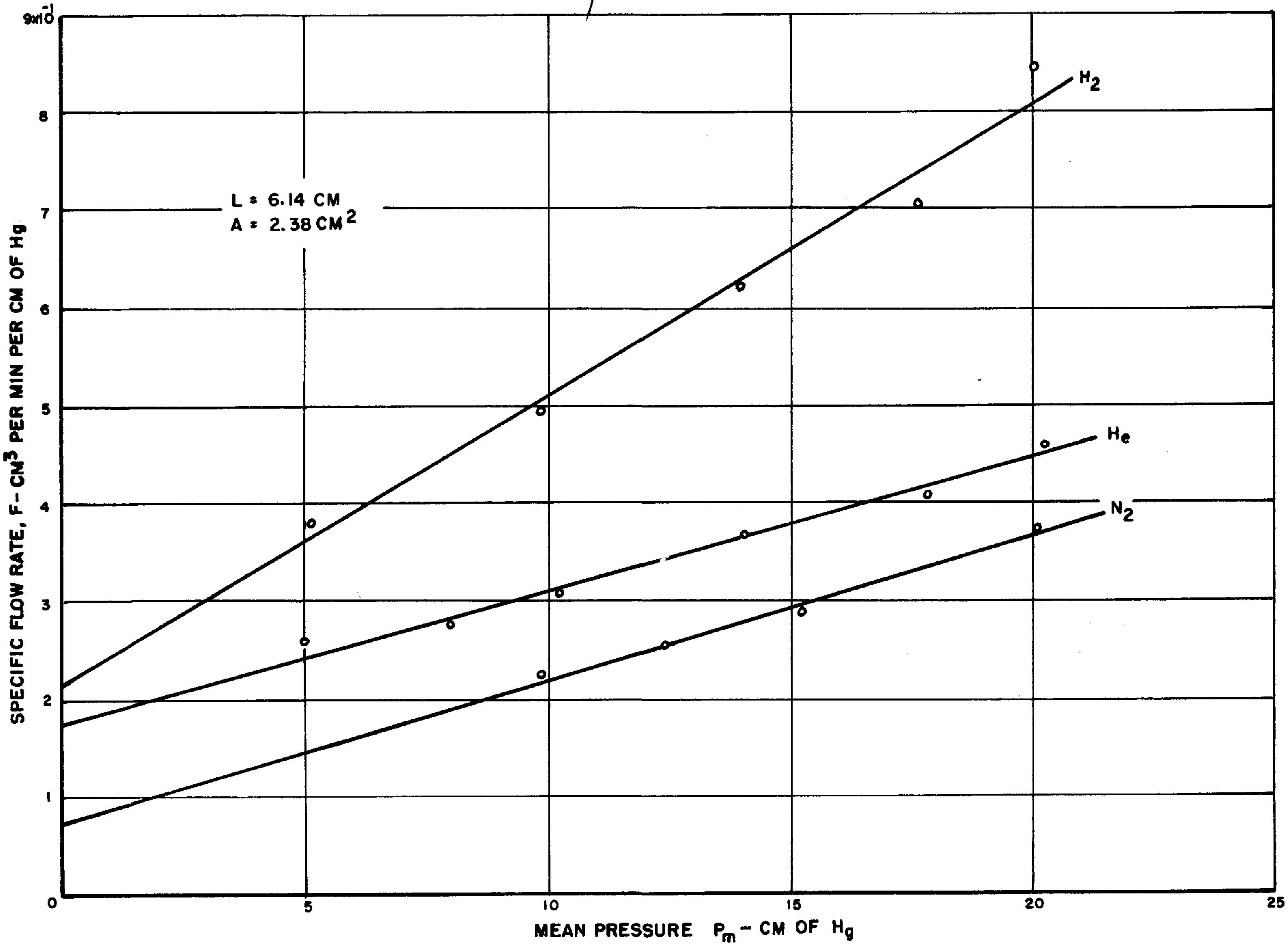

Figure 2. Pore Diffusion.

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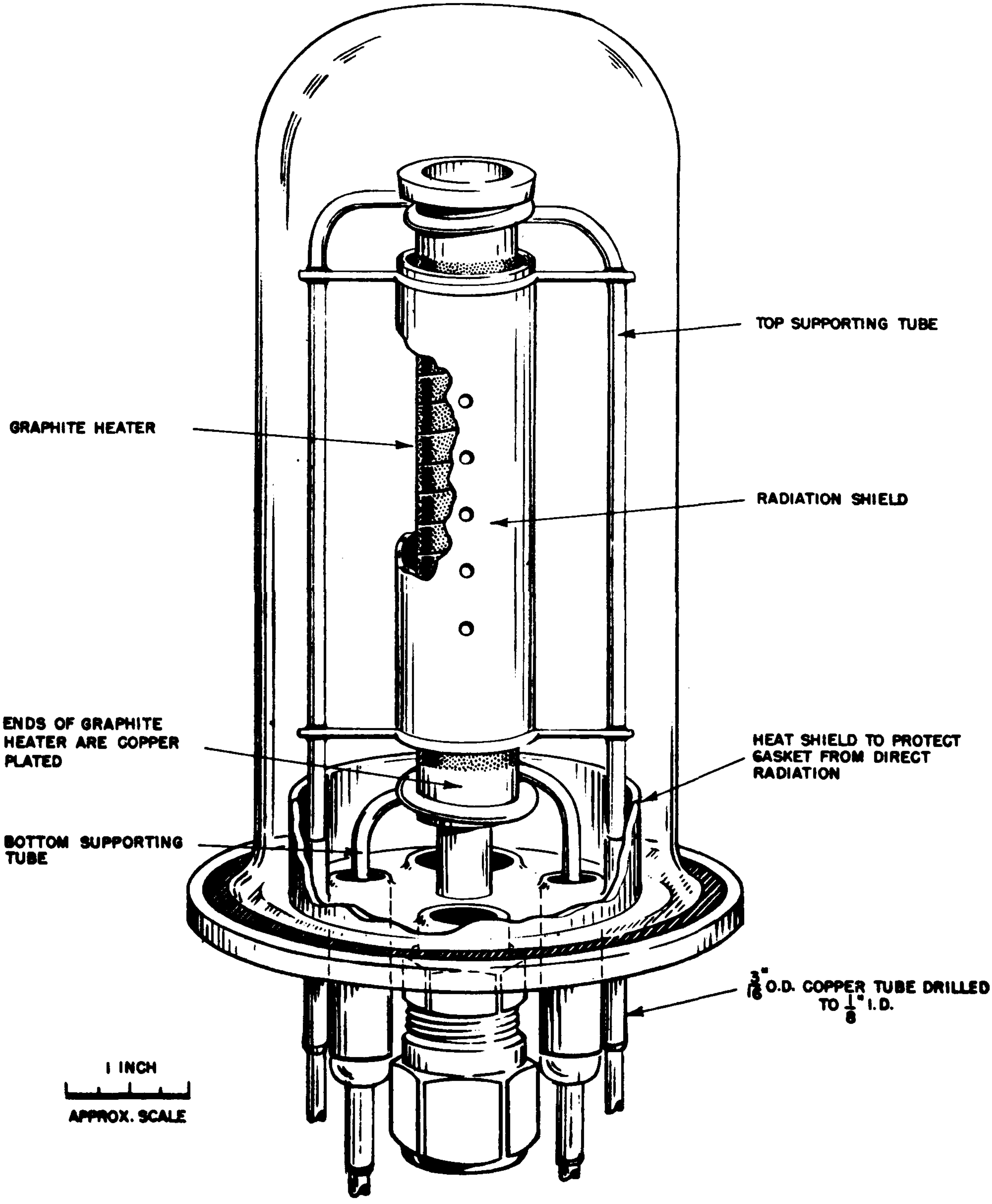

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Figure 3. Furnace Assembly.

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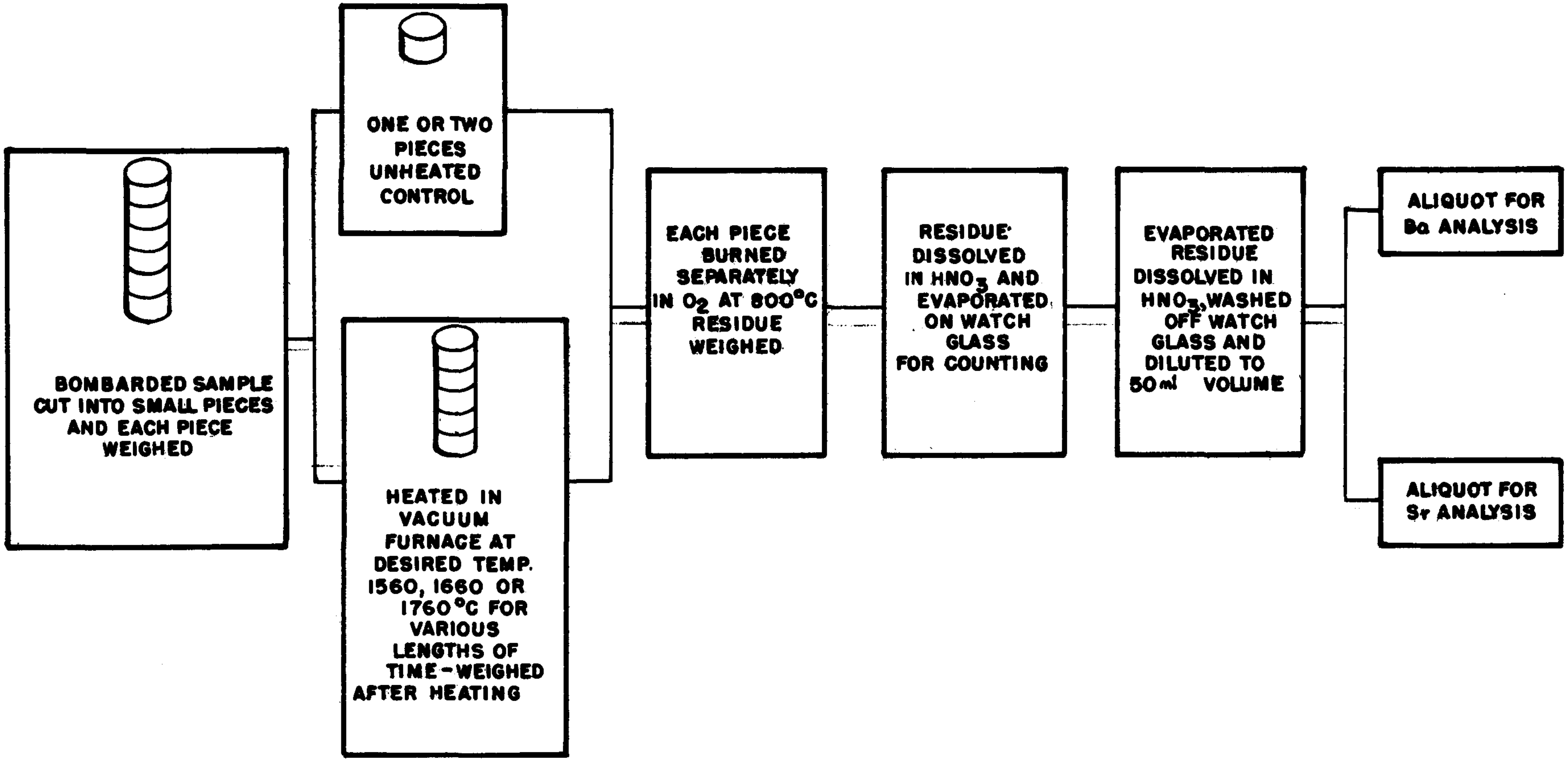

Figure 4. Flow Chart of the Procedure Used for Obtaining 1560, 1660 and 1760° C Data.

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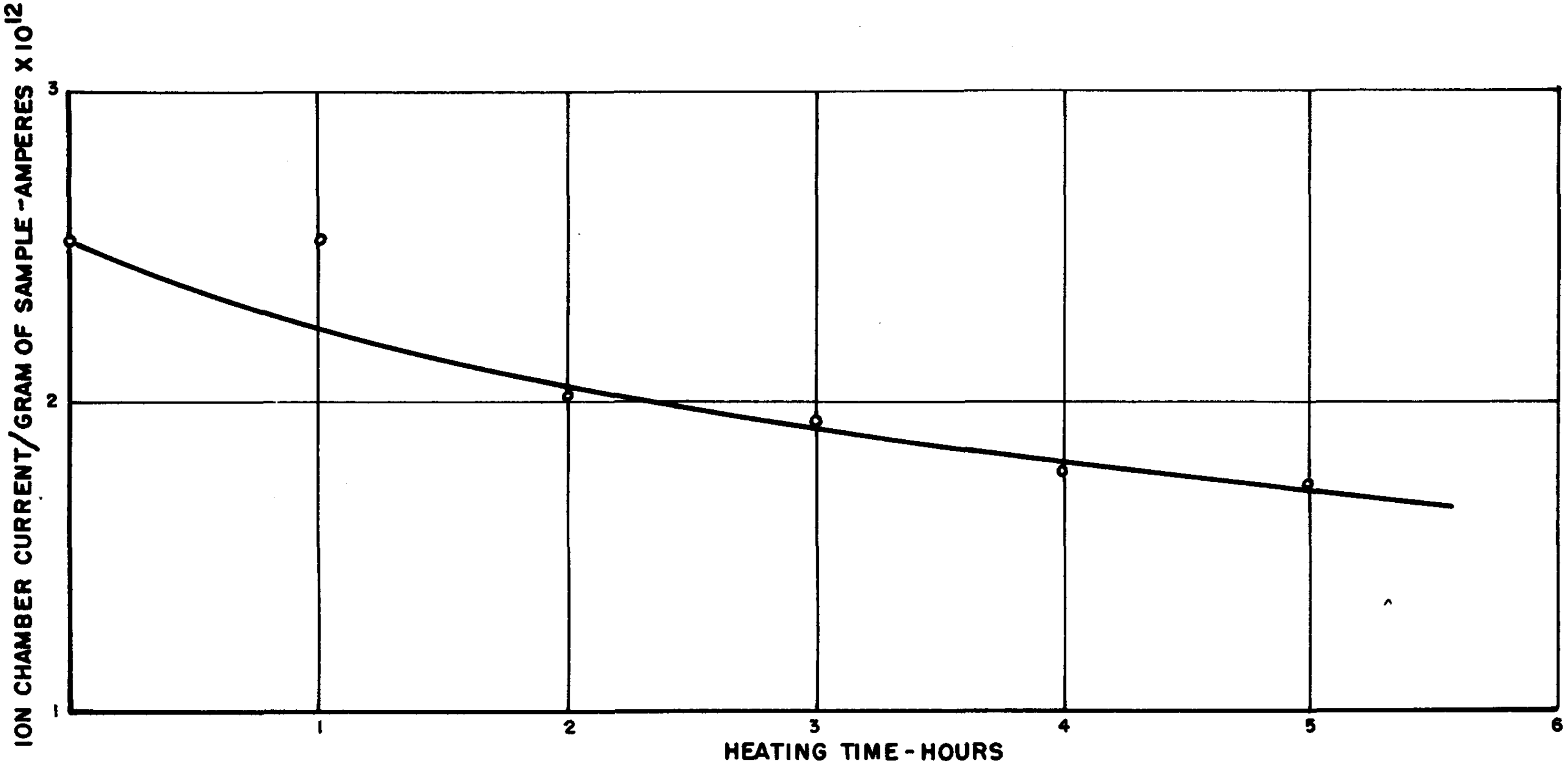

Figure 5. Residual Total Activity vs Heating Time - 1560° C. (Data Correlated with Sample Weights)

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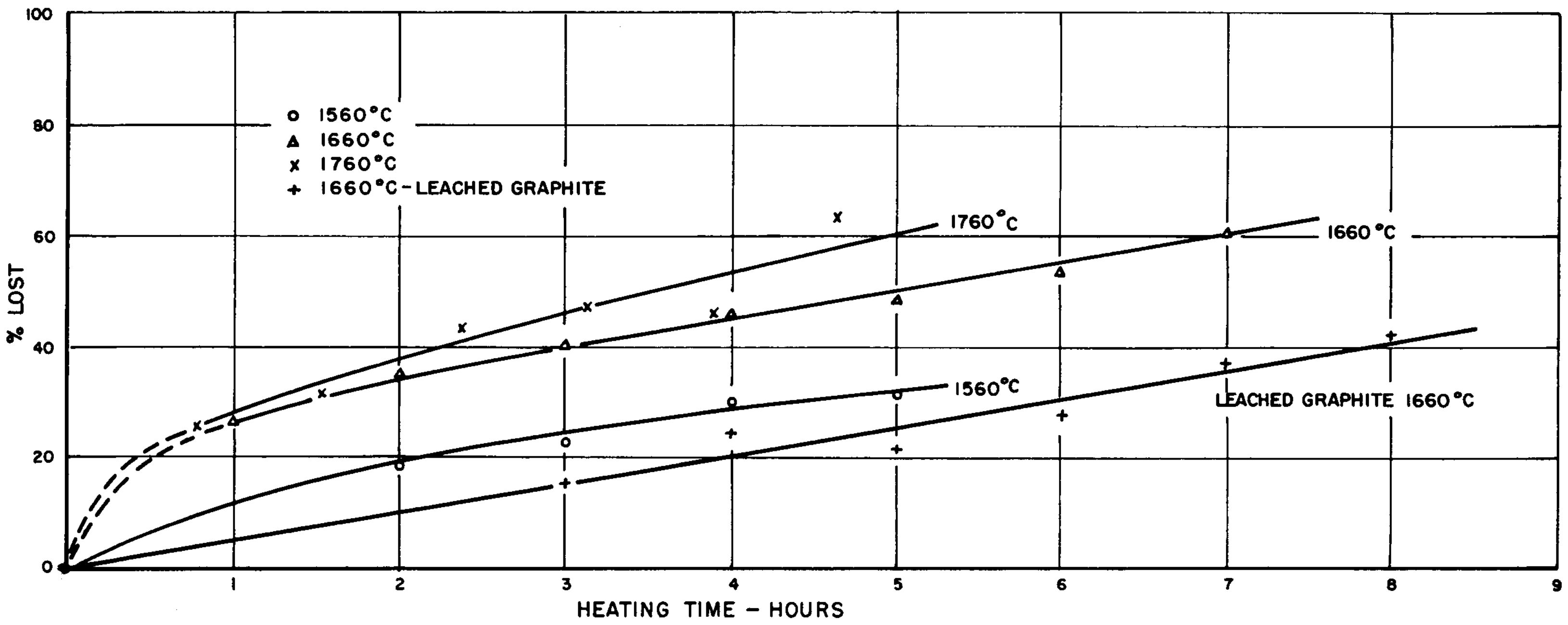

Figure 6. Fraction of Total Activity Lost as a Function of Time and Temperature.

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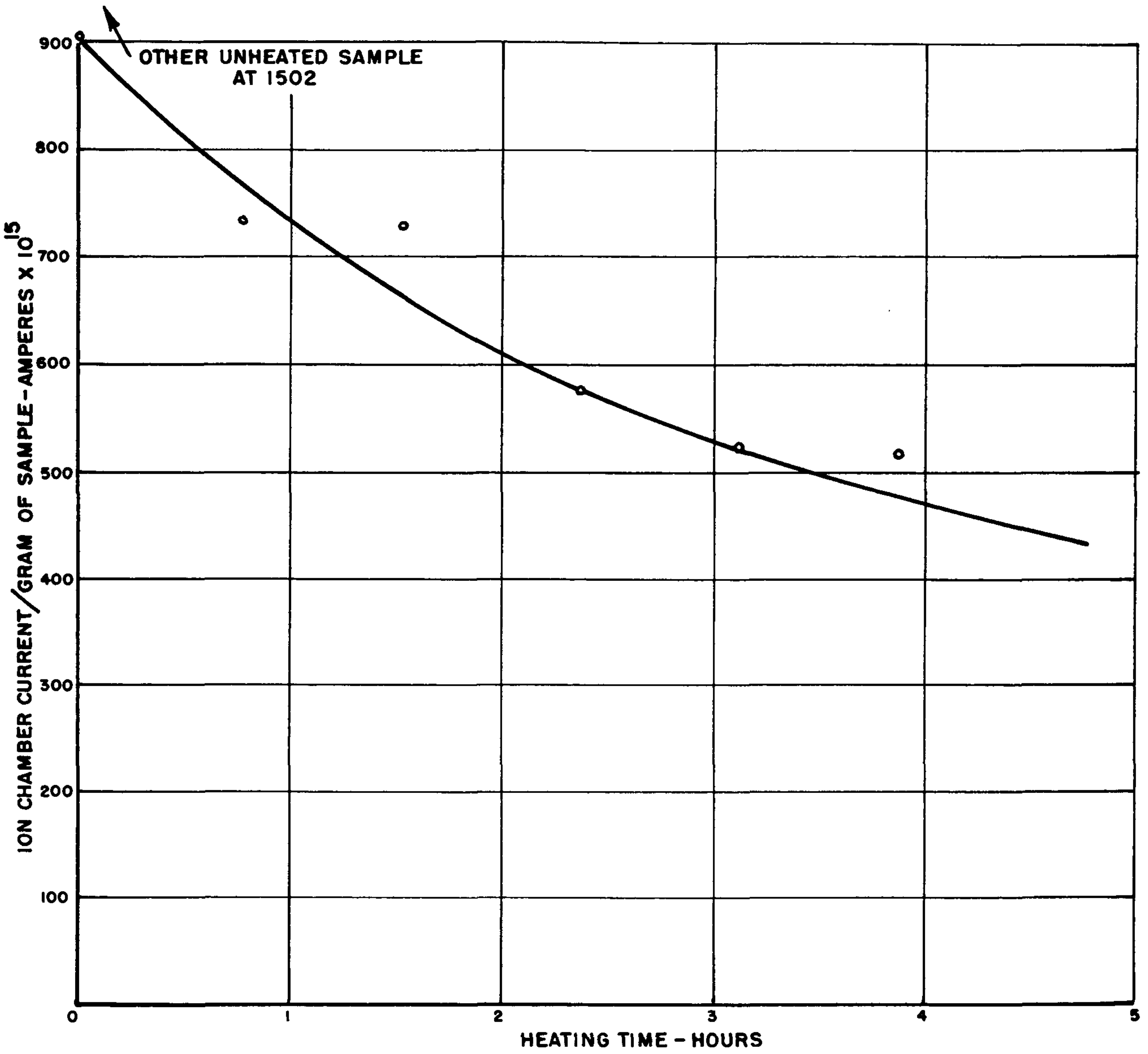

Figure 7. Residual Total Activity vs Heating Time - 1760° C.
(Data Correlated with Sample Weights)

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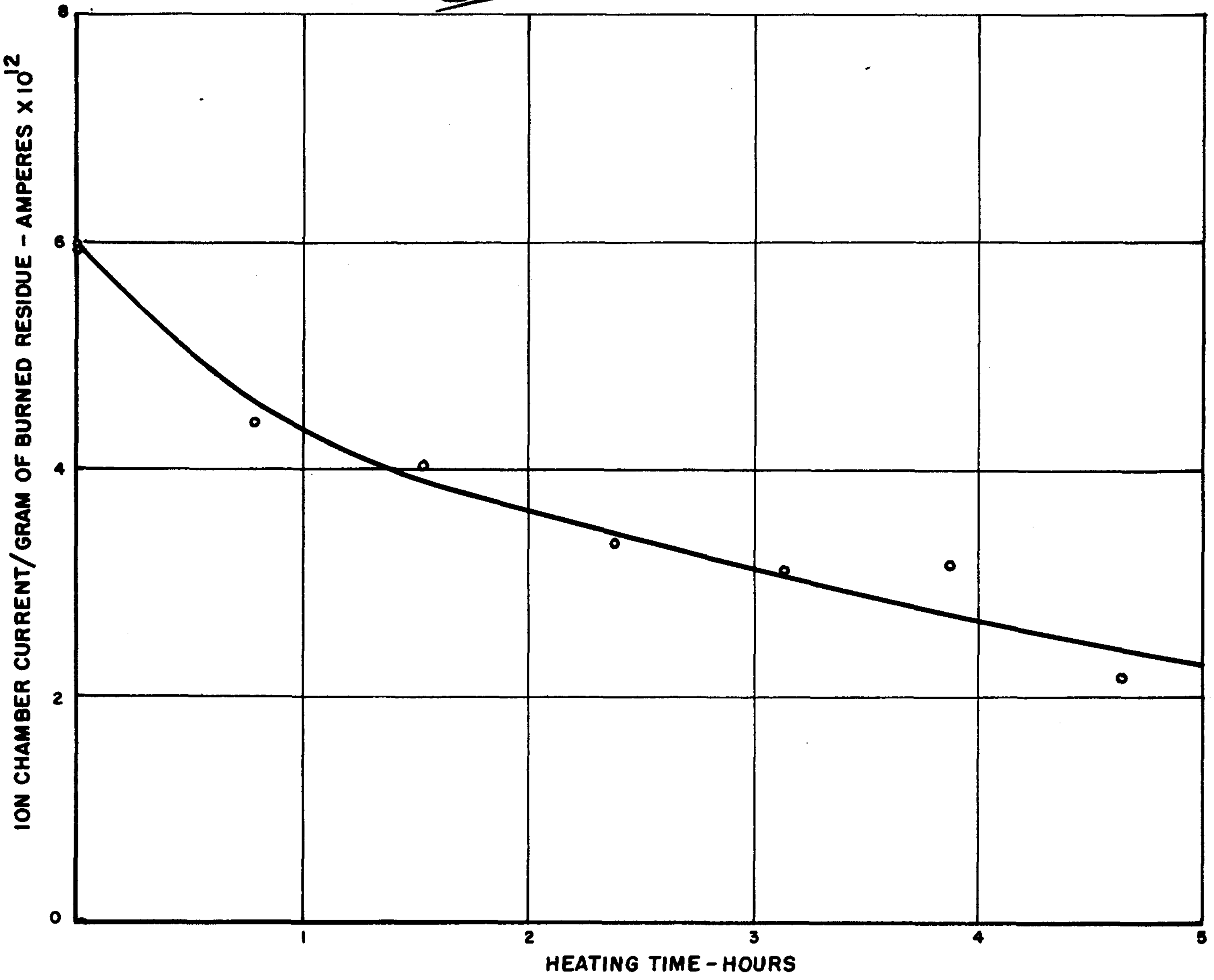

Figure 8. Residue Total Activity vs Heating Time - 1760° C.
(Data Correlated with Weight of Burned Residue)

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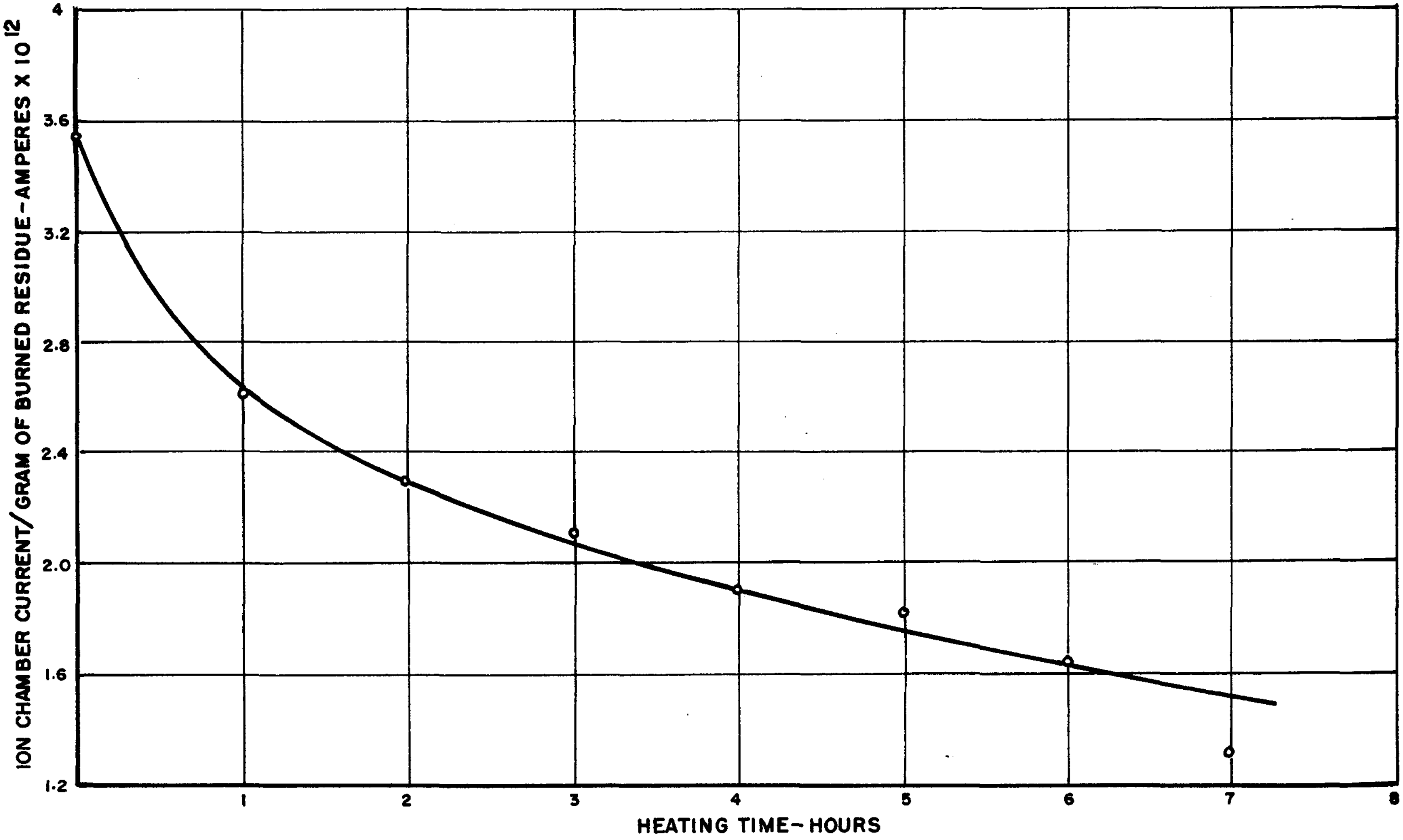

Figure 9. Residual Total Activity vs Heating Time - 1660° C.
(Data Correlated with Weight of Burned Residue)

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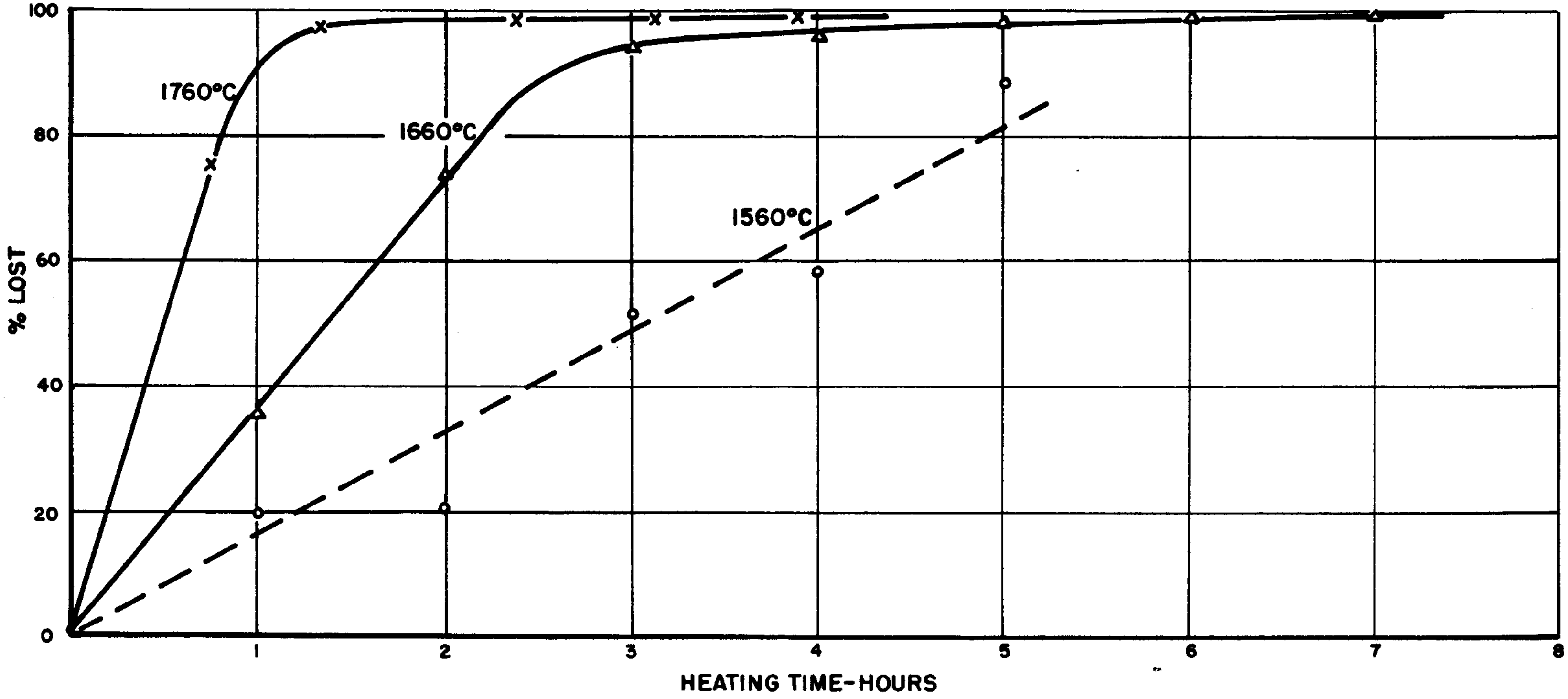

Figure 10. Per Cent of Barium Lost During Heating.

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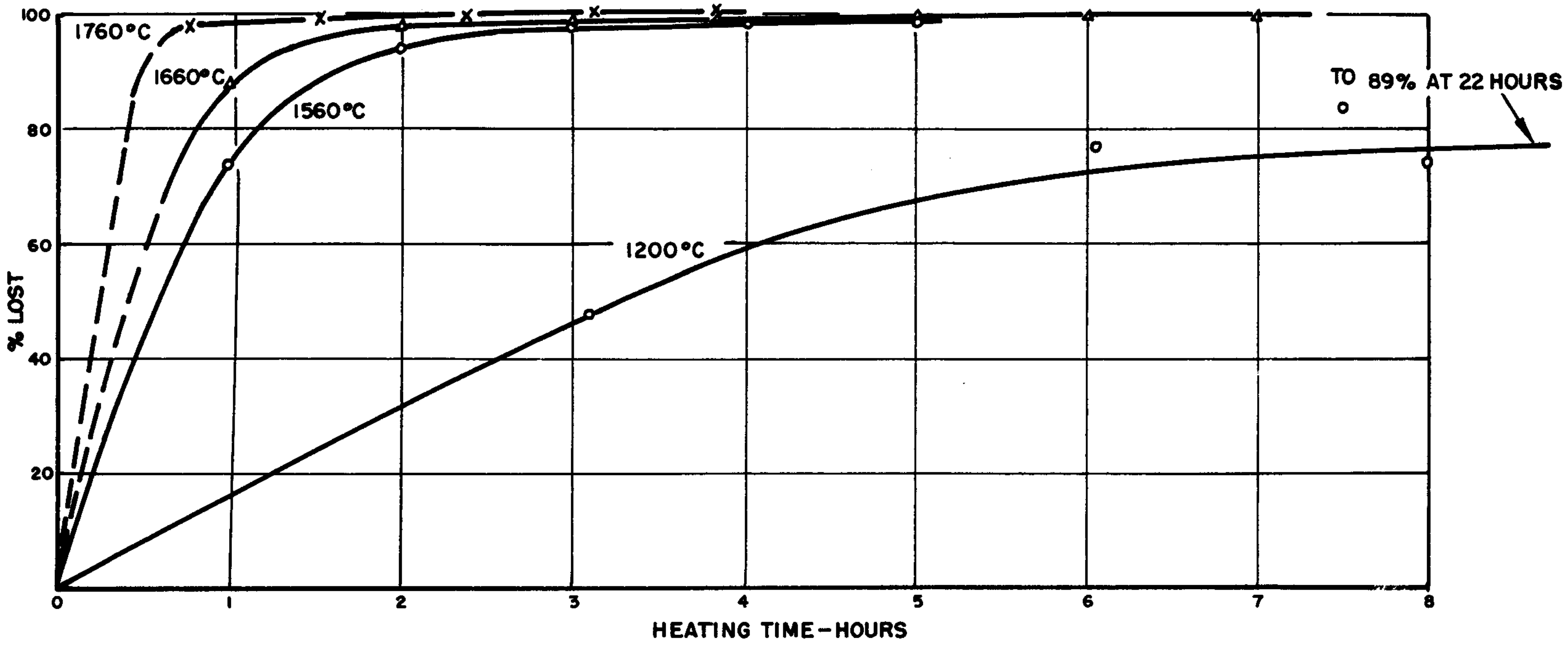

Figure 11. Per Cent of Strontium Lost During Heating.

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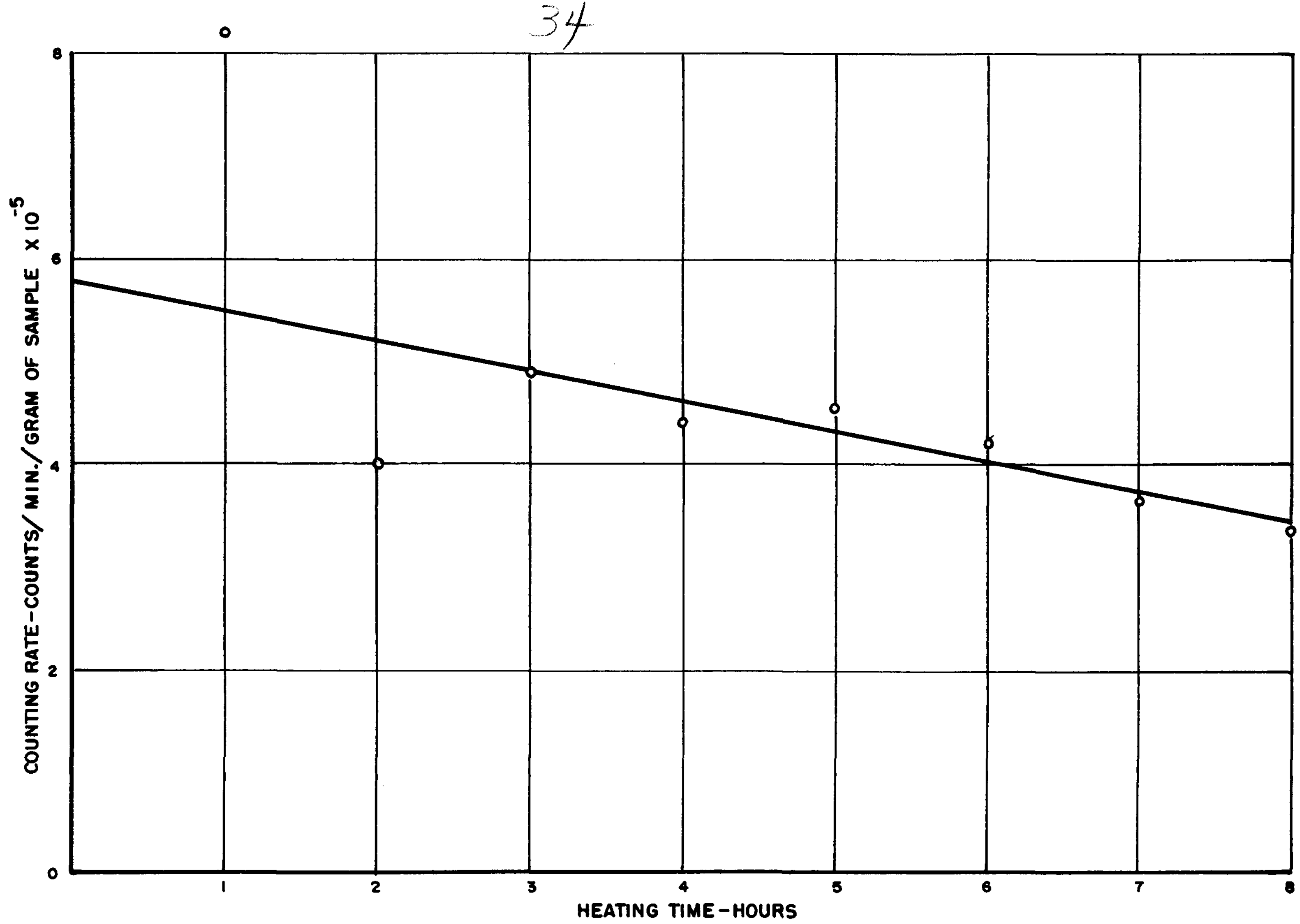

Figure 12. Residual Activity in Leached Graphite After Time at 1660° C.

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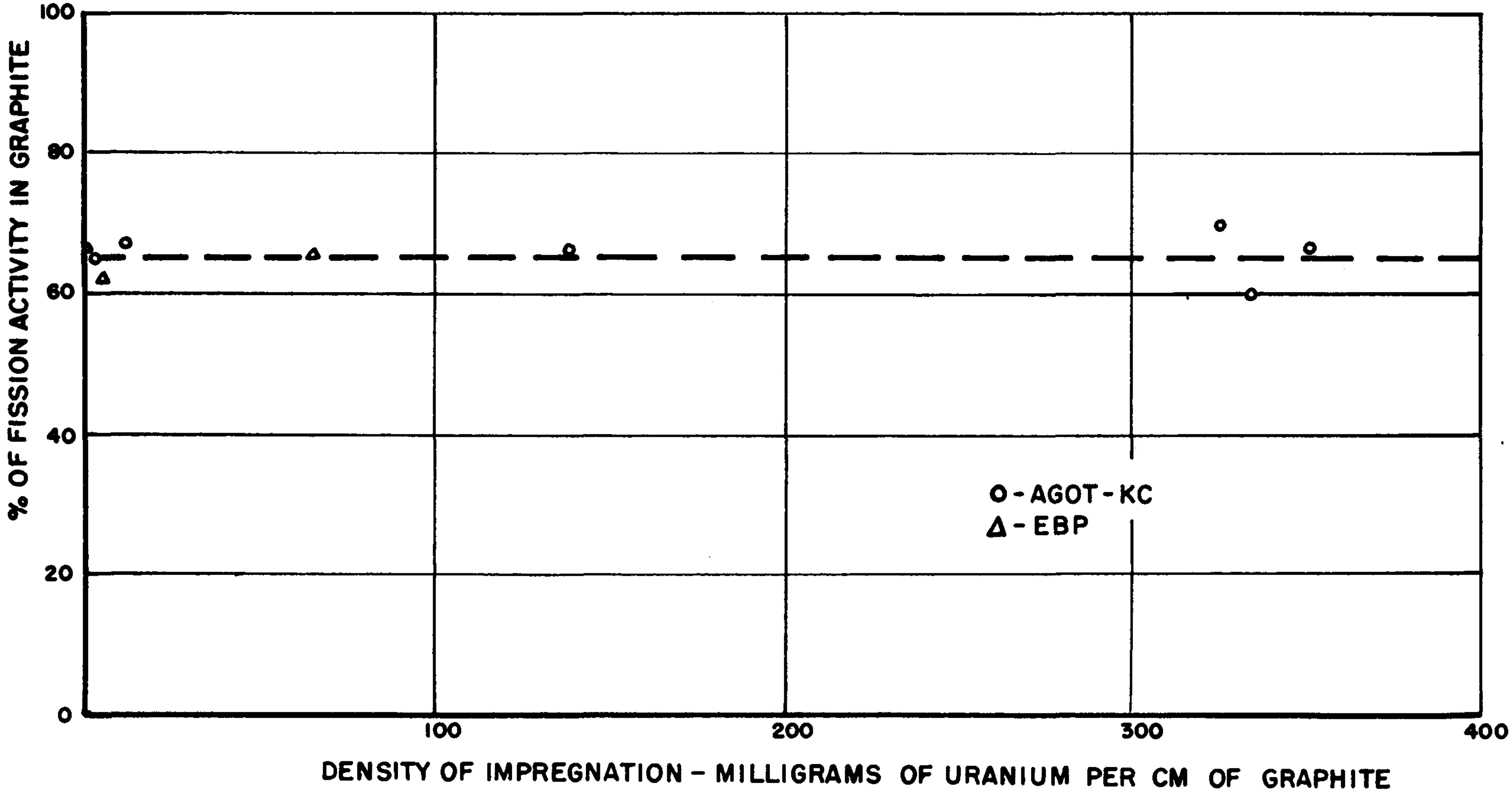

Figure 13. Percentage of the Fission Activity in the Graphite Crystallites as a Function of Density of Impregnation.

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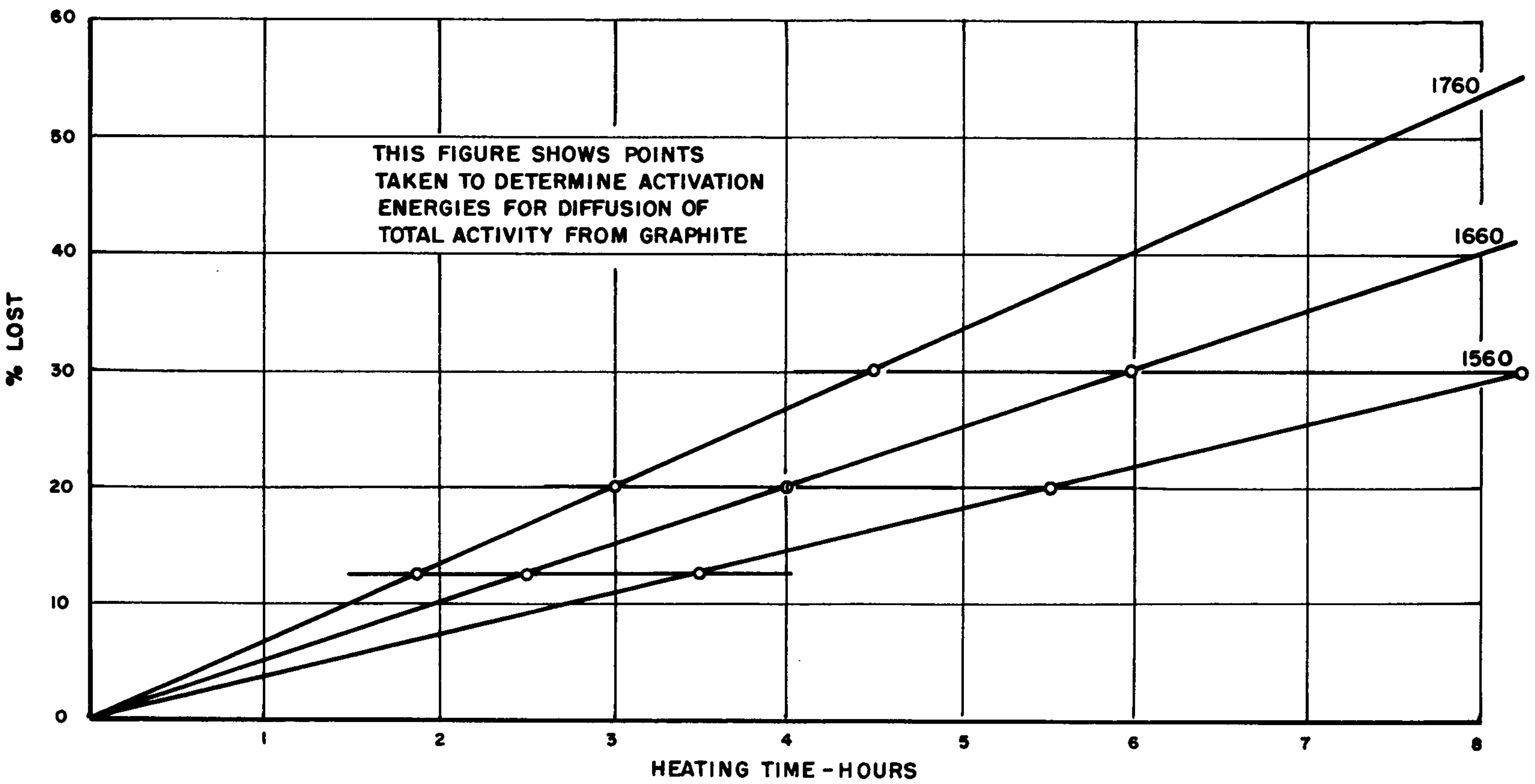

THIS FIGURE SHOWS POINTS TAKEN TO DETERMINE ACTIVATION ENERGIES FOR DIFFUSION OF TOTAL ACTIVITY FROM GRAPHITE

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Figure 14. Final Slopes of Diffusion Curves from Fig. 6 Refered to a Common Origin.

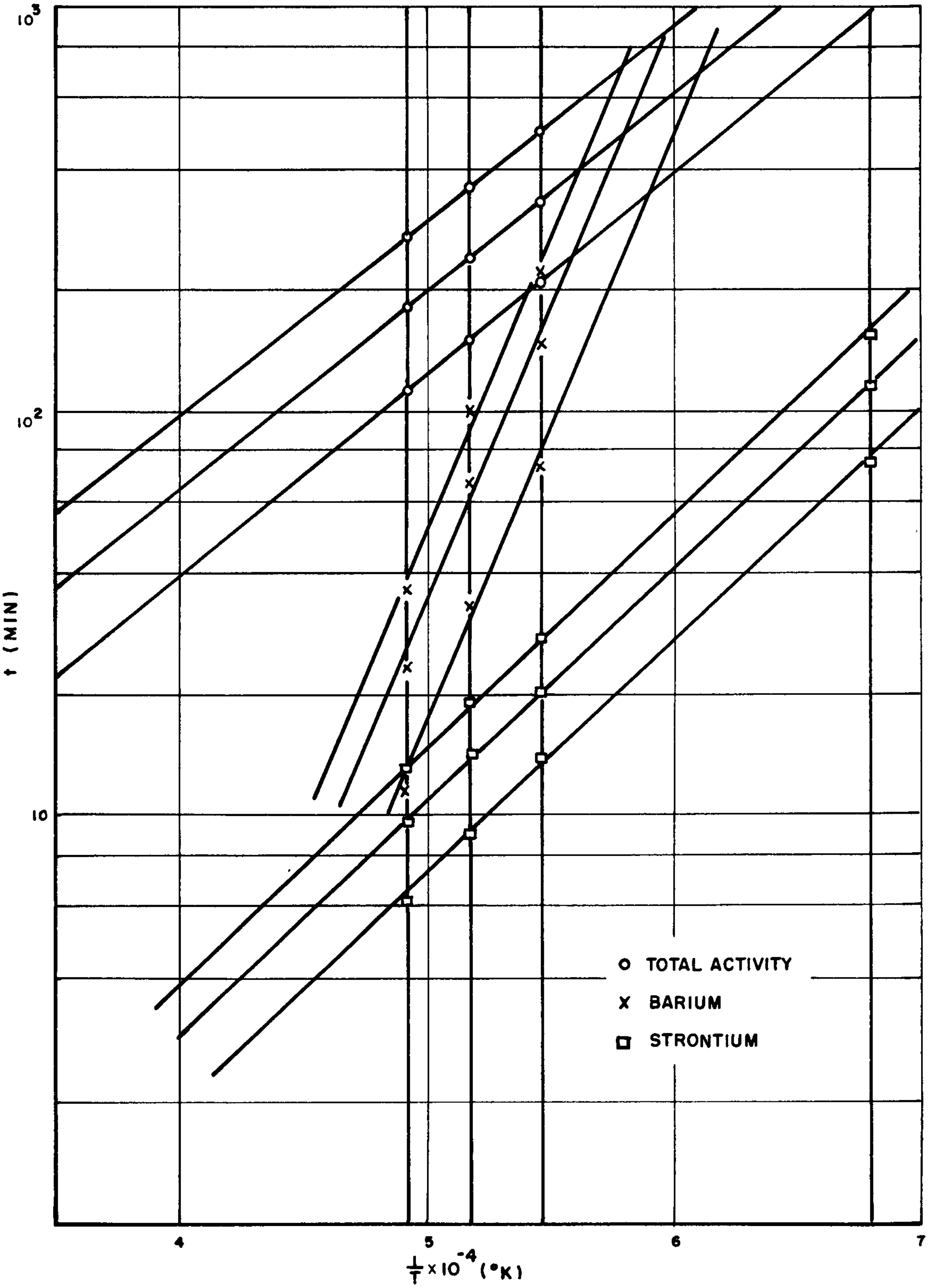

Figure 15. Semilogarithmic Plot of the Time for Diffusion of a Fixed Fraction of Activity vs 1/T, for Total Activity and for Barium and Strontium.

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