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10.1 THE THERMAL DIFFUSION OF FISSION PRODUCTS FROM URANIUM AND URANIUM OXIDE*

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ABSTRACT

The diffusion of fission products from sintered and cast U has been studied at 600° and 1000°C, and the diffusion from pressed U_3O_8 has been studied at 400°, 1000° and 1800°C. Rare gases, I and Te are the predominant elements diffusing from U_3O_8; 13.5 per cent of the rare gas diffuses in 3 hours at 1000°C. The diffusion from sintered metal is of the same order of magnitude as that from pressed U_3O_8.

Diffusion from cast U has been studied in more detail and found to be less in amount and primarily a surface process. In 60 hours at 1000°C diffusion varied from a negligible removal of Mo to a 9 per cent removal of Ce. Other elements were removed in intermediate per cents. The diffusion of rare gases at 600°C was approximately a tenth of that at 1000°C, while the diffusion of other elements was very much less. Data for the diffusion of Xe, I, Ba, Sr, Te, Mo, Np, Ce, La, Y and Pr are reported for a number of experiments, and the diffusion constants for these elements have been calculated at the experimental temperatures.

1. Introduction

When it was shown experimentally that a self-sustaining fission cycle could be attained with natural U as the supporting material, it became necessary to study the factors involved in the actual operation of such a cycle. The fission process heats the supporting pile to a temperature determined by the power generated and the method of heat removal. Early plans contemplated high-temperature piles using air or He cooling, and with such piles the diffusion of radioactive fission products into the gas

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stream, to be carried throughout the cooling system or into the atmosphere, was one of the most serious considerations.

This laboratory undertook the study of fission product diffusion with the realization that the urgent need of the data did not permit the attainment of either the utmost in analytical accuracy or the complete study of each active element produced in fission. The need was a practical one, and the experiments were devised primarily to meet that need. The experiments were performed over a period of several months and with such evolution of techniques that each experiment varied from the preceding ones. However, there are basic techniques which give the experiments a sense of unity and permit their consideration on a general basis. In this report the basic techniques are described fully, while variations in the individual experiments are only considered according to their importance in influencing the results. When these experiments were started, production of U metal had not yet been established and U_3O_8 and UO_2 were being considered for use in the piles. Later, sintered U and finally cast U became available for use. The experimental techniques of the diffusion experiments were improved substantially as the study shifted from U_3O_8 to sintered and then cast U.

2. Apparatus and Experimental Techniques

To determine the amount of fission product diffusion from a sample it was necessary either to collect the diffusing activities cumulatively or to measure their continuous rate of diffusion. The cumulative collection is much the simpler method of the two, and it was the technique first used in this study. With cumulative collection the sample was merely heated in a closed system in a manner that permitted the collection of the diffused material either in the gas phase or on the walls of the apparatus. To allow very rapid diffusion in the gas phase and to make the diffusion rate through the sample the controlling one in the process, the samples were heated in a vacuum. Condensable material in the diffusate deposited on the walls of the apparatus, and the noncondensable rare gases simply remained in the gas phase of the system.

Because of inherent limitations, the cumulative activity measurements did not give a satisfactory insight into the actual diffusion process. The total diffusate gas activity is controlled by two factors. It is

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increased by further diffusion of active gases and decreased by the decay of the activity already present. These factors could not be satisfactorily resolved to measure the actual rate of gas diffusion.

The "argon flow experiments" were devised to sweep the diffusing sample continuously with a constant, known flow of an inert gas. This gas served as a carrier to remove fission products from the neighborhood of the sample, and measuring the activity in a known volume of the gas at the exit end of the furnace permitted a continuous and accurate measure of the rate of rare gas diffusion.

In each case it was attempted to prevent chemical reaction of the sample to make the diffusion as nearly as possible a purely physical process. This attempt was not entirely successful, for in the early experiment with A flow, impurities in the gas reacted with the samples, and in the 1800°C vacuum experiment there was some thermal decomposition of the U_3O_8. In high-temperature experiments there was a tendency for the corners of the metal to react with the surfaces on which they rested.

Since only sub-micro amounts of radioactive fission products were involved, their behavior in diffusion could not be predicted with certainty. It was felt that the only fission products which would show gaseous characteristics were the rare gases and possibly the halogens. Consequently, the rare gases coming out of the furnace were always purified by passing them through a hot copper trap. The activity caught in this trap was primarily I. The other elements were expected to deposit on the cold walls of the furnace, react with the hot walls, or possible be caught in the trap.

2.1 <u>The Induction Furnace Apparatus</u>. The experimental apparatus used in the 1800°C diffusion experiment[1] is shown in Fig. 1. The heating was done in a 4-inch Pyrex tube "a", 2 ft long, placed inside the coil "b" of an induction furnace. This tube was closed at the bottom with a water-cooled brass plate "c" sealed to the glass with sealing wax. The top was all glass, conical with a flat view-window, and with a side arm sealed glass-to-glass to a tube of Corning 172 glass "d" containing Cu and leading through a cotton filled trap "e" to a Cenco megavac pump.

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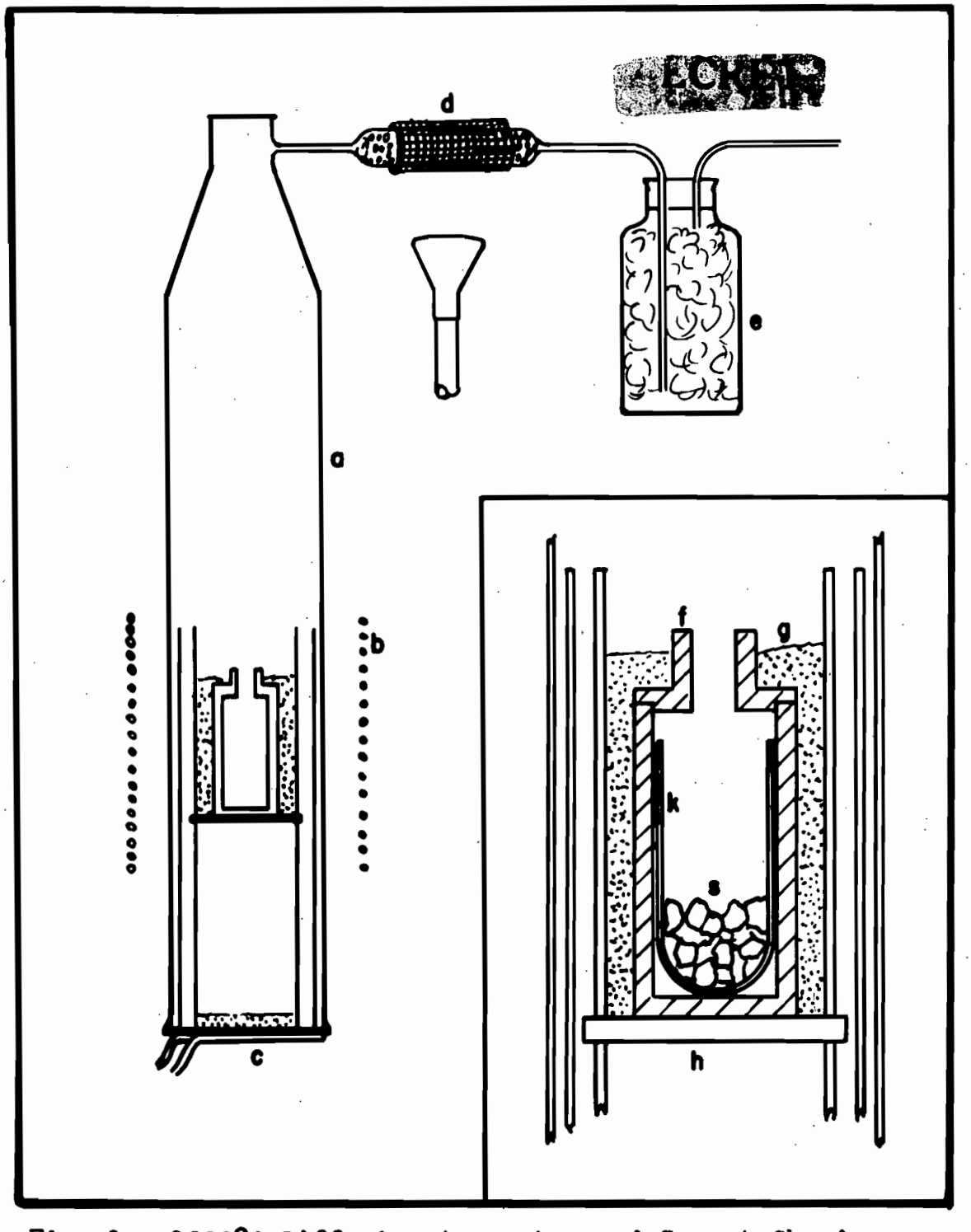

Fig. 1. 1800°C Diffusion Apparatus and Insert Showing Detailed Heating Arrangement.

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Standing inside the 4-in. tube on the bottom brass plate were two concentric quartz cylinders which served as radiation shields and as a support for the crucible. A layer of sea sand protected the brass from direct radiation. The beryllia crucible "k" which held the sample "s" was placed inside a special graphite crucible "f" which was insulated in BeO powder "g" and supported on a beryllia disc "h" resting on the bottom section of the inner quartz cylinder.

When the whole apparatus was assembled, it was evacuated, and the side tube containing Cu was heated by a wing top burner to a dull red heat. As the sample was heated, its temperature was measured through the sight-hole by means of an optical pyrometer. Gases driven off in this apparatus were not caught and their activity was not measured because no pump was available which would maintain the high vacuum required and also trap the gases. The analysis of the diffusate is described in section 5.1(a).

2.2 The Static Vacuum Diffusion Apparatus. The diagram in Fig. 2 shows the furnace arrangement for the closed system experiments[1]. Passing through the center of the resistance furnace "d" is the tube in which the sample was heated. This tube was either of glass or quartz, depending on the temperature to be maintained in the experiment. The 400°C experiment permitted Pyrex glass, the 600°C experiment required Corning 172 glass, and the 1000°C experiment required a quartz tube. The heating tube was 2-3 ft long and 1-2 in. in diameter and was heated over approximately the center half of its length. The ends of the tube were closed with water-cooled, waxed-on glass end caps "c". To the inlet end was sealed a small mercury bubbler "b" beyond which was a 200 ml glass bulb "a" shut off with a stopcock. This bulb was filled with A to be used in collecting the active gases.

To the exit end of the heating tube was sealed a Corning 172 glass tube "e" containing reduced Cu, and in turn, an aluminum finger-type Geiger-Mueller counter tube in a glass housing "f", a liquid air trap "g", and a connection to a vacuum pump. The counter tube was attached to a scaling circuit for a frequent measure of the gaseous activity. The pieces of sample were placed in a short tube smaller in diameter than the furnace tube and of the same material. This sample tube was inserted into the furnace tube to a position in the center of the furnace. Except for the

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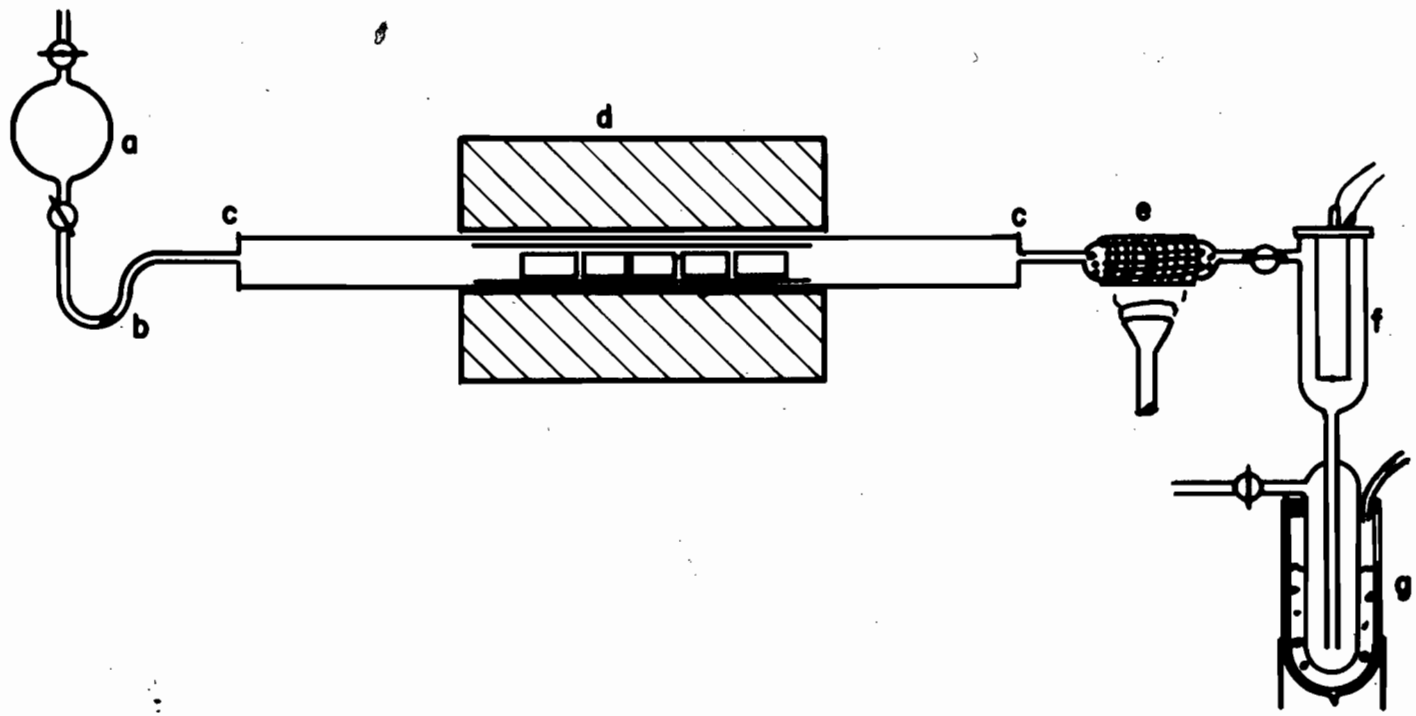

Fig. 2. Closed Vacuum Diffusion Apparatus.

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A bulb, the whole system was evacuated while cold and shut off from the vacuum pump. Since the pressure in the system was low, diffusion took place rapidly and the counter tube gave a measure of the activity in the gas phase. The heating was carried out, measuring the temperature by a chromel-alumel thermocouple; and finally, after the heating was completed, the liquid air trap was immersed in a Dewar of liquid N_2 which was evacuated to about 30 mm. The A in the bulb was bubbled slowly into the system to displace the active gases and condense them in the trap. When this was completed, the counter tube and liquid air trap were sealed off from the furnace tube and taken to the counter room for activity measurements.

The furnace tube and the sample tube were removed and washed with 1N HNO_3 to remove diffused material, and this wash solution was analyzed for fission activities according to the procedure in section 3.

2.3 <u>The Diffusion Apparatus for Continuous A Sweeping</u>. The experiments with continuous A sweeping were carried out in the apparatus[(2)(3)] basically diagrammed in Fig. 3. Heating was obtained by a small resistance furnace "e" 9 inches long, fitted with a tube 14 in. long and 1 in. diameter, of quartz for the 1000°C furnace and Corning 172 glass for the 600°C furnace. The ends of the heating tubes were closed by glass end-pieces "d" sealed with water-cooled wax seals, except for the exit from the Corning 172 tube, which was sealed glass-to-glass. To the exit tube from the furnace, a 10 mm tube "f" of Corning 172 glass containing reduced Cu was attached for removal of halogens from the gas stream. The "halogen trap" tube was sealed to a three-way "Y" stopcock connected to two counter chambers "g". The counter tubes themselves were protected inside lead boxes "h" with 2 in. thick walls. One of the counter tubes in each lead box was used to check the background while the other was used for measuring the activity of the gas. During the experiment the flow of gas could be switched at any time from the counting tube to the background tube and the former replaced by a new tube if it became defective.

On the inlet side of the furnace was an A supply with a constant pressure release "a" containing concentrated H_2SO_4. Tank A (99.6 per cent pure) was passed through a drying tube "b" containing Dessichlora and, in early experiments, directly to the furnace tube. After it was found that

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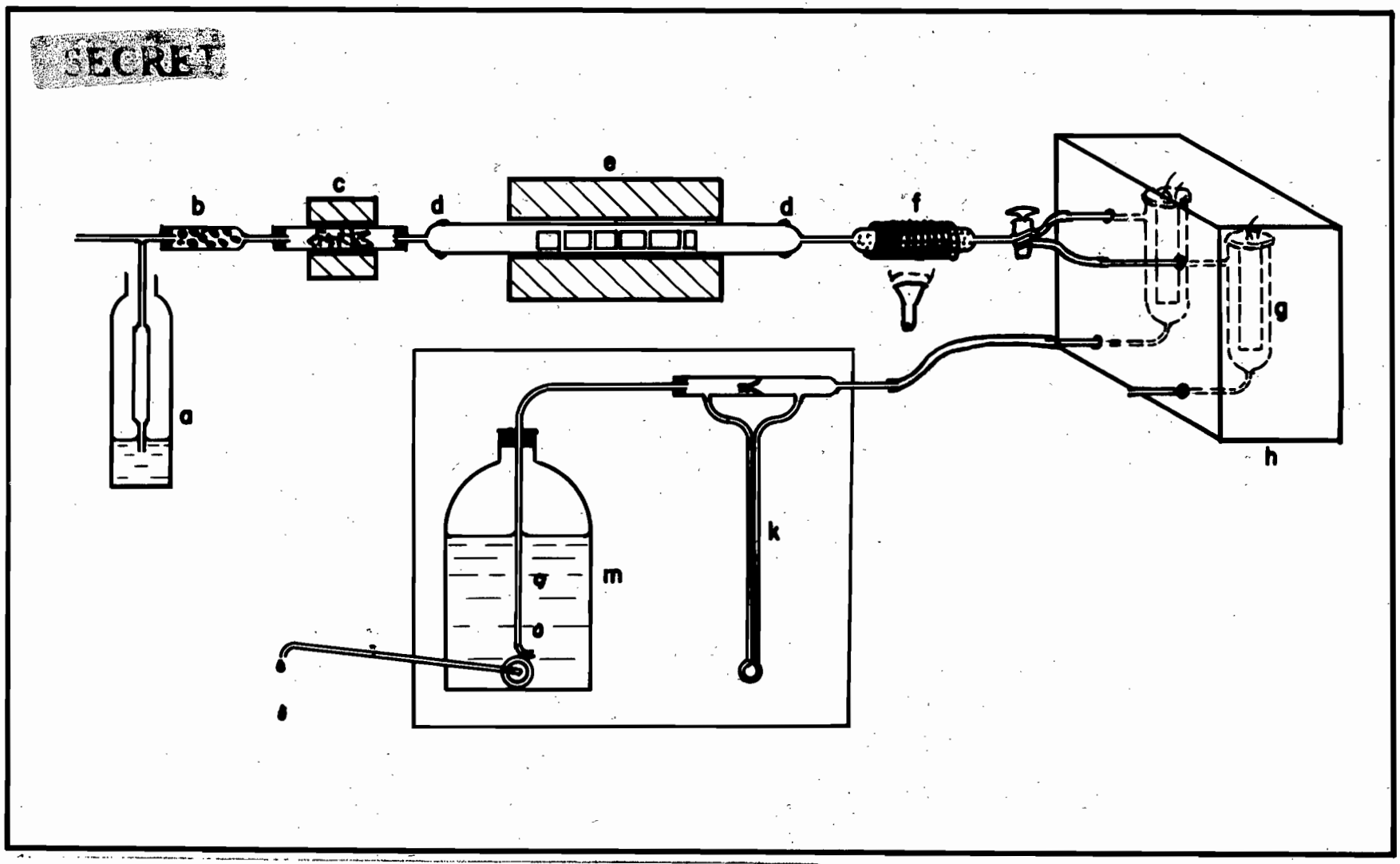

Fig. 3. Argon Flow Diffusion Apparatus.

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the small amount of O_2 and other impurities which the A contained attacked the metal samples during the diffusion experiments, the A was further purified by passing it through a "getter" tube "c" of Corning 172 glass containing freshly cleaned small pieces of U metal heated to 700°C.

The flow of gas through the diffusion apparatus was maintained at 3 ml/min as nearly constant as possible. Hourly measurements of volume and rate of flow were made, gauging the gas volume by the water displaced from a Mariotte flask "m" and the rate of flow by the pressure drop across a capillary-type gas flowmeter "k". The pressure drop was measured by an oil-filled manometer. At first the Mariotte flask and the flowmeter were simply at room temperature, but in subsequent experiments they were thermostatted at 24.7°C in an air thermostat to maintain a more uniform rate of gas flow. Counter tubes were connected to the counter by a multiple choice switch, and the activities of the gases and backgrounds were measured about twice each hour. The furnaces were maintained at 600°-615°C and 1000°-1020°C by manual control of Variac transformers. The temperatures were measured by chromel-alumel thermocouples connected to a Leeds and Northrup potentiometer.

At the end of the heating period the furnaces were cooled, the furnace tube and sample tube were washed out (section 3), and the activities were analyzed and measured. The gaseous activity was measured continuously, so there was no diffusate gas sample to save.

3. The Chemical Separation of Activities

There are three activity measurements, any two of which theoretically facilitate the determination of the amount of diffusion occurring in an experiment. They are the measurements of the activity in the original sample, the diffusate, and the residue sample. Actually in these experiments the per cent diffusion was so small and the non-homogeneity of the samples so great that the difference between original and residue was not a significant one. As a result, "original", "diffusate", and "residue" samples were all analyzed.

The calculation of per cent diffusion based on the activities separated from the diffusate has several limitations which must be considered. Since the activities of the diffusates were low, it was impossible to take

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aliquots for the determination of elemental activities. The entire diffusate had to be used, and the separate activities determined by means of a schematic analysis. The second thing to be considered was the fact that the diffusate activities were deposited over a considerable area in the apparatus, possibly in a form in which their solution would be difficult or impossible.

The elements normally separated from a sample for activity measurements were Sr, Y, Zr, Mo, Te, I, Xe, Ba, La, Ce, Np, and Th for reasons given in section 4. Normally the following carriers for the above elements were used from stock solutions: 20 mg each of Sr, Y, Zr, Ba, La, and Ce as nitrates in HNO_3 solutions; 10 mg I as KI in water; 30 mg each of Mo and Te in HNO_3 solutions.

Since I showed such a significant activity in the diffusate, its retention was important. Accordingly, the furnace tube was first scrubbed with 100 ml of 1N HNO_3 with normal carriers added. The scrubbing was with a rubber policeman on a long glass rod, and the 100 ml were divided among 6 portions. This solution was handled separately for the recovery of I, while in later experiments the furnace tube was washed further with aqua regia to remove activities, particularly Te, which were found to be incompletely removed by the 1N HNO_3. The aqua regia washings were added to the HNO_3 solution after removing the I.

When equilibrium between active isotopes and inactive carrier has been reached before separation processes start, the per cent of added carrier that is mounted is the per cent recovery of an activity. In these experiments it was assumed that such an equilibrium was reached. When no carrier recovery could be measured as with Xe and Np, 100 per cent chemical recovery was assumed.

3.1 <u>The Schematic Separation of Activities</u>[4].

(a) In the case of the diffusate all activities but Xe were recovered from one solution. The separation scheme which this required was adopted as "basic" for all analyses except when modifications were necessary. First the sample was taken into solution in HNO_3, with or without carriers added. If the carriers were not present in the dissolving acid, they were added as soon as possible after solution. The solution was allowed to stand or digest for a few minutes to reach equilibrium between the active

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isotopes and their inactive carriers, and after this the analysis was begun with the assumption that the amount of carrier recovered would correspond to the per cent of activity recovered.

(b) Iodine was separated by oxidizing the iodide in the acid aqueous solution with $NaNO_2$ and extracting the free I produced with CCl_4 in a separatory funnel. After several extractions the I was in turn removed from the CCl_4 solution by shaking it with $NaHSO_3$ solution. The $NaHSO_3$ solution was acidified with HNO_3, boiled to remove SO_2, and the I precipitated as AgI by the addition of a slight excess of $AgNO_3$ solution. The precipitate was filtered on a small, weighed filter paper in a Gooch crucible, dried at 100°C, weighed, and mounted for activity measurements according to the description in section 4.

(c) More than one gram of U interfered with the rest of the separation. If more was present, as in the original and residue samples, it was removed by ether extraction. The solution was evaporated with HNO_3 to the point where $UO_2(NO_3)_2 \cdot 6\ H_2O$ solidified upon cooling. The cool solid residue was then extracted with ether, usually in a beaker. The upper ether solution of $UO_2(NO_3)_2$ was poured off and set aside, while carriers remained in the residue. A second extraction or wash could be made if necessary.

(d) The residue or aqueous fraction was treated with about 15 ml of concentrated HNO_3 and 10 ml of water. The beaker was heated to dissolve the carriers, and the solution was evaporated to about 10 ml, or until the granular precipitate of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ barely began to form. The solution was cooled, treated with an equal voluem of fuming HNO_3, and the precipitation of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ was allowed 30 minutes to reach completion. The time of this precipitation was recorded. The precipitated nitrates were centrifuged from the rest of the solution, the clear supernatant decanted and saved, and the solid washed with 15 ml of 85 per cent HNO_3. The insoluble nitrates contained Ba and Sr, and the combined clear solution contained the remaining activities.

A number of techniques were used for isolating pure Ba and pure Sr activities. Several of the early schemes were not very successful, and in the determined effort to secure pure activities, there was a tendency to use "every separation in the book". Sulfate, carbonate, chloride, and nitrate precipitations of Ba and Sr together were tried, as well as

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chloride and chromate separations of Ba from Sr. Summarized very briefly, the sulfate precipitation was found to be ineffective; the nitrate precipitation was good, but sometimes carried down Ce, Sb, and Te activities. The precipitation of $BaCl_2$ in HCl - ether freed Ba of all activities but Sr, and the carbonate precipitated Ba and Sr well, but to be useful had to be preceded by a scavenger precipitation for the removal of hydroxide-insoluble materials. In this report no detailed account can be given of the Ba-Sr procedures used in each experiment, for in the beginning they varied with each experiment and sometimes with each sample. What are given are the steps which were found to be most effective in producing separations. Other steps, if used, were superfluous.

The $Ba(NO_3)_2$-$Sr(NO_3)_2$ precipitate from the fuming HNO_3 was treated in the centrifuge tube with hot water until soluble nitrates had gone into solution. Any insoluble material was centrifuged down, and the clear nitrates were decanted to a beaker. This simple solution in water left most of the Te and Sb in the insoluble fraction. Several mg of $Fe(NO_3)_3$ were added to the solution, and an excess of NH_4OH was added to precipitate hydroxide-insoluble metals. This removed all rare earths, Th, Y, Zr, La, U, and possibly more Sb and Te. The hydroxides were filtered off and washed, and an excess of $(NH_4)_2CO_3$ was added to the filtrate to precipitate $BaCO_3$ and $SrCO_3$. This precipitate contained rather pure activities.

The mixed carbonates were dissolved in a minimum of dilute HCl after which the solution was neutralized and made barely acid with 2 drops of HCl. The solution was heated and treated with an excess of $(NH_4)_2Cr_2O_7$ followed by $NH_4C_2H_3O_2$. Barium chromate was precipitated. After 30 minutes standing it was centrifuged, the supernatant strontium fraction poured off and saved, the $BaCrO_4$ redissolved in a few drops of hot HCl and reprecipitated by $(NH_4)_2Cr_2O_7$ and $NH_4C_2H_3O_2$. After double precipitation the $BaCrO_4$ contained less than 1 per cent of the Sr activity. The combined supernatant fractions were treated with 2 mg of Ba carrier, several mg of $Fe(NO_3)_3$, and NH_4OH to remove $BaCrO_4$ and insoluble hydroxides. After this scavenger precipitate was filtered off, an excess of $(NH_4)_2CO_3$ was added to precipitate $SrCO_3$. Both $BaCrO_4$ and $SrCO_3$ were filtered on small filter papers in a Gooch crucible, dried at 110°C, and mounted for activity determination in yields of 70-90 per cent.

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(e) The combined centrifugate and washings from the funing HNO_3 separation of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ were in early experiments evaporated to dryness with HCl, but in later experiments more satisfactorily brought down to fuming with a few ml of H_2SO_4 to remove HNO_3. The solution was diluted, brought to a pH of 1, and treated with H_2S to precipitate Te and MoS_3. The sulfide precipitate was filtered on a fine sintered glass crucible, and the filtrate was saved for the determination of other activities. The sulfides were dissolved in aqua regia and evaporated to dryness with HCl several times to remove nitrates.

The residue was dissolved in 15 ml of concentrated HCl; and 25 ml saturated SO_2 water and 1 ml hydrazine hydrate or equivalent of hydrazine hydrochloride were added. The solution was digested just below the boiling point for 10 minutes, and the Te precipitate was filtered off on a small paper filter disc in a Gooch crucible, dried, weighed, and mounted for activity measurements in yields of 70-90 per cent.

(f) The filtrate from the Te was treated with 5 ml of concentrated HNO_3 and boiled 20-30 minutes to oxidize all of the Mo to molybdate, the solution volume being maintained at 75 ml. The solution was cooled to ice temperature and treated with 5 ml of concentrated H_2SO_4 and an excess of α-benzoin oxime solution in 95 per cent ethyl alcohol. The precipitate was allowed to form for several minutes, after which time the solution was treated with 3 ml of saturated bromine water to insure the complete oxidation to molybdate. The precipitate was filtered, washed, and ignited to MoO_3 at 500°-525°C. The weighed sample of MoO_3 was mounted for activity measurement with 50-90 per cent yields.

(g) The filtrate from the original H_2S precipitation of Te and Mo was evaporated to a volume of 25 ml, neutralized with concentrated NH_4OH, and made 6N in HF with 27N HF to precipitate Ce, La, Th, Y, and Np fluorides. These were separated by centrifugation in a Lusteroid tube, and the supernatant liquor containing Zr and U was decanted off. The decanted liquid was treated with 2 ml of concentrated H_2SO_4 and taken to fumes of SO_3, diluted to 50 ml and made up to 20 per cent H_2SO_4 by weight. $ZrO(H_2PO_4)_2$ was precipitated by the addition of a twenty-fold excess of a 6 per cent $(NH_4)_2H_2PO_4$ solution. After an hour's standing, the precipitate was

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filtered, washed with 2-5 per cent NH_4NO_3 solution, ignited to $Zr_2P_2O_7$ at 800°-900°C, and a weighed sample was mounted.

In the 600°C and 1000°C diffusion experiments with cast U, Zr was separated by precipitation and re-precipitation with cupferron followed by ignition to ZrO_2 for weighing. The yield was 50-90 per cent.

(h) The fluoride precipitate of Ce, La, Th, Y, and Np was treated with 2 ml of H_2SO_4 in a platinum dish, heated to persistent fumes of SO_3, cooled, and diluted carefully to 2N H_2SO_4. This solution was treated with an equal volume of saturated $K_2S_2O_8$ solution and 1 mg of Ag^+ added for each ml of solution. After standing an hour in the dark to oxidize Np, the solution was treated with 27N HF to make it 3-6N in HF. The fluorides of Ce, La, Th, and Y were precipitated, leaving Np in the oxidized state in solution. The precipitate was centrifuged down in a lusteroid tube, and the supernatant solution was decanted into a platinum dish and fumed off with several ml of H_2SO_4. The H_2SO_4 was diluted with water and treated with SO_2 to reduce Np, and the Np was precipitated with HF after the addition of 5-10 mg of La carrier. In some experiments the oxidation-reduction-precipitation cycle was repeated to check the complete separation and recovery of the Np.

(i) The Ce, La, Y, and Th fluorides from the previous separation were washed into a platinum dish and fumed with 2 ml H_2SO_4 to remove HF, cooled, diluted with water, and made ammoniacal to precipitate Ce, La, Y, and Th hydroxides. The precipitates were centrifuged and washed with dilute NH_4OH, dissolved in 25 ml of 1:3 HNO_3 and treated with H_2O_2 to reduce Ce. The solution was boiled a few minutes to remove H_2O_2, cooled, and treated slowly with 10 ml of 10 per cent KIO_3 solution in 1:3 HNO_3. The $TH(IO_3)_4$ precipitate was allowed to stand a short time, centrifuged, and washed with the precipitating solution. The supernatant liquor was saved. The $Th(IO_3)_4$ was dissolved in 5-10 ml of saturated SO_2 solution diluted to 50 ml, and $Th(OH)_4$ was precipitated with NH_4OH, filtered, washed, ignited, and mounted for measurement as ThO_2.

(j) The centrifugate from the first $Th(IO_3)_4$ precipitation was treated with 10 mg of Th scavenger solution, and the precipitated $Th(IO_3)_4$ centrifuged off. The cerous ion in the centrifugate was oxidized by the slow addition of 5 ml of hot, 6 per cent $KBrO_3$ solution, and the precipitated

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$Ce(IO_3)_4$ was separated by centrifugation and washing with the solution of 10 per cent KIO_3 in 1:3 nitric acid. The pure $Ce(IO_3)_4$ was dissolved in H_2SO_3 and the Ce reprecipitated as hydroxide, filtered, ignited, and weighed as CeO_2 in 80-90 per cent yields.

(k) Lanthanum, praseodymium, and yttrium hydroxides were precipitated by the addition of NH_4OH to the centrifugate from the $Ce(IO_3)_4$ precipitation. The hydroxides were filtered, washed, and ignited to the oxides. They were mounted together for activity measurements, as the difficulty of further separation was not normally justified. Yields were 80-90 per cent.

3.2 The Analysis of Original and Residue Samples. The original and residue samples were analyzed by the same procedure, one which followed as nearly as possible the schematic analysis of the diffusate. The samples were cut from the bombarded blocks of U_3O_8 or U metal and were dissolved in HNO_3, with a small amount of HCl added to catalyze the solution of the metal. The solution process caused the loss of active I, which was determined by another, direct analysis. All other carriers were added as soon as the sample was in solution. With original and residue samples it was always necessary to remove U by ether extraction.

Since Np activity had to be separated as tracer, with no way of calculating yield, it was more satisfactory and accurate to take a separate sample for this activity alone and make a direct separation of Np. After solution of the sample in HNO_3, the same oxidation-reduction-precipitation cycle was used for the direct separation as was used in the schematic separation. Much better checks were obtained in the direct determination of Np than were obtained in the schematic analysis.

3.3 The Direct Separation of Rare Gases and Iodine. The determination of rare gas and I activities[4] in U and U_3O_8 samples was carried out in the apparatus shown in Fig. 4. A weighed 2 g sample of U or U_3O_8 and 20 mg of iodide carrier were placed in the distillation flask "a". The absorption apparatus was set up and CO_2 swept through for 30 minutes (with the eudiometer liquid in the leveling bulb) to remove air. The eudiometer tube was then filled with 50 per cent KOH, and CO_2 was passed through the system for several more minutes. After the bubbles had been tested to

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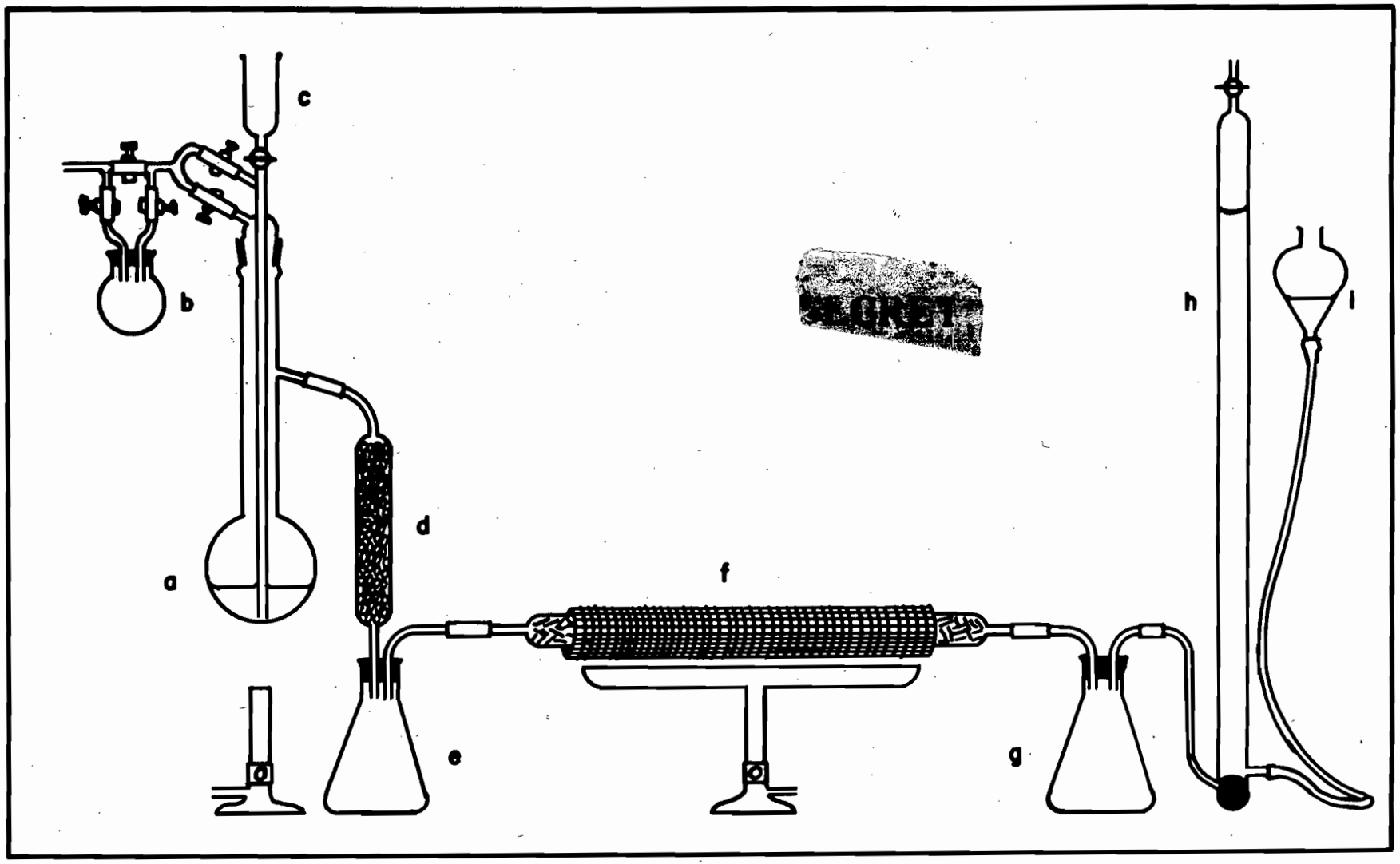

Fig. 4. Apparatus for the Collection of Rare Gases and Iodine.

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insure removal of air, the CO_2 flow was stopped and about 50 ml of hot 92 per cent H_3PO_4 were run into the flask from the dropping funnel "c". The flask was then heated moderately, and as the sample dissolved, the rare gases, I, H_2, and a small amount of Te passed into the absorption train. Iodine and tellurium were absorbed in "d", a glass-bead filled tower wet with saturated $NaHSO_3$ solution. The H_2 was converted to water in the CuO-filled combustion tube "f" and condensed in the trap "g", and the rare gas activity was collected in the eudiometer "h" together with a small amount of other gases. After the solution was complete, CO_2 was passed through the apparatus for 30 minutes, the air in reservoir "b" was swept through, the CO_2 flow was stopped, and the eudiometer was disconnected. The active gas was transferred through a short rubber connection at the top of the eudiometer to an evacuated bulb which was connected to a counting chamber. The stopcock connecting the bulb to the counting chamber was opened after the gas had been quantitatively transferred to the bulb.

About 0.5 ml of 30 per cent H_2O_2 were added to the dissolving flask through the dropping funnel, and the remaining I immediately distilled into the absorption tower. The tower was washed with water, then with 5 per cent HNO_3 solution containing some $NaHSO_3$, and the solutions were transferred to a separatory funnel and made 1N with HNO_3. A few drops of saturated $NaNO_2$ solution were added, and the liberated I was extracted with three 20 ml batches of CCl_4. These extracts were combined, washed twice with 5 ml portions of water, and the I re-extracted with 50 ml of dilute $NaHSO_3$ solution and two 10 ml portions of water. The extract was acidified with 1 ml of 6N H_2SO_4, boiled, and treated with 1 ml of 0.1N $AgNO_3$. The precipitated AgI was filtered, washed, dried, and mounted. Yields of 70-95 per cent were usual.

4. Activity Measurements and their Interpretation

When these experiments were run, only the more important fission products, from the standpoint of fission yield and measureable half-life, were known. While activities of every element except In from Se to Pr are now known to be produced in U fission, early experiments in this laboratory

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indicated that, of the elements Br, Kr, Rb, Sr, Y, Zr, Cb, Mo, 43, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Ce, and Np, only the activities of Kr, Sr, Y, Zr, Mo, Te, I, Xe, Ba, La, Ce, and Np were readily separable schematically and measurable several days after a 100 μah neutron bombardment. These latter elements were given primary consideration in the diffusion experiments. The elements Ru, Rh, Pd, Ag, Cd, In, and Sn were omitted from study because, at the time these experiments were done, they were reported being formed only by fast neutrons. The activities of Cb, 43, Sb, and Cs were found but normally not isolated because they were minor ones and not readily handled in the schematic analysis.

In several experiments Mo and Sb were precipitated together, and normally La, Y, and Pr were precipitated together without further separation. With these exceptions, the activities measured were rather pure. Other activities were simply lost in the chemical separation.

Carrier samples isolated for activity measurements were mounted in onionskin paper packets. A weighed sample of the activity-bearing carrier was spread over a circular area 1 in. in diameter in the center of a 4 x 6 in. sheet of onionskin paper. The sample was carefully stuck into place with either a large gummed label or Scotch tape, and the four edges of the onionskin paper were folded up across the back of the label and stuck in place with another identifying label. The folded edges were spaced so the packet fitted snugly inside the sample holder of a modified Lauritsen electroscope. The one thickness of onionskin paper between the sample and the electroscope gave uniform results with only a small amount of absorption in the paper. All solid samples were mounted as described, for activity measurements on the modified Lauritsen electroscope. The measured activities of solid samples were expressed as divisions per minute (div/min). Gaseous activities were measured on an aluminum finger-type Geiger-Mueller counter tube connected to a scaling circuit of the type produced at that time by the Instrument Division, Chicago. Gaseous activities were expressed as counts per minute (c/min). The background activities of the electroscopes and Geiger-Mueller counters were checked as frequently as possible during measurements. They varied from 0.1-0.4 div/min and from 30-60 c/min, but variations were usually slow,

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and the estimated background was usually correct within ± 10-20 per cent.

All calculations of per cent diffusion in an experiment were based on chosen activities measured at the same time after bombardment. If a chosen activity could not be measured pure at the desired time because of other interfering activities, but could be extrapolated by growth or decay relationships from a measurement at another time, this was done. Calculations were based on specific activities, corrected to 100 per cent chemical recovery.

The complication of the calculations by the presence of secondary activities can be understood when one remembers that in some cases an activity found in the diffusate may have been produced there by the decay of a parent element which itself diffused. The calcualtion of per cent diffusion necessitated knowing the amount of an activity in the sample at the time of diffusion and the amount of that activity which diffused out during the experiment. The considerations given below for each element illustrate the problem.

4.1 Rare Gases. The activities of Kr and Xe could not be separated; they consisted of 3h and 4.6h kryptons and 9.4h and 5.3d xenons. The Kr activities can be considered to behave as primary activities, while the 9.4h Xe is the daughter of 6.6h I, and the 5.3d Xe is the daughter of 22h I. The Kr activities were not of sufficiently long life to last to the completion of the experiment, and in addition, the 3h Kr decayed to a 17m Rb which collected on the counter walls and interfered with activity measurements and interpretation.

Thus it was necessary to rely on Xe activities for measurement. The 5.3d Xe not only has a weak radiation, but is also produced by its 22h I parent for a number of days after bombardment. The 9.4h Xe is produced in good yield and has a strong β-ray, and its parent has decayed to about 1 per cent of its original activity 36-40 hours after bombardment. Thus, except for some 5.3d Xe interference, for which a correction can be made, the rare gas activity is practically a linear function with time on the semi-log paper. Except for early experiments, calculations of rare gas diffusion were based on 9.4h Xe activity in the period more than 40 hours after bombardment.

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4.2 I. Three I half-lives were observed: 2.4h, 22h, and 8d. The 2.4h I is the daughter of 77h Te; the 8d I is the daughter of a 30h Te; while the 22h I has a short-lived parent so that by 30 hours after bombardment no further 22h I is being formed in the sample. Theoretically then, the diffusion calculations should be based on the 22h activity, with the 8d activity subtracted. Actually, the iodide precipitate retained the 5.3d Xe daughter of 22h I, and it took six weeks to establish the 8d background. As a result the calculations were based on total I activities measured as soon as the 2.4h half-life had disappeared and as high on the 22h line as possible.

4.3 Te. The principal Te half-lives were 77h, 30h, 32d, and 90d, all of which can be considered as primary fission products. The measurement was complicated by the retention in the precipitate of the 8d I daughter of the 30h Te. If separation and precipitation of Te were made more than 2-3 days after bombardment, the 30h Te activity was small and a practically pure 77h decay was obtained. The activities upon which calculations were based were those of 77h Te in equilibrium with its 2.4h I daughter.

4.4 Mo and Sb. The 67h Mo and 93h Sb activities are both produced directly in fission. The Mo, which is about 50 times as active as the Sb, has a 6.1h "43" daughter with a weak β-ray, and calculations of Mo diffusion are based on the equilibrium mixture of these two. When Sb was included, it was precipitated and measured with Mo as the sulfide. Otherwise, it was eliminated in the chemical separations.

4.5 Ba. The 12.5d Ba activity was the only activity measured. Produced directly in fission, it was measured in equilibrium with its 40h La daughter.

4.6 Sr. More than a day and less than 7 months after bombardment, the only measurable radio-strontiums are the 10h and 55d activities. Both are primary fission products, 10h Sr being the parent of 57d Y. As a result, separations were preferred after the 10h Sr had decayed, and measurements were based on 55d Sr activity.

4.7 Ce. The 33h, 28d, and 300d Ce isotopes can all be considered primary fission products. The 33h Ce decays to a 13.5d Pr. The activities were total measured activities extrapolated to the same time after bombardment.

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4.8 La, Y, and Pr. The 40h La, the only isotope with long enough half-life to be determined, is produced entirely as a daughter of 12.5d Ba, and its activity calculations are dependent upon that relationship. Its activity in the diffusate was the sum of the La that had diffused plus that which grew from the Ba which diffused. Actually the 40h activities were so low by the time the analyses were complete that the calculations had no significance, and so were not used. Yttrium showed two activities, an 11h activity from a short-lived parent, decaying to 65d Zr, and a 57d daughter of 10h Sr. Separations were not usually complete soon enough after bombardment to measure the 11h Y, so the important Y activity was of 57d half-life. The 13.5d Pr daughter of 33h Ce was the only Pr activity measured. In practice, total La, Y, and Pr activities were measured together because it was felt the difficulty of their further separation was not justified. The total activities were compared at the same time after bombardment.

4.9 Zr. Zirconium activities are primarily the 65d Zr (growing from an 11h Y and decaying to a 35d Cb) and the 17h Zr, a primary fission product which decays to a 75m Cb. Whenever the separation could be made in time, the 17h activity in equilibrium with its 75m daughter was used for calculation. Otherwise, the total activity was taken with comparisons the same time after bombardment.

4.10 The Diffusate Active Gases. The diffusate active gases were measured by two techniques. In the static vacuum experiment the gases were merely caught in the system, and at the end of the experiment they were swept out with A and condensed in a reduced-pressure liquid N_2 trap (see section 2.2). Thus caught, the activity was sealed off from the furnace in a system whose volume had been previously measured. Of the total volume of gas, only a volume of about 37 ml in the counter chamber itself was in a position to be counted, and that counting was with a geometric efficiency of about 25 per cent, neglecting absorption in the counter walls. The quantity $\frac{37 \times 0.25 \times 100}{\text{total gas volume in ml}}$ is analogous to the "per cent recovery" with the solid samples.

The total gaseous diffusate activity in the continuous A-swept diffusion experiment required a different method of calculation. The gas flow was 3 ml/min, and the counter chamber was 37 ml in volume. It can be

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assumed that on the average a change in gas content of the counter chamber occurred every 37/3 or 12.3 minutes. By plotting counting rate as a function of time and summing the activities at 12.3 minute intervals, the total activity actually passing through the chamber could be measured. However, in order to calculate the per cent diffusion of the Xe all measurements must either be made at the same time, or extrapolated to the same time. Thus, each of these interval activities (a 12.5 minute interval was chosen because it was within the limit of accuracy, and more convenient) was extrapolated on a 9.4h decay line to a chosen time. The summation of these extrapolated activities represented the total diffusate Xe activity at that time, and this value was compared with the original Xe activity at the same time to obtain per cent diffusion.

5. Experimental Results

5.1 The Diffusion of Fission Products from U_3O_8[1]. The U_3O_8 used in these experiments consisted of 1/2 x 1/2 x 2 inch blocks of pressed powder weighing about 50 g each, and two 3 in. cylinders weighing 1800 g each. These blocks had been exposed behind paraffin to the slow neutrons from a 100 μah bombardment at the Chicago cyclotron July 28, 1942. The exact arrangement of the blocks is uncertain. The bombardment was not uniform, and the activity of the pieces varied by a factor of two.

(a) Diffusion at 1800°C. In this experiment the sample, weighing 85.50 g, consisted of two blocks of U_3O_8 which had been broken into coarse pieces. The experiment was carried out in the induction furnace apparatus described under section 2.1. The temperature of the crucible was brought rapidly to 900°C and then slowly to 1000°C, where it was held for a time to avoid too rapid evolution of oxygen from the sample. The temperature was raised gradually through short intervals until it had passed 1400°C, and then it was raised rapidly to 1800°C, where it was held for 15 minutes. The walls of the glass cylinder above the crucible were covered with a thin smoky deposit, and the Cu in the side tube was partially oxidized. The apparatus was cooled, and the 4-in. glass cylinder was scoured with 100 ml of 1N HNO_3 in six portions to give a solution containing the diffusate activities.

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The hot Cu trap was found to contain strong I activity, less intense in the strongly heated center portion. No original analyses were made, but the total fission product activity in the original was determined by measuring the specific activity of the bombarded material and subtracting the specific activity of unbombarded U_3O_8. Thus the per cent diffusion of each element could not be calculated, but only the fraction of total activity which ended in the particular diffusate fraction. The diffusate washings were analyzed by a procedure different from that finally used extensively. Although the following procedure was used for all of the experiments with U_3O_8 and sintered U, it was never made to work satisfactorily, and the results of the analyses can only be considered to indicate the order of magnitude of the diffusion. The examinations were as follows:

(1) A 1 ml aliquot was evaporated to dryness and its activity determined. This represented the activity condensed on the furnace tube less the halogens which were lost in HNO_3 evaporation.

(2) An insoluble residue in the washings was filtered off and found to contain principally 77h Te.

(3) To the remaining solution 10 mg each of Br^-, I^-, Sn, Sb, Mo, Cd, Zr, Sr, Ba, Rb, and Cs were added, followed after removal of the halogens by 10 mg each of Ag, Pd, Te, Ru, Rh, Re, La, Ce, In, and Y.

(4) This carrier solution was separated into the following groups:

(a) Halogen was separated by aeration of the hot solution and absorption of the vapors in SO_2 water. Silver halides were precipitated; only I activity was found.

(b) AgCl, Pd, and Te were precipitated by reduction with hydrazine and HCl after removal of HNO_3. AgCl was separated from Pd and Te.

(c) The H_2S group (Sn, Mo, Sb, Ru, Rh, Cd, Re) was precipitated, and Sn, Sb, and Mo were separated by $(NH_4)_2S_x$.

(d) Insoluble hydroxides (Zr, Ce, La, Y, In, Th, U) were precipitated with NH_4OH.

(e) Barium and strontium sulfates were precipitated.

(f) The activity of the final filtrate was determined after evaporation to dryness.

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The activities of the samples recovered in these separations are presented in Table 1 with those of the 1000°C and 400°C experiments. No data were taken on active rare gas diffusion because the gas could not be collected (see section 2.1).

(b) Diffusion at 1000°C. The apparatus used in this experiment was the static vacuum setup described in section 2.2. The sample consisted of two whole blocks of U_3O_8 weighing 91.05 g. In heating, the furnace temperature was raised to 400°C in 1/2 hour, held for 3 hours, raised to 1000°C in 2.67 hours, and held at 1000°C for 2.67 hours. When the apparatus had cooled, it was dismantled, and the diffusate activities were washed from the furnace tube and sample tube. The hot-copper iodine trap was found to be less active than expected, and it was concluded that enough Hg vapor from the bubbler was present in the system to deposit the iodide on the furnace tube walls. Activities in the diffusate solution were separated in a manner similar to that of the 1800°C experiment to give the data in Table 1. An original sample was analyzed for rare gas activities by a method involving solution of the sample in HNO_3 and collection of the gas in an eudiometer. From this analysis and the amount of rare gas collected in the diffusate, it was calculated that 13.5 per cent of the rare gas diffused from the sample at 1000°C.

TABLE 1

FISSION ACTIVITY IN THE 400°, 1000°, and 1800°C DIFFUSATES 68 HOURS AFTER BOMBARDMENT

(div/min)

	400°C	1000°C	1800°C
Fission activity in unheated sample	59,700	60,600	56,800
Activity in the diffusate:			
Insoluble part (Te)	...	8.4	511
I	24	157	814
Te	...	35	172
Sulfides	...	3	5.9
Other	...	0	3
Activity on Cu	...	15	81.5

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(c) Diffusion at 400°C. In an apparatus like that of the 1000°C experiment, except with Pyrex tubes instead of quartz, two blocks of bombarded U_3O_8 weighing 89.6 g were heated. The temperature reached 200°C in 40 minutes, was held at that point for 2-1/2 hours, then was raised to 400°C and held for 4 hours. At the end of the experiment the furnace tube washings were found to be so weakly active they were analyzed for I only. The rare gases were lost when attempting to remove them from the furnace, so no accurate estimate of their diffusion can be made.

5.2 The Diffusion of Fission Products from Sintered U[1]. Two diffusion experiments were run on bombarded sintered U metal. Pieces of sintered (Metal Hydrides) U 1/2 x 1/2 x 2 in. were given a 60 μah bombardment of slow neutrons at Chicago. Although the sample was rotated 6 times during the bombardment, maximum activity variations of 27 per cent were recorded by gold monitors at various places among the blocks.

The experiments at 600°C and 1000°C were run in the static vacuum setup used for pressed U_3O_8, and the techniques for the experiment and the analyses were essentially the same. The greater difficulty of sampling the material and protecting the metal from oxidation during the experiments caused considerable trouble, and the results tabulated below constitute merely a qualitative agreement with the results from the U_3O_8 experiments.

(a) Diffusion at 600°C. The diffusate sample was contaminated with some U when the metal sample oxidized slightly, but strong activities in the Te and I fractions were found, although less than 0.05 per cent of these elements diffused out. Other activities were very weak and not definitely identified.

(b) Diffusion at 1000°C. According to calculations, about 30 per cent of the I activity diffused out of the blocks at 1000°C. This value is surprisingly high, without explanation. About 0.05 per cent of the Te diffused out, but diffusion of other activities was negligible.

The diffusate gas collected per gram of metal at 1000°C was six times that collected at 600°C. The gas collected in the 1000°C experiment was 10 per cent of the total original gas, while the total active gas left in the residue was only 50 per cent of the original. The true amount of gas

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diffusion probably was between 10 per cent and 50 per cent, the discrepancy probably being due to inadequate sampling.

5.3 The Diffusion of Fission Products from Cast U. A number of experiments were performed to study the thermal diffusion of fission activities from cast U. Although they were performed in basically the same A sweeping experimental setup, described in section 2.3, they can best be described by grouping them according to the specific factors receiving most careful attention in each case.

(a) The Effect of Temperature upon Diffusion[2]. Bars of cast Westinghouse U 1/2 x 1/2 x 2 in. were cleaned by sandblasting, cut laterally into blocks and 3/16 in. sample slices and placed together in a square arrangement one block thick for neutron bombardment. Ten gold monitors were regularly spaced about the square to measure the uniformity of the neutron bombardment, which was 150 μah over a 12-hour period ending 10:40 A.M., September 8, 1942. During the bombardment, the sample, which was surrounded with paraffin 2 in. thick, was rotated 90° five times on the axis of the beam.

About 18 hours after the end of the bombardment, the packet was unwrapped and the activities of the 3/16 in. sample slices (which had been given representative positions in the arrangement during bombardment) were determined through a 0.74 gm/cm^2 lead foil. Since the activities were decaying rapidly, they were expressed in terms of the activity of a standard piece, whose decay was measured throughout the period. Specific gamma activities per gram were claculated for the pieces by dividing total relative activity by the piece weight. Of the 16 sample pieces measured, there was a maximum deviation in specific activity of 14 per cent from the average, while most pieces were within a few per cent of the average. The specific activity of a large block of metal was taken as equal to the average of the specific activities of the two adjacent sample slices, and pieces of metal were chosen to form two sample groups of nearly equal surface areas, weights, and total activities. The most representative pieces

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were chosen for original and residue activity analyses. The samples used in the diffusion experiments were:

	Weight	Area	Special Activity	Total Activity
600°C Experiment	426.67 gm	90.4 cm^2	5.70 div/min/gm	2436 div/min
1000°C Experiment	432.53 gm	91.8 cm^2	5.75 div/min/gm	2486 div/min

Each of the samples was heated in its respective apparatus, as described for continuous A sweeping in section 2.3. There were two differences from the drawing (Fig. 3). There was no hot U getter in the A inlet system nor an air thermostat about the flowmeter and Mariotte bottle.

The rare gas activity in the gas stream, while not plotted in this report, followed a curve similar to that in later experiments (Fig. 6, Fig. 7). After the initial peak in rate of diffusion the limiting slope in the 1000°C experiment was 6.8 hours and in the 600°C experiment 9.5 hours. Because the accuracy of measurement of the 600°C gas was more subject to the background variation than that of the 10 times more active 1000°C gas, it was first concluded that the 6.8 hour slope was the significant one, and that most of the diffusion took place in the first few hours of heating. Subsequent gaseous activity was believed to be 9.4h Xe introduced into the gas stream by the decay of its 6.6h I parent, which itself diffused at the beginning of the experiment. This conclusion was only partly true, as indicated in later experiments and described in subsection (c).

At the end of the 30-hour heating period the apparatus was disassembled, and it was noted that the U blocks at the inlet end of the furnace were covered with a thin layer of what appeared to be oxide. The amount of oxidation seemed to be the same in both 1000°C and 600°C experiments. The other blocks in the 600°C furnace showed no change in appearance, but those in the 1000°C furnace had a silvery-white color different from their original appearance. Two of the blocks had sintered together but were easily broken apart. The quartz tube was reduced at the points of contact with the blocks, and two dark lines could be seen. This reaction produced a certain amount of oxide or silicide on the lower edges of the blocks, but it is believed that most of this remained with the blocks and little contaminated the diffusate. In a later experiment,

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7 mg of U remained in the tube, so this magnitude of contamination is likely in this case.

The furnace tube was washed with 1N HNO_3 containing Te and I carriers, and later with aqua regia. The hot copper halogen trap was only very weakly active.

The original samples, residue samples, and diffusate solution were analyzed by techniques essentially those described in section 3. Table 2 gives the amount of diffusion for each element for which the analyses were deemed reliable. The per cent of diffusion was so low that, within the accuracy of the measurements, the residue should be as active as the original. For purposes of comparison, the original and residue analysis are tabulated with the value of "probable original activity" used to calculate the per cent of diffusion. When activity decay curves did not follow the expected pure decay, the best curves were given extra weight; otherwise an average value was taken.

(b) The Effect of Surface Polish[3]. The diffusion experiments with cast sandblasted U at 600°C and 1000°C indicated that only a very small fraction of the fission products diffused, and that the diffusion could be accounted for as primarily a surface phenomenon. Subsequent work with polished and unpolished surfaces of cast U metal indicated[5] that little change occurred in the surface of U heated for 9 hours in purified A at 600°C, but at 700°C, above the first transition point of U, the surface was considerably roughened. The extent and rate of this surface roughening and pitting increased as the temperature increased. It is apparent that any study of the diffusion of fission products from polished and unpolished surfaces must be limited to those temperatures at which the surfaces are not appreciably changed in the process.

In the study of the effect of surface polish, the samples for the two diffusion experiments each consisted of 13 blocks approximately 1 x 1.2 x 1.2 cm. The sandblasted set weighed 359.7 gm and had 106.8 cm^2 gross surface area. The polished set weighed 333.3 gm and had 99.2 cm^2 surface area. The polishing was finished by means of 4-0 carborundum paper to give the surface shown in the photomicrographs (Fig. 5). These blocks, together with 13 pieces 0.1 x 1.2 x 1.2 cm weighing 2.5-3 gm each, were wrapped in paper in three rod-like bundles. The bundles were

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TABLE 2

THE EFFECT OF TEMPERATURE ON THE DIFFUSION OF FISSION PRODUCTS FROM CAST URANIUM (a)

Diffusion at 600°C:	Uranium Specific Activities			Diffusate		
Element	Original	Residue	P.O.A.(b)	Activity	Specific(c) Activity	% Diffusion
I	16.2, 14.2, 16.2	11.6 ..	15	0.06	0.00015	0.001
Te	21.8, 37.0, 35.5	34.9, 27.5	35	0.48	0.0011	0.003
Mo+Sb	21.5, 18.6 ..	20.8 ..	21	0.15	0.0003	0.001
Ba	42.7, 44.5 ..	37.2 ..	40	2.56	0.006	0.015
Sr	.. .. ..	4.0 ..	4	2.7	0.0064	0.16
Xe	74,700 c/m/g				104	0.14

Diffusion at 1000°C:	Uranium Specific Activities			Diffusate		
Element	Original	Residue	P.O.A.(b)	Activity	Specific(c) Activity	% Diffusion
I	16.2, 14.2, 16.2	13.2, 13.6	15	30.4	0.07	0.5
Te	21.8, 37.0, 35.5	34.0, 32.3	35	16.6	0.038	0.11
Mo+Sb	21.5, 18.6 ..	21.6 ..	21	3.6	0.008	0.04
Ba	42.7, 44.5 ..	38.6 ..	40	22.6	0.05	0.13
Sr	.. .. ..	4 ..	4	5.4	0.012	0.3
Xe	74,700 c/m/g				970 c/m/g	1.3

(a) Note: Original and residue activities are in div/min/gm U except Xe activity, which is in counts/min/gm. Since only a small amount of diffusion took place, original and residue analyses were given equal weight in determining "probable original activity". The measured diffusate activity (calculated to 100 per cent chemical recovery) is given to indicate the magnitude of the diffusate activity measured, and to permit estimation of the likely error in measurement. Original and residue samples were generally active enough to permit measurement with an accuracy of a few per cent.

(b) Probable original activity (see text).

(c) The diffusate specific activity is per gram of sample heated in the experiment.

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placed in a wooden cylinder which could be rotated inside a large block of paraffin at the cyclotron by means of a small air turbine and worm gear. During the bombardment the rotation caused the three parts to roll over each other, thus insuring a uniform bombardment and making an element isolated from one block representative of the whole sample. The bombardment was 1100 μah, obtained at the St. Louis cyclotron from 1:15 P.M. to 7:25 P.M., October 29, 1942.

The apparatus and procedure used for the diffusion experiments are described for the A flow diffusion experiments, section 2.3. Heating was begun 30 hours after the end of the bombardment and continued for 30 hours. The rare gas activity which diffused from the samples is plotted in Fig. 6 as a function of time. Correction was made for the time which the gas required to travel from the center of the furnace to the center of the counter tube, so the graph indicates the gas activity at the time it was actually diffusing. The surface of the polished sample showed little transformation in the experiment (Fig. 5). It can be seen from the curves that the gas diffusion from the polished and unpolished samples differed only in magnitude.

Original and diffusate activities for the various elements are given in Table 3. It can be seen that more than twice as much rare gas diffused from the rough-surfaced sample as from the polished one. More of the other activities diffused from the unpolished blocks than the polished ones, but since the total diffusate activities were so low, the results must be considered to represent the order of magnitude of the diffusion rather than its quantitative measure. The amount of diffusion in this experiment was less than in the 600°C experiment described in section 5.3(a). Several factors may have influenced this difference. The slight amount of attack by the unpurified A and the resultant surface change, the possibility of different metal structures due to different casting techniques, and the possibility that the temperature of one furnace was slightly less than that of the other may all be contributing factors to the difference. No positive conclusion can be drawn about which factor was most important.

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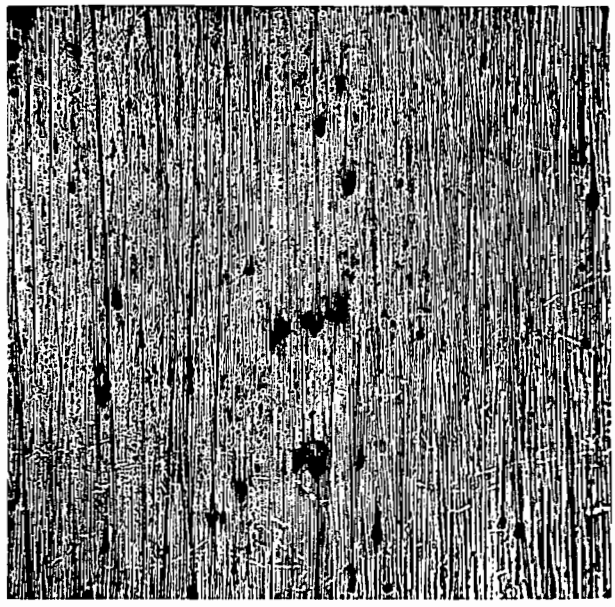
(a)



(b)

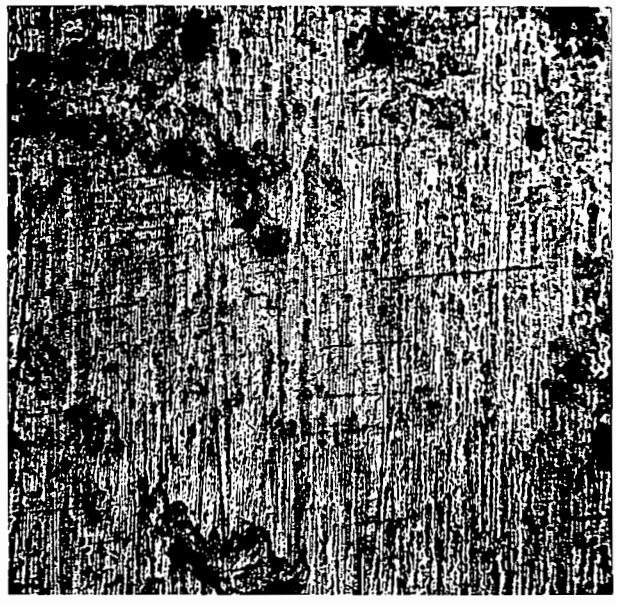


Fig. 5. The Effect of Heating on Surface Polish

(a) Polished Sample, Unheated
Magnification 200X

(b) Polished Sample, Heated 30 Hours at 600°C
Magnification 200X

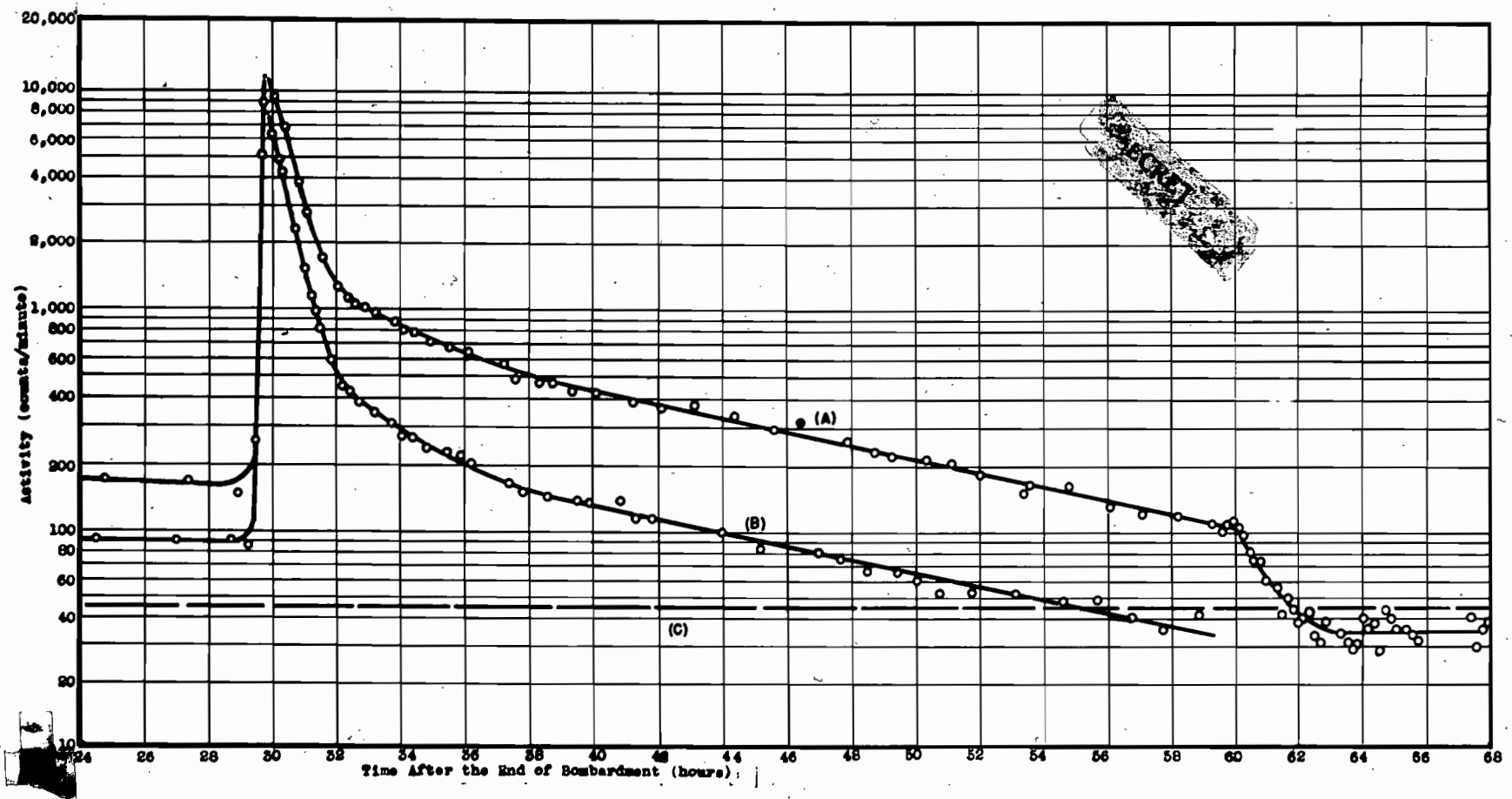


Fig. 8. Rare gas activity in the gas stream on passing argon over polished and unpolished uranium metal at 600°C. The furnace temperature was maintained at 600°C for the 30 hour period beginning 30 hours after the end of bombardment. (A) Activity from unpolished blocks. (B) Activity from polished blocks. (C) Approximate background line.

TABLE 3

THE EFFECT OF SURFACE POLISH ON THE DIFFUSION OF FISSION PRODUCTS FROM CAST URANIUM AT 600°C (a)

Element	Specific Activities		Diffusates					
			Unpolished Uranium			Polished Uranium		
	Original Sample	Average	Activity	Specific Activity	Per Cent Diffusion	Activity	Specific Activity	Per Cent Diffusion
Xe	1.43, 1.51, 1.48($\times 10^6$)	1.47×10^6	...	604	0.04	...	264	0.018
I	66.8, 67.1, 67.8, 66.8	67	0.90	0.0025	0.004	0.10	0.0003	0.0004
Ba	145, 146, 143	145	0.55[b]	0.0016[b]	0.0009[b]	0.02[b]	0.00006[b]	0.00003[b]
Sr	33.7, 32.1, 50.5	39						
Te	352, 308, 328, 278, 283	311	1.17	0.0033	0.001	0.45	0.0014	0.0004
Mo	307, 283, 322	304	1.16	0.0032	0.001	$\ll$0.1	0	0
Zr	911, 833, 968	904	11.0	0.031	0.003	5.3	0.016	0.002
Np	1682, 1775, 887, 1125	1,370	10.4	0.029	0.002	5.0	0.015	0.001
Ce	93, 113	103	...	...	...	...	...	...
La, Y, Pr	167, 168	167[c]	2.3[c]	0.0064[c]	0.0021[c]	0.9[c]	0.0027[c]	0.0009[c]
Th	33.8	34	...	...	...	...	...	...

(a) See footnotes to Table 2 for explanation of conventions.
(b) Because of their very low activity, Ba and Sr in the diffusate were not separated.
(c) The fluorides of Ce, La, Y, Pr, and Th were not separated.

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(c) The Effect of Intermittent Heating[7]. While previous experiments indicated both the magnitude of the diffusion of fission products from U metal and the effect of the metal surface on this magnitude, the mechanism of the diffusion process still posed several important questions. The initial peak in rate of gaseous diffusion was followed by a rapid, then slower regular decrease in rate with a half-life of 6.8-9.8 hours. The activity measured was primarily 9.4h Xe with a small, but up to this time not quantitatively known, amount of 5.3d Xe. The 6.8h slope in the first experiment, section 5.3(a), led to the premature conclusion that the mechanism of the process was simply a rapid diffusion of all materials during the first 6 hours of heating, followed by a period during which the 9.4h Xe in the gas stream was produced by the decay of its parent 6.6h I which had itself diffused. It was first concluded that little Xe diffused from within the metal after the first 6 hours of heating.

The determination of the fission yield and the radiation energy of the 5.3d Xe by Elliott[6], as well as the previous decay curves of the Xe fraction, indicated that this longer-lived activity was being counted. The decay curves, together with the fission yields and decay relationships, made possible the determination of the counting efficiency of this 5.3d activity. Samples of Xe gas were collected from U samples which had neutron bombardments of known time and duration. These samples were transferred to chambers holding the finger-type counter tubes, and the decay curves of the samples recorded. From the duration and time of bombardment and the time of chemical separation, and by using fission yields (9.4h Xe, 9 per cent; 5.3d Xe, 7.6 per cent) and appropriate growth-decay relationships, the actual relative activities of 9.4h and 5.3d xenons were calculated for different times after bombardment. Then from the measured decay curves the relative measured intensities of the two activities were taken. The ratio of 5.3d to 9.4h activity actually found, divided by the ratio theoretically known to be present, gave the relative counting efficiency of 5.3d Xe compared to 9.4h Xe. These relative counting efficiencies varied from about 6-11 per cent, indicating a variation in wall thickness of the finger tubes of from 30-40 mg/cm^2. All of the finger-type counter tubes were calibrated for their relative counting efficiency for these two activities.

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This interrupted heating experiment was devised primarily to determine what part of the diffusate gas activity, after the initial peak rate of diffusion, was produced by direct diffusion from the metal and what part arose from the decay of diffusate I which deposited on the surface of the furnace tube where its decay would project Xe activity into the gas stream. To give the results greater significance, correction was made for the activity of the 5.3d Xe in the gas phase. The experiment also provided a rough estimation of the rate of diffusion of the other fission elements at the beginning and at the end of the heating process.

The samples were taken from 26 sandblasted cylinders of U metal approximately 1.4 cm in diameter and 1 cm long. These were wrapped in 4 cylindrical rolls and placed in a 2-in. hollow wooden cylinder which was rotated slowly within a large block of paraffin at the Chicago cyclotron. The material was given a 150 μah bombardment, ending 7:30 P.M., November 12, 1942. Distributed among the pieces of metal in these rolls were 15 pieces of metal 1.4 cm in diameter and from 0.5-1.5 mm thick, weighing from 1.5-4.2 gm. These were used for the determination of the fission product activities of the original. After the bombardment the pieces were sorted, alternate large pieces from each roll being put together to form the two samples to be heated. Sample A for furnace A consisted of 13 large pieces and one thin piece, with a total weight of 331.6 gm and a surface area of 93.87 cm^2. Sample B for furnace B consisted of 13 large pieces weighing 336.3 gm and with a surface area of 95.54 cm^2.

Three furnaces, as described for the A flow diffusion (section 2.3) were set up side by side. Samples A and B were placed in thin graphite boats to prevent the reaction of the metal with the quartz furnace tubes, and the boats were inserted in the proper furnaces. The furnaces were sealed, swept out with A, which was then maintained at a flow rate of 3 ml/min, and heating was begun 31 hours after the end of the bombardment. The counting rate of the A in the gas stream was measured as often as practicable. Sample A in furnace A was heated continuously at 1000°C for 66 hours. Sample B was heated in furnace B for 12 hours at 1000°C, cooled by a fan to room temperature, transferred to a new graphite boat and put into furnace C, which was then heated to 1000°C for 50 more hours. Furnace B with its original graphite boat was left cold, but A flow was

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maintained through all three furnaces, and the gaseous activity measurements were made as often as possible. At the end of the experiment the gas activity from furnace C tailed off in a way which indicated contamination in the counter chamber. Another tube was substituted, and the old chamber checked. A contamination of approximately 2/3 of the final counted activity was indicated. It could not be determined how or when the activity was deposited in the chamber.

The continuously diffusing gaseous activities are plotted in Fig. 7. The summation of 12.5m extrapolated increments of activity (section 3.2) indicated a diffusion of 2.14 per cent of the total Xe from sample A during the first 30 hours of heating. This compares with 1.3 per cent diffusion in a previous 1000°C experiment (section 5.3(a)). A comparison of corrected curves B' and C shows that after 12 hours of heating, about 42 per cent of the activity in the gas stream arose from the decay of I in the outer tube, and 58 per cent of the total arose from the direct diffusion of gases from the blocks.

In Fig. 7, curve A, the limiting slope of the gaseous activity after the initial peak, corrected to 9.4h Xe by subtraction of the 5.3d Xe background, has a half-life of 7.1h — for 7 half-lives. This is definitely shorter than any value predicted by the theory of Metropolis and Teller[8].

The chemical analyses were systematic and considered two fractions of diffusate activity. Each furnace tube was scrubbed out thoroughly with HNO_3 and carriers, and then with aqua regia (section 3.1). Each graphite boat was burned in O_2 in a clean quartz tube and the tube then scrubbed out with acid and carriers. The diffusate fractions were all analyzed separately by the scheme previously described. (Section 3.1). The activity data are presented in Table 4. The activity of Mo in the diffusates and graphite boats was too low to be identified. It can be concluded that Mo did not leave the metal to a measurable extent.

The gamma activity of the thin slice in sample A was measured through 0.739 gm/cm^2 Pb and compared with the activity of a standard unheated piece before and after the heating experiment. Contrary to expectation, heating produced a slight increase in relative gamma activity. Since measurable percentages of known gamma emitters were driven out by the diffusion process, there should have been a slight decrease in relative activity.

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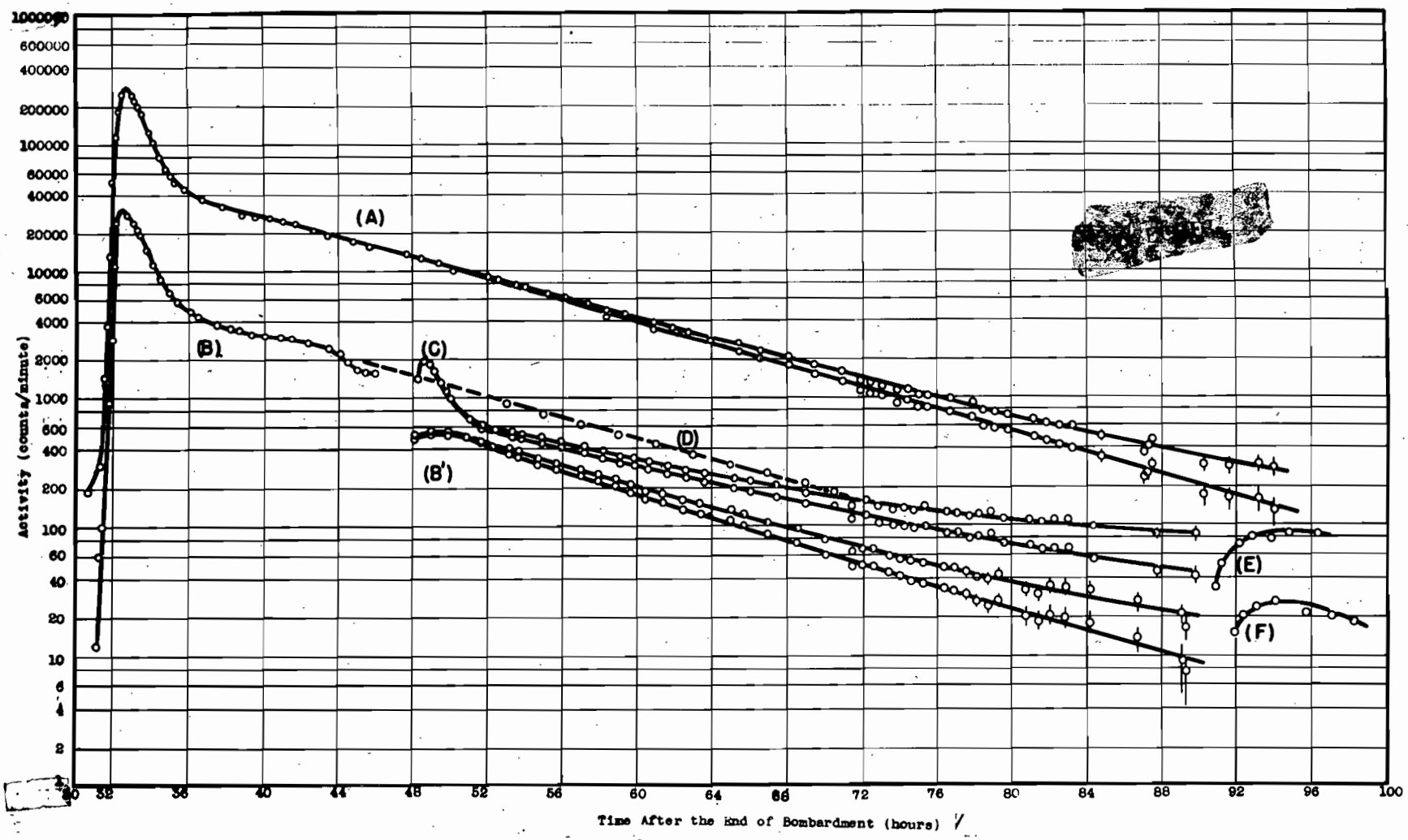

Fig. 7. Xenon activity in the gas stream from uranium metal heated at 1000°C. Blocks reached 1000°C 32.5 hours after the end of the bombardment. The upper curve of each pair is the measured activity corrected for counter tube background; the lower curve is corrected to 9.4 h activity by the subtraction of 5.3 d xenon.

(A) Sample A heated continuously in furnace A, Activity X 10.
(B) Sample B heated in furnace B; furnace turned off 44 hours after bombardment.
(B') Cold diffusate condensed in furnace B.
(C) Sample B reheated in furnace C; temperature reached 1000°C 48.5 hours after the end of the bombardment.
(D) Dotted line is extrapolation of curve B parallel to A; points are summation of B' plus C. Because of suspected contamination in counter chamber C, a new one was substituted, and the original evacuated.
(E) Activity in the original chamber after disconnection and evacuation, showing contamination.
(F) Activity in the new counter chamber when connected to furnace C.

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TABLE 4

THE DIFFUSION OF FISSION PRODUCTS FROM
CAST URANIUM AT 1000°C

Fission Activities of Various Elements in the Original Sample
(div/min/gm)

Sample	I	Ba	Sr	Te	Np	Ce	La, Y, Pr
Original 1	10.74	14.9	3.55	12.1	53	12.22	6.80
Original 2	9.22	10.1	3.54	14.2	41	12.21	6.18
Average	9.98	12.5	3.55	13.2	47	12.22	6.50

Per Cent of Original Elemental Activity Diffusing
into Various Fractions

Sample A	I	Ba	Sr	Te	Np	Ce	La, Y, Pr
Diffusate A	0.94	0.106	0.087	0.020	0.011	2.39	0.63
Graphite A	0.042	0.265	0.163	0.0356	0.063	6.86	3.0
Total Diffusion	0.98	0.371	0.250	0.0556	0.074	9.25	3.63
Sample B	**I**	**Ba**	**Sr**	**Te**	**Np**	**Ce**	**La, Y, Pr**
Diffusate B	1.21	0.060	0.059	0.004	0.003	0.42	0.07
Diffusate C	0.71	0.054	0.059	0.141	0.021	1.88	0.57
(B-C)	1.92	0.114	0.118	0.145	0.024	2.30	0.64
Graphite B	0.042	0.120	0.093	0.0146	0.023	1.38	...
Graphite C	0.055	0.206	0.171	0.138	0.074	4.97	...
(B-C)	0.097	0.326	0.264	0.1526	0.097	6.35	...
Total Diffusion (B-C Graphite and Diffusate)	2.02	0.440	0.382	0.298	0.121	8.65	...

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6. The Calculation of Diffusion Constants

A mathematical treatment of the diffusion results is desirable in order to make them generally useful. This treatment can be given by the calculation of diffusion constants for each of the diffusing elements. The constants recorded in the following tables were calculated by the equation.*

$$D = \pi \frac{f^2 v^2}{s^2 t}$$

where

f = fraction diffusing in time t
v = sample volume in cm^3
s = sample surface area in cm^2
t = time of heating in seconds
D = diffusion constant in cm^2/sec

The agreement among the constants for a given element is reasonably good, and indicates the order of accuracy or reproducibility of the constants. The total activities in diffusate and graphite together were taken for the last two 1000°C experiments, because the analyses indicate that the graphite combined strongly with the diffusion products.

Because the growth of Xe from diffusate I makes such a large contribution to the total Xe activity, the diffusion constant for Xe indicates only an order of magnitude. The diffusion constants for the La, Y, Pr, fraction also indicate only the order of magnitude because of the complexity of their growth-decay relationships.

7. Discussion

The diffusion of a number of the more important fission products from slow-neutron-bombarded pressed U_3O_8, sintered U, and cast U at selected temperatures between 400°C and 1800°C is reported. The data for the fission product diffusion from U_3O_8 and sintered U are for diffusion from a sample heated in a vacuum, and they identify Xe, I, and Te as the elements whose activities predominate in the diffusate. The rough magnitude of the

*(Private communication from Dr. E. Teller).

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diffusion has been determined, but the data do not justify a quantitative treatment.

The diffusion from cast U heated in a slow stream of A at 600°C and 1000°C has been measured more accurately and diffusion constants for various elements have been calculated. Tables 5 and 6 summarize these data and suggest the following conclusions concerning the nature of the diffusion. The diffusion of all elements at 600°C and of some elements at 1000°C is quite small. Since the diffusion process removes the fission activity from the surface of the U and leaves a concentration gradient toward the center of the sample, this indicates that, for those elements whose diffusion is small, the depth from which diffusion takes place is quite small. In these experiments a diffusion of 0.1 per cent could be produced by the activity within 0.003 mm of the sample surface.

TABLE 5

CONSTANTS FOR THE DIFFUSION OF FISSION PRODUCTS FROM CAST URANIUM AT 1000°C

	Section 5.3(a)		Section 5.3(c) A		Section 5.3(c) B+C	
Element	%	D	%	D	%	D
I	0.5	4.9×10^{-11}	0.98	4.6×10^{-11}	2.02	21×10^{-11}
Ba	0.13	3.3×10^{-12}	0.37	6.6×10^{-12}	0.44	10×10^{-12}
Sr	0.3	1.7×10^{-11}	0.25	0.30×10^{-11}	0.38	0.75×10^{-11}
Te	0.1	1.9×10^{-12}	0.056	0.15×10^{-12}	0.30	4.6×10^{-12}
Mo	0.04	3.1×10^{-13}	...	...	...	...
Np	...	...	0.074	2.6×10^{-13}	0.12	7.4×10^{-13}
Ce	...	...	9.25	4.1×10^{-9}	8.65	3.8×10^{-9}
La,Y,Pr	...	...	3.63	6.3×10^{-10}	...	...
Xe	1.3	3.3×10^{-10}	2.12 (30h)	4.7×10^{-10}	...	...
Vol. cm^3	23.4		17.9		18.2	
Area cm^2	91.8		93.87		95.54	
Time, Sec	104,900		237,900		221,700	

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TABLE 6

CONSTANTS FOR THE DIFFUSION OF FISSION PRODUCTS FROM CAST URANIUM AT 600°C

	Unpolished Uranium				Polished Uranium	
	Section 5.3(a)		Section 5.3(b)		Section 5.3(b)	
Element	%	D	%	D	%	D
I	0.001	1.9×10^{-16}	0.004	15×10^{-16}	0.0004	0.15×10^{-16}
Ba	...	...	0.0009	8×10^{-17}	0.00003	9×10^{-20}
Sr, Te	0.003	1.7×10^{-15}	0.001	9.5×10^{-17}	0.0004	1.5×10^{-17}
Mo	0.001	1.9×10^{-16}	0.001	0.95×10^{-16}	...	...
Np	...	...	0.002	3.8×10^{-16}	0.001	9.6×10^{-17}
Zr	...	...	0.003	8.6×10^{-16}	0.002	3.8×10^{-16}
Th, Ce, La, Y	...	...	0.002	3.8×10^{-16}	0.001	1×10^{-14}
Xe	0.14	3.8×10^{-12}	0.04	1.5×10^{-13}	0.018	3.4×10^{-14}
Vol. cm^3	23.1		19.4		18.0	
Area cm^2	90.4		106.8		99.2	
Time sec	106,900		108,000		108,000	

The effect of surface-polishing a sample of cast U is to decrease the diffusion of an element at 600°C by a factor of from 2-10. The mechanism of this decrease is probably the reduction of effective surface area by eliminating the irregular surface of the raw cast metal. Since the diffusion is from such a shallow layer at the surface of the sample, it is critically dependent upon control of surface oxidation, chemical reaction, and thermal rearrangement of the metal structure. More significant than the quantitative values of the diffusion at 600°C is the fact that the diffusion is very small and is essentially a surface process.

At 1000°C the diffusion of fission products has a greater quantitative significance. With the exception of Mo which was not conclusively identified in the 1000°C diffusate, all elements diffused to a much greater extent than at 600°C, the increase being from 10-100 fold. The large diffusion of Xe (2 per cent) and I (1 per cent) was in line with other

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results, but the still larger diffusion of both Ce (9 per cent) and the La, Y, Pr fraction (3.6 per cent) was unexpected. No positive explanation for the large diffusion of these metals is apparent from the data, but it is possible that valence and atomic volume characteristics of these elements permit interchange with U in the lattice, or compound formation with U, and so permit diffusion. Xenon, which has negligible combining affinity, might not be able to break through the bonds of the U lattice in which it is enmeshed. With these cases of more extensive diffusion, the process can no longer be considered a surface one, and the diffusion constants are no longer entirely valid since the derivation of the diffusion equation is based on the assumption of diffusion in one direction only and from a body whose internal concentration is not changed in the process. The true diffusion constants for these elements diffusing in larger amounts must be greater than the ones given in Tables 5 and 6.

The measured diffusion constants can be used to calculate the amount of diffusion from U in piles under similar conditions, taking into account the phenomena of radioactive formation and decay. Ample consideration must be given to the chain relationships of the activities concerned; for when an active element diffuses, it produces in the diffusate not only its own activity but all of its daughter activities as well. Thus, in these experiments it was found that 20 hours after 1000°C heating began, 42 per cent of the diffusate Xe arose from the decay of diffusate I. Since a great many fission elements have either gaseous or diffusable parents, and since in a pile even the short-lived members of the chain have their chance to diffuse, this is a serious consideration. The equations used in this calculation may be derived for any specific case in a manner similar to that used by Metropolis and Teller[8], but the variety of cases makes a discussion here inadvisable.

The object of this research, the determination of the nature and extent of the diffusion of the fission products from U and U_3O_8 with an accuracy sufficient to aid in pile design, was accomplished. With the decision to operate piles at much lower temperatures and to encase the U in a coating of other metal, further studies were not essential, and the work was discontinued.

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