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# DIFFUSION OF URANIUM THROUGH GRAPHITE

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# DIFFUSION OF URANIUM THROUGH GRAPHITE

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## ABSTRACT

Diffusion rates of uranium through graphite were determined in the temperature range 3000 to 4350 F. The diffusion couples consisted of sintered $UC_2$ disks in contact with graphite rods. The observations indicated two distinct types of uranium transport which could be associated with volume diffusion and with migration along pores.

Volume diffusion was characterized by steep concentration gradients and shallow penetration. The diffusion coefficient, $D_v$, in $cm^2$ per sec, between 3300 and 4250 F, is given by the equation:

$$D_v = 7.6 \times 10^{-3} \exp \left(\frac{-82,000}{RT}\right).$$

Above 4250 F, incipient melting of the $UC_2$ was evident and the diffusion coefficients were much higher than those given by the above equation.

As an example of the penetration resulting from volume diffusion, calculations show that, after 1000 hr at 4200 F, the uranium concentration at 0.1 cm from the interface will be 1000 mg per $cm^3$, compared to 10,000 mg per $cm^3$ for pure $UC_2$.

Pore migration resulted in uranium penetration far beyond that arising from volume diffusion at equivalent temperatures and diffusion times. However, uranium concentrations were very small compared to those corresponding to volume diffusion. Pore migration is strongly temperature dependent.

To estimate the practical importance of pore migration, the uranium flow through a graphite wall at 3000 F was measured. With a wall thickness of 0.32 cm, the average flow per unit area was 0.015 mg per $cm^2$ per hr for a 40 hr test.

## INTRODUCTION

Graphite was used in the first nuclear reactor because it is a good moderator and because large amounts of pure graphite were obtainable. The early reactors were designed to operate at relatively low temperatures. However, graphite also is very well suited as a moderator and structural material for power-producing reactors. Except for its poor oxidation resistance, it has generally attractive properties for high-temperature service--high thermal conductivity, good strength, excellent resistance to thermal shock and to creep.

There are several important areas in which more data are needed to extend the use of graphite in power reactors. Among these is the need for information on its compatability with nuclear fuels at high temperatures.

Uranium dioxide and uranium dicarbide are two high-melting fuel compounds which have been considered for use in contact with graphite. As the oxide reacts with graphite at high temperatures to form the carbide, uranium carbide appears to be the more suitable compound to use with graphite.

Uranium dicarbide, $UC_2$, is known to be relatively unreactive with graphite up to its melting point, but few data on the diffusion of uranium from $UC_2$ into graphite have been reported. In fact, prior to this investigation, the only systematic study of the problem appears to be that made by Loftness(1).

Loftness measured the diffusion of uranium from $UC_2$-impregnated graphite into pure graphite at temperatures between 3900 and 4700 F. The impregnated graphite had a uranium concentration of approximately 250 mg per $cm^3$. Loftness concluded that volume diffusion was the only important diffusion mechanism contributing to his results.

The present study deals with diffusion from massive $UC_2$ into graphite. The results should be applicable to a variety of reactor-design problems.

## MATERIALS

Synthetic graphite, designated type AGOT by the manufacturer*, was used in the experiments. This material, made and purified for use in reactor applications, is otherwise a typical high-grade commercial graphite, prepared by heating a mixture of petroleum coke and coal-tar pitch to graphitizing temperatures.

Despite multiple impregnations by pitch to increase the density, the void content ranges from 23 to 27 per cent of the total volume. The pores are largely interconnected and permeable to gases. Figure 1 gives the mercury pore spectrum of AUF graphite, which is structurally similar to AGOT. The grains of AUF and AGOT graphites range from 1 to 20 microns and contain crystallites 2000 A long in the direction of the basal plane, and the majority of the pores, 80 per cent, are in the same size range as the grains.

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*The National Carbon Company.

Massive $UC_2$ was crushed in a steel mortar to pass a 200-mesh sieve. All handling of the $UC_2$ was performed under carbon tetrachloride to prevent oxidation. Chemical analysis of the $UC_2$ showed 8.44 per cent carbon, compared to the theoretical carbon content of 9.16 per cent.

To prepare specimens, the graphite was machined into cylinders, 3.8 cm long and 2.2 cm in diameter. The axes of the cylinders were parallel to the direction of extrusion. End surfaces were polished with 600-grit SiC abrasive paper.

The $UC_2$ powder and 0.75 wt % paraffin, added as a carbon tetrachloride solution, were thoroughly mixed, and then the carbon tetrachloride was evaporated in air. The resultant powder was pressed at 22,600 psi into disks which were sintered in vacuum at 4200 F for 1-1/2 hr. One side of each disk was polished under carbon tetrachloride with 600-grit SiC paper. The finished disks were 0.3 cm thick and 1.8 cm in diameter. They were stored under carbon tetrachloride until used.

## EXPERIMENTAL PROCEDURES

Each diffusion couple consisted of a sintered $UC_2$ disk resting on one end of a graphite cylinder. The $UC_2$ was held in place temporarily by an organic adhesive which carbonized during heating. The diffusion couple was placed in a carbon-tube resistor furnace with the axis of the cylinder vertical and heated to maximum temperature in about 2 hr. Furnace temperatures were read to ± 20 F with a Leeds-Northrup optical pyrometer.

Corrections were made in the temperature readings for losses in the glass lens and mirror used in sighting. The furnace was cooled overnight to room temperature before the couple was removed.

Argon entering the furnace was passed over heated titanium granules to remove nitrogen and was dried with anhydrous magnesium perchlorate. Traces of CO were present in the furnace atmosphere.

After each diffusion couple was removed from the furnace, the $UC_2$ disk was detached, and the graphite was sectioned on a lathe in accordance with the diagram in Figure 2. In every case, part of the graphite stuck to the $UC_2$ upon separating the couple leaving an irregular graphite surface. Therefore, the distance of each cut from the original interface was measured with reference to the periphery of the graphite face, which was undamaged. As the $UC_2$ disks were smaller in diameter than the graphite rods, the peripheral area was not in contact with $UC_2$ during heating.

The cutting operation permitted an accuracy of ± 0.0005 cm in measuring the thickness and penetration distance after each cut. Penetration distance was recorded as the distance between the original interface and the midpoint of the cut.

Material shaved off by the lathe tool was collected carefully and its uranium content analyzed by a fluorophotometer.(2) The accuracy of the analyses was ± 10 per cent of the uranium content. The center cuts shown in Figure 2 were used to obtain concentration-penetration curves. The outer cuts were analyzed only to determine whether radial diffusion had an effect on the uranium concentrations resulting from linear diffusion.

## RESULTS AND DISCUSSION

The heating conditions and concentration-penetration data for the experiments are shown in Table 1. Representative penetration curves for the first few cuts are shown in Figure 3. The curves for Specimens 15 and 23 in Figure 3 are typical of those obtained at and below 4250 F. Experiments at 4300 and 4350 F produced curves similar to that shown in Figure 3, for Specimen 19.

Figure 3 shows a strong dependence of penetration distance on temperature. At 4350 F, which is near the melting point of $UC_2$(3), the penetration was 0.04 cm after only 2 hr, while heating for 16 hr at 3800 F produced a penetration of less than 0.02 cm.

An unusual feature of the results was the appearance of two types of concentration gradients: (1) large gradients near the interface, as shown in Figure 3, and (2) small gradients at deeper penetrations. The two types of gradients are illustrated in Figure 4 for Specimen 15. Even though the concentrations at the deeper penetrations were small, they were significant. The data are plotted in Figure 4 as log concentration versus distance only for convenience; the straight lines should not be taken as an indication that linear relationships were obtained with this type of plot.

The dependence of concentrations near the interface on depth and time was found to be consistent with diffusion equations, and sufficiently well defined to permit the determination of diffusion coefficients. However, the data were not sufficient to answer secondary questions, such

TABLE 1. URANIUM CONCENTRATION-PENETRATION DATA

| | Sample 14<br>4250 F<br>8 hr | | Sample 1<br>4300 F<br>5 hr | | Sample 20<br>4200 F<br>12 hr | |
|---|---|---|---|---|---|---|
| Cut Number | Uranium Concentration, mg per cm$^3$ | Depth of Cut,(1) cm | Uranium Concentration, mg per cm$^3$ | Depth of Cut, cm | Uranium Concentration, mg per cm$^3$ | Depth of Cut, cm |
| 1 | N.D.(2) | 0.004 | N.D. | 0.004 | N.D. | 0.004 |
| 2 | 700 | 0.014(3) | 920 | 0.013(3) | 700 | 0.011 |
| 3 | 84 | 0.019 | 130 | 0.019 | 100 | 0.019 |
| 4 | 4.0 | 0.027 | 7.3 | 0.027 | 4.4 | 0.027 |
| 5 | 2.9 | 0.034 | 4.9 | 0.034 | 2.8 | 0.034 |
| 6 | 2.1 | 0.045 | 5.3 | 0.045 | 2.1 | 0.045 |
| 7 | 1.4 | 0.061 | 4.7 | 0.061 | 2.1 | 0.061 |
| 8 | 0.98 | 0.076 | 4.2 | 0.076 | 1.7 | 0.076 |
| 9 | 0.98 | 0.099 | 3.3 | 0.099 | 1.7 | 0.099 |
| 10 | 0.93 | 0.130 | 2.6 | 0.130 | 1.7 | 0.130 |
| 11 | 1.0 | 0.160 | 2.3 | 0.160 | 1.3 | 0.160 |
| 12 | 0.778 | 0.252 | 1.4 | 0.252 | 0.87 | 0.252 |
| 13 | 0.622 | 0.405 | 1.1 | 0.405 | 0.62 | 0.405 |
| 14 | 0.570 | 0.558 | 0.85 | 0.558 | 0.61 | 0.558 |
| -- | -- | -- | -- | -- | -- | -- |

| | Sample 19<br>4350 F<br>2 hr | | Sample 24<br>4350 F<br>1 hr | |
|---|---|---|---|---|
| Cut Number | Uranium Concentration, mg per cm$^3$ | Depth of Cut, cm | Uranium Concentration, mg per cm$^3$ | Depth of Cut, cm |
| 1 | N.D. | 0.004 | N.D. | 0.004 |
| 2 | 920(3) | 0.011 | 1080 | 0.013(4) |
| 3 | 973 | 0.019 | 870 | 0.019 |
| 4 | 600 | 0.027 | 200 | 0.027 |
| 5 | 254 | 0.034 | 10.4 | 0.034 |
| 6 | 50 | 0.042 | 3.0 | 0.042 |
| 7 | 5.3 | 0.050 | 2.0 | 0.050 |
| 8 | 2.9 | 0.058 | 1.7 | 0.058 |
| 9 | 2.6 | 0.069 | 1.5 | 0.069 |
| 10 | 2.0 | 0.079 | 1.0 | 0.079 |
| 11 | 1.5 | 0.092 | 1.0 | 0.092 |
| 12 | 0.97 | 0.117 | 2.0 | 0.117 |
| 13 | 1.1 | 0.140 | 1.5 | 0.140 |
| 14 | 0.88 | 0.170 | 1.3 | 0.170 |
| 15 | 1.08 | 0.261 | 0.62 | 0.261 |
| 16 | 0.61 | 0.413 | 0.49 | 0.413 |
| 17 | 0.55 | 0.505 | 0.39 | 0.505 |

(1) The depth was taken as the center of each cut, except when otherwise noted.

(2) N.D. - No determination.

(3) This point was not shown in Figure 3 since it was in obvious error and is less reliable than deeper

(4) In these cuts, the center of the cut could not be used as the depth because a substantial portion of in thin slices (0.0025 cm), and the average depth of those slices which contained substantial amounts

| Sample 23<br>3800 F<br>16 hr | | Sample 32<br>3600 F<br>8 hr | | Sample 29<br>4000 F<br>16 hr | |
|---|---|---|---|---|---|
| Uranium Concentration, mg per $cm^3$ | Depth of Cut, cm | Uranium Concentration, mg per $cm^3$ | Depth of Cut, cm | Uranium Concentration, mg per $cm^3$ | Depth of Cut, cm |
| 1200 | 0.004 | 73.0 | 0.004 | 74.0 | 0.005(3) |
| 110 | 0.011 | 2.0 | 0.011 | 7.0 | 0.011 |
| 6.1 | 0.019 | 0.83 | 0.019 | 2.3 | 0.019 |
| 3.6 | 0.027 | 0.46 | 0.027 | N.D. | 0.027 |
| 2.2 | 0.034 | 0.31 | 0.034 | 1.1 | 0.034 |
| 1.8 | 0.045 | 0.41 | 0.045 | N.D. | 0.045 |
| 0.84 | 0.061 | 0.36 | 0.061 | 0.62 | 0.061 |
| 0.64 | 0.076 | 0.41 | 0.076 | N.D. | 0.058 |
| 0.46 | 0.099 | 0.57 | 0.099 | 1.2 | 0.069 |
| 0.40 | 0.130 | 0.54 | 0.130 | N.D. | 0.130 |
| 0.36 | 0.160 | 0.39 | 0.160 | 83 | 0.160 |
| 0.24 | 0.252 | 0.16 | 0.252 | N.D. | 0.252 |
| 0.11 | 0.405 | 0.01 | 0.405 | 62 | 0.405 |
| 0.03 | 0.558 | 0.006 | 0.558 | N.D. | 0.558 |
| -- | -- | 0.006 | 0.611 | 4.2 | 0.611 |

| Sample 13<br>4300 F<br>8 hr | | Sample 15<br>4250 F<br>12 hr | | Sample 21<br>3300 F<br>56 hr | |
|---|---|---|---|---|---|
| Uranium Concentration, mg per $cm^3$ | Depth of Cut, cm | Uranium Concentration, mg per $cm^3$ | Depth of Cut, cm | Uranium Concentration, mg per $cm^3$ | Depth of Cut, cm |
| 980 | 0.005(3) | N.D. | 0.004 | 420 | 0.005(3) |
| 980 | 0.011 | 850 | 0.011 | -- | -- |
| 760 | 0.019 | 115 | 0.019 | -- | -- |
| 138 | 0.027 | 3.3 | 0.027 | -- | -- |
| 14.5 | 0.034 | 2.8 | 0.034 | -- | -- |
| 5.9 | 0.042 | 2.1 | 0.042 | -- | -- |
| 3.8 | 0.050 | 2.5 | 0.050 | -- | -- |
| 3.6 | 0.058 | 2.6 | 0.058 | -- | -- |
| 2.7 | 0.069 | 2.3 | 0.069 | -- | -- |
| 2.0 | 0.079 | 1.8 | 0.079 | -- | -- |
| 1.5 | 0.092 | 1.7 | 0.092 | -- | -- |
| 1.7 | 0.117 | 1.7 | 0.117 | -- | -- |
| 1.7 | 0.140 | 1.2 | 0.140 | -- | -- |
| 1.2 | 0.170 | 1.3 | 0.170 | -- | -- |
| 1.0 | 0.261 | 1.1 | 0.261 | -- | -- |
| 0.73 | 0.413 | 0.73 | 0.413 | -- | -- |
| 0.70 | 0.505 | 0.67 | 0.505 | -- | -- |

points.

the cut had been removed with the $UC_2$ disk. To estimate the real depth of these cuts, the graphite was removed of material was used as the depth of the cut.

as whether the diffusion coefficient in the carbide was the same as in the graphite where the uranium concentration was much lower. Accordingly, analysis of the data was based on the equation:

$$C\ (x,t) = \frac{C_o}{2}\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right].$$

Where $C_o$ = 10,000 mg per $cm^3$ is the original concentration in the carbide. This equation is applicable to the results of the present investigation provided: (1) there is no very large dependence of the diffusion coefficient on concentration, (2) no appreciable change in concentration occurs at the extremities of the couple, and (3) the effect of radial diffusion is negligible. Auxiliary experiments showed that the diffusion times used in this work were sufficiently short to prevent depletion of uranium at the outer extremities of the $UC_2$ disks. Also, the center cuts which were taken for analysis were shown to be close enough to the center line so that radial diffusion could be ignored.

In accordance with the above equation, the concentration-penetration data were plotted as 100 $C/C_o$ on the probability scale versus $x/(t)^{1/2}$ on a linear scale. Straight lines were drawn through the data for the shallow penetrations so as to intersect the point 100 $C/C_o = 50$ and $x/(t)^{1/2} = 0$. In most cases it was not necessary to force this intersection, showing that the assumption of constant D on both sides of the interface was not unreasonable. The plots obtained for the experiments at 4200 and 4300 F are shown in Figure 5. All of the plots showed a definite tail marking the transition from shallow penetration to deep penetration noted in Figure 4.

For the experiments at 4200 F and above, there were enough points available and the straight-line fit was sufficiently good to calculate a diffusion coefficient with some certainty. In doing this for Specimens 13 and 19, however, very little weight was given to the first cut because of the uncertainties in the concentration and in the penetration distance.

For the experiments at 3300, 3600, 3800, and 4000 F, the first cut again was doubtful, leaving only one or two reliable points in each case. Straight lines were drawn to fit the points as well as possible. Under the circumstances, the values of D obtained from these experiments are not so reliable as those at the higher temperatures.

The values of D obtained for shallow penetration are shown in Table 2. A plot of log D versus 1/T is shown in Figure 6 along with values obtained by Loftness(1) for comparison.

TABLE 2. DIFFUSION COEFFICIENTS FOR SHALLOW PENETRATION

| Temperature, F | Diffusion Coefficient D, $cm^2$ per sec |
|---|---|
| 4350 | $1.9 \times 10^{-8}$ |
| 4300 | $3.6 \times 10^{-9}$ |
| 4250 | $1.0 \times 10^{-9}$ |
| 4200 | $7.4 \times 10^{-10}$ |
| 4000 | $6.8 \times 10^{-11}$ |
| 3800 | $1.6 \times 10^{-10}$ |
| 3600 | $4.1 \times 10^{-11}$ |
| 3300 | $2.4 \times 10^{-11}$ |

A least-squares treatment of these data was not made because the substantial uncertainties at the four lowest temperatures could not be estimated at all well. The line shown in Figure 6 was drawn by inspection. Using this line, the diffusion coefficient, D, in $cm^2$ per sec, between 3300 and 4250 F, is given by the equation:

$$D = 7.6 \times 10^{-3} \exp(-82,000/RT).$$

On the basis of close inspection of the data, it is estimated that this activation energy of 82,000 cal per g-atom may be in error by as much as 20,000 cal per g-atom, which is not unduly high for diffusion experiments of this type.

The rather high value of the activation energy suggests that volume diffusion is the major contributor to shallow penetration by uranium.

The results obtained in this investigation are in general agreement with those reported by Loftness. His activation energy of 53,000 cal per g-atom is not significantly different. The only important difference is seen in the results at temperatures above 4250 F, where Loftness did not observe the sharp increases in diffusion rates noted in the present investigation. A possible reason for this may be that, in Loftness' experiments, the $UC_2$ initially was distributed in thin layers on the pore walls in the graphite. Thus, it easily could take up excess carbon, which prevented melting of the carbide(3). In the present experiments, the amount of carbon available to the $UC_2$ was limited, so some melting occurred at 4300 F and above.

Calculation of uranium penetrations by volume diffusion for long times indicate that this type of diffusion may be of less practical importance than the type referred to as deep penetration. For example, after 1000 hr at 3200 F, the uranium concentration would be expected to decrease from 10,000 mg per $cm^3$ in the $UC_2$ to 1000 mg per $cm^3$ 0.01 cm inside the graphite. After 1000 hr at 4200 F, the concentration should be 1200 mg per $cm^3$ at 0.1 cm from the interface. Deep penetration, on the other hand, reaches a depth of a centimeter or more in a few hours at these temperatures.

Deep penetration must occur by way of the pores and may logically be called pore migration. Although it is presumably a type of diffusion, the available data give no evidence for this and do not justify the estimation of diffusion coefficients. To obtain some conception of the temperature dependence of the process, the data were plotted as log Q/t versus 1/T, where Q is the amount of uranium absorbed by the graphite as a result of pore migration and t is the time. In the present experiments, volume diffusion was negligible at depths greater than 0.05 cm; only the uranium which penetrated deeper than 0.05 cm was used in calculating Q. The resultant plot is shown in Figure 7.

Pore migration shows a temperature-penetration which is qualitatively similar to that observed for volume diffusion. A sharp increase in rate again was noted above 4250 F.

One experiment was made to estimate the uranium loss through a graphite wall due to this form of transport. The uranium flow was measured through a thin-walled tube, 1/2 in. in diameter and 4 in. long, closed at one end. Minus 325-mesh $UC_2$ powder was tightly packed in the 1/4-in. bore of the tube to a depth of 1/2 in. and the bore closed with a graphite plug. The tube was placed in a carbon black absorption bed contained by a tube 1 in. in diameter. The assembly was placed vertically in a vacuum furnace similar to that described by Smith(4) so that only that portion of the inner tube which contained the $UC_2$ was in the hot zone of the furnace. In this manner, uranium leakage around the plug was minimized.

The uranium lost per unit area was 0.6 mg per $cm^2$ after 40 hr at 3000 F. Under these conditions, the penetration depth by volume diffusion would be about 0.004 cm compared to the wall thickness of 0.32 cm. Therefore, the uranium picked up in the carbon black must have reached the outer wall of the graphite tube by pore migration.

## SUMMARY AND CONCLUSIONS

Uranium transport through polycrystalline graphite was measured in the temperature range of 3000 to 4350 F. Two forms of transport were observed: volume diffusion and pore migration.

The volume-diffusion coefficients obtained in this investigation are in good agreement with those reported by Loftness(1). The activation energy of 82,000 ± 20,000 cal per g-atom is not significantly different from Loftness' value of 53,000 cal per g-atom.

Within the time and temperature ranges studied, depths of penetration by pore migration were of the order of 100 times as great as those by volume diffusion. Therefore, for practical purposes, pore migration may be the more important type of uranium transport.

A better understanding of pore migration is needed. More experiments, using graphites of widely different pore structures, will be helpful. It is of particular interest to determine whether pore migration occurs to the same extent in very dense graphites as it does in ordinary graphites.

IDL:JRG:WHD/hmo
August 23, 1955

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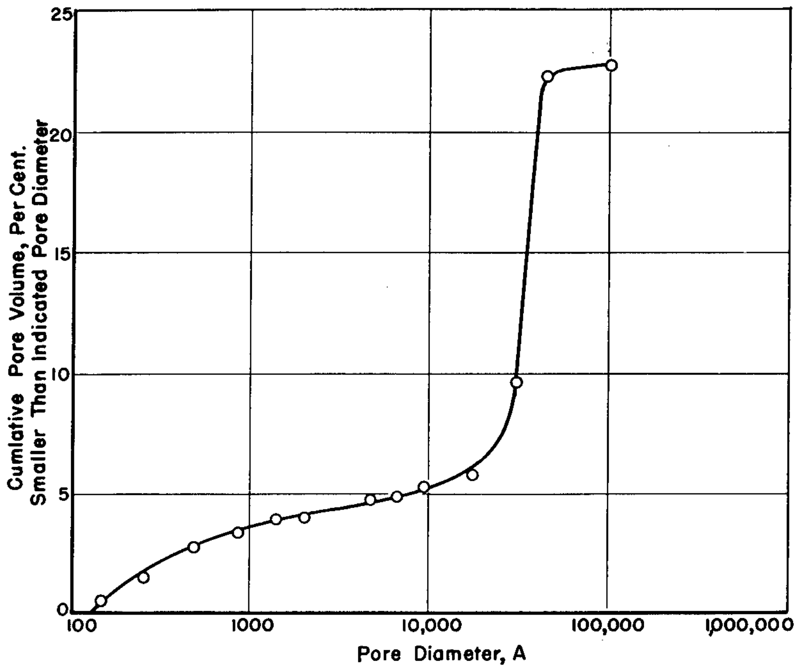


FIGURE 1. PORE SIZE DISTRIBUTION IN AUF GRAPHITE

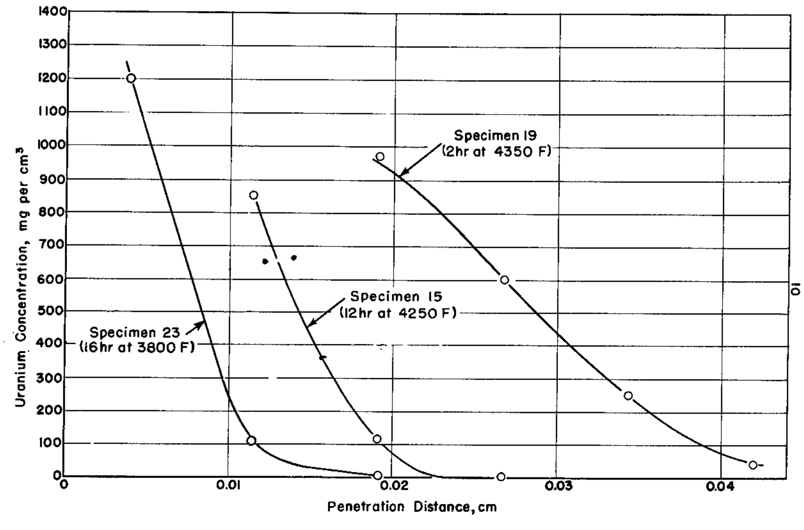
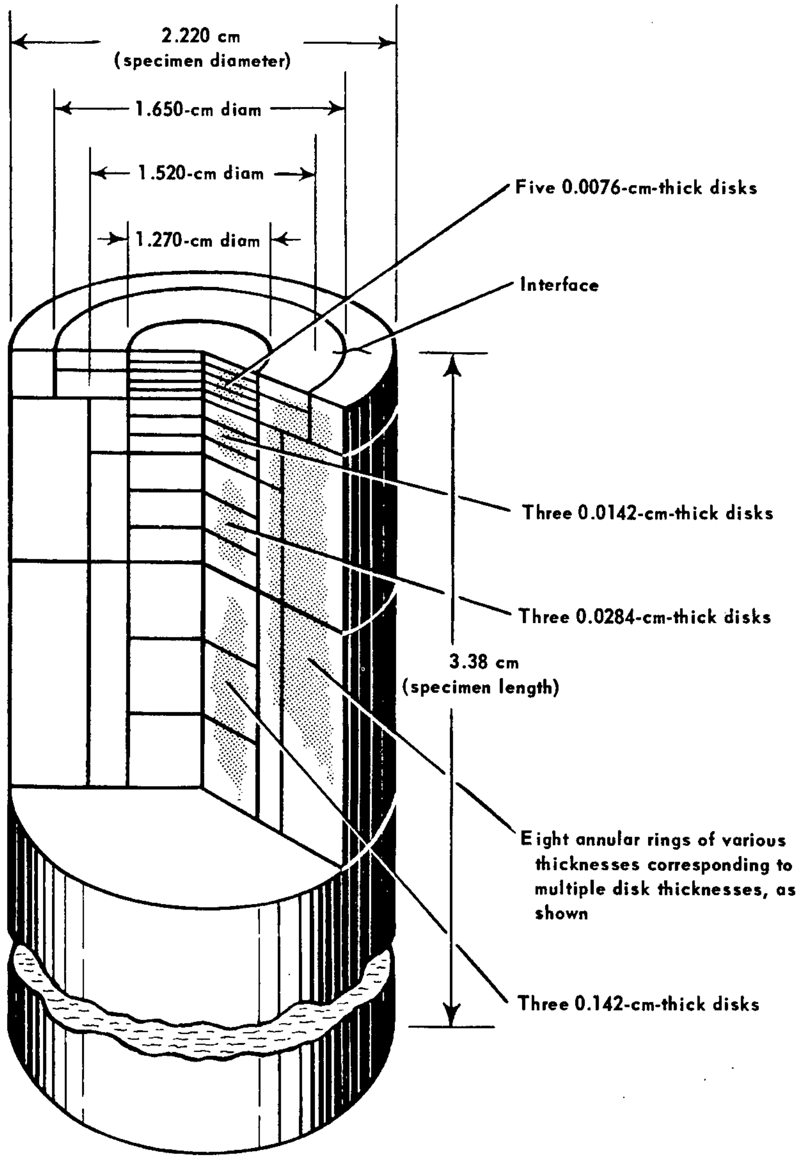


FIGURE 3. REPRESENTATIVE CONCENTRATION-PENETRATION CURVES FOR SHALLOW PENETRATION



Exaggerated view (no scale)
to show relative locations

FIGURE 2. CUTTING SCHEME FOR DIFFUSION COUPLES

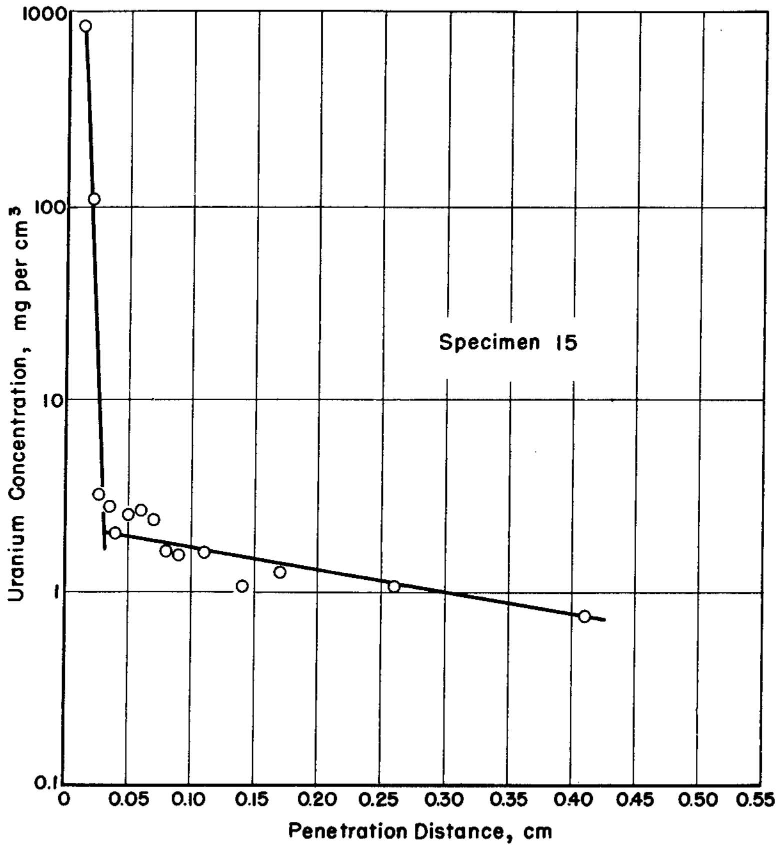


FIGURE 4. COMPARISON OF THE TWO TYPES OF CONCENTRATION GRADIENTS

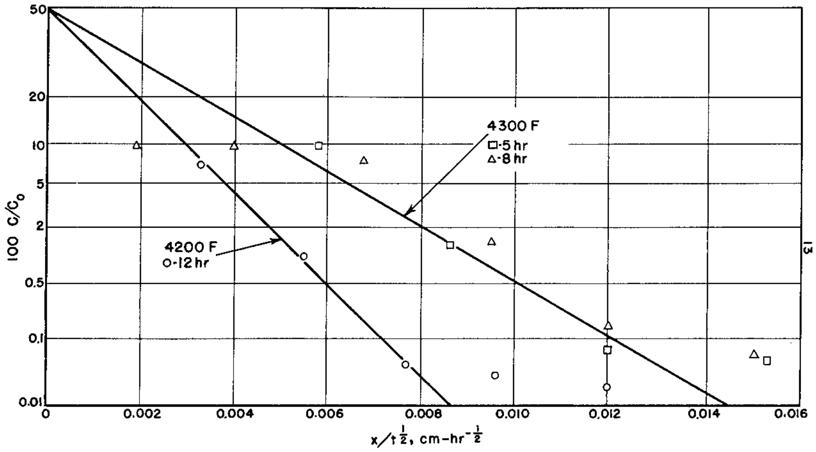


FIGURE 5. PLOTS SHOWING AGREEMENT OF SHALLOW—PENETRATION DATA WITH FICK'S LAW

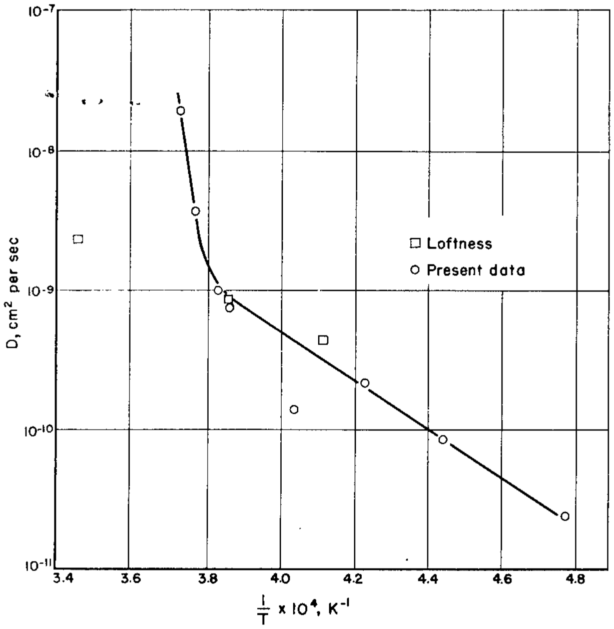


FIGURE 6. DEPENDENCE OF DIFFUSION COEFFICIENT ON TEMPERATURE FOR SHALLOW PENETRATION

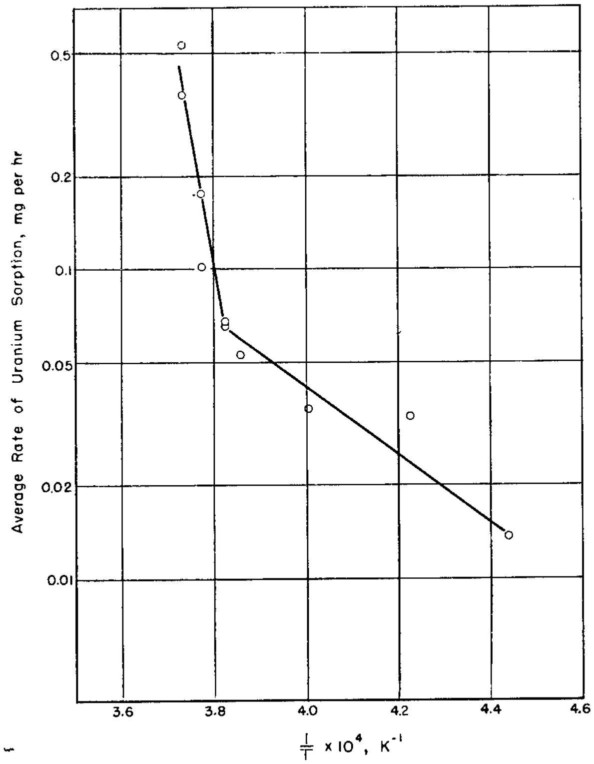


FIGURE 7. DEPENDENCE OF PORE MIGRATION ON TEMPERATURE