We carry through exactly the same manipulations as in Sec. 4 to obtain from the first Born approximation to (3.2):

$$\frac{R_{\mathrm{ac}}}{R_{\mathrm{dc}}}\cong\frac{1+1.280\alpha^2+0.410\alpha^4}{1+1.415\alpha^2+0.500\alpha^4}, \tag{5.6}$$

which is plotted in Fig. 2. We remark that using the first Born approximation to (3.2) directly in (5.5), without assuming a variational parameter, gives a curve almost identical to (5.6), which actually fits the experimental results of Broudy and Levinstein[8] slightly better for $\alpha>1$.

6. CONCLUSIONS

If $\alpha\equiv fRW\epsilon_0(1+b)$ is small, say less than 0.5, the methods used in this paper are quite accurate since the approximate expression obtained for $R_{\mathrm{ac}}/R_{\mathrm{dc}}$ will differ from the true expressions by terms of the order of α^4. In this region the fit with the experimental curve of Broudy and Levinstein is excellent, as can be seen from Fig. 2. For larger values of α, the two curves evidently still agree within the accuracy attained. On the other hand, the curves obtained from previous experiments and from the Howe theory lie considerably lower. We may conclude that the present theory is an adequate explanation of the data for films which have no barriers. Furthermore, since we have made no assumptions other than those of the Howe theory, it is clear that the agreement between the Howe theory and earlier experiments was partially accidental, as suggested by Broudy and Levinstein.

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Diffusion of Carbon Atoms in Natural Graphite Crystals[*]

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Diffusion in purified natural graphite crystals was studied by two techniques. Crystals with C^{14} atoms on the surface were prepared by heating at 1575°C for thirty minutes in a mixture of radioactive carbon monoxide and helium. These crystals were heated at diffusion temperatures *in vacuo*, and the C^{14} distribution within the crystals was determined by burning them slowly and measuring the radioactivity in the carbon dioxide produced. Diffusion measurements were carried out for times up to twenty-five hours in the temperature range 1995°–2195°C. The results indicated that simultaneous diffusion into single-crystal regions and into disordered regions occurred.

Diffusion was also studied by measuring the rate at which C^{14} atoms were taken up by graphite crystals heated in radioactive carbon monoxide whose C^{14} concentration was maintained constant. Experiments were carried out for times up to eighty hours at temperatures in the range 1995°–2347°C. The results indicated that the greatest part of the flow of atoms into the crystals occurred by the process of volume diffusion at temperatures above 2150°C. The volume diffusion coefficient for graphite is $D=40f^2\exp[(-163\,000\pm12\,000)/RT]$, where f is a geometry factor used because of the irregular shape of the crystals and is estimated to be between 0.1 and 0.6. The volume diffusion coefficient reported appears to be that for the direction parallel to the layer planes.

INTRODUCTION

KNOWLEDGE of diffusion rates in metals and in ionic solids has been an important key to the understanding of many properties of those solids. Measurements of the volume diffusion coefficient and its temperature dependence have indicated the mechanisms by which atoms move through the crystal lattice and have made the correlation of phenomena related to atom movement possible. Relatively little work on covalently bonded solids has been reported.[1,2]

Graphite is known to have a layer lattice.[3] The carbon atoms are bound in a hexagonal plane lattice by strong covalent bonds and the planes are held together by relatively weak Van der Waals forces. The distance between atoms in the basal plane is 1.42 A and that between the planes is 3.35 A. Dienes[4] has made a theoretical study of self-diffusion in graphite and has estimated the activation energies for self-diffusion by direct interchange, vacancy, and interstitial mechanisms. Feldman, Goeddel, Dienes, and Gossen[5] have reported experimental studies of diffusion in artificial graphite in which C^{14} was used as a tracer. Because their results showed simultaneous diffusion into graphite crystallites and along grain boundaries in the temperature range studied, the volume diffusion coefficient could not be evaluated.

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[*] Based on work performed under the auspices of the U. S. Atomic Energy Commission and submitted to the Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry.

[1] Letaw, Portnoy, and Slifkin, Phys. Rev. **102**, 636 (1956).

[2] N. H. Nachtrieb and G. S. Handler, J. Chem. Phys. **23**, 1187 (1955).

[3] J. D. Bernal, Proc. Roy. Soc. (London) **A106**, 749 (1924).

[4] G. J. Dienes, J. Appl. Phys. **23**, 1194 (1952).

[5] Feldman, Goeddel, Dienes, and Gossen, J. Appl. Phys. **23**, 1200 (1952).

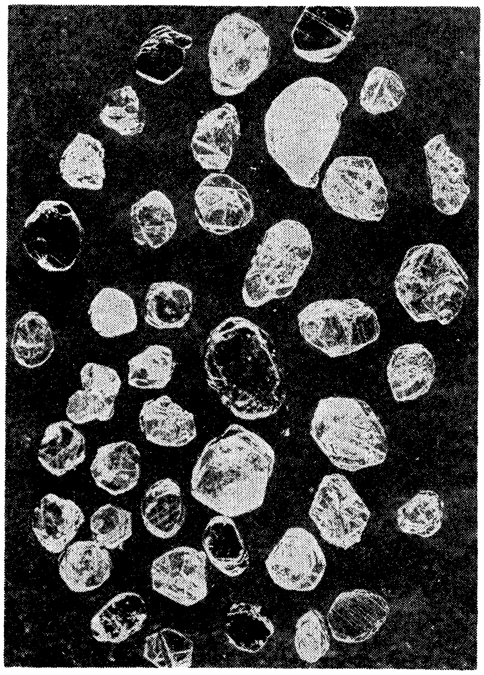

FIG. 1. Photomicrograph of Ogdensburg graphite crystals at approximately 10× magnification.

In order to determine the volume diffusion coefficient, we have studied diffusion in well-formed natural graphite crystals. Because the available well-formed graphite crystals were quite small and because of the anisotropy of the graphite crystals, the conventional methods for studying diffusion in solids could not be used. Hennig and Pattin[6] have shown that exchange between graphite and $C^{14}O$ is very rapid at 1700°C and that the resulting radioactive surface carbon atoms can be removed by oxidizing only a very small fraction of the graphite. This work suggested the use of exchange between $C^{14}O$ and graphite to provide a source of tracer atoms for diffusion and the use of partial oxidation as a method for the determination of concentration profiles. Therefore, an attempt was made to carry out diffusion experiments in which an "instantaneous source" of tracer atoms was placed on the outer surfaces by exchange prior to diffusion and concentration profiles were determined by partial oxidation. In subsequent experiments, measurement of the uptake of C^{14} atoms by crystals whose surface concentration was maintained constant by exchange with $C^{14}O$ proved more tractable and allowed determination of the self-diffusion coefficient.

MATERIALS

Graphite Crystals

Well-formed graphite crystals were obtained by dissolving limestone mined from a commercial quarry at Ogdensburg, New Jersey. Separation and purification of the crystals was carried out by the method described by Primak and Fuchs.[7] The crystals were sieved prior to purification and that portion which passed a No. 20 standard screen but was retained on a No. 40 screen was used for diffusion measurements.

A representative sample of the Ogdensburg crystals is shown in Fig. 1. Many of the crystals are clearly not single, some have dull pitted surfaces, and nearly all show prominent twin zones. X-ray observations on a few representative crystals indicated that the crystals contained as many as ten single crystallites at approximately the same orientation and some very small crystallites randomly oriented. A spectroscopic analysis of the crystals is given in Table I.

The areas of the basal planes of 119 of these crystals were measured using a microscope fitted with a net reticule calibrated against a stage micrometer. From the average area and average weight, other average dimensions were calculated. In particular, it was necessary to know the ratio of the peripheral area (area of the surface generated by the edge of the basal plane) to the volume in order to evaluate the diffusion coefficient. Since the outlines of the crystals were not regular, this ratio was calculated for a flat circular cylinder having the same weight and basal area as these crystals. These dimensions were as follows: Average area of basal plane per crystal—$6.4\times10^{-3}\text{cm}^2$; average weight per crystal—1.57×10^{-4} g; ratio of peripheral area to volume for a flat cylinder having these dimensions—44 cm^{-1}.

Artificial Graphite

Reactor-grade graphite which was used for fabrication of crucibles and radiation shields has been described elsewhere.[8]

TABLE I. Spectroscopic analysis of purified Ogdensburg graphite crystals.[a]

Element	Concentration (ppm)	Element	Concentration (ppm)
Ag	< 1	Mg	< 5
Al	< 5	Mn	< 1
As	<20	Na	< 5
B	< 0.1	Ni	< 2
Ba	< 2	P	<20
Be	< 0.5	Pb	< 1
Bi	< 1	Sb	< 1
Ca	<10	Si	<10
Co	< 2	Sn	< 5
Cr	< 1	Sr	<20
Cu	2	Ti	< 2
Fe	< 2	V	< 2
Hg	< 1	Zn	<20
K	<20	Zr	<10
Li	< 1		

[a] Analysis performed by Joseph Goleb.

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[6] G. R. Hennig and H. S. Pattin, Argonne National Laboratory Report ANL-4288, July 28, 1949, unpublished.

[7] W. Primak and L. Fuchs, Phys. Rev. **95**, 22 (1954).

[8] Currie, Hamister, and MacPherson, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, September, 1955* (United Nations, New York, 1956), Paper No. 534.

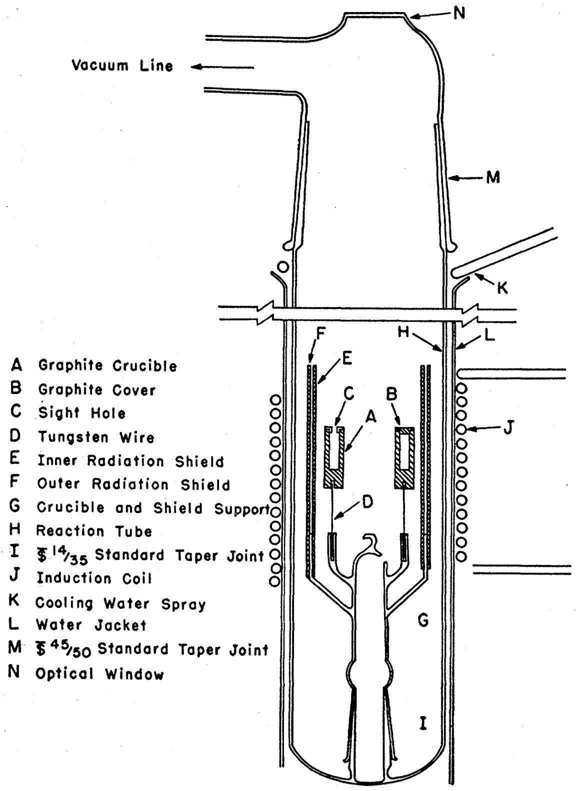

FIG. 2. Diffusion apparatus for the instantaneous-surface-source experiments.

Carbon Monoxide

Concentrated sulfuric and formic acids which had been rendered air-free by alternate freezing and melting *in vacuo* were allowed to react in an evacuated system at 40°C to form carbon monoxide. The gas was dried by passing through a trap at liquid nitrogen temperature and into a storage bulb.

Radioactive Carbon Monoxide

A mixture of C^{14} labeled barium carbonate and lead chloride[9] was heated in an evacuated silica tube at 400°C for thirty minutes. The carbon dioxide given off was condensed in a trap at liquid nitrogen temperature and evaporated from this trap at dry ice temperature to eliminate traces of water. It was then condensed into a storage bulb. At the start of each experiment, the required amount was introduced into the diffusion apparatus where it was quickly converted to carbon monoxide upon contact with graphite above 1575°C.

APPARATUS

The apparatus in which the crystal samples were heated is shown in the drawings. The apparatus for the instantaneous surface-source measurements is shown in Fig. 2 and that for the constant surface-source experiments is shown in Fig. 3. In both cases the graphite crucibles were heated with a General Electric electronic heater and the temperature was kept constant by manual adjustment of the power output.

Temperature measurements were made with a Leeds and Northrup Model 8622–C optical pyrometer through a prism and optically flat window. The readings were taken by sighting on a small hole in the cover of the graphite crucible in which the crystals were heated. No emissivity correction was needed since the crucibles were blackbody cavities. The pyrometer was calibrated by comparison with one standardized using rotating sectors and the freezing points of both platinum and copper.[10] Window and prism corrections were determined by reading the temperature of a lamp both directly and through the window and prism. A magnetically actuated shutter protected the window from carbon deposition.

C^{14} determinations were made on samples of carbon monoxide or carbon dioxide. A mica end-window Geiger-Mueller counter was sealed into the open end of a bell-shaped counting chamber with a beeswax-rosin mixture. Victoreen Model VG–10 and Nuclear-Chicago Model D–34 counter tubes were used with a Nuclear-Chicago

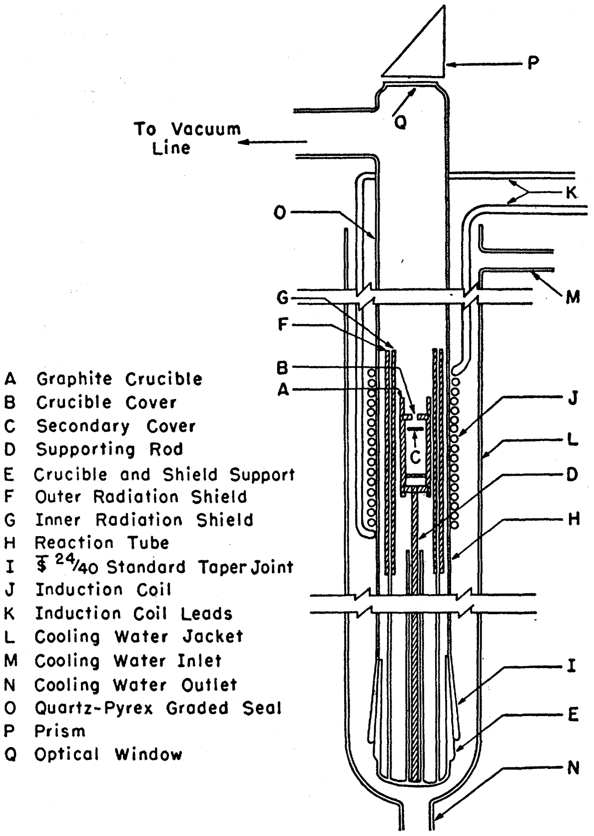

FIG. 3. Diffusion apparatus for the constant-surface-concentration experiments.

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[9] Zwiebel, Turkevich, and Miller, U. S. Atomic Energy Commission Report AECU–72 (unpublished).

[10] The standardized pyrometer was made available by R. J. Thorn, who carried out the standardization.

Model 166 scaling circuit. The tube and counting chamber were held in a two-inch-thick lead shield, and the counting chamber was connected to a vacuum line by Pyrex tubing passing through a small hole in the shield. The counting efficiency of this arrangement was approximately one percent. From the volume of the chamber, the pressure of the gas, and the counting rate, the relative specific activity of the samples was determined. Since all the radioactivity measurements were relative ones, no absolute standardization of the counter was necessary.

INSTANTANEOUS SURFACE SOURCE EXPERIMENTS

A sample containing 0.25 g of graphite crystals was heated in the apparatus of Fig. 2. After outgassing at 2150°C for about two hours, it was heated at 1575°C for thirty minutes in a mixture of radioactive carbon monoxide and helium at a pressure of 10 mm of mercury to obtain a surface source of C^{14} atoms. The system was evacuated and the sample was heated at the diffusion temperature for a measured time. The pressure during this time was maintained below 2×10^{-6} mm of mercury.

After cooling, the sample was removed from the apparatus, weighed into a silica capsule, and placed into an evacuated combustion tube. It was heated at 700°C and exposed to successive small amounts of CO_2-free air for times sufficiently short that not more than 25% of the oxygen in a single portion was used up. The capsule, magnetically coupled to a motor outside the combustion tube, was rotated at one rpm during the combustion to agitate the crystals. Each portion of gas withdrawn from the combustion tube was passed through hot copper oxide to oxidize carbon monoxide and through a series of three traps at liquid nitrogen temperature to condense the carbon dioxide. This carbon dioxide was passed into a container of known volume in which its pressure was measured with a tilting McLeod gauge and then into the counting chamber in which its radioactivity was measured. From these measurements the distribution of C^{14} in the crystals was determined.

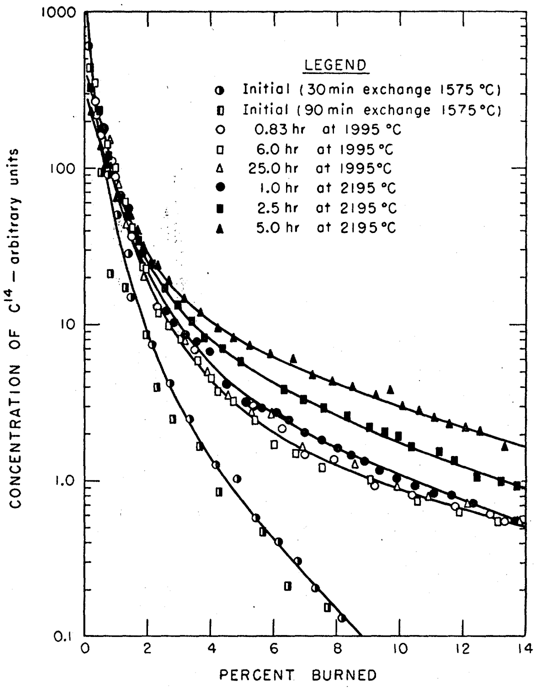

FIG. 4. Distribution of C^{14} in Ogdensburg graphite crystals after diffusion from instantaneous surface source.

C^{14} distributions in Ogdensburg graphite crystals obtained in these experiments are shown in Fig. 4. Data are given showing the effect of the time of exchange on the initial distribution, the effect of heating at 1995°C for times up to 25 hours and the effect of heating at 2195° for times up to five hours. Since strength of the initial source could not be controlled, the data have been normalized to the same total C^{14} content.

Although the method used to determine the C^{14} distribution has been shown to burn graphite crystals uniformly at the outer surfaces,[11] it is not possible to relate quantitatively the percent burned to a distance x from the surface in the basal plane because of the irregular shape of the crystals and the uncertainty of the relative rates of oxidation at the peripheral and basal surfaces. It may be shown that the logarithm of the concentration, C, is nearly linear in the distance x, from the surface; hence, the concentration profiles show that $\log C$ is not proportional to x^2 as would be expected for diffusion in a uniform semi-infinite solid with an instantaneous source at the boundary. The rapid initial penetration of tracer atoms at 1995°C can be attributed to diffusion along grain boundaries whereas the slow rise in internal C^{14} concentration at 2195°C can be attributed to diffusion into the single-crystallite regions. The constant-surface-source experiments which could be performed at somewhat higher temperatures permitted a more complete interpretation of diffusion in these crystals.

CONSTANT-SURFACE-SOURCE EXPERIMENTS

An empty graphite crucible was heated at 2475°C in carbon monoxide containing about one millicurie of C^{14} at a pressure of 50 mm of mercury. The heating was continued until the activity of the gas became constant. The activity of the gas was determined by transferring an aliquot to the counter used for assaying the crystals. This occurred after approximately eighty hours for a completely new assembly but only thirty hours were required for an assembly consisting of a new crucible and radiation shields which were already radioactive.

The radioactive crucible was then filled with crystals to about 2 mm from the top. It was heated at the diffusion temperature for the desired time in carbon mon-

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[11] M. A. Kanter, Argonne National Laboratory Report ANL-5433 (unpublished); Ph.D. thesis, Illinois Institute of Technology, 1955 (unpublished).

oxide of that C^{14} concentration which was approximately in equilibrium with the graphite crucible at a pressure of 50 mm of mercury. At appropriate intervals an aliquot of gas and a sample of the crystals were taken. The transfers were made quickly to minimize exposure to air.

The radioactive crystals were washed on a screen with petroleum ether to remove very fine particles which presumably came from the crucible inner wall. After drying, they were weighed and placed in an evacuated combustion tube in which they were oxidized completely in oxygen at 1000°C. The C^{14} in the carbon dioxide was then determined. The counting rates ranged from 300 counts/min to 3000 counts/min above background with a standard error of 1.5% or better.

It was assumed that, in these experiments, the tracer concentration of the gas in contact with the crystals was maintained constant by rapid exchange with the radioactive crucible. The crucible served as a source of tracer atoms that was not seriously depleted as the experiment proceeded since it contained much more carbon than was present in the crystals or the carbon monoxide. The constancy of the C^{14} concentration in the gas measured after each run confirms this assumption.

Table II. Summary of results of the constant-surface-source experiments.

Temperature (°C)	Parameters of the equation $R=a+b\sqrt{t}$ fitted to the data by the method of least squares $10^3\times a$	 $10^3\times b$ ($hr^{-\frac{1}{2}}$)
2347	0.77 ± 0.35	3.09 ± 0.03
2299	0.80 ± 0.21	2.18 ± 0.06
2242	0.92 ± 0.39	1.52 ± 0.10
2185	0.75 ± 0.10	1.10 ± 0.03
2131	0.20 ± 0.40	0.87 ± 0.12
1995	-0.31 ± 0.30	0.29 ± 0.05

When the experiments were carried out in carbon monoxide at a pressure of 5 mm of mercury, local overheating occurred at incipient cracks in the crucible. Carbon was lost from these spots by sputtering until these cracks became large enough that the crucible could no longer be heated. The C^{14} content of crystals from these runs was irreproducible and, in general, higher than the results reported here. By carrying out the heating in carbon monoxide at 50 mm of mercury pressure, these effects were eliminated. The crucibles heated at this pressure could be used for a much longer time, the life being limited by a gradual loss of carbon from the outside wall of the crucible to the cooler parts of the system.

The graphite container was designed to minimize temperature gradients in the mass of crystals by confining the crystals to the center and providing an extra cover and double bottom. In one set of observations, the temperature at a constant power input was measured through the hole in the cover with the crucible filled to several different levels. No change in temperature was observed.

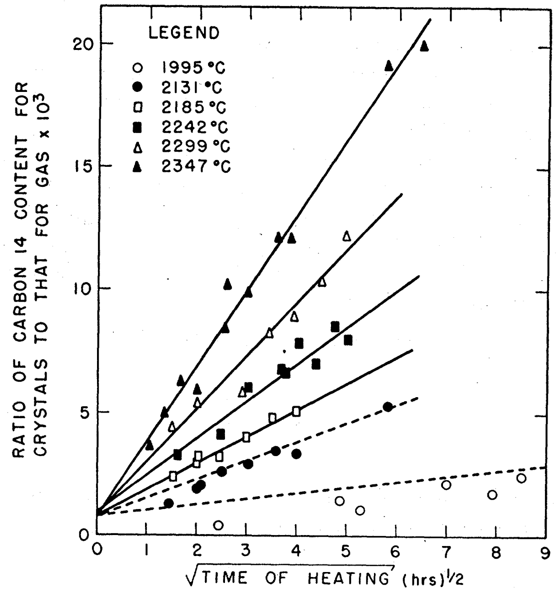

Fig. 5. Carbon 14 content of Ogdensburg graphite crystals after heating in $C^{14}O$.

In another experiment, crystal samples were carefully taken from different levels within the crucible after diffusion. The radioactivity determination showed that the samples had the same C^{14} content within experimental error and also demonstrated that the mass of crystals was heated at a nearly uniform temperature.

The constant-surface-source experiments were carried out using Ogdensburg crystals at six temperatures in the range 1995°–2347°C. The experimental data are shown in Fig. 5 where the ratio R of the average C^{14} concentration of the crystals to that of the gas in which they were heated is given as a function of the square root of time of diffusion. The experimental points for each temperature have been fitted to the equation, $R=a+b\sqrt{t}$. The parameters of this equation, derived by the method of least squares,[12] are listed in Table II.

The full lines in Fig. 5 represent the best straight-line fit to the experimental points for the four higher temperatures. These lines have a common intercept at zero time. The dotted lines show a calculated relationship between the C^{14} content of the crystals and the time for the two lower temperatures, as discussed in a later section. The experimental points approach the calculated behavior at long times.

The mean absolute deviation in the data is five percent which is twice the estimated experimental error. It is not unreasonable to attribute this deviation to the statistical fluctuations in the area and perfection of the crystals from one experiment to another.

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[12] R. T. Birge, Phys. Rev. **40**, 207 (1932).

CALCULATIONS

Diffusion in a perfect graphite crystal can be treated as a one-dimensional problem subject to the assumptions that diffusion in the direction parallel to the basal plane is much faster than in the direction perpendicular to it and that the mean diffusion length, $\frac{1}{2}(\pi Dt)^{\frac{1}{2}}$ for this geometry, is much smaller than the extent of the basal plane. For one-dimensional diffusion in a semi-infinite solid with initial concentration zero and the surface concentration maintained constant at C_0, the concentration at time t is given by [13]

$$C(x,t)=C_0\,\mathrm{erfc}[x/2(Dt)^{\frac{1}{2}}], \tag{1}$$

where

$$\mathrm{erfc}x\equiv\frac{2}{\sqrt{\pi}}\int_x^\infty \exp(-t^2)dt;$$

and the average concentration for a crystal with volume V and area of surface source A is

$$\frac{A}{V}\int_0^\infty C dx=\frac{2C_0A(Dt)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}V}. \tag{2}$$

The ratio R of the average concentration of the crystal to the surface concentration is then

$$R=2A(Dt)^{\frac{1}{2}}/(\pi^{\frac{1}{2}}V). \tag{3}$$

For graphite crystals the surface which serves as a source of diffusing atoms is the peripheral surface since it is assumed that diffusion in the direction perpendicular to the basal plane can be neglected. Since the crystals are irregular in shape, the area of the peripheral surfaces is not known accurately. Therefore, a factor f is defined as the ratio of the peripheral area of a thin circular cylinder which has the same dimensions as the average crystal to that area which serves as the actual source of diffusing atoms.

From the x-ray observations, it is known that the Ogdensburg crystals are composed of large crystallites oriented nearly parallel to one another and very small crystallites randomly oriented and concentrated largely at surfaces. It seems reasonable to assume that they also contain disordered carbon on the flat surfaces, at the edges, and along the boundaries between the perfect regions. Diffusion into single crystallites follows Eq. (3) only when the mean diffusion length is small compared with the size of the single crystallites. When it is of comparable magnitude, the amount of diffusing species taken up tends to saturate. In regions composed of disordered carbon atoms, diffusion can be much faster than in single crystals.

TABLE III. Volume diffusion coefficients for graphite.

Temperature (°C)	Diffusion coefficient $\times10^{12}$ Experimental (cm²/sec)	Diffusion coefficient $\times10^{12}$ Calculated from Eq. (7) (cm²/sec)
2347	1.07 ± 0.03	···
2299	0.54 ± 0.03	···
2242	0.26 ± 0.03	···
2185	0.135 ± 0.006	···
2131	···	0.062
1995	···	0.0082

If the imperfect regions, the very small crystallites and the disordered carbon, attain the surface concentration in a time shorter than the shortest experiment, the amount of C^{14} taken up will follow the equation

$$R=a+b\sqrt{t}, \tag{4}$$

where the first term represents the C^{14} in the imperfect regions and the second term is the C^{14} taken up in the large single crystallites [see Eq. (3)].

Inspection of the data for the four higher temperatures (2185°C, 2292°C, 2299°C, and 2347°C) shows a linear relationship between the ratio of average C^{14} concentration attained in the crystals to the surface concentration and the square root of the time. The straight lines have a common positive intercept at zero time. From Eq. (4) the intercept, 8×10^{-4}, is the fraction of the carbon in the crystals present in imperfect regions. The slope of the line, b, can be related to the diffusion coefficient by Eq. (3). For the present case,

$$D=1.12\times10^{-7}f^2b^2, \tag{5}$$

an expression obtained by substituting the proper numerical values in Eq. (3) $(A/V=44.2/f)$ and noting that D has the units cm²/sec whereas b is given in $(\mathrm{hr})^{-\frac{1}{2}}$. The values of D are listed in Table III.

The diffusion coefficients for the four temperatures follow a simple Arrhenius expression of the form

$$D=D_0\exp(-\Delta H/RT) \tag{6}$$

as shown in Fig. 6. The equation of the straight line is

$$D=40f^2\exp(-163\,000/RT). \tag{7}$$

The uncertainty in the activation energy, ΔH, is 12 000 cal/mole, and the corresponding uncertainty in D_0 is a factor of ten. The parameters of the Arrhenius expression were determined by a least-squares analysis in which the individual points were weighted for the uncertainty in both diffusion coefficients and temperature readings. The magnitude of these uncertainties is shown by the size of the points in Fig. 6.

DISCUSSION

In Fig. 5[2] the data for the two lower temperatures (1995°C and 2131°C) do not lie on straight lines which can be extrapolated to the same intercept as the lines for the higher temperature data. The experimental points for 2131°C show a definite curvature at short times whereas those for 1995°C are too scattered for a precise determination of the functional relationship between the average C^{14} concentration and the time. It

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[13] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1947), p. 45.

is clear that for both of these temperatures extrapolation of the data to zero time gives a lower intercept than for the higher temperatures. If, at the lower temperatures, diffusion into imperfect regions occurs in times which are comparable to the times of the experiments, the C^{14} content of these regions would not be constant, and the C^{14} uptake of the whole crystal would follow a somewhat more complicated law than Eq. (4). The extrapolated volume diffusion coefficients for these temperatures were calculated from the Arrhenius expression [Eq. (7)] and are given in Table III. By using Eqs. (4) and (5), the C^{14} taken up in the large crystallites was calculated. The dashed lines in Fig. 5 represent this calculated C^{14} content added to the limiting C^{14} concentration of the imperfect regions. The experimental data for long diffusion times can be fitted to these lines as one would expect. However, the role of the imperfect regions must be considered further.

Diffusion along intercrystalline boundaries has been discussed by Smoluchowski,[14] who concludes that it is faster than volume diffusion only for boundaries between crystals which have a large angle of misalignment or for those having a width greater than several atom distances. From x-ray observations, it is known that the misalignment of the single crystals is small but nothing is known of the width of the boundaries. Because of the anisotropy of graphite, two distinct types of boundaries must be considered, those parallel to the basal plane and those having any other orientation. Both types provide a path along which tracer atoms may diffuse faster than in the single crystal but, since the volume of the boundaries is small compared to the single-crystal regions, this process in itself has just the effect noted in the experimental data, namely, a small increase in the C^{14} uptake which causes a deviation from the square root of time dependence at short times and low temperatures. However, those boundaries which are not parallel to the basal plane may also serve as additional sources for tracer atoms diffusing into the single crystals. Since the area of these boundaries is comparable to the peripheral area, one could explain the observed dependence of the C^{14} uptake on the square root of time only if diffusion along them is so slow that they do not act as sources or if it is so fast that they act as sources of constant strength. The concentration profiles, Fig. 4, from the instantaneous-source experiments indicate that there was a penetration of the crystals which was rapid even at 1995°C. However, since this penetration may have occurred along either or both types of boundaries, one cannot determine from these experiments whether sources other than on the peripheral surfaces were present.

The role of those boundaries which are not parallel to the basal plane affects the evaluation of the diffusion coefficient since the area of the source of tracer atoms must be known. If these boundaries do not act as sources, the peripheral area must be used; but, if they do, twice their area must be included. Since the crystals are irregular, one can only estimate these areas. The peripheral area is estimated to be about 1.5 times as large as that of the equivalent flat circular cylinder described earlier. The area is estimated to be about six times as large if the boundaries are considered as sources. Since the area enters only into the evaluation of the pre-exponential term in the volume diffusion coefficient, the choice between these estimates is not of critical importance.

Another possible type of imperfect region which must be considered is a layer of disordered carbon on the peripheral surface which has a diffusion coefficient different from that of the single crystals. The treatment of this two-zone case is qualitatively similar to that for diffusion in a semi-infinite solid where the transfer between the solid and the gas of constant composition is proportional to the concentration difference. If the surface layer is thin, the solution to the diffusion equation is identical to that for a first-order surface reaction. The solution for this case has been determined.[11] It is concluded that there is a range of parameters over which the uptake of tracer atoms follows the square root of the time and that in this range the correction in diffusion coefficient which must be made to include the effect of a surface barrier is less than 8%. Therefore, since the precision of the data is of this order, the effect of a surface barrier may also be neglected.

The assumption was made in interpreting the data that diffusion in the direction perpendicular to the basal plane can be neglected. If such diffusion occurs, the amount of C^{14} taken up can be considered, in first approximation, as the sum of that diffusing in from the plane surfaces and from peripheral surfaces. In that

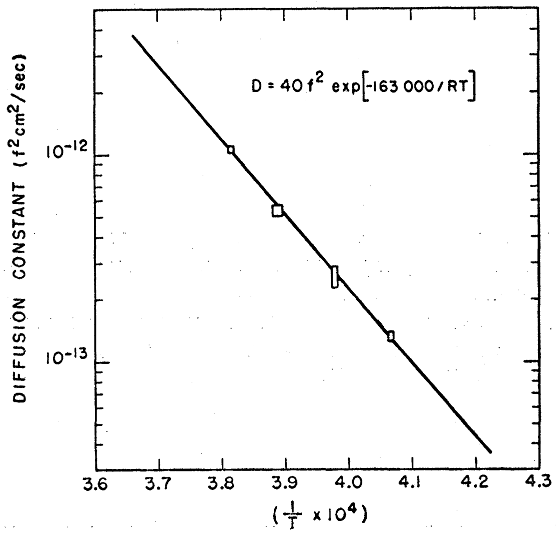

FIG. 6. Temperature dependence of the volume diffusion coefficient of graphite.

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[14] R. Smoluchowski, Phys. Rev. 87, 482 (1952).

TABLE IV. Activation energies for diffusion in graphite calculated by Dienes' method.[a]

Process	Energy (kcal/mole) (a)	(b)
Formation of a vacancy	119.4	170
Motion of a vacancy	71.4	93
Total activation energy for diffusion by vacancy mechanism	190.8	263
Direct interchange	90.4	113
Interstitial mechanism	417.0	467

[a] The value of the heat of sublimation of graphite used in the calculation was (a) 124 kcal/mole and (b) 170 kcal/mole.

case, the C^{14} content would vary as

$$R=a+\frac{2}{\pi^{\frac{1}{2}}V}(A\sqrt{D}+A'\sqrt{D'})\sqrt{t}. \qquad (8)$$

A system described by Eq. (8) could exhibit the observed temperature dependence of Fig. 5 if the two diffusion coefficients had comparable activation energies or if one diffusion coefficient was much smaller than the other. The first of these possibilities seems very unlikely.

Volume Diffusion Coefficient of Graphite

The theory of the self-diffusion coefficient in solids has been reviewed by Zener[15] who has shown that diffusion may occur by direct interchange of atoms on adjacent lattice sites, by migration of atoms onto adjacent vacant lattice sites, by migration of atoms via interstitial positions, and by a number of more complicated mechanisms requiring the cooperative movement of several atoms. The diffusion coefficients for the various mechanisms all have the form

$$D=\gamma a^2\nu \exp(\Delta S/R)\exp(-\Delta H/RT), \qquad (9)$$

where γ is a coefficient depending on the lattice geometry and the diffusion mechanism, a is a lattice parameter, ν is the characteristic lattice-vibration frequency, and ΔS is the entropy change associated with the process which determines ΔH, the activation energy. For interchange mechanisms, the activation energy for diffusion is the activation energy of the elementary jump process, whereas for vacancy and interstitial mechanisms it is the sum of the activation energy of the elementary jump process and the energy of formation of the mobile unit.

The end result of the experiments is the evaluation of the volume diffusion coefficient as given in Eq. (6) where $D_0=40f^2$ and $\Delta H=163\pm 12$ kcal/mole and where the value of f is between 0.1 and 0.6. These values can be compared with those for other substances on the basis of empirical correlations often used in evaluating diffusion data.

One of these correlates the activation energy for diffusion, ΔH, and the latent heat of sublimation, ΔH_s. The value of the ratio, $\Delta H/\Delta H_s$ is approximately 0.65 for a large number of metals,[16] 0.67 for white phosphorus,[2] and 0.76 for germanium.[1] The ratio determined here for graphite is considerably higher, 0.96.

Another empirical correlation is that of the activation energy for diffusion with the melting temperature, T_m. This correlation is not as well founded as others involving the heat of fusion but the heat of fusion is not known for graphite. The ratio $\Delta H/T_m$ is approximately 38 cal/mole °K for many metals,[16] 30 cal/mole °K for white phosphorus,[2] and 55 cal/mole °K for germanium.[1] The value for graphite is 33 cal/mole °K, for which the value of T_m used was 5000°K, a minimum value estimated by Brewer.[17]

It is not to be implied that these correlations should properly be extended to graphite. On the contrary, testing them with diffusion data for substances other than the metals for which they were first found to apply indicates that, whereas the energies involved in fusion, sublimation, and diffusion are related, the lattice structure of the solid must be taken into consideration.

Because the value of D_0 may be in error by a factor of twenty, any extensive consideration of its significance is of doubtful value. However, calculation of the entropy change, using Eq. (10) and taking $f=\frac{1}{3}$, $\gamma=\frac{1}{4}$, $a=1.42\times 10^{-8}$ cm, and $\nu=5\times 10^{13}$ sec^{-1}, shows that $\Delta S=3.8$ cal/mole °K, a positive number indicating that the diffusion observed in these experiments was volume diffusion and did not involve "short-circuiting" paths.[15]

Dienes[4] has attempted the calculation of these activation energies for graphite by consideration of nearest-neighbor interactions for the appropriate atom configurations. The potential used for calculating atomic interactions between the layer planes consisted of a Born-Mayer repulsive term and a Van der Waals attractive term, where the constants have been evaluated from the measurements of Nelson and Riley on the thermal expansion of graphite.[18] The potential function used for calculating interactions between atoms within the layer planes was merely an empirical expression of the change in energy with length for carbon-carbon bonds of different order. Dienes' calculated activation energies are given in Table IV. The data on carbon-carbon bonds were taken from Pauling[19] and are based on the value 124 kcal/mole for the heat of sublimation of graphite. Data based on the more reliable value of the heat of sublimation, 170 kcal/mole,[20]

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[15] C. Zener, in *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), Paper 11.

[16] A. D. LeClair, *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1949), Vol. 1, Chap. 7.

[17] L. Brewer, *Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1950), Paper No. 3, National Nuclear Energy Series, Plutonium Project Record, Vol. 4, Div. 19B.

[18] J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) **57**, 477 (1945).

[19] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1944), p. 53, 131.

[20] G. Glockler, J. Chem. Phys. **22**, 159 (1954).

are given by Coulson.[21] Dienes' calculations have been repeated, and the corrected values are also presented in Table IV. Comparison of these calculations and the experimental result shows best agreement for the direct-interchange mechanism but the agreement is not sufficiently good to exclude the vacancy mechanism especially in view of the assumptions made in Dienes' theory. The calculated energy for the vacancy mechanism is undoubtedly high since relaxation effects were neglected.

The interstitial mechanism involving motion of atoms in the interplanar spaces can be ruled out on experimental grounds as well as from theoretical considerations. It is known from irradiation damage studies[22] that single interstitial atoms become mobile at temperatures near 200°C so that at temperatures above 2000°C such atoms could move freely over the whole extent of the interplanar space within the crystal. The movement of tracer atoms from the surface to the interior would be controlled by the process of exchange either between surface-source atoms and the interstitials or between the interstitial atoms and the lattice atoms. Such a process would lead to a nonzero concentration gradient only in the vicinity of traps for interstitial atoms and the uptake of tracer atoms would be described by first-order kinetics. Neither effect is observed.

Diffusion by the direct-interchange mechanism or by one of the more complicated mechanisms described by Zener cannot be ruled out since the relatively open structure of graphite may make such mechanisms energetically favorable. It should be pointed out, however, that no entropy calculations have been made for such mechanisms in graphite.

The value, 163 kcal/mole, for the activation energy for diffusion seems compatible with a vacancy mechanism. A simple calculation given by Mott and Gurney[23] shows that the energy of formation of a vacancy in a nonpolar crystal is equal to the heat of sublimation. This calculation neglects the effect of relaxation around a vacancy. It seems reasonable to assume that the energy of formation of the vacancy in graphite could be substantially lower than the heat of sublimation due to the relaxation, so that the sum of the energy of formation of the vacancy plus the activation energy for its motion would be of the order of the energy of sublimation. However, a definitive determination of the mechanism of diffusion in graphite will depend on the calculation of the energy involved in the relaxation process.

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[21] C. A. Coulson, *Valence* (Clarendon Press, Oxford, 1953), p. 181.

[22] Montet, Hennig, and Kurs, Nuclear Sci. and Eng. 1, 33–52 (1956).

[23] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940).

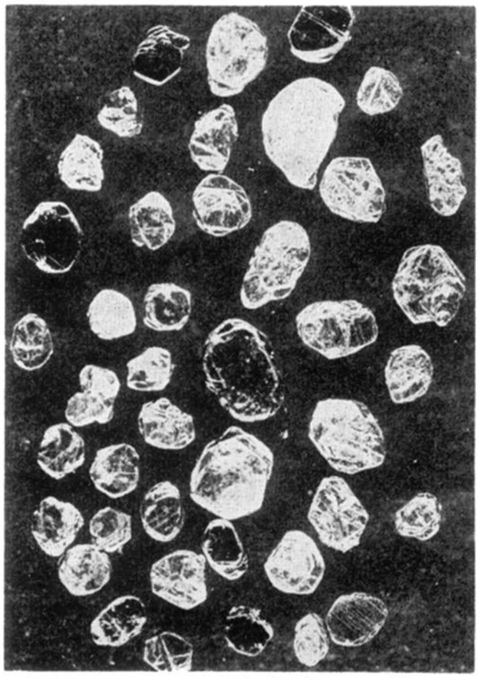

Fig. 1. Photomicrograph of Ogdensburg graphite crystals at approximately 10× magnification.