The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. VII. The Activation Energy of the Diffusion of Iodine-131 in Graphite

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The authors have studied the behavior of fission products captured in graphite by fission recoil and have obtained much interesting information. For example, fission products do not leach out of graphite into nitric acid to any extent, unless the graphite is heated to a high temperature before the leaching assay[1]. Xenon, iodine, and tellurium diffuse more rapidly out of natural graphite than out of artificial graphite[2]. The heating curve and the activation energy of the diffusion of xenon indicate that the diffusion mechanism is not simple, but is related to imperfections in the graphite crystal[3]. The distribution of the activation energy of the diffusion shifts to higher temperatures with an increase in the concentration of fission products in graphite crystal[4]. Iodide is the chemical form of iodine diffusing out of graphite crystal[5].

These studies have been carried out in connection with the development of a semi-homogeneous fuel, that is, a dispersion-type fuel of uranium dioxide or uranium carbide in a graphite base; at the same time, they brought out many facts very interesting from the standpoint of hot atom chemistry.

Taking account of the fact that the iodide is the chemical form of iodine diffusing out of a graphite-uranium dioxide-system fuel, the authors undertook to determine the activation energy of the diffusion of iodine in graphite crystal and to elucidate the mechanism of the diffusion and formation of the iodide.

Experimental

Preparation of Samples.—Natural graphite (NG-1) was used throughout the experiments. The use of natural graphite, which has fewer imperfections than artificial graphite, made analysis of the experimental results clearer and easier; our studies made it clear that the diffusion rates of xenon, iodine, and tellurium in the natural graphite specimen were much larger than those in artificial graphite. Its properties are given in Table I, and those of the uranium dioxide used, in Table II.

A mixture of 1 g. of graphite and 0.5 g. of uranium dioxide powder was irradiated for 15 hr. in a JRR-1 reactor (water boiler type; thermal neutron flux: about 5×10^{11} n/cm^2/sec.) and cooled for 5 days. This cooling time facilitated the analysis of the behavior of iodine-131 by allowing short-lived iodine nuclides and the precursor of iodine-131 to decay out. The cooled sample was then treated with a hot nitric acid solution to separate

TABLE I. ANALYTICAL DATA OF IMPURITIES IN GRAPHITE

Impurities	NG-I
Ash	0.8%
SiO_2	3700 p.p.m.
Al_2O_3	3500 p.p.m.
Fe_2O_3	300 p.p.m.
MgO	100 p.p.m.
CaO	300 p.p.m.
V_2O_5	0.5 p.p.m.
Na_2O	25 p.p.m.
K_2O	20 p.p.m.
B_2O_3	0.5 p.p.m.

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1) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, This Bulletin, 33, 494 (1960).

2) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, ibid., 33, 497 (1960).

3) S. Yajima, S. Ichiba, Y. Kamemoto, K. Shiba and M. Kori, ibid., 34, 697 (1961).

4) S. Yajima, S. Ichiba, K. Iwamoto and K. Shiba, ibid., 35, 1263 (1962).

5) S. Yajima, K. Shiba and M. Handa, ibid., 36, 253 (1963).

TABLE II. ANALYTICAL DATA OF IMPURITIES IN URANIUM DIOXIDE

	%
Content	99.85
Alkalies and alkaline earths	0.13
Heavy metals (Pb)	0.005
Fe_2O_3	0.013
Cl^-	0.004
NO_3^-	Trace
SO_4^{2-}	0.002

uranium dioxide from the graphite; this was then filtered off, washed with water and acetone, and dried at about 100°C. It was shown that about 60 per cent of the fission products are captured in graphite under these experimental conditions.

Apparatus Used.—The flow system of the apparatus used is shown in Fig. 1. It may be divided broadly into three parts: an argon gas purifier, diffusion equipment, and a trapping device for the diffused iodine.

In the argon gas purifier, carbon dioxide, water, and the major portion of oxygen in the argon gas were eliminated with potassium hydroxide, phosphorus pentoxide, and copper net, heated to 400°C, respectively. Copper oxide heated to 300°C was effective in oxidizing carbon monoxide and hydrogen to carbon dioxide and water, which were then absorbed in potassium hydroxide and phosphorus pentoxide respectively. Finally, nitrogen gas and a trace of oxygen gas were removed with uranium turnings heated to 900°C.

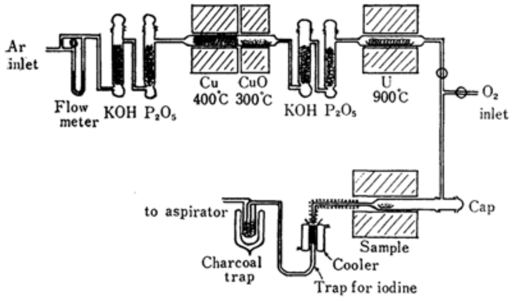

Fig. 1. Apparatus.

A graphite sample placed in a quartz tube was heated in a resistance furnance with nichrome windings. The temperature was controlled with a slide transformer. Diffused iodine-131 was carried by the purified argon gas and introduced into a slender quartz pipe heated to 600°C with a nichrome heater to prevent the iodine-131 from depositing on the wall of the pipe. The absence of such deposits was verified by gamma-assay of a sodium hydroxide solution with which the wall had been rinsed at the end of the experiments.

The trapping of the iodine was given the most careful consideration in setting up the apparatus. It has been established that iodide is the chemical form of iodine diffusing out of graphite into an inert atmosphere and that the iodide deposits on the copper powder surface at about 700°C under certain conditions[5]. Consequently, these facts must be taken into consideration in trapping iodine-131.

A trapping tube for iodine-131 was replaced by a new one at short intervals, whenever a heating curve was obtained or when the activation energy was determined, because a gap was then left between the trap and the pipe. The iodine-131 caught in the trap must be stable in air at room temperature. Such stability was obtained with iodine-131 deposited on copper metal. Before reaching the trap, a portion of the diffused iodine would be oxidized to iodine (I^0) by air entering through the gap. Iodine (I^0) is converted into silver iodide by contact with silver metal at any temperature above that of the room, and the product is stable in air at room temperature. Copper metal also combines with iodine (I^0) at room temperature to form cuprous iodide. The metal, however, is oxidized to copper oxide at a high temperature by air. The authors, therefore, used a trap comprising a glass tube (10 mm. inner diameter; 100 mm. long) stuffed with silver-plated copper netting to a depth of 10 mm. from the end of the tube facing the opening of the pipe, beyond which was copper netting to a depth of 30 mm. The trap was cooled with water circulating through a jacket surrounding the glass tube.

The flow rate of the argon stream through the quartz tube was 150 ml./min.; the narrow opening of the pipe caused the iodine-131 carried with the argon stream to be injected past the gap into the trap. The gas was evacuated through the trapping materials by an aspirator with a capacity of 170 ml./min. With this arrangement, a preliminary experiment showed that all the iodine-131 diffusing out of graphite was in the trap within a depth of 10 mm. from the inlet end.

Making the Heating Curves.—A graphite sample was placed in a quartz boat, which was then inserted through the entrance into the heating part of the diffusion apparatus after taking off the cap. After replacing the cap, the purified argon gas was introduced into the apparatus at a flow rate of 150 ml./min. in order to scavenge the air. At the same time, the slender pipe was set to heat up. As soon as the pipe temperature reached 600°C, the sample was made to start heating, beginning at a temperature of approximately 40°C in all the experiments due to the effect of the slender, highly-preheated pipe. The sample was heated at a rate of 5°C/min., this rate being controlled with a transformer adjusted by hand. The temperature was measured with a platinum-platinum rhodium thermocouple. After reaching 1100°C, the temperature of the sample was lowered to 1000°C, and the argon gas stream was replaced by oxygen gas, flowing at a rate of 150 ml./min., in order to burn out the graphite and to catch remaining iodine-131. Throughout this experiment, the trapping tube was renewed every 10 min. The activity of the iodine-131 caught in each trap was measured with an RCL 256 channel gamma-ray spectrometer equipped with a sodium iodide crystal (3 inch diameter × 3 inch thickness). Errors due to the absorption of gamma-ray from iodine-131 by the glass wall and copper netting of the traps cancelled out, because the glass tube thickness and diameter, as well as the packing conditions of the trapping materials in the traps, were identical.

The ratio of the iodine-131 counts of each trapping tube to the aggregate count of all the tubes was divided by the temperature increment covering the trap in question, the quotient being plotted against the absolute temperature. The histogram thus obtained was redrawn in the form of a smooth curve equivalent in area, as shown in Fig. 2.

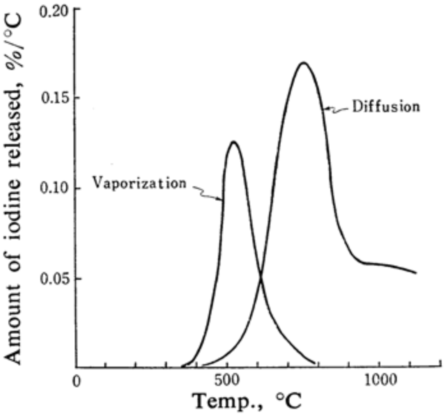

Fig. 2. Heating curves (5°C/min.) of iodine-131.

It is believed that iodine-131, after having diffused, interacts physically or chemically with the graphite crystal on the surface and then leaves the graphite. It would, therefore, be useful to obtain the heating curve of the iodine-131 which, having diffused out of the graphite crystal, has then deposited on the surface of graphite powder of a similar nature. For this purpose, an iodine sample was prepared by means of the thermo-chromatographic method described in a previous report[5]. The heating curve obtained is also shown in Fig. 2.

Determination of Acitivation Energy.—The heating curve of iodine-131 diffusion in graphite crystal has a peak at 750°C, indicating the existence of a mechanism of diffusion predominant at that temperature. Consequently, isotherms for diffusion were determined at 676, 718, 746, and 780°C, temperatures selected in the vicinity of 750°C.

Before putting a sample in the diffusion apparatus, the slender connecting pipe was preheated and kept at 600°C, and the heating section was kept at the designated temperature, while argon gas was allowed to flow at 150 ml./min. through the apparatus. As soon as the graphite sample, placed on a quartz boat, was inserted in the heating section under these conditions, the cap was fastened and the sample heated. The trap was renewed at appropriate intervals. The time of the beginning of diffusion was taken to be the instant the cap was in position.

After being kept at a constant temperature from 2 to 4 hr. in order to get an isotherm, the temperature of the sample was raised to 1000°C and the sample was fired by replacing the argon atmosphere with oxygen gas; the iodine-131 remaining in the graphite was caught in the trap. The trapping tubes were handled and put through spectrometry in the same way as has been described for making heating curves. The amount of diffused iodine-131 is plotted against the diffusion time in Fig. 3.

According to Dienes[6], in the relaxation process, the relaxation time, *t*, and the activation energy, *E*, are related by the equation:

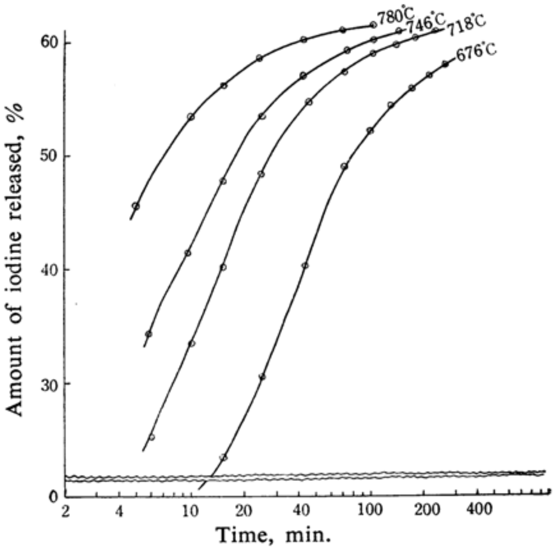

Fig. 3. Isotherms for diffusion of iodine-131.

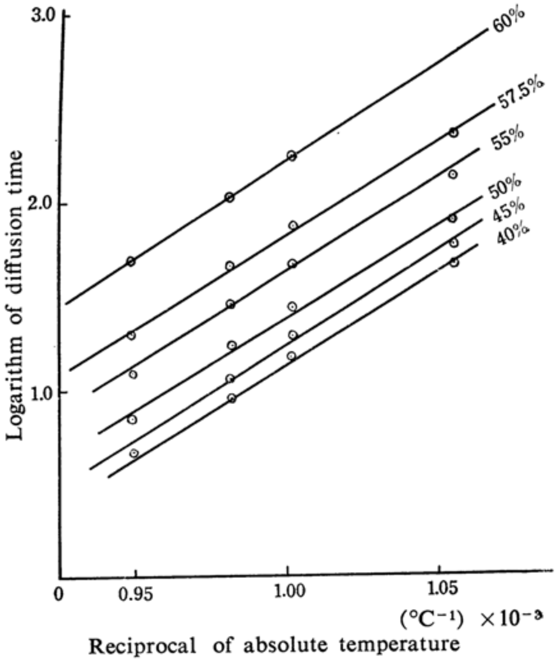

Fig. 4. Activation energies of diffusion of iodine-131.

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[6] G. J. Dienes and W. E. Parkins, "An Improved Method for Determining Activation Energies of Relaxation Process", NAA-SR-60 (1950).

$$t\times\exp(-E/\boldsymbol{R}T)=\text{constant}$$

where $\boldsymbol{R}$: gas constant

T: absolute temperature.

In order to apply this to diffusion phenomena and to determine activation energy, the logarithms of diffusion time corresponding to 40, 45, 50, 55, 57.5, and 60 per cent of the total iodine-121 content on each isotherm were plotted against the reciprocal of the absolute temperature, as is shown in Fig. 4. The groups of points stand along lines with the same gradient. This evidently means that the activation energy of the diffusion of iodine-131 is single. The activation energy calculated from each gradient is given in Table III.

TABLE III. ACTIVATION ENERGIES OF DIFFUSION OF IODINE-131

Per cent	Slope, deg.	Activation energy, kcal./mol.
40	1.01×10^4	46.3
45	1.02×10^4	46.7
50	1.00×10^4	45.8
55	1.02×10^4	46.7
57.5	1.02×10^4	46.7
60	1.05×10^4	49.2

Discussion

It has been clarified that iodide is the chemical form of iodine-131 diffusing out of graphite in an inert atmosphere. In the heating curve of the iodide deposited on graphite powder, a peak appears at 530°C, as is shown in Fig. 2. If there should be no chemical interaction between the iodide diffused out of graphite and graphite crystals on the surface, the heating curve is to be related to the vaporization of the iodide. Most compounds have a measurable vapor pressure in the neighborhood of their melting points; therefore, by a first approximation, the iodide can be considered to have its melting point in the range between 400 and 600°C.

The heating curve of deposited iodide has a peak at 530°C, while the peak of the heating curve of "diffusion" is found at 750°C, which is 200°C higher than that of the iodide. This leads to the conclusion that the iodide which had diffused in graphite and had reached the surface did not stay there, but was carried immediately off by the argon gas stream; that is, the peak at 750°C originated in the very diffusion of iodine-131.

Figures 2 and 3 and Table III show that the bulk of the iodine-131 diffusion in graphite at temperatures lower than 1100°C occurs around 750°C, based on a single mechanism with an activation energy of 47 kcal./mol.

In order to compare the diffusion in graphite crystal of iodine with that of xenon, a typical heating curve and the activation energies of the diffusion of xenon have been reproduced from the fourth and fifth papers of this series; they are given in Fig. 5 and Table IV. Whereas, in the heating curve of xenon, peaks appear at 200, 500, 750, 1000 and 1400°C, that of iodine has only one, at 750°C. Attention is drawn to the fact that a peak at 750°C appears also in the xenon diffusion curve and that the activation energies are approximately equal, as is seen in Table IV. This means that the diffusion of xenon and iodine are governed by one and the same mechanism.

It is also interesting to compare the heating curves of volatile fission products, xenon and iodine, diffusing out of graphite, with the annealing curves of graphite irradiated with fast neutrons. To depict the neutron damage to artificial graphite, differential annealing curves of several physical properties are shown in Figs. 5 and 6, based on work carried out by Woods et al.7) and by Kinchin8). In Table

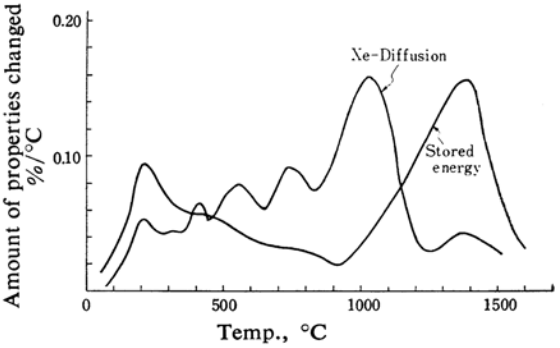

Fig. 5. Heating curve (5°C/min.) of diffusion of xenon and differential annealing curve of neutron damage.

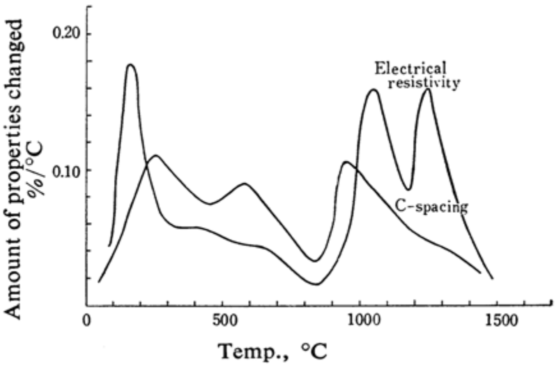

Fig. 6. Differential annealing curves of neutron damage.

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7) W. K. Woods, L. P. Bupp and J. F. Fletcher, Geneva Conference Paper, P/746, 7, 455 (1956).

8) G. H. Kinchin, ibid., P/442, 7, 472 (1956).

TABLE IV. ACTIVATION ENERGIES FOR ANNEALING OF DAMAGE (kcal./mol.)

Phenomena	Exposure	Temperature range, °C			Remark
		150~200	650~850	1000~1200	
Electrical resistivity	8.1×10^{18} n/cm^2	23.8		69.5	Woods[7]
	1.5×10^{19} n/cm^2	29.2		58.2	Woods[7]
	5.4×10^{20} n/cm^2	39.6			Woods[7]
	$\sim10^{19}$ n/cm^2	27.6		69	Kinchin[8]
Xenon diffusion	1.4×10^{13} fp/cm^3	23.8	49	68.4	Yajima[3]
	1.4×10^{13} fp/cm^3			65.5	Yajima[4]
Iodine diffusion	2.6×10^{14} fp/cm^3		47		Present work

IV is given the activation energy of the annealing of electrical resistivity determined by using a pulse-annealing technique.

The peaks of the heating curve of the diffusion of xenon and those of the annealing of neutron damage coincide very well with each other except for the one at 750°C; this coincidence is the more remarkable when one considers the differences in such factors as irradiation conditions of the samples, experimental method, and treatment of data. This indicates that the xenon-tracer technique can match other methods with respect to high sensitivity and simplicity when studying the process of the annealing of imperfections in graphite crystal. Furthermore, the activation energies of the diffusion of xenon at 200 and 1000°C are nearly equal to those of the annealing of electrical resistivity. This means that, so far as these peaks are concerned, the damage due to fast neutrons is the same as that due to fission fragments, and that xenon is released on the annealing of these imperfections.

It has been established that fission fragment damage caused by the recoil of fission fragments into graphite crystal is far greater than fast neutron damage[4,9]. The absence of a peak at 750°C in the annealing curves of the neutron damage would indicate either that this damage is characteristic of fission fragment damage or that other methods less sensitive than the xenon-tracer technique obscure the presence of the 750°C-peak caused by fast neutron damage. However, the latter suggestion cannot be easily affirmed. Therefore, the imperfection corresponding to the 750°C-peak may have its origin in the fission fragments themselves or in fissionable materials, in the present instance, uranium atoms brought into the graphite crystal by fission fragments, because the physical interaction of fission fragments with graphite atoms is not considered to be fundamentally different from those of fast neutrons with graphite atoms.

These assumptions lead to the conclusion that iodine-131 was initially distributed evenly over the various imperfections in the graphite crystal, as was the xenon which had recoiled. However, because of the chemical affinity of iodine, iodine-131 caught in the imperfections (C_2, C_3, C_4,—clusters)[10] corresponding to temperatures below 750°C had a very small probability of migrating between layers or of diffusing out of the graphite crystal, and so tended rather to combine successively with clusters corresponding to higher temperatures at the time of the disappearance of the imperfections. Thus, as clusters begin to disappear at lower temperatures, iodine-131 shifts to clusters corresponding to higher temperatures and is trapped there. Consequently, in the case of iodine, no peak is observed at temperatures lower than 750°C. Finally, iodine-131 combines with those foreign atoms which constitute imperfection corresponding to the peak at 750°C to form the iodide species and to diffuse out. This assumption is supported by the fact that, at 2.6×10^{14} fission products per cubic centimeter of graphite, the amounts of iodine and xenon diffusing at temperatures below 900°C are 42 and 44 per cent respectively, which figures are nearly equal. Another evidence is that many halides of metals like UCl_4, UO_2Cl_2 intercalate graphite in the vicinity of 300°C[11]; this quite low temperature facilitates the diffusion of the iodide species in graphite crystal. To confirm the presence of uranium atoms and to determine the concentrations of the atoms along the range of fission fragments in graphite would further consolidate this assumption.

The authors intend further to pursue their studies of the chemical form and diffusion behavior of the iodine-131 remaining in the graphite without diffusing out at temperatures over 900°C.

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9) R. J. Harrison, CF-53-3-276 (Del.), Radiation Damage Conference, Part I, 93 (1954).

10) T. Iwata and H. Suzuki, "A Model of Radiation Damage in Graphite", I.A.E.A. Symposium on Radiation Damage in Solid and Reactor Materials, Venice (1962).

11) R. C. Croft, *Aust. J. Chem.*, **9**, 184 (1956).

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