The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. IV. Further Studies on the Diffusion of Xenon-133 in Graphite

By Seishi YAJIMA, Sumio ICHIBA, Yuichiro KAMEMOTO,
Koreyuki SHIBA and Masaharu KORI

(Received September 3, 1960)

Several papers have been published on the diffusion of fission products in graphite$^{1-7)}$. Only artificial graphite in a form similar to a fuel element, a disk or a pellet, was used in those experiments. On the other hand, the authors have studied the diffusion of fission products in many kinds of graphite such as amorphous carbon, artificial graphite, and natural graphite. The diffusion of xenon$^{6)}$, iodine$^{7)}$, and tellurium$^{7)}$ in graphite was previously reported. However, more recent study by the authors suggests that in the determination of activation energy of diffusion in such a complicated material as graphite the use of Fick's law is not entirely satisfactory and that fission products in graphite have many energy states. Consequently, this experiment has been undertaken to determine the diffusion rate of fission product xenon-133 in graphite and the distribution of xenon-133 among such energy states as mentioned above.

Theoretical Consideration

In general, the escape rate v of fission products captured in imperfections with energy E is given by

$$v=-\frac{\mathrm{d}n}{\mathrm{d}t}=-\int\frac{n(x,y,t)}{a(x,y)}\mathrm{d}x\mathrm{d}y\,\nu \times\exp[-(E_D+E)/kT] \qquad (1)$$

where

$n(x,y,t)$: number of fission products captured in a small region between x and $x+\mathrm{d}x$, and y and $y+\mathrm{d}y$.

$a(x,y)$: number of jumps of fission products required to escape from the graphite.

E_D : activation energy of diffusion of fission products.

T : temperature in °K.

ν : frequency of vibration of a fission product in the graphite.

k : Boltzmann constant.

If an isothermal escape rate of a fission product in a sample is determined at T_1,

$$v_1=-\int\frac{n_1(x,y,t)}{a(x,y)}\mathrm{d}x\mathrm{d}y\,\nu \times\exp[-(E_D+E)/kT_1] \qquad (2)$$

After time t, if T_1 is instantly increased to T_2 and an isothermal escape rate is determined at the temperature,

$$v_2=-\int\frac{n_2(x,y,t)}{a(x,y)}\mathrm{d}x\mathrm{d}y\,\nu \times\exp[-(E_D+E)/kT_2] \qquad (3)$$

When being extrapolated to t, n_1 is equal to n_2. Then,

$$\ln(v_2/v_1)=\frac{E_D+E}{k}\,\frac{T_2-T_1}{T_1T_2} \qquad (4)$$

or

$$E_D+E=\frac{2.303\,kT_1T_2}{T_2-T_1}\log(v_2/v_1) \qquad (4')$$

When the fission products are caught in imperfection distributed over various energy states of graphite, Eq. 4 must be carefully applied to the calculation of activation energies. As Mugnuson et al.$^{8)}$ discussed, however, if the difference of temperature T_1 and T_2 is taken as small as possible, the most important activation energy of the diffusion of fission products within the range of T_1 and T_2 is calculated according to Eq. 4.

Experimental

Preparation of Samples.—A mixture of 1 g. of graphite powder and 60 mg. of uranium dioxide was irradiated with thermal neutrons (thermal

---

1) D. Schulz, "Summary Report for January, February, and March, 1947", ANL-4006, Sec. 1. 6, 62 (Oct. 3, 1947).

2) C. A. Smith and C. T. Young, "Diffusion of Fission Fragments from Uranium-Impregnated Graphite", NAA-SR-72 (May 4, 1951).

3) D. Cubicciotti, "The Diffusion of Xenon from Uranium Carbide-Impregnated Graphite", NAA-SR-194 (Oct. 13, 1952).

4) C. T. Young and C. A. Smith, "Preliminary Experiments on Fission Product Diffusion from Uranium-Impregnated Graphite in the Range 1800~2200°C", NAA-SR-232 (March 25, 1953).

5) L. B. Doyle, "High-Temperature Diffusion of Individual Fission Element from Uranium Carbide-Impregnated Graphite", NAA-SR-255 (Sept. 11, 1953).

6) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, This Bulletin 33, 497 (1960).

7) S. Yajima, S. Ichiba, Y. Kamemoto and K. Shiba, ibid., 34, 493 (1961).

8) G. D. Mugnuson, W. Palmer and J. S. Koehler, *Phys. Rev.*, 109, 1990 (1958).

neutron flux, about 5×10^{11} neutrons/cm²/sec.) for five hours in an experimental hole of JRR-1 reactor. After irradiation the mixture was treated with a hot 4 N nitric acid solution to dissolve uranium dioxide and neptunium-239 produced. In order to measure the activity of xenon-133 without any influence of other fission xenon nuclides and iodine-133, the irradiated graphite samples were cooled for four days before use.

Particle sizes of graphite samples used in this experiment and the analytical data on impurities are shown in Table I.

TABLE I. PARTICLE SIZES OF GRAPHITE SAMPLES AND ANALYTICAL DATA OF IMPURITIES

	Sample		
	AG (Artificial graphite)	NG-1 (Natural graphie-1)	NG-2 (Natural graphite-2)
Particle size (micron)	30	1	50
Impurity			
Ash (total)	0.07%	0.3%	0.8%
SiO_2	250 p.p.m.	220 p.p.m.	3700 p.p.m.
Al_2O_3	210	60	3500
Fe_2O_3	130	24	300
MgO	15	24	100
CaO	70	36	300
V_2O_5	—	0.12	0.5
MnO	—	—	—
Na_2O	20	12	25
K_2O	15	12	20
NiO	—	0.06	—
ThO_2	—	2.4	—
CuO	—	—	—
B_2O_5	0.1	0.02	0.5

Determination of Activation Energy.—A flow system is illustrated in Fig. 1. Furnace-C_1 and Furnace-C_2 consisted of an alundum tube with a nichrome winding. The temperature of the furnaces could be increased to 1150°C and kept constant at a temperature with a transformer. The temperature was measured with a platinum-platinum rhodium thermocouple. The temperature of Furnace-C_2 was always kept about 50°C higher than that of Furnace-C_1.

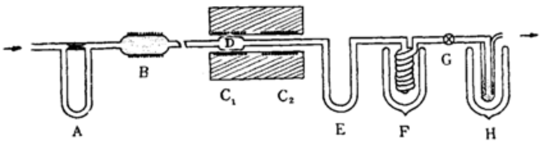

Fig. 1. Flow system.

A Flow meter B Sponge titanium
C_1, C_2 Furnace D Diffusion cell
E Phosphorus pentoxide
F Dry ice trap G Stopcock
H Charcoal trap cooled with dry ice

Each part of the system was made of hard glass except a silica tube in the furnace in which samples were heated, and each part was connected with a polyethylene tube.

Helium gas at a constant flow rate (100 ml./min.) was purified with sponge titanium heated at 800°C to eliminate a trace amount of oxygen. Phosphorus pentoxide was used to remove water in the gas which had swept over a sample. A dry ice trap was set to remove volatile fission products other than rare gases. Xenon-133, which was released, was adsorbed on charcoal cooled with dry ice which was set next to the trap without charcoal. When the charcoal trap was exchanged for a new one at appropriate intervals, a change-over cock was serviceable for the continuous catch of xenon-133 on charcoal.

A typical experiment was as follows. The graphite powder described above was placed in a silica boat which was slid into the silica tube. Then, helium gas was introduced into the system. After confirming that helium gas took the place of air, the tube was slid into Furnace-C_1. The graphite sample was heated at a constant temperature for 30 min. During this period the charcoal trap was exchanged every 5 min. Just 30 min. after the beginning of the heating, the sample together with the tube was slid into Furnace-C_2 whose temperature had been about 50°C higher than that of Furnace-C_1. The trap was exchanged every 2 min. and the sample was heated at a constant temperature for 12 min. The temperature was measured with a platinum-platinum rhodium thermocouple adjacent to the sample. Such a procedure was repeated at a set of increased temperatures.

Making of Heating Curve.—In order to make a heating curve, a graphite sample was heated with a constant increment of temperature and xenon-133 released during a constant period of time was adsorbed on charcoal.

The amount of the released nuclide was plotted versus temperature. The flow system is the same as that shown in Fig. 1 except a furnace and a tube in which a sample was heated. Because the temperature of samples must be continuously increased to temperatures as high as possible, silicon carbide was used as the heater of the furnace.

The sample described above was placed in an alundum boat which was slid into the alundum

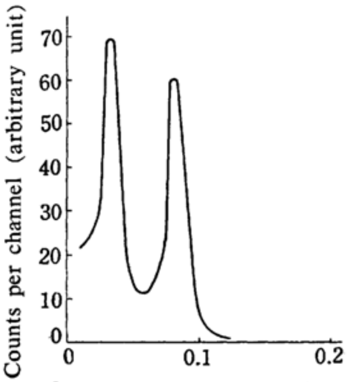

Fig. 2. Gamma-ray spectrum of xenon-133 in a charcoal trap.

tube. Then, helium gas was introduced into the system. After confirming that helium gas took the place of air, the tube was slid into the furnace. The sample was heated with a contsant increment of temperature, 3°C/min. Xenon-133 released was adsorbed charcoal in a trap cooled with dry ice, the trap being exchanged every 10 min.

Activity Measurement.—Activity of xenon-133 adsorbed on charcoal was measured with a RCL 256 channel gamma-ray spectrometer with a well type NaI scintillator (2 inch diameter×1.75). The charcoal was placed in the well, with its trap made of glass, and the activity was measured. The gamma-ray spectrum of xenon-133 is illustrated in Fig. 2.

Results

The absolute value of v_1 and v_2 is not always necessary but the ratio of v_2/v_1 is necessary for determining the activation energy according to Eq. 4. Therefore, when amounts of xenon-133 remaining in graphite are plotted versus diffusion time, the ratio v_2/v_1 is equivalent to a ratio of tangential slopes at a discontinuous point of temperature. A typical plot is shown in Fig. 3. The values obtained from these plots are given in Table II, and the apparent activation energy versus absolute temperature is illustrated in Fig. 4.

Heating curves obtained by another experiment are illustrated in Figs. 5—7. The axis

Table II. Activation energies of diffusion of xenon-133 in graphite

AG (Artificial graphite)

T_1 °C	T_2 °C	v_2/v_1	$E+E_D$ kcal./mol.
228	269	5.48	23.8
400	447	4.72	31.8
490	539	4.48	37.4
606	675	6.37	40.6
725	780	4.94	60.7
815	870	3.74	59.2
910	950	2.55	67.7
1023	1082	3.88	80.2

NG-1 (Natural graphite-1)

T_1 °C	T_2 °C	v_2/v_1	$E+E_D$ kcal./mol.
380	418	3.58	30.3
500	560	4.28	32.0
656	696	2.17	34.6
786	840	3.06	48.6
915	956	2.12	53.3
1041	1090	1.81	68.4

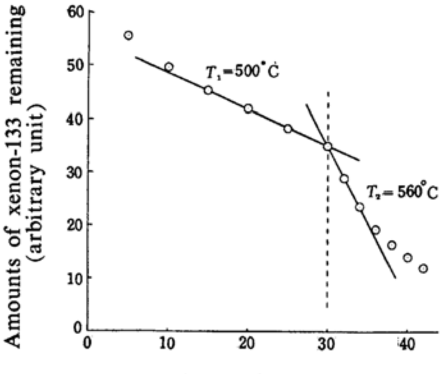

Fig. 3. Isothermal escape rates of xenon-133 in natural graphite-1 at 500 and 560°C.

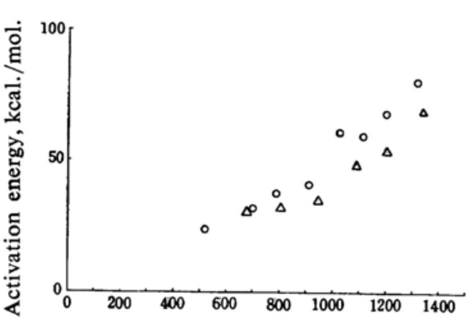

Fig. 4. Apparent activation energy versus temperature.

○ AG △ NG-1

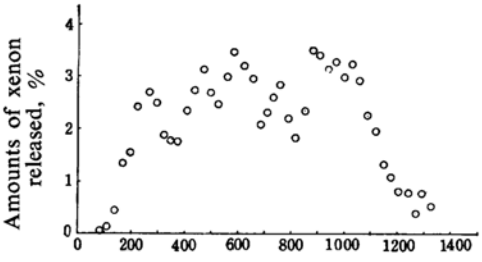

Fig. 5. Heating curve (3°C/min.) of natural graphite-1.

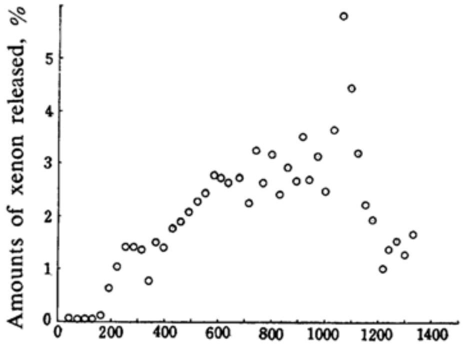

Fig. 6. Heating curve (3°C/min.) of natural graphite-2.

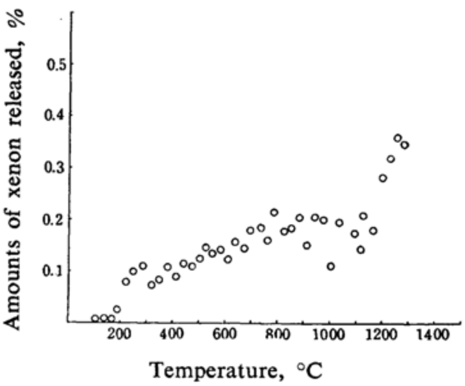

Fig. 7. Heating curve (3°C/min.) of artificial graphite.

of abscissa is temperature and the axis of ordinate is percent xenon-133 released from graphite every 10 min.

Discussion

In the previous experiment⁶⁾, it was observed that the diffusion of xenon consisted of a rapid diffusion and a slow diffusion, and from the latter, the activation energy of the interstitial diffusion was calculated. But it is inadquate to treat the diffusion of xenon in graphite from the slow diffusion alone.

The tendency of the diffusion was observed by Argonne workers¹⁾ and Cubicciotti³⁾. The Argonne workers interpreted that there were two mechanisms for the diffusion, a rapid "pore" diffusion and a slow "crystallite" diffusion. However, as pointed out by Cubicciotti, if the above interpretation were correct, there would be a truly rapid diffusion which would eventually give way to a slow diffusion at one temperature; that is, all the rapidly diffusing material would have been gone in a short time and then, an increase in temperature would result in the simple diffusion of the slowly diffusing material. Experimentally, however, it is found that with each increase in temperature there is a rapid escape of xenon. Cubicciotti explains that the initial rapid escape is attributed to a rapid temperature increase of the sample. On the other hand, our experiment on natural graphite-2 showed no striking effect of the rate of temperature increase: the amount (46.3%) of xenon-133 released when the temperature of a graphite sample was increased from room temperature to 800°C in 3 min. and kept constant at 800°C for 90 min. was nearly equal to the amount (41.7%) of xenon-133 released when the temperature of another sample was increased from room temperature to 800°C at a rate of 3°C/min. This fact suggests that the amount of xenon-133 released is mainly determined by a final temperature.

Circles and triangles in Fig. 4 are not on a straight line parallel to the axis of abscissa but on ascending lines, respectively. In other words, the activation energy of the diffusion is not simple but consists of various values, say, 20∼40 kcal. at 500 to 1000°K and higher at temperatures over 1000°K. This tendency is the same both in artificial and natural graphite except the fact that the activation energy of diffusion in artificial graphite is a little higher than that in natural graphite.

Heating curves in Figs. 5—7 show the distribution of the amount of released xenon over a wide range of temperature. These figures also indicate the distribution of the energy of xenon in graphite, when the relation shown in Fig. 3 is taken into account. The energy is considered to correspond to E in Eq. 4 because E_D is far smaller than E. From these observations, the fact that the diffusion rate of xenon in natural graphite was greater than that in artificial graphite will be explained as follows. Xenon atoms in natural graphite are distributed more in sites of a low activation energy while xenon atoms in artificial graphite are more in sites of a high activation energy. Therefore, the amount of xenon diffusing out at a temperature is greater in natural graphite than in artificial graphite. Although not studied thoroughly, it is supposed that xenon atoms exist on vacant sites of graphite lattice and that the above mentioned activation energies are determined according to the position of such xenon atoms, because the activation energy of the interlaminar diffusion in graphite is known to be very low. It is obvious by the X-ray diffraction and the electron diffraction methods that artificial graphite is more imperfect than natural graphite. This means that the number of vacancies is larger in artificial graphite than in natural graphite. In this sense, a heating curve is considered to show also the distribution of the vacancies among sites of various energies.

On the basis of discussion described above, a rapid diffusion and a slow diffusion in an isothermal curve are easily interpreted. When a graphite sample is rapidly heated to a certain temperature, a xenon atom existing in a site with an activation energy which corresponds to the temperature diffuses out through the interlaminar space: this is a rapid diffusion. During the maintenance of the temperature, xenon existing in a site with a larger activation energy escapes out with a certain probability: this is a slow diffusion. It is evident that Fick's law can not be applied to such a system, because the law deals with diffusion only in terms of concentration gradient.

The authors wish to thank Dr. H. Suzuki of Solid State Physics Laboratory of JAERI for helpful discussions.

Division of Chemistry
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken
(S. Y., S. I., Y. K. & K. S.)
Mitsubishi Atomic Power Industries
Inc. Laboratory
Omiya-shi Saitama-ken
(M. K.)