*On the Permeation of Iodine through Graphite**

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(Received March 7, 1963)

Gas permeation through artificial graphite can occur, because of its porous nature, via three paths: through the pore volumes, along pore surfaces, and through the graphite structure. The relative importance of these paths depends on the pore structure of the graphite bodies and on the chemical nature of the diffusing substances.

We have previously reported on the permeation of inert gases through graphite(1) and also on the absorption of bromine to carbonaceous materials(2); each report was concerned with a limiting case of the gas permeation processes through graphite.

In the present paper, the behavior of iodine permeating through graphite is discussed. It is known that iodine is non-reactive with graphite at any temperature and that it does not form a lamellar compound(3), in contrast to the well-known case of bromine.

Nevertheless, iodine possibly has some such weak interaction with graphite as chemisorption(4), and it is expected to show some interesting behavior upon its permeation through graphite because of its condensable character. Moreover, as one of the main fission products of uranium, the behavior of iodine in graphite neutron moderators has attracted recent attention(5,6).

The purpose of the present paper is to discuss the character of the iodine diffusion through graphite at temperatures ranging from 90 to 160°C on the basis of its dependence on temperature and pressure. The effect of the presence of inert gas on the rate of iodine permeation is also investigated.

Experimental

Preparation of the Graphite Specimens.—Samples of graphite were cut to disks, 3 mm. thick and 15 mm. in diameter, which had a ring-shaped depression on one side. As is shown in Fig. 1, glass tubes were cemented to the graphite specimens with silver chloride. The procedure of the cementing was as follows: The surface of the depression on the graphite specimens was electroplated with silver, using the electrolyte of a silver cyanide aqueous solution with which the depresssion was filled. After being washed and dried thoroughly, silver chloride powder was mounted on the electroplated silver and heated indirectly and slowly, until it melted. Then, a moderately preheated glass tube was immersed in the melt and cooled very slowly.

The glass-to-graphite seal was verified to be leakproof by preliminary experiments, in which the values of the air permeability of the same graphite

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* Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

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4) P. Connor, J. B. Lewis and W. J. Thomas, "Proceedings of the 5th Conference on Carbon", Vol. 1, Pergamon, New York (1962), p. 120.

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6) L. B. Doyle, NAA-SR-255 (1953).

TABLE I. CHARACTERISTICS OF THE GRAPHITE SAMPLES AND A COMPARISON OF THE FLOW RATES FOR AIR AND IODINE

Graphite sample	Characteristics of the sample			Flow rate (NTP. cc./sec.)		Ratio
	Apparent density g./cm^3	Porosity %	Permeability at stand. condition K, cm^2/sec.	Air Q_{air}	Iodine Q_{I_2}	$\frac{Q_{air}}{Q_{I_2}}$
A	1.49	32.2	6.5×10^{-1}	4.35×10^{-2}	1.57×10^{-2}	2.77
$B_{\parallel}$*	1.78	19.6	1.5×10^{-1}	1.17×10^{-1}	3.34×10^{-2}	2.85
$B_{\perp}$*	1.78	19.6	8.4×10^{-2}	4.75×10^{-2}	1.77×10^{-2}	2.68
D**	1.82	11.8	3.2×10^{-3}	$7.5\ \times10^{-4}$	$(\sim2\times10^{-4})$†	(~3.5)†

* The subscripts $\parallel$ and $\perp$ designate directions of the flow parallel and perpendicular, respectively, to the plane pressed on molding.

** This sample was doubly impregnated.

† This value includes an experimental error of ±50% because of the difficulties of measuring the flow rate of such a small order.

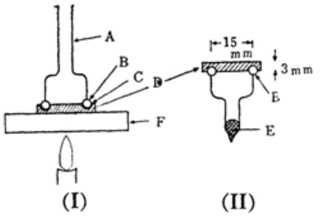

Fig. 1. The sample capsule. The preparation of the glass-to-graphite seal (I) and the complete form of the capsule (II).

A : Glass tube
B : AgCl binder
C : Electroplated silver
D : Graphite specimen
E : Iodine
F : Graphite plate for indirect heating

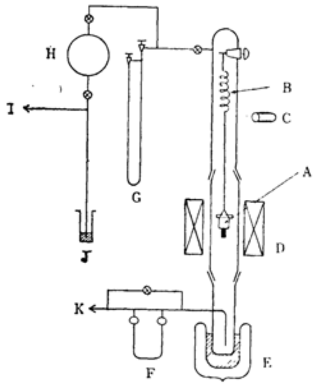

Fig. 2. Apparatus for iodine permeation experiments.

A : Sample capsule
B : Quartz-spring balance
C : Running microscope
D : Electric furnace
E : Dewer vessel
F : Flow meter
G : Manometer
H : Gas reservior
I : To argon bomb
J : Manostat
K : To vacuum line

specimen were compared between two cases with different seals, silver chloride and Araldite†. The results of the two cases agreed very well*.

Measurement of the Rate of Iodine Permeation.—About 1 g. of GR-grade iodine was sealed in a glass tube fitted to the graphite specimen. The capsule thus prepared (as shown in Fig. 2) was suspended by a quartz-spring balance in a reaction tube. The reaction tube was evacuated for about one hour, until the air in the capsule had also been evacuated through the graphite specimen.

The capsule was then heated in vacuo or in argon flow, and the rate of the weight loss of the capsule, which was caused by the iodine permeation through the graphite specimen, was measured at controlled temperatures. The whole apparatus is shown in Fig. 2.

The air permeability of each specimen was also measured by the method described in a previous report[2)].

Samples.—Graphite samples were ordinary artificial graphite and high-density nuclear graphite, produced by the Nippon Carbon K. K. and the Tokai Denkyoku Seizo K. K.*

The characteristics of the samples are listed in Table I.

Results and Discussion

Iodine Permeation into a Vacuum.—The rate of iodine permeation was determined from the gradient of a plot of the weight change of the sample capsule vs. time. The plots were found to be linear in a steady state for every run of the experiments.

The results are summarized in Fig. 3, which

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† Epoxy resin produced by Ciba, Ltd.

* Typical results of the preliminary experiments were as follows:

Graphite sample	Air permeability, cm^2/sec.	
	AgCl seal	Araldite seal
A	1.93	1.88
B	3.51×10^{-2}	3.52×10^{-2}

* The authors wish to express their gratitude to the Nippon Carbon K. K, and the Tokai Denkyoku Seizo K. K. for kindly providing us with the samples.

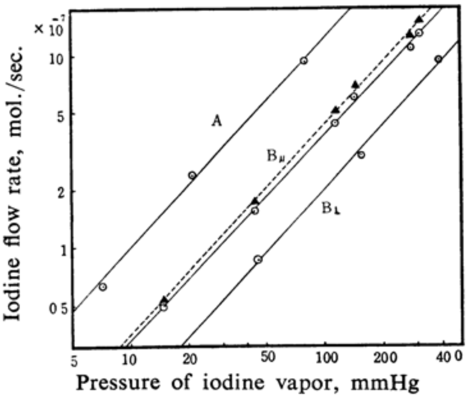

Fig. 3. Iodine flow rate as a function of the pressure of iodine vapor in log-log plot. The broken line is modified with respect to temperatures.
A, B∥ and B⊥ designate the graphite sample, characteristics of which are listed in Table I.

is a log-log plot of the rate of iodine permeation and the pressure of iodine vapor, which was equilibrated with solid or liquid iodine at each temperature of the experiments. The gradients of the plots in Fig. 3 have the same value, 1.06, for all samples. Accordingly, it was concluded that the rate of iodine permeation increased roughly proportionally to the pressure of iodine vapor at pressures lower than 400 mmHg.

It is natural to suppose, as a first appoximation, that the iodine permeation through graphite consists mainly of gas flow through the pore volumes of the media. When a single gas flows isothermally and in a steady state through the pore volumes of the media, the flow is usually considered to consist of two types, namely viscous and Knudsen flows; at any rate, it is known that it can be expressed by the following equation[1]:

$$q_m P_m = vRT = \frac{A}{L}(B_o P_m + K_o)\varDelta P \tag{1}$$

In Eq. 1, the viscous flow rate is expressed by the first term, characterized with the coefficient B_o, and the Knudsen flow by the second term, involving the coefficient K_o. q_m means the volume flow rate, cm³/sec., at a pressure of P_m, and v means the molar flow rate, mol./sec., A and L are the cross-section and the thickness of the specimen respectively.

For the present experiments, where the flowing gas consisted of the iodine gas only, P_m and $\varDelta P$ in Eq. 1 were replaced by $P_{I_2}/2$ and P_{I_2} respectively. Thereby Eq. 1 becomes:

$$v = \frac{1}{RT} \cdot \frac{A}{L}\left(\frac{1}{2} B_o P_{I_2} + K_o\right) P_{I_2} \tag{2}$$

Two limiting cases are derived from Eq. 2, pure viscous flow and pure Knudsen flow. In the case of the pure viscous flow, at a definite temperature, v increases with $(P_{I_2})^2$. On the contrary, v increases with P_{I_2} for the pure Knudsen flow.

The experimental resuls of Fig. 3, showing that v increased almost linearly with P_{I_2}, lead to the plausible conclusion that, for the iodine permeation through graphite, the Knudsen flow is predominant. This conclusion was further examined by considering the temperature dependence of the flow rate in Eq. 2. As the coefficient, K_o, for the Knudsen flow is also proportional to the spuare root of T, the values of v, which were measured at different temperatures, ought to be normalized as follows:

$$v_o = v\left(\frac{T}{T_o}\right)^{1/2} \tag{3}$$

where v_o is the normalized molar flow rate at the temperature of T_o.

The re-plot of v_o normalized at $T_o = 300°\text{K}$ is presented in Fig. 3 as a broken line, which gives the gradient of 1.09. This result revealed that the conclusion mentioned above was appropriate.

The Knudsen model for iodine permeation was also supported by the comparison of the flow rates for air and iodine. The obtained values of the flow rates, which are normalized to the same condition of temperature and pressure for both air and iodine, are tabulated in Table I. It was also confirmed experimentally that the air flow at the normalized condition consisted mainly of the Knudsen flow.

Provided that the flows of both air and iodine are those of the Knudsen type, the ratio of the flow rates, (Q_{air}/Q_{I_2}), ought to be equal to the square root of (M_{I_2}/M_{air}), namely, 2.96 (where M means the molecular weight of the gases). The experimental values obtained were 2.68~2.85. The values of theory and experiments agree fairly well. The small discrepancies are possibly due to the small contributions of the viscous part to the total flow, since the mean free path of air is about 1.5 times longer than that of iodine at the same pressure and so the contribution of the viscous part of the air flow is probably smaller than that of the iodine flow.

Iodine Permeation in Argon Gas.—The rate of iodine permeation was measured also in an argon gas flow of controlled pressure in order to clarify the effects of inert gases on the behavior of gas permeation through porous media such as graphite. The apparatus used and the method of measurements were just the same as above, except that argon gas streamed at the mean flow rate of 1 cm./sec. in the reaction tube shown in Fig. 2.

It was found that the rate of iodine permeation was depressed markedly in the stream of argon gas. As is clear from Fig. 4, in which a plot of $1/v$ vs. mean gas pressure ($P_{I_2}/2 + P_{Ar}$) is presented, even at the mean pressure of the Knudsen diffusion region (at pressure below 400 mmHg), the rate of iodine permeation decreased with an increase in argon gas pressure. This fact seems to be rather curious, because in the Knudsen region the flow rate of one species might not be affected by the presence of the other species.

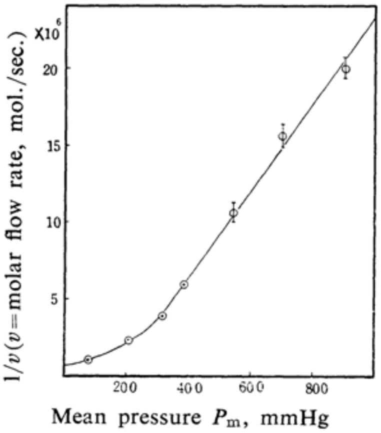

Fig. 4. The dependence of iodine flow rate on the pressure of argon gas.

It has been reported by Korsmeyer⁷⁾ and Evans et al.⁸⁾, however, that the same phenomena as have been described above were observed in the measurement of the counter-current mutual permeation of helium and argon through graphite septum. They pointed out that, for the gas flow through porous media such as graphite, even at the pressure of the Knudsen region, a pure Knudsen flow is not realized and that the mutual diffusion effect must be taken into account. The Knudsen coefficient, K_0, in Eqs. 1 and 2 is, therefore, replaced by a total diffusion coefficient, $(K_1)_{eff}$, and is represented by the Bosanquet type of an equation⁹⁾ as follows:

$$(K_1)_{eff}^{-1} = (D_{12})_{eff}^{-1} + K_0^{-1} \tag{4}$$

where $(D_{12})_{eff}$ is the effective mutual diffusion coefficient proportional to D_{12}, the usual diffusion coefficient of the gases. The constant of proportionality is charcteristic of the internal geometry of the porous medium. Evans et al.⁸⁾ have theoretically derived just the same formula as Eq. 4, applying the "dusty gas model" for the diffusion of gases in porous media.

Since D_{12} in Eq. 4 is roughly inversely proportional to the mean pressure of gases, the relationship of $1/v$ vs. P_m obtained in the present study (as shown in Fig. 4), especially at the linear part of the figure, is explained reasonably by this model. The reason for the discrepancy in the lower pressure region is not clear, but it is likely that this is due to the character of the flow in this region, which is supposed to be intermediate between the capillary model and the "dusty gas model".

Summary

The rate of iodine permeation through graphite has been studied and the following results were obtained:

(1) The process of iodine permeation through graphite has been found to consist mainly of a simple gas flow through the pore volumes, just as in the case of inert gases. The chemical interaction between iodine and graphite has been observed to be negligibly small.

(2) At tempeatures ranging from 90 to 160°C, and under a corresponding pressure of iodine vapor below 400 mmHg the rate of iodine permeation has been observed to be almost linearly proportional to the pressure of iodine. It has been concluded that the Knudsen flow was the predominant element of the total flow.

(3) The ratio of the flow rates for air and iodine, which were interpolated to the value under the same conditions, has been calculated to be 2.68~2.85, close to the value 2.96, namely $(M_{I_2}/M_{air})^{1/2}$, as was expected from the Knudsen flow model.

(4) The rate of iodine permeation has been observed to decrease in the presence of argon gas, even in the region of Knudsen flow. It has been found that the rate is roughly inversely proportional to the pressure of argon gas. The "dusty gas model" discussed by Evans et al. has been adapted to give a reasonable explanation of this phenomena.

The authors are indebted to Mr. O. Lee for help in a part of the measurements.

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