Interdiffusion of Helium and Argon in a Large-Pore Graphite

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MEASUREMENTS of the mutual diffusion coefficients for binary gas mixtures have been conducted for many years, utilizing the classical diffusion experiment (*11*) in which the diffusion rates of the components are forced to equality through the use of closed diffusion cells of known geometry (*5, 8*). A more complicated problem is posed when diffusion takes place in a porous medium. The internal geometry of the medium may be difficult to define and the over-all diffusion mechanism could be comprised of several individual mechanisms. Excellent summaries of these and of similar situations as they might influence chemical reactions taking place in the pores of catalysts have been given by Wheeler (*17*) and Weisz (*16*).

The present experiments were a part of a series of survey experiments designed to aid in the selection of flow equations applicable to the movement of gases within components of a helium-cooled nuclear reactor. The experimental method selected for these studies was originally developed by Wicke (*18*), who was primarily interested in the surface diffusion rates of adsorbed CO_2 through porous media. A mixture of N_2 and CO_2 was impacted on one face of a porous pellet while N_2, which was present as a diluent, was impacted on the opposite face to maintain a uniform total pressure. The CO_2 diffusion rates were measured; the N_2 rates were neglected. In subsequent work, Wicke (*19*) turned to forced flow experiments with CO_2; however, the original method closely simulates many applied diffusion situations and offers the advantage of performing steady-state rate measurements. Several investigators have employed this technique to determine diffusion mechanisms within porous media (*13, 16, 17*) as well as the anisotropic flow properties of graphites (*15*).

Although exhaustive studies had been made on net drift effects in large pore material with ternary gas mixtures (*2, 12*), Hoogschagen (*9*) appears to be the first to observe this effect for binary systems. This worker utilized Wicke's method with the additional precaution of measuring the rates of both gases at uniform total pressure. The net drift was such that the ratio of the rates was inversely proportional to the square root of the molecular weights of the gases. Elementary discussions and equations for net-drift situations with binary mixtures are available in the literature (*7, 13*).

MATERIALS

National Carbon Co. AGOT (CS Grade) graphite was selected as the diffusion medium for this study. Typical pore size distribution data for this material are available (*6*). These data were used to prepare the plot of Figure 1, which indicates that the pore spectrum is bimodal with a maximum differential volume at a radius of 2.5 microns.

The experimental diffusion medium consisted of a cylindrical septum. The axis of the septum was perpendicular to the axis of extrusion of the source material which was in the form of a 4-inch × 4-inch × 4-foot block. Permeability data obtained with the septrum after it had been sealed into the diffusion cell are shown on Figure 2. The variable constant, k, is a measure of the admittance of the material to forced fluid flow (*1*). The definitive equation relating k and the variables measured is

$$k = \frac{Q_a P_a \mu L}{P_m A \Delta P} \qquad (1)$$

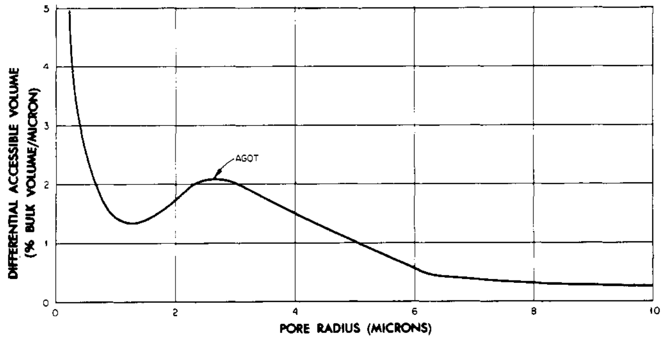

Figure 1. Differential accessible volume as a function of pore radius for AGOT graphite

where Q_a is the flow rate, cc. per second, measured at a pressure P_a, atm.; μ is the viscosity, centipoise; L is the septum thickness, cm.; A is the cross-sectional area of the septum, square cm.; P_m is the average pressure of the gas within the septum, atm.; and ΔP is the pressure drop across the septum, atm. Using the units mentioned, one obtains k in darcys. The pressure dependence of k is measured by the slope of the curves. A slight slope, as shown, indicates the presence of some "slippage" or Knudsen effects with the majority of the flow taking place as classical viscous flow.

Samples of the same source were utilized to obtain porosity (*14*), surface area, and adsorption data. The open-pore porosity was found to be 22 volume % using a helium density method; the total porosity was 26 volume %. The latter value was based on a theoretical graphite density of 2.25 grams per cc. Surface area determinations resulted in a value of 0.64 square meter per gram. The equations for the adsorption isotherms of argon and xenon at 0° C. are (*4*)

$$y = 1.60 \times 10^{-5} p^{0.8} \qquad (2a)$$

for argon, and

$$y = 2.14 \times 10^{-4} p^{0.8} \qquad (2b)$$

for xenon; y is the amount of gas absorbed, cc. STP per gram of graphite, and p is the partial pressure of the absorbed gas, mm. of Hg.

On the basis of the curves of Figure 1, it was concluded that a small amount of Knudsen flow (*10*) might be present.

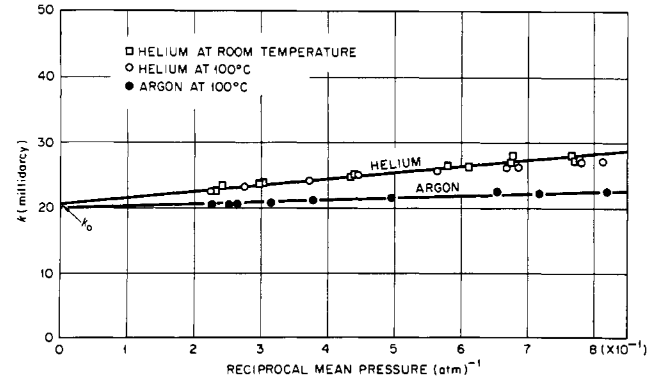

Figure 2. Generalized permeability constants for diffusion septum

However, the data of Equation 2a combined with estimates of the surface diffusion rates to be expected revealed that surface diffusion of argon could not be detected in this material under the conditions of these experiments.

Cylinders of analyzed helium and argon were used as the sources of gas for the experiments. The free oxygen content of these gases ranged from 1 to 4 p.p.m. The water concentrations encountered were 10 to 15 p.p.m. as determined by a dew point method. No attempts at additional purification were made. The good reproducibility of data obtained before and after the diffusion experiments demonstrated that the flow properties of the graphite remained unaltered during the experimental period.

APPARATUS AND PROCEDURE

A photograph of the diffusion cell assembly is shown on Figure 3. The components, from bottom to top, are: the argon outlet which contains the thermocouple, the container, the diffusion septum, and container cap, and the inner helium flow guide. The graphite septum was attached to the end caps shown with National Carbon Co. No. 14 cement. An exposed length of 4 inches was left uncoated. The outer diameter was 0.8 inch and the inner diameter was 0.5 inch. This gave a logarithmic mean area to length ratio of 135.8 cm.

For a diffusion experiment helium was forced into the upper tee, down the ¼-inch to ⅛-inch tubing annulus, along the inner graphite surface and out the ⅛-inch tubing. Argon was forced into the lower tee, around the outer graphite surface, and out the bottom. A drawing of the entire system is shown on Figure 4. The gases were admitted at the nonbleed regulators, passed through the cell, and throttled to atmospheric pressure at the needle valves. Gas samples for mass spectrometer analyses were taken at A and A_1. After the gases were passed through the thermal conductivity cell, they were passed through the wet-test meter, then vented. All the results reported here are based on mass spectrometer analyses, as the thermal conductivity arrangement was undergoing calibration during these experiments.

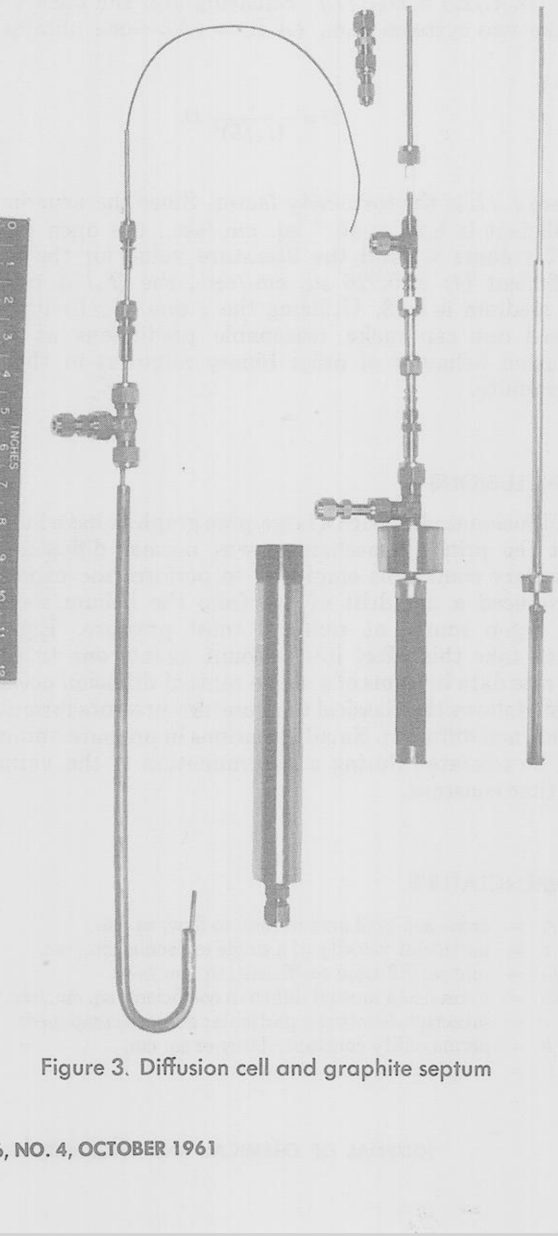

Figure 3. Diffusion cell and graphite septum

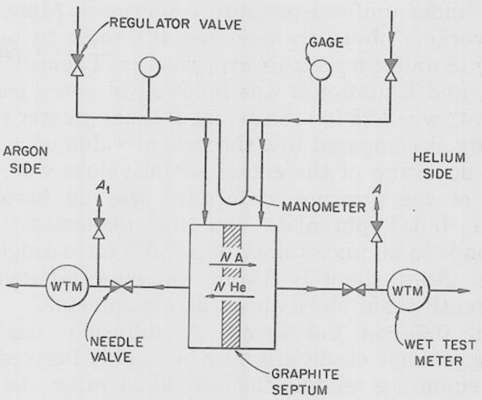

Figure 4. Diagram of diffusion apparatus

A series of blank runs was performed with partial cells or "dummies" to determine pressure drops in the system between the manometer taps and the exposed graphite. These data led to small corrections (2 to 8 mm. of butyl phthalate) which were applied to the manometer readings during diffusion determinations. The entire cell (with preheating coils) was suspended in a thermostat for the 100° C. experiments. All thermometers, thermocouples, gages, and meters were calibrated before the experiments. Based on all the uncertainties associated with the experiment, the estimated maximum error in the measured coefficient was ±5%.

RESULTS AND DISCUSSION

The results of three sets of experiments performed during this investigation are presented in Tables I and II. Experimentally determined values of temperature, pressure, the average gas concentrations at each face of the septum, the measured diffusion rates of helium-argon and net drift, and a single mutual diffusion coefficient for the helium-argon mixtures in this particular graphite are shown. Before presenting the methods employed to calculate the coefficient, it is pertinent to discuss the net drift (η_T) value and the η_{He}/η_A ratios for the uniform pressure experiments as tabulated in Tables I and II.

Net Drift. The net molecular flow (from the helium to argon side) at uniform total pressure is, as stated earlier, a result of the boundary conditions of the experiment. Flow equations by Present (*13*) and Hirschfelder (*7*) clearly indicate that the interdiffusion rates can be equal under this condition only when transient experiments are conducted in closed containers. Although the presence of a net molecular drift has been discussed in textbooks, no theoretical derivations have been encountered which would enable one to predict the value of the net drift or the η_{He}/η_A ratio for large conduits. Fortunately, a few rather definitive experiments were noted by Hoogschagen (*9*), for which the rate ratio was given as

$$\eta_1/\eta_2 = (M_2/M_1)^{1/2} \qquad (3)$$

for the interdiffusion of three binary mixtures (subscript 1 refers to the lightest component) through a large pore medium under uniform pressure conditions. Many of the earlier workers obviously assumed the rates to be equal.

Of the 18 uniform pressure experiments (Tables I and II). $\eta_{He} > \eta_A$ and Equation 3 was followed in every case. The helium rate was 3.28 (on the average) times greater than the argon rate as compared to a theoretical value of 3.16. The average deviation of the experimental values was ±5.5%. Control of the pressure uniformity was no better than ±2 mm. butyl phthalate (on the manometer) which corresponds to an uncertainty of ±7.0% for a single measurement. Approximately 1-mm. pressure difference was inadvertently maintained during all experiments.

Mutual Diffusion Coefficient. A diffusion relationship involving a single coefficient may be readily derived on the basis of equations relating the individual rates, the sum of the mole fractions, N, Fick's first diffusion law, and an equation which involves a mixed drift term and a Fick term. The applicability (and validity) of these equations for correlating the data are based on the observation of the presence of net flow and negligible Knudsen flow with respect to the graphite under investigation. The basic equations are:

$$\eta_T = \eta_1 - \eta_2 \tag{4}$$

$$1 = N_1 + N_2 \tag{5}$$

$$D_{12}\frac{dN_1}{dx} = -D_{12}\frac{dN_2}{dx} \tag{6}$$

and *(7, 13)*

$$\eta_1 = N_1\eta_T - D_{12}A\frac{P}{RT}\frac{dN_1}{dx} \tag{7}$$

The positive direction, x, is taken as the direction of η_1 where $\eta_1 > \eta_2$. An equation similar to Equation 7 can be written for η_2; however, this is not required. The integrated form of Equation 7 is

$$\eta_T = D_{12}\frac{A}{L}\frac{P}{RT}\ln\left[\frac{\eta_{He} - \eta_T N_{He}(L)}{\eta_{He} - \eta_T N_{He}(0)}\right] \tag{8}$$

where the helium concentrations at the surfaces, $x = 0$ and $x = L$, have been inserted. This equation was used to obtain D_{12}, since all other quantities shown were measured. All the measured quantities required to compute the individual D_{12} appear in the tables. The experimental D_{12} values were then normalized to 20° C. and 1 atm. according to the classical formulation *(5)*.

$$(D_{12})_{T,P} = D_0\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)^{1.75} \tag{9}$$

which is based on consideration of the intermolecular collisions of gas particles of a binary gas mixture. The collision diameter and the reduced mass are contained in D_0. The normalized values are shown as functions of pressure in the last columns of Tables II and III. An average value of 6.21×10^{-3} sq. cm. per sec. was obtained for the uniform pressure experiments. The constant values obtained for the normalized coefficient, regardless of the experimental temperature and pressure, indicate that Equations 8 and 9 are applicable to the mechanism under study.

To predict rates at other temperatures and pressures one may utilize Equation 9 and a combined form of Equations 3 and 8. The latter is

$$\eta_{He}\beta = \eta_T = D_{12}\frac{A}{L}\frac{P}{RT}\ln\left[\frac{1 - \beta N_{He}(L)}{1 - \beta N_{He}(0)}\right] \tag{10}$$

where

$$\beta = \left[1 - \left(\frac{M_{He}}{M_A}\right)^{1/2}\right]$$

Nonuniform Pressure Experiments. Although Equation 10 is restricted to uniform total pressure conditions, Equation 8 is not under certain limitations. A small total pressure drop across the septum will superpose a forced flow component on the net diffusive drift. The pressure drop must be small, so that the molar density of the gas will not vary appreciably along L. Four additional experiments were conducted with the pressure on the argon side greater than that on the helium side-the difference being equal to 1.43 mm. of Hg in each case. The results are shown in Table II. These data show that the rates are considerably altered by small pressure drops; however, a comparison of the corresponding diffusion coefficients of Table II with those of Table I indicates that, within the precision of the experiment, small pressure drops do not affect changes in the coefficient. In other words, the value of the coefficient does not depend on the magnitude of η_T. However, η_T must appear in the calculations.

Internal Geometry of the Medium. One may convert the flow parameters, k and D, which are based on the gross dimensions of the porous medium, to values applicable to straight circular conduits by means of an assumed model. To accomplish this a knowledge of the tortuosity factor and porosity of the medium is required. A model frequently used is a bundle of capillaries of equal average diameters and lengths. If the bundle contains ζ capillaries and the porous material has a porosity ϵ, then $\zeta\,(\eta RT)_{cap.} = (\eta RT)$ or $\zeta\,(D_c A_c/L_c) = D(A/L)$. Equating also the open volume of the two systems—i.e., $\zeta A_c L_c = \epsilon AL$—one obtains *(10)*

$$D = \frac{\epsilon}{(L_c/L)^2}D_c \tag{11}$$

where L_c/L is the tortuosity factor. Since the experimental coefficient is 6.21×10^{-3} sq. cm./sec., the open porosity is 22 volume %, and the literature value for the mutual coefficient *(4)* is 0.726 sq. cm./sec., the (L_c/L) ratio for the medium is 5.08. Utilizing the ϵ and (L_c/L) data presented one can make reasonable predictions as to the diffusion behavior of other binary mixtures in this type of graphite.

CONCLUSIONS

Diffusion studies with a large-pore graphite have indicated that the primary mechanism was normal diffusion. The boundary conditions employed to perform the experiment introduced a net drift of gas from the helium source to the argon source at uniform total pressure. Equations which take this effect into account enable one to express the rate data in terms of a single mutual diffusion coefficient which follows the classical temperature-pressure formulation for normal diffusion. Small variations in pressure uniformity can be tolerated during a determination if the variations are time constant.

NOMENCLATURE

A = cross-sectional area normal to flow, sq. cm.
c = particular velocity of a single molecule, cm./sec.
D_{12} = mutual diffusion coefficient, sq. cm./sec.
D_0 = normalized mutual diffusion coefficient, sq. cm./sec.
i = subscript denoting a particular gaseous component
k = permeability constant, darcy or sq. cm.
L = length along path of flow, cm.

Table I. Results of Uniform Pressure Experiments Conducted at Room Temperature

Temp., ° K.	Pressure, Atm.	Mole Fraction of Helium		Diffusion Rates, Moles/Sec.			η_{He}/η_A	Difusion Coeff.[a] D_{12}, Sq. Cm./Sec.
		At $x = 0$	At $x = L$	η_{He}	η_A	η_T		
299.7	1.249	0.9935	0.0232	6.07×10^{-5}	1.72×10^{-5}	4.35×10^{-5}	3.53	6.17×10^{-3}
298.4	1.251	0.9866	0.0446	5.75	1.73	4.02	3.32	6.17
297.1	1.251	0.9867	0.0439	5.66	1.71	3.94	3.31	6.11
301.1	1.475	0.9874	0.0454	5.78	1.61	4.17	3.59	5.97
299.3	1.475	0.9862	0.0434	5.52	1.77	3.75	3.12	6.06
300.5	1.500	0.9947	0.0169	6.18	1.94	4.24	3.19	6.47
298.7	1.740	0.9962	0.0132	6.14	1.80	4.34	3.41	6.28
295.7	1.740	0.9863	0.0419	5.45	1.79	3.66	3.04	6.07
295.4	1.975	0.9862	0.0440	5.69	1.80	3.90	3.16	6.28
297.3	1.992	0.9958	0.0132	6.03	1.92	4.11	3.14	6.40
298.7	3.005	0.9872	0.0442	5.79	1.70	4.09	3.41	6.11
300.5	3.005	0.9861	0.0421	5.49	1.84	3.64	2.98	6.14
298.1	3.704	0.9950	0.0146	6.18	2.13	4.05	2.90	6.76
298.2	6.351	0.9857	0.0358	6.35	1.64	4.71	3.87	6.42

[a] Normalized to 20° C. and 1 atm. by relationship, $D = D_0(P_0/P)(T/T_0)^{1.75}$.

Table II. Experiments Conducted at 100° C.

Pressure, Atm.	Mole Fraction of Helium		Diffusion Rates, Moles/Sec.			Ratio of Helium to Argon Diffusion Rate	Diffusion Coeff.[a] D_{12}, Sq. Cm./Sec.
	At $x = 0$	At $x = L$	η_{He}	η_A	η_T		
			Results at Uniform Pressure				
1.25	0.9851	0.0485	6.30×10^{-5}	1.95×10^{-5}	4.35×10^{-5}	3.23	5.80×10^{-3}
1.48	0.9846	0.0507	6.50	2.00	4.51	3.25	6.10
1.96	0.9844	0.0508	6.63	2.02	4.61	3.29	6.09
2.51	0.9842	0.0532	6.93	2.05	4.88	3.39	6.31
			Results with $P_A - P_{He} = 1.43$ Mm. Hg at Various Total Pressures				
1.98	0.9834	0.0375	5.89	2.51	3.38	2.34	6.49
1.51	0.9789	0.0489	5.78	2.36	3.42	2.45	6.48
1.27	0.9829	0.0423	5.77	2.30	3.47	2.51	5.91
2.97	0.9783	0.0397	5.59	2.90	2.69	1.93	6.46

[a] See footnote Table I.

L_e/L = tortuosity factor
M_i = molecular weight of component i
N_i = mole fraction of component i
$N_i(x)$ = mole fraction of a component at a point x
p = partial pressure, atm.
P = total pressure, dyne/sq. cm. or atm.
P_a = pressure at which effluent Q_a is measured, dyne/sq. cm. or atm.
P_m = mean flowing pressure, dyne/sq. cm. or atm.
Q_a = volumetric flow rate of effluent gas (generally at P_a = barometric pressure), cc./sec.
R = gas constant 82.05 cc. atm./mole ° K.
T = temperature, ° K.
x = variable position along L, cm.
y = volume of gas adsorbed, cc. STP/g. graphite
β = diffusive flow factor
ΔP = pressure drop along L, dyne/sq. cm. or atm.
ϵ = open or connected porosity
η_i = total flow rate of component i, mole/sec.
η_T = net flow rate, mole/sec.
ζ = number of capillaries
μ = fluid viscosity, dyne-sec./sq. cm.

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