

Measurements of Diffusion Coefficients in Porous Solids by Inverse Gas Chromatography

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The relatively new methodology of reversed-flow gas chromatography has been applied to measure the diffusion coefficients of gaseous species into porous solid material. The necessary experimental arrangements and the theoretical analysis were described, and the appropriate mathematical analysis which leads to equations describing the diffusion coefficients as a function of the experimental data and other measurable experimental conditions was developed. All of the calculations were performed using a simple software for a personal computer. The methodology was applied to pentane, hexane, and heptane diffusing into porous α - and γ -alumina as well as of sulfur dioxide diffusing into porous marble at various temperatures. The results were compared with those obtained by the Knudsen formula or those given by other researchers.

1. Introduction

One of the most fascinating phenomena associated with porous solids is the ability of the absorbed surface species to diffuse into the porous solid. This phenomenon is of great importance in catalysis, metallurgy, environmental studies, and many other industrial and natural processes.

There are few experimental data referring to diffusion into porous media, although for calculating diffusion coefficients in porous solids theoretical approaches have been adopted such as the well-known formula of Knudsen.^[1] In 1997, Reyes et al.^[2] reported a new application of frequency-modulated perturbation methods for measuring dynamic parameters and capacities pertaining to diffusion and adsorption within mesoporous solids. These methods needed corrections to translate the apparent diffusion coefficients into their true values due to adsorption uptakes. On the other hand, the van't Hoff equation and Henry's law constants were used for considering experimental enthalpies and entropies of adsorption.

In contrast to the latter, a subtechnique of inverse gas chromatography can be used without any perturbation of the system (except in the sampling procedure taking place far from the gas-solid interface) to show the time distribution of adsorption energies, local monolayer capacities, and local isotherm on heterogeneous solid surfaces^[3] as well as to determine the surface diffusion coefficients for physically adsorbed or chemisorbed substances. This technique, which is called reversed-flow gas chromatography (RF-GC), has

been reviewed recently for catalytic studies,^[4] diffusion coefficients,^[5] and isotherm determination.^[6]

In this work, the appropriate mathematical analysis and experimental arrangements for the application of RF-GC for the calculation of diffusion coefficients in porous solids are developed.

The diffusion of hydrocarbons (i.e., pentane, hexane, and heptane) into common porous absorbents (i.e., α - and γ -alumina) at various temperatures was studied as a reference model for evaluating the methodology. The developed methodology was then applied to a more complicated system such as sulfur dioxide-marble with great environmental significance.

2. Theory

The experimental arrangement on which the following theoretical analysis is based has already been published^[3-7] and is repeated here in Fig. 1 for convenience.

The necessary mathematical model is based on three mass balance equations, an adsorption isotherm, and an initial condition. These equations are as follows.

The mass balance equation of the solute gas A in the free region y of the tube outside of the porous particles species on heterogeneous surfaces^[7] is:

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial y^2} - D_1 \left(\frac{\partial^2 c_1}{\partial r^2} + \frac{2}{r} \frac{\partial c_1}{\partial r} \right) \quad (\text{Eq 1})$$

where c_1 is the gaseous concentration (in moles per cubic centimeter) in the free of solid region of section y , and D_1 is the diffusion coefficient (in square centimeters per second) of the injected solute in the region filled with solid particles, with r being the particle radius ranging from 0 (at the surface) to R (in the center of the particles).

The mass balance equation of the solute inside the porous volume is:

$$\frac{\partial c_2}{\partial t} = D_1 \left(\frac{\partial^2 c_2}{\partial r^2} + \frac{2}{r} \frac{\partial c_2}{\partial r} \right) + k_R \frac{a_s}{a_y} (c_s - c_s^*) \quad (\text{Eq 2})$$

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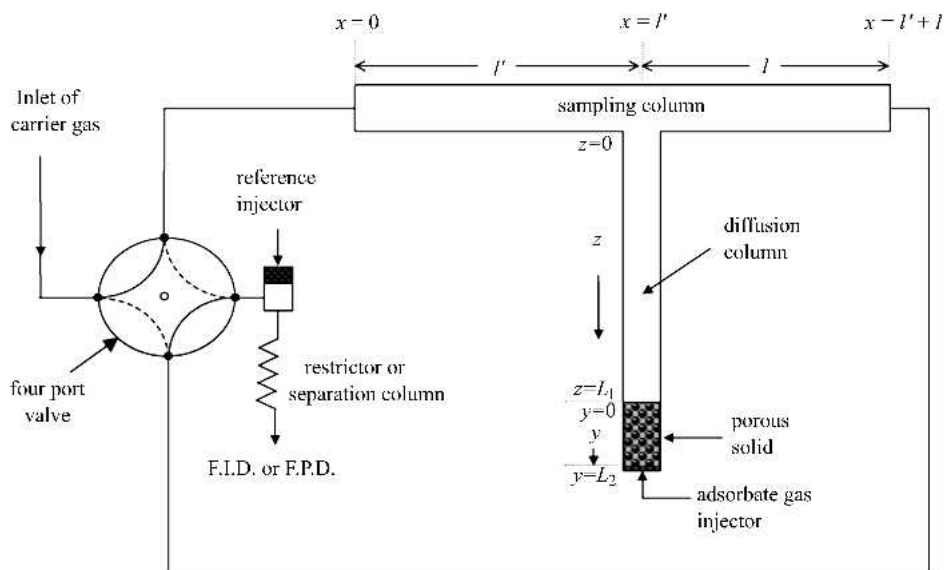


Fig. 1 Experimental arrangement of the RF-GC technique for measuring diffusion coefficients in porous solids

where c_2 is the gaseous concentration inside the porous particles (in moles per cubic centimeter), c_s is the adsorbed concentration of A (in moles per gram), c_s^* is the adsorbed equilibrium concentration (in moles per gram), a_s is the amount of solid per unit length of bed (in grams per centimeter), a_y is the free cross-sectional area of the region y (in square centimeters), and k_R is the adsorption/desorption rate constant on the solid adsorbent (in seconds), which is related to the forward rate constant k_1 and the equilibrium constant K by the equation^[8]:

$$k_R = \frac{k_1(K + 1)}{K} \quad (\text{Eq 3})$$

A mass balance equation, which describes the irreversible change of the adsorbed concentration c_s to other species (if this does happen), by a catalytic or other process:

$$\frac{\partial c_s}{\partial t} = k_R(c_s^* - c_s) - k_2 c_s \quad (\text{Eq 4})$$

where k_2 is the relevant first-order or pseudo-first-order catalytic constant or other rate constant (in seconds). The sum $k = k_R + k_2$ may be termed the *overall rate constant of transference*, pertaining to the overall disappearance of the solute from the gas phase.

The nonlinear adsorption isotherm of the locally adsorbed equilibrium concentration is:

$$c_s^* = \frac{a_y}{a_s} k_1 \int_0^t c_2 d\tau \quad (\text{Eq 5})$$

where k_1 is a dynamic rate constant (in seconds), pertaining to the isotherm point active at each moment, t . The symbol τ is a dummy variable for time.

Finally, the initial condition describing the injection of the solute as a pulse (Dirac's delta function) at the point $y = L_2$ is given as:

$$c_1(L_2) = \frac{n_A}{a_y} \delta(y - L_2) \quad (\text{Eq 6})$$

where $c_1(L_2)$ is the gaseous concentration (in moles per cubic centimeter) of A at the point L_2 , and n_A is the amount injected (in moles).

Solving the above system of the three partial differential equations is very difficult, if not impossible, owing mainly to the spherical diffusion terms. To find an acceptable solution, the functions c_1 , c_2 , c_s , and c_s^* which depend on r , are substituted by the functions u_1 , u_2 , u_s , and u_s^* , respectively, by resorting to the following equations as suggested by Crank^[9]:

$$u_1 = c_1 r, \quad u_2 = c_2 r, \quad u_s = c_s r, \quad u_s^* = c_s^* r \quad (\text{Eq 7})$$

Using the above expressions and after simple mathematical arrangements, Eq 1, 2, 4, and 5 become partial differential equations of u instead of c .

By applying a Laplace transformation with respect to time t , particle radius r , and diffusion coordinate y , the resultant equations, after algebraic manipulations taking into account all of the boundary conditions that are defined by the experimental arrangement, describe the experimental concentration $c(l', t)$ of the solute in the detector as a function of time:

$$c(l', t) = \frac{n_A}{v a_z Q_3} (A_1 e^{B_1 t} + A_2 e^{B_2 t} + A_3 e^{B_3 t}) \quad (\text{Eq 8})$$

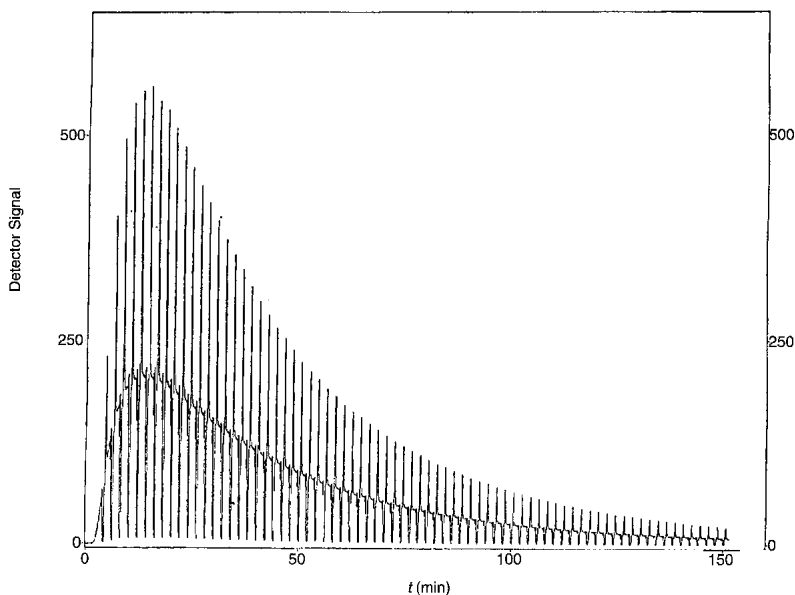


Fig. 2 A reversed-flow gas chromatograph showing sample peaks for the interaction between SO_2 and marble at 323.2 K

where v is the linear flow velocity of the carrier gas through column x (in centimeters per second), a_z is the cross-sectional area of the diffusion column, Q_3 is equal to:

$$Q_3 = \frac{1}{a_1} + \frac{2}{a_2} + 2Q_1 \quad (\text{Eq 9})$$

and the dimensionless quantities A_1 , A_2 , and A_3 are given by the relations:

$$A_1 = \frac{B_1^2 + kB_1}{(B_1 - B_2)(B_1 - B_3)}; \quad A_2 = \frac{B_2^2 + kB_2}{(B_2 - B_1)(B_2 - B_3)}; \\ A_3 = \frac{B_3^2 + kB_3}{(B_3 - B_1)(B_3 - B_2)} \quad (\text{Eq 10})$$

while $k = k_R + k_2$. The other parameters of Eq 9 are given as follows:

$$a_1 = 2D_z/L_1^2; \quad a_2 = 2D_1/L_2^2; \quad Q_1 = \varepsilon \frac{\alpha_y L_1 L_2}{\alpha_z D_z} \quad (\text{Eq 11})$$

where D_z denotes the diffusion coefficient of the injected solute into a solute-free solid section z , L_1 and L_2 are the lengths of the sections z and y , respectively, and ε denotes the void fraction of the solid bed in section y .

Finally, the exponential coefficients of time B_1 , B_2 , and B_3 are combined with the diffusion parameters α_1 and α_2 according to the relation:

$$-(B_1 + B_2 + B_3) = \frac{1}{Q_3} + k = X_1 \quad (\text{Eq 12})$$

The exponential coefficients of time B_1 , B_2 , and B_3 as well as the preexponential coefficients A_1 , A_2 , and A_3 are extracted by means of a program for the personal computer that was recently published elsewhere.^[7] These values are applied to the above-mentioned equations, and the diffusion coefficients can be calculated. The only experimental data needed for these calculations are the geometrical characteristics of the experimental cell and the values of the pairs H , t (i.e., the peak height H and the moment t of reversing the flow as measured from the moment of injection of the diffusing solute at the end L_2 of the y section of the column) (cf. Fig. 1). All of the other necessary quantities can be given by values obtained from the literature.

3. Experimental

3.1 Apparatus

The experimental arrangement of the RF-GC technique has been reported many times in detail elsewhere.^[3-7] The chromatograph used was the Shimadzu 14A (Columbia, MD) with a flame ionization detector (FID) when the system under study was hydrocarbons/ α - or γ -alumina, and a flame photometric detector (FPD) for the system SO_2 -marble. The L_1 section (53.5-57 cm) had no solid material, while the L_2 section (5.1-5.8 cm) contained the porous material. The cross-sectional areas of the regions z and y were $\alpha_z = \alpha_y = 0.096 \text{ cm}^2$. Both sections L_1 and L_2 were of pyrex glass with an inside diameter (i.d.) of 4.0 mm. The sampling column ($l = l' = 62 \text{ cm}$) was a stainless steel chromatographic tube with an i.d. of 4.0 mm.

3.2 Materials

Hydrocarbons (pentane, hexane, and heptane) were supplied by Carlo Erba (Milano, Italy), while SO_2 was supplied

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by Aeroskopio (Athens, Greece). The marble was a Penteli marble (Athens, Greece), the γ -alumina was from Akzo Chemicals (Amsterdam, The Netherlands), and the α -alumina was prepared from γ by heating it in situ at 1373.15 K for 8 h.

3.3 Procedure

After conditioning the porous material by heating it in situ at 573.6 K for 20 h under a continuous carrier gas flow, the solid was cooled to the working temperature. Then, 1 cm³ (under the atmospheric pressure) of hydrocarbons or SO₂ was introduced through the injector at $y = L_2$ (Fig. 1).

After the appearance of the continuously rising concentration-time curve, the reversing procedure for the nitrogen carrier gas flow started, with each reversal always lasting 6 s. This is shorter than the gas hold-up time in the section of the sampling column. The above procedure was performed automatically by using an electronic valve supplied by Shimadzu. The narrow, fairly symmetrical sample peaks created by the flow reversals were stored in a personal computer and were integrated by using the CLASS VP chromatography data system (Shimadzu), and finally they were printed using an ink-jet printer (Fig. 2). By treating the pair values of H , t as explained above, the diffusion coefficients were calculated and printed.

4. Results and Discussion

The results obtained by treating the experimental data, are collected in Table 1. From these results, it is fairly obvious that the values of the diffusion coefficients have the same order of magnitude (10^{-3} cm²/s) as those calculated by the well-known formula of Knudsen diffusion coefficients (cf. Eq 5.79 of Ref 1).

Furthermore, from the above-mentioned results it is obvious that the porous size of the solid is a critical parameter controlling the diffusion of gases into porous solids. All D_1 values for the three hydrocarbons (except for pentane at 353.2 K) were higher when α -alumina (mean porous radius 108 Å) was the solid under study rather than γ -alumina (mean porous radius 53 Å).

The size of the molecule is another essential parameter for the diffusion of gases into porous solids. In all cases (except for pentane at α -alumina), the increase of the molecular size implies a decrease in the diffusion coefficients.

Finally, a comparison of the calculated diffusion coefficients with those determined by Reyes et al.^[2] follows. They gave values of 0.103 and 0.110 s for what they called *diffusivity constants*, D/R_0^2 (s⁻¹), for isobutene at 348 and 398 K, respectively, diffusing into mesoporous silica spheres, which are commonly used as catalyst supports. Their mean particle radius was $R_0 = 0.135$ cm, and thus, by multiplying their D/R_0^2 values by 0.1352 cm², one obtains 1.88×10^{-3} and 2.00×10^{-3} cm²/s for the diffusion coefficient of isobutane into silica spheres at 348 and 398 K, respectively. These two values are of the same order of magnitude as our D_1 values for pentane in α - and γ -alumina, at 353.2 and

Table 1 Diffusion coefficients (D_1) of pentane, hexane, and heptane diffusing into α - and γ -alumina and SO₂ diffusing into marble at different temperatures

Variables	T, K	D_1 , 10 ³ cm ² /s ⁻¹
Pentane on α -alumina	353.2	2.76
	363.2	2.91
	373.2	3.68
Hexane on α -alumina	363.2	3.14
	373.2	2.92
Heptane on α -alumina	383.2	2.63
	393.2	2.68
	403.2	2.71
Pentane on γ -alumina	353.2	3.01
	363.2	2.37
	373.2	2.83
Hexane on γ -alumina	393.2	3.32
	353.2	2.22
	363.2	1.93
	373.2	2.66
Heptane on γ -alumina	393.2	2.90
	373.2	1.94
	383.2	1.93
SO ₂ on marble	403.2	2.05
	303.2	2.667
	313.2	3.000
	323.2	3.166
	333.2	2.883
	343.2	3.365
	353.2	3.232

393.2 K, respectively (Table 1). They are 2.76×10^{-3} and 3.32×10^{-3} , respectively. One should take into account the vastly different methodology of the present work compared with that of Reyes et al.^[2]

Acknowledgments

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