

Diffusion and Adsorption Measurements in Porous Solids by Inverse Gas Chromatography

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The new inverse gas chromatography methodology of reversed-flow gas chromatography has been applied to measure diffusion and adsorption in porous solids. The theoretical analysis leads to equations describing the experimental data with very few approximations. From these, the total overall rate constant of transference ($k = k_R + k_2$), its probable error, the diffusion coefficient (D_1) into porous solids (α -alumina and γ -alumina), and its probable error are calculated by means of a simple PC program. The methodology was applied to pentane, hexane, and heptane diffusing into porous α - and γ -alumina at various temperatures. A comparison of the results is made with those obtained by the Knudsen formula and with those of other researchers.

Introduction

In 1997, Reyes et al.¹ reported a new application of frequency-modulated perturbation methods for measuring dynamic parameters and capacities pertaining to coupled diffusion and adsorption within mesoporous solids. Their measurements required a wide frequency range and theoretical response functions to account for the dynamic coupling between adsorption and diffusion phenomena. Corrections were needed to translate the apparent diffusion coefficients into their true values because of adsorption uptakes. However, their experimental enthalpies and entropies of adsorption had been considered on the old basis of the van't Hoff equation and Henry's law constant. In contrast to the latter, a time distribution of adsorption energies, local monolayer capacities, and local isotherms on heterogeneous solid surfaces show up clearly by inverse gas chromatography² without any perturbation of the system under study, except of the sampling procedure taking place far from the gas–solid interface. This procedure, called reversed-flow gas chromatography (RF-GC), has been reviewed recently^{3–5,16} for catalytic studies,³ diffusion coefficients,⁴ and isotherm determination,⁵ so it is worthwhile to try its use for diffusion and adsorption measurements in porous solids. This is the object of the present paper, exemplified by some representative results.

Theory

The experimental arrangement, on which the following theoretical analysis is based, has been published before^{2,3,6,7,16} and is repeated here in Figure 1 for convenience.

The necessary mathematical model is based on the following partial differential equations. First, the solute gas (A) is injected as a pulse (Dirac's delta function) at the point $y = L_2$

$$c_1(L_2) = \frac{n_A}{a_y} \delta(y - L_2) \quad (1)$$

where $c_1(L_2)$ is the gaseous concentration (mol/cm³) of A at

point L_2 , n_A is the amount injected (mol), and a_y is the free cross sectional area of region y (cm²).

The mass balance equation of A in region y of the tube cannot be given as in our previous work (e.g., eq 6 of ref 3) because in our previous work no term describing the radial diffusion of the solute inside the porous particles had been included. Now including radial diffusion (i.e., eq 6.1 of ref 8), old eq 6 of ref 3 splits up into the following two eqns (2 and 3)

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

where c_1 is the gaseous concentration (mol/cm³) in the free-of-solid region of section y and D_1 is the diffusion coefficient (cm²/s) 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 second mass balance equation refers only inside the porous volume as

$$\frac{\partial c_2}{\partial t} = D_1 \left(\frac{\partial^2 c_2}{\partial r^2} + \frac{2}{r} \frac{\partial c_2}{\partial r} \right) + k_R \frac{a_s}{a_y} (c_s - c_s^*) \quad (3)$$

where c_2 is the gaseous concentration inside the porous particles (mol/cm³), c_s is the adsorbed concentration of A (mol/g), c_s^* is the adsorbed equilibrium concentration (mol/g), a_s is the amount of solid per unit length of bed (g/cm), and k_R is the adsorption/desorption rate constant on the solid adsorbent (s⁻¹), related to the forward-rate constant (k_1) and the equilibrium constant (K) by the following equation:¹⁹

$$k_R = \frac{k_1(K + 1)}{K}$$

A third mass balance in the adsorbed state is needed because some of the adsorbed concentration (c_s) irreversibly changes to other species by a catalytic or other process

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

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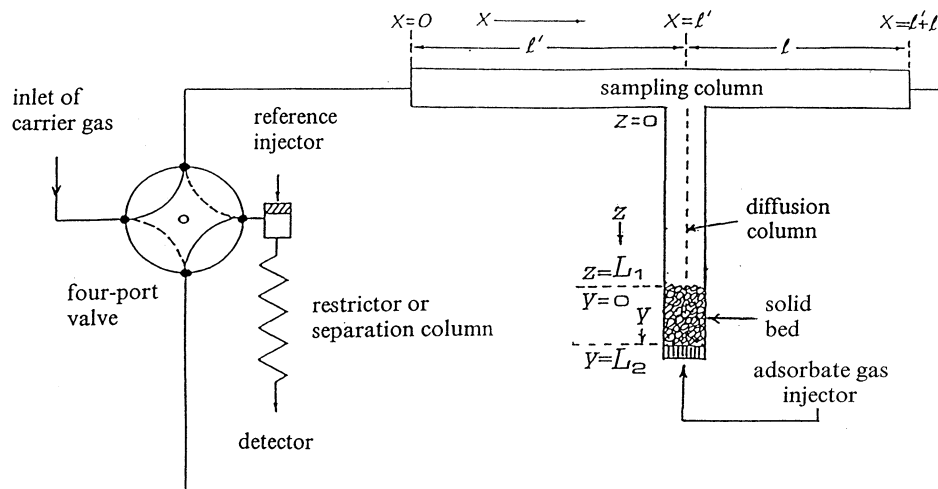


Figure 1. Schematic representation of columns and gas connections of the reversed-flow technique for diffusion and adsorption measurements.

with k_2 being the relevant first or pseudo-first-order catalytic or other rate constant (s^{-1}). 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.

Finally, the adsorption isotherm of the locally adsorbed equilibrium concentration can be written as

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

with k_1 being a dynamic rate constant (s^{-1}) pertaining to the isotherm point active at each moment, t . The symbol τ is a dummy variable for time.

Solving the above system of the three differential equations (2–4), initial condition 1 and integral eq 5, is a difficult if not impossible task, owing mainly to the spherical diffusion terms in eqs 2 and 3. Previous solutions such as those given in refs 3–5 and 16 cannot be applied in the present case because of these radial diffusion terms. A great simplification, however, arises by changing the functions dependent on r , c_1 , c_2 , c_s and c_s^* , to other functions, u_1 , u_2 , u_s and u_s^* , respectively, following the suggestion of Crank⁸ by putting

$$u_1 = c_1 r \quad u_2 = c_2 r \quad u_s = c_s r \quad u_s^* = c_s^* r \quad (6)$$

Then, eqs 2–5 become, respectively

$$\frac{\partial u_1}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial y^2} - D_1 \frac{\partial^2 u_1}{\partial r^2} \quad (7)$$

$$\frac{\partial u_2}{\partial t} = D_1 \frac{\partial^2 u_2}{\partial r^2} + \frac{a_s}{k_R a_y} (u_s - u_s^*) \quad (8)$$

$$\frac{\partial u_s}{\partial t} = k_R (u_s^* - u_s) - k_2 u_s \quad (9)$$

$$u_s^* = \frac{a_y}{a_s} k_1 \int_0^t u_2 d\tau \quad (10)$$

Now, the way is open to use Laplace transformations with respect to t (parameter p) on the above equations to find an acceptable solution. By denoting the time transformed functions, u_1 , u_2 , u_s , and u_s^* , with capital letters, U_1 , U_2 , U_s , and U_s^* ,

respectively, one obtains the following from transformed eqs 9 and 10, respectively

$$U_s = \frac{k_R U_s^*}{p + k_R + k_2} \quad \text{and} \quad U_s^* = \frac{a_y}{a_s} k_1 \frac{U_2}{p} \quad (11)$$

assuming that no adsorbed concentration (c_s) existed initially ($t = 0$). Now transforming eq 8, which is also valid inside the porous solid particles, with respect to t and then by substituting in it eq 11, one obtains after rearrangement

$$\frac{d^2 U_2}{dr^2} = j^2 U_2 \quad (12)$$

where j^2 is given by the relation

$$j^2 = \frac{p}{D_1} + \frac{k_R k_1 (p + k_2)}{D_1 p (p + k_R + k_2)} \quad (13)$$

with all of the symbols on the right-hand side having been explained before.

Equation 12 can now be solved easily in regard to the independent variable r , by taking Laplace transforms with respect to this variable (parameter g) and then by inverting the r transforms after rearrangement. The result is

$$U_2 = U_2(r=0) \cosh jr + \frac{U_2'(r=0)}{j} \sinh jr \quad (14)$$

where $U_2(r=0)$ is the value of U_2 at the particle external surface and

$$U_2'(r=0) = \left(\frac{\partial U_2}{\partial r} \right)_{r=0}$$

From eq 14, one can calculate the second derivative of U_2 with respect to r

$$\frac{d^2 U_2}{dr^2} = U_2(r=0) j^2 \cosh jr + U_2'(r=0) j \sinh jr \quad (15)$$

which at $r = 0$ becomes

$$\left(\frac{d^2 U_2}{dr^2}\right)_{r=0} = U_2(r=0)j^2 = U_1 j^2 \quad (16)$$

Now by taking the t transform of eq 7

$$pU_1 - u_1(t=0) = D_1 \frac{d^2 U_1}{dy^2} - D_1 \left(\frac{d^2 U_1}{dr^2}\right)_{r=0} \quad (17)$$

and replacing the derivative $(d^2 U_1/dr^2)_{r=0}$ on the far right-hand side with eq 16, for boundary condition reasons, one obtains

$$\frac{p}{D_1} U_1 - \frac{u_1(t=0)}{D_1} = \frac{d^2 U_1}{dy^2} - U_1 j^2 \quad (18)$$

after a small rearrangement.

It is now about time to return to the concentration domain “ c ” from “ u ”, simply through division of every u and U by r , according to eq 6. Equation 18 then becomes

$$\frac{p}{D_1} C_1 - \frac{c_1(t=0)}{D_1} = \frac{d^2 C_1}{dy^2} - C_1 j^2 \quad (19)$$

Then

$$c_1(t=0) = \frac{n_A}{a_y} \delta(y - L_2) \quad (20)$$

according to eq 1.

Independent variable y remains in the column section filled with the porous solid (cf. Figure 1), appearing in the above relations. Now by taking the Laplace transformation with respect to variable y (transform parameter s) in eq 19, rearranging the result, and inverting the s transform, one finds the following for C_1

$$C_1 = -\frac{n_A}{a_y D_1 q_3} \sinh q_3(y - L_2) \cdot u(y - L_2) + C_1(0) \cosh q_3 y + \frac{C_1'(0)}{q_3} \sinh q_3 y \quad (21)$$

where $u(y - L_2)$ is a unit step function, $C_1(0)$ is the value of C_1 at $y = 0$, $C_1'(0) = (dC_1/dy)_{y=0}$, and q_3 is given by the relation

$$q_3^2 = \frac{2p}{D_1} + \frac{k_R k_1(p + k_2)}{D_1 p(p + k_R + k_2)} \quad (22)$$

Because the system is closed at the end point $y = L_2$ (cf. Figure 1), the derivative $((dC_1/dy)_{y=L_2})$ equals 0 and thus from eq 21 one obtains

$$C_1'(0) \cosh q_3 L_2 = \frac{n_A}{a_y D_1} - C_1(0) q_3 \sinh q_3 L_2 \quad (23)$$

From the free-of-solid section (z) of Figure 1, it is derived easily⁹ that (in the form of t Laplace transformation)

$$C_z(L_1) = C_z(0) \cosh q_1 L_1 + \frac{C_z'(0)}{q_1} \sinh q_1 L_1 \quad (24)$$

$$\left(\frac{dC_z}{dz}\right)_{z=L_1} = C_z(0) q_1 \sinh q_1 L_1 + C_z'(0) \cosh q_1 L_1 \quad (25)$$

where C_z is the t transformed concentration $c_z(\text{mol}/\text{cm}^3)$, $C_z(0)$

refers to $z = 0$, $C_z'(0) = (dC_z/dz)_{z=0}$, and $q_1^2 = p/D_z$, D_z denoting the diffusion coefficient of the injected solute in the free-of-solid section, z .

At $z = 0$ and $x = l'$ (cf. Figure 1), the following boundary conditions are valid

$$C_z(0) = C(l', p) \text{ and } D_z \left(\frac{\partial C_z}{\partial z}\right)_{z=0} = v C(l', p) \quad (26)$$

where $C(l', p)$ refers to the concentration at the junction of columns x and z and v is the linear flow velocity of the carrier gas through column x (cm/s), with all of the C values being Laplace transformed concentrations with respect to time, t , measured from the moment of injection of the gaseous solute at $y = L_2$.

Substitution of the boundary conditions of eq 26 into eqs 24 and 25 and omission of $\cosh q_1 L_1$ as compared to $(v/D_z q_1) \sinh q_1 L_1$ and of $\sinh q_1 L_1$ as compared to $(v/D_z q_1) \cosh q_1 L_1$, justified before,¹⁰ leads to

$$C_z(L_1) = \frac{v C(l', p)}{D_z q_1} \sinh q_1 L_1 \quad (27)$$

$$C_z'(L_1) = \frac{v C(l', p)}{D_z} \cosh q_1 L_1 \quad (28)$$

At $z = L_1$ and $y = 0$, boundary conditions other than those at $z = 0$ are valid, namely

$$C_1(0) = C_z(L_1) \text{ and } a_y D_1 C_1'(0) = a_z D_z C_z'(L_1) \quad (29)$$

These, combined with the previous ones (27 and 28), lead to

$$C_1(0) = \frac{v C(l', p)}{D_z q_1} \sinh q_1 L_1 \quad (30)$$

$$C_1'(0) = \frac{a_z v C(l', p)}{a_y D_1} \cosh q_1 L_1 \quad (31)$$

Substitution of eqs 30 and 31 for $C_1(0)$ and $C_1'(0)$, respectively, into eq 23 and solving algebraically for $C(l', p)$, one obtains

$$C(l', p) = \frac{n_A}{a_y v} \left[\frac{a_z}{a_y}, \cosh q_1 L_1 \cdot \cosh q_3 L_2 + \frac{D_1 q_3}{D_z q_1} \sinh q_1 L_1 \cdot \sinh q_3 L_2 \right]^{-1} \quad (32)$$

This gives the desired experimental concentration, $c(l', t)$, in the detector in the form of t Laplace transform, $C(l', p)$. An inverse p transformation of eq 32 remains in order to find $c(l', t)$ as a function of experimental time.

For a similar function, but a different content of q_3 (cf. eq 22), a different form of products $\cosh q_1 L_1 \cdot \cosh q_3 L_2$ and $\sinh q_1 L_1 \cdot \sinh q_3 L_2$ was adopted,¹¹ namely

$$\cosh q_1 L_1 \cdot \cosh q_3 L_2 = \frac{1}{2} [\cosh(q_1 L_1 + q_3 L_2) + \cosh(q_1 L_1 - q_3 L_2)] \quad (33)$$

$$\sinh q_1 L_1 \cdot \sinh q_3 L_2 = \frac{1}{2} [\cosh(q_1 L_1 + q_3 L_2) - \cosh(q_1 L_1 - q_3 L_2)] \quad (34)$$

By applying McLaurin's expansion on the right-hand side of

these functions, retaining the first two terms in each, eq 32 becomes

$$C(l', p) = \frac{n_A}{a_y v} p(p+k) \left[\left(\frac{1}{a_1} + \frac{2}{a_2} + 2Q_1 \right) p^3 + \left(1 + \frac{k}{a_1} + \frac{2k}{a_2} + 2kQ_1 \right) p^2 + \left(k + \frac{k_R k_1}{a_2} + k_R k_1 Q_1 \right) p + \left(\frac{k_R k_1 k_2}{a_2} + k_R k_1 k_2 Q_1 \right) \right]^{-1} \quad (35)$$

after simple algebraic manipulations, where

$$k = k_R + k_2 \quad (36)$$

$$a_1 = \frac{2D_z}{L_1^2} \quad (37)$$

$$a_2 = \frac{2D_1}{L_2^2} \quad (38)$$

$$Q_1 = \epsilon \frac{a_y L_1 L_2}{D_z} \quad (39)$$

with ϵ denoting the void fraction of solid bed in section y.

With the coefficient of p^3 in eq 35 denoted by Q_3

$$Q_3 = \frac{1}{a_1} + \frac{2}{a_2} + 2Q_1 \quad (40)$$

one can write eq 35 as

$$C(l', p) = \frac{n_A}{v a_z} \frac{p(p+k)}{Q_3} \left\{ p^3 + \left(\frac{1}{Q_3} + k \right) p^2 + \left[\frac{k + k_R k_1 \left(\frac{1}{a_2} + Q_1 \right)}{Q_3} \right] p + \frac{k_R k_1 k_2 \left(\frac{1}{a_2} + Q_1 \right)}{Q_3} \right\}^{-1} \quad (41)$$

after rearrangement. If the roots of the above third-degree polynomial of p in the denominator are denoted as B_1 , B_2 , and B_3 , then eq 41 simply becomes

$$C(l', p) = \left(\frac{n_A}{v a_z Q_3} \right) \frac{p^2 + kp}{(p - B_1)(p - B_2)(p - B_3)} \quad (42)$$

where

$$-(B_1 + B_2 + B_3) = \frac{1}{Q_3} + k = X_1 \quad (43)$$

The inverse p transformation of eq 42, used to find the respective function of t , is found easily from the tables in ref 12 and reads

$$c(l', t) = \frac{n_A}{v a_z Q_3} (A_1 e^{B_1 t} + A_2 e^{B_2 t} + A_3 e^{B_3 t}) \quad (44)$$

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

$$A_1 = \frac{B_1^2 + kB_1}{(B_1 - B_2)(B_1 - B_3)} \quad (45)$$

$$A_2 = \frac{B_2^2 + kB_2}{(B_2 - B_1)(B_2 - B_3)} \quad (46)$$

$$A_3 = \frac{B_3^2 + kB_3}{(B_3 - B_1)(B_3 - B_2)} \quad (47)$$

Calculations

The calculation of the diffusion coefficients and other rate constants pertaining to adsorption starts from the diffusion band of RF-GC experiments, comprising the values of the (H, t) pairs, that is, 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. Figure 1). From these, the preexponential coefficients (A_1 , A_2 and A_3) together with their respective standard errors and the exponential coefficients of time t (B_1 , B_2 , B_3) with their respective standard errors, all of eq 44, are extracted by means of a PC program published recently elsewhere³ and also given here as Supporting Information.

From the A_i ($i = 1-3$) values found and printed in lines 900–1030 of that program, the k value of eq 36 is calculated from the ratios obtained from eqs 45–47

$$\frac{A_2(B_2 - B_1)(B_2 - B_3)}{A_1(B_1 - B_2)(B_1 - B_3)} = \frac{B_2^2 + kB_2}{B_1^2 + kB_1}$$

$$\frac{A_3(B_3 - B_1)(B_3 - B_2)}{A_1(B_1 - B_2)(B_1 - B_3)} = \frac{B_3^2 + kB_3}{B_1^2 + kB_1} \quad (48)$$

Using the mean of the k values obtained from the above two equations and the X_1 value found by eq 43 from the exponential coefficients of time (B_1 , B_2 , and B_3), one calculates Q_3 by the relation

$$Q_3 = \frac{1}{X_1 - k} \quad (49)$$

obtained directly from eq 43.

The diffusion coefficient (D_z) in the free-of-solid section (z) is either calculated by the literature^{13,14} or found experimentally by performing the same experiment in the absence of solid particles. In that case, q_3^2 of eq 22 simply becomes $2p/D_1$. In either case, D_z is used in eq 37 to find a_1 and in eq 39 to find Q_1 . Based on eq 40 then, one uses the values of a_1 and Q_1 to find a_2 and from that, by eq 38, to find the diffusion coefficient (D_1) of the injected gas into the solid particles.

In conclusion, by the simple algebra described above, the physicochemical quantities k and D_1 are calculated from the (H, t) pairs as recorded by reversing the carrier gas flow repeatedly for a few seconds (5–60).

Clearly, the first quantities calculated from the experimental (H, t) pairs, together with their standard errors, are A_1 , A_2 , A_3 , B_1 , B_2 , and B_3 of eq 44.

The text following that relation and eqs 45–49 clearly indicate that both k and D_1 are functions of A_i and B_i . If these functions are written explicitly, then their probable error (P) can be calculated by the well-known relation¹⁵

$$P = \sqrt{\left(\frac{P_X \partial Z}{\partial X} \right)^2 + \left(\frac{P_Y \partial Z}{\partial Y} \right)^2 + \dots} \quad (50)$$

where

$$Z = f(X, Y, \dots) \quad (51)$$

Here Z stands for k or D_1 and X, Y, \dots for A_1, A_2, A_3, B_1, B_2 , and B_3 .

In the case of k , one finds the following easily from eq 48:

$$k_{12} = \frac{A_2 B_1^2 (B_3 - B_2) + A_1 B_2^2 (B_3 - B_1)}{A_2 B_1 (B_2 - B_3) + A_1 B_2 (B_1 - B_3)} \quad (52)$$

$$k_{13} = \frac{A_3 B_1^2 (B_2 - B_3) + A_1 B_3^2 (B_2 - B_1)}{A_3 B_1 (B_3 - B_2) + A_1 B_3 (B_1 - B_2)} \quad (53)$$

The value of k is the average of the two above, namely,

$$k = \frac{(k_{12} + k_{13})}{2} \quad (54)$$

The probable errors (P_{12} and P_{13}) of k_{12} and k_{13} , respectively, are found easily by using eq 50 and by using the right-hand side of eqs 52 and 53, respectively, in place of eq 51. Then, the probable error of k from eq 54 is

$$P_k = \frac{\sqrt{P_{12}^2 + P_{13}^2}}{2} \quad (55)$$

The probable error of the diffusion coefficient into the solid (D_1) is found as follows. First, D_1 is written as a function of variables whose probable errors are known or can be found, namely, $D_1 = a_2 L_2^2 / 2$ from eq 38. Then, a_2 is obtained from eq 40 as $2 / (Q_3 - 1/a_1 - 2Q_1)$. Combining these two expressions, one finds

$$D_1 = \frac{L_2^2}{Q_3 - \left(\frac{1}{a_1} + 2Q_1 \right)} \quad (56)$$

In this expression, L_2 , a_1 , and Q_1 are constants with no probable errors, as eq 37 and 39 show. Only Q_3 has a probable error, which can be found from eq 49 since P_k is found by eq 55 and P_{X_1} by means of eq 43

$$P_{X_1} = \sqrt{P_{B_1}^2 + P_{B_2}^2 + P_{B_3}^2} \quad (57)$$

Keep in mind that P_{B_1} , P_{B_2} , and P_{B_3} are calculated from the experimental data and printed in lines 910, 940, and 970 of the PC program in the Supporting Information. By applying eq 50 to eq 49 for P_{Q_3} , one finds

$$P_{Q_3}^2 = \left[\frac{-P_{X_1}}{(X_1 - k)^2} \right]^2 + \left[\frac{P_k}{(X_1 - k)^2} \right]^2 \quad (58)$$

Having found P_{Q_3} , P_{D_1} can be calculated using eq 50, as $D_1 = f(Q_3)$ only, given by eq 56

$$P_{D_1}^2 = \left\{ \frac{-L_2^2}{\left[Q_3 - \left(\frac{1}{a_1} + 2Q_1 \right) \right]^2} \right\}^2 P_{Q_3}^2 \quad (59)$$

All of the calculations described in this section can be carried out easily using the GW-BASIC program given in the Supporting Information of this work. One simply enters the pair values (H , t) into the 3000–3040 DATA lines, together with some

other known quantities asked by INPUT lines 160–240. The running of the program prints the values of A_1, A_2, A_3, B_1, B_2 , and B_3 with their standard errors of eq 44, the square of the maximum correlation coefficient, r^2 , the optimum values of the points for the 1st, 2nd, and 3rd exponential term of eq 44, and finally the calculated values of k and D_1 , together with their probable errors.

Experimental Section

The experimental arrangement of the RF-GC technique can be found in previous publications,^{2,6,7} in three recent reviews,^{3,4,5} or in a recent book.¹⁶ The instrument was a Shimadzu GC-8A gas chromatograph equipped with a FID detector. The diffusion column (z) had a length (L_1) of 53.5–57 cm and an internal cross sectional area (a_z) of 0.096 cm². It was free of any solid or liquid material and filled only with a stagnant column of carrier gas (nitrogen 99.99% pure, dried with silica gel).

The solid bed column (y) was 5.1–5.8 cm long (L_2) with an internal cross sectional area (a_y) of 0.096 cm². It was filled with 10–22 mesh solid particles of γ -alumina from Akzo or α -alumina prepared from γ as follows. The γ -alumina was heated in situ at 1373.15 K for 8 h and converted to α -alumina as shown by XRD analysis.

The amount of solid material per unit length of bed (a_s) was 0.051 g/cm in the case of γ - and 0.053 g/cm in α -alumina experiments.

The macrovoid fraction of the solid bed (ϵ_M) was 0.690 in the γ -alumina case and 0.721 in the α -alumina.

The mean pore radius for γ -alumina was measured as 53 Å, whereas for α -alumina it was found to be 108 Å.

Three adsorbates were used, namely, pentane, hexane, and heptane from Carlo Erba.

After conditioning of the solid bed by heating in situ at 573.6 K for 20 h, under a continuous carrier gas flow through the sampling column, the bed was cooled to the working temperature for 1 h, not necessarily the same as the temperature of the empty diffusion column. Then, the adsorbates were introduced through the injector at $y = L_2$ as liquids (2 μ l).

Following the appearance of the continuously rising concentration–time curve in the detector signal, the reversing procedure for the carrier gas flow was started, lasting 6 s for each reversal, which is shorter than the gas hold-up time in both column sections, l' and l . The narrow, fairly symmetrical sample peaks created by the flow reversals (cf. Figure 2 of ref 3 or Figures 3.2 and 3.3 of ref 16) were recorded, and their height (H), or the area under the curve, was calculated and printed, together with the corresponding time (t) by a C-R6A Shimadzu Chromatopac. By treating the (H , t) pair values as explained in the calculations section, all of the physicochemical parameters exposed and defined in the Theory section are calculated and printed.

Results and Discussion

The results obtained by treating the experimental data as described in the Calculations section are collected in Table 1. Some characteristics of the results are fairly obvious, concerning both k and D_1 values pertaining to the diffusion coefficients within the porous solid beds. First, these coefficients have the same order of magnitude (10^{-3} cm² s⁻¹) as those calculated by the well-known formula of Knudsen diffusion coefficients (eq 5.79 of ref 17). However, they are significantly smaller as expected because the Knudsen flow regime occurs when the

TABLE 1: Total Overall Rate Constant of Transference ($k = k_R + k_2$) and Diffusion Coefficient (D_1) into Porous Solids (α -Alumina and γ -Alumina) of Saturated Unbranched Acyclic Hydrocarbons (C_5H_{12} , C_6H_{14} , C_7H_{16}), Together with Their Probable Errors and the Number of Experimental Points (N) Used for Each Calculation

temp, K	$10^4 k, s^{-1}$	$10^3 D_1, cm^2 s^{-1}$	N
pentane on α -alumina			
353.2	8.83 ± 2.78	2.76 ± 0.239	62
363.2	9.02 ± 2.19	2.91 ± 0.274	49
373.2	9.32 ± 1.18	3.68 ± 0.131	61
hexane on α -alumina			
363.2	4.04 ± 3.73	3.14 ± 0.251	29
373.2	5.70 ± 0.968	2.92 ± 0.234	76
heptane on α -alumina			
383.2	5.16 ± 0.547	2.63 ± 0.090	51
393.2	6.24 ± 1.08	2.68 ± 0.212	60
403.2	7.50 ± 0.735	2.71 ± 0.149	55
pentane on γ -alumina			
353.2	8.75 ± 0.429	3.01 ± 0.106	58
363.2	5.53 ± 0.872	2.37 ± 0.140	60
373.2	7.72 ± 0.700	2.83 ± 0.085	45
393.2	7.02 ± 0.531	3.32 ± 0.082	59
hexane on γ -alumina			
353.2	2.99 ± 0.197	2.22 ± 0.069	54
363.2	3.67 ± 0.644	1.93 ± 0.184	57
373.2	4.65 ± 0.497	2.66 ± 0.129	75
393.2	5.58 ± 0.402	2.90 ± 0.083	57
heptane on γ -alumina			
373.2	6.64 ± 0.247	1.94 ± 0.085	38
383.2	4.53 ± 0.805	1.93 ± 0.186	60
403.2	4.05 ± 1.03	2.05 ± 0.329	50

Knudsen number (N_{Kn}) is of the order of 100 or greater

$$N_{Kn} = \frac{\lambda_A}{d_o} \quad (60)$$

where λ_A is the mean-free-path of the gas and d_o is the diameter of the pore in the porous solid. In the present work, this diameter was measured and found to be 216 Å in α -alumina and 106 Å in γ -alumina. Using these values for d_o in eq 60, one finds $N_{Kn} = 3.22 \times 10^{-2}$ for α - and 6.56×10^{-2} for γ -alumina, respectively, using C_5H_{12} at 373.2 K, whose the λ_A was found by eq 5.74 of ref 17, using a viscosity (μ_A) of 84.1 micropoise for pentane at 100 °C, given in ref 18. These values are definitely smaller than 100, the criterion stated before, leading to the definite conclusion that the diffusion coefficients calculated from the experimental data do not belong to the Knudsen flow regime. If they were, then they could be calculated by the well-known relation

$$D_{KA} = 48.5 d_o \left(\frac{T}{M_A} \right)^{1/2} \quad (61)$$

where M_A is the molar mass of the gas. In the example of pentane at 373.2 K used above, eq 61 gives $D_{KA} = 2.38 \times 10^{-2}$ and $1.17 \times 10^{-2} cm^2 s^{-1}$ for α - and γ -alumina, respectively. These values are 6.5 and 4.1 times bigger than those found in the present work (cf. Table 1).

A comparison of our diffusion coefficients with those determined by Reyes et al.¹ in 1997 by frequency-modulated perturbation methods seems in order now. They give the values of 0.103 and 0.110 s^{-1} for what they call diffusivity constants D/R_o^2 (s^{-1}), for isobutane at 348 and 398 K, respectively, diffusing into mesoporous silica spheres commonly used as

catalyst supports. Their mean particle radius (R_o) was 0.135 μm , and thus by multiplying their D/R_o^2 values by 0.135² cm^2 one obtains 1.88×10^{-3} and $2.00 \times 10^{-3} cm^2 s^{-1}$ 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 393.2 K, respectively, given in Table 1. They are $(2.76 \pm 0.239) \times 10^{-3}$ and $(3.32 \pm 0.082) \times 10^{-3}$, respectively. One must not forget the tremendously different methodology of the present work as compared to that of Reyes et al.¹

One final comment is that the probable errors pertaining to physicochemical quantities, as those determined by inverse gas chromatography methods, have never been determined before. These errors, given in Table 1, can be used in conjunction with the numbers (N) of the experimental points given in the last column to calculate the t statistic for the difference between two values of k or D_1 and see whether this is significant or not. It can be done by means of the well-known formula

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{P_1^2}{N_1} + \frac{P_2^2}{N_2}}} \quad (62)$$

and a table of the t statistic, where \bar{x}_1 and \bar{x}_2 stand for k or D_1 in Table 1 and P_1 and P_2 are their respective probable errors. For example, $t = 2.29$ for the last two values of D_1 in Table 1. This means that their difference is highly significant at the 5% significance level.

An explanation of decreasing the value of k with increasing temperature in some cases of Table 1 may be the fact that k is a complex constant pertaining to adsorption, desorption, and permanent immobilization of hydrocarbons on porous solids defined by the complex relation

$$k = k_R + k_2 = \frac{k_1(K + 1)}{K} + k_2 \quad (63)$$

as stated after eq 3. This combination of two rate constants (k_1 and k_2) with an equilibrium constant (K) may cause an irregular change of the resulting complex (k) with temperature in some cases. Also, this may be due to the unpredicted inhomogeneity of porous solids.

The errors for the reported quantities, suggesting rather high reliability of the reported data, cannot possibly exclude a decrease of the complex rate constant (k) with temperature.

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Supporting Information Available: The small PC program in GW-BASIC for calculating the various physicochemical quantities and their probable errors directly from the (H , t) experimental pairs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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