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# Determination of Diffusivities in Catalyst Particles

This paper describes a method for the determination of the diffusivities of molecules within heterogeneous catalyst particles under the conditions (temperature, pressure, etc.) that prevail during catalysis. © 1988 Academic Press, Inc.

## INTRODUCTION

The knowledge of the diffusion coefficients of reactant and product molecules within the structure of a heterogeneous catalyst is important for an understanding of its kinetic behavior as well as for the proper design of the catalyst and optimal process conditions.

In general catalytic practice, one wishes to provide conditions whereby the characteristic diffusion time into or out of the particle is small (fast) compared to the characteristic conversion time. This will provide maximum utilization of the catalyst mass and often provide optimal selectivity by allowing equally rapid exit of products before reconversion to secondary products (*1*, *2*).

On the other hand, in shape-selective catalysis by zeolites, one wishes to provide discrimination between two species of molecules, by supplying favorably fast diffusion for one but not the other species, relative to the characteristic conversion times (*3*).

In "classical" (i.e., nonzeolitic) porous solids, it is possible to estimate diffusivities from independent determination of porosity fraction and average pore size, and the application of classical laws of diffusion (ordinary or Knudsen, depending on pore size range) (*1*, *2*). At times it is possible to make direct measurements of diffusivity on mounted specimens (*2*, *4*, *5*). Sometimes these methods are not available or practicable.

In zeolite catalysts, we deal with crystallites in which mass transport occurs in the "configurational" regime of diffusion (*6*), where classical laws of estimation or extrapolation do not apply, due to the close approach of molecular and pore dimensions. Furthermore, it is rarely possible to "mount" such (usually micrometer-sized) crystals for direct diffusive transport observations.

The mounting of specimens of zeolite crystals has been accomplished (*7*, *8*). However, this requires special crystals of unusual size and operating conditions rarely matching those in catalysis.

The derivation of a diffusivity from sorption rate depends on the assumption that all molecules sorbed participate in diffusion; and again, sorption rates and catalysis cannot easily be measured under the same conditions, thus requiring extrapolations (*9*).

A method of determination of diffusivities from catalytic measurements themselves has general utility. This has been discussed and demonstrated (*2*), including with reference to zeolite catalysts (*9*, *10*). It employs the characteristics of the functional relationship between the reaction rate (or utilization factor $\eta$) and the Thiele modulus $\phi$, using a graphical curve-fitting procedure termed the "triangle method."

We have now formalized this method by numerical computer solutions so that experimental observations of comparative catalytic rates on catalysts of different Thiele modulus, i.e., of different particle size, or of different reactivity, can be readily translated into quantitative information on diffusivities.

## METHOD

Intraparticle catalyst diffusivities can be derived from the *observed* ratio of reaction

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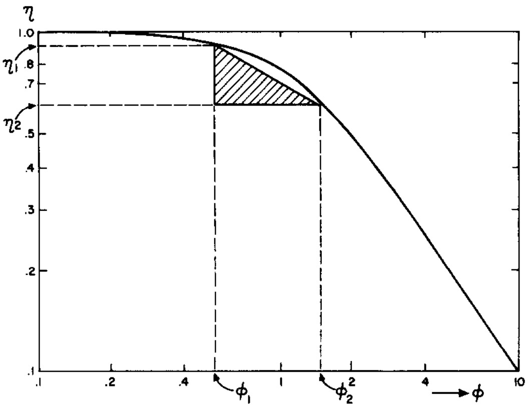

FIG. 1. The graphical "triangle method." The observed ratio of activities, representing a length on the logarithmic ordinate, and the known ratio of the Thiele modulus, on the logarithmic abscissa, is fitted to the $\eta$ vs $\phi$ relationship.

rates $(dn/dt)_1/(dn/dt)_2$ on two catalyst samples that are characterized by different particle (crystallite) sizes of *known* ratio $R_1/R_2$, which means that the ratio of the Thiele moduli $\phi_1/\phi_2$ is known, i.e.,

$$\phi_1/\phi_2 = R_1/R_2, \quad \text{since } \phi = R(k/D)^{1/2}. \quad (1)$$

The reaction rate ratio also equals the ratio of the effectiveness factors $\eta$,

$$\eta_1/\eta_2 = (dn/dt)_1/(dn/dt)_2, \quad \text{since } dn/dt = \eta * k * c_0. \quad (2)$$

The two quantities, the observed ratio $X_\eta = \eta_2/\eta_1$ and the known ratio $X_\phi = \phi_2/\phi_1$, allow us to locate the actual values of the pairs $\phi_1$, $\eta_1$ and $\phi_2$, $\eta_2$ by locating the proper fit of the data pairs on the known functional forms of ln $\eta$ vs ln $\phi$. This is exemplified by the "triangle" in Fig. 1, which pictures that relationship for first-order reaction and slab geometry (one-dimensional entry).

Once a pair $\eta$, $\phi$ has been determined (one of the two suffices), the applicable diffusivity is derived from

$$D = (dn/dt) * (1/c) * R^2 * (1/\eta * \phi^2), \quad (3)$$

which follows directly from (1) and (2).

## GENERAL MATHEMATICAL FORMULATION

### *Solutions*

We have developed the general numerical solutions applicable to nearly any geometry that is likely to be of interest; they are summarized in Figs. 2 and 3 for slab and spherical partical geometries. They do not differ greatly. We therefore omit the cylinder geometry which lies in between and close to that of the sphere.

For any given experimental value of $X_\eta$ and known value of $X_\phi$, $(= R_2/R_1)$ will provide $\phi_1$, which will give $\eta_1$. Thus all information is available to determine diffusivity $D$ from formula (3). If desired, one can obtain a second check via $\phi_2$ (which follows from $\phi_1$ and $X_\phi$).

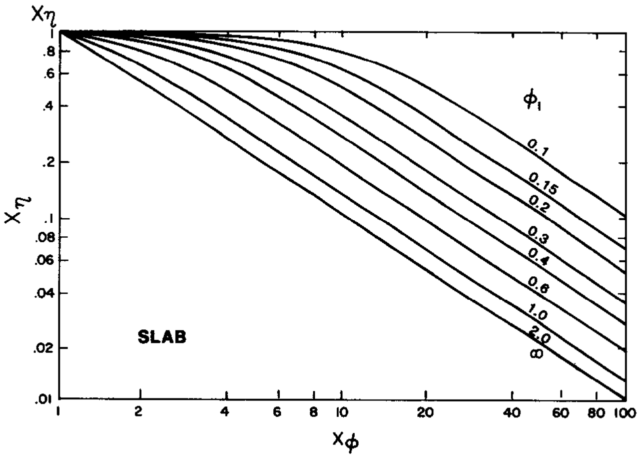

FIG. 2. Solutions allowing direct determination of the Thiele modulus of one catalyst from the observed activity ratio $X_\eta$ and known Thiele modulus ratio, $X_\phi$; for slab geometry.

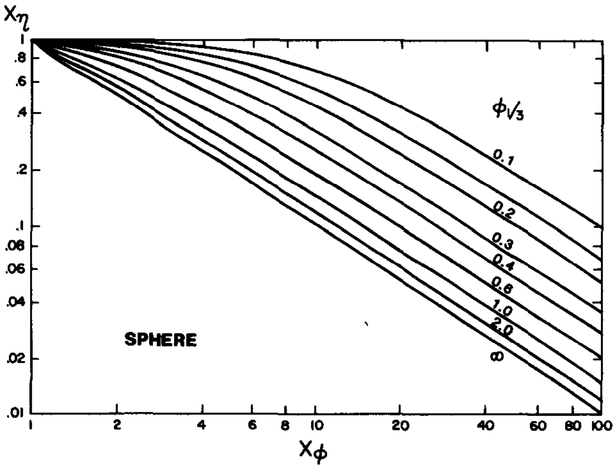

FIG. 3. Solutions for spherical geometry.

## Derivation

The analytical solutions for the functions

$$\eta = f(\phi) \tag{4}$$

depend on geometry. The functional expressions (for first-order reaction) are (*11*)[1]

$$\eta = (\tanh \phi)/\phi \quad \text{(slab)} \tag{5a}$$

$$\eta = 2 * I_1(\phi)/I_0(\phi) * \phi \quad \text{(cylinder)} \tag{5b}$$

$$\eta = 3 * (\coth(\phi) - 1/\phi)/\phi \quad \text{(sphere).} \tag{5c}$$

In this treatment we have used a "normalized" Thiele modulus, defined by

$$\phi = R * (k/D)/G, \quad \text{where} \begin{cases} G = 1 \text{ for slab} \\ G = 2 \text{ for cylinder} \\ G = 3 \text{ for sphere.} \end{cases} \tag{6}$$

Conceptually, this takes into account the relative ease or multidimensionality of the diffusion paths, for a given characteristic length dimension $R$ for the three geometries, analytically it results in a near match of the functions (5) for all geometries, as pointed out by Aris (*11*). It demonstrates the great insensitivity of diffusional effects in catalysis to the exact knowledge of geometry.

We have, for any given geometry (i.e., function (5) above),

$$X_\eta = f(\phi_2)/f(\phi_1),$$

and since $X_\phi$ is known, $\phi_2 = \phi_1 * X_\phi$, and

$$X_\eta = f(X_\phi * \phi_1)/\mathrm{f}(\phi_1). \tag{7}$$

$X_\eta$ and $X_\phi$ are known; thus formula (7) serves to determine $\phi_1$. ($\eta_1$ then follows, and $D$ becomes determined through formula (3).)

The convention $\phi_2 > \phi_1$ will be used throughout. Consequently, $\eta_2 < \eta_1$.

Our numerical procedure used Newton's method; an initial guess for the iterative solution of Eq. (5) is easily obtained, since, for given $X_\phi$ and $X_\eta$, either bounding value of $\phi_1$ will lead to convergence of Newton's method.

## EXAMPLE OF EXPERIMENTAL DIFFUSIVITY DETERMINATION

Haag *et al.* (*10*) measured the rate of reaction of paraffins and olefins of various structures on ZSM-5 zeolite catalyst, including on catalysts of similar intrinsic activity but having two different crystallite sizes, in the ratio $X_\phi = 54$ for all cases, and with $R_2 = 1.35 \times 10^{-4}$ cm for the half-thickness of the slab-like crystals.

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[1] $I_0$ and $I_1$ are modified Bessel functions of order 0 and 1.

TABLE 1

Diffusivities of Zeolite ZSM-5 Calculated from Experimental Reaction Rate Data (Ref. *10*)

| Reactant | $k_{1,\mathrm{obs}}$ | $X_\phi$ | $X_\eta$ | $\phi_1$ | $\phi_2$ | $\eta_1$ | $\eta_2$ | $D$ ($\mathrm{cm^2/s}$) |
|---|---|---|---|---|---|---|---|---|
| 2,2-Dimethylbutane | 29 | 54 | 0.30 | 0.06 | 3.33 | 0.99 | 0.30 | $2.0 \times 10^{-8}$ |
| 2,2-Dimethylheptane | 63 | | 0.13 | 0.14 | 7.55 | 0.99 | 0.13 | $2.0 \times 10^{-8}$ |
| 1-Hexene | 7530 | | 0.86 | 0.013 | 0.71 | 1.00 | 0.85 | $2.7 \times 10^{-4}$ |
| 3-Methylpentene | 7420 | | 0.49 | 0.04 | 1.98 | 1.00 | 0.49 | $3.5 \times 10^{-5}$ |
| 3,3-Dimethylbutene | 4350 | | 0.032 | 0.65 | 35.1 | 0.88 | 0.03 | $7.3 \times 10^{-8}$ |

Table 1 contains the values of the observed rate constant (they are proportional to observed rates) for the smaller particles,

$$k_{1,\mathrm{obs}} = (1/c) * (dn/dt)_1;$$

the fractional decrease $X_\eta$ is obtained for the larger particles and for several hydrocarbons, all at 810 K, on ZSM-5 catalyst; then $\phi_1$ is obtained from Fig. 2, followed by $\phi_2$ from $\phi_1 * X_\phi$; $\eta_1$ and $\eta_2$ are obtained from the associated $\phi$'s.

Diffusivities are obtained from pairs $\phi_1$, $\eta_1$ or $\phi_2$, $\eta_2$, using formula (3), and are listed in Column f.

## METHOD SENSITIVITY AND LIMITATIONS

It can be seen from inspection of Fig. 1, which demonstrates the general diffusion behavior of catalysts, that useful determinations depend on obtaining a substantially measurable decrease in activity (i.e., $X_\eta < 1$) when increasing particle size (i.e., by $X_\phi \gg 1$). When this is not the case, the experiment must be repeated under more severe conditions, i.e., usually by increasing temperature, thereby increasing the reaction rate constant $k$ and thus the magnitudes of the Thiele modulus $\phi$.

Alternatively, when the fractional decrease in activity approaches the fractional increase in particle size, i.e., when $X_\eta * X_\phi \approx 1$, the asymptotic condition of the diffusion effect will yield only a value of minimum diffusivity, based on $\phi_1 > 2$. If a quantitative solution is desired, the experiment should be repeated under milder conditions, such as lower temperature or still smaller particle sizes.

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J. F. MARSHALL[1]
PAUL B. WEISZ[2]

*Central Research Laboratory*
*Mobil Research and Development Corporation*
*Princeton, New Jersey 08540*

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[1] Present address: P.O. Box 31, Mechanicsville, PA 18934.

[2] Present address: University of Pennsylvania, Department of Chemical Engineering, Philadelphia, PA 19104-6393.