DIFFUSION PHENOMENA IN HETEROGENEOUS CATALYSIS

T. K. SHERWOOD

Department of Chemical Engineering, Massachusets Institute of Technology, Cambridge, Mass., U.S.A.

Many of the most important industrial chemicals are produced by catalytic processes. Ammonia, sulphuric acid, phthalic anhydride, acrylonitrile and many other chemicals are manufactured in very large volumes by heterogeneous catalysis. Catalysis has proved enormously successful in practice, and its promise for new and better products and processes is so great that industry now spends many millions of dollars each year on research and development in the area of applied catalysis.

The successful development of the many important catalytic processes has been accomplished in spite of the fact that the mechanism of catalysis is not well understood, and catalysts must be selected or developed largely on the basis of empirical knowledge and experience. The elucidation of the mechanism of surface reactions is proving to be an exceedingly complex and difficult scientific problem. Progress would be more rapid were simpler and better techniques available to measure directly the state of the reacting species on the catalytic surface, as the reaction proceeds. The gross kinetics of the surface reaction, however, can often be developed if information is available concerning the concentrations of reactants and products in the fluid immediately adjacent to the catalyst surface.

Almost all industrial and most academic studies of heterogeneous catalysis depend on measurement of the concentrations of reactants and products in the ambient fluid. Part of the chemical potential corresponding to the reactant concentration in the ambient fluid is dissipated in transporting the reactants and products to and from the surface of the solid; the potential of interest in the study of the surface kinetics may be quite different from that measured and reported. In the extreme case of a very active catalyst and a large resistance to mass transfer, the results are relevant to the mass transfer phenomena but not to catalysis. There are, in fact, studies reported in the scientific literature in which the investigator measured mass transfer resistances in the belief that he was studying catalysis. Studies providing ambient fluid concentrations can be analysed more rationally if methods are available to estimate the difference between the reactant concentration at the surface and that in the ambient fluid; some of the methods available for this purpose are summarized in this paper.

As a simple example of the problem, consider a first order irreversible reaction catalysed by a single spherical pellet of porous catalyst. In the steady state the rate of transport of reactant from fluid to outer pellet surface must be equal to the rate of reaction:

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = k_c A_s (C_o - C_s) = \eta_p k_V V_c C_s = \eta_o k_V V_c C_o \tag{1}$$

where $-\mathrm{d}n/\mathrm{d}t$ is the rate of reaction in mole/sec, C_o is the reactant concentration in the ambient fluid in g mole/cm^3, C_s is the reactant concentration in fluid adjacent to outer pellet surface in g mole/cm^3, A_s is the outer pellet surface in cm^2, k_c is the mass transfer coefficient, fluid to pellet in cm/sec, V_c is the pellet volume in cm^3, and k_V is the chemical rate constant applicable throughout the porous pellet in sec^{-1}.

The effectiveness factor η_p is the ratio of the reaction rate to that which would be attained if all of the pore surface were exposed to the concentration C_s; the "overall" effectiveness factor η_o is the ratio of the actual reaction rate to the rate attainable with all of the pore surface exposed to the reactant concentration C_o. The following relation is easliy obtained:

$$\eta_o = \frac{1}{Rk_V/3k_c + 1/\eta_p} \tag{2}$$

where R is the radius of the spherical pellet.

The overall effectiveness factor is unity if there is no mass transfer resistance ($3k_c \gg Rk_V$, $\eta_p = 1$); mass transfer resistances within the pellet structure ($\eta_p < 1$), or around the pellet ($k_V/k_c > 3/R$) reduce η_o to a fraction.

MASS TRANSFER BETWEEN A FLUID AND A SOLID SURFACE

If the mass transfer resistance is significant, that is, if part of the available chemical potential is dissipated in transporting the reacting species, then the temperature and concentrations at the solid surface are not those of the ambient stream. The observed activation energy of the overall process is not that of the surface reaction (it is usually less). If competing chemical reactions are involved, the selectivity of the catalyst will depend on the value of the mass transfer resistance.

The foregoing is intended to emphasize the need to know the magnitude of the mass transfer resistance in order that one may interpret experimental data properly, or "scale up" laboratory data for industrial purposes. Fortunately, there are reasonably reliable methods, some theoretical and some empirical, to use in the prediction of k_c and of the chemical potential lost in promoting mass transfer. These methods cannot be described in this brief review, since there are so many of them, each applying to a particular geometry and to either laminar or turbulent flow of the fluid. Two or three will be mentioned as examples of the useful correlations now available, mostly in the literature of chemical engineering. In many cases it is not necessary to be able to estimate k_c with great accuracy; situations in which the mass transfer resistance is either negligible or dominant are common, so that approximate methods often serve to define the role of diffusion.

Fluid motion is laminar at low flow velocities and each element of the fluid follows a definite path, which, in principle, is known or can be calculated. Mass transfer from a fluid in laminar flow to a solid surface can, again in principle, be calculated, though the analysis is often difficult. Levich[1], for example, presents the theory for the case of mass transfer between the surface of a rotating disc and a fluid in laminar motion, and obtains the relation:

$$\frac{2k_cR}{D} = 1{\cdot}24 \left(\frac{\nu}{D}\right)^{1/3} \left(\frac{\omega R}{\nu}\right)^{1/2} \tag{3}$$

where D is the molecular diffusion coefficient, ν is the kinematic viscosity of the fluid, R is the radius of the disc, and ω is the angular speed of rotation. The quantity on the left is the Nusselt number for mass transfer, ν/D is the Prandtl number for mass transfer (often referred to as the Schmidt number), and the dimensionless ratio $\omega R/\nu$ is a version of the Reynolds number. The rotating disc and the very long rotating cylinder are examples of the relatively few cases in which the surface is "uniformly accessible": k_c is the same at all points on the surface. The analysis of experimental data is simplified greatly if uniformly accessible surfaces are employed, with or without surface catalysis.

Laminar flow over a flat plate is a case in which the surface is not uniformly accessible: the local value of k_c decreases sharply with distance x from the leading edge. The average value of k_c, from which the mass transport to the entire plate may be calculated, is given by [1, 2]:

$$\frac{k_ch}{D} = 0{\cdot}66 \left(\frac{\nu}{D}\right)^{1/3} \left(\frac{hU}{\nu}\right)^{1/2} \tag{4}$$

where h is the length of the plate in the direction of flow, and U is the ambient velocity of the fluid.

Of more interest in catalysis, however, is the case of mass transfer between a solid sphere and a flowing gas or liquid. As for most bluff objects, transition from laminar to turbulent flow is gradual, and attempts have been made to correlate the existing experimental data by means of single equations covering the entire range of Reynolds numbers. Several of the proposed correlations are of the form:

$$\frac{2k_cR}{D} = 2{\cdot}0 + K \left(\frac{2RU}{\nu}\right)^{1/2} \left(\frac{\nu}{D}\right)^{1/3} \tag{5}$$

where R is the sphere radius. Values of the constant K reported by various authors fall in the range 0·3–1·0. A recent review[3] of existing data in the range of Reynolds numbers from 20 to 2000 (commonly employed in studies of catalysis) suggests $K = 0{\cdot}63$ for gases and $K = 0{\cdot}76$ for liquids.

At negligibly small flow $2k_cR/D$ is 2·0, as may be readily calculated for radial molecular diffusion from a sphere to an infinite stagnant medium. At very low fluid velocities, as for a solid sphere falling freely in a fluid, the group $2k_cR/D$ is best expressed as a function of the Péclet number $2UR/D$, as indicated by *Figure 1*[4]. This shows the asymptote of 2, a curved intermediate section based on theory, and an upper asymptote represented by:

$$\frac{2k_cR}{D} = 0{\cdot}99 \left(\frac{2UR}{D}\right)^{1/3} \tag{6}$$

This last, with slightly different constants, is given by Levich[1] and by Aksel'rud[5]. Equation (6) may be combined with Stokes law to eliminate U and so obtain:

$$k_c^* = 0{\cdot}38 \left(\frac{g\,\Delta\rho}{\rho_f}\right)^{1/3} \left(\frac{\nu}{D}\right)^{-2/3} \tag{7}$$

where ρ_f is the fluid density, $\Delta\rho$ is the difference in density between fluid and solid, and k_c^* is the coefficient of mass transfer from a fluid to a sphere in free fall. *Figure 1* suggests that this should apply at values of the Péclet number greater than about 500. At lower values of the Péclet number the curved portion of *Figure 1* may be similarly combined with Stokes relation to obtain k_c^*. From equation (7), and from the fact that $2k_c^*R/D$ approaches 2 as the particle radius approaches zero, it is evident that k_c^* is independent of R for large particles, but inversely proportional to R in the case of very small particles.

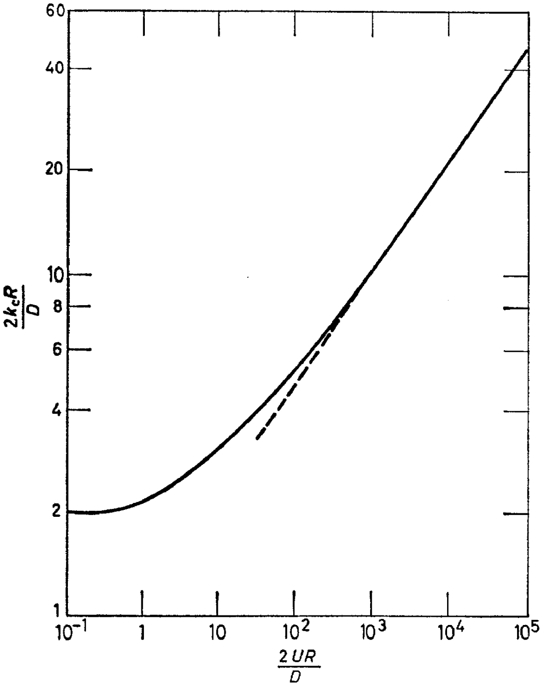

Figure 1. Mass transfer to a single sphere moving in a fluid at low velocity

Suspensions of dispersed solid catalysts are commonly employed for hydrogenations and other catalytic processes. Agitation tends to improve mass transfer, but the effect is surprisingly small. Very small particles tend to follow the motion of the fluid and stirring does not increase k_c; k_c for larger particles is increased by stirring or agitation, but Harriott[6] has shown that k_c/k_c^* for suspensions in liquids ordinarily falls in the range 1–4.

An approximate value of k_c can thus be obtained by employing a calculated or measured settling velocity, (*Figure 1*), and an assumption that k_c/k_c^* is about 2.

For very finely divided solids in suspension, both the area per unit mass and the mass transfer coefficient are inversely proportional to the particle size, so the slurry or fluid bed can provide enormous reaction capacity compared with other reactor designs.

It has proved difficult to develop a simple method to characterize the shapes of broken and irregular solid particles, and to relate their size and form to the sphere radius employed in mass transfer correlations. The recent papers of Lochiel and Calderbank[7] represent an important contribution in this direction, but the use of a particle radius corresponding to a sphere having the same ratio of external surface to volume is often adequate for technical calculations.

The value of mass transfer correlations in the analysis of kinetic data is illustrated by a recent study of the hydrogenation of α-methyl styrene. This was carried out in this laboratory by Farkas[8] who employed a 2·5 cm i.d. "bubble column" containing 0·5–3 g/l. of palladium black suspended in a liquid mixture of α-methyl styrene and cumene. Hydrogen, supplied at the bottom at atmospheric pressure, served not only to keep the catalyst in suspension, but to maintain the liquid thoroughly mixed from top to bottom of the column.

At steady state the rate of cumene formation is equal to the rate of solution of hydrogen in the liquid and to the rate of transport of hydrogen from the liquid solution to the surface of the catalyst particles. If the reaction at the surface is first order in hydrogen, then:

$$\text{mole/h} = (k_c)_g A_g (C_o^* - C_o) = (k_c)_p A_p (C_o - C_s) = k_R A_p C_s \qquad (8)$$

The symbol C refers to concentration of hydrogen in the liquid, C_o^* is the value at equilibrium with the gas, C_o is the value for the bulk liquid, and C_s is the concentration at the surface of the solid particle. The coefficient of mass transfer from gas to liquid is $(k_c)_g$ and from liquid to particle is $(k_c)_p$; k_R is the chemical rate constant expressed in terms of the particle surface A_p.

Eliminating C_o and C_s, these relations lead to the following:

$$\text{mole/h} = C_o^* \left[\frac{1}{(k_c)_g A_g} + \frac{1}{(k_c)_p A_p} + \frac{1}{k_R A_p}\right]^{-1} \qquad (9)$$

This suggests that data obtained with different catalyst loadings (which are proportional to A_p) might be correlated by plotting the reciprocal of the rate per unit volume *vs.* the reciprocal of the catalyst loading. *Figure 2* shows Farkas' data plotted as suggested; it is seen that the analysis is well substantiated.

Figure 2 would appear to provide a good correlation of kinetic data for a case of heterogeneous catalysis. This correlation is ambiguous, however, since the indicated effect of loading may be due to the effect of variation of particle surface on either mass transfer or surface reaction; there is no indication of the relative importance of the second and third terms in the square brackets of equation (9).

As noted earlier, *Figure 1* provides a basis for the estimation of $(k_c)_p$. The calculation of $(k_c)_pA_p$, however, can be expected to be good only to an order of magnitude, since the particles are not spheres but variable agglomerates, and the median diameter obtained from settling measurements cannot provide a reliable value of A_p. Carrying out the calculation, it is found by the use of *Figure 1* that the predicted maximum rate $[(k_c)_pA_pC_o^*)]$ of mass transfer to the particles is only one-tenth of the observed rates. The conclusion that the diffusional resistance was important is inescapable. In all probability, the work described should be considered as an investigation of mass transfer to suspended particles, and not a study in catalysis.

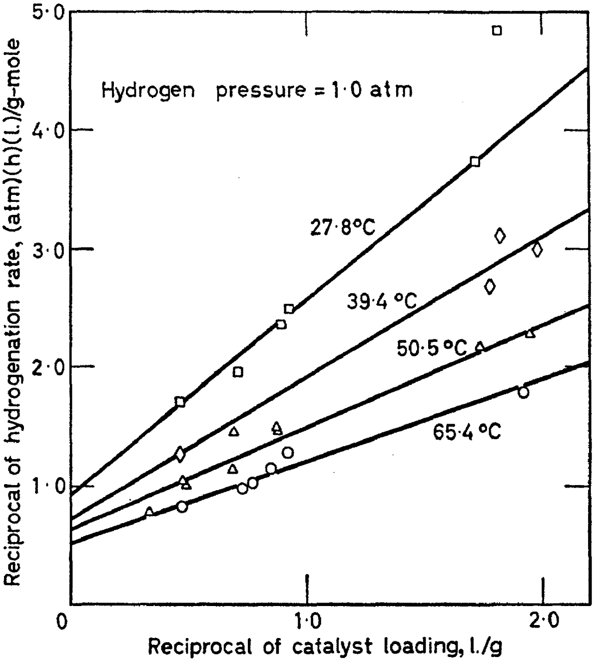

Figure 2. Hydrogenation of α-methyl styrene

Large-scale continuous catalytic processes commonly employ fixed beds of extrudates or pressed pellets. The flow passages in such beds are quite complex, and it has been found necessary to develop empirical correlations of data on mass transfer between the pellets and the flowing gas or liquid. Many such correlations appear in the literature; *Figure 3* is representative of those which relate the Chilton–Colburn "*J*-factors" to the Reynolds number based on particle diameter. The dimensionless quantities appearing as ordinates are defined by:

$$J_D \equiv \frac{k_c\rho}{G}\left(\frac{}{D}\right)^{2/3}; J_H \equiv \frac{h}{C_fG}\left(\frac{C_f\rho v}{k}\right)^{2/3}$$

The lower line provides a basis for estimating k_c and the upper line an estimation of the coefficient of heat transfer, h. Similar correlations for mass and heat transfer particles in fluidized beds are available[9, 10], though these are probably less reliable than the fixed bed correlations.

The mass velocities usually employed with gas flow in fixed beds are large enough to cause the mass transfer resistance to be quite small. In fact it seems safe to generalize by stating that the resistance to mass transfer from gas to the outer surface of the particles cannot be important if more than 25–40 cm of bed height are required to cause a first order reaction to be carried 90 per cent of the way to equilibrium. This does not hold for liquid flow in a bed, since ν/D can be 10^3 or 10^4 as great in liquids as in gas mixtures; the mass transfer resistance may be dominant in single-phase liquid flow in beds if the catalyst is reasonably active.

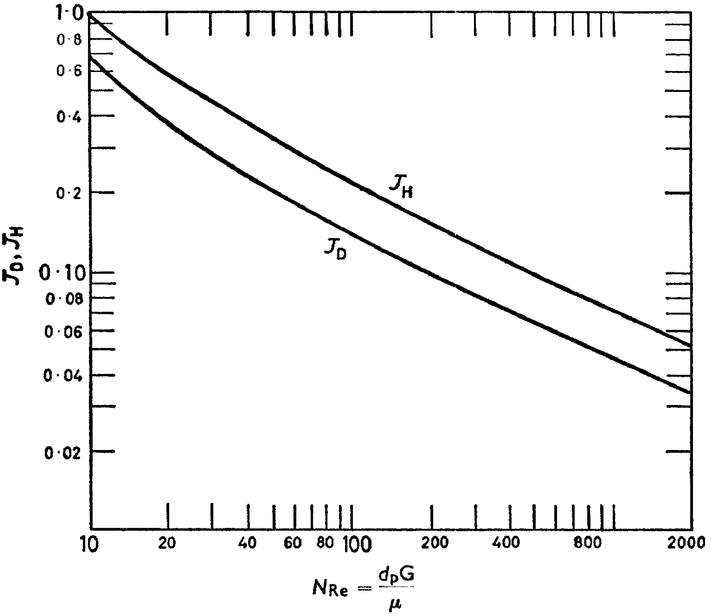

Figure 3. Variation of J_H and J_D with Reynolds number in fixed beds

Mixed-phase operation of fixed beds is becoming increasingly common, with down-flow of a mixture of gas and liquid. No adequate correlations of mass transfer data for such systems have been published, and it is evident that the process is complicated. Liquid flows over and probably saturates the porous pellets, so that reactants in the gas must first diffuse across a flowing liquid film and then into the liquid filled pores to reach the internal catalyst surface.

The thickness of the liquid film on the pellets is evidently quite small in these "trickle beds". If the void volume is 40 per cent with 5 mm pellets, and if the "dynamic hold-up" of liquid is one-third the void volume, then the average thickness of the liquid layer is only 0·185 mm. The diffusional resistance of this film is small compared with that of the porous pellet of radius 2·5 mm.

As noted earlier, the temperature of the catalyst surface may be quite different from that of the ambient fluid. If the rate and enthalpy of the reaction are known, then the difference in the temperatures of fluid and solid may be calculated if the heat transfer coefficient h is known. Correlations of heat transfer data exist for many geometries and flow systems, and are generally somewhat more complete and reliable than those available for mass transfer. One example is the line on *Figure 3* representing J_H for packed beds. If the fluid velocity is low, the catalyst active, and the reaction highly exothermic, the catalyst surface may be 100°C or more above the temperature of the ambient fluid.

DIFFUSION AND REACTION IN POROUS CATALYSTS

Porous catalysts are employed in order to provide a very large catalytic surface in a small volume, at low cost. The pores are very small, however, and diffusion of reactants into the catalyst, and products back out, may dissipate a large part of the available chemical potential. The theory of simultaneous diffusion and reaction in porous catalyst is now more than 25 years old[11–14], and has been discussed extensively in the literature. It has not been employed widely in engineering practice, however, since the surface kinetics can seldom be predicted, and there are as yet no adequate methods to define the structure of porous solids in such a way as to make it possible to predict diffusion coefficients with confidence. This theoretical development has proved, nevertheless, to be a major contribution to the understanding of catalyst systems.

The nature of the theory will be described by summarizing the relations which have been developed for diffusion into a spherical porous pellet in which there is an irreversible surface reaction which follows power law kinetics.

Diffusion is assumed to be described by the relation:

$$N = D_E \frac{dC}{dr} \tag{10}$$

where N is the molal diffusion flux of reactant into a pellet of radius R, per unit of total cross section normal to the radius; D_E is the "effective" diffusion coefficient, and dC/dr is the reactant concentration gradient at $r = r$. A reactant balance for a differential shell leads to the basic differential equation, which is integrated with the boundary conditions $C = C_s$ at $r = R$ and $dC/dr = 0$ at $r = 0$. The result for a first order reaction is:

$$-\frac{dn}{dt} = 4\pi R D_E\, C_s\, \phi \left[\frac{1}{\tanh \phi} - \frac{1}{\phi}\right] \tag{11}$$

where:

$$\phi = R \left(\frac{k_V}{D_E}\right)^{1/2} \tag{12}$$

The total reaction rate is $-\,dn/dt$ mole/sec; k_V is the reaction rate constant defined on the basis of unit volume of the porous catalyst.

If all of the interior surface were exposed to reactant at the concentration C_s (that at the outer surface of the pellet), the reaction rate would be:

$$-\frac{dn}{dt} = \frac{4}{3}\pi R^3 k_V C_s = V_c k_V C_s \tag{13}$$

The "effectiveness factor" of the pellet, defined in connection with equation (1), is obtained by dividing equation (11) by equation (13):

$$\eta_p = \frac{3}{\phi}\left[\frac{1}{\tanh \phi} - \frac{1}{\phi}\right] \tag{14}$$

The nature of the relation between η_p and ϕ is illustrated by the curves shown on *Figure 4* for spheres with reaction orders of zero, one, and two.

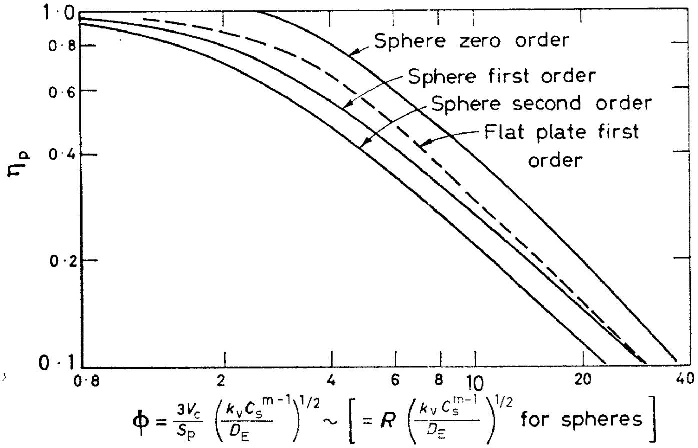

Figure 4. Effectiveness factor with power-law kinetics

Cases involving bulk flow in the pores, due to volume change on reaction have also been analysed[15, 16].

If the reaction rate is small and D_E large ϕ is small and η_p approaches unity. This means that essentially all of the internal catalytic surface is "effective". If the reaction rate is large or D_E quite small ϕ becomes large and η_p may be quite small. In this case much of the internal surface is ineffective; most of the reaction occurs near the outer pellet surface as reactant diffuses in through the pores.

The theory which has been outlined briefly would clearly be of great practical value if it could be employed quantitatively. Unfortunately, the diffusion process is complex and there are but limited data on D_E for porous catalysts of interest. The data required to fix the chemical rate constant k_V and the order of reaction are often difficult to obtain. Nevertheless, the semi-quantitative analysis of a heterogeneous reaction may point the way to process improvements. If ϕ is known to be very large or very small, even though its exact value is known quite imprecisely, η_p can be shown to be either very small or near unity. If η_p is near unity little will be lost by employing larger pellets, thereby reducing bed pressure drop and probably reducing the cost of pellet manufacture. If η_p is small the pellet size should be reduced if that is practical. A change in the method of manufacture to substantially increase the effective diffusivity may also be possible. Other things being equal, highly active catalysts will show low effectiveness factors, and poor catalysts will show effectiveness factors approaching unity.

Considerable progress has been made in recent years in the development of methods of predicting D_E, but there is much yet to be done. Knudsen diffusion takes place at low pressures in small pores, but ordinary molecular or "bulk" diffusion prevails at higher pressures and in the larger pores. The transition region between the two extends over a rather wide range of pressures in a given pore structure[17, 18]. The Knudsen coefficient for diffusion in a straight round pore (based on the pore cross-section) is given by:

$$D_K = 9700\, r_e\, (T/M)^{1/2} \tag{15}$$

where r_e is the pore radius in cm. The usual binary diffusion coefficients apply for ordinary molecular diffusion in pores. An approximate equation for D in a straight pore in the transition region is[19]:

$$D = \frac{1}{1/D_M + 1/D_K} \tag{16}$$

where D_M is the value for molecular diffusion.

The difficulty in applying these simple relations to diffusion in porous solids lies in the complex pore structure of common catalysts. Pores are neither straight nor of uniform cross-section. Pellets formed by compressing powders usually have a bimodal pore structure, a portion of the pores being very small and most of the remainder relatively large. Knudsen diffusion may prevail in the smaller pores and diffusion in the transition or bulk region takes place at the same time in the large pores. Models of the structure have been proposed[20] which have shown promise of providing a basis for a useful theory and correlation, but it is extremely difficult to characterize a complex pore structure in a simple way. Surface diffusion along the pore walls has been the subject of a number of recent papers, but it would appear that this phenomenon will require more study before its importance in pore diffusion can be described quantitatively.

Flow and diffusion in porous materials have sometimes been analysed by introducing an empirical "tortuosity factor", by which the rate calculated for a straight round pore is divided. Thus for Knudsen diffusion in a material having a porosity θ;

$$D_E = \frac{D_K\theta}{\tau} = 19{,}400\,\frac{\theta^2}{S_g\rho_p\tau}\left(\frac{T}{M}\right)^{1/2} \tag{17}$$

This follows from equation (15), with r_e replaced by $2\theta/S_g\rho_p$, where S_g is the pore surface per gram and ρ_p is the pellet density. *Figure 5* shows data collected from various literature sources (*Table 1*) plotted for comparison with the solid line representing equation (17). The empirical factor τ evidently varies from approximately 0·3 (the top line) to 5·9 for porous, unfused Vycor glass. The data of Weisz and Schwartz[21] on porous oxide-derived gels (not shown) give values of τ ranging from 1 to 3. Catalysts with

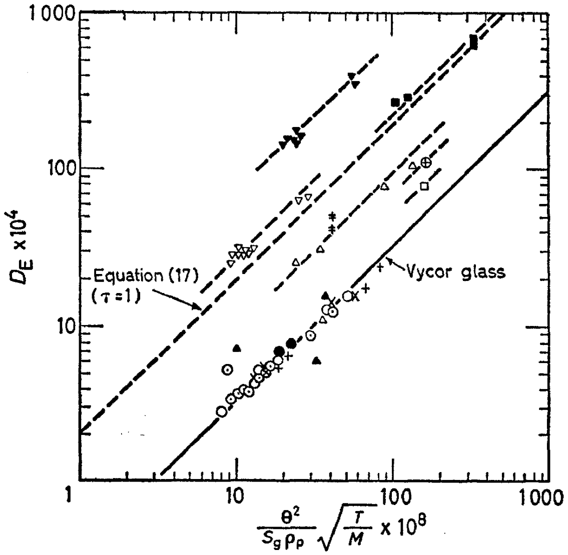

Figure 5. Data on diffusion of gases in consolidated porous media compared with equation (17) for Knudsen diffusion in straight round pores. For full experimental data and key *see Table 1*

Table 1. Diffusion and flow in porous media (experimental data shown on *Figure 5*)

Material	*Technique*	*Gases*	*Temperature* (0°K)	r_e (Å)	θ	τ
■ Alumina pellets	Diffusion	N_2, He, CO_2	303	96	0·812	0·85
△ Fresh and regenerated silica–alumina cracking catalyst	Flow	H_2, N_2	298	31–50	0·464 0·447	2·1
× Vycor glass	Flow	H_2, He, A, N_2	298	30·6	0·31	5·9†
⊕ Water–gas shift catalyst	Diffusion	O_2, N_2	298	177	0·52	2·7
□ Ammonia synthesis catalyst	Diffusion	O_2, N_2	298	203	0·52	3·8
○ Vycor glass	Flow	He, Ne, H_2, A, N_2, O_2, Kr, CH_4, C_2H_6	292 294	30	0·298	5·9†
+ Vycor glass	Flow	H_2, He, A, N_2	298	50	0·28	5·9†
▲ Silica–alumina cracking catalyst various treatments	Reaction	Gas oil	755	28–71	—	3–10
● Vycor glass	Flow	A, N_2	298	46	0·305	5·9†
▽ Alumina–silica cracking catalyst	Flow	He, Ne, A, N_2	273–323	16	0·40	0·725
▼ Alumina–silica cracking catalyst	Flow	He, Ne, N_2	273–323	24	0·53	0·285
⊙ Vycor glass	Flow	He, CO_2, N_2, O_2, A	298	44	0·31	5·9†
⊗ Silica–alumina cracking catalyst	Reaction	Cumene	420	(24)	(0·50)	5·6
‡ Nickel–alumina‡	Reaction	*o*–H_2, *p*–H_2	77	(30)	(0·44)	1·8

† Average value for the five sets of data on Vycor.

‡ Data were obtained in the transition region. D_E for Knudsen diffusion was calculated from the observed D_E by equation (16).

bimodal pore structure give the smallest values of τ. Poor as this simple correlation is, it can provide rough estimates of D_E which are often quite useful.

Values of D_E are usually obtained by measuring the diffusion of a gas through a porous sample, or the flow resulting from a pressure gradient. Data obtained in these ways are of doubtful application to the theory of pellet effectiveness, since there may be many dead-end pores which provide useful catalytic surface but do not contribute to steady-state flow or diffusion. The best source of values of D_E is data on the catalytic activity of the material.

The pellet effectiveness factor η_p is defined by:

$$-\frac{dn}{dt} = \eta_p V_c k_v C_s \tag{18}$$

This may be combined with equation (12) to eliminate k_v and obtain

$$\phi^2 \eta_p = \frac{R^2}{D_E C_s}\left(-\frac{1}{V_c}\frac{dn}{dt}\right) \tag{19}$$

The effectiveness factor η_p is a function of $\phi^2.\eta_p$, as can easily be obtained from equation (14). A graph of η_p *vs.* $\phi^2.\eta_p$ looks very much like *Figure 4.* To obtain a value of D_E, from reaction rate studies, several catalyst tests are run under identical reaction conditions but with different pellet sizes, and also with a bed of small particles or powder. The data are used with equation (19) to obtain several values of $\phi^2.\eta_p$, and with equation (18) to obtain corresponding values of $k_v\,\eta_p$. There should then be only one value of k_v and one value of D_E which cause the data to fit both equation (18) and the theoretical curve of η_p *vs.* $\phi^2.\eta_p$. Such data demonstrate clearly the pellet size range where the effectiveness factor falls to a fraction, even though they may not be used to calculate k_v and D_E individually.

It has been emphasized that analyses of reaction kinetics based on concentrations in the ambient fluid can be quite misleading. Furthermore, the temperature T_s of the outer pellet surface is usually different from that (T_0) of the following fluid. The temperature difference $T_s - T_0$ can be estimated by the use of existing correlations of heat coefficients, just as $C_s - C_0$ is estimated from correlations of data on k_c. Thus *Figure 3* provides a basis for the estimation of $T_s - T_0$ in packed beds, and other correlations are available for many geometries and flow patterns.

Temperatures within the interior of porous catalyst particles may be greater or less than the temperature T_s at the surface, depending on whether the reaction is exothermic or endothermic. Under steady-state conditions, if the reactants diffuse into the particle across the same surface as the heat must be dissipated, then the maximum internal temperature $T_{max.}$ is given by:

$$T_{max.} = T_s + \frac{(-\Delta H) D_E C_s}{\lambda} \tag{20}$$

where ΔH is the enthalpy of the reaction, and λ is the thermal conductivity of the porous catalyst. This maximum occurs when the values of D_E and

k_V are such that reactant is consumed before it diffuses to the interior, where C is then zero.

In the case of exothermic reactions the effectiveness factor η_p, as defined by equation (18), may be greater than unity if k_V is taken to be the rate constant at T_S, where the reactant concentration is C_S. This occurs when the increase in rate caused by increased temperature towards the centre of the pellet more than compensates for the drop in concentration.

Several cases of diffusion and reaction in pores have been analysed to determine the manner in which the heat of reaction affects the effectiveness factor of the pellet[22-24]. Wiesz and Hicks[24] represent their calculated results for first order reaction in spheres in the form of graphs relating η_p to three dimensionless groups:

$$\eta_p = \mathrm{f}\left(\phi, \frac{E}{RT_S}, \frac{C_S(-\Delta H)D_E}{\lambda T_S}\right) \qquad (21)$$

where E is the activation energy and R is the gas constant. These analyses, compared with that for isothermal pellets, show that the apparent activation energy, based on C_S and T_S, can be greatly different from the true value E.

The selectivity of a porous catalyst may be very different from that for a smooth surface of the same material. In the case of a sequential irreversible reaction, for example, the internal pores are exposed to the first products for an extended time and the production of the second products may be greater than desired in relation to the amount of the first products. Though the theory of selectivity in such cases has been discussed by Wheeler[16] and others, there have been very few experimental studies to confirm the predicted variation of selectivity with pellet size, pore structure, and reaction path. It is obviously a subject of great practical importance in industry.

Only recently has the theory of diffusion and reaction beeen extended to incorporate Langmuir–Hinshelwood instead of power law kinetics[25-27]. Assuming the rate expression to be:

$$\left(-\frac{1}{V_c}\frac{\mathrm{d}n}{\mathrm{d}t}\right)_A = \frac{kK_Ap_A}{1 + K_Ap_A + \sum_i k_ip_i} \quad (i \neq A) \qquad (22)$$

Roberts and Satterfield[27] present a graph of η_p *vs.* $L(k'_vRT/D_A)^{1/2}$ with curves for various values of Kp_{AS}. The derivation was for a flat porous plate of thickness $2L$; p_A is the partial pressure of reactant A disappearing at the rate given by equation (22), p_{AS} is the value of p_A at the plate surface, and K is given by:

$$K = \frac{K_A - D_A\sum_i(K_iB_i/D_i)}{1 + \sum_i K_i\left[P_{iS} + (p_{AS}B_iD_A/D_i)\right]} \quad (i \neq A) \qquad (23)$$

Here D_A and D_i are the effective diffusion coefficients for A and the species i, and the B_i are the corresponding stoichiometric coefficients (taken as positive unity for reactant A, negative for the other reactants, and positive for products). K is zero for a simple first order reaction, negative for strong product adsorption, and positive for strong reactant adsorption. The results show η_p to be very much less for large negative than for large positive values of Kp_{AS}; pore diffusion becomes important with much smaller particle sizes if the products are adsorbed more strongly than the reactants.

Roberts and Satterfield have extended their analysis to the case of a second order reaction for which the rate expression is:

$$-\frac{1}{V_c}\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_A = \frac{kp_Ap_B}{(1+\sum_i K_ip_i)^2} \qquad (24)$$

Their study shows that in this case it is possible for η_p to be greater than unity and, in some cases, to be triple-valued, even though the system is isothermal.

Both theoretical and experimental studies of reaction in porous catalysts have been largely confined to gas systems, though the basic concepts apply also to liquids. An interesting study of a liquid system is reported by O'Connell[28], who employed the hydrogen form of an ion exchange resin (Dowex 50W × 8) in the inversion of sucrose at 50°, 60°, and 70°C, using four sizes of resin beads (0·004, 0·027, 0·055 and 0·077 cm diameter).

O'Connell's data are plotted in *Figure* 6 as η_p *vs*, ϕ, with a solid line shown to represent equation (14). Values of k_V/D_E of 90,000, 149,000 and 372,000 were used in calculating ϕ at 50°, 60°, and 70°C respectively. Separate measurements of D_E by transient adsorption of sucrose into the sodium form of the resin enabled k_V to be calculated; these values of k_V agreed well with k_V calculated from the results with the finest resin, for which η_p was assumed to be essentially unity. D_E was found to be $26{\cdot}9 \times 10^{-8}$ cm^2/sec at 50°C, and the activation energy for diffusion was 5·5 kcal/g mole; the activation energy for the overall process varied from 25 kcal for the very small beads to 18 kcal for the 0·077 cm beads. The theoretical relation is seen to provide an excellent basis for the correlation of data on such systems.

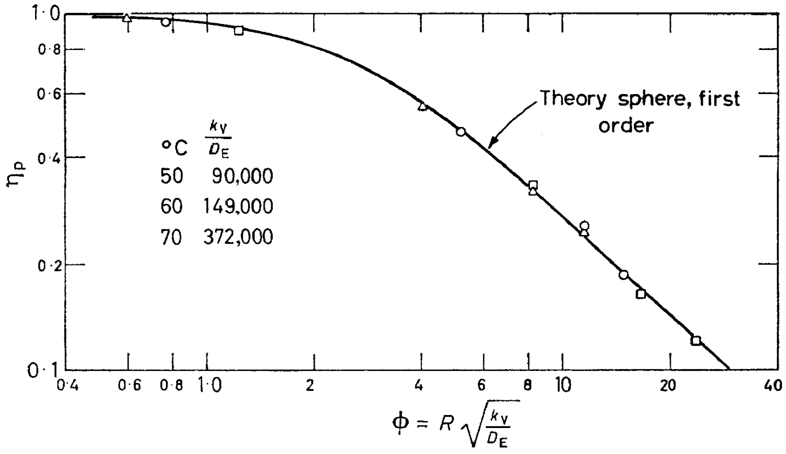

Figure 6. Sucrose inversion in ion exchange resin beads

CONCLUSION

Published analyses of experimental data on heterogeneous catalysis are frequently misleading because of failure to allow for diffusion from fluid to solid, and within porous solids. Existing correlations of mass transfer data provide means of estimating the surface concentrations for many geometries and flow systems. Though these are incomplete and frequently imprecise, they can often be employed to show that the diffusional resistances are either negligible or dominant. Where it is possible, investigations of heterogeneous catalysis in flow systems should be carried out with "uniformly accessible" surfaces under conditions for which reliable mass and heat transfer correlations are available.

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