Mass Transfer Effects in Surface Catalysis

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In studying the kinetics of a chemical reaction that is surface-catalyzed, it is essential to evaluate the relative contributions of mass transfer and true surface reaction. Such a distinction is necessary both for practical-reactor design and for theoretical work.

From the practical viewpoint, a decision as to whether a particular design is in the diffusion controlled or surface-rate controlled region leads to different predictions on the effects of major variables. A diffusion-controlled reaction rate would be greatly affected by changes in the degree of agitation (flow rate is the index of agitation in a fixed bed), but would show relative independence of temperature or pressure. True chemical-rate control would show the reverse: independence of agitation, but sharp variation with temperature (depending on the activation energy), and possibly pressure.

For more mechanistic analyses of surface kinetics, it is common procedure to compare rate data with composition and temperature relations predicted from several likely mechanisms. It is evident that such comparisons can be meaningful only when applied to true surface rates. Current treatments of this problem attempt to assess the importance of mass transfer by either an independent computation based on published correlations, or a judicious qualitative interpretation of the experimental-rate measurements. These approaches will be referred to as *method no. 1* and *method no. 2* in the discussion which follows.

The independent computation method (no. 1) is based upon the mass transfer studies of Hougen and Watson (*10*), Yang and Hougen (*24*), and many other workers (*3, 6, 23*). The mass transfer correlations used are generally expressed in terms of dimensionless groups:

$$k = \alpha (N_{Sc})^a (N_{Re})^b \qquad (1)$$

The greatest number of these correlations are formulated for the very important packed-bed geometry; however, information is also available for other physical arrangements. Several typical literature reports are summarized in Table 1. It is of interest to note that the correlating exponent b does not show great variability in spite of radical changes in geometry and in the grouped variables that form the Reynolds number.

Method no. 1 yields a value of the concentration gradient which is based upon mass transfer experiments done in the absence of reaction, and depends on the physical properties of the bulk phase and the catalyst dimensions. Temperature gradients between the catalyst and the bulk fluid are ignored, although it has been shown that this gradient may be significant (*18*). A specific application may require considerable extrapolation of physical data or reactor geometry. It was pointed out by Hoelscher (*8*) that these calculations seldom yield values of concentration gradient of significant size; however, examples of larger gradients can be found in the literature (*16, 25*).

The other method of dealing with mass transfer (method no. 2) depends upon experimental data and is based on the expectation that all systems become surface-rate controlled (reaction or adsorption) at sufficiently high agitation rates. If there is no porous diffusion in the catalyst, it is reasoned that increased turbulence must eventually become adequate to supply reactant at the rate at which it is consumed at the surface. In the usual application of this method (for a packed-bed reactor), true surface rates are found by extrapolating measured rates to the limit of infinite flow rate. In practice, this is often done by extrapolating a reciprocal scale to zero, although Perkins and Rase (*15*) and Butt, Bliss, and Walker (*2*) have achieved the same end by external recirculation of product.

If, on the other hand, reaction rate is constant as agitation is varied, the concentration in the bulk phase is assumed to be the same as that at the catalyst surface, and it is reported that no mass transfer resistance exists. Kayser and Hoelscher (*13*) have pointed out that if flow rate is to be the independent variable, such a study can only be accurate if the variation is made at constant residence time. Otherwise, the effect of agitation upon reaction rate is complicated by the changes in reaction rate due to residence time differences. This effect is aggravated under conditions which approach equilibrium.

The experimental method (no. 2), when properly applied, deals with the mass transfer question without recourse to the physical constants of the reacting system, but a serious limitation is the fact that no quantitative estimate of the effect is possible. This paper describes in a quantitative way the maximum concentration gradient which can be expected with a given relationship between reaction rate and agitation.

The analysis which follows is based upon the assumption that diffusion within the catalyst is not significant, and that there are no appreciable temperature or concentration gradients perpendicular to the flow direction. The results should therefore be applicable to plug-flow tubular reactors or to stirred reactors in which the homogeneous mass transfer resistance is not significant.

Under steady state conditions the observed reaction rate of any species is equal to the rate of mass transfer of that component:

$$r = k\,(P - P_i) \qquad (2)$$

A mass transfer parameter w will be used to represent a generalized agitation variable; it could represent flow rate in a packed bed, or stirrer speed in the case of a stirred reactor. Differentiation of Equation (2) with respect to w gives

$$\frac{dr}{dw} = -k\frac{dP_i}{dw} + (P - P_i)\frac{dk}{dw} \qquad (3)$$

$$\Delta P = \frac{\dfrac{dr}{dw} + k\dfrac{dP_i}{dw}}{\dfrac{dk}{dw}} \qquad (4)$$

The usual qualitative argument of method no. 2 is based on experimental evidence indicating that $(dr)/(dw)$ is approximately equal to zero. It is reasoned that $(dP_i)/(dw)$ is zero, since otherwise a change in overall reaction rate would be observed. Then, from Equation (4), $\Delta P = 0$, and the system is classified as reaction controlled. To replace this test with a quantitative

TABLE 1. SUMMARY OF MASS TRANSFER CORRELATIONS IN THE FORM*: $k = \beta(N_{Sc})^a(w)^b$

Geometry	Agitation variable	System type	Exponent b	Reference
Stirred vessel	Stirrer speed	Solid-liquid	0.710	*11*
Rotating cylinder	Cylinder rotation	Solid-liquid	0.70†	*5*
Slurry suspension	Stirrer speed	Solid-liquid	0.833	*1*
Flow past a single sphere	Flow rate	Solid-liquid	0.5	*7*
Packed bed	Flow rate, $Re > 350$	Gas-solid	0.59†	*7*
Packed bed	Flow rate, $Re < 350$	Gas-solid	0.49	*23*

* For the purposes of the text, it is advantageous to factor the variable w out of the Reynolds number. The other terms are considered constant and included in β.

† The correlations reported in these references were rearranged to fit the form of this table.

criterion it is necessary to note that the experimental observation cited above is more properly $(dr)/(dw) = \epsilon$ where ϵ can be related to the analytical accuracy or the actual mass transfer effect. The problem, therefore, is to formulate an expression for ΔP given some finite ϵ.

FIRST-ORDER REACTION

The simple first-order mechanism

$$r = k_1 P_i \tag{5}$$

in which the rate of surface reaction is proportional to the partial pressure of reactant above the catalyst has been commonly used in interpreting catalytic-reaction data. While the corresponding surface concentration is perhaps a more logical variable from a theoretical standpoint, the relative ease with which partial-pressure equations can be handled mathematically has led to their retention in kinetic models. The use of exponents on partial pressures has been advocated by Weller (*22*) as a preferred and sufficiently accurate simplification. To develop the needed quantitative criterion, Equation (5) is differentiated with respect to w:

$$\frac{dr}{dw} = k_1 \frac{dP_i}{dw} \tag{6}$$

Equation (6) is substituted in (4):

$$\Delta P = \frac{\dfrac{dr}{dw} + \dfrac{k}{k_1}\left(\dfrac{dr}{dw}\right)}{\dfrac{dk}{dw}} = \frac{\left(\dfrac{1}{k_1} + \dfrac{1}{k}\right)\dfrac{dr}{dw}\, w}{\dfrac{d \ln k}{d \ln w}} \tag{7}$$

The denominator of this expression can be evaluated from an appropriate mass transfer correlation of the type discussed above [Equation (1) and Table 1]. It is precisely b, the slope of the log-log plot arising from the use of correlating equations in the form of Equation (1). If w is considered to be mass velocity in a packed bed, $b = 0.5$ (*6, 23*). If w is stirrer speed in a stirred vessel, $b = 0.75$ (*11*).

The numerator of Equation (7) can be simplified by the use of the defining Equations (2) and (5):

$$\frac{1}{k_1} + \frac{1}{k} = \frac{P}{r} \tag{8}$$

Substituting (8) in (7) one obtains

$$\frac{\Delta P}{P} = \frac{d \ln r / d \ln w}{b} \tag{9}$$

This solution will immediately give the value of $(\Delta P/P)$ over a range of w if the variation of r vs w is found to be linear on log-log coordinates. In general, however, this is not to be expected. Equation (9) can be used to evaluate $(\Delta P)/(P)$ at specific w values if a curve of r vs w is available. Otherwise, if analytical inaccuracies or a lack of data preclude the determination of the complete relationship, Equation (9) may be replaced by an inequality. Since mass transfer effects become less significant as agitation increases, the measured rate must level off. Experimentally a curve such as that in Figure 1 will be obtained. The following inequality then exists

$$\frac{\Delta \ln r}{\Delta \ln w} \geq \frac{d \ln r}{d \ln w} \tag{10}$$

at the higher w value. Therefore

$$\frac{\Delta P}{P} \leq \frac{\Delta \ln r / \Delta \ln w}{b} \tag{11}$$

Thus if only a few points are available, or if random effects obscure the smooth curve, a straight line may be drawn through the points and (11) may be adopted. The numerator of the right-hand term of inequality (11) can be evaluated in either of two ways, depending on whether or not the rate is observed to change with w. If over a range w_1 to w_2, no change is observed in reaction rate, r, then Δr may be as great as, but no greater than, the probable error in analysis, expressed in *terms of equivalent rate. Then the* computation is based on the rearranged form

$$\frac{\Delta \ln r}{\Delta \ln w} = \frac{\ln r_2 - \ln r_1}{\ln w_2 - \ln w_1} = \frac{\ln\left(\dfrac{r_1 + \Delta r}{r_1}\right)}{\ln\left(\dfrac{w_2}{w_1}\right)} \tag{12}$$

in which Δr is equal to the expected error due to analysis. The value of $(\Delta P)/(P)$ computed in this way may be considered as an average within the w range.

If the rate exhibits a uniform variation with the agitation variable, the required ratio of differences can be found directly from a graph such as Figure 1. In this case an average gradient in the observed range can be computed from (11), or point values of $(\Delta P)/(P)$ may be calculated from Equation (9). Since the actual mass transfer resistance may be considerably smaller than that calculated from (11), it will usually be preferable to use Equation (9) when this is possible. If points A and B in Figure 1 are used in inequality (11), the computed effect will be much greater than if points B and C are used, even though the range of w covered is much smaller in the second case. As expected, it is found that diffusion resistance may be neglected in certain ranges of the agitation variable, while it must be taken into account in other ranges. A graph such as Figure 1 can serve as a basis for designing the experiment; data taken in Region A-C should not be used in deriving the rate mechanism. Experimental work will be more accurate if the smaller w range B-C is used.

The derivation given above applies only to first-order reactions in which the reaction rate is proportional to the partial pressure of reactant above the catalyst. Two additional cases are considered next. Since Equation (9) is

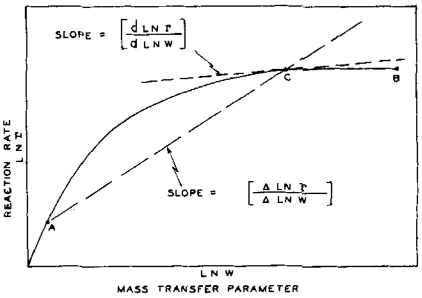

Fig. 1. Reaction rate vs. mass transfer parameter (on logarithmic scales).

preferred over inequality (11), further derivations will be in the form of equations, although it should be noted that the inequality form can be used when made necessary by the data.

SECOND-ORDER REACTION

Consider a reaction of the type

$$r = k_2 P_{Ai} P_{Bi} \tag{13}$$

With the single additional assumption that the effect of agitation is the same on the partial pressure of each of the reactants, that is, that

$$\frac{dP_{Bi}}{dw} = \frac{dP_{Ai}}{dw} \tag{14}$$

an analysis similar to that described above gives the following result:

$$\frac{\Delta P}{P} = \frac{d \ln r/d \ln w}{b} \left[1 - \left(\frac{P_{Ai}}{P_A} \right) \frac{P_{Ai}}{P_{Ai} + P_{Bi}} \right] \tag{15}$$

If component B is in great excess the reaction becomes first order in A, and (15) reduces to (9). Moreover, since partial pressures are necessarily positive, the bracketed term may be omitted if a simpler inequality is desired. Thus inequality (11) is applicable also to second-order reactions at any level of the component partial pressures.

SURFACE-CONCENTRATION KINETICS

The widely used Hougen and Watson (*10*) method for the evaluation of postulated rate mechanisms includes the assumption that the surface reaction rate is proportional to the surface concentration of reactant. If the effect of reverse reaction is neglected

$$r = k_s C \tag{16}$$

This step is considered to be in series with a reversible adsorption step

$$r = k_f C_v P - k_r C \tag{17}$$

The previous mechanisms in which partial pressures are used can be considered a special case of Equation (17) in which C_v is constant and adsorption is at equilibrium. This would be true for a catalyst with many vacant sites or for a reaction with a small surface concentration of reactant. Alternatively, the assumption of adsorption equilibrium can be avoided if a second-order approximation is made concerning the surface concentrations:

$$C_A + C_v = \text{constant} \tag{18}$$

A derivation similar to that previously presented yields the following result for this case:

$$\frac{\Delta P}{P} = \frac{(d \ln r/d \ln w)}{b} \left[\frac{1 + (C/C_v)}{1 + (d \ln r/d \ln w)(C/C_v)} \right] \tag{19}$$

As expected, Equation (19) reduces to (9) as C/C_v approaches 0.

The region of greatest interest is that in which the mass transfer resistance becomes very small, that is, where $[d \ln r/d \ln w] << 1$. With this restriction, Equation (19) reduces to

$$\frac{\Delta P}{P} = \frac{(d \ln r/d \ln w)}{b} \left[1 + \frac{C}{C_v} \right] \tag{20}$$

Since C and C_v are not ordinarily measured quantities, it is advantageous to replace their ratio by rearranging Equation (17)

$$\frac{C}{C_v} = KP_i - \frac{r}{C_v k_f} \tag{21}$$

where

$$K = \frac{k_f}{k_r} \tag{22}$$

the adsorption equilibrium constant for the component in question as used in the Hougen and Watson analysis. When the last term in Equation (21) is omitted, the result is the inequality

$$\frac{C}{C_v} \leqq KP_i \tag{23}$$

If $P_i < 1$, substitution of (23) into (20) gives

$$\frac{\Delta P}{P} \leqq \frac{(d \ln r/d \ln w)}{b} [1 + K] \tag{24}$$

In an investigation in which this analysis was used to test hypothetical mechanisms, a value of K would be found. It would therefore be available for substitution in Equation (24). However, computed values of K are commonly less than one; as a result it is often satisfactory to neglect K in computing $(\Delta P/P)$. In view of the possible range in K, this decision must be left to the application in a specific case. It should be pointed out, however, that in the process of replacing (C/C_v) by K, a sequence of inequalities was needed. The use of K may therefore give values of $(\Delta P/P)$ many times larger than the ratio actually existing. The adsorption equilibrium constants have been neglected in the computations given in this article.

DISCUSSION

The literature on catalytic reactions affords a ready source of data for testing the relationships derived here. Results from five representative articles are shown in Table 2. In each case the $(\Delta P/P)$ value claimed by the authors of the reference is compared with the result computed from either Equation (9) or inequality (11), as noted. Whenever Equation (9) was used, the derivative on the right-hand side was computed at both extremes of the available flow-rate range. The two values are denoted in Table 2 as *maximum* and *minimum*. The table also indicates whether mass transfer correlations (method no. 1) or experimental data (method no. 2) were used in the reference to estimate the concentration gradient, and notes whether the solution to inequality (11) was based upon experimental-reaction-rate vs. flow-rate data or upon analytical accuracy.

The comparisons indicate that inequality (11) is an extremely conserv-

TABLE 2. REPRESENTATIVE $\left(\frac{\Delta P}{P}\right)$ VALUES

			From references		From methods derived in this study				
Reaction	Catalyst	Ref.	$\frac{\Delta P}{P}$, %*	Method used (see text)	$\frac{\Delta P}{P}$, %*	Relation used	Comment†	Justification for the relation used	Source of data used
Sec-butyl alcohol dehydrogenation	Brass	*16*	4	Method no. 1	158	(9)	Maximum	Point values available	r vs. w reported
					71	(11)	Average		
					11	(9)	Minimum		
SO_2 oxidation	Platinum	*14*	11	Method no. 1	106	(9)	Maximum	Point values available	r vs. w reported
					42	(11)	Average		
					13	(9)	Minimum		
NO decomposition	Alumina	*19*	0	Method no. 2	3	(11)	Average	No data reported for r vs. w	Analytical accuracy reported
Phosgene formation	Activated carbon	*17*	0	Method no. 2	30	(11)	Average	Relatively few points reported	r vs. w reported
Ethanol dehydration	Alumina	*2*	0	Method no. 2	1	(11)	Average	No data reported for r vs. w	Analytical accuracy reported
Ethanol dehydration	Cation exchange resin	*12*	0	Method no. 2	40	(11)	Average	Relatively few points reported	r vs. w reported

* These figures are averages over the entire temperature range studied.

† Maximum gradients are found from Equation (9) evaluated at the lowest w studied.
Minimum gradients are found from Equation (9) evaluated at the highest w studied.
Average gradients are found from inequality (11) with the lowest and highest w's.

ative criterion, if the mass transfer computations are used as a standard (references *16, 14*). This is not surprising in view of the repeated inequalities which were used in its derivation. Equation (9), a more rigorous computation, appears to agree much more closely with the mass transfer correlation result if the figures at the maximum flow rate are compared. However, in both cases this method offers considerable advantage over the crude yes-or-no qualitative judgment. In references *19* and *2*, for example, the mass transfer conclusions are based upon the no-rate-change observation. The quantitative estimates of 3% and 1% were made by considering the range in reaction rate that could escape detection with the analytical system used.

In reference *17* there is a scatter of points over a narrow range of mass velocity More exact or more extensive data might have resulted in a lower computed value of $(\Delta P/P)$ since a smooth curve might have made possible the use of Equation (9). The mass transfer effect may in fact be negligible, but the data presented are not sufficient to draw this conclusion. The computation shows that $(\Delta P/P)$ may be as great as 30%. There is a good reason to vary the agitation parameter over a fairly wide range before a conclusion is reached regarding the importance of mass transfer.

A complete analysis of the complex matters of accuracy and precision in kinetics measurements can be found in the literature (*18*), and is beyond the scope of this paper. However, the error referred to in the preceding paragraph, that error which results from the use of too small a range of the agitation variable, may be treated by a simple rearrangement of the equations derived above. Equation (9) may be rearranged to yield a quantitative value for the range of agitation which should be studied:

$$\left(\frac{w_2}{w_1}\right) \geq \left(\frac{r_2}{r_1}\right)^{\left(\frac{1}{b\,(\Delta P/P)}\right)} \qquad (25)$$

As an illustration of this consider a packed-bed reactor ($b = 0.5$) for which it is desired that no $(\Delta P/P)$ larger than 0.1 can escape detection. Then

$$\left(\frac{w_2}{w_1}\right) \geq \left(\frac{r_2}{r_1}\right)^{20} \qquad (26)$$

If now the measurement of r is only reproducible to within 5%, whether because of analytic accuracy, random fluctuation, or some other cause, the required flow-rate range is

$$\frac{w_2}{w_1} \geq (1.05)^{20} = 2.65 \qquad (27)$$

The use of this range will insure that random effects do not totally obscure a real agitation-dependent change in reaction rate.

Reference *12* can be used to elaborate this point. In this investigation reproducibility was 5 to 10% (as computed from the data), and a mass-velocity range of 19 to 60% was used in studying the mass transfer effect at constant contact time. The authors apparently concluded that the observed range in measured reaction rate was due to experimental error. The computation above indicates that a range of 265% would have been needed in order to distinguish a mass transfer effect at this level of accuracy. Thus the mass transfer question remains unanswered.

CONCLUSIONS

The results of this study indicate that it is possible to make reasonably quantitative estimates of mass transfer effects from experimental kinetics data. A yes-or-no decision based on the apparent flatness of a reaction-rate curve may in fact be an unwarranted conclusion: an approximately constant reaction rate is not enough to insure a negligible value of $(\Delta P/P)$. The equations derived here set a quantitative value on this ratio and should be used in conjunction with experimental data in evaluating mass transfer effects. If the data over a large range are to be used in deriving the rate mechanism, the safest method of evaluating $(\Delta P/P)$ is to use Equation (9) at the lowest w value at which data were taken. If this is not possible, inequality (11) should be applied between the lowest and highest w values.

NOTATION

C = concentration on catalyst surface
C_v = concentration of vacant sites on catalyst surface
K = adsorption equilibrium constant = k_f/k_r
P = partial pressure of component in bulk phase
P_i = partial pressure of component at catalyst-fluid interface
N_{Re} = Reynolds number
N_{Sc} = Schmidt number
a = Schmidt number correlating exponent
b = mass transfer parameter correlating exponent
k = mass transfer coefficient
k_f = forward adsorption rate constant
k_r = reverse adsorption (desorption) rate constant
k_s = surface concentration reaction rate constant
k_1 = first-order reaction rate constant
k_2 = second-order reaction rate constant
r = observed over-all reaction rate
w = mass transfer parameter
ΔP = $P - P_i$
α = constant
β = constant
ϵ = an error of measurement = $(dr)/(dw)$

Subscripts

A = component A in reaction mixture
B = component B in reaction mixture

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LITERATURE CITED

1. Barker, J. J., and R. E. Treybal, *A.I.Ch.E. Journal*, **6**, 289 (1960).
2. Butt, J. B., Harding Bliss, and C. A. Walker, *ibid.*, **8**, 42 (1962).
3. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, **26**, 1138 (1935).
4. Dodd, R. H., and K. M. Watson, *Trans. Am. Inst. Chem. Engrs.*, **42**, 263 (1946).
5. Eisenberg, Morris, C. W. Tobias, and C. R. Wilke, *Chem. Eng. Progr. Symposium Ser. No. 16*, **51**, 1 (1955).
6. Gamson, G. W., George Thodos, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **39**, 1 (1943).
7. Garner, F. H., and R. D. Suckling, *A.I.Ch.E. Journal*, **4**, 114 (1958).
8. Hoelscher, H. E., *ibid.*, **3**, 144 (1957).
9. *Ibid.*, **4**, 300 (1958).
10. Hougen, O. A., and K. M. Watson, "Chemical Process Principles," Part 3, Wiley, New York (1947).
11. Johnson, A. I., and Chen-Jung Huang, *A.I.Ch.E. Journal*, **2**, 412 (1956).
12. Kabel, R. L., and L. N. Johnson, *ibid.*, **8**, 621 (1962).
13. Kayser, R. F., and H. E. Hoelscher, *Chem. Eng. Progr. Symposium Ser. No. 10*, **50**, 109 (1954).
14. Olson, R. W., R. W. Schuler, and J. M. Smith, *Chem. Eng. Progr.*, **46**, 614 (1950).
15. Perkins, T. K., and H. F. Rase, *A.I.Ch.E. Journal*, **4**, 351 (1958).
16. Perona, J. J., and George Thodos, *ibid.*, **3**, 230 (1957).
17. Potter, Charles, and Seymour Baron, *Chem. Eng. Progr.*, **47**, 473 (1951).
18. Pozzi, A. L., and H. F. Rase, *Ind. Eng. Chem.*, **53**, 813 (1961).
19. Sakaida, R. R., R. G. Rinker, Y. L. Yang, and W. H. Corcoran, *A.I.Ch.E. Journal*, **7**, 658 (1961).
20. Tschernitz, J. L., Sidney Bornstein, R. B. Beckmann, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*. **42**, 883 (1946).
21. Weger, Eric, and H. E. Hoelscher, *A.I.Ch.E. Journal*, **3**, 153 (1957).
22. Weller, Sol, *ibid.*, **2**, 59 (1956).
23. Wilke, C. R., and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **41**, 445 (1945).
24. Yang, K. H., and O. A. Hougen, *Chem. Eng. Progr.*, **46**, 146 (1950).
25. Yoshida, Fumitake, P. Ramaswami, and O. A. Hougen, *A.I.Ch.E. Journal*, **8**, 5 (1962).

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