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Testing the Relative Importance of Temperature and Concentration Gradients in Catalyst Pellets

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The intrapellet concentration and temperature gradients within a catalyst pellet cause the reaction rate to vary with position. To predict the average rates, simultaneous solution of the differential equations for the temperature and concentrations is required. The temperature and the concentration dependence of the rate expressions are generally nonlinear. Also, for many systems more than one chemical reaction has to be considered. For such systems, it is difficult to predict the observed rates by the solution of the energy and species conservation equations. The mathematical theory of diffusion and reaction in porous catalysts is discussed in detail by Aris (1975). Treatment of nonisothermal conditions within a pellet is also reviewed by Petersen (1965a), Smith (1970), Froment and Bischoff (1979), and Carberry (1979).

When the activation energy of the rate constants is not small, the impact of thermal gradients on the activity and selectivity of catalysts is much more important than the concentration gradients. For an exothermic reaction, the increase of the rate due to temperature rise within the pellet can more than offset the decrease in rate due to drop in reactant concentration. From the practical point of view it is quite important to know the relative importance of diffusion and heat transfer on the observed rates and the conditions under which the effects of temperature and concentration gradients can be neglected.

Anderson (1963) derived a criterion to test the isothermal behavior of a catalyst pellet. The Anderson criterion

$$R_{(i)_a} \, |-\Delta H_r| \, \frac{r_o^2}{T_s \lambda_e} < \frac{3}{4} \frac{T_s R_g}{E_a} \, , \qquad (1)$$

assumes that the rate of reaction depends on temperature in the Arrhenius fashion and does not consider the effect of temperature rise on the concentration gradients and diffusion limitations. Weisz and Hicks (1962) also considered the nonisothermal behavior of the catalyst pellet, and a set of computations were reported for the prediction of effectiveness factors under nonisothermal conditions. Weisz and Prater (1954) proposed a criterion to test the importance of diffusional limitations on the observed rates for isothermal pellets. This criterion is later generalized by Petersen (1965), Hutchings and Carberry (1966), Schneider and Mitschka (1966), Bischof (1967), Hudgins (1968), and Narshimhan and Guha (1972). The criterion developed by Hudgins is also applicable for reactions having other than power-type rate expressions.

$$R_{(i)_a} \frac{r_o^2}{C_{d,s} D_j} < \frac{1}{C_{j,s}} \frac{R_{(i)_s}}{\left(\dfrac{\partial R_{(i)}}{\partial C_j}\right)_s} \qquad (2)$$

Doğu and Doğu (1980, 1982) generalized the Hudgins criterion to bidisperse porous catalysts and to multiple reaction systems. In this work, a general criterion is developed to test the relative importance of diffusion and heat transfer limitations on the observed rates of reactions catalyzed by porous solids. The criterion is applicable to reactions conforming to any rate law. It can be used even if there are more than one temperature-dependent parameters in the rate expression, and it is derived for the general case of a multiple reaction system.

For a multiple reaction system with n-independent reactions and m species, the intrinsic rate of reaction i can be given by a Taylor expansion about the surface temperature and concentrations. The terms higher than the first are neglected considering small deviations of these variables from the surface values.

$$R_{(i)} = R_{(i)_s} + \sum_{j=1}^{m} \left(\frac{\partial R_{(i)}}{\partial C_j}\right)_s (C_j - C_{js}) + \left(\frac{\partial R_{(i)}}{\partial (1/T)}\right)_s \left(\frac{1}{T} - \frac{1}{T_s}\right) \qquad (3)$$

For such systems temperature and concentration profiles can be approximated as

$$\frac{1}{T} - \frac{1}{T_s} = \delta \left(1 - \frac{r^2}{r_o^2}\right) \qquad (4)$$

and

$$C_j - C_{j,s} = -\beta_j \left(1 - \frac{r^2}{r_o^2}\right) \qquad (5)$$

The effectiveness factor,

$$\eta = \frac{R_{(i)_a}}{R_{(i)_s}} = 3 \int_0^1 \frac{R_{(i)}}{R_{(i)_s}} \rho^2 d\rho \qquad (6)$$

is then obtained by substituting Eqs. 3, 4 and 5 into Eq. 6 and carrying out the integration

$$\eta = 1 - \frac{2}{5R_{(i)_s}} \sum_{j=1}^{m} \beta_j \left(\frac{\partial R_{(i)}}{\partial C_j}\right)_s + \frac{2}{5R_{(i)_s}} \delta \left(\frac{\partial R_{(i)}}{\partial \left(\dfrac{1}{T}\right)}\right)_s \qquad (7)$$

TABLE 1. KINETIC DATA REPORTED BY MAYMO AND SMITH (1966) AND THE CALCULATED VALUES OF α FOR $2H_2 + O_2 \rightarrow 2H_2O$

Run No.	T_s(°C)	$P_{O_{2,s}}$(kPa)	$R_a \left(\frac{\text{mol}}{\text{cm}^2\cdot\text{s}}\right)$	γ	β	$\frac{\gamma\beta}{n}$	α
11.2	100.8	5.34	1.42×10^{-6}	7.03	0.116	1.014	0.048
11.3	99.5	0.92	0.27×10^{-6}	7.06	0.025	0.219	2.96
E-1	117.6	10.84	4.0×10^{-6}	6.75	0.339	2.846	9.31

By equating the observed rate of formation of species j and the rate of heat generation to the diffusion and heat conduction rates at the surface, respectively as,

$$-D_j \left(\frac{\partial C_j}{\partial r}\right)_s = \frac{r_o}{3} \sum_{i=1}^{n} R_{(i)_a} \nu_{ij} \tag{8}$$

and

$$\lambda_e \left(\frac{\partial T}{\partial r}\right)_s = \frac{r_o}{3} \sum_{i=1}^{n} R_{(i)_a} \Delta H_{(i)} \tag{9}$$

and using the concentration and temperature profile expressions given in Eqs. 4 and 5, the parameters β_j and γ are evaluated.

$$\beta_j = -\frac{r_o^2}{6D_j} \sum_{i=1}^{n} R_{(i)_a} \nu_{ij} \tag{10}$$

$$\delta = \frac{r_o^2}{6\lambda_e T_s^2} \sum_{i=1}^{n} R_{(i)_a} \Delta H_i \tag{11}$$

For exothermic reactions it is possible to have η values greater or smaller than one. Using the expressions given in Eqs. 10 and 11 in Eq. 7 and by setting up $1.05 > \eta > 0.95$, following criterion is obtained for small deviations of observed rates from the rates evaluated at surface conditions.

$$\alpha_i = \left| -r_o^2 \left\{ \sum_{j=1}^{m} \frac{\left(\frac{\partial R_{(i)}}{\partial C_j}\right)_s}{R_{(i)_s} D_j} \sum_{i=1}^{n} R_{(i)_a} \nu_{ij} + \frac{\left(\frac{\partial R_{(i)}}{\partial (1/T)}\right)_s}{R_{(i)_s} \lambda_e T_s^2} \sum_{i=1}^{n} R_{(i)_a} \Delta H_{(i)} \right\} \right| < \frac{3}{4} \tag{12}$$

In this criterion, the first term gives information about the diffusion limitations and the second term about the heat effects. For endothermic reactions both of these terms have the same sign, and both of these limitations result in the decrease of observed rates compared to rates evaluated at the surface conditions. On the other hand, these terms have opposite signs for exothermic reactions. For some systems the absolute values of these terms may be about the same and consequently the criterion may be satisified indicating η is close to one. For such a system the decrease in rate due to diffusion limitations is compensated by the increase in rate due to the increase of temperature within the pellet. The order of magnitudes of the two terms in Eq. 12 give information about the relative importance of diffusion and heat transfer limitations. This is illustrated by the application of the criterion to the catalytic oxidation of hydrogen.

$$2H_2 + O_2 \rightarrow 2H_2O \qquad \Delta H_{298\,K} = -483{,}790 \text{ J/gmol} \tag{13}$$

The rate expression for this reaction is given by Maymo and Smith (1966) as

$$R_{H_2O} = 0.655\, P_{O_2}^{0.804} \exp\left(-\frac{21{,}888}{R_g T}\right) \tag{14}$$

They used platinum-alumina catalyst pellets of 1.86 cm in diameter and density of 0.57 g/cm^3. The effective diffusivity of oxygen and the effective thermal conductivity for this catalyst are reported as 0.166 cm^2/s and 2.55×10^{-3} J/cm·s·°C, respectively.

For a single reaction with a simple power law rate expression and Arrhenius fashion temperature dependence of the rate constant, the criterion derived in Eq. 12 reduces to

$$\alpha = \left| \frac{r_o^2 R_a n}{D_A C_{A,s}} \left\{ 1 - \frac{\gamma\beta}{n} \right\} \right| < \frac{3}{4} \tag{15}$$

where

$$\beta = \frac{-\Delta H D_A C_{A,s}}{\lambda_e T_s} \tag{16}$$

$$\gamma = \frac{E_a}{R_g T_s} \tag{17}$$

and n is the order of reaction. For $\gamma\beta/n < 1$ heat effects are expected to be less than the diffusion limitations. On the other hand, for $\gamma\beta/n > 1$ effect of temperature rise within the pellet on the rate of reaction is expected to be more than the decreasing effect of diffusion limitations. Consequently, effectiveness factor values of greater than 1 are observed. Using the data reported by Maymo and Smith (1966), the dimensionless parameter α is calculated and the results are reported in Table 1.

As it is seen in Table 1, the value of $\gamma\beta/n$ is less than one, and consequently the magnitute of the parenthesis in the criterion (Eq. 15) is positive for Run No. 11.3. This indicates that the effect of temperature rise within the pellet on the observed rate is less than the effect of diffusion limitations. On the other hand, the value of α is larger than $3/4$ for this run indicating that there are considerable concentration gradients within the pellet. Such concentration gradients cause a decrease in the observed rate of reaction. In fact, the value of the effectiveness factor calculated from Maymo and Smith's results is 0.73. The temperature rise within the pellet for this run is reported by Maymo and Smith as 7.7°C which is quite small compared to the other runs.

The value of $\gamma\beta/n$ is very close to one and the value of α is much less than $3/4$ ($\alpha = 4.8 \times 10^{-2}$) for Run No. 11.2. These results show that, although diffusion limitations are not negligible for this run ($r_o^2 R_a n / D_A C_{A,s} > 3/4$), increase of the rate due to increase in temperature (reported as 46.7°C) is sufficient to offset the decrease due to drop in reactant concentration. Consequently, no significant deviation of η from one is expected.

For Run No. E.1, the value of $\gamma\beta/n$ is much greater than one, and consequently the magnitute of the term in parenthesis in Eq. 15 is negative. This shows that the temperature effects are much more significant than diffusion limitations for this pellet. The value of α is 9.31. There are significant diffusion limitations but the increase of rate due to temperature rise in the pellet is expected to be much more than the decrease due to drop in oxygen concentration. In fact, the value of the effectiveness factor is predicted as 1.42 and the temperature rise in the pellet is measured as 102.5°C by Maymo and Smith.

All these results show that the criterion derived here can be successfully used to test the relative importance of diffusion and heat transfer limitations on the observed rates of catalytic reactions. The criterion does not have any limitations as far as the number of reactions, number of species, form of rate expressions, number and form of temperature-dependent parameters in the rate expression are concerned.

NOTATION

C_j = concentration

$C_{j,s}$ = concentration of species j at the external surface of the catalyst
D_j = effective diffusivity of species j
E_a = activation energy
m = number of species in the system
n = number of independent reactions
$R_{(i)}$ = intrinsic rate of reaction i, based on catalyst volume
$R_{(i)_a}$ = apparent rate of reaction i
$R_{(i)_s}$ = rate of reaction i evaluated at the external surface concentration and temperature of the catalyst
R_g = universal gas constant
r = radial coordinate for the catalyst particle
r_o = radius of the catalyst particle
T = temperature
T_s = temperature at the external surface of the catalyst

Greek Letters

α = defined by Eq. 15
α_i = defined by Eq. 12
β = defined by Eq. 16
β_j = defined by Eq. 10
δ = defined by Eq. 11
γ = defined by Eq. 17
ρ = dimensionless radial coordinate, r/r_o
λ_e = effective thermal conductivity
η = effectiveness factor
ν_{ij} = stoichiometric coefficient of jth species in the ith reaction (+ for products, − for reactants)
$\Delta H_{(i)}$ = heat of reaction of ith reaction

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Diffusion Coefficients Near the Spinodal Curve

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The study of diffusion coefficients in supersaturated solutions is of fundamental importance in further understanding the mechanism of diffusion and for the rational design of crystallization processes. Sorell and Myerson (1982) measured the diffusivity of urea in supersaturated aqueous solution employing Gouy interferometry. Results of this study show a very rapid decline in the diffusion coefficient with increasing concentration in the supersaturated region. This behavior is similar to behavior noted in liquid-liquid systems near the consolute point. Claersson and Sundelof (1957) and Haase and Siry (1969) reported that the binary diffusion coefficient drops rapidly to zero in the region of the critical solution temperature or consolute point. An explanation of this phenomenon can be made on thermodynamic grounds by employing the thermodynamic criterion for a critical point:

$$\frac{\partial^2 g_1}{\partial x_1^2} = 0 \frac{\partial \mu_1}{\partial x_1} \qquad (1)$$

$$\frac{\partial^3 g_1}{\partial x_1^3} = 0 = \frac{\partial^2 \mu_1}{\partial x_1^2} \qquad (2)$$

Equations normally used to calculate concentration-dependent diffusion coefficients such as the Gordon equation (1957) or modification of the Stokes Einstein relation (Turner 1975a,b) consist of the product of an infinite dilution diffusivity and a thermodynamic correction term:

$$D = D^0 \left(1 + \frac{\partial ln \gamma_1}{\partial ln x_1}\right) \frac{\mu_1}{\mu_{12}} \text{ (Gordon)} \qquad (3)$$

$$D = D^0 \left(\frac{\partial ln a_1}{\partial ln x_1}\right) \text{ (Stokes-Einstein modified)} \qquad (4)$$

The thermodynamic correction terms in Eqs. 3 and 4 are

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