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Falsification of Activation Energies by Pore Diffusion in Parallel Reaction Networks

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The effect of pore diffusion on the behavior of a slow, irreversible reaction that takes place in parallel with a fast, reversible reaction has been analyzed for the case where the reactions are first order in a common reactant. When the resistance to pore diffusion is significant, the apparent activation energy of the slow reaction generally is not equal to one-half of the true activation energy. Rather, the difference between the true and apparent activation energies of the slow reaction depends on the equilibrium constant and on the enthalpy change of the fast, reversible reaction. If the equilibrium constant is small compared to one, or if the enthalpy change of the fast, reversible reaction is close to zero, a significant resistance to pore diffusion will not cause a falsification of the activation energy of the slow reaction. The true activation energy will be observed in these situations. However, if the equilibrium constant of the reversible reaction is large compared to one and if the enthalpy change of this reaction is large, the observed activation energy for the slow, irreversible reaction in the presence of a significant pore diffusion resistance can range from negative for an endothermic reaction to much greater than the true activation energy for an exothermic reaction. The analysis is applied to recent data on the skeletal isomerization and parallel cracking of *n*-hexane.

INTRODUCTION

It is well known that pore diffusion, also referred to as internal and intraparticle diffusion, can affect the behavior of heterogeneous catalytic reactions taking place in porous solid catalysts. In 1951, Wheeler (1) pointed out that the reaction order that is observed experimentally may be different from the true reaction order when pore diffusion is a significant resistance, i.e., when there are severe concentration gradients of reactants and products within the catalyst particle. In the same paper, Wheeler also showed that the observed activation energy of a reaction will generally be about one-half of the true activation energy when the resistance to pore diffusion is significant. These effects commonly are referred to as falsification of the reaction order and falsification of the activation energy, respectively. Weisz and Prater (2) and Gupta and Douglas (3) later extended Wheeler's analysis and developed a relationship between the apparent and true activation energies that is valid over the complete range of pore diffusion resistance.

The selectivity of a network of reactions also can be altered by the presence of a pore diffusion resistance. Wheeler (1, 4) analyzed the effect of internal diffusion on the selectivity of two simple reaction networks

$$A \rightarrow B \rightarrow C \quad \text{(series or consecutive reactions)}$$

$$\begin{matrix} A \rightarrow R \\ B \rightarrow S \end{matrix} \quad \text{(independent parallel reactions)}$$

and derived expressions for the apparent selectivity of these two networks in the presence of pore diffusion. Wheeler also discussed qualitatively the effect of pore diffusion on parallel reactions involving a common reactant, i.e.,

$$\begin{matrix} A \rightarrow R \\ \searrow S \end{matrix} \qquad \text{(A)}$$

Roberts (5) later provided a quantitative analysis of this network.

Extensive theoretical literature has developed over the last four decades on interactions between chemical reaction and pore diffusion. At various times, Satterfield and Sherwood (6), Satterfield (7), and Froment and Bischoff (8) have provided useful summaries of the state of the art. Much of the existing analysis has concerned single, irreversible reactions. Reversible reactions, especially ones that are part of a network of reactions, have probably received less attention than warranted by their frequency of occurrence and by their practical significance.

Recently, Otten *et al.* (9) studied the isomerization of *n*-hexane over platinum mordenite catalysts in the presence of hydrogen at atmospheric pressure and at temperatures that ranged from 513 to 573 K. They observed that the primary and kinetically rapid reac-

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tions, the skeletal isomerizations of *n*-hexane to 2- and 3-methyl pentane, were accompanied by a slower cracking of hexane to lighter paraffins. Under the conditions of their study, the skeletal isomerization is thermodynamically reversible, with an equilibrium constant on the order of unity. The cracking reactions are essentially irreversible. Although the actual chemistry is much more complex, the overall reaction network for this system may be represented as

$$\begin{array}{l} n\text{-C}_6\text{H}_{14} \rightleftharpoons i\text{-C}_6\text{H}_{14}\,(\text{fast}) \\ \quad\searrow \text{light paraffins (slow)} \end{array}$$

Otten *et al.* (9) found that the apparent (experimentally measured) activation energy for the fast reaction, the skeletal isomerization, was about one-half of the activation energy that had been reported by other investigators. However, the apparent activation energy of the parallel reaction, hexane cracking, was close to that reported in the literature. These results are summarized in Table 1.

Otten *et al.* (9) attributed the decreased activation energy for the skeletal isomerization reaction to a strong pore diffusion influence. However, this hypothesis contradicts the existing body of theory in one important respect. Specifically, for two parallel, irreversible reactions with a common reactant, i.e., reactions A above, it can be shown (14) that the apparent activation energy of *both* reactions should be reduced significantly by the presence of a strong pore diffusion resistance. Thus, the high activation energy of the cracking reactions that was measured by Otten *et al.* (9) appears to contradict their hypothesis that a strong pore diffusion resistance was responsible for the lower apparent activation energy of the isomerization reactions.

The objective of this paper is to provide a theoretical basis to support the interpretation provided by Otten *et al.* (9). Obviously, this analysis must rest on the reversibility of one of the parallel reactions, e.g., the isomerization reactions in the referenced study.

TABLE 1

Measured Activation Energies for *n*-Hexane Reactions

Reaction	Activation energy (Kcal/mol) Otten *et al.* (9)	Activation energy (Kcal/mol) Literature[a]
Isomerization	14–16	29–36 (10–12)
Cracking	35–40	35 (13)

Note. Reference numbers are given in parentheses.

METHODS AND RESULTS

Analytical Approach

Consider the reactions

$$\begin{array}{l} \text{A} \rightleftharpoons \text{R} \\ \;\searrow \text{S} \end{array}$$

taking place in a porous catalyst. All three reactions are assumed to be first order in their respective reactants. A rigorous, general analysis of simultaneous diffusion and reaction inside a porous catalyst particle for this system is beyond the scope of this paper and will be presented elsewhere (14). For the present purpose, a simplifying assumption will be made that avoids much of the mathematics and also provides physical insight into the phenomena that give rise to the observed results (9). This assumption is that the net rate of the reversible reaction, i.e., the difference between the rates of the forward and reverse reactions A → R and R → A, is large compared to the rate of the slow reaction A → S throughout most of the interior of the catalyst particle. When this assumption is valid, the concentration profile of reactant A inside the particle is determined almost totally by the kinetics of the reversible reaction and by the rate of pore diffusion. The kinetics of the slow, irreversible reaction have little effect on this concentration profile. However, the overall rate of the slow reaction will be determined by the profile of reactant A since the reaction A → S is first order in A.

This simplifying assumption can be valid over a broad range of pore diffusion resistances, e.g., catalyst particle sizes. However, it will not apply when the resistance to pore diffusion is extremely high, such that A cannot diffuse into the particle as rapidly as it is consumed by the slow reaction, A → S. This limitation is described in more detail below.

For mathematical simplicity, the catalyst particle is assumed to be an infinite slab of thickness $2L$, as shown in Fig. 1 and is assumed to be isothermal. The differential equation that describes the simultaneous diffusion and reaction of species A within the particle is

$$D_\text{A}\frac{d^2C_\text{A}}{dx^2} = k_1C_\text{A} - \frac{k_1}{K}C_\text{R} + k_3C_\text{A},$$

where C_i is the concentration of species i, D_i is the diffusion coefficient of species i, k_1 is the forward rate constant for the reaction A → R, k_3 is the rate constant for the reaction A → S, K is the equilibrium constant for the reaction A → R, and x is the distance from the centerline of the catalyst particle. Since the reaction A → S is assumed to be very slow compared to the net rate of the reversible reaction, the last term on the right-hand side

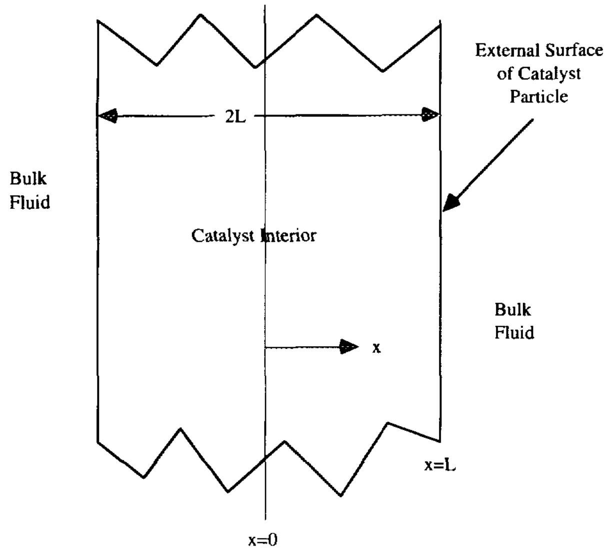

FIG. 1. Geometry of catalyst particle.

of this equation may be neglected to give

$$D_A \frac{d^2C_A}{dx^2} = k_1 C_A - \frac{k_1}{K} C_R. \qquad [1]$$

As implied in the preceeding paragraph, it is not valid to neglect k_3C_A relative to $[k_1C_A - (k_1/K)C_R]$ once the resistance to pore diffusion becomes so high that the maximum rate of diffusion into the interior of the catalyst particle is comparable to the intrinsic rate of the slow reaction. In that case, C_R/K can exceed C_A, such that the A that is converted to S is provided to some extent by the reaction R → A (14).

Equation [1] is subject to the boundary conditions

$$\frac{dC_A}{dx} = 0, \quad x = 0 \qquad [1a]$$

$$C_A = C_{A,s}, \quad x = L. \qquad [1b]$$

The subscript s denotes a condition at the surface of the catalyst particle, i.e., at $x = L$.

The differential equation that describes the simultaneous diffusion and reaction of species R within the particle is

$$D_R \frac{d^2C_R}{dx^2} = -k_1 C_A + \frac{k_1}{K} C_R, \qquad [2]$$

which is subject to the boundary conditions

$$\frac{dC_R}{dx} = 0, \quad x = 0 \qquad [2a]$$

$$C_R = C_{R,s}, \quad x = L. \qquad [2b]$$

The system of Eqs. [1], [1a], [1b], [2], [2a], and [2b] has been solved by Smith and Amundson (15). The solution is

$$C_A(x) = \frac{D_R T_c}{(KD_R + D_A)} + \left[C_{A,s} - \frac{T_c D_R}{(KD_R + D_A)}\right] \frac{\operatorname{Cosh} \alpha x}{\operatorname{Cosh} \phi}, \qquad [3]$$

where

$$T_c \equiv C_{R,s} + \left(\frac{D_A}{D_R}\right) C_{A,s} \qquad [4]$$

$$\phi \equiv L \sqrt{k_1\left(\frac{1}{D_A} + \frac{1}{KD_R}\right)} \qquad [5]$$

$$\alpha \equiv \sqrt{k_1\left(\frac{1}{D_A} + \frac{1}{KD_R}\right)}. \qquad [6]$$

The parameter ϕ defines the Thiele modulus for this system of reactions. Equation [3] gives the value of C_A at every position, x, inside the catalyst particle.

The rate of disappearance of reactant A per unit of geometric surface area of catalyst is

$$R_A = D_A \left[\frac{dC_A}{dx}\right]_{x=L}. \qquad [7]$$

Differentiating Eq. [3] with respect to x, evaluating the resulting expression at $x = L$, and substituting into Eq. [7] gives

$$R_A = \frac{\operatorname{Tanh} \phi}{\phi} \left\{ Lk_1 \left[C_{A,s} - \frac{C_{R,s}}{K} \right] \right\}. \qquad [8]$$

Equation [8] has the expected form, i.e., R_A = (effectiveness factor) × (rate that would be observed if there were no concentration gradients inside the catalyst particle). The effectiveness factor, η, is given by Tanh ϕ/ϕ. The rate that would exist if there were no gradients is given by the expression within the outermost brackets on the right-hand side of Eq. [8].

When the resistance to pore diffusion is high, ϕ is large (e.g., > about 3) so that

$$\frac{\operatorname{Tanh} \phi}{\phi} \cong \frac{1}{\phi}.$$

If, as assumed, the reaction A → S is very slow, the rate of disappearance of A is essentially equal to the rate of formation of R, i.e., $R_A \cong R_R$, so that Eq. [8] becomes

$$R'_R \cong R'_A = \frac{1}{\phi} \left\{ Lk_1 \left[C_{A,s} - \frac{C_{R,s}}{K} \right] \right\}.$$

In the above, the prime designates a region of "moderate" pore diffusion resistance. This equation will be a reasonable approximation for $\phi >$ about 3 and for $\phi_3 <$ about 0.5, where ϕ_3 is the Thiele modulus for the slow reaction, i.e.,

$$\phi_3 = L\sqrt{k_3/D_A}.$$

The latter criterion results from the requirement, outlined earlier, that the rate of pore diffusion be rapid compared to the rate of the slow reaction. The region $\phi >$ about 3 and $\phi_3 <$ about 0.5 constitutes a reasonable working definition of the regime of "moderate" pore diffusion resistance.

Substituting Eq. [5] for ϕ gives

$$R'_R \cong R'_A = \frac{\sqrt{k_1}}{\sqrt{\left(\frac{1}{D_A} + \frac{1}{KD_R}\right)}}\left[C_{A,s} - \frac{C_{R,s}}{K}\right]. \quad [9]$$

The rate of formation of species S is given by

$$R_S = \int_0^L k_3 C_A \, dx = k_3 \int_0^L C_A \, dx.$$

Substituting the expression for C_A, Eq. [3], into the above and integrating gives

$$R_S = \left(\frac{k_3 D_R T_c L}{KD_R + D_A}\right)\left(1 - \frac{\text{Tanh}\,\phi}{\phi}\right) + k_3 L C_{A,s}\frac{\text{Tanh}\,\phi}{\phi}. \quad [10]$$

Since $k_3 \ll k_1$ and since $\eta = \text{Tanh}\,\phi/\phi \ll 1$ in the region of moderate pore diffusion resistance, Eq. [10] reduces to

$$R'_S = \left(\frac{k_3 D_R T_c L}{KD_R + D_A}\right) \quad [11]$$

The physical significance of this equation is easier to understand if it is assumed that $D_A = D_R$. This simplies Eq. [11] to

$$R'_S \cong k_3 L\left(\frac{C_{R,s} + C_{A,s}}{K + 1}\right). \quad [12]$$

The quantity $(C_{R,s} + C_{A,s})/(K + 1)$ is the equilibrium concentration of A, $C_{A,eq}$. Equation [12] shows that, for large ϕ and small ϕ_3, the rate of formation of S is simply the product of the rate constant, k_3, the half-width of the catalyst particle, L, and the equilibrium concentration of A. This equation implies that, when the resistance to pore diffusion is sufficiently large, C_A reaches its equilibrium concentration a very short distance into the pellet, as shown in Fig. 2. The driving force for the reaction A → S then is a constant concentration of A ($C_{A,eq}$) throughout the whole catalyst particle.

Temperature Dependence

The analysis of the temperature dependence of R_A and R_S can be simplified by assuming that $D_A \cong D_R$. This assumption is already embodied in Eq. [12]. To simplify further, it will be assumed that $(C_{R,s}/K) \ll C_{A,s}$. This inequality will be met when the composition of the fluid at the catalyst surface is far from the equilibrium composition. In the studies of Otten *et al.* (9), there were no branched hexanes in the feed to the reactor and the fractional conversion of *n*-hexane was very low so that $C_{R,s} \cong 0$. The assumptions that $(C_{R,s}/K) \ll C_{A,s}$ and $D_A \cong D_R$ reduces Eq. [9] to

$$R'_R = \sqrt{k_1 D_A}\sqrt{\frac{K}{(K + 1)}}C_{A,s} \quad [13]$$

and the former assumption reduces Eq. [12] to

$$R'_S \cong k_3 L\left(\frac{C_{A,s}}{K + 1}\right). \quad [14]$$

The parameters k_1, k_3, and D_A may be written in Arrhenius form, i.e.,

$$k_1 = A_1 e^{-E_1/RT} \quad [15]$$

$$k_3 = A_3 e^{-E_3/RT} \quad [16]$$

$$D_A = A_D e^{-E_D/RT}, \quad [17]$$

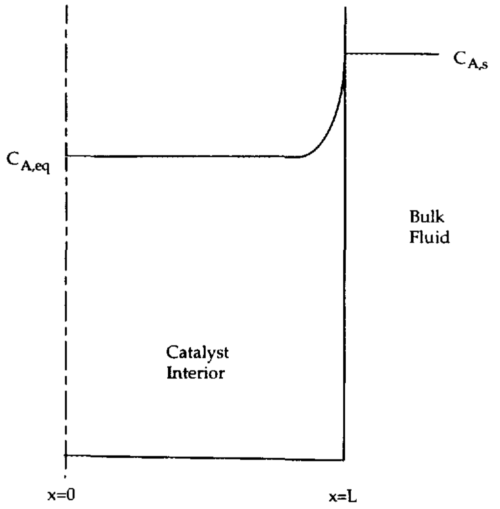

FIG. 2. Concentration profile of reactant A inside the catalyst particle in the regime of moderate pore diffusion.

and the equilibrium constant can also be written in exponential form as

$$K = A_E e^{-\Delta H_R/RT}, \qquad [18]$$

where ΔH_R is the enthalpy change for the reaction A → R.

Now consider two cases:

Case A ($K \ll 1$). Neglecting K in the term $(K + 1)$ and substituting Eqs. [15], [17], and [18] into Eq. [13] gives

$$R'_R = \sqrt{k_1 D K}C_{A,s} = [A_1 A_D A_E e^{-(E_1+E_D+\Delta H_R)/RT}]^{1/2} C_{A,s}$$

so that the apparent activation energy for the fast reaction (A → R) in the regime of moderate pore diffusion is

$$E_{app}(\text{fast}) = (E_1 + E_D + \Delta H_R)/2. \qquad [19]$$

In general, the "activation energy" for diffusion, E_D, is of the order of a few Kcal/mol and may be neglected relative to E_1, the true or intrinsic activation energy of the reaction A → R. However, Gupta and Douglas (16) have provided an example where this assumption is not valid, i.e., where E_D cannot be neglected relative to E_1.

The heat of reaction for A → R, ΔH_R, can vary over a wide range. If this reaction is exothermic, $\Delta H_R < 0$ and its effect will be to reduce the apparent activation energy to less than $E_1/2$. This reduction can be very significant with a reaction that is highly exothermic, such that the magnitude of ΔH_R is comparable to that of E_1. For some reversible reactions, e.g., methanol synthesis, the magnitude of ΔH_R can exceed that of E_1, making the apparent activation energy of the reversible reaction zero or even negative.

When the reaction A → R is endothermic, $\Delta H_R > 0$, which tends to increase the apparent activation energy according to Eq. [19]. In this case, the expected diminution of the apparent activation energy by pore diffusion is moderated, or perhaps even eliminated. On balance, the activation energy of the fast reversible reaction exhibits relatively "normal" falsification behavior, although the situation is more complex than with an irreversible reaction because of the added effect of ΔH_R.

For the reaction A → S, when $K \ll 1$, Eq. [14] becomes

$$R'_S = k_3 L C_{A,s}$$

and the apparent activation energy is simply

$$E_{app}(\text{slow}) = E_3. \qquad [20]$$

For this case, there is no falsification of the activation energy of the slow, irreversible reaction.

Case B ($K \gg 1$). This case must be approached with some caution. If K is too large, it may no longer be valid to neglect the third term on the right-hand side of Eq. [10]. With this disclaimer, Eq. [13] becomes

$$R'_R = \sqrt{k_1 D_A}C_{A,s} = [A_1 A_D e^{-(E_1+E_D)/RT}]^{1/2} C_{A,s}$$

and the apparent activation energy of the fast reaction is

$$E_{app}(\text{fast}) = (E_1 + E_D)/2. \qquad [21]$$

This result shows "normal" falsification behavior; i.e., the apparent activation energy is reduced by a factor of about 2.

For $K \gg 1$, Eq. [14] reduces to

$$R'_S \cong \frac{k_3}{K} L C_{A,s} = \frac{A_3}{A_E} e^{-(E_3-\Delta H_R)/RT} L C_{A,s}$$

and the apparent activation energy for the reaction A → S in the regime of moderate pore diffusion is

$$E_{app}(\text{slow}) = E_3 - \Delta H_R. \qquad [22]$$

The value of the apparent activation energy for the slow reaction depends on the value of the enthalpy change of the fast, reversible reaction. The apparent activation energy will deviate significantly from the true activation energy if the magnitude of ΔH_R is large compared to that of E_3. If the fast, reversible reaction is exothermic, the apparent activation energy of the slow reaction will be higher than the true activation energy, by a factor of 2 or more for highly exothermic reactions. The exact opposite is true for endothermic reactions, where a large positive value of ΔH_R can make the apparent activation energy negative. If $\Delta H_R \cong 0$, there will be essentially no falsification of the activation energy of the slow reaction.

DISCUSSION

In the regime of moderate pore diffusion, the apparent (experimentally observed) activation energy of the slow reaction shows some very unusual behavior, which apparently has not been recognized previously. None of the cases examined in this paper leads to a "conventional" relationship, where the apparent activation energy of the slow reaction is approximately one-half of the true activation energy when pore diffusion is significant. Instead, the apparent activation energy of the slow reaction varies from a negative value to a value that exceeds the true activation energy, depending on the thermodynamic properties of the fast, reversible reaction.

The strong influence of these thermodynamic parameters can be understood by referring to Fig. 2. In the regime of a moderate resistance to pore diffusion, the concentration gradient of reactant A inside the catalyst particle is very steep, and the concentration of A falls to its equilibrium value, $C_{A,eq}$, a very short distance from the external surface of the catalyst particle. Therefore, essentially the whole interior of the particle is at this equilibrium concentration. The rate of formation of S is the product of the rate constant, k_3, the half-width of the particle, L, and $C_{A,eq}$. The temperature dependence of this reaction rate arises from a combination of the temperature dependencies of k_3 and $C_{A,eq}$. The equilibrium concentration depends on the equilibrium constant, K, which, in turn depends exponentially on $\Delta H_R/RT$. If the enthalpy of reaction is negative, i.e., the reaction is exothermic, $C_{A,eq}$ will increase towards a limit of $C_{A,s}$ as the temperature increases. Directionally, this increase reinforces the increase of the rate constant k_3 with temperature, causing the apparent activation energy of the slow reaction to exceed the true value.

Conversely, if the reversible reaction is endothermic, $C_{A,eq}$ decreases with increasing temperature, which offsets the effect of temperature on the rate constant k_3 to some extent. If the endothermic heat of reaction is sufficiently large, the decrease of $C_{A,eq}$ with temperature can be the dominant effect, leading to an apparent negative activation energy.

Finally, if the equilibrium constant K is very small compared to unity, an unlikely situation in actual practice, $C_{A,eq}$ will be essentially equal to $C_{A,s}$ and will not vary with temperature. Also, if $\Delta H_R \cong 0$, K and $C_{A,eq}$ will not vary with temperature. For these cases, the only effect of temperature on the rate of formation of product S will occur via the rate constant k_3, so that the true activation energy for the slow reaction will be experimentally observed for these two circumstances.

The *n*-hexane isomerization and cracking reaction system studied by Otten *et al.* (9) does not correspond exactly to either of the limiting cases treated above ($K \gg 1$ and $K \ll 1$). At their conditions, the equilibrium constant of the reversible hexane isomerization was about one. However, the enthalpy of reaction for the skeletal isomerization of *n*-hexane is only a few Kcal/mol, and is negligible compared to the values of E_1 given in Table 1. For $\Delta H_R \cong 0$, there is no falsification of the activation energy of the slow reaction for either limiting case, as shown by Eqs. [20] and [22]. Moreover, Eqs. [19] and [21] show that there should be a normal falsification of the activation energy of the hexane isomerization reaction; i.e., $E_{app} \cong E_1/2$ for both cases. Thus, the results and interpretation presented by Otten *et al.* (9) are consistent with the present analysis.

CONCLUSIONS

The effect of pore diffusion on the behavior of a slow, irreversible reaction that takes place in parallel with a fast, reversible reaction has been analyzed. The apparent activation energy of the reversible reaction exhibits relatively normal falsification behavior, complicated to some extent by the effect of the enthalpy change of the reaction. The apparent activation energy of the slow reaction generally is not equal to one-half of the true activation energy. Rather, in the regime of moderate pore diffusion resistance, the difference between the apparent and true activation energies of the slow, irreversible reaction depends primarily on the equilibrium constant and the enthalpy change for the fast, reversible reaction.

If the equilibrium constant is small compared to one, or if the change in enthalpy of the reversible reaction is close to zero, there will be no falsification of the activation energy of the slow reaction. The true activation energy of this reaction will be observed, even when the resistance to pore diffusion is significant. For the hexane isomerization reaction studied by Otten *et al.* (9), the enthalpy of reaction is of the order of a few Kcal/mol. Therefore, the observed activation energy of the parallel, slow cracking reaction should be close to the true activation energy. Thus, this analysis supports their interpretation of the experimental data.

If the equilibrium constant of the fast, reversible reaction is large compared to one and if the magnitude of the enthalpy change of this reaction is large, the observed activation energy of the slow, irreversible reaction can range from negative for an endothermic reaction to much greater than the true activation energy for an exothermic reaction.

APPENDIX: NOMENCLATURE

A_1, A_3	pre-exponential factors in Arrhenius relationships for k_1 and k_3 (s^{-1})
A_D	pre-exponential factor in Arrhenius relationship for D_A (m^2/s)
A_E	pre-exponential factor in expression for K (Eq. [18]) (dimensionless)
C_i	concentration of species i (mol/m^3)
D_i	diffusion coefficient of species i (m^2/s)
E_1, E_3, E_D	activation energies for k_1, k_3, and D_A, respectively (cal/mol)
k_1, k_3	rate constants for $A \rightarrow R$ and $A \rightarrow S$, respectively (s^{-1})
K	equilibrium constant for $A \leftrightarrow R$ (dimensionless)
L	half-thickness of catalyst particle (m)
R_i	rate of disappearance of species i per unit

	geometrical surface area of catalyst particle (mol/s, m^2)
R	gas constant (cal/mol, K)
T	temperature (K)
T_C	parameter defined by Eq. [4] (mol/m^3)
α	parameter defined by Eq. [6] (m^{-1})
η	effectiveness factor (dimensionless)
ϕ	Thiele modulus, defined by Eq. [5] (dimensionless)
ϕ_3	Thiele modulus for reaction A → S (dimensionless)
ΔH_R	enthalpy change for reaction A → R (cal/mol)

Subscripts

app	apparent
A	reactant A
eq	equilibrium
R	product R
s	catalyst surface, i.e., $x = L$
S	product S

Superscript

/	region of moderate pore diffusion resistance

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