Analyses of Nonisothermal Effectiveness Factors Using a Generalized Langmuir-Hinshelwood Rate Expression

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For a monomolecular, heterogeneous catalyzed reaction, $A \rightleftharpoons B$, analyses of nonisothermal effectiveness factors were made using a Langmuir-Hinshelwood rate expression based on the three mutually rate-determining steps of adsorption, surface reaction and desorption. The parameters in the rate expression were quantified in terms of temperature with internal thermodynamic consistency. The occurrence of maxima points in the effectiveness factor-modulus curves, as observed by several previous investigators using empirical rate expressions, appears to be a physically plausible phenomenon not strongly dependent on the form or degree of thermo-kinetic completeness of the rate expression used in the analyses. However, the same is not true of the appearance of multiple steady-state solutions. The study revealed that the multiplicity of steady-state solutions, as reported previously by several investigators, was absent in the more generalized treatment. This latter result did appear, however, to be influenced by the degree of thermo-kinetic completeness of the Langmuir-Hinshelwood rate expression used in the analyses.

NOMENCLATURE

A	reactant species
A'	defined in text, Eq. (18)
A·s	reactant A chemisorbed on site s
B	product species
B'	defined in text, Eq. (19)
B·s	product B chemisorbed on site s
C'	defined in text, Eq. (20)
C_A	variable concentration of the reactant (mole/cm³)
C_{AS}, C_{BS}	concentration of reactant and product at surface (mole/cm³)
C_0	$C_{AS} + C_{BS}$, total concentration (mole/cm³)
D'	defined in text, Eq. (21)
D_{eff}	effective diffusion coefficient (cm²/sec)
eu	entropy units (cal/mole °K)
E	defined in text, Eq. (8)
Δf	thermodynamic driving force
ΔH_a^0	heat of adsorption (cal/mole)

k_A, k_B	adsorption rate constants (mole/g atm sec)
k_S	surface reaction rate constant, mole/g sec
K_A, K_B	adsorption equilibrium constants (1/atm)
K_p	overall equilibrium constant, dimensionless
K_S	surface reaction equilibrium constant, dimensionless
K_{eff}	effective thermal conductivity (cal/cm °K sec)
$K_i \; (i = 1\text{–}6)$	defined in text, Eqs. (22) to (25)
K_ϕ	defined in text, Eq. (33)
l	variable distance from center of the pellet (cm)
L	radius of the pellet (cm)
N	defined in text, Eq. (9)
P_A, P_B	partial pressures (atm)
P_t	total pressure (atm)
r	overall reaction rate (mole/g sec)
r_A	adsorption rate for A (mole/g sec)

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r_B	desorption rate for B (mole/g sec)
r_S	surface reaction rate (mole/g sec)
R	gas law constant (atm cm³/ mole °K)
R'	overall resistance (g atm sec/ mole)
s	active site on the catalyst
ΔS_a^0	entropy of adsorption (eu)
S_g^0	absolute entropy of the gas phase (eu)
T	variable temperature (°K)
T_S	surface temperature (°K)
X	dimensionless variable distance from center, defined in text, Eq. (15)
Y	dimensionless variable concentration of the reactant, defined in text, Eq. (16)
Y_S	dimensionless surface concentration of the reactant
Z	dimensionless variable temperature in the pellet, defined in text, Eq. (17)
Z_S	dimensionless surface temperature

Greek Symbols

ρ_p	density of catalyst pellet (g/cm³)
θ_A, θ_B	dimensionless concentration of species A and B chemisorbed on site s
θ_v	dimensionless concentration of active vacant sites
β	thermicity factor, defined in text, Eq. (26)
η	effectiveness factor, defined in text, Eqs. (30) and (31)
ϕ	modulus, defined in text, Eq. (32)
γ	$E/R \cdot T_S$, dimensionless activation energy

Subscripts

a	adsorption
A, B	reactant, product
g	gas phase
s	at the surface
v	vacant active site

1. INTRODUCTION

The analyses of nonisothermal effectiveness factors for heterogeneous catalyzed reactions in spherical pellets have evolved over the past years utilizing incomplete or empirically based rate expressions in the mass and thermal energy transport models. The kinds of rate expressions which have been used in the analyses have been based, for the most part, on pseudo-homogeneous, integer, power-law kinetics (5, 7, 8, 11, 13, 18) or some limiting form of the Langmuir-Hinshelwood kinetics (9, 15, 17). Very often the use of integer, power-law kinetics leads to different and misleading interpretations (12). The fundamental physicochemical interpretations of effectiveness factor results have therefore been limited primarily by the built-in lack of detail in the rate model. It is realized that there remains a basic need to recompute the results of previous nonisothermal effectiveness factor studies using a complete rate expression. The complete rate expression features built-in thermodynamic constraints for internal consistency as was shown by Bradshaw and Davidson (4) to be warranted for Langmuir-Hinshelwood type kinetic systems.

One of the truly remarkable and unexpected results from the computation of nonisothermal effectiveness factors using incomplete rate expressions has been the appearance of multiple steady states in the region of effectiveness factors greater than unity. Weisz and Hicks (18) and several other researchers (5, 8, 13) have encountered multiple steady-state solutions while computing nonisothermal effectiveness factors using first-order kinetics and different particle geometries. The reproduction of the same results using a complete rate expression of the Langmuirian type has not been attempted, although Roberts and Satterfield (15), Kao and Satterfield (9), and Luss and Lee (10) have performed isothermal effectiveness factor studies using a limiting form of the Langmuirian rate expression.

The purpose of the present study was to attempt a detailed case study analysis of

the characteristics of nonisothermal effectiveness factors using a complete rate expression and thermodynamically consistent parameters. By complete rate expression is meant a rate model in which all steps are mutually rate-controlling as conceived by Bradshaw and Davidson (4) and Shah (16). Once the kinetic model is properly set theoretically with respect to a mechanism with all the parameters quantified in terms of temperature, with internal thermodynamic consistency, a real advantage is gained in attempting to obtain fundamental results. The analysis can cover a wide range of values of parameters without concern for violating certain thermodynamic limitations. When the parameters of the rate model are expressed as functions of temperature according to Arrhenius and van't Hoff laws, the condition of mutual rate-controlling steps shifts automatically in the direction of a particular rate-controlling step depending upon the relative magnitudes of the individual activation energies of the various reaction steps as the temperature changes throughout the pellet.

The contributions of this work are summarized in Table 1. Compared to the chief cognate works in the field, use of a generalized Langmuir-Hinshelwood rate model in combination with a nonisothermal analysis of the effectiveness factor marks the novel features of this work.
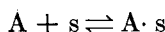
2. THE GENERALIZED RATE EXPRESSION AND THERMO-KINETIC PARAMETERS

Consider a general, reversible monomolecular reaction represented by:

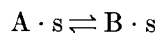$$A \rightleftharpoons B \qquad (1)$$

Based on the Langmuir-Hinshelwood, Hougen-Watson approach, the following sequence of elementary steps is postulated to occur.

(i) Adsorption of the reactant
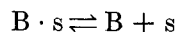
$$A + s \rightleftharpoons A \cdot s$$

(ii) Surface reaction of the adsorbed reactant

$$A \cdot s \rightleftharpoons B \cdot s$$

(iii) Desorption of the product

$$B \cdot s \rightleftharpoons B + s$$

The corresponding equations describing the individual one-step rate processes are:
Adsorption of the reactant

$$r_A = k_A \left[P_A \theta_v - \frac{\theta_A}{K_A} \right] \qquad (2)$$

Surface reaction of the adsorbed reactant

$$r_S = k_S \left[\theta_A - \frac{\theta_B}{K_S} \right] \qquad (3)$$

Desorption of the product

$$r_B = k_B \left[\frac{\theta_B}{K_B} - P_B \theta_v \right] \qquad (4)$$

An inventory balance on the active sites produces

$$\theta_A + \theta_B + \theta_v = 1 \qquad (5)$$

Bradshaw and Davidson (4) have demonstrated that, in the steady state, the rate of each step may be governed by a finite resistance and a nonzero driving force. Therefore, it is possible to view the rate of reaction for the general case as

$$r = \frac{\Delta f}{R'} = \frac{[P_A - (P_B/K_p)]}{R'} \qquad (6)$$

where Δf is the gas phase thermodynamic driving force and R' is the overall resistance.

The generalized rate expression, as we have defined it, is obtained by simultaneous solution of the nonlinear equations (2), (3), (4), and (5). Details of the derivation can be found elsewhere (16). The solution gives the generalized rate expression as

$$r = \frac{[P_A - (P_B/K_p)]}{E(1 + K_A P_A + K_B P_B) - N[P_A - (P_B/K_p)]} \qquad (7)$$

TABLE 1

SURVEY OF STUDIES ON NONISOTHERMAL EFFECTIVENESS FACTORS

	Weisz and Hicks (18)	Roberts and Satterfield (15)	Sneider and Mitschka (17)	Kao and Satterfield (9)	Cresswell (5)	Hlavacek and Kubicek (8)	Paterson and Cresswell (13)	This work
Kinetic model	First-order, irreversible $A \to B$	L-H,[a] one step controlling, irreversible $A \to B$	L-H, one step controlling, reversible $A \rightleftharpoons B$	L-H, one step controlling, reversible $A \rightleftharpoons B$	First-order, irreversible $A \to B$	First-order, irreversible $A \to B$	First-order, irreversible $A \to B$	L-H, all steps controlling, reversible $A \rightleftharpoons B$[b]
Transport model: lumped parameter, steady-state, deterministic diffusion model	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Isothermal	Yes	Yes	Yes	Yes	No	No	No	Yes
Nonisothermal	Yes	No	No	No	Yes	Yes	Yes	Yes[b]
External mass transfer	No	No	No	No	Yes	Yes	Yes	No
Single maximum in η–ϕ curves	Yes	No	No	No	Yes	Yes	Yes	Yes
Multiple steady states	Yes	No	No	No	Yes	Yes	Yes	No[b]

[a] Langmuir-Hinshelwood.
[b] Unique contributions of this work.

where

$$E = \frac{1}{K_A}\left[\frac{1}{k_S} + \frac{K_A}{k_A} + \frac{K_B}{k_B K_S}\right] \quad (8)$$

and

$$N = \left[\frac{K_A}{k_A} - \frac{K_B}{k_B}\right] \quad (9)$$

The use of first-order kinetics presumes the overall resistance to be a reciprocal Arrhenius function of temperature. In the present study the overall resistance R' is a highly nonlinear combination of reaction velocity and thermodynamic equilibrium constants which are, in turn, functions of temperature. R' also depends on partial pressures which are variables during the course of the reaction process.

Boudart, Mears and Vannice (2) have suggested a set of criteria which can be used to assess the physical significance of parameters for nonenzymic heterogeneous catalyzed reactions. The four rules which test entropy and enthalpy changes against feasible upper and lower limits apply to the thermodynamic equilibrium constants and are given by

$$0 < -\Delta S_a{}^0 < S_g{}^0 \quad (10)$$

$$-\Delta S_a{}^0 > 10 \text{ eu} \quad (11)$$

$$-\Delta S_a{}^0 < 12.2 - 0.0014 \, \Delta H_a{}^0 \quad (12)$$

The inequalities given by expressions (10) and (11) provide that: (i) entropy must decrease with adsorption, (ii) the decrease must not be larger than the initial entropy content, and (iii) the decrease should exceed 10 eu. A hypothetical set of physically plausible thermodynamic equilibrium constants K_A, K_B, and K_S is selected without violating any of these rules. They are presented in graphical form in Fig. 1.

Boudart (1) has further shown that from a practical viewpoint for such a system of elementary steps, there exists a temperature at which values of all the reaction velocity constants k_A, k_B, and k_S may be numerically identical. A reasonably realistic value of 500°K for this unique temperature, known as the isokinetic point, was chosen. Fixing the isokinetic point in the
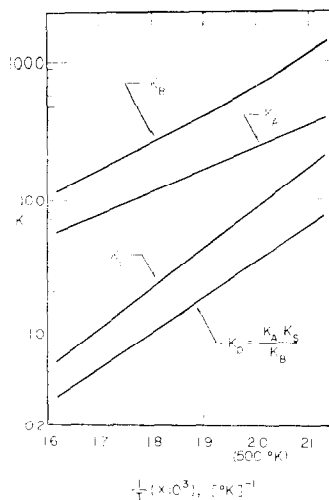

FIG. 1. Natural logarithm of equilibrium constants versus reciprocal temperature.

middle of the range of temperatures of industrial importance makes it possible to examine the practical situations in a more general way. Typical magnitudes are then assigned to the activation energies. The reaction velocity constants are presented in graphical form in Fig. 2.

One more physical criterion was applied to check the validity of the selected parameters. It states that the initial rate should be several orders of magnitude smaller than the collision rate of molecules as predicted by the kinetic theory of gases. Also, it was verified that the magnitudes of initial and finite rates fall in the range of observed values for typical monomolecular reactions of industrial importance.
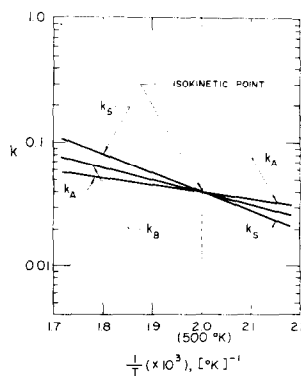

FIG. 2. Natural logarithm of reaction velocity constants versus reciprocal temperature.

3. The Transport Model

The interaction of effective mass diffusion, effective heat conduction, and reversible monomolecular reaction in a spherical catalyst pellet is represented mathematically by the following system of conservation equations written in dimensionless form.

$$\frac{d^2Y}{dX^2} + \frac{2}{X}\frac{dY}{dX} = \frac{A'Y + B'}{C'Y + D'} \qquad (13)$$

$$\frac{d^2Z}{dX^2} + \frac{2}{X}\frac{dZ}{dX} = \beta \cdot \frac{A'Y + B'}{C'Y + D'} \qquad (14)$$

where

$$X = \frac{l}{L} \qquad (15)$$

$$Y = \frac{C_A}{C_{AS} + C_{BS}} \qquad (16)$$

$$Z = \frac{T}{T_S} \qquad (17)$$

$$A' = \left[K_4 + \frac{K_6}{K_5}\right]Z \qquad (18)$$

$$B' = -\frac{K_6}{K_5} \cdot Z \qquad (19)$$

$$C' = \left[\left(\frac{1}{K_3} + \frac{K_6}{K_2} + \frac{K_6}{K_5 K_2}\right)K_4 \right.$$
$$\left. - \left(\frac{1}{K_3} + \frac{K_4}{K_1} + \frac{K_4}{K_3 K_1}\right)K_6\right]Z \qquad (20)$$

$$D' = \left[\frac{1}{K_3} + \frac{K_4}{K_1} + \frac{K_6}{K_5 K_2}\right]$$
$$+ \left[\frac{1}{K_3} + \frac{K_4}{K_1} + \frac{K_4}{K_5 K_1}\right]K_6 Z \qquad (21)$$

$$K_1 = k_A\left[\frac{\rho_p L^2 R T_S}{D_{eff}}\right] \qquad (22)$$

$$K_2 = k_B\left[\frac{\rho_p L^2 R T_S}{D_{eff}}\right] \qquad (23)$$

$$K_3 = k_S\left[\frac{\rho_p L^2 R T_S}{D_{eff}P_t}\right] \qquad (24)$$

$$K_4 = K_A P_t, \quad K_5 = K_S, \quad K_6 = K_B P_t \qquad (25)$$

$$\beta(\text{thermicity factor}) = \left[\frac{D_{eff}(-\Delta H)P_t}{K_{eff}R T_S^2}\right] \qquad (26)$$

With the assumption that the gas phase velocities are high, external film resistances to mass and thermal energy transport can be neglected without great loss in generality. The boundary conditions are therefore given by

$$X = 0; \frac{dY}{dX} = \frac{dZ}{dX} = 0 \qquad (27)$$

$$X = 1; Y = Y_S, Z = Z_S = 1 \qquad (28)$$

Following the technique of Prater (14), it is possible to obtain an algebraic expression relating concentration and temperature at any point in the pellet in terms of the surface conditions. The expression is

$$Z = \beta(Y - Y_S) + 1 \qquad (29)$$

The problem now reduces to obtaining the steady-state solution(s) of Eqs. (13) and (29) subject to the boundary conditions given by (27) and (28). This highly nonlinear, two-point boundary value problem is solved numerically using a fourth-order, Runge-Kutta technique. The increment in the independent variable X was sufficiently small so as to obtain a desired four-decimal-place accuracy. Equations (13) and (29) are integrated forward for different specified conditions with an assumed value of Y at the center of the pellet, which is varied from the equilibrium value to a value of Y at the surface (i.e., Y_S) in sufficiently small increments so that multiple steady-state solutions are not lost. An effectiveness factor is then calculated based on the following definition:

$$\eta = \frac{\text{Actual reaction rate}}{\text{Reaction rate at surface conditions}} \qquad (30)$$

Mathematically it reduces to the following dimensionless form:

$$\eta = \frac{3[dY/dX]_{X=1}}{\phi^2\left[\dfrac{Y + (B'/A')}{Y + (D'/C')}\right]} \qquad (31)$$

where

$$\phi = L\left(\frac{\rho_p K_\phi}{D_{eff}C_0}\right)^{1/2} = \left(\frac{A'}{C'}\right)^{1/2} \qquad (32)$$

and

predict the behavior of effectiveness factor-

$$K_\phi = \frac{[K_A + (K_B/K_S)]}{K_A\left[\dfrac{1}{k_{Si}} + \dfrac{K_B}{k_B} + \dfrac{K_B}{K_S k_B}\right] - K_B\left[\dfrac{1}{k_S} + \dfrac{K_A}{k_A} + \dfrac{K_A}{K_S k_A}\right]} \tag{33}$$

Modulus ϕ is varied in small increments so as to obtain reasonably smooth η–ϕ curves.

For the isothermal case only Eq. (13), a type of the Embden Equation (6), needs to be solved. This does not have a closed-form analytical solution. If, for some limiting cases, the constant C' is small compared to the constant D' in Eq. (13), the kinetics can be considered as pseudo-first-order and Eq. (13) yields to an analytical solution. For all possible combinations of the rate-controlling steps and the equilibrium constants, it was observed that the constant C' is comparable or even greater than the constant D' in magnitude.

4. RESULTS

The dependence of the effectiveness factor on the basic properties of the catalyst material, catalyst activity, and imposed surface conditions is displayed in graphical form in Figs. 3 through 5. These basic properties are represented by the modulus ϕ and the thermicity factor β which, together with imposed surface conditions, are varied over a large range of values of interest.

With the use of a highly nonlinear kinetic term in the model, it is difficult to

modulus curves. These curves, for specific magnitudes of parameters, could display one or more maxima, with or without the existence of multiple steady states. The fact that the curves in Figs. 3 to 5 show only a single maximum, as also observed by several other investigators using first-order kinetics, establishes it as a physically plausible result not strongly dependent on the form of the rate expression. As the magnitude of the modulus increases, the effectiveness factor rises to a value greater than unity and then drops down to a value near zero. Since the average internal temperature is greater than the surface temperature for nonisothermal conditions, values of effectiveness factors greater than unity are physically plausible.

The analysis uncovered a rather interesting result totally different from those of previous researchers. The multiplicity of steady-state solutions is absent from any of the cases. We are therefore led to conclude that, for a thermo-kinetically complete formulation of the Langmuir-Hinshelwood rate expression, it is shown that multiple steady-state effectiveness factor values are not obtained for a monomolecular reversible reaction. The discrepancy between this result and those of previous
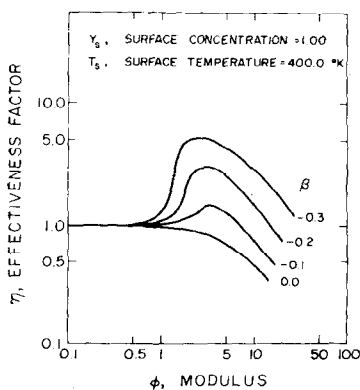
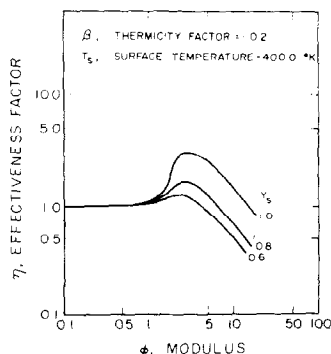FIG. 3. Effectiveness factors η at different thermicity factors β.

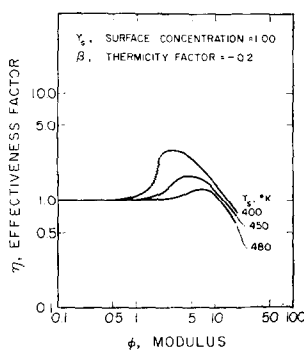FIG. 4. Effectiveness factors η at different surface concentrations Y_S.

FIG. 5. Effectiveness factors η at different surface temperatures T_S.

investigators can be attributed to a number of factors. The rate models previously employed have little physical basis for existence. The rate model presently employed, however, has an overall resistance term R' which varies in a fundamental way with temperature and extent of reaction. The pseudo-reciprocal exponential temperature relationships used in previous models do not adequately reflect the true variation in R' during the course of the reaction process. Another contributing factor in the explanation of this anomaly is the physical validity of the range of parameters used. For instance, a temperature rise of over 150°C within a pellet is physically unrealistic, as was used erroneously by several previous investigators (18).

Implicit in the use of the rate model are a number of restrictions which, if not observed, lead to violation of some physical law. One subtle point to notice is that the overall heat of reaction, by Hess's law, is the sum of the individual heat effects of each of the reaction steps. Therefore, neither sign nor magnitude of the overall heat of reaction can change without changing the individual-step heat effects. In addition, the thermicity factor β can have only one sign for a set of individual-step activation energies. Furthermore, a parameter γ involving the activation energy, as used by previous researchers, cannot be employed in a generalized study as there is no single activation energy which controls the rate of reaction.

5. CONCLUSIONS

The results of this study verify the occurrence of a single maximum in the η–ϕ curves and indicate the nonexistence of multiple steady states. A clear, one-to-one comparison of the results with those of previous researchers is rendered difficult by the nonappearance of like parameter groupings in the dimensionless terms. The use of complete rate expressions for studies of this kind tends to smooth out the interpretations and reduces uncertainties associated with unusual behavior.

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