The Apparent Chemical Kinetics of Surface Reactions in External Flow Systems: Diffusional Falsification of Activation Energy and Reaction Order

DANIEL E. ROSNER

AeroChem Research Laboratories, Incorporated, Princeton, New Jersey

If the temperature level or free stream reactant concentration is deliberately changed, the resulting change in the observed global reaction rate on a catalytic surface in a flow system will not necessarily reflect the true chemical kinetics at the fluid/solid interface. General expressions, reminiscent of those applicable to a static system, are derived for the relation between the diffusional falsification of activation energy and reaction order in terms of a logarithmic derivative of the isothermal diffusion correction (effectiveness factor). Approximate solutions are given for the case of the thin, nonturbulent diffusion layer which develops along an impermeable catalytic flat plate, for arbitrary values of the true reaction order and Prandtl number for diffusion (Schmidt number). Comparisons with exact solutions to the boundary-layer equations and alternate approximate methods are given for the special case of first-order surface reactions. Of the various quantities of interest in the diffusional theory of heterogeneous reactions in flow systems, it is shown that the accuracy of the Frank-Kamenetskii quasi-stationary method can become unacceptably poor for the calculation of these falsification parameters. The physico-chemical conditions under which these errors are likely to be largest are discussed. Applications are given to the study of the chemical kinetics of fast surface reactions.

While chemical kinetic studies of surface reactions are most often carried out under conditions for which diffusional transport of reactant is sufficiently rapid to play no role in the observed kinetics [as in a Schwab type of reactor (*1*)], this extreme is not always experimentally accessible. In the latter case any interpretable macroscopic kinetic experiment must be conducted with a geometry for which the magnitude of the diffusional (bottle neck) effect is accurately calculable. In static systems several such geometries exist (*2*). However when one turns to flow systems for studying the kinetics of faster interfacial reactions, the choice is far more limited. Even for those flow systems which have been discussed in the past, few treatments have been carried as far as providing numerical results which allow one to extract meaningful chemical kinetic parameters from experimental measurements of overall conversion. This paper will investigate a simple isothermal flow system for which this is possible and, in particular, study the influence of external reactant diffusion on the resulting reaction rate distribution, the integrated reaction rate, the apparent activation energy, and apparent reaction order. Emphasis will be placed on the general scaling (similitude) properties of this class of problems. In the course of the discussion the accuracy of two approximate computational methods will be investigated. The first of these is the well-known quasi-stationary method of Heymann (*3*) and Frank-Kamenetskii (*4*), which leads to the so-called *series-resistance* concept. The second method, developed in references 5 and 6, is a rational improvement of this procedure which nevertheless retains much of its simplicity. In the light of this work, and related results in the field of convective heat transfer, an attempt is made to extract some general conclusions as to the physical and chemical conditions under which the simple quasi-stationary assumption is likely to be adequate. Finally possible experimental applications of the solutions presented are outlined, from the point of view of macroscopic chemical kinetics.

PHYSICO-CHEMICAL HYDRODYNAMIC MODEL

When an incompressible viscous fluid flows past a solid body of characteristic dimension L, owing to the non-slip condition at the stationary fluid/solid interface, the surface generates vorticity which diffuses out into the surrounding fluid at a rate dependent upon the kinematic viscosity $\nu = \mu/\rho$ of the fluid.* If the rate of bodily convection is large compared with the rate at which vorticity can diffuse laterally, that is when the Reynold's number $N_{Re} = UL/\nu$ is large compared with unity, a thin vorticity layer envelops the body (*7*). Outside of this boundary layer viscosity plays a minor role in determining the flow field; within it convective and viscous terms in the equations of fluid motion are of comparable importance.

In a similar way, when a stream of fluid containing a reactant flows past an active catalyst with characteristic dimension L, the surface generates a region of reactant depletion which can be said to diffuse out into the surrounding fluid at a rate depending on the molecular diffusion constant appropriate to the reactant/foreign fluid system. When the characteristic rate of bodily convection is large compared with the rate of diffusion, that is when the diffusional Reynolds number UL/D is large compared with unity, a thin diffusion boundary layer envelops the catalytic solid. Outside of this layer diffusional transport plays a minor role in determining the steady state reactant concentration distribution; within it convective and diffusive transport terms in the conservation equation for the reactant are of comparable magnitude. This division of the concentration field into two more or less distinct regions enables the partial differential equations of convective diffusion to be simplified in the manner of Prandtl (*7*). The solution of these boundary-layer equations, subject to prescribed physico-chemical conditions at the outer edge of the layer and along the catalytic surface, will then provide the steady state concentration field in the immediate vicinity of the catalyst, from which the local and global (integrated) rates of diffusional transfer (and hence reaction rate) can be determined.

Now, while the rate of the surface reaction will everywhere be influenced both by the conditions of convective

---

[*] The Navier-Stokes equations of fluid motion may be regarded as vorticity transport equations (see reference 7, pp. 54-55). Thus for a two dimensional viscous flow the vorticity vector $\zeta \equiv$ curl $\mathbf{v}$, whose magnitude is everywhere equal to $(\partial v/\partial x) - (\partial u/\partial y)$, satisfies a linear diffusion equation of the form $d\zeta/dt = \nu\nabla^2\zeta$ in which the kinematic viscosity ν plays the role of the diffusion coefficient.

diffusion and the catalytic activity (or appetite so to speak) of the surface, at any point along the catalyst the conditions at the interface will determine the rate of reaction, in accordance with some phenomenological rate law. What the rate of reaction will be at some point downstream will likewise depend both upon the rate at which reactant can be supplied to the interface from the free stream by convective diffusion over the intervening distance, as well as the appetite of the surface. Thus while the magnitude of the local reaction rate is not known a priori, it is known that whatever its magnitude the reaction rate per unit area must be identically equal to the local rate at which the reactant can be supplied by reactant diffusion across streamlines. This statement provides the required physico-chemical boundary condition at the interface. Owing to the functional form of Fick's law of diffusion this condition will be seen to provide a relation between the normal gradient of reactant concentration and the absolute value of the reactant concentration at the boundary.

Historically the first application of Prandtl's boundary-layer theory was to the laminar flow along a very thin flat plate (*8*). The merit of this specific example is that it provides maximum simplicity and yet retains most of the fundamental features of two-dimensional boundary-layer flows. Moreover velocity, skin friction, and heat transfer measurements on isothermal plates in the laminar regime have provided striking confirmation of the theory. Because the nonturbulent flow over an impermeable flat plate is so well understood, this example provides a logical starting point for an investigation of the diffusion-surface reaction problem in steady viscous flows.*

In accordance with the discussion above the following mathematical model is adopted. An incompressible carrier fluid is assumed to move near the catalyst surface (see Figure 1) in accordance with the two-dimensional continuum equations of momentum and continuity. If the flow in this vorticity layer is laminar and the kinematic viscosity ν is constant, then these equations may be written (*7*)

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = u_e\frac{du_e}{dx} + \nu\frac{\partial^2 u}{\partial y^2} \qquad (1)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \qquad (2)$$

where u and v are, respectively, the x (tangential) and y (normal) components of the velocity field, and $u_e(x)$ is the asymptotic value of u for large distances y from the plate surface. For the case of a flat plate at zero incidence $u_e \equiv U$ is independent of the distance x along the stream from the leading edge, causing the first term of the right-hand side of Equation (1) to vanish.

In the carrier fluid (diluent) there is a reactant present in dilute amounts. The reactant concentration field established in the vicinity of the catalyst is assumed to satisfy the diffusion boundary-layer equation

$$u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} = D\frac{\partial^2 c}{\partial y^2} \qquad (3)$$

where c is the local nondimensional reactant concentration (mass fraction) and the Fick diffusivity D is taken to be constant. The conditions of no net mass transfer or slip at the fluid/solid interface then require that both $u(x,0)$ and $v(x,0)$ vanish identically. If no chemical reaction takes place in the fluid itself, the free stream (external) reactant concentration, written c_e, will be a constant. Finally a chemical kinetic boundary condition is prescribed on the behavior of the reactant concentration field at the surface and for this purpose it will be assumed that the intrinsic kinetics at the interface are well described by a power function of the local reactant concentration (*9*). Then the interfacial reactant conservation equation takes the form

$$D\rho\frac{\partial c}{\partial y}\bigg|_{y=0} = k\cdot(\rho c)^n\bigg|_{y=0} \qquad (4)$$

Here k represents the intrinsic interfacial phenomenological rate constant. For the present the rate constant k is assumed to be independent of position on the catalyst surface. This usually, but not necessarily, implies that the surface temperature is uniform. If one imagines the properties of the carrier fluid-reactant mixture, the flow velocity, and the interfacial kinetics to be prescribed, the problem posed here is to find the corresponding steady state distribution of reaction rate along the catalytic surface. When this is done, it is then possible to obtain the integrated reaction rate for a catalyst of prescribed length as well as the effect of diffusional transport on the apparent chemical kinetics. In practice of course one or more parameters prescribed here will not be known, but several of the computed parameters will be accessible to direct measurement. By suitably combining the analysis with experiment one can then extract the fundamental macroscopic kinetic parameters of interest. Methodologically this process would be no different from that of using the Hagen-Poiseuille pressure drop-volume flow law to experimentally determine the viscosity of fluids.

SIMILITUDE PROPERTIES

A number of fairly general conclusions can immediately be drawn concerning the effect of various physical parameters on the solution (*5, 6*). Let N_{Sh_x} represent the diffusional mass transfer coefficient at nondimensional position $\tilde{x} \equiv x/L$ along the plate $(d \ln u_e/d \ln x = 0)$ in the absence of chemical surface reaction. From the now classical work of Polhausen (*10*) and Levich (*11*) one can write the well-known laminar boundary-layer result

$$N_{Sh_x} = \frac{x}{c_e - c_w}\left(\frac{\partial c}{\partial y}\right)_{y=0} = [\Theta_w'(0, N_{Sc})](N_{Re})^{1/2}(\tilde{x})^{-1/2} \qquad (5)$$

where the function $\Theta_w'(0, N_{Sc})$ of the Schmidt number alone has also been computed by Eckert (*12*), Merk (*13*), Sparrow (*14*), Fisher and Knudsen (*15*), Evans and Spalding (*16*), and others over a very wide range of Schmidt (Prandtl) numbers. An immediate consequence of the present mathematical model is that local values of any nondimensional dependent variable constructed from the reactant concentration field at $y = 0$ can depend only upon the independent variable $z \propto G_n \cdot (x/L)^{1/2}$ and the parameter n, where G_n (9) is given by

$$G_n \equiv \frac{k\cdot(\rho c_e)^n}{N_{Sh^*_x}\cdot D\rho c_e/L} \qquad (6)$$

and $N_{Sh^*_x}$ is the value of the local mass transport coefficient N_{Sh_x} evaluated at $x = L$ (the trailing edge of the plate). Thus the dependent variable of greatest interest, that is the local rate of reaction R'', can be written in the separable form

$$\dot{R}'' = k[\rho c_e]^n \cdot \eta(z; n) \qquad (7)$$

which defines a local nondimensional reaction rate coefficient If the local reaction rate given by Equation (7) is integrated over the length of the catalyst, then the actual overall reaction rate will be given by an expression of the form

$$\bar{\dot{R}} = k[\rho c_e]^n L \cdot \bar{\eta}(G_n, n) \qquad (8)$$

This likewise defines a nondimensional reaction rate coefficient $\bar{\eta}$. The meaning of the nondimensional coefficients η and $\bar{\eta}$ is made clear as follows. If the reactant concentration c_w at the catalyst surface were c_e everywhere, then $k[\rho c_e]^n$ would represent the resulting local reaction rate, and $k[\rho c_e]^n \cdot L$ the overall rate of reaction (per unit plate depth). However the actual rates $\dot{R}''$ and $\bar{\dot{R}}$ are given by the corresponding products with η and $\bar{\eta}$.

---

* Results given herein can also be applied to the case of catalysts deposited on the interior or exterior of short impermeable cylindrical ducts with sharp edged entrance sections.

These nondimensional functions η and $\bar{\eta}$ must embody the effects of convective diffusion on the observed reaction rate, since neither $k[\rho\, c_e]^n$ nor $k[\rho\, c_e]^n \cdot L$ involve any reference to diffusion. Moreover η and $\bar{\eta}$ are each less than unity since the reactant is depleted locally by the interfacial reaction and the catalytic activity k remains constant. This leads to an interesting interpretation of the product $\bar{\eta} \cdot L$ as the effective length [or more generally effective area (per unit depth)] of the catalyst in the presence of convective diffusion. Since a catalytic plate of length L in the presence of convective diffusion causes the same total amount of conversion as a catalytic plate of length $\bar{\eta}L$ in the absence of a diffusional limitation, the factor $\bar{\eta}$ is sometimes referred to as the catalyst effectiveness or utilization factor. The normalized reaction rate coefficient η may likewise be regarded as a local effectiveness factor.

To the chemist interested in the interfacial reaction itself, diffusion is a falsifier, an intruder. Thus while one is usually interested in the true activation energy and the true reaction order characterizing the chemical reaction, these will not be observed (in the presence of slow reactant diffusion) when the temperature level and free stream reactant concentration are intentionally changed. The extent of this falsification may be conveniently discussed in terms of two new parameters: the apparent activation energy and the apparent reaction order. Expressions for these quantities are suggested by formal analogy with E and n; that is, if the temperature dependence of the intrinsic rate constant k is characterized by a single activation energy parameter E given by

$$E = -R\frac{d(\ln k)}{d(1/T)} \tag{9}$$

then the apparent activation energy E_a, based on the observed temperature sensitivity of the overall reaction rate $\bar{R}$, is taken to be

$$E_a \equiv -R\frac{d(\ln \bar{R})}{d(1/T)} \tag{10}$$

that is, the slope of an Arrhenius plot of observed rate data. Similarly an apparent reaction order is defined by the relation

$$n_a \equiv \frac{d[\ln \bar{R}]}{d[\ln\,(\rho\, c_e)]} \tag{11}$$

The normalized apparent activation energy E_a/E and normalized apparent reaction order n_a/n are related to the isothermal effectiveness factor $\bar{\eta}$ in much the same way as in static systems. Consider for example an isothermal catalysis problem in which an n^{th} order surface reaction takes place along a solid immersed in a stream of foreign gas. The gas will be considered to have a total density which depends inversely on the temperature level at a fixed level of the total pressure; however the nondimensional reactant concentration c_e will remain invariant under such a change. When the temperature level of the system is increased by a small amount dT, the density, kinematic viscosity, reactant/carrier gas binary diffusion coefficient, and, most important, the intrinsic chemical rate constant, are all altered in magnitude. In particular consider the case for which $\nu \propto T^{3/2}$, $D \propto T^{3/2}$, $k \propto \exp[-E/(RT)]$. From the definitions of $\bar{\eta}$ and E_a one has

$$\frac{E_a}{E} = \frac{d(\ln k) + n\, d(\ln \rho) + d(\ln \bar{\eta})}{d(\ln k)} \tag{12}$$

Since the basic equations governing the physico-chemical-hydrodynamic model reveal that $\bar{\eta} = \bar{\eta}(\mathcal{C}_n, n)$, one may write

$$d(\ln \bar{\eta}) = \frac{d(\ln \bar{\eta})}{d(\ln \mathcal{C}_n)} \cdot d(\ln \mathcal{C}_n) \tag{13}$$

Considering all rates of change to be with respect to the reciprocal of the absolute temperature, and making use of the definition of the catalytic parameter $\mathcal{C}_n$, one obtains (*6*)

$$\frac{E_a}{E} = \left[1 - n\left(\frac{E}{RT}\right)^{-1}\right] + \left[1 - \left(n - \frac{1}{4}\right)\left(\frac{E}{RT}\right)^{-1}\right] \times \frac{d(\ln \bar{\eta})}{d(\ln \mathcal{C}_n)} \tag{14}$$

This relation allows the calculation of the normalized apparent activation energy E_a/E for each value of the catalytic parameter $\mathcal{C}_n$, as soon as the dependence of the global diffusion correction $\bar{\eta}$ on $\mathcal{C}_n$ has been determined.[*] As a commonly occurring special case it is observed that when $E >> RT$, Equation (14) specializes to

$$\frac{E_a}{E} = 1 + \frac{d(\ln \bar{\eta})}{d(\ln \mathcal{C}_n)} \tag{15}$$

The ratio of apparent to true reaction orders n_a/n is treated in a similar way. Imagine a small change $d(\rho c_e)$ in the free stream reactant concentration with the total density ρ held constant. Then the global reaction rate $\bar{R}$ will change in accordance with

$$d(\ln \bar{R}) = n\, d[\ln(\rho c_e)] + d(\ln \bar{\eta}) \tag{16}$$

Introducing the definition of the apparent reaction order n_a one has

$$\frac{n_a}{n} = 1 + \frac{1}{n}\,\frac{d(\ln \bar{\eta})}{d(\ln \mathcal{C}_n)} \cdot \frac{d(\ln \mathcal{C}_n)}{d(\ln \rho c_e)} \tag{17}$$

The dependence of the catalytic parameter $\mathcal{C}_n$ on $\rho\, c_e$ then implies

$$\frac{n_a}{n} = 1 + \frac{n-1}{n} \cdot \frac{d(\ln \bar{\eta})}{d(\ln \mathcal{C}_n)} \tag{18}$$

With regard to the dependence of the normalized apparent reaction order n_a/n on the catalytic parameter $\mathcal{C}_n$, it is observed that the falsification of reaction order depends upon the same differential coefficient of the effectiveness factor $\bar{\eta}$ as does the activation energy ratio E_a/E.[*] It is remarked that, in the special case of first-order surface reactions ($n = 1$), the second term on the right-hand side of Equation (18) vanishes regardless of the magnitude of the parameter $\mathcal{C}_n$. This means the apparent and observed reaction orders[†] will always be identical if the true reaction order is unity. For this reason one cannot conclude that a surface reaction is diffusion controlled on the basis of reaction order data alone.

It is interesting to compare Equations (15) and (18) with Equations (35) and (45), respectively, of reference *1*. While the equations given here apply to surface reactions occurring along catalytic solids immersed in a stream of reactant, and the equations given by Weisz and Prater (*1*) are derived for diffusion within porous catalysts, one cannot help but be struck by their formal similarity.

APPROXIMATE SOLUTIONS

The real work of the solution remains to be done, since the actual form of each isothermal diffusion correction $\eta(z; n)$ and $\bar{\eta}(\mathcal{C}_n, n)$ is, as yet, unknown. This information can only be obtained of course by solving the boundary-layer conservation equations subject to the constraints discussed earlier. While the diffusion Equation (3) is itself linear, the chemical kinetic boundary condition (4) at the interface is not (except for $n = 0, 1$). Furthermore the velocity field $u(x, y)$, $v(x,y)$ within the layer is not generally expressible in closed form. Under these conditions one has no practical alterna-

---

[*] Since the dependence on catalyst geometry is absorbed in $\bar{\eta}(C_n, n)$, Equation (14) will hold for bodies of arbitrary shape and catalytic activity provided the boundary layers are laminar. Available evidence indicates that laminar boundary-layer flow may prevail about individual catalyst particles in fixed bed catalytic reactors (see reference *17*). In the limit $E >> RT$ Equation (14) will apply to turbulent boundary layers as well, provided the definition of C_n is suitably modified.

[*] Again this result will therefore formally apply to catalytic solids of arbitrary geometry.

[†] One can also define an apparent order with respect to catalyst surface area which will vary between unity in the absence of a diffusional limitation and ½ in the presence of a rate limiting laminar diffusion layer. For intermediate values of C_n this apparent order is readily found to be given by $1 + ½(d \ln \bar{\eta}/d \ln C_n)$, when the diffusion layer is laminar.

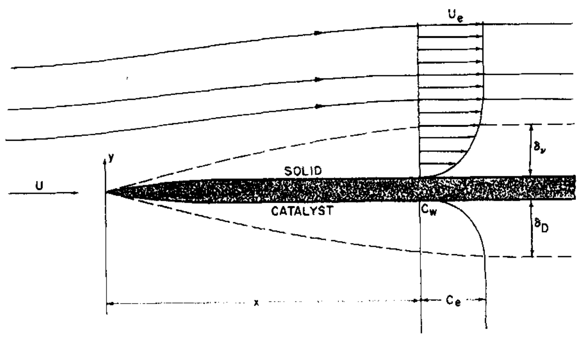

Fig. 1. Vorticity and concentration diffusion boundary layers developing along a catalytic flat plate.

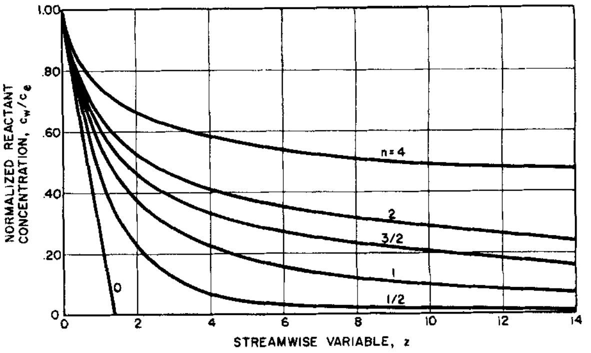

Fig. 2. Normalized, steady state reactant concentration distributions along a catalytic flat plate for several reaction orders.

tive but to seek approximate solutions whose accuracy can be checked only in certain extreme (asymptotic) cases.

The most straightforward approach to this problem would be that of Heymann (*3*), as adapted to flow systems by Frank-Kamenetskii (*4*). In accordance with this approach a steady state reactant concentration c_w would be established at each point along the surface such that the local rate of diffusional transport, taken to be simply proportional to the local concentration driving force $c_e - c_w$, is identically equal to the local chemical rate of conversion at the interface. The fundamental approximation is that the nonreactive diffusional transport coefficient given by Equation (5), and derived under the condition $c_e - c_w =$ constant, is applicable even when the diffusional driving force $c_e - c_w$ is increasing with axial distance as the reaction proceeds. When one considers distance and time to be related by the free stream velocity, in spirit then this is indeed a quasi-stationary method.

Without pausing to justify this procedure one may quickly obtain its consequences since only algebraic manipulations are involved. The basic reactant conservation equation at the interface takes the form

$$N_{Sh_x} \cdot D\rho \cdot (c_e - c_w)/x = k \cdot (\rho c_w)^n \tag{19}$$

where N_{Sh_x} is taken over from Equation (5). Again defining $\mathcal{G}_n$ by Equation (6) one finds the local diffusion correction $\eta = (c_w/c_e)^n$ from the solution of the algebraic equation

$$z\,\eta + \eta^{1/n} - 1 = 0 \tag{20}$$

where $z \equiv \mathcal{G}_n \cdot (\tilde{x})^{1/2}$. The global diffusion correction $\bar{\eta}$ is then obtained from the integral

$$\bar{\eta} \equiv \frac{\int_0^L \dot{R}''(x)\,dx}{k \cdot (\rho c_e)^n L} = \left(\frac{1}{\mathcal{G}_n}\right)^2 \int_0^{\mathcal{G}_n} 2z\eta(z)\,dz \tag{21}$$

For instance in the special case $n = 1$ (first-order surface reaction), the results are simply (*5*)

$$\eta = \frac{1}{1+z} \tag{22}$$

and

$$\bar{\eta} = (2/\mathcal{G}_1)\,[1 - (1/\mathcal{G}_1)\ \ln\,(1 + \mathcal{G}_1)] \tag{23}$$

The differential coefficient $d(\ln \bar{\eta})/d(\ln \mathcal{G}_1)$ appearing in the expressions for the apparent chemical kinetic parameters E_a/E and n_a/n is readily obtained in explicit form from Equation (23). In dimensional form Equation (22) has an interesting interpretation. Defining the local diffusion velocity $k_D \equiv N_{Sh_x} \cdot D/x$, one has the well-known resistance additivity law (*4*)

$$\frac{1}{k_a} = \frac{1}{k} + \frac{1}{k_D} \tag{24}$$

for the apparent rate constant $k_a = \eta\, k$ defined by $\dot{R}'' = k_a\, \rho\, c_e$ at each axial station $\tilde{x}$ along the catalyst. Since this local resistance law is a consequence of the underlying uncoupling approximation of the quasi-stationary method, it is of interest to examine its accuracy and in particular the conditions under which it is likely to be inadequate. Generally speaking the fact that the extent of the diffusional falsification of chemical kinetic parameters depends upon a differential coefficient of the diffusion correction (effectiveness or utilization factor) suggests that any errors introduced in the determination of $\bar{\eta}$ itself will be amplified in the calculation of E_a/E and n_a/n. An object of the present work will be to evaluate this error by comparison with at least one exact solution of the original set of equations.*

A qualitative understanding of the nature of the quasi-stationary assumption may be obtained from a consideration of the diffusional driving force history. If one confines his attention to reactant concentrations in the immediate vicinity of the catalyst, the fact that the action of the catalyst causes the local reactant concentration c_w to decrease monotonically with increasing stream distance implies that fluid parcels near any particular point on the surface have come from upstream regions where the concentration c_w was somewhat higher. Considering the local diffusional rate of transfer to the surface per unit driving force Δc (that is the coefficient), one sees that this invasion of reactant near the wall causes the local concentration profile to be distorted for the same local value of c_e and c_w in such a way that the local transfer coefficient $(x/\Delta c)(\partial c/\partial y)_{y=0}$ is increased. In this sense the reactant depletion process produced by the presence of the catalyst is self-regulating, since the more vigorously the catalyst causes the reactant concentration c_w to decrease spatially, the more this enhances the local diffusional mass transfer coefficient. Clearly then any method which neglects this phenomenon will *underestimate the reaction rate* everywhere along the catalyst surface and therefore underestimate the overall rate of interfacial reaction (hence $\bar{\eta}$) as well. In short quasi-stationary methods of this type will always tend to give an exaggerated estimate of the effects of diffusion on the total conversion of a catalytic surface. When it comes to the apparent activation energy and reaction order however it will be seen that it can cause overestimates or underestimates of the effect of diffusion depending on the extent of the diffusional limitation itself (that is the magnitude of $\mathcal{G}_n$ and hence $\bar{\eta}$).

It may be asked whether these properties of the quasi-stationary method constitute the price of its simplicity

---

* An important start in this direction was made in reference *18* where the accuracy of the quasi-stationary $\eta(z;1)$ distribution was examined in the asymptotic extreme $N_{Sc} \to \infty$ for small z. The author wishes to carry such a comparison through to the stage where the accuracy of E_a/E and n_a/n can be investigated over the entire range of the diffusion-reaction modulus C_n, since these falsification parameters are of particular practical interest.

and formal generality. In particular one is tempted to ask whether the quasi-stationary method can be quantitatively improved without forfeiting these appealing features. Fortunately a significant improvement can be effected if one invokes an approximate method introduced by Ambrok *(19)* in his treatment of a related heat transfer problem, namely the convective heat transfer properties of nonisothermal surfaces. It is suggested, although admittedly with some hesitation, that this improved method be called *quasi-quasi-stationary,* since this seems to best describe its essential property, namely that of using the quasi-stationary method to generate its own improvement. While this quasi-quasi-stationary method is applied here only for the laminar diffusion boundary layer on a flat plate, it is readily generalized to include transition flows and turbulent flows along catalytic wedges (*5, 6, 20*). For the case studied the method allows rapid and reasonably accurate calculation of the local and integrated reaction rates, apparent activation energies, and apparent reaction orders for arbitrary values of the reaction order. Moreover the results are formally applicable over the entire range of Schmidt numbers. In contrast to the integral equation approach adopted by Chambré and Acrivos *(18)* the author has preferred casting this method into its differential form. In the present case this is readily done, and it offers some advantages in studying and displaying the qualitative behavior of solutions (*9*).

Consider first the problem of determining the diffusional mass transfer distribution, but for the present imagining the distribution $c_w(x)$ to be prescribed. Of course in the actual catalysis problem this is not the case, for if it were the solution to the problem would simply be $\eta = (c_w/c_e)^n$.

By formally integrating the laminar diffusion boundary layer Equation (3) over y from $y = 0$ to $y \to \infty$, and making use of the continuity equation, it can be shown that the convective diffusion layer thickness defined by

$$\delta \equiv \int_0^\infty \frac{u}{u_e}\left(1 - \frac{c - c_w}{c_e - c_w}\right) dy \qquad (25)$$

satisfies the ordinary differential equation

$$\frac{d\delta}{dx} + \delta\frac{d}{dx}\{\ln[u_e(c_e - c_w]\} = N_{St} \qquad (26)$$

where N_{St} is the local diffusional Stanton number, defined by

$$N_{St} \equiv D\left(\frac{\partial c}{\partial y}\right)_{y=0} \cdot [u_e(c_e - c_w)]^{-1} \qquad (27)$$

If this nondimensional transfer coefficient were known as a function of say $u_e\,\delta/\nu$, ν/D etc., then Equation (26) would provide a relation for the growth of the diffusion layer thickness, from which the coefficient N_{St} could in turn be determined at each point x along the surface. While for arbitrary free stream velocity distribution $u_e(x)$ and concentration distribution $c_w(x)$, N_{St} is not known, there exists a class of free stream velocity distributions $u_e(x)$ for which exact solutions of the boundary-layer equations are available (in numerical form), provided c_w = constant. These are the so-called *isothermal wedge solutions* (*7*) for which $u_e \propto x^m$, where the exponent m is sometimes called the *Euler number.* In particular the flat plate problem is a member of this class, corresponding to an Euler number of zero. As in the Frank-Kamenetskii quasi-stationary method these exact solutions will be enlisted to obtain approximate solutions to the catalysis problem, but in a somewhat less direct manner.

Consider the introduction of the nondimensional axial coordinate $\tilde{x} \equiv x/L$ and the nondimensional, stretched diffusion layer thickness $\tilde{\delta} \equiv (\delta/L)\cdot(N_{Re})^{1/2}$, where again $N_{Re} \equiv UL/\nu$. Then with $m = 0$ Equation (26) becomes

$$\frac{d\tilde{\delta}}{d\tilde{x}} + \tilde{\delta}\frac{d}{d\tilde{x}}[\ln(c_e - c_w)] = N_{St}\,(N_{Re})^{1/2} \qquad (28)$$

Since exact numerical solutions to the boundary-layer equations exist (*10, 12, 16*) for $m = 0$, c_w = constant, one can in particular obtain the functions

$$N_{Sh_x}\,(N_{Re_x})^{-1/2} \equiv \Theta_w'(0, N_{Sc})$$

and (29)

$$(\delta/x)\,(N_{Re_x})^{1/2} \equiv \Delta(0, N_{Sc}) = (2/N_{Sc})\cdot\Theta_w'(0, N_{Sc}) \qquad (30)$$

In terms of the function $\Theta_w'(0, N_{Sc})$ one finds the corresponding local Stanton number depends upon the diffusion layer thickness in accordance with

$$N_{St}\,(N_{Re})^{1/2} = 2(\Theta_w'/N_{Sc})^2/\tilde{\delta} \qquad (31)$$

For a flat plate with c_w = constant Equation (28) reveals that the convective diffusion layer thickness grows in accordance with the first-order differential equation

$$\frac{d\tilde{\delta}}{d\tilde{x}} = 2\left(\frac{\Theta_w'}{N_{Sc}}\right)^2 \cdot \frac{1}{\tilde{\delta}} \qquad (32)$$

However for a flat plate with variable c_w a first approximation to the convective diffusion layer thickness distribution can be obtained from the solution to the complete equation

$$\frac{d\tilde{\delta}}{d\tilde{x}} + \tilde{\delta}\frac{d}{d\tilde{x}}[\ln(c_e - c_w)] = 2\left(\frac{\Theta_w'}{N_{Sc}}\right)^2 \frac{1}{\tilde{\delta}} \qquad (33)$$

where the presence of the second term on the left-hand side corrects $\tilde{\delta}(\tilde{x})$ for the axial variation in the diffusional driving force $c_e - c_w$, and it is assumed that the local relation between N_{St} and $\tilde{\delta}$ is not appreciably changed by the altered boundary condition. The result is a nonlinear first-order differential equation for $\tilde{\delta}(\tilde{x})$ which is of the Bernoulli type. Therefore a solution can be obtained which gives the explicit dependence of $\tilde{\delta}$ on the concentration

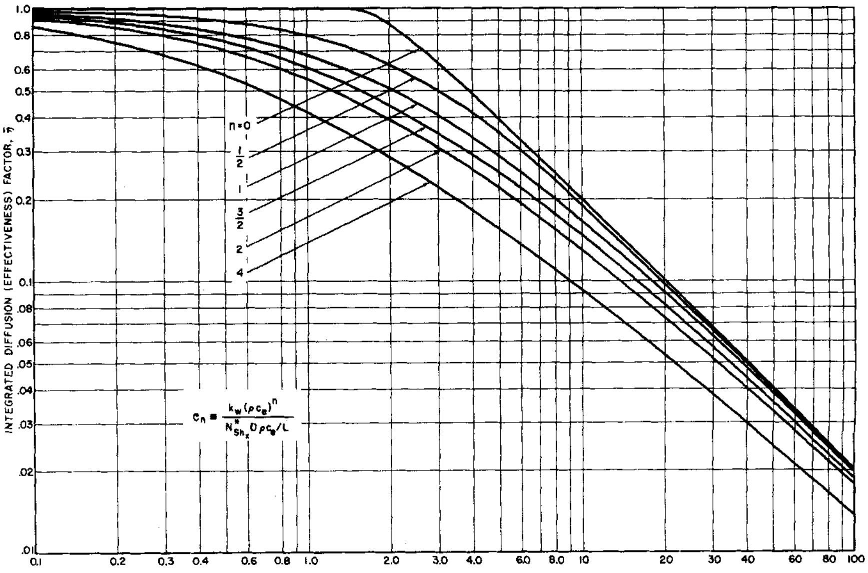

Fig. 3. Dependence of global catalyst effectiveness factor on the composite catalysis-diffusion parameter C_n for several reaction orders.

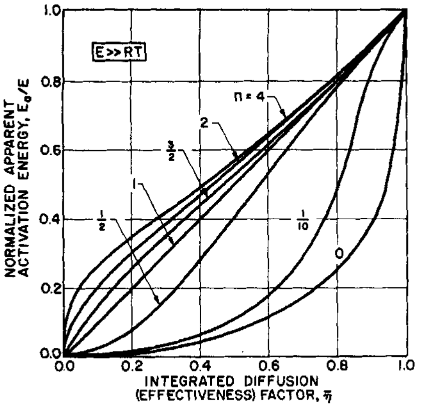

Fig. 4. Influence of convective diffusion on the apparent activation energy for chemical surface reactions on catalytic plates of finite length.

distribution along the surface. Returning to Equation (31) one finds that the solution to the intermediate problem becomes

$$N_{St}\,(N_{Re})^{1/2} = (\Theta_w'/N_{Sc}) \times$$
$$\left[(c_e - c_w)^{-2} \int_0^{\tilde{x}} (c_e - c_w)^2\, d\tilde{x}_1 \right]^{-1/2} \tag{34}$$

This result is now applied to the catalysis problem initially posed. When the surface of the plate is catalytically active, the diffusional driving force distribution is not prescribed; in fact it is sought. The actual boundary condition to be satisfied is given by Equation (4). When one makes use of the definition of the local Stanton number, this condition becomes

$$k[\rho\, c_w]^n = N_{St} \cdot \rho\, U \cdot (c_e - c_w) \tag{35}$$

But since N_{St} is now given by Equation (34), Equation (35) represents a nonlinear integral equation of the Volterra type for the normalized reactant concentration $\tilde{c} \equiv c_w/c_e$ along the surface.* In terms of the following nondimensional quantities

$$c \equiv c_w/c_e$$
$$G_n \equiv \frac{k \cdot (\rho\, c_e)^n}{\Theta_w' \cdot (N_{Re})^{1/2}\, D\, \rho\, c_e/L} =$$
$$\frac{k \cdot (\rho\, c_e)^n}{N^*_{Sh_x}\, D\, \rho\, c_e/L} \tag{36a, b, c}$$
$$z \equiv G_n \cdot (x/L)^{1/2}$$

the equation reads

$$c^n = (1-c)^2 \times$$
$$\left[2 \int_0^z (1-c)^2 z_1\, dz_1 \right]^{-1/2} \tag{37}$$

This nonlinear integral equation for $c(z)$ can be transformed into the following separable first-order differential equation

$$-2z\, dz = c^{-(2n+1)}\, (1-c) \times$$
$$[2n - 2(n-2)\, c] \cdot dc \tag{38}$$

with the initial condition $c(0) = 1$. Therefore if the reaction order is not $n = 0$, 1/2, or 1, the normalized reactant concentration c and axial variable z are related by

$$z^2 = \left[\frac{1 - c^{2n}}{c^{2n}} \right] -$$
$$\frac{2(n-1)}{n - \frac{1}{2}} \left[\frac{1 - c^{2(n-1/2)}}{c^{2(n-1/2)}} \right] -$$
$$\frac{2-n}{n-1} \left[\frac{1 - c^{2(n-1)}}{c^{2(n-1)}} \right] \tag{39}$$

If the reaction is of zeroth order, c and z are (linearly) related in accordance with

$$z^2 = 2(1-c)^2 \quad c \geqslant 0 \tag{40}$$

If the reaction is of order 1/2, then c and z are related in accordance with

$$z^2 = \frac{1-c}{c} + \ln \frac{1}{c^2} - 3(1-c) \tag{41}$$

and finally if the reaction is of the first order ($n = 1$) then c and z are related in accordance with

$$z^2 = \frac{1-c^2}{c^2} - \ln \frac{1}{c^2} \tag{42}$$

The normalized, steady state reactant concentration distributions $c(z; n)$ along the catalyst surface are shown in Figure 2.* The corresponding normalized reaction rate distributions $\eta(z; n)$ are simply given by $[c(z; n)]^n$. A number of interesting properties of the solution are now discussed in terms of this example.

Generality With Respect to Schmidt Number

Since the same differential equation must be solved for all values of the Schmidt (diffusional Prandtl) number, the results (39), (40), (41), and (42) apply for all Schmidt numbers. Only the nature of the axial variable z changes. For very large values of the Schmidt number Lighthill (*21*) has shown that

$$\Theta_w'(0; N_{Sc}) \sim 0.3387\, (N_{Sc})^{1/3} \tag{43}$$

For Schmidt numbers not far from unity Polhausen (*10*) observed that

$$\Theta_w'(0; N_{Sc}) \cong 0.33206\, (N_{Sc})^{1/3} \tag{44}$$

In this latter case the relevant catalytic parameter G_n therefore becomes explicitly

$$G_n = \frac{k \cdot (\rho c_e)^{n-1}}{0.33206 (N_{Re})^{1/2}\, (N_{Sc})^{1/3}\, D/L} \tag{45}$$

Over a much wider range of large Schmidt numbers Merk (*13*) obtained the asymptotic expansion

$$\Theta_w'(0, N_{Sc}) = 0.3387\, (N_{Sc})^{1/3} \times$$
$$\left[1 - \frac{1}{45} (N_{Sc})^{-1} + \frac{2}{675} (N_{Sc})^{-2} + \ldots \right] \tag{46}$$

in which the leading term had been given earlier by Lighthill (*21*). On the other hand when the diffusional Prandtl number becomes very small ($N_{Sc} << 1$), the leading term in $\Theta_w'(0, N_{Sc})$ is supplied by Boussinesq's treatment of heat transfer in inviscid flow (*22*); that is

$$\Theta_w'(0, N_{Sc}) \to \frac{1}{\sqrt{\pi}} (N_{Sc})^{1/2} \tag{47}$$

In this latter case ($N_{Sc} \to 0$) however it will be seen that an exact solution in closed form is obtainable (*23*) when the surface reaction is of first order. This solution will therefore be called on later to check the accuracy of the approximate method described above.

Spatial Transition from Activation to Diffusion Control (18)

The solutions presented have the property that sufficiently near the leading edge of the catalytic plate the local reaction rate is always given by $k \cdot (\rho c_e)^n$; that is, it is independent of diffusion or convection parameters. This reflects the fact that reactant supply by convection near the sharp leading edge is always more than adequate to cope with the tendency of the catalyst to locally deplete the reactant concentration. As a result the diffusion layer starts with zero thickness at the leading edge. Far downstream the local reactant concentration at the catalyst itself becomes very small compared with the free stream reactant concentration. The reaction is said to become diffusion controlled in the sense that the magnitude of actual catalytic activity k no longer limits the result; that is the surface has the chemical kinetic capacity for greater local conversion (if it were exposed to the free stream reactant concentration). However by the very fact that it has consumed reactant at a rate at which it cannot be adequately replenished, the surface must content itself with converting

---

* c will be used hereafter (in place of $\tilde{c} \equiv c_w/c_e$) for notational convenience.

* The case $n = 4$ is included primarily because of its heat transfer analogue (*24*), namely radiation cooling of flat plates with forced convection.

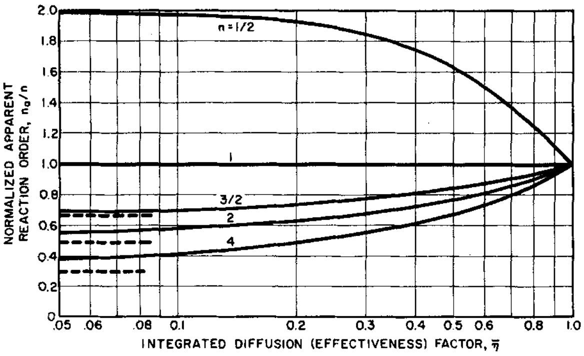

Fig. 5. Influence of convective diffusion on the apparent reaction order for chemical surface reactions on catalytic plates of finite extent.

only what can reach it by diffusion from the free stream across the diffusion boundary layer. With regard to the local apparent kinetics the reaction rate near the leading edge will therefore always respond to changes in free stream reactant concentration and temperature level in a way which reflects the true n^{th} order kinetics and temperature dependent rate constant $k(T)$. Further downstream however diffusion begins to mask the true reaction order and temperature dependence of k. Ultimately the local reaction rate responds to changes in free stream reactant concentration as if a first order, temperature insensitive, interfacial reaction were taking place, regardless of the true reaction order and activation energy. Looking at the catalytic surface from an overall point of view one may see that the observed kinetics will then be intermediate between that characterizing the interfacial process itself and that corresponding to the pure physical process of convective diffusion. By summing up the local reaction rates along the catalyst (that is regarding the plate as an integral reactor), one may quantitatively examine the extent of the resulting falsification for catalysts of finite length and activity.

Computation of $\bar{\eta}$, E_a/E, and n_a/n

In order to calculate the diffusional falsification parameters it is first necessary to obtain the integrated diffusion correction $\bar{\eta}$ (catalyst effectiveness factor). This is readily done in terms of the local reaction rate distributions $\eta(z;n) = c^n$ already given, since integration along the catalyst surface yields Equation (21). The integral of $2\eta(z)z \cdot dz$ appearing in Equation (21) need not be evaluated numerically since $\eta = c^n$ and $2z \cdot dz$ can be replaced by its value in terms of c alone [see Equation (38)], enabling term-by-term quadratures for all values of the reaction order n. Letting c^* and $z^* = \mathcal{G}_n$ be the values of c and z, respectively, at the trailing edge of the plate ($x = L$), one then finds

$$\bar{\eta} = \frac{2}{c^{*n}} \cdot \left(\frac{1-c^*}{z^*}\right)^2 \qquad (48)$$

In this manner the overall reaction rate coefficient $\bar{\eta}(\mathcal{G}_n, n)$ may be found from the known function $z^*(c^*, n)$ alone. Results are shown graphically in Figure 3 for the reaction orders $n = 0, 1/2, 1, 3/2, 2, 4$.* Since both scales are logarithmic, it is seen from Equations (15) and (18) that the local slope of this curve is all that is needed to compute the falsification parameters E_a/E and n_a/n. Fortunately the calculation of these parameters can proceed without having to carry out a numerical differentiation, since it is easily shown that

$$\frac{d(\ln \bar{\eta})}{d(\ln \mathcal{G}_n)} = -2\left[1 - \frac{\eta}{\bar{\eta}}\right] \qquad (49)$$

Values of E_a/E for $E >> RT$ have been computed from these relations, and the results are shown graphically as a function of the effectiveness factor $\bar{\eta}$ in Figure 4 for several true reaction orders ($n = 0, 1/2, 1, 3/2, 2, 4$). For values of E which are not large compared with RT, one can construct E_a/E by introducing these values of $d(\ln \bar{\eta})/d(\ln \mathcal{G}_n)$ into Equation (14). It is observed that under conditions of strong diffusional limitation the apparent activation energy E_a will become negligible compared with the true activation energy E. This is in contrast to the well-known limit $E_a \rightarrow E/2$ for chemical surface reactions in porous spherical pellets and can be shown to be a consequence of the absence of chemical reaction over the diffusion path in the external flow problem (*1*).

Similarly the normalized apparent reaction order n_a/n is shown plotted as a function of the effectiveness factor $\bar{\eta}$ in Figure 5 for these same true reaction orders. The tendency of all interfacial reactions to masquerade as first-order reactions in the presence of a strong diffusional limitation is illustrated by the $\bar{\eta} = 0$ asymptotes $1/n$ (shown dashed).

For values of the effectiveness factors $\bar{\eta}$ near unity it is seen from these plots that the diffusional falsification of activation energy and reaction order is most pronounced for true reaction orders which are smaller than unity. It is also interesting that diffusional effects are observed even for the zeroth order case (*6*) provided the parameter $\mathcal{G}_o$ exceeds some threshold value ($\sqrt{2}$ in accordance with the method presented).

With the exception of a discussion of accuracy this completes the problem of determining the macroscopic chemical kinetic consequences of diffusion on isothermal catalytic plates of finite length in the laminar boundary-layer flow regime. As has already been remarked, since the falsification of kinetic parameters involves the rate of change of $\bar{\eta}$ with changes in the modulus $\mathcal{G}_n$, it is to be expected that the improvement offered by the present method over the straightforward quasi-stationary method will be more marked in comparing these quantities than in comparing the predicted diffusion corrections η or $\bar{\eta}$ alone. Furthermore in view of the physical origin of the error introduced in the quasi-stationary approximation (as discussed earlier) it can also be expected that the errors inherent in the quasi-stationary method will become larger as the Prandtl number for diffusion becomes smaller, that is as convective processes near the surface become comparatively more important in determining the structure of the diffusion layer; this is where the maximum reactant concentration nonuniformities along the stream indeed exist. Fortunately the extreme $N_{Sc} \rightarrow 0$ is most tractable mathematically, particularly when $n = 1$, and the accuracy of each approximation in predicting the falsification parameter E_a/E can now be investigated in the worst possible hydrodynamic case.

AN EXACT SOLUTION

In the asymptotic extreme $N_{Sc} \rightarrow 0$ the vorticity boundary-layer thickness becomes negligible with respect to the diffusion layer thickness with the result that the fluid velocity everywhere within the diffusion layer may be considered to be uniform and equal to the free stream velocity. When one inserts $u = u_e = U =$ constant and $v = 0$ into Equation (3), the diffusion

---

* See footnote, page 326.

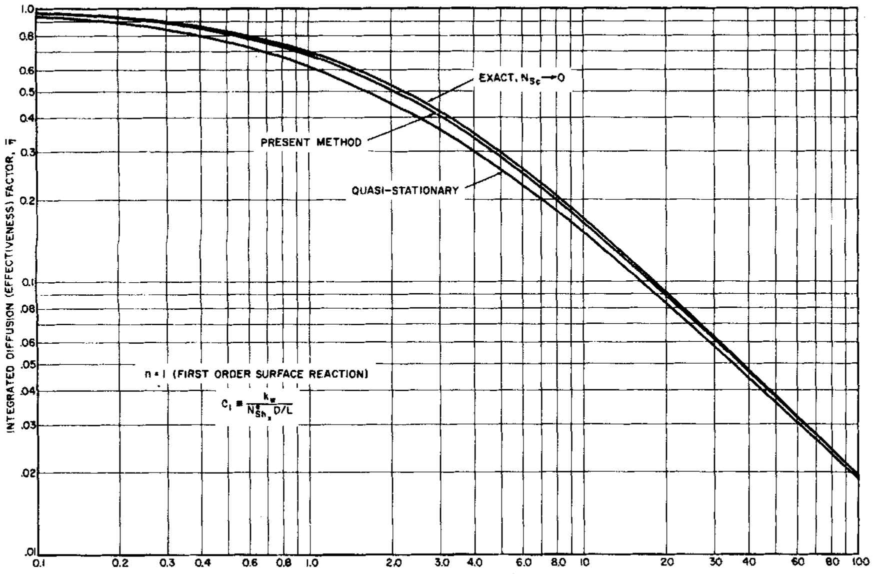

Fig. 6. Dependence of global catalyst effectiveness factor on the composite catalysis-diffusion parameter for first-order surface reactions; a comparison of three methods.

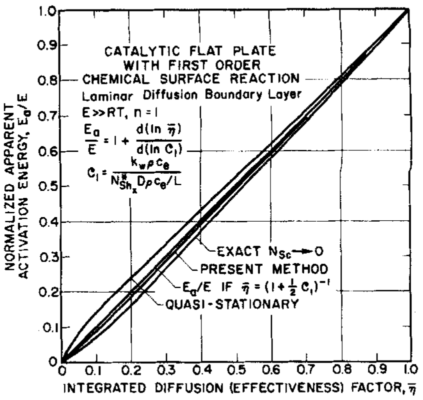

Fig. 7. Influence of convective diffusion on the apparent activation energy for first-order surface reactions on catalytic plates of finite length; a comparison of four methods.

boundary-layer equation takes the extremely simple form

$$U \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2} \tag{50}$$

With the substitution of the transit time (or contact time) variable $t = x/U$ the problem of solving Equation (50) subject to a chemical kinetic boundary condition of the form (4) becomes mathematically equivalent to that of determining the transient radiation cooling of a semi-infinite solid slab (in one spatial dimension).

A well-known result used in experimental heat flux determinations relates a transient surface temperature measurement $T_w(t)$ to the instantaneous heat flux $\dot{q}''(t)$ and thermal properties of the backing material

$$\dot{q}''(t) = \frac{\lambda}{\sqrt{\pi}} \int_0^t \frac{1}{\sqrt{\alpha \cdot (t-\tau)}} \left(\frac{dT_w}{d\tau}\right) d\tau \tag{51}$$

The mass transfer analogue of this relation is

$$D\rho \left(\frac{\partial c}{\partial y}\right)_{y=0} = -\frac{D\rho}{\sqrt{\pi}} \int_0^t \frac{1}{\sqrt{D \cdot (t-\tau)}} \left(\frac{dc_w}{d\tau}\right) d\tau \tag{52}$$

If one now makes use of the local reactant conservation relation (4) at the interface, the solution to the problem posed is equivalent to the solution $c(z)$ of the nonlinear, singular, Volterra integral equation (*21*)

$$[c(z)]^n = -\int_0^z \frac{1}{\sqrt{z^2 - z_1^2}} \left(\frac{dc}{dz_1}\right) dz_1 \tag{53}$$

where c has again been written for c_w/c_e. In this case the catalytic parameter $\mathcal{G}_n$ appearing in the stretched distance coordinate $z \equiv \mathcal{G}_n \cdot (x/L)^{1/2}$ is given by

$$\mathcal{G}_n \equiv \frac{k \cdot (\rho c_e)^{n-1}}{(1/\sqrt{\pi})\,(N_{Re})^{1/2}(N_{Sc})^{1/2}\, D/L} \tag{54}$$

in accordance with Equation (47).

One of the simplest, but most important, special cases of Equation (53) is that of first-order chemical kinetics ($n = 1$). Then the integral Equation (53) becomes linear and has the closed form solution

$$c = \exp\left[(z/\sqrt{\pi})^2\right] \cdot \operatorname{erfc}(z/\sqrt{\pi}) \tag{55}$$

This function ($\exp \xi^2 \cdot \operatorname{erfc} \xi$) is well-known in the theory of transient diffusion processes in solids.[*] A short table is given in Carslaw and Jaeger's treatise on heat conduction (*25*). A more complete table has recently been reported by Sunderland and Grosh (*26*). The overall reaction rate for the entire surface can be obtained from Equation (55) by integration over $z (0 \leq z \leq \mathcal{G}_1)$ to give

$$\bar{\eta} = \left(\frac{\mathcal{G}_1}{\sqrt{\pi}}\right)^{-2} \left\{ \exp\left[\left(\frac{\mathcal{G}_1}{\sqrt{\pi}}\right)^2\right] \operatorname{erfc}\left(\frac{\mathcal{G}_1}{\sqrt{\pi}}\right) - 1 + \frac{2}{\sqrt{\pi}}\left(\frac{\mathcal{G}_1}{\sqrt{\pi}}\right) \right\} \tag{56}$$

The differential coefficient required for determining the extent of diffusional falsification of chemical kinetic parameters is then found from Equation (49). It is now possible to compare the values of $\bar{\eta}$ and E_a/E predicted by the quasi-stationary and quasi-quasi-stationary methods with the exact solution given above. This is done[†] in Figures 6 and 7. Also shown in Figure 7 is the result one would obtain by making the physically unrealizable assumption that the reactant concentration everywhere along the catalyst surface is constant[*] and proceeding to solve for $\bar{\eta}$. In this way one readily obtains the simple formula

$$\bar{\eta} = \frac{1}{1 + \frac{1}{2}\mathcal{G}_1} \tag{57}$$

where $\mathcal{G}/2$ will be recognized as a diffusion-reaction parameter $\bar{\mathcal{G}}_1$ based on a global instead of a local mass transfer coefficient.

A comparison of predicted global effectiveness factors $\bar{\eta}$ reveals that the Frank-Kamenetskii quasi-stationary method gives the largest maximum error (14.6%), while the present (quasi-quasi-stationary) modification gives the smallest maximum departures (3.55%) from the exact values of $\bar{\eta}$. It is indeed interesting that the maximum error in using Equation (57) is only about 4.77%. With regard to predictions of the diffusional corrections to apparent chemical kinetic parameters the quasi-stationary estimate of E_a/E can be in error by more than a

---

[*] It is interesting to note that this solution is identical to that governing the distribution of slip velocity along a flat plate, as determined by means of the Rayleigh impulsive plate analogy in viscous fluid theory (*27*). Thus for example the overall drag force on flat plates in constant density slip flow is related to the overall (first order) reaction rate on catalytic plates of arbitrary activity. This is one manifestation of an underlying similarity which unites seemingly unrelated problems in surface catalysis, slip flow, and radiation cooling (*6, 24*).

[†] Tabular data and comparisons are given in reference *6*.

[*] In the analogous heat transfer problem (*24*) this result would pertain to a plate of infinite thermal conductivity, that is one which becomes isothermal owing to internal heat conduction despite spatial nonuniformity of the fluid-side heat transfer coefficient.

factor of 2 in the region of strong diffusional limitation. In the region of moderate diffusional limitation, say for $\bar{\eta} \geqq 0.5$, the maximum error in E_a/E as predicted by the quasi-stationary method is found to be 7.98% as contrasted to the maximum error of 2.04% obtained with the quasi-quasi-stationary improvement. In this respect the present method represents a substantial improvement in accuracy with virtually no sacrifice in ease of computation. Interestingly enough the maximum error in using Equation (57) to calculate E_a/E in the range $\bar{\eta} \geqq 0.5$ is only 2.59%. In each of the above cases, with $\bar{\eta} \geqq 0.5$, the approximate methods underestimate the value of E_a/E (overemphasize the importance of diffusion). In a kinetic investigation this would cause the inferred value of the true activation energy E to be overestimated by the corresponding percentages.

From the work reported on here, as well as previous theoretical studies of heat transfer to or from nonisothermal solid surfaces (*28*), several general conclusions can be drawn as to the hydrodynamic and physico-chemical conditions under which the quasi-stationary approximation is likely to lead to appreciable errors. In particular the conditions leading to large errors will include laminar as opposed to turbulent diffusion boundary layers, adverse pressure gradients (decelerating flows), small reaction orders, and laminar boundary-layer flows with small Schmidt numbers.*

As shown earlier in this section these errors become particularly serious in the computation of the apparent activation energy and reaction order. Acrivos and Chambré (*18*) have convincingly demonstrated that the ability to predict reaction rate distributions when, for example, sequential surface reactions ($A \rightarrow B \rightarrow C$) are involved represents another severe test of any approximate method. This can be traced to the fact that the steady state reactant distribution $c(z)$ sought in the present paper is, in turn, necessary as input information for determining subsequent product distributions. An investigation of the ability of quasi-quasi-stationary and alternative approximate methods to predict the apparent selectivity of catalysts in flow systems is being undertaken and will be reported in the near future. It can also be anticipated that the errors will likewise be more serious in treating the coupled problem of simultaneous exothermic reaction and heat transfer. This more general problem is however also beyond the scope of the present paper and will be discussed elsewhere (*29*).

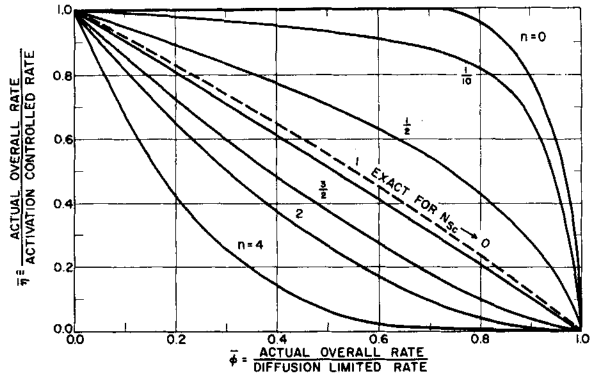

Fig. 8. Relation between the two global reaction rate coefficients $\bar{\Phi}$ and $\bar{\eta}$ for chemical surface reactions on catalytic plates of finite length.

APPLICATIONS

If the reaction were completely diffusion controlled everywhere along the catalyst, then the total reaction rate would be equal to the total rate of reactant diffusion through the laminar layer to the catalytic plate when $c_w = 0$:

$$\bar{R} \rightarrow 2\, N^*_{Sh_x} \cdot D \rho c_e \qquad (58)$$

The ratio of the actual rate to this limiting rate constitutes another important nondimensional coefficient $\bar{\Phi}$ which is related to the effectiveness factor $\bar{\eta}$ through

$$\bar{\Phi} \equiv \frac{\bar{R}}{2\, N^*_{Sh_x} D \rho c_e} = \bar{\mathcal{G}}_n \cdot \bar{\eta} \qquad (59)$$

This relation $\bar{\Phi}(\bar{\eta})$ is shown graphically in Figure 8. In a chemical kinetic study the use of the coefficient $\bar{\Phi}$ has the advantage that it can be calculated from observables if the Fick diffusivity D can be accurately estimated. A knowledge of the true reaction order then enables the determination of $\bar{\eta}$ and hence the falsification parameter E_a/E (Figure 4). When the diffusivity is not accurately known or estimable, the calculation of the coefficient $\bar{\Phi}$ from the observed rate data is precluded. Nevertheless the catalyst effectiveness factor could be determined by means of a triangle method of the type used in static systems (*30, 1*).

The basic technique is described below for a first-order surface reaction. One makes two rate determinations with the same catalyst by varying some physical (hydrodynamic) parameter such as the catalyst length or the free stream velocity. Since the dependence of the catalytic parameter $\mathcal{G}_1$ on hydrodynamic factors is known, the ratio of this parameter for the two experiments will be known. On a logarithmic plot the ratio $\mathcal{G}_{1,1}/\mathcal{G}_{1,2}$ represents a line segment of fixed length. From the ratio of observed reaction rates one can similarly calculate the ratio $\bar{\eta}_1/\bar{\eta}_2$ independent of any knowledge of the rate constant k. Again on a logarithmic plot of $\bar{\eta}(\mathcal{G}_1)$ the ratio $\bar{\eta}_1/\bar{\eta}_2$ represents a line segment of fixed length. These two line segments form a triangle which can be fitted to the $\bar{\eta}$ vs. $\mathcal{G}_1$ plot, resulting in the determination of $\bar{\eta}$ and $\mathcal{G}_1$ for each experiment. The actual rate constant k can then be obtained from either of the effectiveness factors $\bar{\eta}$ so determined. Thus the procedure outlined in reference *1* for determining the activity of porous catalyst pellets carries over, with minor modifications, to external flow systems. As in the case of porous catalysts the result is determinate only when the rate data is obtained in the regime of moderate diffusion effect, that is where the $\bar{\eta}(\mathcal{G}_1)$ plot is not asymptotically straight.

When the intrinsic reaction order n is not known beforehand, application of triangle method must be preceded by additional experiments in which the free stream reactant concentration is varied. In this case however, with an analogous approach, the relation between n_a/n and $\bar{\Phi}$ could readily be used to extract the true value of n. This would enable one to proceed with the triangle method for determining the true interfacial rate constant k as outlined earlier, thereby completing the description of the macroscopic kinetics of the interfacial rate process. It should be added in closing however that these possible applications are cited only as examples. By no means do they exhaust the methodological alternatives open to the experimentalist.

CONCLUSIONS

Boundary-layer flows are shown to form an important class of well-defined flow systems which a complete theoretical treatment of the role of physical

---

* It should be noted that gas/solid catalytic reactions ordinarily involve Schmidt numbers of unity or less. For turbulent boundary-layer flows the accuracy of the quasi-stationary method degenerates with increasing Schmidt number (*20*), since the bulk of the diffusion boundary layer becomes submerged within the laminar sublayer.

phenomena in determining the apparent kinetics of surface reaction is feasible (*31*). Between the chemically (activation) controlled and diffusion controlled extremes lies a transition regime within which the observed kinetics are determined by the intrinsic activity of the surface as well as hydrodynamic and diffusive parameters. From a study of the similitude properties of the boundary layer conservation equations this transition or exchange of control is shown to be governed by the magnitude of a nondimensional composite catalytic-diffusive parameter G_n of the form $G_n =$ (characteristic chemical rate at the interface)/(characteristic rate of diffusion to the interface). Two important nondimensional reaction rate coefficients $\bar{\eta}$ and $\bar{\Phi}$ depend upon the magnitude of this parameter. The coefficient $\bar{\eta}$ (the integrated catalyst effectiveness factor) may be regarded as a correction (to the activation controlled rate) for the effects of convective diffusion, becoming unity only when G_n becomes very small. Similarly the coefficient $\bar{\Phi}$ may be regarded as a correction (to the integrated diffusion limited rate) for the effects of finite catalytic activity, becoming unity only when G_n becomes very large. It is shown that general expressions, reminiscent of those applicable to static systems, can be derived relating the falsification of the activation energy and reaction order to a logarithmic derivative of the isothermal diffusion correction (effectiveness factor). Improved approximate solutions have been given for the case of the thin, nonturbulent diffusion layer which develops along an impermeable catalytic flat plate, applicable to arbitrary values of the true reaction order and diffusional Prandtl number. Comparisons with an exact solution to the boundary-layer equations and the well-known quasi-stationary method have been made for the special case of first-order surface reactions. Of the various quantities of interest in the diffusional theory of heterogeneous reactions in flow systems it is found that the accuracy of the Frank-Kamenetskii quasi-stationary approximation can become unacceptably poor for the calculation of the falsification of kinetic parameters. Arguments have been given which show that these errors should be most severe for laminar diffusion layers in small pressure gradient fields, particularly when the Prandtl number for diffusion, as well as the true reaction order, are small. Finally it is shown that solutions of the type presented can be applied to the experimental inference of chemical kinetic parameters (when a diffusion limitation is present) in much the same way as in static systems; specifically the triangle method of activity determination carries over (limitations included) almost without change to the case of catalytic reactions in external flow systems.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of F. Kuehner in carrying out the calculations presented herein. This research was supported in part by the United States Air Force Office of Scientific Research, Office of Aerospace Research, Air Force Systems Command, Propulsion Division, under Contracts AF 49(638)-300 and AF 49(638)-1138. The author is grateful to this agency for making this work possible.

NOTATION

c = mass fraction of reactant in fluid phase or c_w/c_e
G_n = catalytic-diffusive parameter for n^{th} order surface kinetics [Equation (6)]; $\bar{G}_n = G_n/2$
D = Fick diffusion coefficient (diffusivity)
E = activation energy
k = intrinsic chemical rate constant
k_a = $\eta\, k$
k_D = local diffusion velocity [Equation (24)]
L = characteristic dimension of catalyst
m = pressure gradient parameter (Euler number)
n = intrinsic reaction order
N_{Sh} = nondimensional mass transfer coefficient (Sherwood, or diffusional Nusselt number)
N_{Sc} = Schmidt number $\equiv \nu/D$ (diffusional Prandtl number)
R = universal gas constant
$\dot{R}''$ = mass rate of surface reaction (reactant consumption) per unit area
$\bar{\dot{R}}$ = total mass rate of reaction (one side of plate)
N_{Re} = Reynolds number
N_{St} = Stanton number [Equation (27)]
T = absolute temperature level
u = component of fluid velocity parallel to catalyst surface
U = approach velocity of fluid
v = component of fluid velocity normal to catalyst surface
x = coordinate (distance) along catalyst surface
y = coordinate (distance) normal to catalyst surface
z = stretched coordinate along catalyst surface
z_1 = dummy (integration) variable; [Equations (37) and (53)]

Greek Letters

α = thermal diffusivity $\equiv \lambda/(\rho\, c_p)$
δ = convective diffusion layer thickness [Equation (25)]
$\tilde{\delta}$ = $(\delta/L)(N_{Re})^{1/2}$
Δ = nondimensional convective diffusion layer thickness
ζ = vorticity = $\partial v/\partial x - \partial u/\partial y$ for two-dimensional flow
η = $\dot{R}''(x)/[k(\rho\, c_e)^n]$ = local diffusion correction
$\bar{\eta}$ = $\int_0^L \dot{R}''(x)dx/[k \cdot (\rho\, c_e)^n\, L]$ = isothermal catalyst effectiveness factor
Θ_w' = function describing dependence of N_{Sh} on N_{Sc}
λ = thermal conductivity of fluid
μ = dynamic viscosity of fluid
ν = μ/ρ = kinematic viscosity of fluid
ρ = mass density of fluid
τ = dummy (integration) variable
$\bar{\Phi}$ = nondimensional coefficient defined by Equation (59)

Subscripts

a = apparent (observed)
D = pertaining to molecular diffusion
e = at outer edge of boundary layer
n = pertaining to reaction order n
w = at surface (wall) of catalyst
x = based on the distance x
1, 2 = pertaining to experiments no. 1 and 2

Special Symbols

d = operator for ordinary differentiation
exp = exponential function
erfc = complementary error function
$*$ = pertaining to the trailing edge of the catalyst
ln = natural logarithm
Δ = change in (across the diffusion boundary layer)
∇^2 = Laplacian operator

LITERATURE CITED

1. Weisz, P. B., and C. D. Prater, "Advances in Catalysis," pp. 143-196, Academic Press, New York (1954).
2. Wise, H., and C. M. Ablow, *J. Chem. Phys.*, **29**, 634-639 (1958); see also Tsu, K., and M. Boudart, *Can. J. Chem.*, **39**, 1239-1246 (1961).
3. Heymann, H., *Z. physik. Chem.*, **81**, 204-222 (1913).
4. Frank-Kamenetskii, D. A., *Zhur. Fiz. Khim.*, **13**, 756-758 (1939).
5. Rosner, D. E., *AeroChem TP-14*, AFOSR TN 60-887 (September, 1959, Revised July, 1960).* Presented at the 1959 American Chemical Society—I/EC Symposium: "Mechanics of In-

---

* Copies of most AeroChem Research Laboratories Reports, when not available through the Armed Services Technical Information Agency, Arlington, Virginia, can be obtained by writing to the author.

terfacial Reaction," Johns Hopkins University, Baltimore, Maryland (December, 28-29, 1959).
6. ———, Ph.D. dissertation, Princeton Univ., Princeton, New Jersey (October, 1960), University Microfilms, Ann Arbor, Michigan, Order No. 61-4825 (Microfilm $5.00; Xerox $17.55).
7. Schlicting, Hermann, "Boundary Layer Theory," Pergamon Press, London, England (1955).
8. Blasius, H., *Z. Math. u. Phys.*, **56**, 1 (1908).
9. Rosner, D. E., *J. Aero/Space Sci.*, **26**, 281-286 (1959).
10. Polhausen, E., *Z. angew. Math. Mech.*, **1**, 115-121 (1921).
11. Levich, B. G., *Acta Physicochim., U.R.S.S.*, **17**, 257-307 (1942); *ibid.*, **19**, 117-138 (1944); *Zhur. Fiz. Khim.*, **18**, 335-355 (1944).
12. Eckert, E. R. G., *VDI Forschungsheft 416* (1942).
13. Merk, H. J., *J. Fluid Mech.*, **5**, 460-480 (1959).
14. Sparrow, E. M., and J. L. Gregg, *Natl. Aeronaut. Space Admin. Memo. 2-27-59E* (February, 1959).
15. Fisher, F. D., and J. G. Knudsen, *Chem. Eng. Progr. Symposium Ser., No. 29*, **55**, 209 (1959).
16. Evans, H. L., *Intern. J. Heat Mass Transfer*, **5**, 35-57 (1962).
17. Carberry, J. J., *A.I.Ch.E. Journal*, **6**, 460 (1960).
18. Chambré, P. L., and Andreas Acrivos, *J. Appl. Phys.*, **27**, 1322-1328 (1956); *Ind. Eng. Chem.*, **49**, 1025-1029 (1957).
19. Ambrok, G. S., *Soviet Phys.—Tech. Phys.*, **2**, 1979-1986 (1957).
20. Rosner, D. E., *Chem. Eng. Sci.* to be published.
21. Lighthill, M. J., *Proc. Roy. Soc. (London)*, **202**, 359-377 (1950).
22. Boussinesq, J., *Gauthier-Villars*, Paris (1903); *J. Math Pures Appl.*, **1**, 285 (1905); Mixon, F. O., and J. J. Carberry, *Chem. Eng. Sci.*, **13**, 30 (1960).
23. Rosner, D. E., *AeroChem TP-16*, AFOSR TN 60-690, ASTIA AD 237-929 (April, 1960).
24. ———, *AeroChem TM-18*, AFOSR TN 60-331 (November, 1959).
25. Carslaw, H. S., and J. C. Jaeger, "Heat Conduction," Oxford, London, England (1947).
26. Sunderland, J. E., and R. J. Grosh, Document 6157, American Documents Institute, ADI Aux. Public. Project Photodup. Service, Library of Congress, Washington 25, D. C. ($1.25 for photoprints).
27. Shaaf, S. A., and F. S. Sherman, *J. Aeronaut. Sci.*, **21**, 85-90 (1954).
28. Levy, S., *ibid.*, **19**, 341 (1952).
29. Rosner, D. E., *AeroChem TP*, to be published.
30. Hougen, O. A., and K. M. Watson, *Ind. Eng. Chem.*, **35**, 529-541 (1943).
31. Rosner, D. E., Chemical Engineering Monograph, to be published.

Manuscript received January 30, 1962; revision received July 25, 1962; paper accepted July 30, 1962. Paper presented at A.I.Ch.E. New York meeting.

Effective Interfacial Area in Packed Columns for Absorption with Chemical Reaction

FUMITAKE YOSHIDA and YOSHIHARU MIURA

Kyoto University, Kyoto, Japan

A number of theoretical studies have been reported on gas absorption accompanied by a chemical reaction since the pioneering work of Hatta (*9, 10*). However the method of designing the packed column for chemical absorption has not been well established, partly because of insufficient knowledge of the effective interfacial area for chemical absorption. In the present work the effective interfacial area for chemical absorption was evaluated from data on absorption of carbon dioxide into aqueous solutions of sodium and potassium hydroxides in a packed column and in a bead column, that is a column of spheres connected in a vertical row. Theoretical relationships for the reaction factor, the ratio of the coefficient for chemical absorption to that for physical absorption, were confirmed. Physical absorption experiments were also performed to obtain the necessary data on the mass transfer rates in the liquid and gas phases.

EXPERIMENTAL

The setup of the apparatus for the physical absorption experiments was similar to the one reported elsewhere (*30, 31*). Figure 1 shows a schematic diagram of the apparatus for the chemical absorption experiments with the bead column. Carbon dioxide from a cylinder was absorbed into water in the saturating column, and the gas was stripped from the solution by air in the stripping column to give an air-carbon dioxide mixture of a given composition, which could be varied by controlling the rate of water to the stripping column. The bead column consisted of a jacketed glass tube, 40 mm. I.D. and a vertical row of porcelain spheres connected with a stainless steel wire at the axis of the column. Thirty 1-in. spheres, with 4-mm. clearances between adjacent spheres, and sixty ½-in. spheres, with 2-mm. clearances, were used. The temperature of the liquid through the bead column was controlled by means of the liquid feed preheater and the column jacket, through which water from a thermostated tank was passed.

The apparatus for the packed column experiments was similar to the one shown in Figure 1 except for the use of a packed column in place of the bead column. The packed column, made of glass, was 12.1 cm. I.D. and was packed with 1-in. and ½-in. porcelain Raschig rings to a

---

Yoshiharu Miura is at Himeji Technical College, Himeji, Japan.