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Convective Diffusion as an Intruder in Kinetic Studies of Surface Catalyzed Reactions

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Nomenclature

a = radius of circular disk
A,B,C = individual chemical species
c = mass fraction of reactant in fluid phase
c_0 = mass fraction of reactant at beginning of active section
$\hat{c}$ = c_w/c_∞, Eq (3 20)
$\bar{\mathfrak{C}}_n$ = catalytic parameter for nth order surface reaction, Eq (2 12)
c_p = heat capacity of carrier fluid
d = diameter of tubular reactor
D = Fick molecular diffusion coefficient, Eq (2 1)
$D^{(t)}$ = eddy diffusivity for species transport, Eq (2 1)
D_0 = pre exponential factor, Eq (2 7)
E = activation energy, Eq (2 6)
E = dimensionless universal eddy diffusivity distribution, Eq (4 12)
E_a = apparent activation energy, Eq (2 16)
E_D = parameter describing temperature dependence of D, Eq (2 7)
E_ν = parameter describing temperature dependence of ν, Eq (2 8)
F = dimensionless universal axial velocity profile, Eq (4 11)
H = dimensionless transverse velocity distribution, Eqs (3 1) and (3 12)
$-j''$ = diffusional mass flux of reactant toward interface per unit area, Eq (2 2)
K = function defined by Eq (3 17)
k_w = intrinsic chemical rate constant, Eq (2 4)
k_a = apparent rate constant, Eq (2 15)
k_0 = pre-exponential factor in Arrhenius equation, Eq (2 6)
L = characteristic length, e g , length of catalytic plate
l = parameter in the diffusional driving force law $\vartheta_e \propto x^l$
$\overline{Nu}$ = $\overline{Nu}_D$ unless otherwise specified
$\overline{Nu}_\lambda$ = nondimensional average heat transfer coefficient
$\overline{Nu}_D$ = nondimensional average diffusional-transfer coefficient
$\dot{m}''$ = net mass-transfer rate away from interface
n = true reaction order, Eq (2 4)
n_a = apparent reaction order, Eq (2 18)
p = parameter in Eq (3 19)
Pr = Pr_D unless otherwise specified
Pr_λ = Prandtl number for heat conduction, ν/α Eq (5 1)
Pr_D = Prandtl number for diffusion, ν/D
Q = heat release per unit mass of reactant, Eq (5 2)
q = parameter in Eq (3 19)
$\mathbf{r}$ = position vector
r = radial coordinate
r_0 = radius of coated portion of disk
R = universal gas constant, Eq (2 6)
R'' = local rate of reaction per unit area, Eq (2 3)
$\bar{R}$ = over-all rate of reaction for surface area S
Re = Reynolds number = $U_\infty x/\nu$, $U_\infty L/\nu$, or Ud/ν
r_D = recovery factor for chemical energy, Eq (5 1)

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S = total wetted surface area, Eq (2 15)
St = Stanton number = $Nu/(Re\,Pr)$
T = absolute temperature
U_∞ = approach velocity of fluid at upstream infinity
U = average axial velocity within reactor
v_x = component of fluid velocity along x axis of tubular reactor
v_y = component of fluid velocity normal to catalyst surface, Eq (3 1)
x = longitudinal coordinate
y = transverse coordinate
z = stretched nondimensional coordinate, Eq (3 21)
α = thermal diffusivity of carrier fluid, $\lambda/(\rho c_p)$
β = heat release parameter, Eq (5 4)
β = inviscid velocity gradient at forward stagnation point, Eq (3 12)
γ = activation energy parameter, Eq (5 4)
δ = convective diffusion-layer thickness, Eqs (3 3, 3 4, and 3 13)
ϵ_w = total hemispheric emittance of surface, Eq (5 6)
ζ = dummy variable, Eq (3 19)
η = local catalyst effectiveness factor $\equiv R''/R''_{\mathrm{h\ m}}$
$\bar{\eta}$ = global catalyst effectiveness factor, Eq (2 10)
ϑ_e = local diffusional driving force, $\vartheta_e \equiv c - c_w$
θ = dimensionless residence time in reactor, Eq (4 10)
Θ = normalized concentration excess variable, $(c - c_w)/(c - c_w)$
λ = thermal conductivity of carrier fluid
μ = dynamic viscosity of carrier fluid
ν = kinematic viscosity of carrier fluid
ν_0 = pre-exponential factor, Eq (2 8)
ξ = dummy variable, Eq (3 4)
ξ = upstream position of sudden change in driving force, Eq (3 16)
ρ = fluid density
σ = Stefan-Boltzmann radiation constant, Eq (5 5)
τ_w = shear stress at wall, Eqs. (4 11) and (4 12)
ϕ = local correction for finite catalyst activity $\equiv R''/R''_{\mathrm{diff}}$
$\bar{\phi}$ = global correction for finite catalyst activity, Eq (2 11)
ω = rotational speed of disk, Eq (3 1)

Subscripts

a = apparent (observed)
b = pertaining to bulk (flow rate-averaged) value
D = pertaining to diffusion
e = at the outer edge of the boundary layer
eq = pertaining to local thermochemical equilibrium
n = pertaining to reaction order n
w = at the wall (surface of catalyst)
λ = pertaining to heat transfer
∞ = at upstream infinity
chem = pertaining to chemical control
diff = pertaining to diffusion control
iso = pertaining to constant diffusional driving force
loc = local value
1 = integration variable

1 Introduction

FORCED convection flow systems are frequently used to study the kinetics of fast heterogeneous reactions, since improved rates of reactant transport make it difficult for the active surface to become "reactant starved" (i e , induce appreciable local concentration gradients) However, in most cases the conditions of convective transport are not uniform at all points along a catalytic surface, and, for sufficiently active catalysts (e g , at sufficiently high surface temperatures), local reactant depletion can cause the apparent (observed) kinetics of the surface reaction to differ drastically from the true kinetics Thus, although one is usually interested in the true activity k_w, the true activation energy E, and the true reaction order n, these parameters will not be obtained as the temperature level and freestream reactant concentration are intentionally changed Fortunately, however, in many well-defined flow systems the magnitude of this falsification is predictable, so that diffusional effects can be removed from kinetic measurements made in the intermediate regime where both the chemical kinetics and diffusion govern the observed reaction rates This paper reviews the current state of knowledge in this regime and outlines chemical kinetic and aerodynamic applications of available theory as well as areas in need of further development

1 1 Phenomenological Heterogeneous Catalysis

The term heterogeneous in chemical kinetics refers to reactions occurring at interfaces, i e , phase boundaries In this review we shall deal primarily with the apparent kinetic behavior of gas/solid and liquid/solid interfaces in flow systems where the active solid represents either a confining surface (i e , the internal problem) or the surface of a completely immersed body (i e , the external problem) The term *catalysis* implies that the extent of the active surface's participation in the chemical reaction is severely limited since, strictly speaking, the products of a heterogeneously catalyzed reaction cannot include atoms that were originally bound in the lattice of the catalyst itself Thus, neither the catalyst's bulk properties nor its gross external geometry are changed by virtue of the chemical reaction

Since a catalytic solid cannot initiate a chemical reaction that is thermodynamically impossible, we must, in general, expect simultaneous chemical change to occur in the fluid or homogeneous phase without the participation of the catalyst However, it is frequently true that the eligible homogeneous reactions proceed at rates that are simply negligible by comparison to the surface reaction The interface may then be singled out as effectively the site of all of the chemical change in the system, and we therefore look to conditions at the interface as governing the "velocity" of change However, observational techniques are insufficiently refined to follow the course of each participating atom or molecule throughout its entire reaction history on the surface What occurs at this microscopic level must usually be inferred from what can be readily observed, such as the temperature and concentration dependence of the over-all reaction rate

Therefore, if the relative slowness of reactant transport to the catalytic surface causes the reactant concentrations to be locally depleted, this already difficult task becomes further complicated To the chemist interested in the interfacial reaction itself, diffusion will be seen to be a skillful falsifier and certainly an undesired intruder For this reason, every attempt is made to carry out experiments on the kinetics of heterogeneous reactions under a set of conditions which relegates diffusion effects to a small or negligible correction It is then important that we have available both a priori theoretical criteria for use in the design of such experiments and simple a posteriori experimental tests for the absence of the effects of external transport phenomena However, it must not be concluded that kinetic information cannot be obtained in the presence of a simultaneous diffusional limitation This is quite important, because the extreme in which diffusional transport is sufficiently rapid to play no role in the observed kinetics is not always experimentally accessible, even in forced convection flow systems Interpretable kinetic experiments can be carried out in certain well-defined flow systems for which the magnitude of the diffusional effect is accurately calculable

1 2 Importance of Flow Systems in Kinetic Studies

Although the advantages of flow reactors for carrying out catalytic processes on an industrial scale were recognized immediately, the acceptance of flow reactors for carrying out small-scale fundamental kinetic studies has been more gradual However, current theoretical and practical interest in reactions that are too fast to study by conventional means is inevitably leading to the widespread use of flow systems in kinetic investigations These flow systems take diverse forms For the purposes of this brief review, however, they may be broken down into two broad categories depending on whether the chemically active fluid/solid interface is moving or at rest in a laboratory coordinate system In the first class, the solid under investigation may be mechanically rotated in the reactant containing fluid or may be falling through it, for example, under the action of gravity In the second class, sometimes referred to as fixed catalytic systems, are to be found steady flow reactors (in which the reactant containing fluid flows past or through the catalyst under study) as well as batch reactors where fluid agitation is accomplished by means of some mechanical stirrer or agitator Particularly when transport phenomena cannot be completely avoided, it is important that the investigator understand the fluid mechanics of his system since, in the absence of convective transport information, it will not be possible to extract true kinetic data from such experiments or to generalize the data to apply to different situations

In the design of experiments one has, therefore, two alternatives The first consists of attempting to calibrate out these transport phenomena by, say, first studying the behavior of a reaction that is known to be completely diffusion controlled and then bringing these data to bear on an intermediate regime reaction carried out in the same reactor The second alternative is to obviate the need for an experimental calibration by choosing a class of reactors in which the convective transport situation is well understood theoretically It would appear that each of these alternatives has merits of its own; however, it will be shown that for most flow systems a simple calibration procedure previously implied is, in fact, inadequate, particularly if one is interested in inferring the true kinetic parameters characterizing the reaction Although the appropriate calibration is within the realm of possibility, its complexity makes this a research project in itself One is therefore led to adopt a geometry in which this calibration has in a sense already been carried out, either theoretically or experimentally Thus, for example, one can use the information presented in the following sections to extract kinetic parameters accurately from experiments carried out in the intermediate regime in which transport phenomena are not negligible; indeed, it is possible simultaneously to infer transport parameters (such as the diffusion coefficient for the reactant) that may be difficult to obtain by other methods

1 3 Historical Background

In 1904 an apparently general theory of reaction velocity in heterogeneous systems was set forth[6 51 52] Developing an idea first advanced by Noyes and Whitney[54] (1897) to account for the results of dissolution experiments, Nernst and Brunner postulated that interfacial reactions are fast enough to cause the over-all reaction rate to be limited by the rate at which reactants can diffuse across an effectively stagnant film of thickness δ_N, subsequently called the Nernst film or Nernst layer The consequences of this postulate were readily deduced and compared with experiment Three of the most important implications are 1) the apparent kinetics should be first order with respect to bulk reactant concentration, i e , the rates should depend linearly on this concentration; 2) the temperature dependence of the observed reaction rate should be characteristic of a molecular diffusion process and not that of a chemical reaction; and 3) fluid-dynamic effects on the rate of reaction, i e , the effects of agitation, stirring, feed rate, turbulence, etc , should occur by virtue of their effects on the effective diffusion film thickness δ_N alone

In discussing this theory it should be recognized that, as stated, it constituted a qualitative theory, amounting essentially to a dimensional analysis based on the original postulate, i e , no means of calculating the effective diffusion-layer thickness from first principles was, in fact, suggested In the years immediately following its formulation, the theory served as the target for a relentless series of critical papers[8 42–47 93] Excellent reviews of this material have been given by Levich[42] and by Bircumshaw and Riddiford[4] Fundamentally, the critical papers could be divided into two schools Contributors in the first school accepted the essential Nernst-Brunner idea but were unhappy with the oversimplification of a "stagnant" layer, particularly in the face of evidence on the detailed structure of viscous fluid layers near solid surfaces which was accumulating since the groundbreaking research of Prandtl[82] On the other hand, those in the second school produced surface reactions that were either paradoxes or that displayed inconsistencies They suggested that, although the theory was sometimes valid, more often it was not Conceptually, the second category of objections is more significant, since the cornerstone of the Nernst-Brunner theory is the notion of diffusion control; to be dissatisfied only with the notion of stagnant layer is, in fact, merely to be dissatisfied with numerical values However, the theory was qualitative to begin with, and dimensional analysis cannot supply absolute values Therefore, this criticism of the Nernst-Brunner theory led only to more rigorous quantitative formulas for the effective diffusion-layer thickness in particular cases[42 93 111]; the "diffusion-controlled consequences" remained essentially unaltered On the other hand, the second group displayed a number of important catalytic reactions upon which hydrodynamic factors exerted virtually no influence at all Temperature coefficients were observed which exceeded anything that could reasonably be attributed to diffusion processes alone Reaction orders not equal to unity were also cited, and, even in those cases for which the apparent order was unity, it was cautioned that this by itself did not necessarily confirm the Nernst-Brunner theory, i e , there are indeed first-order surface reactions Haber[24] remarked that the Nernst-Brunner theory "teaches us, then, how the rate of diffusion is determining the velocity when other influences are excluded " He added that the theory "by no means shows that the chemical velocity must be great as compared with the diffusional velocity but instead, when rightly considered, leaves the point wholly undecided " Heymann[29] in 1913 was among the first to make a rational attempt at quantitatively reconciling the apparent contradictions just cited He, as had Haber,[24] Van Name,[92] and others, correctly reasoned that the Nernst-Brunner mechanism must be a limiting case Heymann's method of generalizing the diffusional theory to include an intrinsic chemical rate constant was imaginatively exploited and extended to flow systems of practical interest about three decades later by Frank-Kamenetskiĭ[21] As a result, in the theory of heterogeneous reactions, the so-called *quasi-stationary method* is commonly attributed to him According to this view, a steady-state reactant concentration c_w is quickly established at the surface such that the rate of diffusional transport to the surface, which is taken to be proportional to the local or instantaneous concentration difference $c - c_w$ across the diffusion layer, is identically equal to the chemical rate of conversion at the interface The latter is, in turn, usually proportional to some power n of the reactant concentration c_w, where n is the reaction order The method is extremely simple to use but is seductive in that, when it is applied to flow systems, one is tempted to introduce a coefficient of diffusional transport which has been experimentally or theoretically determined in the absence of surface reaction[21] Indeed, this is the *suggestion* of Frank-Kamenetskiĭ[21] However, for developing flows in which chemical change is occurring in the streamwise direction, the problem of determining the actual local coefficient of diffusional transport is strictly coupled to the kinetics problem Thus, the error one makes in applying the quasi-stationary method will depend on chemical kinetic as well as fluid-dynamic parameters Rigorous attacks on this particular problem awaited advances in boundary-layer theory and were independently reported by Levich and Meiman,[47] Chambré and Acrivos,[1 9] and others Because of the increasing importance of flow systems in kinetic studies and the longstanding importance of flow systems in technical operations, a reasonably unified presentation of some recent theoretical developments is in order, particularly since these developments have been the result of research in many disciplines where the goal and points of view have been widely different Although the chemist has been interested in how convective diffusion influences the apparent kinetics of rapid surface reactions, the fluid dynamicist is often concerned with the perturbing effects of the kinetics of surface reactions on such quantities as heat-transfer rates The two groups often find themselves entering the transition region but through different doors, as it were—the former from the chemically controlled side, the latter from the diffusion controlled side It should also be kept in mind that mathematical analogs of the convective diffusion-surface reaction problem exist,[66 68 76] particularly in the fields of convective heat transfer and rarefied gasdynamics (cf Sec 5 6) Thus, not only are the mathematical methods of these fields of interest here, but the boundary-value-problem solutions themselves will often be seen to be directly applicable, requiring only trivial notational changes

In each case presented below the quantitative relations provided by the theory can and should be used in many distinct ways In typical *design* applications, one presumes an independent knowledge of the kinetics and some physical parameters and perhaps calculates the required catalyst size, geometry, or flow rate to accomplish the desired amount of chemical reaction On the other hand, in applications to the problem of kinetic *analysis*, the relations can be used to transform accessible measurements into meaningful kinetic parameters characterizing the reactant/surface system Thus, it should be remembered that, in practice, one or more of the parameters usually prescribed in the examples below may not be known, but several of the parameters computed will be accessible to direct measurement By suitably combining the analysis with experiment, one can then extract fundamental macroscopic parameters of interest We will deliberately focus our attention on several tractable yet realistic examples, but the principles and methods elucidated by these examples indeed carry over to more complex geometries, and for this reason some attempt has been made to express the results in a form applicable to such cases Scaling properties of solutions are emphasized throughout, since these properties reveal the kind of correlations apt to be useful in more complex cases as well The external flow configurations dealt with in Sec 3 include the rotating disk in laminar flow, the forward stagnation point, and, finally, the flat plate aligned with the flow In Sec 4, internal flow configurations are described with attention to tubular reactors in which the fully developed flow is either laminar or turbulent In each of the preceding cases it is assumed that either 1) a negligible amount of heat is released in the surface reaction or 2) provision has been made by some external means to withdraw precisely the amount of heat generated by the surface reaction Thus the systems considered in Secs 3 and 4 will be isothermal in the forementioned sense In Sec 5, nonisothermal effects attributable to the exothermicity of chemical surface reactions will be briefly described, together with applications of these effects in the chemical analysis of mixtures Section 5 concludes with remarks on the occurrence of spatially nonuniform catalyst activity, sequential reactions, the effects of reactions in the fluid phase as well as on the surface, the effects of mass transfer at surfaces that are not strictly catalytic, and, finally, analogies between chemical surface catalysis and other problems in heat-transfer theory

2 Mathematical Model

2 1 Basic Assumptions

We will limit ourselves to the simplest class of problems exhibiting the basic interaction between convective transport and chemical surface catalysis In some respects, generalizations to more complicated cases will be relatively straightforward; however, in many instances these extensions constitute new research problems in themselves Although the discussion will be generally applicable to liquid/solid or gas/solid systems, some of the underlying assumptions will be seen to be more restrictive than others as to the range of validity of the results for either liquids or gases Thus, let us consider steady flows of incompressible carrier fluids over impermeable catalytic solids Contained in the carrier fluid is a reactant present in dilute amounts, as measured by its mass fraction c, which will be everywhere considerably less than unity The catalyst is considered to be the site of all chemical change in the system, so that in the absence of the catalyst the concentration of reactant would be constant in both time and space * Implicit in the diluteness assumption is the property that the fluid motion is unaffected by the presence of reactant diffusion and chemical surface reaction, so that the fluid motion is obtainable directly from experiments in the absence of reaction or from an independent study of the equations of over-all continuity and motion For laminar flows, only concentration (Fick) diffusion is considered, and the pertinent diffusion coefficient D is taken to be a scalar quantity independent of the reactant concentration itself For turbulent flows, the effective diffusion coefficient will be greater than D by an amount $D^{(t)}$, which will, in general, be position-dependent in accord with the local condition of turbulence

2 2 Conservation Equations

Subject to these assumptions, the steady-state concentration field $c(\mathbf{r})$ will satisfy the species conservation equation[5]:

$$\mathbf{v} \quad \mathbf{grad}\, c = \mathrm{div}\{[D + D^{(t)}]\, \mathbf{grad}\, c\} \qquad (2\ 1)$$

where $\mathbf{v}$ represents the local fluid mass-averaged and time-averaged velocity At the surface of the catalyst, $\mathbf{v}$ vanishes identically since there is no slip, and there is no *net* mass transfer across the interface This implies that the mass rate of reactant transport to a unit area of surface $y = 0$ is given by

$$-j'' = D\rho(\partial c/\partial y)_{y=0} \qquad (2\ 2)$$

This local rate of diffusional transport must be identically equal to the rate of reaction for this species as given by a phenomenological chemical kinetic rate law of the form

$$R'' = R''(\rho c_w, T_w, \text{surface}, \quad) \qquad (2\ 3)$$

where we will limit this discussion to cases for which Eq (2 3) is well represented by the simple power law form

$$R'' = -k_w \ (\rho c_w)^n \qquad (2\ 4)$$

Here k_w is called the *intrinsic chemical rate constant* for the reaction/catalyst in question, and n is the corresponding *true reaction order* For first-order surface reactions ($n = 1$), k_w will be seen to have the dimensions of velocity (centimeters per second) In heterogeneous catalysis, values of n between 0 and 2 are of particular interest, with most reactions falling in the range between 0 and unity Thus, the boundary

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* For boundary-layer flows, this implies the equivalence of c_∞ (the reactant concentration at upstream infinity) and c (the reactant concentration at the outer edge of the boundary layer) Thus c_∞ and c may be used interchangeably throughout this paper

condition on the concentration field may be written as

$$D\rho(\partial c/\partial y)_{y=0} = k_w\ (\rho c_w)^n \qquad (2\ 5)$$

which is nonlinear unless $n = 0$ or unity The use of the molecular diffusion coefficient D in the foregoing relation implies that 1) the turbulent contribution $D^{(t)}$ is negligible at the fluid/solid interface, and 2) the reaction product does not itself limit the forward rate of reaction, say, by influencing the local magnitude of the coefficient for reactant diffusion through the local mixture The absence of a "back" reaction term for the reactant in Eq (2 4) implies that conditions existing at the interface are far removed from local thermochemical equilibrium,[61] i e , $c_w \gg c_{w,\mathrm{eq}}(T_w;\ p)$

Not only is the magnitude of the rate constant k_w of interest in a chemical kinetic investigation, but also its temperature dependence In many cases, this dependence is well represented by the simple two-parameter Arrhenius relation

$$k_w = k_0 \exp[-E/(RT_w)] \qquad (2\ 6)$$

where k_0 is a constant for the reactant/catalyst system under investigation and E is the *true activation energy* for the reaction The ratio of E to the universal gas constant R may be considered to be a characteristic temperature for the reaction/catalyst system, and this temperature is, in most cases, considerably larger than the actual surface temperature level T_w Thus the rate "constant" k_w is usually strongly dependent on catalyst surface temperature This is not true for the temperature dependence of the effective Fick diffusion coefficient D or of the fluid kinematic viscosity ν For low-density gases, simple kinetic theory reveals that these quantities increase as about the $\frac{3}{2}$ power of the absolute temperature In contrast, for most liquids both D and ν are themselves[69] exponential functions of temperature, i e ,[42]

$$D = D_0 \exp[-E_D/(RT)] \qquad (2\ 7)$$

$$\nu = \nu_0 \exp[E_\nu/(RT)] \qquad (2\ 8)$$

However, the corresponding characteristic temperatures E_D/R and E_ν/R are very frequently smaller than E/R The consequences of this fact are discussed in Sec 2 4

In Secs 3 and 4 we will restrict ourselves to systems in which the temperature level is uniform throughout Experimentally, this can be accomplished even for surface reactions that are not thermoneutral by sufficiently diluting the reactant/carrier fluid mixture If this condition is not met, then the catalyst temperature (and hence k_w) may become nonuniform and different from the supply temperature; the steady-state reaction rate will thus become dependent upon conditions of heat exchange as well as diffusional transport (cf Sec 5 2)

2 3 Similitude Properties[42 62 65 71 74]

Dimensional analysis reveals that, in addition to the parameters $Re \equiv U_\infty L/\nu$ (Reynolds number based on characteristic velocity U_∞ and length L) and $Pr = \nu/D$ (diffusional Prandtl number) which occur in any convective diffusion problem for a given configuration (shape), two new parameters now enter the isothermal problem discussed here, namely,

$$k_w\ (\rho c_\infty)^n/[D\ (\rho c_\infty)/L] \quad \text{and } n \qquad (2\ 9)$$

Thus, the actual over-all reaction rate $\bar{R}$ will be related to the reaction rate $\bar{R}_{\mathrm{chem}}$ corresponding to no transport effects by an equation of the form

$$\bar{R}/\bar{R}_{\mathrm{chem}} \equiv \bar{\eta}\left(k_w\ (\rho c_\infty)^{n-1}L/D;\ n, Re, Pr, \text{shape}\right) \qquad (2\ 10)$$

where $\bar{\eta} \to 1$ when its first argument approaches zero

Alternatively, the actual over-all reaction rate $\bar{R}$ will be related to the reaction rate $\bar{R}_{\mathrm{diff}}$ corresponding to diffusion control ($c_w = 0$ everywhere) by an equation of the form

$$\bar{R}/\bar{R}_{\mathrm{diff}} \equiv \bar{\phi}\left(k_w\ (\rho c_\infty)^{n-1}L/D;\ n, Re, Pr, \text{shape}\right) \qquad (2\ 11)$$

where $\bar{\phi} \to 1$ when its first argument approaches infinity

Since the average Nusselt number $\overline{Nu}_{\mathrm{iso}}$ for the same configuration† is a function of Re and Pr alone, with no loss in generality, the first of the two new parameters [cf Eq (2 9)] may be replaced by

$$\bar{\mathfrak{C}}_n \equiv k_w\ (\rho c_\infty)^n L/[\overline{Nu}_{\mathrm{iso}}(Re, Pr)D\ (\rho c_\infty)] \qquad (2\ 12)$$

where $\bar{\mathfrak{C}}_n$, the basic nondimensional group characterizing this class of problems, has the evident interpretation of being the characteristic rate of interfacial reaction divided by characteristic rate of convection diffusion

It will be seen that, in several cases, apart from their appearance in $\bar{\mathfrak{C}}_n$, the explicit dependence of the nondimensional reaction rate coefficients $\bar{\eta}$ and $\bar{\phi}$ on Re and Pr is negligible, so that one then has the useful similitudes

$$\bar{\eta} = \bar{\eta}(\bar{\mathfrak{C}}_n;\ n) \qquad (2\ 13)$$

$$\bar{\phi} = \bar{\phi}(\bar{\mathfrak{C}}_n;\ n) \qquad (2\ 14)$$

Such relations, as a matter of fact, are not very shape dependent (cf Secs 3 and 4)

2 4 Falsification of Kinetics[59 71 74 78]

For very small values of the basic dimensionless group $\bar{\mathfrak{C}}_n$, the reaction rate $\bar{R}$ will be very close to its maximum value $\bar{R}_{\mathrm{chem}}$, since, owing to the slow interfacial reaction and the favorable conditions of convection, the reactant concentration c_w at the fluid/solid interface will be everywhere negligibly different from the concentration c_∞ existing in the supply system For intermediate values of $\bar{\mathfrak{C}}_n$, the steady-state reactant concentration c_w will drop below that existing in the supply system, and this is associated with a reduction of the over-all reaction rate $\bar{R}$ to a value less than $\bar{R}_{\mathrm{chem}}$ (i e , $\bar{\eta} < 1$) If one were unaware of this reactant depletion effect, the chemical surface reaction would appear to be characterized by a (smaller) rate constant

$$k_a = \bar{R}/[(\rho c_\infty)^n\ S] = \bar{\eta} k_w \qquad (2\ 15)$$

where S is the wetted area of the catalyst However, in practice, it would soon become evident that one was not measuring a chemical kinetic property of reactant/catalyst system, since, even at constant surface temperature, the apparent rate constant k_a would depend upon the conditions of convective diffusion (through $\bar{\eta}$) The relative values of the activation energies E, E_ν, and E_D discussed earlier imply that, even if the diffusion-reaction parameter $\mathfrak{C}_n$ is much smaller than unity at one surface temperature level, this may not be true at a somewhat higher surface temperature because of the large increase in the specific rate constant k_w This has important implications for experiments designed to obtain the value of the true activation energy E, particularly at elevated surface temperatures As is well known, one typically does this by constructing a so-called Arrhenius plot of the observed reaction rate data (cf solid curve on Fig 1) in which $\ln\bar{R}$ is displayed (cf asymptote) as a function of $1/T_w$ and the slope is taken to be‡ $-E/R$ But if the actual rate $\bar{R}$ is different from $\bar{R}_{\mathrm{chem}}$, then the *apparent activation energy* E_a so determined will be less than the true activation energy E, and, moreover, E_a will depend upon conditions of convective diffusion For $E/R \gg T_w$, the previous definitions imply

$$E_a/E = 1 + (\partial \ln\bar{\eta}/\partial \ln\bar{\mathfrak{C}}_n) \qquad (2\ 16)$$

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† The subscript "iso" will be used to denote quantities pertaining to a flow configuration in which the driving force ϑ for the diffusion of species or heat is independent of position along the surface

‡ Actually, in a gas/solid catalytic system, the dependence of density level on temperature at fixed total pressure implies that the slope of this plot will rigorously equal $-E/R$ only if $E/R \gg T_w$ or if the reaction is of zeroth order

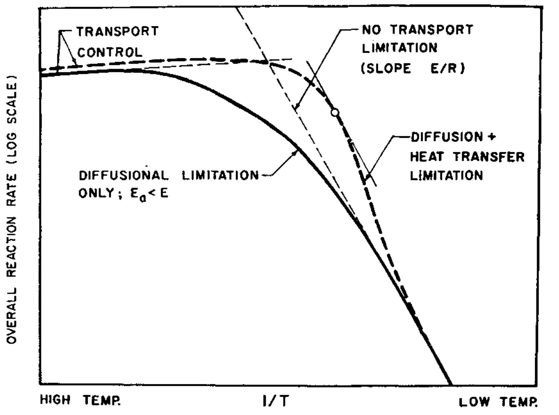

Fig 1 Arrhenius plot of observed reaction-rate data

and, owing to the properties of the $\bar{\eta}(\bar{\mathfrak{C}}_n,n)$ relation, it will be seen that E_a may be identified with E only in the limit $\bar{\mathfrak{C}}_n \rightarrow 0$, whereas $E_a \rightarrow 0$ as $\bar{\mathfrak{C}}_n \rightarrow \infty$ One can correct for the effect of convective diffusion in activation energy measurements only if the dependence of $\bar{\eta}$ on $\bar{\mathfrak{C}}_n$ is known and if the value of $\bar{\eta}$ is determined The relation between $\bar{\eta}$ and $\bar{\mathfrak{C}}_n$ is obtainable from the theory; hence an experimental determination of this correction is, in fact, possible for the systems to be described below It should be remarked that, if thermochemical effects are not negligible, the Arrhenius plot can display the behavior represented by the dashed transition curve of Fig 1 In such situations the apparent activation energy E_a can actually exceed the true activation energy, a situation that will be discussed in greater detail in Sec 5

A corresponding falsification of reaction order is caused by a diffusional limitation, for if the reactant concentration c_∞ is deliberately changed, the reactant/catalyst system will appear to be characterized by a reaction order[71 74]

$$n_a \equiv \partial \ln\bar{R}/\partial \ln(\rho c_\infty) \qquad (2\ 17)$$

This *apparent reaction order* is, in general, different from the true reaction order n As in the derivation of Eq (2 16), the definitions given here lead to the simple quantitative relation

$$n_a = n + (n - 1)(\partial \ln\bar{\eta}/\partial \ln\bar{\mathfrak{C}}_n) \qquad (2\ 18)$$

where the second term vanishes identically for first-order surface reactions Indeed, convective diffusion tends to make all chemical surface reactions look like first-order reactions, i e , in the limit $\bar{\mathfrak{C}}_n \rightarrow \infty\ (\bar{\phi} \rightarrow 1)$ the apparent order, n_a approaches unity Using Eq (2 18), the dependence of n_a/n on the conditions of convective diffusion can be obtained from the theoretical results outlined below; hence, experimental measurements complicated by diffusional effects can nevertheless be used to extract the true value of the reaction order when the latter is different from unity

Almost each property presented in this section has a parallel in the theory of surface reactions *within* porous catalyst pellets[31 88 95 100] Solid catalysts are often used commercially in the form of granular pellets with the active material supported on a porous carrier and distributed throughout the pellet In this case diffusional effects within the pellet can be quite important, since a highly active catalyst will cause entering molecules to react before they can diffuse very far into the pellet The concentration of reactant thus falls off sharply in the interior, and, as a result, these regions cannot make their full contribution to the over-all reaction rate Owing to the work of Thiele,[88] Zeldovich,[100] Wheeler,[97] Hougen,[31] and others who followed in their path, it is now well established that the intervention of transport phenomena can lead one far astray in the interpretation of reaction rate data for high-surface-area, active catalysts Although quantitative theories are available for predicting the magnitude of these effects in catalyst pellets of simple form, known activity, and known pore structure, the parameters appearing in these theories are, more often than not, only inaccurately known to the experimenter Consequently, where possible, experimental determinations of reaction models are carried out on the exterior surfaces of impermeable pellets or in pellets that are small and/or permeable enough to be unaffected by the slowness of internal diffusional transport Of course, even in the former case one is not guaranteed of the absence of external diffusional limitations, as will be illustrated by the examples of Sec 3 Perhaps the most important qualitative difference between the internal and external diffusional problems arises because, for internal diffusion, chemical reaction occurs during the diffusional process, whereas, for external diffusion, chemical reaction occurs subsequent to diffusion This profoundly affects corresponding properties of the respective "diffusion controlled extremes," as illustrated by the fact that the apparent activation energy E_a approaches $E/2$ for pore diffusion control, whereas E_a approaches a value that can bear no relation to E for external diffusion control

3 External Flow Configurations

Although it is clear that the rates of diffusional transport can be enhanced by turning to systems with forced flow or some kind of mechanical agitation, more often than not the systems of greatest practical interest are precisely those which defy accurate theoretical treatment Thus, although it is possible to extract some general a priori conclusions about transfer rates in mechanically stirred reactors or, say, packed bed flow reactors, formidable mathematical obstacles stand in the way of making accurate predictions of the absolute value of transfer rates However, there also exists a class of flow systems which can now be said to be so well understood that theoretical predictions are more frequently used to test the validity of experimental measurements than vice versa It is this latter class of well-defined flow systems with which we shall concern ourselves here, since its very existence has had profound implications not only in fluid mechanical research per se but also in the field of transport theory and experimental chemical kinetics

As is well known, the fundamental conservation laws of continuum fluid mechanics were cumulatively formulated by Euler, Fourier, Poisson, Stokes, Navier, and others during the eighteenth and nineteenth centuries[5 82] The time lag between their formulation and the deduction of useful numerical consequences for nontrivial flow fields may be traced to the presence of nonlinear terms in these partial differential equations However, important classes of solutions have been discovered by the method of combination of variables This method reduces the computational problem to the more tractable one of numerical integration of one or more ordinary

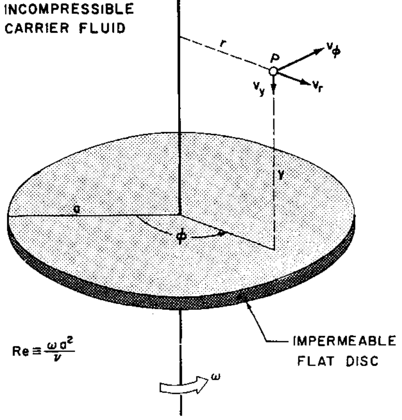

Fig 2 Rotating disk configuration

differential equations and will be illustrated by the example of the uniformly rotated plane disk This exact solution of the Navier-Stokes equations, to be discussed in Sec 3 1, is also of interest because it illustrates the boundary-layer property anticipated by Noyes and Whitney,[54] Nernst,[51 52] Brunner,[6] and Prandtl,[82] i e , for surrounding fluids of small kinematic viscosity ν, and for disks in rapid rotation, the influence of viscosity extends only over a very small neighborhood of disk surface The same is true of any temperature or concentration nonuniformities established in the system by the presence of the disk Although many interesting properties of the rotating disk solution recur in apparently dissimilar flow fields, in at least one important property this case, together with the forward stagnation-point problem to be described in Sec 3 2, is singular with respect to the diffusion-catalysis problem This arises from the observation that both the rotating disk in *laminar* flow and the forward stagnation region of a blunt-nosed, symmetrical body have the rarely encountered property that the coefficient of convective transport is uniform over the surface § In flow systems, spatially nonuniform transfer coefficients are the rule, as typified by the classical problem of the flat plate aligned parallel with the approach flow (cf Sec 3 3) This implies that a catalyst of uniform activity will usually establish a nonuniform reactant concentration distribution along its surface, so that the driving force for diffusion $\vartheta \equiv c_e - c_w$ will vary with position x measured along the catalyst surface It is well known from studies of heat transfer to/from nonisothermal surfaces that such variations themselves affect the values of the local transfer coefficient Thus, in general, the transfer problem cannot be solved independently of chemical kinetic considerations at the fluid/solid interface This coupling will be examined more closely in Sec 3 3

3 1 Rotating Disk[38 39 42]

The physical configuration considered here is that shown in Fig 2 Although a flat disk of finite radius a is depicted, the exact solution cited below is strictly applicable only to disks of infinite radius ¶ However, since the zone of strong influence of the disk will be seen (a posteriori) to be confined to relatively small distances from it, one anticipates that this solution will be applicable to disks of finite radius provided the disk radius is large compared with the zone of influence ** Local reactant depletion caused by the presence of the disk gives rise to a steady-state diffusive influx of reactant to the disk surface The rate of transport is enhanced considerably by the rotation, since the disk acts like a centrifugal fan that draws fluid rich in reactant toward the disk surface and then ultimately throws it outward by its centrifugal action This convective transport of reactant decreases the disk's ability to maintain an appreciable zone of reactant depletion The resulting increased concentration gradient is, in turn, associated with an increased rate of diffusional transport to the impermeable disk itself, where the normal velocity of the fluid vanishes identically When the entire flow field is laminar,†† von Kármán[33] pointed out that an exact self-similar solution to the equations of axisymmetric motion can be found in which the pressure and the normal component v_y of the fluid velocity are independent of radius r, being dependent only on the stretched dimensionless ordinate $(\omega/\nu)^{1/2}y$ Numerical solutions to the resulting nonlinear system of ordinary differential equations were subsequently obtained by Cochran,[82] and, in particular, the normal velocity distribution became available in the form

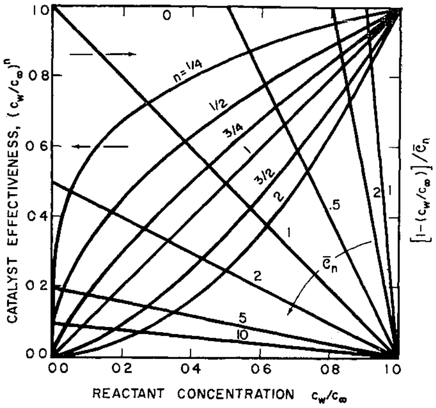

Fig 3 Diffusional reactant depletion for surface-catalyzed reactions of arbitrary kinetic order

$$v_y = -(\omega\nu)^{1/2}\, H(y(\omega/\nu)^{1/2}) \tag{3 1}$$

where H is a well-tabulated function of its single argument Levich pointed out that an exact solution to the reactant diffusion problem is readily obtainable for a catalytic disk subject to the chemical kinetic boundary condition expressed by Eq (2 5) As suggested by the structure of the velocity field, a compatible reactant concentration field independent of radius can be found which satisfies the appropriate specialized version of the species continuity equation [cf Eq (2 1)], namely,

$$v_y(y)\ (dc/dy) = D(d^2c/dy^2) \tag{3 2}$$

This linear ordinary differential equation is easily solved for the entire concentration field $c(y)$ and, in particular, the value of the reactant concentration c_w established at the boundary ($y = 0$) If one imposes the boundary condition (2 5), the latter concentration must satisfy the algebraic equation

$$k_w\ (\rho c_w)^n = D\rho\ (c_\infty - c_w)/\delta \tag{3 3}$$

where the length δ is the effective film thickness‡‡ related to the dimensionless normal velocity field $H(y(\omega/\nu)^{1/2})$ by§§

$$\delta = \left(\frac{\nu}{\omega}\right)^{1/2}\left\{\int_0^\infty \exp\left[-Pr\int_0^\xi H(\xi_1)d\xi_1\right]d\xi\right\} \tag{3 4}$$

The rate of transfer $-j''$ per unit area of disk is then constant over the surface and given by either the right-hand side or the left-hand side of Eq (3 3)

Solutions to the algebraic equation (3 3) have been conveniently displayed by Frank-Kamenetskii[21] in the form shown in Fig 3 Here curves of $(c_w/c_\infty)^n$ and $[k_w\ (\rho c_\infty)^{n-1}\ \delta/D]^{-1}\ [1 - (c_w/c_\infty)]$ are plotted against c_w/c_∞ At the appropriate intersection, Eq (3 3) is evidently satisfied For sufficiently small values of the nondimensional group $k_w\ (\rho c_\infty)^{n-1}\delta/D$, the reactant concentration c_w will be close to the bulk reactant concentration c_∞, and hence the catalyst

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§ Such a surface is often called "uniformly accessible"[21 42] Another system of this type is that of the rotating cylinder (cf Ref 54)

¶ Or, with minor modifications, to circular cones rotated about their axis (cf Refs 101 and 102) the disk representing the special case of a cone with half angle $\pi/2$

** Similarly, the fluid-dynamical effects of other surfaces containing the fluid will also be small if they are sufficiently far removed from the rotating disk In any particular experimental configuration, these geometric effects can be eliminated by extrapolation procedures in the design stage

†† This is found to be the case for finite radius disks if the Reynolds number $\omega a^2/\nu$ based on tip velocity ωa is less than about 10^5 The actual value in practice will depend upon the surface finish and dynamical balancing of the disk

‡‡ End effects for a finite radius disk will be negligible if the disk radius a is very large compared with δ; cf Ref 42

§§ Significantly, δ is independent of chemical kinetic parameters and hence pertinent to nonreactive transfer problems as well

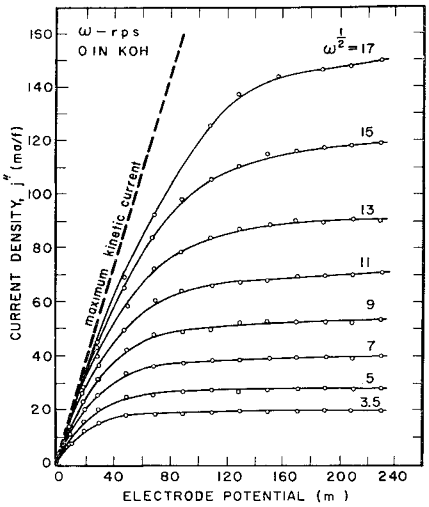

Fig 4 Current density-voltage characteristics for a rotating disk electrode [48]

effectiveness factor $\bar\eta$ defined in Sec 2 3 will be close to unity However, for very large values of the rate parameter $k_w\ (\rho c_\infty)^{n-1}\delta/D$, the steady-state reactant concentration c_w will become negligible compared with c_∞, and the rate of reactant transfer to the surface will approach the diffusion controlled value j''_{diff} given by

$$-j''_{\text{diff}} = D\rho c_\infty/\delta \tag{3 5}$$

More explicitly, for Prandtl numbers that are very large compared to unity, this is equivalent to the exact asymptotic law

$$-j''_{\text{diff}} = 0\ 62048(Pr)^{1/3}(\omega/\nu)^{1/2}D\rho c_\infty \tag{3 6}$$

the validity of which is now well established from experimental studies of rotating disk electrodes [23 42 48 91] In this class of applications, it is found that increasing the voltage on such an electrode immersed in a suitable electrolyte increases the current to the electrode until the current becomes diffusion-limited ¶¶ Here increases in applied potential are analogous to increases in the chemical rate constant k_w, so that one observes a transition between a kinetically controlled electrode reaction and a diffusion-controlled electrode reaction at constant disk speed A recent quantitative example of this behavior is provided by the work of Lewis and Reutschi,[48] on which Fig 4 is based It is seen that an increase in rotational speed ω delays the onset of diffusion control to higher applied voltages; however, the current density ultimately reaches a plateau whose height depends linearly on $\omega^{1/2}$ The intrinsic rate of the electrode reaction is obtained from initial slope of these curves, and the pertinent diffusion coefficient D can be determined from the plateau regions, in accord with Eq (3 6) The linear dependence of $-j''_{\text{diff}}$ on the bulk concentration c_∞ can be used to analyze mixtures of ions in solution, a technique known as solid surface polarography [42]

Recapitulating, it is seen that, for this convective flow problem, 1) the reactant concentration, and hence reaction rate, is uniform over the entire surface*; 2) one can then identify $\bar{\mathscr{C}}_n$ (cf Sec 2 3) with the nondimensional group

$$\bar{\mathscr{C}}_n \equiv \frac{k_w\ (\rho c_\infty)^{n-1}}{0\ 62048\ Pr^{1/3}(\omega/\nu)^{1/2}D} \qquad (\text{for } Pr \gg 1) \tag{3 7}$$

and 3) the effectiveness factor $\bar\eta \equiv \bar R/\bar R_{\text{h m}}$ satisfies the simple algebraic equation

$$\bar{\mathscr{C}}_n\bar\eta = 1 - \bar\eta^{1/n} = \bar\phi \tag{3 8}$$

obtained directly from Eq (3 3) In particular, for $n = 1$ (first-order surface reaction),

$$\bar\eta = (1 + \bar{\mathscr{C}}_1)^{-1} \tag{3 9}$$

It can be verified directly from Eqs (2 16) and (3 9) that, for this special case ($n = 1$),

$$E_a/E = \bar\eta \qquad (E/R \gg T_w) \tag{3 10}$$

and, of course, $n_a = n = 1$

In two important situations, these simple properties break down First, if the disk does not have a uniform activity but is instead "coated" up to $r = r_0$ and catalytic thereafter (cf Sec 5 1), then even in the diffusion-controlled extreme the reactant flux will have a radial dependence, as given by Zaidel's solution† (for $r > r_0$, $Pr \gg 1$):

$$-j''_{\text{diff}} = 0\ 62048(Pr)^{1/3}(\omega/\nu)^{1/2}D\rho c_\infty[1 - (r_0/r)^3]^{-1/3} \tag{3 11}$$

Second, if the flow becomes turbulent,[33] then the reaction rate will also acquire a radial dependence In both of these cases the solution to the intermediate regime kinetics problem becomes less straightforward, since a nonuniform reactant concentration $c_w(r)$ would be established at the disk surface, and this itself alters the magnitudes of the local convective transport coefficient ‡ Results of this type of coupling between the kinetic and transport problems will be illustrated in Sec 3 3 for the case of boundary-layer flow over a flat plate

3 2 Forward Stagnation Point

The physicochemical situation at the forward stagnation point of a blunt-nosed object immersed in a uniform stream is very similar to that described in the preceding section, since, at least locally, the normal fluid velocity v_y in the viscous layer is a function only of the distance y measured perpendicular to the surface Hence, the diffusion equation admits solutions of the form $c(y)$ and specializes to that given by Eq (3 2) The solution procedure then parallels that outlined in Sec 3 1

According to laminar boundary-layer theory, the normal velocity distribution may be obtained in the functional form

$$v_y = -(\nu\beta)^{1/2}\ H\left(y(\beta/\nu)^{1/2}\right) \tag{3 12}$$

where the inviscid velocity gradient $\beta \equiv (dv_{x\ e}/dx)_{x=0}$ is seen to play the same role as the rotational speed ω in the disk problem The corresponding expressions for the boundary-layer thickness δ are relatively well known For Prandtl numbers of order unity, we have[84 87]

$$\delta = \begin{cases} [0\ 763(\beta/\nu)^{1/2}(Pr)^{0\ 4}]^{-1} & (3\ 13\text{a}) \\ [0\ 570(\beta/\nu)^{1/2}(Pr)^{0\ 4}]^{-1} & (3\ 13\text{b}) \end{cases}$$

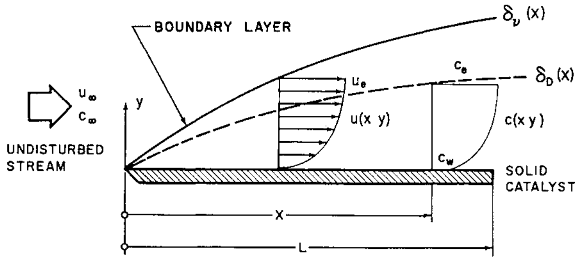

Fig 5 Catalytic flat-plate configuration

¶¶ At which point the electrode is said to be fully polarized

* The coefficients ϕ and $\bar\phi$ may then be identified with the ratio $\Delta c/c_\infty$, where Δc is the drop in reactant concentration across the diffusion boundary layer

† Reported on page 108 of Ref 42

‡ See, for example, Hartnett's solution[25] for heat transfer from a nonisothermal disk rotating in still air

for three-dimensional and two-dimensional§ stagnation points, respectively Thus, for example, the boundary-layer solution reported by Goulard[22] for a first-order surface-catalyzed reaction at a three-dimensional stagnation point is readily generalized to arbitrary reaction order ¶ Defining a *local* catalyst effectiveness factor $\eta \equiv (c_w/c_\infty)^n$ and a *local* catalysis-diffusion parameter[64]**

$$\mathfrak{C}_n \equiv k_w \ (\rho c_\infty)^{n-1}/[0\ 763(\beta/\nu)^{1/2}(Pr)^{0\ 4}D] \qquad (3\ 14)$$

one then finds that the $\eta(\mathfrak{C}_n;\ n)$ relation is identical to the $\bar{\eta}(\bar{\mathfrak{C}}_n;\ n)$ relation for the rotating disk [cf Eq (3 8)], so that the remarks following Eq (3 8) apply equally well to this flow configuration As before, the simplicity of this solution may be traced back to the fact that the convective transfer coefficient at a stagnation point is (locally) uniform; thus a catalyst of uniform activity will establish a (locally) uniform reactant concentration at the fluid/solid interface, and there will be no coupling between the convective and chemical kinetic parts of the problem

3 3 Catalytic Flat Plate[1 10 42 47 62 66 67 71 74]

For viscous flow over a flat plate at high Reynolds numbers, one encounters the more usual property that conditions of convective transport vary with position along the surface, i e , the effective film thickness $\delta_{\text{iso}}(x)$ grows with streamwise distance, as depicted schematically in Fig 5 One thus expects a transition from chemical to diffusion control to take place *along* the surface, since $k_w\ (\rho c_\infty)^{n-1}\ \delta_{\text{iso}}/D$ is very small near the leading edge but may become quite large far downstream A catalytic plate of finite length L can therefore be regarded as a series of back-to-back differential reactors with each element of surface operating in a different intermediate regime of diffusional depletion The fact that the steady-state reaction rate will, in general, be spatially nonuniform implies that the steady-state reactant concentration at the fluid/solid interface will be a function of x; hence the driving force for diffusion, $\vartheta_e(x) \equiv c_e - c_w$, will be spatially nonuniform If, for the moment, one imagined that the distribution $\vartheta\ (x)$ were prescribed, then it is well known that the local rate of transfer at any point x along the surface would depend upon the upstream history $\vartheta_e(\xi)$ of the diffusional driving force Indeed, if $\vartheta_e(x)$ increased as the lth power of x, then local transfer coefficients would be larger than the values corresponding to ϑ_e = const by the amounts shown in Fig 6 But, for the convective-diffusion chemical-surface-reaction problem of interest here, the distribution $\vartheta_e(x)$ is sought as part of the solution, so that an expression for the local transfer rate $j''(x)$ valid for arbitrary $\vartheta\ (x)$ is required Owing to the linearity of the convective diffusion equation, it is readily demonstrated that, if the solution to a boundary-value problem with a step-function distribution†† of $\vartheta_e(x)$ is obtainable, then the solution for arbitrary $\vartheta\ (x)$ can be constructed from this fundamental solution by simple superposition[80 90] Let us denote by $\Theta(x,y,\xi)$ the normalized concentration excess field, $(c - c_w)/(c_\infty - c_w)$ satisfying 1) the step-function boundary condition, and 2) the appropriate boundary-layer equation

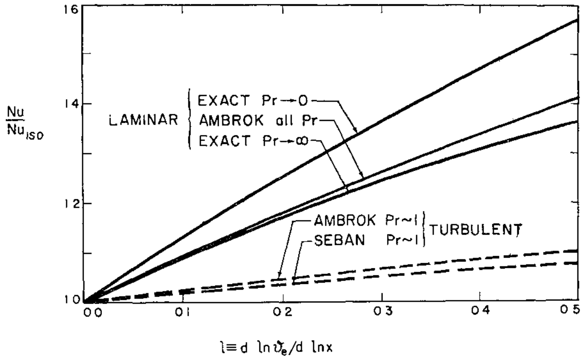

Fig 6 Effect of variable diffusional driving force on the magnitude of the local transfer coefficient; boundary-layer flow over a flat plate [76]

Table 1 Parameters, *p*,*q* for boundary-layer flow over a catalytic flat plate[74]

Flow	Pr	p	q
Laminar	$\ll 1$	2	$-\frac{1}{2}$
Laminar	0(1)	$\frac{3}{2}$	$-\frac{1}{3}$
Laminar	$\gg 1$	$\frac{3}{2}$	$-\frac{1}{3}$
Turbulent	0(1)	$\frac{9}{2}$	$-\frac{1}{9}$
Turbulent	$\gg 1$	$\frac{9}{4}$	$-\frac{1}{3}$

$$v_x \frac{\partial \Theta}{\partial x} + v_y \frac{\partial \Theta}{\partial y} = \frac{\partial}{\partial y} \left\{ [D + D^{(t)}] \frac{\partial \Theta}{\partial y} \right\} \qquad (3\ 15)$$

If this boundary-value problem‡‡ can be solved, then, by superposition, the transfer-rate distribution $-j''(x)$ for the more general problem in which $\vartheta_e = \vartheta_e(x)$ is given by the Stieltjes integral[90]:

$$-j''(x) = D\rho \int_{\xi=0}^{\xi=x} \left(\frac{\partial \Theta}{\partial y} \right)_{y=0} d\vartheta\ (\xi) \qquad (3\ 16)$$

Several such fundamental solutions for incompressible boundary-layer flow over a flat plate are available in the heat-transfer literature,[10 90] some of which are exact and some approximate Typically, these solutions have the property that $(\partial\Theta/\partial y)_{y=0}$ is expressible in the form[58]

$$(\partial\Theta/\partial y)_{y=0} = K(\xi/x)/\delta_{\text{iso}}(x) \qquad (3\ 17)$$

where $K(1) = \infty$ and the behavior of the dimensionless kernel for $\xi/x < 1$ depends upon both the Prandtl number and the role of turbulence in the convective transport process For these cases, the transfer rate is then calculable from a Stieltjes integral[90] of the form

$$j''(x) = \frac{D\rho}{\delta_{\text{i o}}(x)} \int_{\xi=0}^{\xi=x} K\left(\frac{\xi}{x}\right) dc_w(\xi) \qquad (3\ 18)$$

To apply this result to the chemical surface reaction problem for which the distribution $c_w(x)$ is as yet unknown, one must set the left-hand side of Eq (3 18) equal to $-k_w\ (\rho c_w)^n$ in accord with the kinetic boundary condition (2 5) For most of the available kernels,[10 49 58 83 90] this leads to the following class of singular nonlinear Volterra integral equations[74] for $c_w(x)$:

$$\hat{c}^{\,n} = -\frac{1}{z} \int_0^z \left[1 - \left(\frac{\zeta}{z} \right)^p \right]^q \frac{d\hat{c}}{d\zeta}\ d\zeta \qquad (3\ 19)$$

where we have introduced the notation

$$\hat{c} \equiv c_w/c_\infty \qquad (3\ 20)$$

$$z \equiv k_w\ (\rho c_\infty)^{n-1}\delta_{\text{iso}}(x)/D \qquad (3\ 21)$$

and some pertinent values of the exponents p and q are collected in Table 1

If there were no coupling between the chemical kinetic and diffusional process, the local diffusion correction§§ $\eta \equiv (c_w/$

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§ For $Pr \to \infty$, replace $0\ 570(Pr)^{0\ 4}$ by $0\ 661(Pr)^{1/3}$; cf Ref 102

¶ Or, for that matter, to cases not described by simple power law kinetics [70]

** Given here for the axisymmetric case [64]

†† For example, one for which $\vartheta_e = 0$ for $x < \xi$ and $\vartheta = 1$ thereafter

‡‡ For the boundary-layer-type flow, the remaining condition on $\Theta(x,y;\xi)$ is, of course, $\Theta(x, \infty;\xi) = 1$

§§ Which may be identified with the reaction rate distribution normalized by the value at the leading edge

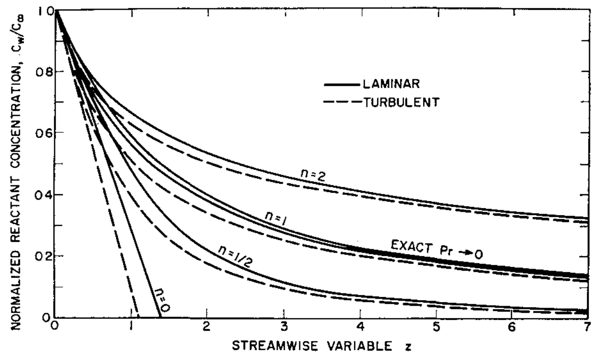

Fig 7 Normalized steady-state reactant concentration distributions along a catalytic flat plate for several reaction orders[71 74]

$c_\infty)^n$ would be calculable from the local analog of Eq (3 8), viz ,

$$z\eta = 1 - \eta^{1/n} \qquad (3\ 22)$$

from which $\bar{\eta}$ could then be obtained by an integration However, solutions to the Volterra integral equation are found to differ markedly from Eq (3 22), particularly for laminar boundary-layer flows with reaction orders less than unity ¶¶ It is also found that small errors in the calculation of the reaction rate distribution can lead to large errors in the predicted apparent reaction order and activation energy Thus, solution methods that accurately account for the chemical kinetic-convective diffusion coupling described earlier are of considerable interest Exact solutions to the nonlinear integral equation (3 19) can, of course, be obtained numerically by adapting the procedures outlined for special cases by Acrivos and Chambré[1] and by Chung, Liu, and Mirels[13] In certain cases,* power-series solutions for small and large z may be useful, although the convergence is found to be slow An approximate method that combines reasonable accuracy with considerable computational convenience and generality has been used by the writer for studying both laminar and turbulent cases over the entire range of reaction orders of interest As described in Refs 65, 71, and 74, use is made of Ambrok's relation[2] generalizing Nu_{is} to account for streamwise variations in diffusional driving force $\vartheta(x)$ An indication of the accuracy of this approximation is obtained by applying it to the familiar power-law case, $\vartheta(x) \propto x^l$, for which exact (similar) solutions are available[49] Results are included in Fig 6, where it is seen that the accuracy is quite good, except perhaps for laminar flow with very small Prandtl numbers † When this method is applied to the diffusion-surface catalysis problem, the resulting nonlinear integral equation can be transformed to a separable ordinary differential equation for all reaction orders, and calculations of the important integrated catalyst properties ($\bar{\eta}$, $\bar{\Phi}$, E_a/E, and n_a/n) proceed using algebraic relations alone for all reaction orders Results for both laminar and turbulent‡ boundary-layer flow[71 74] are displayed in Figs 7–10, where the reaction order has been varied between zero and two § Figure 7 displays an important local property of the solutions, namely the steady-state distribution of reactant concentration (c_w/c_∞) Figures 8–10 contain the important properties of catalytic flat plates when viewed as integral reactors A double logarithmic representation (cf Fig 8) has been adopted for the relation between the catalyst effectiveness factor $\bar{\eta}$ and the composite diffusion-catalytic parameter $\bar{\mathcal{C}}_n$, since the slope of each curve is then what is required to calculate the diffusional falsification of activation energy and reaction order, in accord with the general relations presented in Sec 2 4 A very interesting result is that *with this choice of abscissa* ($\bar{\mathcal{C}}_n$), both laminar and turbulent contours are virtually coincident; moreover, they differ but slightly from the familiar algebraic relation (3 8) ¶ For example, the maximum departure of the $n = 1$ results shown in Fig 8 from Eq (3 8) is 1 34% for the laminar boundary-layer case and only 0 075% for turbulent boundary-layer case However, the corresponding percentage departures in calculating the falsification of activation energy (Fig 9) and reaction order (Fig 10) are considerably larger, particularly for reactions of small kinetic order in the regime of strong diffusional limitation In Fig 10, the tendency of all interfacial reactions to masquerade as first-order reactions in the presence of a strong diffusional limitation is illustrated by the $\bar{\Phi} = 1$ asymptotes, $1/n$ For values of the catalyst effectiveness factor $\bar{\eta}$ near unity, it is also seen that the diffusional falsification of activation energy and reaction order is most pronounced for the reaction orders n that are smaller than unity **

Before leaving the problem of the flat-plate catalytic reactor, it should be emphasized that the proximity of results for laminar and turbulent boundary layers shown in Figs 7–10 is one of the important consequences of a "natural" choice of coordinates rather than a true independence of diffusional falsification on the conditions of turbulence within the boundary layer Thus, the fact that the integrated transfer coefficient $\overline{Nu}_i$ for a plate of length L is much larger for turbulent boundary-layer flow than for laminar flow means that one can study faster interfacial chemical reactions in the former case without encountering strong diffusional effects On the other hand, the accuracy with which a priori theoretical predictions can be made is, of course, better for laminar boundary-layer flow than for turbulent flow As one would anticipate from the transfer coefficient results already displayed in Fig 6, the coupling between the diffusion and chemical kinetic processes is strongest for the laminar case This is perhaps best illustrated by the normalized reaction rate distributions shown in Fig 11 for first-order reactions Neglect of the coupling leads one to predict that the laminar and turbulent boundary-layer results should be coincident (with this choice of abscissa), as indicated by the solid curve [$\eta = (1 + z)^{-1}$] marked "quasi-stationary" The more accurate method of Refs 71 and 74 predicts a noticeable difference between the two cases, with the approach to diffusion control being somewhat more gradual in the laminar case because of the stronger self-regulating effect of increases in $\vartheta_e \equiv c - c_w$ on the local transfer coefficient itself Although the exact solution for laminar flow with very small Prandtl number falls slightly above the distribution calculated using the approximate

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¶¶ The coefficients p listed in Table 1 apply only to flow over a flat plate (zero pressure gradient) Effects of pressure gradients are currently under investigation[79] using the integral equation approach[20] outlined in this section It is found that the accuracy of Eq (3 22) improves for strongly accelerated flows Heat-transfer aspects of the diffusion-surface reaction problem with pressure gradient have been treated by Rae[57] and Inger[32]

* The singular case $n = 0$ admits closed form solutions for all sets of (p,q) in terms of incomplete beta functions[77]

† In this latter case, a closed-form exact solution to the diffusion-surface reaction problem is obtainable for first order surface reactions[67 71]

‡ Here the boundary layer is assumed to be tripped at the leading edge of the plate

§ The case $n = 4$, not shown, is of special interest because of its heat transfer analog,[66 68 76] namely, radiation cooling of constant emittance flat plates heated by forced convection; cf Sec 5 6

¶ This implies that the diffusional reduction of integrated reaction rate is almost equal to that predicted by a naive analysis that considers c_w = const and evaluates its magnitude by means of an over all species conservation relation

** Interestingly enough, diffusional effects are observed even for the zeroth-order case, provided the parameter $\bar{C}_0$ exceeds a threshold value ($= 2^{1/2}$ for the approximate method used in constructing Figs 7–10)

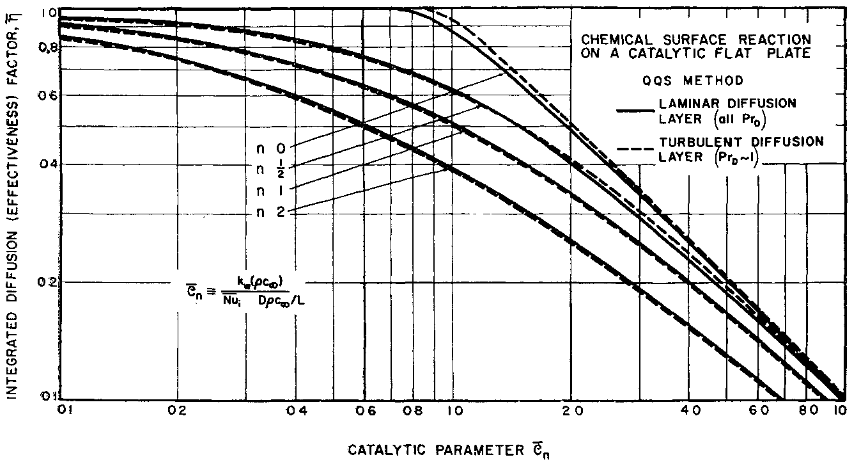

Fig 8 Dependence of global catalyst effectiveness factor on the composite catalysis-diffusion parameter $\overline{\mathscr{C}}_n$ for several reaction orders [71] [74]

method of Ref 71, the latter result is practically coincident with the exact power-series result for $Pr \to \infty$ given by Chambré and Acrivos [9] The reader interested in a more detailed discussion of accuracy under various combinations of physicochemical conditions is referred to Refs 1, 12, 13, 57, 67, 71, and 74 Such studies help delineate those problems for which similar approximations can be used with some confidence in more complex situations Several methods of applying these results to the inference of catalytic activities are discussed in Ref 71

4 Internal Flow Configurations

In the area of diffusion effects on chemical surface reactions, the simplest internal flow system, and no doubt the most important from a practical point of view, is the *tubular reactor* This is particularly true in those cases for which the fluid flow is fully developed, i e , when the chemically active section is downstream of the duct inlet by at least one hydrodynamic entry length, as shown in Fig 12 For incompressible fluids without swirl, this implies that the time-averaged velocity within the reactor is axially directed and is a function of radius r alone Apart from these latter properties, it will be realized that the growth of the concentration boundary layer immediately downstream of the chemically active section inlet is closely related to the external catalysis problem discussed in Sec 3 3 †† Further downstream, however, the thickness of these boundary layers becomes comparable to the duct radius $d/2$, and an interaction occurs which causes the reactant concentration along the duct centerline to decay axially Mathematically, one is then not able to prescribe this distribution, unlike the case of external boundary-layer flows Instead, a symmetry condition is imposed at the duct axis, namely, $(\partial c/\partial r)_{=0} = 0$ This, together with the inlet distribution $c(0,r) = c_0 =$ const, the chemical kinetic boundary condition, and the species conservation equation

$$v_x(r)\,\frac{\partial c}{\partial x} = \frac{1}{r}\,\frac{\partial}{\partial r}\left[r(D + D^{(t)})\,\frac{\partial c}{\partial r}\right] + \frac{\partial}{\partial x}\left[(D + D^{(t)})\,\frac{\partial c}{\partial x}\right] \qquad (4\ 1)$$

essentially completes the mathematical statement of the problem ‡‡ However, in any particular case the velocity distribution $v_x(r)$ and the corresponding turbulent diffusivity distribution $D^{(t)}(r)$ must also be specified

4 1 Tubular Reactors with Laminar Flow[3 16 20 30 34 55]

If the Reynolds numbers Re based on the diameter d and average velocity U does not exceed about $2\,1 \times 10^3$, then the flow will be laminar throughout, and the turbulent diffusivity $D^{(t)}$ vanishes everywhere The fluid velocity distribution of greatest interest is then parabolic, i e ,

$$v_x(r) = 2U[1 - (2r/d)^2] \qquad (4\ 2)$$

However, because of its relative simplicity, considerable attention has been devoted to so-called "slug"-flow (or "plug"-flow) reactors[16 30] for which $v_x \equiv U =$ const §§ In either case, it is commonly assumed that axial diffusion is negligible, so that Eq (4 1) specializes to

$$v_x(r)\,\frac{\partial c}{\partial x} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\,\frac{\partial c}{\partial r}\right) \qquad (4\ 3)$$

When $v_x(r) \equiv U =$ const and x/U is replaced by a new transit time variable t, Eq (4 3) will be recognized as the equation describing transient radial diffusion through a quiescent medium If one considers the first-order chemical kinetic boundary condition

$$D(\partial c/\partial r)_{r=d/2} = k_w\ (c)_{=d/2} \qquad (4\ 4)$$

it is found that linear boundary-value problems of this type

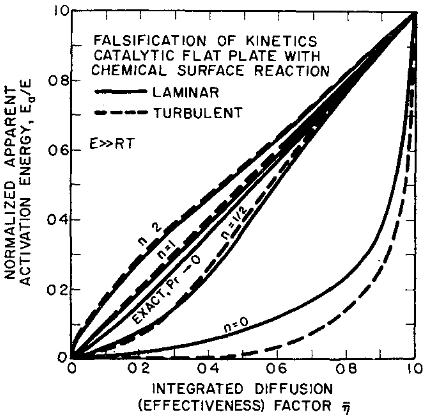

Fig 9 Influence of convective diffusion on the apparent activation energy for chemical surface reactions on catalytic plates of finite length [71] [74]

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†† Indeed, Eq (3 19) is applicable in this region if one sets $p = 3$, $q = -\frac{1}{3}$ The significance of the property $pq = -1$ is discussed in Ref 74 and Sec 5 1

‡‡ It is usually assumed that the turbulent diffusivity $D^{(t)}$ is independent of x, so that the last term of Eq (4 1) is written as $[D + D^{(t)}]\,(\partial^2 c/\partial x^2)$

§§ This approximation would be most accurate for short reactors whose active section starts at the hydrodynamic tube inlet if the reactant/carrier fluid transport is characterized by very small diffusional Prandtl numbers, $Pr_D \ll 1$

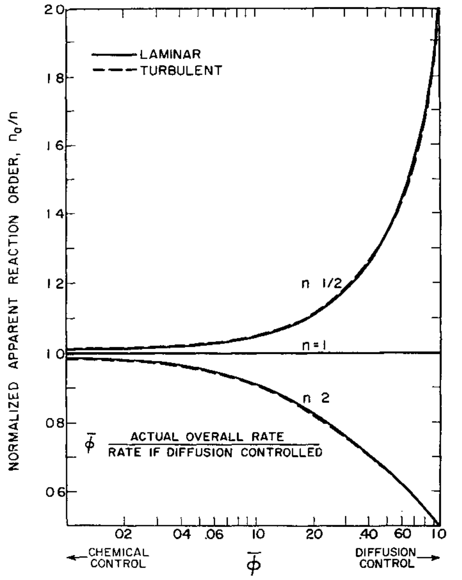

Fig 10 Influence of convective diffusion on the apparent reaction order for chemical surface reactions on catalytic plates of finite length [71] [74]

are readily handled by the classical Fourier method of separation of variables, as illustrated in Refs 16, 30, and 55 ¶¶ Solutions to this problem for circular boundaries have been reported by Newman,[53] Paneth and Hertzfeld,[55] and more recently by Damköhler[16] and Hoelscher [30] For example, using the tabular data of Ref 53, one can readily construct the dependence of the catalyst effectiveness factor $\bar{\eta}$ on the conditions of flow rate, diffusion, and surface activity The results are shown in Fig 13, where the ordinate is defined as

$$\bar{\eta} \equiv \frac{\pi d \int_0^x k_w \rho c_w(x) dx}{\pi d \; k_w \rho c_0 x} = \frac{1}{x} \int_0^x \left(\frac{c_w}{c_0}\right) dx \qquad (4\ 5)$$

and the abscissa will be recognized as the ratio of the residence time x/U to the characteristic diffusion time $d^2/4D$ across the reactor It should be remarked that the catalyst effectiveness factor defined here would not be close to unity for any considerable reactor length even in the absence of radial nonuniformities in reactant concentration This is because the bulk* reactant concentration $c_b(x)$ must decay

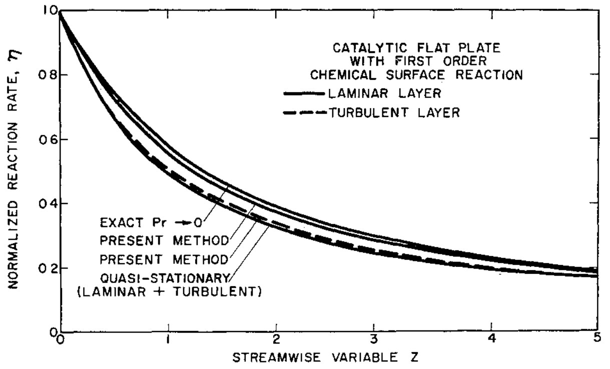

Fig 11 Comparison of normalized steady-state reaction rate distributions along a catalytic plate for first-order surface reactions [74]

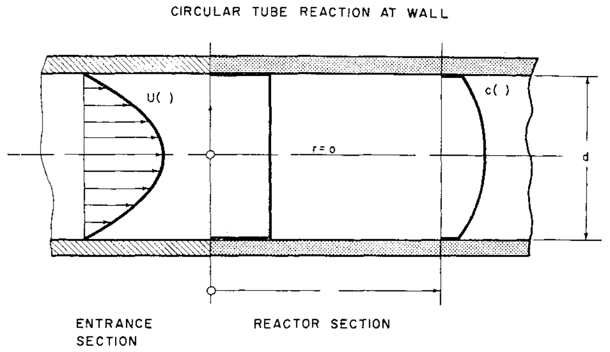

Fig 12 Tubular reactor configuration; fully developed flow

in accord with a species conservation equation governing the reactor as a whole When 1) the wall reaction is first order, 2) radial concentration gradients are small, and 3) axial diffusion is neglected, then the bulk reactant concentration $c_b(x)$ would decay with length as though a first-order *homogeneous* reaction were occurring, i e ,

$$c_b/c_0 = \exp[-4(k_w/U)(x/d)] \qquad (4\ 6)$$

This familiar result leads to the practice of reporting $4k_w/d$ as an *equivalent first-order homogeneous rate constant* †

By introducing the notion of a local[5] diffusional transfer coefficient Nu_{loc} defined by

$$-j''(x) = Nu_{\text{loc}} \; D\rho \; (c_b - c_w)/d \qquad (4\ 7)$$

Eq (4 6) may then be generalized to include the effect of transverse concentration nonuniformities For first-order surface reactions, the chemical kinetic boundary condition then implies

$$c_w(x)/c_b(x) = [1 + (k_w d/Nu_{\text{loc}} D)]^{-1} \qquad (4\ 8)$$

which is identical in form to Eq (3 9) ‡ Combining this relation with the equation relating local reaction rate to dc_b/dx immediately gives

$$\frac{c_b}{c_0} = \exp\left\{-4\left(\frac{k_w}{U}\right)\int_0^{x/d}\left[1 + \frac{k_w d}{Nu_{\text{loc}} D}\right]^{-1} d\left(\frac{x}{d}\right)\right\} \qquad (4\ 9)$$

This expression is not exact for the diffusion-surface reaction problem, since (as in the flat-plate case) the local transfer coefficient defined by Eq (4 7) is itself dependent in the reactant concentration distribution along the wall § (which is not known a priori) However, with the introduction of available transfer coefficient predictions or measurements, Eq (4 9) does provide a useful means for making rapid quantitative estimates of the dominant effects of interest For the nonlinear cases ($n \neq 1, 0$), simple closed-form approximate results of this type are not available unless one can reasonably assume that Nu_{loc} is independent of x/d

Exact solutions applicable to the nonlinear cases ($n \neq 0, 1$) for which separation of variable techniques are not available may be obtained using the integral equation approach of Chambré[10] (cf Sec 3 3) or by a direct numerical attack on the partial differential equation (4 3) with machine methods [20] [41] In the former case, the necessary kernels for slug flow and Poiseuille flow are available in the heat-transfer literature [10] [90] An example of the use of numerical methods is provided by the recent work of Fetting et al ,[20] in which Eq (4 3) is treated as a difference equation in the radial di-

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¶¶ For a comprehensive review of the eigenvalue problems arising in the treatment of the first-order case, including axial diffusion, see Ref 103

* Defined such that c_b is the concentration that one would measure if the reactor were severed at x and the effluent mixture were collected in a container and thoroughly mixed [5]

† Particularly in chemical kinetic investigations in which homogeneous and heterogeneous reactions proceed simultaneously[35] (cf Sec 5 4)

‡ For any reaction order n, one can obtain a simple algebraic equation relating c_w/c_b to $k_w\,(\rho c_b)^{n-1}\,d/[Nu_{\text{loc}} D]$

§ Particularly for small Prandtl numbers rection and the distance variable is left continuous Solutions are then obtained on an analog computer for any reaction order and velocity profile assumption

Before leaving the laminar tubular reactor problem, mention should be made of Katz's[34] interesting inversion of the integral equation governing $c_w(x)$ For parabolic (Poiseuille) flow¶ in a tubular reactor, and regardless of the concentration dependence of the local reaction rate, $c_w(\theta)$ may be expressed in the form

$$c_w = c_0 - \int_0^{\theta} M(\theta - \theta_1) \left[\frac{-dc_b}{d\theta_1}\right] d\theta_1 \tag{4 10}$$

where $\theta \equiv 8(Re\ Pr)^{-1}\ (x/d)$, and the kernel $M(\theta)$ has been computed recently by Dranoff [18] The spatial decay of *bulk* reactant concentration, $dc_b/d\theta$, is presumed to be determined as a result of a series of traverse measurements From these latter measurements the local rate of reaction is, of course, readily calculated, and from Eq (4 10) the corresponding local concentration at the fluid/solid interface can be obtained In this way the function $R''(c_w)$ can be constructed without ever having to measure reactant concentrations accurately at the catalyst surface itself Alternate methods of using the theoretical results discussed in this section to infer heterogeneous rate constants may be found, for example, in Refs 3 and 81

4 2 Tubular Reactors with Turbulent Flow[81 99]

Turbulent flow reactors may be of interest for the study of fast interfacial reactions, since the conditions of convective diffusion are better and the fluid flow itself is less likely to be affected by small amounts of radial heat transfer than in the laminar case However, from a theoretical point of view, the turbulent reactor problem is less well defined owing to uncertainties in the velocity profile itself and, perhaps more important, in the relation between the eddy diffusivity $D^{(t)}$ and the velocity profile Yet, available pipe flow data suggest the validity of semiempirical universal profiles having the functional forms

$$v_x = (\tau_w/\rho)^{1/2}\ F\Big((\tau_w/\rho)^{1/2}(\tfrac{1}{2}d - r)/\nu\Big) \tag{4 11}$$

$$D^{(t)} = \nu\ E\left(\frac{(\tau_w/\rho)^{1/2}(\frac{1}{2}d - r)}{\nu}, \frac{(\tau_w/\rho)^{1/2}(\frac{1}{2}d - r)^2}{\nu\ \frac{1}{2}d}\right) \tag{4 12}$$

where τ_w, the shear stress at the wall, is well known from available pressure drop measurements in pipes over a wide range of Reynolds numbers Wissler and Schechter[99] have recently carried out calculations for tubular reactors using the function F recommended by Deissler[17] and the function E adopted by Sparrow, Hallman, and Siegel [86] For first-order wall reactions and neglecting axial diffusion, the method of separation of variables is applicable, and tabular values of the first six eigenvalues and Fourier coefficients are provided for calculating concentration distributions at two Reynolds numbers (0 7003 × 10^4 and 1 4017 × 10^4), two Prandtl numbers (Pr_D = 0 7 and 2), and two values of the chemical kinetic parameter k_wd/D (20 and 200) Their results for the higher Reynolds number and the smaller Prandtl number are shown in Fig 14, together with the results (at $x = 100d$) of a simple approximate method equivalent to the use of Eqs (4 8) and (4 9) with Nu_{loc} set equal to a constant ** At this station, the agreement between the two calculations is quite good, suggesting that in many applications the more refined calculation method may not be necessary for turbulent flow reactors †† Indeed, most available work in this field is based on the approximate applicability of nonreactive heat- and mass-transfer coefficients

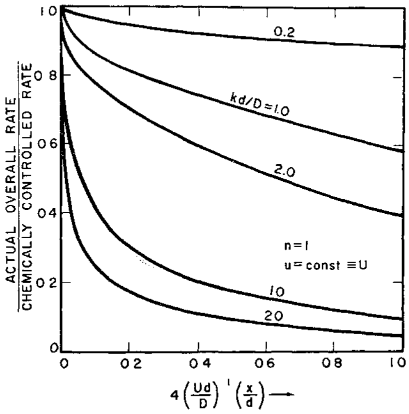

Fig 13 Global catalyst effectiveness factors for long, plug-flow tubular reactors [68]

For the case of surface reactions of arbitrary kinetic order, an integral equation of the type (4 10) can be derived, and the kernel $M(\theta - \theta_1)$ can be computed using the methods of Ref 99 ‡‡ These authors give the first six coefficients in the Fourier expansion of M for Re = 0 7003 × 10^4 and 1 4017 × 10^4 and for Pr = 0 7 and 2

5 Remarks on More General Problems

In view of the deliberately restricted class of physicochemical problems included in Secs 2–4, it may be of interest to amplify somewhat on important generalizations of current research interest These would include the important effects of spatially variable catalyst activity,[13 32 42 62] thermochemical heat release,[78] reversible and sequential reactions,[1] simultaneous homogeneous phase reaction,[14 36 41 75 94 98] and effects of net mass transfer at the fluid/solid interface [11 85 107] Although a detailed review of progress in each of these areas cannot be attempted here, the nature

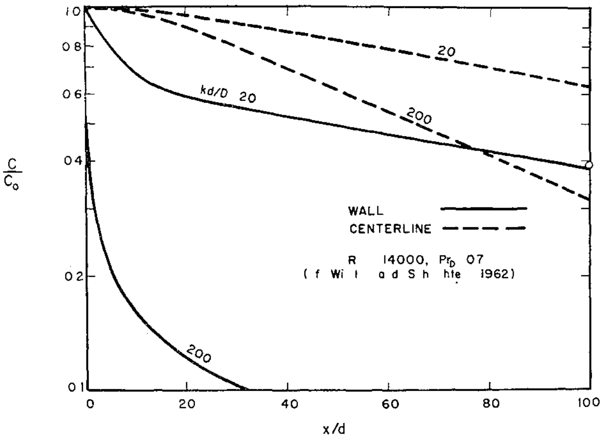

Fig 14 Steady-state reactant concentration distributions; long tubular reactor with fully turbulent flow [99]

¶ Although the results of Ref 34 are also applicable with more general velocity profiles, the author's assumptions of constant radial diffusivity (D) and, to a lesser extent, negligible axial diffusion would appear to rule out their application to turbulent flows

** If the dependence of Nu_{loc} on x/d is neglected, then this method gives very poor results near the start of the active section (e g , in the first 10 diameters) For this reason we have not included the points calculated in Ref 99 for $x/d = 0$

†† Particularly at large values of the Prandtl number, ν/D

‡‡ Actually, because of the truncation error in the computation of the kernel $M(\theta)$, Wissler and Schechter[99] recommend the use of a similar integral equation related to Eq (4 10) by a single integration by parts However, this would appear to place greater demands on the precision of the experimental data, since one then requires accurate values of $d^2c_b/d\theta^2$ instead of $dc_b/d\theta$

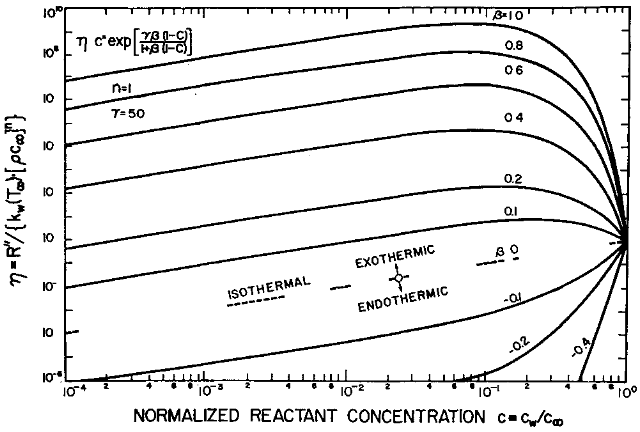

Fig 15 Simultaneous effect of heat and species transport limitations on local catalyst effectiveness for exothermic and endothermic surface reactions [78]

of the problems can be outlined and several pertinent references cited in the hope that among the readers of this section will be those who will wish to pursue some of these questions further The paper concludes with some remarks on well-defined flow configurations not included in Secs 3 and 4 and with analogies between the diffusion-surface reaction problem and other well-known problems in transport theory

5 1 Spatially Variable Catalyst Activity

In practice, the case of spatially variable catalyst activity is commonly encountered due to 1) the method of model or reactor fabrication,[23 42] 2) catalyst poisoning by constituents of the fluid mixture, or 3) heat release modifying the steady-state temperature distribution of the catalyst[76 78] and hence the specific rate constant k_w We will confine our attention here to the first case and will discuss the effects peculiar to heat release in Sec 5 2, which follows

Either out of necessity or by design, one frequently encounters the noncatalytic "patch" problem or what Levich[42] terms the partially "coated" surface Here the catalyst activity is piecewise uniform but is discontinuous The simplest problem of this type is that in which the active surface is preceded by a noncatalytic "run," $x \leqslant x_0$, such that the hydrodynamic boundary layer begins to grow upstream of the origin of the concentration boundary layer Some general characteristics of the piecewise uniform catalytic plate problem were discussed by the writer in Ref 62 More recently, Chung, Liu, and Mirels[13] have provided quantitative predictions of the effect of an upstream run of zero or infinite activity on downstream reactant concentrations for laminar boundary-layer flow over simple shapes Studies of the effects of such variations on the apparent kinetics of the over-all surface reaction are currently in progress at AeroChem §§ In addition, continuous variations of catalyst activity are of interest, particularly since this is usually the result of catalyst poisoning after extended operation This problem also arises in connection with certain aerodynamic heating applications and is discussed from this point of view by Inger[32] in a recent paper dealing with polynomial or simple power-law variations of k_w

5 2 Nonisothermal Phenomena and Applications

When heat is released at the catalyst surface and provision has not been made to remove the heat at an adequate rate, the local temperature of the catalyst increases until the surface can lose enough heat by convection to achieve a steady state [60 63 70 73 76] Since the rate constant k_w is very sensitive to temperature, we therefore encounter a strong nonlinear interaction between the heat-transfer and diffusional-transfer problems [78] Now in a wide class of flow systems, transfer coefficients for heat transfer and species diffusion are simply proportional to one another In the absence of internal heat removal or other forms of heat loss (e g , radiation), this leads to the existence of a useful relation between the steady-state catalyst temperature and reactant concentration distribution (a first integral) which can be written down before the actual spatial distribution of either quantity is obtained If, for a given configuration, we denote by the symbol r_D the transfer coefficient ratio¶¶

$$r_D \equiv (Pr_\lambda/Pr_D)\ \ (Nu_{D\ \mathrm{iso}}/Nu_{\lambda\ \mathrm{is}}\ ) \tag{5 1}$$

then this surface temperature-reactant concentration relation is usually of the simple form[63]

$$T_w/T_\infty = 1 + r_D\ \ (c_\infty Q/c_pT_\infty)\ \ [1 - (c_w/c_\infty)] \tag{5 2}$$

where Q represents the heat release per unit mass of reactant, and c_p is the specific heat of the carrier fluid In view of the strong temperature dependence of the specific rate constant k_w, one then finds that the local reaction rate $k_w\ (\rho c_w)^n$ can *increase* despite a local depletion of the reactant concentration, since the accompanying increase in the rate constant can more than offset the concentration factor * This effect is illustrated in Fig 15 in terms of the local reaction rate coefficient η defined by $R''(\mathrm{actual})/R''(\text{no transport effects})$ or, explicitly,

$$\eta \equiv \{k_w(T_w)\ \ [\rho c_w]^n\}/\{k_w(T_\infty)\ \ [\rho c_\infty]^n\} \tag{5 3}$$

Combining Eqs (5 2, 2 6, and 5 3), one finds that the local and hence global catalyst effectiveness factor will depend not only on the parameters of Sec 2† but also on

$$\gamma \equiv E/RT_\infty \qquad\qquad \beta \equiv r_D\ \ (c_\infty Q/c_pT_\infty) \tag{5 4}$$

i e , one recovers the "isothermal" results of Secs 3 and 4 only if *either* of these parameters vanishes identically or is simply negligible ‡ When this is not the case, the steady-state reactant concentration $\hat{c} \equiv c_w/c_\infty$ must first be obtained from the following Volterra integral equation[78]:

$$\hat{c}^{\,n} \exp\left[\frac{\gamma\beta(1 - \hat{c})}{1 + \beta(1 - \hat{c})}\right] = \\ -\frac{1}{z}\int_0^z \left[1 - \left(\frac{\zeta}{z}\right)^p\right]^q \frac{d\hat{c}}{d\zeta}\ \ d\zeta \tag{5 5}$$

which represents the generalized form of Eq (3 19), where the left-hand side is again recognized as the relevant local value of the reaction rate coefficient $\eta \equiv R''/R''_{\mathrm{chem}}$ (cf Fig 15) The small z expansion of Eq (5 5) reveals that a

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§§ In this case, one is led to generalized form of Eq (3 19) in which the lower integration limit takes on a nonzero value z_0, given by the magnitude that z would have for a uniform activity surface at the location $x = x_0$ Whenever the velocity field with the diffusion boundary layer is "structureless" in the x direction (e g , entry 1 of Table 1, or the region immediately downstream of the catalytically active section in a fully developed pipe flow configuration), then $pq = -1$, and the solution to this more general problem is obtained from the solutions of Eq (3 19) by merely replacing z with $(z^p - z_0{}^p)^{-q}$ wherever it appears

¶¶ Which is unity if $Pr_\lambda = Pr_D$, i e , if $D = \alpha$ (unit Lewis number)

* Clearly, this effect is greatest for reactions of small kinetic order, since the rate becomes insensitive to the magnitude of c_w

† In which the rate constant k_w is now presumed to be evaluated at the supply temperature T_∞

‡ As seen from the definition of β, the kinetics of strongly exo- or endothermic reactions ($|Q| \gg c_pT_\infty$) may still be determined using isothermal theory provided the reactant concentration c_∞ and Lewis number D/α are sufficiently small

sufficient condition for the attainment of $\eta > 1$ is that the product $\beta\gamma$ exceeds the reaction order n Thus, thermochemical heat release coupled with simultaneous limitations on heat and species transfer can result in catalyst effectiveness factors that exceed unity, as illustrated by the normalized reaction rates shown in Fig 16 Since η and hence $\bar{\eta}$ can increase above unity before decreasing to small values at large values of $\bar{c}_n$, positive values of $\partial \ln\bar{\eta}/\partial \ln\bar{c}_n$ are readily achieved, implying that the apparent activation energy E_a [cf Eq (2 16)] can actually *exceed* the true activation energy E This behavior is indicated by the dashed contour included in the Arrhenius plot (Fig 1) and is completely analogous to the effects of heat release within porous catalyst pellets of finite thermal conductivity[7 28 56 89 96] Similarly, Eq (2 18) reveals that, in these same conditions, the apparent reaction order can 1) exceed the true reaction order even when the true order is greater than unity, and 2) be smaller than the true order even when the true order is less than unity

The existence of a relation such as Eq (5 2) is the basis of most thermometric methods in analytical chemistry[73] An alternative to the technique of using a surface temperature measurement to infer local values of c_∞ is to measure the difference in heat flux to catalytic and noncatalytic surfaces maintained at the same temperature[26 73] In both probe types, an understanding of the intermediate kinetic regime is required in order to predict correction factors and to calibrate the device in an absolute sense The dependence of steady-state surface temperatures[63 70] and aerodynamic heat flux[11 12 22 64 75] on surface-catalyzed atom recombination reactions has, in fact, motivated much of the recent theoretical work in this field

It should also be stressed that in solving many problems of aerodynamic interest the compressible boundary-layer equations are first transformed to those governing the development of an equivalent incompressible boundary layer Thus, in the absence of gas-phase reactions, the results and methods described in the foregoing are directly applicable in making predictions of heat-transfer distributions around hypersonic vehicles (cf , eg , Ref 12) The accuracy of this procedure has been investigated in Ref 112

5 3 Reversible and Sequential Reactions

Although most of the previous discussion has been confined to the case of single-step irreversible reactions with a rate law of the form (2 4), in kinetic studies there is considerable interest in *reversible* reactions for which the net rate of reaction is comprised of two terms, each of the form (2 4), the sum of which is zero at equilibrium For example, Baron et al[3] have given the solution for a slug flow catalytic reactor for which the surface reaction is reversible and first order in each direction Another commonly occurring situation is the sequence of surface-catalyzed reactions[1]: $A \rightarrow B \rightarrow C$ where 1) B is a reaction intermediate§ that may either diffuse away, back-react to form A, or form the desired product C, or 2) B is the desired product and C a minor by-product Such cases have been investigated by Acrivos and Chambré[1] for laminar boundary-layer flow over flat plates This work suggests that the ability to predict reaction rate distributions in the intermediate kinetic regime will constitute a severe test of any approximate method This may be traced to the fact that the steady-state reactant concentration distribution sought in Sec 3 3 is, in turn, necessary as input information for determining product distributions, thereby magnifying the chemical-kinetic/convective-diffusion coupling effects described in that section Since catalysts are often characterized by their *selectivity*, e g , by the ratio of the rate constants for each step of a sequence of the type $A \rightarrow B \rightarrow C$, in situations where the rate of the second step ($B \rightarrow C$) is competitive with diffusional transfer of B away from the catalyst, the product distribution will depend both on the true kinetics of each step and on the conditions of convective diffusion Thus *apparent selectivity* can be used as a test for the presence or absence of diffusional limitations in both static and flow systems[78]

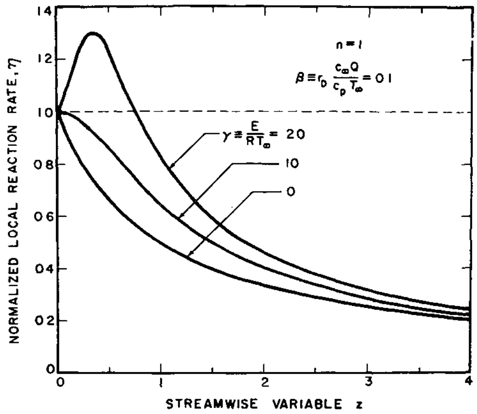

Fig 16 Normalized steady-state reaction rate for first-order exothermic reactions; quasi-stationary method

5 4 Simultaneous Homogeneous Reactions

Studies of the effects of fluid-phase reactions in catalytic reactors have been motivated primarily by the need to predict correction factors in certain simple experimental configurations, as well as the possibility of performing experiments to extract simultaneously fluid phase and heterogeneous chemical kinetic data Thus Wise and Ablow[98] have treated a particular class of slug flow tubular reactors¶ including the effects of first-order wall reactions and second-order (in reactive species) homogeneous reactions Krongelb and Strandberg,[41] Walker,[94] and Kaufman[35 36] have recently discussed the effects of simultaneous homogeneous and heterogeneous reactions on the validity of simple one-dimensional approximations for tubular reactors with Poiseuille flow It is found that homogeneous reactions can produce very large radial concentration gradients owing to the large difference in residence times implied by Eq (4 2) at various radial locations The combined effects of homogeneous and heterogeneous exothermic reactions are also of interest in predicting heat fluxes to high-speed objects entering the earth's atmosphere Aspects of this problem are considered in Refs 14 and 75 **

5 5 Mass-Transfer Effects

The considerations of Secs 3 and 4 are frequently applied to processes that are not strictly catalytic, e g , the oxidation of metals forming volatile oxides[50] In these cases, there will be a net interfacial velocity[85] that may or may not affect the accuracy of computed rate constants In any case, this can be determined by evaluating the magnitude of a

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§ Levich[42] discusses an interesting application of piecewise uniform disk electrodes for studying the individual rate constants in a reaction sequence of this type

¶ Characterized by the presence of a porous catalytic surface (simulating a calorimetric atom detector) at $x = L$

** Chung and Liu[14] derived an approximate correlation equation for the heat flux to an atom recombination catalyst by considering the homogeneous reaction to be similar in its effect to an additional surface reaction with an appropriate concentration dependence This provides an interesting contrast with the more frequently encountered treatment of a wall reaction as an "equivalent" homogeneous reaction (cf Sec 4 1) An alternative approximate approach, which should prove more accurate, has been adopted by Inger[104] for relating the complete solution to the frozen flow solution dimensionless mass-transfer parameter such as $\dot{m}''/[\rho_e v_{x,e} St_{\text{loc}}]$ (where St_{loc} is evaluated in the absence of mass transfer) and comparing it to values known to produce significant effects on the convective transfer coefficients themselves Available similar solutions to the laminar boundary-layer equations[40] suggest that, if mass-transfer effects are *not* negligible, then there will be a stronger convection-chemical kinetic coupling than in the purely catalytic case, since transfer coefficients are more sensitive to streamwise variations in diffusional driving force when there is *blowing* at the wall The situation is simpler for the configurations treated in Secs 3 1 and 3 2 (rotating disk†† and forward stagnation point, respectively), since solutions for which c_w = const are then compatible with the condition of a constant blowing rate Indeed, Chung[11] has provided a quantitative study of the effects of blowing on stagnation-point heat transfer to an atom recombination catalyst Some experimentally observed effects of simultaneous homogeneous reactions‡‡ in such a case are discussed in Ref 72

5 6 Other Configurations and Analogous Problems

In closing, it should be emphasized that the examples cited in Secs 3 and 4 by no means exhaust the well-defined flow systems for which exact solutions of the conservation equations are either readily obtainable or experimentally useful §§ Thus, the possibility of calibrating oxygen atom catalytic probe surfaces at gas pressures in the range of 1–10 torr led Hartunian and Liu[27] to investigate the problem of low Reynolds number (Oseen) flow over a catalytic sphere ¶¶ Chung[15] has treated the problem of wall recombination of shock-produced atoms for application to shock tube sidewall heat-transfer experiments In addition, the boundary-value problems of interest in the theory of diffusion and surface reaction recur in seemingly unrelated fields of transport theory such as the radiation cooling of surfaces heated by convection,[66 68 76] as well as slip-flow and temperature-jump problems in slightly rarefied gas flows over solids [68] For example, the first of these analogies, investigated in Refs 66, 68, and 76, follows immediately from the heat flux boundary condition

$$[\lambda(\partial T/\partial y)]_{y=0} = \epsilon_w \sigma T_w{}^4 \qquad (5\ 6)$$

where ϵ_w is the total hemispheric emittance of the surface and σ is the Stefan-Boltzmann radiation constant Neglecting the temperature dependence of the thermal conductivity, this is seen to be identical in form to Eq (2 5), with the quantity

$$4 + d(\ln \epsilon_w)/d(\ln T_w) \qquad (5\ 7)$$

playing the role of the effective "order " The coefficient $\bar{\eta}$ for this problem is the radiative "fin efficiency" of the surface, i e , it compares the actual radiative flux to the radiative flux had the surface temperature been T_∞ everywhere From a study of the conservation equations and boundary conditions alone, it follows that several classes of momentum and heat-transfer solutions already exist which, with minor notational changes, can be applied to the problems discussed in Secs 3 and 4

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†† Rotating disks have recently been used in the study of ablation rates (cf Ref 105) and diffusion-controlled homogeneous reactions (cf Ref 106)

‡‡ Interactions between homogeneous reactions and heterogeneous reactions with net mass transfer have recently been studied by Kulgein[107] for the case of laminar boundary-layer flow over a flat plate

§§ Tubular reactors with *annular* cross section have recently been discussed by Schmidt [108]

¶¶ The low Reynolds number catalytic sphere problem has been independently treated by Taylor [109] Results for catalytic spheres in the boundary-layer regime have been given by Kusik and Happel [110]

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