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EFFECTS OF THE STEFAN–NUSSELT FLOW ON THE APPARENT KINETICS OF HETEROGENEOUS CHEMICAL REACTIONS IN FORCED CONVECTION SYSTEMS

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Abstract—The effect of the interfacial *mass* velocity normal to surfaces undergoing heterogeneous reaction on the apparent kinetics of such reactions is quantitatively investigated. A simple algebraic model is developed which enables all pertinent non-dimensional reaction-rate coefficients to be obtained over the entire range from reaction rate ("chemical") control to diffusion control for one-step irreversible heterogeneous reactions of arbitrary kinetic order. Illustrative results are presented for the case of turbulent boundary layers on flat surfaces undergoing first-order reaction. The effect of this interfacial flow (the Stefan–Nusselt flow) is found to be significant whenever the reaction rate is not completely chemically controlled *and* the quantity $[\ln(1 + B_{\text{diff}})]/B_{\text{diff}}$ departs appreciably from unity, where B_{diff} is a diffusion-controlled dimensionless mass-transfer parameter obtainable *a priori* in terms of the reactant mass fraction in the feed and the reaction stoichiometry. The Stefan–Nusselt flow is found to (i) destroy the time-honored notion that diffusional limitations ultimately cause all surface reactions to masquerade as first order reactions, (ii) introduce a connection between the profile drag on reacting surfaces and the true kinetics of the reaction and (iii) leave unaltered the form of a potentially useful relation between the power required to maintain a reacting surface at a prescribed temperature and the true kinetics of the chemical reaction at that temperature. Applications of the theory to specific heterogeneous reactions (e.g. oxidation, chlorination, chemical vapor plating) are facilitated by the compilation of representative values of the mass-transfer parameter B_{diff}. The errors committed by neglecting the Stefan–Nusselt flow are discussed for two cases of current interest, viz. the high temperature oxidation of graphite and molybdenum in air. The results of the theory are presented and discussed in such a way as to emphasize their generality as well as the physicochemical conditions under which simple computational procedures are likely to be acceptable.

NOMENCLATURE

A,	wetted area of surface;
b,	constant appearing in equation (7) which determines sensitivity of the Stanton number to interfacial mass transfer;
B,	dimensionless mass-transfer parameter defined by equation (6);
c,	species mass fraction, or $c_{R,w}/c_{R,e}$, cf. equation (13);
c_f,	skin-friction coefficient defined by equation (41);
c_p,	specific heat of fluid per unit mass;
D,	effective Fick diffusion coefficient for reactant diffusion in the prevailing mixture, cf. equation (5);
$\mathscr{D}$,	profile drag defined by equation (42);
E,	activation energy, equation (23);
$-j_i''$,	diffusional mass flux of species i toward surface, cf. equation (5);
k_o,	pre-exponential factor appearing in equation (23);
k_w,	true chemical rate constant, defined by equation (2);
$k_{w,a}$,	apparent rate constant, defined by equation (20);
L,	characteristic length (of surface);
m,	pressure-gradient parameter, $d \ln u_e / d \ln x$;
$\dot{m}''$,	interfacial mass flux, cf. equation (3);

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M,	molecular weight, cf. equation (38);
n,	reaction order, cf. equation (2);
n_A,	"order" with respect to surface area, defined by equation (29);
n_U,	"order" with respect to flow velocity, defined by equation (28);
P,	symbol for product species;
Pr,	Prandtl number for heat conduction;
Pr_D,	Prandtl number for diffusion, $\equiv \nu/D$;
Q,	chemical heat release per unit mass of reactant (R) consumed;
$\mathcal{Q}$,	power requirement to maintain given surface temperature, cf. equation (44);
r,	stoichiometric mass ratio, defined by equation (1);
R,	symbol for reactant species;
R,	universal gas constant, cf. equation (23);
St,	Stanton number, defined by equation (5);
S,	symbol for surface species;
T,	absolute temperature;
t,	time;
u,	component of fluid velocity parallel to surface;
U,	characteristic velocity (e.g. velocity of approach stream);
$\dot{w}''_i$,	chemical source term for species i at the interface [g/cm^2 s];
W,	symbol for the element tungsten;
x,	streamwise distance along surface;
y,	distance normal to surface;
z,	stretched dimensionless distance along surface, defined by equation (14);
$\bar{z}$,	$[(\omega - 1)/\omega]z$.

Greek Symbols

β,	generalized pressure gradient parameter, cf. equation (38);
δ,	diffusion boundary-layer thickness;
ζ,	dummy variable, equation (21);
η,	normalized local reaction-rate coefficient, defined by equation (15);
$\bar{\eta}$,	overall effectiveness factor, $\equiv \dot{w}_R/\dot{w}_{R,\text{chem}} = \dot{m}/\dot{m}_{\text{chem}}$;
ν,	kinematic viscosity of fluid;
ξ,	dummy variable, equation (42);
ρ,	fluid density;
τ_w,	local skin friction (shear stress), cf. equation (42);
ϕ,	local reaction-rate coefficient, defined by equation (18);
$\bar{\phi}$,	overall reaction-rate coefficient, cf. equation (22);
ω,	diffusion boundary-layer growth parameter, defined by $\omega \equiv (\mathrm{d}\ln\delta_{B=0}/\mathrm{d}\ln x)^{-1}$.

Subscripts

a,	apparent (observed);
chem,	pertaining to chemical control ($c_w = c_e$);
diff,	pertaining to diffusion control ($c_w \to 0$);
eff,	effective value, cf. equation (38);
D,	pertaining to species transport;
e,	at outer edge of the diffusion boundary layer;
w,	at reactive surface;
R,	pertaining to reactant R;
$B = 0$,	pertaining to the case of zero interfacial mass flux;
ref,	reference value, cf. equation (38).

Miscellaneous

(g),	gaseous species, cf. equation (37);
(s),	condensed phase, cf. equation (37);
$O(1)$,	of order unity, i.e. not very different from unity.

INTRODUCTION

CHEMICAL kinetic studies of rapid heterogeneous reactions are frequently complicated by the intervention of diffusional limitations (on reactant supply, product escape, heat removal) which introduce a dependence of the observed reaction rates on fluid dynamic and transport parameters [4, 27, 30]. However, these physical phenomena need not preclude the inference of reaction-rate parameters if the reactor behavior is well understood from a theoretical point of view. Indeed, fast-flow reactors in which *both* transport and kinetic processes play an important role enable the kinetic study of surface reactions which simply could not be studied in a static system at reactant partial pressures and surface temperatures of interest. Recognition of this fact has motivated the author's previous quantitative studies of the apparent kinetics of surface-catalyzed reactions in flow systems [27, 29, 30, 34]. In addition, an understanding of these phenomena is necessary to *design* large reactors whose surfaces operate in this interesting transition region between kinetic and diffusion control.

Previous studies of this regime have been concerned, for the most part, with *surface-catalyzed* reactions as opposed to heterogeneous reactions in which the solid material is a bonafide reactant. This has simplified previous analyses since the absence of a *net* mass transfer at the fluid/solid interface ensures the applicability of a vast amount of fluid-dynamic and heat-transfer information available from earlier studies on nonreactive surfaces. However, there is a need for comparable analyses of the behavior of more general reactions in which there is a nonzero net mass transfer, and hence, a normal mass-averaged velocity (the so-called Stefan–Nusselt flow) at the boundary. In addition to defining the limits of validity of the previous work (when applied to such reactions) a more comprehensive theory can be useful in anticipating new phenomena, suggesting more general correlation procedures, and, ultimately, enabling the extraction of accurate reaction-rate parameters from measurements made in the "exchange of control" regime. The present simplified treatment is intended as a first step in this program. As such, an attempt has been made to introduce a general algebraic model (at the expense of some accuracy) which will bring out the essential new features of this class of reactions in a unified way. More accurate treatments are thus anticipated (particularly for laminar boundary-layer flows, and for fractional-order surface reactions forming volatile products) but these must of necessity contain the phenomena described herein, and will probably be best described in terms of the dimensionless variables found useful in the present analysis. In many cases, however, more accurate treatments with some pretense of generality will *not* be justified because numerous complications are associated with specific surface reactions which would be difficult to adequately account for (e.g. geometry changes during reaction, variable property effects due to the formation of heavy product molecules, product condensation within the cooler parts of diffusion boundary layers, etc.). Further remarks on these and other complicating phenomena are best postponed to the Discussion section. As in all problems, preoccupation with difficulties at too early a stage would discourage even an attempt at a comprehensive theory.

APPROXIMATE PHYSICOCHEMICAL-HYDRODYNAMIC MODEL

We consider the quasi-steady, constant property boundary-layer flow of a fluid over a reactive surface S (Fig. 1). Contained in the fluid is a reactant R which diffuses to the surface and reacts there* with S to form the product P in accord with the stoichiometry:

$$1 \text{ gram } S + r \text{ gram } R \rightarrow (1 + r) \text{ gram } P. \quad (1)$$

The product P may volatilize (or dissolve) and enter the fluid boundary layer, or, alternatively,† may adhere to the surface and possibly impede further progress of the reaction. In either event an interfacial *mass* velocity (the Stefan–Nusselt flow) is established normal to the surface as a result of these mass-transfer processes. Our object here is to incorporate the major effects of this velocity on the convective-transfer coefficients and hence, the steady-state reaction rate in the regime in which *both* kinetic and transport factors influence the observed reaction rates. Having done this, it will then be possible

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* Reactions in the fluid phase are not considered here.

† As will be discussed later on, the theory outlined here is readily extended to the class of vapor-deposition (plating) reactions in which reactant R is heterogeneously decomposed into two (or more) products P_1, P_2, ..., some of which are volatile, and some of which are adherent.

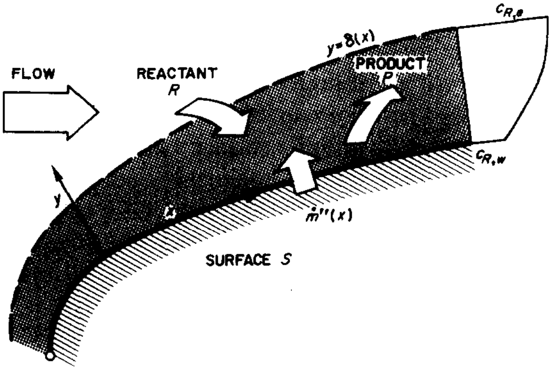

FIG. 1. Schematic of physicochemical model.

to investigate the *apparent chemical kinetics* of such reactions, i.e. the kinetics as they would appear to an observer unaware of the intervention of these transport phenomena [27, 29, 30, 34].

PHENOMENOLOGICAL KINETIC MODEL

For many surface reactions of practical interest the *rate* of reactant consumption at the surface is found to depend on a power of the *local* reactant concentration, and is independent of the local reaction-produced concentration. Considering this case,* for a constant surface-temperature system, we write the mass rate of reactant consumption $-\dot{w}''_R$ (per unit geometric surface area) as

$$\dot{w}''_R = -k_w\cdot(\rho c_{R,w})^n \tag{2}$$

where n is the (true) *reaction order*, k_w is the (true) *reaction-rate constant* and $c_{R,w}$ is the reactant mass fraction prevailing at the gas/solid interface. In accord with the stoichiometry, this rate of consumption will produce a *net* mass flux

$$\dot{m}'' = (1/r)k_w\cdot(\rho c_{R,w})^n \tag{3}$$

directed away from the surface when the (only) product P is volatile, or a net mass flux

$$\dot{m}'' = -k_w\cdot(\rho c_{R,w})^n \tag{4}$$

directed toward the surface when the (only) product P is nonvolatile.*

FLUID DYNAMIC MODEL

If one defines a local convective transfer coefficient (the Stanton number), $St(x)$, using the relation

$$D\rho(\partial c_R/\partial y)_{y=0} \equiv \rho_e u_e St\cdot(c_{R,e}-c_{R,w}) \equiv -j''_R \tag{5}$$

then an exact theory must account for

(i) the effects of both the local and *upstream* mass transfer rate $\dot{m}''$ on the local value of St;
(ii) the effects of both the local and *upstream* variations in the diffusional driving force $c_{R,e}-c_{R,w}$ on the local value of St.

In the approximate theory presented here the effect of the *local* value of the mass flux $\dot{m}''$ on the *local* value of the Stanton number *will* be accounted for, but the remaining phenomena are neglected. With regard to the mass-transfer effect this is equivalent to a *local similarity* approximation, the accuracy of which has been discussed [43] for particular cases (none of which deal with surface reactions, however). Neglecting the influence of the actual diffusional driving-force history for this class of problems is equivalent to the well-known *quasi-stationary approximation*, extensively exploited by Frank-Kamenetskiĭ [12]. The accuracy of this approximation when applied to surface-catalyzed reactions has been the subject of recent investigation by the writer [26, 27, 29, 30, 33, 34] and others [1, 6, 8, 9, 13, 15, 25, 36]. As indicated in [30], for surface reactions with nonzero Stefan–Nusselt flow, its accuracy remains to be explored. However, we anticipate (see Discussion section) that

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* That is, reactions which are effectively irreversible.

* In the latter case the rate constant k_w appearing in equation (2) may be a decreasing function of time, reflecting the partially protective role of the adherant, inert product film on the reactive surface S. This film may, alternatively, be a liquid which runs off the surface, as in the oxygen cutting of metals [39, 42]. However, for the oxidation of many materials (e.g. Mg(s), Ca(s), Ce(s), U(s)) the product film, although solid, is sufficiently porous to be completely nonprotective.

the errors will be smallest for turbulent boundary-layer flows with diffusional Prandtl numbers of order unity, for reactions orders, n near (or larger than) unity, and for surface reactions characterized by negative or small positive interfacial mass fluxes.

As has been especially emphasized by the work of Spalding [37–42], it is convenient to discuss the effects of mass transfer on the boundary layer in terms of a dimensionless mass-transfer parameter, B, defined by

$$B \equiv \dot{m}''/\rho_e u_e \cdot St. \tag{6}$$

Several investigators [11, 14, 20, 21] have shown that, for boundary layer flows, the effect of interfacial mass transfer on the magnitude of St is accurately* given by an implicit relation of the simple form †

$$St/St_{B=0} = (1 + bB)^{-1} \tag{7}$$

where the constant b is dependent on the type of boundary layer (laminar or turbulent) and is only weakly dependent on the diffusional Prandtl number. As will be seen (see Discussion section), b is a number typically near $\frac{1}{2}$, being somewhat larger for most laminar boundary-layer flows and smaller for turbulent boundary-layer flows. Equation (7) expresses the well known fact that "blowing" ($B > 0$) reduces the Stanton number, whereas "suction" ($-1 < B < 0$) increases it. The Stanton number in the absence of mass transfer, written $St_{B=0}$, is available from numerous theoretical and experimental boundary-layer studies of heat transfer (or mass transfer for $B \approx 0$) in nonreactive situations.

REACTANT CONSERVATION AT THE FLUID/SOLID INTERFACE

The central equation in the present theory is that expressing reactant conservation at the fluid/solid interface. Figure 2 shows a control volume ("pillbox") which moves in such a way as to always straddle the interface. Relative to a coordinate system fixed with respect to this interface, one notices convective fluxes as well as diffusive fluxes at the interface. In the steady state (no accumulation of reactant within the control volume) the net influx of reactant per unit area: $-j''_{R,w} - \dot{m}''c_{R,w}$ (comprised of a diffusive and convective term) must be equal to the net rate of reactant consumption, $-\dot{w}''_R$. Thus, the conservation relation may be written:

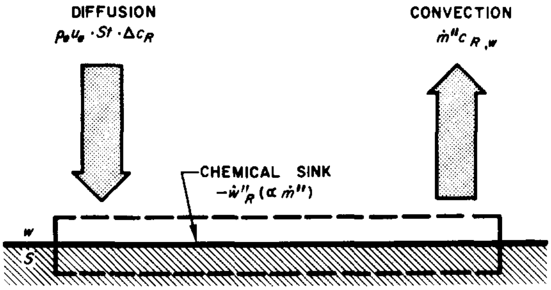

FIG. 2. Reactant conservation at the fluid/solid interface.

$$\rho_e u_e \cdot St \cdot (c_{R,e} - c_{R,w}) - \dot{m}''c_{R,w} = k_w \cdot (\rho c_{R,w})^n \tag{8}$$

where $\dot{m}''$ and the reactant "sink" term $-\dot{w}''_R$ (right-hand side) are related in accord with equations (2–4). An important limiting case occurs when the steady-state reactant concentration at the wall, $c_{R,w}$, becomes negligible (compared to $c_{R,e}$) due to the rapidity of the surface reaction and/or poor conditions of convective diffusion. In this case, which we call the *diffusion-controlled limit,* the convective term $-\dot{m}''c_{R,w}$ drops out of equation (8) and we are left with

$$\rho_e u_e \cdot St_{B=B_{\text{diff}}} \cdot c_{R,e} = \begin{cases} r\dot{m}''_{\text{diff}} \\ \qquad\qquad \text{or} \\ -\dot{m}''_{\text{diff}} \end{cases} \tag{9}$$

where the choice of the right-hand side depends on the volatility of the product P (see above).

Introducing the definition of the dimensionless mass-transfer parameter B it follows that, for volatile reaction products,

$$B_{\text{diff}} = c_{R,e}/r \tag{10}$$

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* The accuracy degenerates, however, as one approaches the limit $B \to -1$. In this extreme $St/St_{B=0} \sim (1 + B)^{-\frac{1}{2}}$ for laminar boundary-layer flows [2, 3, 38].

† Equation (7) is equivalent to the frequently cited explicit relation: $St/St_{B=0} = 1 - b(\dot{m}''/\rho_e u_e St_{B=0})$.

whereas, for nonvolatile products

$$B_{\text{diff}} = -c_{R,e}. \tag{11}$$

Since the reactant *mass fraction* at the outer edge of the boundary layer, $c_{R,e}$, cannot exceed unity (this limit being obtained in the absence of a "carrier" fluid) we see that for the present class of surface reactions.

$$-1 \leqslant B_{\text{diff}} \leqslant 1/r. \tag{12}$$

The fact that the parameter, B_{diff}, which governs the severity of the Stefan–Nusselt flow effect in any particular system, depends linearly on the undisturbed stream-reactant mass fraction obviously justifies the often quoted result that this effect is minimized by reactant dilution.*

CALCULATIONS OF STEADY-STATE REACTION RATE DISTRIBUTIONS

For most geometries of interest, the conditions of convective diffusion are not equally good at all points along the reactive surface, i.e. St has an appreciable dependence on the position x along the surface. For this reason alone a transition from near reaction-rate control rate to near diffusion control can occur along a single, isothermal surface [30]. Thus, in convective flow environments overall surfaces generally behave like integral reactors comprised of a series of back-to-back differential reactors, each of which operates somewhere between the extremes of reaction-rate control and diffusion control. We illustrate this behavior later on for the case of (non-blunted) surfaces having the property that $St(x)$ is large enough for small x so that the leading (or inlet) region always operates chemically controlled,† i.e. $c_{R,w} \approx c_{R,e}$ locally.

To treat this problem with some generality our previous work [27, 29, 30] suggests that it will prove convenient to introduce the following dimensionless quantities:

$$c \equiv c_{R,w}/c_{R,e} \tag{13}$$

$$z \equiv k_w \cdot (\rho c_{R,e})^n/\rho_e u_e \cdot St_{B=0}(x) c_{R,e} \tag{14}$$

$$\eta \equiv \dot{w}_R''(x)/\dot{w}_{R,\text{chem}}'' = c^n. \tag{15}$$

Here c is a normalized local reactant concentration, z is a stretched distance along the surface (proportional to the local diffusion boundary-layer thickness $\delta(x)$ on a nonreactive surface of the same geometry), and η is a normalized local reaction rate. The steady-state reactant conservation equation (8), and equations (2–4, 10, 11) can then be combined to yield the simple result

$$z = (1 - c)c^{-n}. \{1 + B_{\text{diff}}[c + b(1 - c)]\}^{-1} \tag{16}$$

which implicitly defines the steady-state reactant concentration distribution $c(z; n, B_{\text{diff}})$ along the surface, and, through equation (15), the steady-state *reaction-rate distribution*, $\eta(z; n, B_{\text{diff}})$, along the surface. To this solution there corresponds a steady-state distribution of the mass transfer parameter B, obtained, *a posteriori*, from:

$$B/B_{\text{diff}} = z\eta/(1 - bB_{\text{diff}} z\eta). \tag{17}$$

It will be noted that $B(z)$ approaches B_{diff} as $z \to \infty$ since the normalized reaction rate falls off like $\eta \sim [(1 + bB_{\text{diff}})z]^{-1}$ in this limit.

One further dimensionless reaction-rate variable of interest is

$$\phi \equiv \dot{w}_R''/\dot{w}_{R,\text{diff}}'' = \dot{m}''/\dot{m}_{\text{diff}}'' \tag{18}$$

which is a measure of the approach to local diffusion control along the surface. Using the preceding definitions we obtain the interrelation:

$$\phi = (1 + bB_{\text{diff}})z\eta. \tag{19}$$

Thus, a simple algebraic equation, equation (16), contains all relevant information on the steady state *distributions* of reactant concentration, reaction rate, transfer coefficient, etc.,

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* Several investigators [2, 7] imply that these effects will be important for surface-*catalyzed* reactions. However, for a surface-catalyzed reaction (e.g. H atom recombination on solid surfaces) the *net* mass flux, $\dot{m}''$ vanishes despite the fact that the *reactant* consumption rate, $-\dot{w}_R''$, is nonzero. Thus [cf. equation (3)] r is infinite and $B_{\text{diff}} = 0$.

† Quantities evaluated in the chemically controlled extreme will be denoted hereafter by the subscript chem.

along reactive surfaces. Equation (16) also contains, as a special case ($B_{\text{diff}} = 0$), the previously discussed [30] quasi-stationary equation governing external diffusion effects in heterogeneous *catalysis*.

SURFACES VIEWED AS INTEGRAL REACTORS

By adding up the contributions of the reaction rate at each point, $\dot{w}_R'''(x)$, we obtain the *total* reaction rate $\dot{w}_R$ for the surface in question. In any case it is of interest to compare this rate to the two calculable* extreme rates. The first of these is the rate $\dot{w}_{R,\text{chem}}$ which would exist if the reaction were everywhere chemically controlled. The second is the rate $\dot{w}_{R,\text{diff}}$ which would exist if the reaction rate were everywhere diffusion-limited. These comparisons define two dimensionless reaction-rate coefficients $\bar{\eta}$ and $\bar{\phi}$, analogous to η and ϕ. As discussed in [29, 30] the factor $\bar{\eta} \equiv \dot{w}_R/\dot{w}_{R,\text{chem}}$ can be viewed in two distinct ways. Since the rate $\dot{w}_{R,\text{chem}}$ is linearly related to the wetted surface area A, the product $\bar{\eta}A$ may be regarded as an *effective surface area* operable in the presence of the diffusional limitation (hence, the name *effectiveness factor* for $\bar{\eta}$). Alternatively, if one defines an *apparent reaction-rate constant*, $k_{w,a}$, by the expression

$$k_{w,a} \equiv (-\dot{w}_R)/(\rho c_{R,e})^n A \tag{20}$$

(cf. equation (2)) then $\bar{\eta}$ may be interpreted as the ratio of this apparent reaction-rate constant to the true specific reaction-rate constant k_w. In what follows we briefly consider the calculation of $\bar{\eta}$ for a particular class of boundary-layer flows which will be referred to later in the numerical examples.

For many geometries of interest the Stanton number $St_{B=0}$ varies as a simple power of the streamwise distance x, corresponding to a diffusion boundary-layer thickness, $\delta_{B=0}$ which also varies as a power of the distance x. If, say, $\delta_{B=0} \propto x^{1/\omega}$ ($\omega = 2, 5$ for laminar and turbulent boundary layers, respectively) and the streamwise variation of b can be neglected, we can readily obtain $\bar{\eta}$ from the solutions for the local reaction rate distribution $\eta(z; n, B_{\text{diff}})$ outlined in the previous section. The required relation is*

$$\bar{\eta} = z^{-\omega} \int_0^z \eta(\zeta; n, B_{\text{diff}})\omega\zeta^{\omega-1}\,\mathrm{d}\zeta. \tag{21}$$

Upon carrying out this integration the reaction rate coefficient $\bar{\phi} \equiv \dot{w}_R/\dot{w}_{R,\text{diff}} = \dot{m}/\dot{m}_{\text{diff}}$ is readily obtained from $\bar{\eta}$. In fact, if one defines† $\bar{z} \equiv [(\omega - 1)/\omega]z$ then $\bar{\phi}$ may be expressed

$$\bar{\phi} = (1 + bB_{\text{diff}})\bar{z}\bar{\eta} \tag{22}$$

which is identical in form to equation (19).

FALSIFICATION OF KINETICS DUE TO TRANSPORT LIMITATIONS

Together with the reduction in the apparent rate constant, there is an accompanying reduction in apparent activation energy, as well as a deviation between the true and apparent reaction order. General quantitative expressions for these important deviations, obtainable using the approach of [27, 29, 30, 34], are given and discussed below.

Consider the class of reaction-rate constants of the two-parameter Arrhenius form:

$$k_w = k_0 \exp[-E/(RT_w)] \tag{23}$$

where the pre-exponential factor, k_0, is a constant, and the ratio of the true activation energy, E, to the universal gas constant, R, may be considered a characteristic temperature of the reaction in question. In experiments designed to evaluate E one usually varies the temperature of the system (or surface) and plots of logarithm of the observed reaction rate as a function of the reciprocal surface temperature. The apparent

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* For the present we assume the true kinetic constants of the reaction are known. In applying the theory one may invert the procedure and determine these constants from those reaction-rate coefficients which are experimentally accessible.

* Here ζ is a dummy (integration) variable.

† Which is a coordinate identical to z [cf. equation (14)] except based on the average coefficient $\overline{St}_{B=0}$ for the surface up to location x.

activation energy will therefore be[*]

$$E_a \equiv -R[\mathrm{d}\ln \dot{m}/\mathrm{d}(1/T_w)]. \qquad (24)$$

In the limit $E \gg RT_w$, the previous definitions reveal that[*]

$$E_a/E = 1 + (\mathrm{d}\ln \bar{\eta}/\mathrm{d}\ln \bar{z}). \qquad (25)$$

Thus, E_a will depart from E whenever $\bar{\eta} \equiv \dot{m}/\dot{m}_{\mathrm{chem}}$ departs from unity. Aside from the fact that $\bar{\eta}$ depends parametrically upon B_{diff}, this result is formally identical to the corresponding result for surface-catalyzed reactions. The reason is simply that the new parameter B_{diff} is temperature-independent.[†] However, consideration of the apparent reaction order presents an interesting new aspect, as outlined below.

If the reactant concentration in the feed, $c_{R,e}$, is systematically varied, the chemical reaction will appear to be characterized by the reaction order

$$n_a \equiv \mathrm{d}\ln \dot{m}/\mathrm{d}\ln c_{R,e} \qquad (26)$$

where $\dot{m} = \dot{m}_{\mathrm{chem}} \cdot \bar{\eta}(\bar{z};\, n,\, B_{\mathrm{diff}})$. Now one must account for the fact that in addition to changing $\dot{m}_{\mathrm{chem}}$ a change in $c_{R,e}$ changes $\bar{\eta}$, not only because of its effect on $\bar{z}$ (when $n \neq 1$), but also because of its effect on B_{diff} [cf. equations (10, 11)]. accord with the chain rule one then finds

$$n_a = n + (n-1)(\partial \ln \bar{\eta}/\partial \ln \bar{z})_{B_{\mathrm{diff}} = \mathrm{const}} + (\partial \ln \bar{\eta}/\partial \ln B_{\mathrm{diff}})_{\bar{z} = \mathrm{const.}} \qquad (27)$$

In the absence of this last term we recall [30] that the approach to diffusion control is always characterized by an approach to apparent first order kinetics.[‡] This is *not* the case for surface reactions with nonzero mass velocity at the interface, as will be numerically illustrated later on.

Since B_{diff} is also independent of flow-rate and reactor dimensions one finds that the expressions for the dependence of reaction rate on flow rate and wetted area are formally identical to those cited in [34], i.e. for two-dimensional diffusion boundary layers which grow according to $\delta_{B=0} \propto x^{1/\omega}$

$$n_U \equiv \mathrm{d}\ln \dot{m}/\mathrm{d}\ln U = -[(\omega - 1)/\omega](\mathrm{d}\ln \bar{\eta}/\mathrm{d}\ln \bar{z}) \qquad (28)$$

and[*]

$$n_A \equiv \mathrm{d}\ln \dot{m}/\mathrm{d}\ln A = 1 + (1/\omega)(\mathrm{d}\ln \bar{\eta}/\mathrm{d}\ln \bar{z}). \qquad (29)$$

The presence of nonzero B_{diff} will be seen to have no effect on the asymptotic values (small $\bar{z}$ and large $\bar{z}$) of d ln $\bar{\eta}$/d ln $\bar{z}$. We therefore conclude that the Stefan–Nusselt flow does *not* change the *limiting* values of n_U and n_A but only the *shape* of the transition between their limiting values. Thus, for example, if a surface-catalyzed reaction rate in a given reactor exhibits a variation with approach flow velocity which ranges between U^0 (chemical control) and $U^{\frac{1}{2}}$ (diffusion control) these same limiting exponents are to be expected for reactions with nonzero interfacial mass velocity.

ILLUSTRATIVE RESULTS

To illustrate the nature of the Stefan–Nusselt flow effect on the transition from reaction-rate control to diffusion control we concentrate here on a particular case. Since the errors inherent in the present approximate theory are expected to be smallest for (i) turbulent boundary-layer flow over nearly flat surfaces with diffusional Prandtl numbers (ν/D) near unity and (ii) reactions whose true kinetic order, n, is not too small, all illustrative numerical results collected here (in the form of dimensionless graphs) will pertain to the following choice

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[*] In this, and all subsequent formulae containing d ln $\dot{m} \equiv \mathrm{d}\dot{m}/\dot{m}$, the absolute value of $\dot{m}$ is implied.

When $E \gg RT$ then $E_a/E = \mathrm{d}\ln \dot{m}/\mathrm{d}\ln k_w$, hence equation (25) predicts the sensitivity of the observed reaction rate to a change (or uncertainty) in the reaction-rate coefficient.

[†] In applying the present theory to the calculation of E_a/E it is assumed that the effective stoichiometry (hence, product distribution) does not change with temperature level. In regimes where changes in product distribution occur, B_{diff} would be temperature-dependent (through the quantity r appearing in equation (10), see Discussion section).

[‡] For the case of concentration-independent Fick diffusion coefficient.

[*] For a two-dimensional surface $\mathrm{d}A = \mathrm{d}x$.

of parameters: $n = 1$, $\omega = 5$, i.e. to first-order surface reactions in a fluid dynamic situation for which $\delta_{B=0} \propto x^{\frac{4}{5}}$ (hence, $St_{B=0} \propto x^{-\frac{1}{5}}$). For constant property turbulent boundary layers with small streamwise pressure gradients the constant b is estimated as 0·34, based on [44]. Calculations are then carried out for selected values of the mass transfer parameter B_{diff} (with results shown here for $B_{\text{diff}} = -1{\cdot}0$,* $-0{\cdot}5$, 0, 0·5, 1·0, 2·0, 4·0). A discussion of the magnitude of B_{diff} encountered for some specific reactions of current interest will be given in the Discussion section.

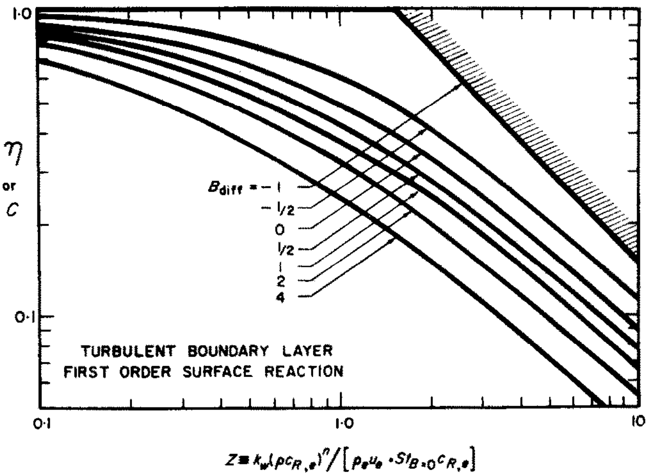

FIG. 3. Normalized reaction-rate (and reactant-concentration) distributions along a flat plate.

Figure 3 shows the results for the normalized *distributions* of both reactant concentration and reaction rate [these are identical for first order reactions; cf. equation (15)], as obtained from equation (16). Except for the singular case (limit) $B_{\text{diff}} = -1$, one notices a gradual decay of reaction rate down the isothermal surface, with large departures from local chemical control occurring earlier in the case of large values of the mass transfer B_{diff}. It is interesting to note that the small-z behavior is independent of the boundary-layer constant b, and hence, is similar (in these coordinates)* for both laminar and turbulent boundary layers. Explicitly, for small z we find:

$$c \sim 1 - (1 + B_{\text{diff}})z \tag{30}$$

$$\eta \sim 1 - n(1 + B_{\text{diff}})z. \tag{31}$$

In contrast, the *product* bB_{diff} governs the large z behavior, which is found to be

$$c \sim [(1 + bB_{\text{diff}})z]^{-1/n}. \tag{32}$$

Correspondingly,

$$\eta \sim [(1 + bB_{\text{diff}})z]^{-1}. \tag{33}$$

Thus, for any reaction order n, η ultimately falls off like $1/z$, with a spacing determined by the factor $(1 + bB_{\text{diff}})^{-1}$. Corresponding results for the reaction-rate function $\bar{\Phi}$ can be obtained from equation (18).

Similar remarks can be made about the integrated reaction-rate coefficient $\bar{\eta}(\bar{z}; n, B_{\text{diff}})$, shown in Fig. 4 (for the case $\omega = 5$, $n = 1$). For

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* The limiting case. $B_{\text{diff}} = -1$ is singular, and will be discussed later on.

* Note that in these coordinates the boundary-layer growth parameter ω does not appear explicitly in determining the distributions of reactant concentration and reaction rate.

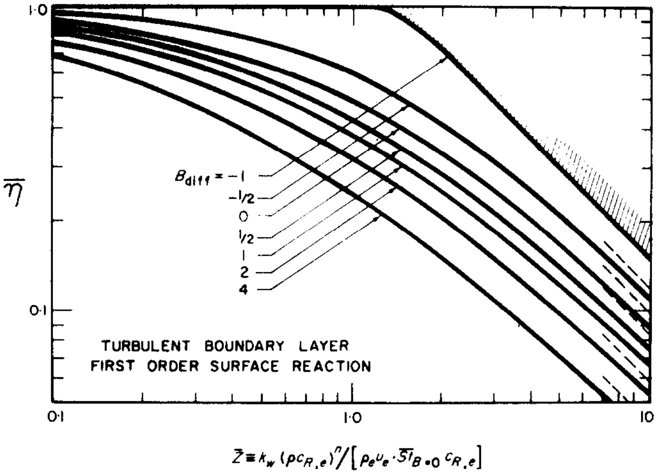

FIG. 4. Reduction in overall reaction rate on a flat plate due to external diffusional limitations.

small values of $\bar{z}$ the total reaction rate is not much smaller than the chemically controlled value, and

$$\bar{\eta} \sim 1 - n(1 + B_{\text{diff}})[\omega^2/(\omega^2 - 1)]z. \qquad (34)$$

This result (which does not contain b) is valid for both laminar and turbulent boundary layers. For very large values of $\bar{z}$, the bulk of the surface is operating near the diffusion-controlled limit, and, asymptotically* (as $\bar{z} \to \infty$)

$$\bar{\eta} \sim [(1 + bB_{\text{diff}})\bar{z}]^{-1} \qquad (35)$$

[cf. equation (33)]. The ratio, $\bar{\phi}$, of the actual total reaction rate to the rate which will be obtained if local diffusion control prevailed everywhere, is readily obtained from equation (22). The relation between the two dimensionless reaction rates, $\bar{\eta}$ and $\bar{\phi}$, is shown in Fig. 5. Since diffusion-controlled reaction rates can often be calculated *a priori*, a knowledge of the theoretical dependence of $\bar{\phi}$ on $\bar{z}$ (through $\bar{\eta}$) can be used to infer the rate constant from observed kinetic data in the intermediate regime.

A reduction in the overall reaction rate due to diffusional limitations is, of course, accompanied by a reduction in the apparent activation energy of the reaction. This correlation (between E_a/E and $\bar{\eta}$) is shown in Fig. 6, again for the case $\omega = 5$, $n = 1$. One notices that increasing B_{diff} *reduces* the departure of E_a from E that accompanies a given reduction in the absolute value of the reaction rate.

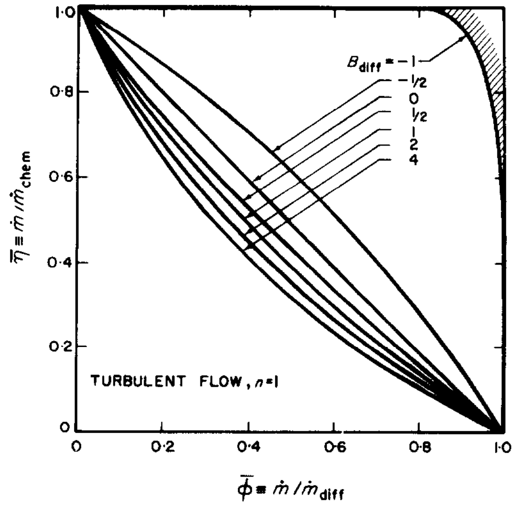

FIG. 5. Relation between the dimensionless reaction-rate coefficients $\bar{\eta}$ and $\bar{\phi}$.

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* This result implies that $\bar{\eta}$ at a given value of $\bar{z}(\gg 1)$ will be approximately the same for both laminar and turbulent boundary-layer situations, provided $\bar{\eta}$ is evaluated *at the same value of the product* bB_{diff}.

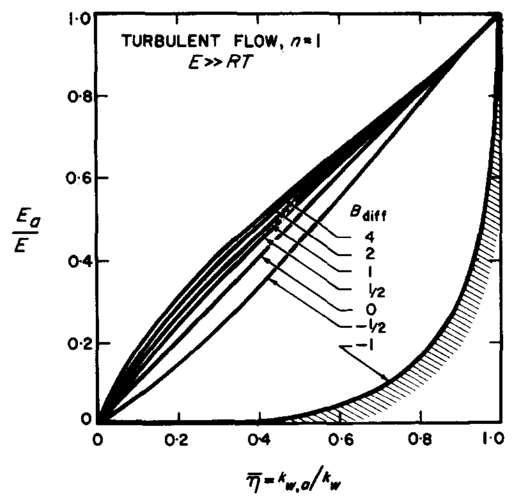

FIG. 6. Relation between the reduction in apparent activation energy and apparent rate constant.

Perhaps the most interesting new phenomenon to emerge in considering the effects of the Stefan–Nusselt flow concerns the apparent kinetic order of surface reactions. One normally expects isothermal diffusional phenomena to ultimately cause all reactions to masquerade as first-order reactions, regardless of their true kinetic order [4, 30]. This is *not* the case here since the diffusion-limited rates depend on B_{diff} which itself depends (linearly) on the reactant concentration in the feed. Figure 7 demonstrates the resulting behavior for surface reactions which have a *true* kinetic order of unity. One notices that in the diffusion limit ($\bar{\phi} \to 1$) such reactions may appear to have reaction orders which are greater than, or less than, unity, depending on the nominal value of B_{diff}. It is also clear from Fig. 7 that deviations from the true kinetic order are *not* necessarily greatest in the diffusion-controlled extreme.

DISCUSSION

To appreciate the importance of the effects contained in the previous relations it is first necessary to consider the magnitudes of the parameters B_{diff} and b encountered in practice. Values of the diffusion-limited blowing parameter B_{diff} are therefore collected below for a number of chemical systems, including oxidation reactions and so-called chemical vapor-plating systems. Likewise, suggested values of the boundary layer (mass-transfer sensitivity) parameter b are summarized, and corrections for the effects of pressure gradient and variable properties (e.g. unequal molecular weights) indicated. We then consider two particular implications of the present theory; viz. (i) the modification of profile drag on reactive solids, and (ii) the use of energy transfer to characterize chemical surface reactions which are not thermoneutral. Previous work on the nature of the transition between chemical control and diffusion control for the surface combustion of graphite, and the high-temperature oxidation of molybdenum is criticized in the light of the present theory, and the role of the Stefan–Nusselt flow is clarified in each case. We conclude with a discussion of the expected accuracy of the approximations introduced in the present work, and areas in need of improvement and/or generalization.

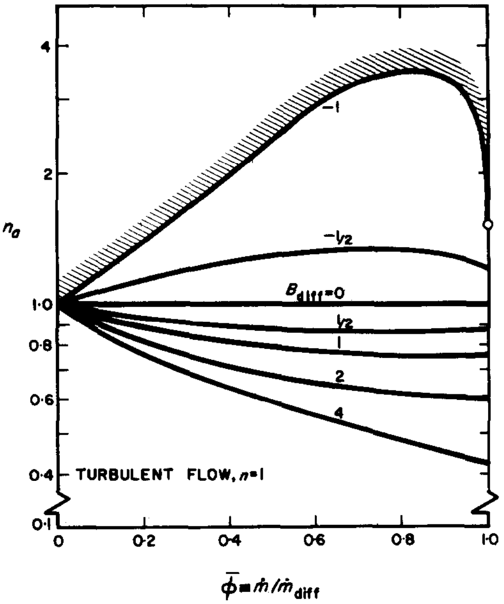

FIG. 7. Diffusional falsification of reaction order.

THE MASS-TRANSFER PARAMETER B_{diff}

Values of B_{diff} for representative chemical surface reactions are collected below. Two tables are given, Table 1 pertaining to reactants which are undiluted (i.e. $c_{R,e} = 1$). Table 2 pertains to the values of B_{diff} encountered for various heterogeneous oxidation processes in *air* (the ubiquitous oxidizer). In both tables we include a column giving the ratio of the gaseous product molecular weight, M_P, to the molecular weight, M_e, of the fluid at the outer edge of the diffusion boundary layer. As will be seen, when this ratio departs appreciably from unity it is necessary to modify the absolute value of b. Note that two values of B_{diff} are given for the same reactants (R and S) depending on the identity of the principal product P. In these systems values of B_{diff} intermediate between the extremes tabulated are therefore possible, reflecting the simultaneous presence of both stable products.

As already indicated, the present theory can be generalized* to include vapor deposition reactions [24] which yield several products $P_1, P_2, \ldots$, some of which are volatile and one of which (identical to S) remains behind. Thus, if r g of reactant R are needed to deposit 1 g of nonvolatile product S, ($r > 1$) we find

$$B_{\text{diff}} = -\,c_{R,e}/r \qquad (36)$$

[which, apart from the sign, is identical to

Table 1. Some values of B_{diff} for surface reactions in streams of pure gaseous reactant ($c_{R,e} = 1$, $M_e = M_R$)

Surface S	Reactant R	Product(s) P	M_P/M_R	B_{diff}
$C(s)$	$O_2(g)$	$CO(g)$	0·876	+0·751
$C(s)$	$O_2(g)$	$CO_2(g)$	1·375	+0·375
$C(s)$	$H_2O(g)$	$CO(g) + H_2(g)$	0·833	+0·667
$C(s)$	$CH_4(g)$	$C(s) + 2H_2(g)$	0·125	−0·750
$W(s)$	$O_2(g)$	$WO_2(g)$	6·746	+5·74
$W(s)$	$O_2(g)$	$WO_3(g)$	7·246	+3·83
$W(s)$	$Cl_2(g)$	$WCl_2(g)$	3·593	+2·59
$W(s)$	$H_2O(g)$	$WO_3(g) + 3H_2(g)$	3·301	+3·40
$W(s)$	$H_2O(g)$	$WO_2 + 2H_2(g)$	4·068	+5·10
$Mo(s)$	$O_2(g)$	$MoO_2(g)$	3·998	+3·00
$Mo(s)$	$O_2(g)$	$MoO_3(g)$	4·498	+2·00
$Mo(s)$	$Cl_2(g)$	$MoCl_2(g)$	2·353	+1·35
$Mo(s)$	$H_2O(g)$	$MoO_3(g) + 3H_2(g)$	2·082	+1·78
$Ni(s)$	$O_2(g)$	$NiO(g)$	2·335	+3·67
$Ni(s)$	$Cl_2(g)$	$NiCl_2(g)$	1·830	+0·828
$Ge(s)$	$O_2(g)$	$GeO(g)$	2·769	+4·54
$Si(s)$	$Cl_2(g)$	$SiCl_4(g)$	2·396	+0·198
$Ir(s)$	$O_2(g)$	$Ir_2O_3(g)$	13·51	+8·01
$Ir(s)$	$O_2(g)$	$IrO_3(g)$	7·506	+4·00
$Ta(s)$	$O_2(g)$	$Ta_2O_5(s)$	—	−1·00
$Nb(s)$	$O_2(g)$	$Nb_2O_5(s)$	—	−1·00
$Pt(s)$	$H(g)$	$H_2(g)$	2·000	0·000

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* Another generalization of interest is to the kinetics of condensation, sublimation or dissolution, for which [39, 42] $B_{\text{diff}} = (c_{S,w\,\text{eq}} - c_{S,e})/(1 - c_{S,w\,\text{eq}})$.

Table 2. Some values of B_{diff} for surface oxidation in air ($R = O_2(g)$, $c_{R,e} = 0{\cdot}231$, $M_e = 28{\cdot}97$)

Surface	Product	M_P/M_e	B_{diff}
$C(s)$	$CO(g)$	0·9669	+0·174
$C(s)$	$CO_2(g)$	1·519	+0·0868
$W(s)$	$WO_2(g)$	7·451	+1·33
$W(s)$	$WO_3(g)$	8·003	+0·887
$Mo(s)$	$MoO_2(g)$	4·417	+0·694
$Mo(s)$	$MoO_3(g)$	4·969	+0·463
$Ni(s)$	$NiO(g)$	2·579	+0·849
$Ir(s)$	$Ir_2O_3(g)$	14·92	+1·85
$Ir(s)$	$IrO_3(g)$	8·291	+0·927
$Ta(s)$	$Ta_2O_5(s)$	—	−0·231
$Nb(s)$	$Nb_2O_5(s)$	—	−0·231

equation (10)]. As an example, consider the deposition of solid graphite [22] by passing a stream of methane gas over a heated mandrel. In this case the principal chemical reaction may be represented as

$$CH_4(g) \rightarrow C(s) + 2H_2(g). \qquad (37)$$

To deposit 12·00 g of carbon one must pyrolyze 16 g ($=M_{CH_4}$) of methane, hence $r = 1{\cdot}333$. If the gas stream passing over the mandrel is pure methane, we then have $B_{diff} = -0{\cdot}750$. Similar examples occur in the deposition of tungsten from $WF_6(g)$-containing gases, the deposition of boron from $BBr_3(g)$-containing gases, etc.*

THE BOUNDARY-LAYER CONSTANT *b*

Many experimental and theoretical investigations have been concerned with the effects of interfacial mass transfer on the magnitude of convective heat- and mass-transfer coefficients. Since not all of the correlations obtained can be cast in the form of equation (7) over the entire range of the parameter $B(-1 < B < \infty)$ it is convenient to compare the available findings for $B^2 \ll 1$. This is done in Table 3 for the case of two-dimensional constant-property boundary layers in the absence of large streamwise velocity gradients. For treating the effects of variable properties, velocity gradient [46], etc., the approach that has been taken by most investigators is to suitably modify the values of b given in Table 3. Upon surveying available predictions for *laminar* boundary layers in the absence of chemical reaction, Eckert [11] suggested a relation equivalent (in the present notation) to

$$b_{eff} = b(\rho_e/\rho_{ref})(1 - \tfrac{1}{2}\beta)^{\frac{1}{2}} (M_e/M_P)^{\frac{1}{3}}. \qquad (38)$$

Here ρ_{ref} is a reference density of the approach fluid (computed at a static temperature about mid-way between the approach stream temperature and the surface temperature), β is a generalized velocity-gradient parameter* (taking on the values 0 for flat plate flow, 1 for two-dimensional stagnation-point flow and $\frac{1}{2}$ for axially symmetric stagnation-point flow) and M_P is the molecular weight of the transferred fluid. For turbulent boundary-layer flow a similar relation was suggested [11]:

$$b_{eff} = b(\rho_e/\rho_{ref})(M_e/M_P)^{\frac{2}{3}} \qquad (39)$$

Table 3. Values of the parameter b for B near zero (constant properties, zero pressure gradient)

Boundary layer	Pr_D	b	Ref.
laminar	$\gg 1$	0·566	[19, 20]
laminar	$O(1)$	0·724	[19, 20]
laminar	$O(1)$	0·73	[11]
laminar	$O(1)$	0·71	[44]
turbulent	$O(1)$	0·37	[11]
turbulent	$O(1)$	0·34	[44]
turbulent	$O(1)$	0·16	[14]
turbulent	$O(1)$	0·50	[39, 42]
turbulent	$O(1)$	0·414	[18]

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* In using the gaseous halides one commonly introduces hydrogen as well, to tie up the reactive halogen [24].

* For two-dimensional boundary-layer flow

$$\beta = 2m/(m + 1),$$

where $m \equiv \mathrm{d} \ln u_e/\mathrm{d} \ln x$.

where the absence of the factor β reflects an insensitivity of the turbulent boundary layer to nonzero values of the pressure-gradient parameter β. While those correlations will probably require refinement in the light of new information (obtained for extreme property variations) it is clear that the effective value of b is increased for the flow over heated surfaces ($\rho_{\text{ref}} < \rho_e$) at which lightweight products are generated ($M_P < M_e$). Reference to Tables 1 and 2 shows that the *largest* values of B_{diff} correspond to the attack of relatively high-molecular-weight solids, and hence the generation of *heavy*-product molecules (e.g. the oxidation of iridium). In these cases b, and hence the product bB_{diff}, should be reduced in accord with the abovementioned molecular weight effect.

It should be reiterated that the relation $St/St_{B=0} = (1 + bB)^{-1}$ exploited herein cannot be used for values of B near the "suction" limit, -1. For laminar boundary layers on surfaces of arbitrary shape, Acrivos [2] has shown that in this limit the proportionality constant $St \cdot (1 + B)^{\frac{1}{2}}$ contains all of the effects of variable properties.

With regard to the need for a rough criterion for the importance of the Stefan–Nusselt flow, the film-theory relation [42]

$$St/St_{B=0} \approx [\ln(1 + B)]/B \qquad (40)$$

[which implies $b = \frac{1}{2}$ ($B^2 \ll 1$)] suggests itself. Thus, we can state that unless $[\ln(1 + B_{\text{diff}}]/B_{\text{diff}}$ is near unity, or diffusional limitations are negligible, it will be necessary to account for the Stefan–Nusselt flow effect in the analysis of heterogeneous reactions.

PROFILE DRAG ON REACTING SURFACES

In heterogeneous combustion systems it has frequently been reported that burning and/or evaporating droplets do not accelerate at the rate which would be predicted from available nonreactive sphere-drag data [39]. More generally, as a consequence of the Stefan–Nusselt flow, we can expect both the profile- and form-drag on reacting surfaces to be different from the corresponding drag on nonreactive surfaces of the same geometric shape. Form-drag alteration will not be considered here, although it is clear that changes in the location of boundary-layer separation and detachment can produce large changes in the prevailing pressure distribution. On the other hand the change in profile drag (due to the integrated effect of the component of the local frictional drag in the direction of flow) can be estimated using the theory presented earlier, together with Reynolds analogy [5]. This extension is outlined below, with particular attention to the change in profile drag associated with the transition from chemical control to local diffusion control.

For $Pr_D \approx 1$, in the absence of streamwise pressure gradients, the simplest form of Reynolds analogy is applicable, and may be concisely stated:*

$$\tfrac{1}{2}c_f \equiv \tau_w(x)/\rho_e u_e^2 = St \qquad (41)$$

where c_f is the dimensionless skin friction coefficient. Since this result holds with or without mass transfer at the interface, $c_f/c_{f,B=0}$ may be taken as equal to $St/St_{B=0}$ [cf. equation (7)]. Utilizing these properties, we consider the integrated drag force (per unit depth) on a flat plate:

$$\mathscr{D}(x) \equiv \int_0^x \tau_w(\xi)\,\mathrm{d}\xi \qquad (42)$$

and examine the ratio $\mathscr{D}(x)/\mathscr{D}_{B=0}(x)$. In this way we find that, for either laminar or turbulent boundary-layer flow, the alteration in overall drag bears a simple relation to the reaction-rate coefficient $\bar{\phi}(\equiv \dot{m}/\dot{m}_{\text{diff}})$ introduced earlier. The result is

$$\mathscr{D}/\mathscr{D}_{B=0} = [1 + bB_{\text{diff}}(1 - \bar{\phi})]/(1 + bB_{\text{diff}}) \qquad (43)$$

which is seen to vary monotonically between

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* The definition of c_f given here corrects a typographical omission (the factor $\frac{1}{2}$) in the Nomenclature of [29].

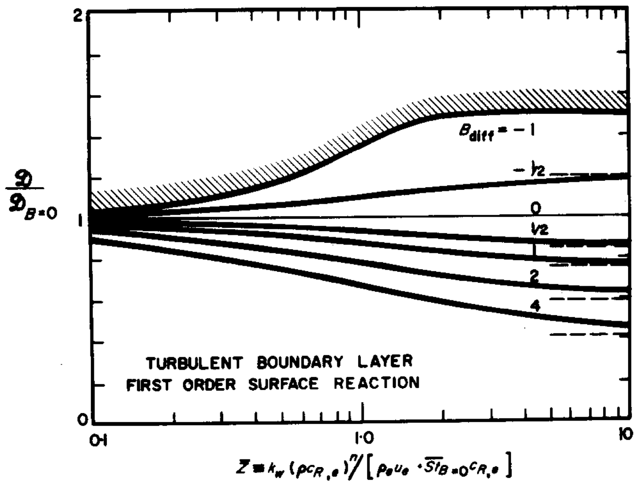

FIG. 8. Drag alteration on reactive surfaces in the transition regime.

unity (when $\bar{\phi} = 0$) and $(1 + bB_{diff})^{-1}$ (when $\bar{\phi} = 1$). This transition behavior is shown in Fig. 8, for the case of turbulent boundary-layer flow.* It will be recalled that the abscissa, $\bar{z}$, contains the reaction-rate constant k_w as a multiplier. Thus, for example, if the product bB_{diff} were sufficiently large, it is conceivable that a measurement of actual drag reduction could provide an estimate of $\bar{\phi}$ and, hence, other reaction-rate parameters of interest. Conversely, relations of this kind might be used to estimate the alteration in pressure drop anticipated within tubular reactors and similar equipment.

ENERGY TRANSFER REQUIREMENTS FOR REACTING SURFACES

In addition to changing the profile drag, heterogeneous chemical reaction will generally alter the amount of power required to maintain the surface at any prescribed, elevated temperature $T_w(> T_e)$. This altered power requirement can be calculated using the present theory provided internal heat conduction renders the surface temperature *uniform*. Heterogeneous chemical reaction alters the energy requirement in two ways: (i) by altering the local Stanton number for heat transfer (as a result of the Stefan–Nusselt flow)* and (ii) by generating (or absorbing) heat locally at the rate $-\dot{w}_R''Q$. The relative importance of the latter mechanism is found to be governed by a dimensionless exothermicity parameter, $c_{R,e}Q/c_p(T_w - T_e)$, which appears here for the first time. We consider here the heat balance in the absence of appreciable radiation loss, and for values of the Lewis number (Pr/Pr_D) near unity. Combining the energy and species balance with equation (7), for the flat plate geometry we find

$$\mathcal{Q}/\mathcal{Q}_{B=0} = (\mathcal{D}/\mathcal{D}_{B=0}) - [c_{R,e}Q/c_p(T_w - T_e)]\,\bar{\phi}(1 + bB_{diff})^{-1} \qquad (44)$$

a result which likewise applies to either laminar or turbulent boundary-layer flow. One notes here the individual contributions of mechanisms (i), (ii) above—the alteration in convective heat transfer being identical to the drag alteration $\mathcal{D}/\mathcal{D}_{B=0}$ already given by equation (43).

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* Predictions of the reduction in drag for laminar boundary-layer flow over a flat plate with first-order surface reaction have been made by Kulgein [17].

* It is sometimes stated, or implied, that the Stefan–Nusselt flow destroys the analogy between convective heat transfer and mass transfer. This is *not* the case, as has recently been reiterated by W. E. Stewart [46]. Mass transfer merely becomes analagous to heat transfer *in the presence of blowing or suction at the wall.*

Because of the presence of the additional term (weighted by the heat release parameter) the change in power requirement can be used as a sensitive indicator[*] of the reaction rate coefficient $\bar{\phi} \equiv \dot{m}/\dot{m}_{\text{diff}}$ (and, hence, the true kinetics) whenever the remaining parameters in equation (44) are independently measurable or estimable. This result can be written in the simple inverted form:[†]

$$\bar{\phi} = [1 - (\mathcal{Q}/\mathcal{Q}_{B=0})]/[1 - (\mathcal{Q}/\mathcal{Q}_{B=0})_{\text{diff}}] \quad (45)$$

which clearly brings out the relation between the reaction rate coefficient $\bar{\phi}$ and the power requirement ratio $\mathcal{Q}/\mathcal{Q}_{B=0}$.

EFFECT ON TRANSITION-REGIME PREDICTIONS AND DIFFUSION CORRECTIONS

Among other assumptions, several investigators have (implicitly) neglected the effect of the Stefan–Nusselt flow in cases where non-negligible systematic errors may be incurred. Since incorporation of the dominant effects of this flow would seem to entail no appreciable difficulty, cruder approximations cannot be justified on the grounds of their simplicity alone. Two specific examples will be critically considered here. The first deals with predictions of the ablation rate of graphite in the transition regime between chemical control and diffusion control. The second deals with the proper treatment of rate data obtained in the presence of diffusional limitations.

Accurate calculations of the diffusion-limited ablation rate, $\dot{m}''_{\text{diff}}$, have been reported for graphite in air [35]. However, since this upper limit is frequently not achieved in practice it is necessary to incorporate kinetic limitations, by availing oneself of true reaction-rate data, say, in the form $\dot{m}''_{\text{chem}}(T_w, p_{O_2,w})$. It was originally recommended [23] that the required "interpolation" be done in accord with the familiar *resistance-additivity* result

$$1/\dot{m}'' = (1/\dot{m}''_{\text{chem}}) + (1/\dot{m}''_{\text{diff}}). \quad (46)$$

This equation not only neglects the effect of the Stefan–Nusselt flow, but it also ignores the fact that the true kinetic order of the graphite reaction is frequently found to be $\frac{1}{2}$ (whereas equation (46) implies $n = 1$).[*] At the suggestion of the writer [28] equation (46) was readily altered to account for the effect of nonunity reaction order, however, an additional approximation was made[†] to obtain the simple result [35]:

$$1/\dot{m}''^2 = (1/\dot{m}''^2_{\text{chem}}) + (1/\dot{m}''^2_{\text{diff}}). \quad (47)$$

Using the formalism of the present paper, it is now possible to rapidly assess the accuracy of this equation as applied to the ablation of graphite in air ($B_{\text{diff}} = 0{\cdot}174$ if CO(g) is the dominant reaction product,[‡] see Table 2). The result is shown in Fig. 9 for the case of a two-dimensional stagnation point flow ($b = 0{\cdot}71(\frac{1}{2})^{\frac{1}{2}}$). The coordinates $\dot{m}''/\dot{m}''_{\text{chem}}$ and $\dot{m}''_{\text{chem}}/\dot{m}''_{\text{diff}}$ are, in the present notation, equivalent to η and $(1 + bB_{\text{diff}})z$, respectively.[§] The maximum error is found to be about 18 per cent, most of which is attributable to the assumption mentioned in the footnote rather than neglect of the Stefan–Nusselt flow *per se*. Interestingly enough, this maximum error (in these coordinates) remains bounded as $B_{\text{diff}} \to \infty$, and cannot exceed about 31 per cent. For the ablation of

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[*] When the two terms in equation (44) act in the same direction [i.e. exothermic reactions forming volatile products ($B_{\text{diff}} > 0$), or endothermic reactions forming adherent products ($B_{\text{diff}} < 0$)].

[†] A similar result was obtained by the writer in an analysis of catalytic heat exchangers [34].

[*] Similar remarks would apply to the expression $t = t_{\text{chem}} + t_{\text{diff}}$ commonly used to describe the time required to burn carbon particles ([39], p. 110).

[†] viz. $\dot{m}_{\text{diff}} \propto (p_{O_2,e} - p_{O_2,w})^{\frac{1}{2}}$ (cf. Scala, S. M., Chapter 16, p. 431, *Developments in Heat Transfer*, W. M. Rohsenow, ed., M.I.T. Press, 1964) which is not justified.

[‡] The nature of the transition in the presence of both $CO_2(g)$ and CO(g) as primary reaction products has been considered by Welsh and Chung [47].

[§] The stagnation point ($x \to 0$) formally corresponds to the limit ($\omega \to \infty$; i.e. the boundary layer thickness (hence z) is finite and locally constant there. In this limit $\eta = \bar{\eta}$, $z = \bar{z}$.

graphite in pure oxygen ($B_{\text{diff}} = 0{\cdot}75$) the corresponding error is about 21 per cent. In each case equation (47) is seen to systematically *overestimate* the actual ablation rate $\dot{m}''$.

Our second example is drawn from the work of Modisette and Schryer [21] on the oxidation rate of high temperature molybdenum in both air and 21·5% O_2/78·5% He gas mixtures.*

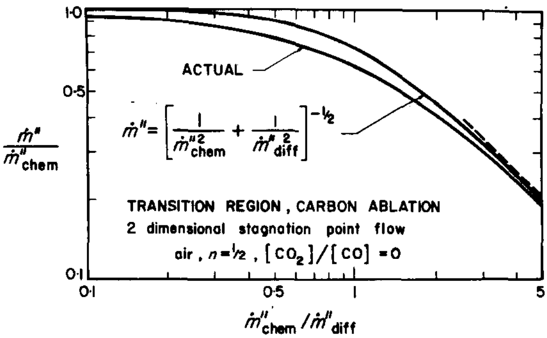

FIG. 9. Comparison of alternate predictions of the transition between chemically controlled and diffusion-controlled graphite ablation.

These authors correct their apparent rate data ($k_{w,a}$, E_a) for the effects of oxygen diffusional limitations using a procedure which, among other things [32], neglects the effect of the Stefan–Nusselt flow. Since the diffusion corrections are not small ($E_a/E \approx 0{\cdot}65$ for the 1330°K–1670°K data treated most extensively) it is of interest to inquire how the reported value of the true activation energy ($E = 21$ Kcal/mole) would be influenced by the Stefan–Nusselt flow effect. Unfortunately, this cannot be done accurately since the experiments were performed at Reynolds numbers below which the laminar boundary-layer values of the constant b (cf. Table 3) are applicable. However, if use is made of the present theory for *laminar* boundary layers with assumed first order kinetics* ($n = 1$) it appears that the effect of the Stefan–Nusselt flow is to increase diffusion correction (and hence, the reported activation energy) for the air oxidation results by almost 10 per cent. In the case of molybdenum oxidation by 21·5% O_2/78·5% He mixtures the effect is greater than 25 per cent. Neglect of systematic effects of this magnitude in a parameter as important as the true activation energy can clearly lead to enormous errors in even modest extrapolations of such rate information to higher temperatures.

ACCURACY LIMITATIONS, REFINEMENTS AND EXTENSIONS

The accuracy of the approximate method exploited here depends in a rather complex way on the many fluid-dynamic and chemical-kinetic parameters that enter the results. Pending comparisons with exact solutions to special cases (which do not yet exist for this class of problems) one can only estimate the regimes in which the accuracy is likely to break down based on previous work on related problems [30] and on *a posteriori* comparisons using data from analogous problems in fluid mechanics and heat transfer [16]. Indeed, it is hoped that the present work, which, perhaps, gains in generality† what is lost in accuracy, will stimulate more detailed investigation of this class of coupled chemical kinetic–convective mass-transfer problems.

At a fixed value of the parameter B_{diff} the accuracy should exhibit behavior similar to that encountered in the writer's previous investigations on surface-catalyzed reactions [27, 29, 30, 34]. In that case ($B_{\text{diff}} = 0$) the approximations exploited here are best‡ for turbulent

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* Interestingly enough, this substitution (He for N_2) not only affects the diffusivity of O_2 through the carrier gas, it also increases B_{diff} [for the production of $MoO_3(g)$] from 0·462 to 1·37. This may explain why the increase in reaction rate associated with the substitution of N_2 by He was some 16 per cent less than that anticipated [21] neglecting the Stefan–Nusselt flow effect.

* Actually, the true reaction order is probably not quite unity under these conditions [31, 32].

† For example, while boundary-layer concepts and results have been extensively invoked, the present approach should prove useful even when (thin) boundary-layer theory, in the conventional sense, breaks down.

‡ The present approach should be extremely accurate when applied locally to symmetrical stagnation-point situations (where local similarity is exact) provided the values of B are such that equation (7) for $St/St_{B=0}$ is accurate.

boundary layers with $Pr_D = O(1)$, and for reaction orders near unity or larger. The accuracy is poorest for small pressure gradient, laminar boundary layer flow with $Pr_D \to 0$ and for very small reaction orders. Moreover, these errors are most serious in the computation of quantities like E_a/E, n_a, etc., since they involve logarithmic derivatives of $\bar{\eta}$ [cf. equations (25, 27–29)]. For $B_{\text{diff}} > 0$ we expect these errors to be larger than those already discussed, owing to the increased sensitivity of transfer coefficients to a spatially variable diffusional driving force in the presence of blowing [16]. The local similarity treatment for the effects of blowing is also expected to be most accurate for turbulent boundary layers.

The difficulties encountered using equation (7) near $B_{\text{diff}} = -1$ have already been mentioned, hence, the curves labeled* $B_{\text{diff}} = -1$ herein should *not* be used quantitatively, but merely used as an indication of trends as one begins to approach the suction limit. It is clear from equation (16) that the case $B_{\text{diff}} = -1$ is singular even in the present formulation, despite the fact that $St/St_{B=0}$ predicted by equation (7) remains finite as $B_{\text{diff}} \to -1$. Variable property effects will probably be most important in the suction limit as well [2].

While the theory presented is a steady-state theory, it may be applied to time-varying problems (e.g. shape changes, reactivity changes) provided the time scale of the variation of interest is sufficiently large (compared with the "transit time" L/U) and provided other fundamental assumptions (e.g. k_w independent of the distance x) are not simultaneously violated. In such cases the time, t, will merely play the role of a parameter.

Owing to its simplicity, the present formulation is seen to lend itself well to (i) preliminary studies of parametric dependencies, (ii) the definition of problems worthy of more careful investigation, or (iii) making quantitative estimates of the kind given above for the oxidation of graphite and molybdenum. In this regard work is currently being done on extension of the present theory to the so-called non-isothermal case [30], in which both diffusion and heat-transfer limitations determine steady-state surface temperatures, reaction rates, etc. More accurate computations of special cases are also in progress to assess the validity of the underlying approximations (cf. also [17]).

CONCLUSIONS

A simple algebraic model has been adopted which, in a unified way, reveals the dominant effects of the Stefan–Nusselt flow on the apparent kinetics of heterogeneous reactions in the transition regime between chemical control and reaction-rate control. These effects will be important whenever the reaction is not chemically controlled *and* the quantity $[\ln(1 + B_{\text{diff}})]/B_{\text{diff}}$ departs significantly from unity, where B_{diff} is a diffusion-limited mass-transfer parameter $(-1 \leqslant B_{\text{diff}} < \infty)$ whose magnitude is directly proportional to the free stream reactant *mass* function. The apparent kinetics for reactions of arbitrary kinetic order are readily obtained for a variety of convective flow situations in terms of natural dimensionless coordinates of the problem. Illustrative results have been presented [in the range $(-1 \leqslant B_{\text{diff}} \leqslant 4)$] for turbulent diffusion boundary-layer flow along flat surfaces being attacked in accord with first-order kinetics by a reactant present in the free stream. Several consequences of the theory of particular interest are: (i) The Stefan–Nusselt flow not only affects the nature of the transition between known asymptotic values (e.g. apparent activation energy, dependence of reaction rate on flow velocity and on wetted-surface area, etc.) for chemical control and diffusion control, but it can also affect the asymptotic values themselves (as in the case of the apparent reaction order in the diffusion limit). Thus, diffusional limitations do *not* cause all heterogeneous chemical reactions to masquerade as first-order reactions when the Stefan–Nusselt flow effect is appreciable. (ii) In any particular

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* The shadings in Figs. 3–8 indicates that smaller values of B_{diff} are of no physical interest.

flow configuration there will be a relation between the fluid-dynamic drag on the surface and the true kinetics of the surface reaction, which for sufficiently large absolute values of B_{diff}, would be measurable. (iii) For surface reactions which are not thermoneutral there will be a more sensitive relation between the power required to maintain a surface at a prescribed surface temperature and the true kinetics of the reaction at that temperature. This relation can be cast in a form identical with that pertaining to surface-catalyzed reactions. Representative values of the parameter B_{diff} encountered in practice have been assembled (cf. Tables, 1, 2) and specific applications of the theory to the oxidation of graphite and molybdenum in air reveal the extent of the errors typically committed in neglecting the Stefan–Nusselt flow, and illustrate the way in which the present theoretical development and correlations can be utilized in a straightforward way. It is hoped that the present theory, which attempts to provide a useful overall conceptual framework, will stimulate more detailed investigation of particular cases of practical or theoretical interest.

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Résumé—L'effet de la vitesse *massique* interfaciale normale aux surfaces sur-lesquelles se produit une réaction hétérogène sur la cinétique apparente de ces réactions est étudié d'une façon quantitative. Un modèle algébrique simple est présenté qui permet d'obtenir les coefficients non dimensionnels de vitesse de réaction dans toute la gamme allant du contrôle ("chimique") de la vitesse de réaction au contrôle par la diffusion pour des réactions irréversibles en une seule étape d'ordre cinétique arbitraire. Des résultats sont présentés comme exemple dans le cas de couches limites turbulentes sur des surfaces planes sur-lesquelles se produit une réaction du premier ordre. L'effet de cet écoulement interfacial (écoulement de Stefan–Nusselt) est sensible toutes les fois que la vitesse de réaction n'est pas complètement contrôleé chimiquement *et* que la quantité $[\ln(1 + B_{\mathrm{diff}})]/B_{\mathrm{diff}}$ diffère d'une façon appréciable de l'unité, B_{diff} étant un paramètre sans dimensions pour le transport de masse contrôlé par la diffusion qu'on peut obtenir *a priori* en fonction de la fraction massique du réactif dans le fluide d'alimentation et les relations stoechiométriques de la réaction. On trouve que l'écoulement de Stefan–Nusselt:

1° bat en brèche l'idée ancienne que les limitations produites par la diffusion conduisent en dernier lieu toutes les réactions superficielles à se déguiser en réactions du premier ordre;

2° introduit une relation entre la traînée de profil sur les surfaces en réaction et la cinétique réelle de la réaction, et

3° laisse sans changement la forme d'une relation, qui pourrait être utile, entre la puissance nécessaire pour maintenir une surface en réaction à une température fixée et la cinétique réelle de la réaction chimique à cette température. Les applications de la théorie à des réactions hétérogènes spécifiques (par ex. l'oxydation, la chloruration, le plaquage chimique par une vapeur) sont facilitées par la compilation des valeurs représentatives du paramètre de transport de masse B_{diff}. Les erreurs commises en négligeant l'écoulement de Stefan–Nusselt sont discutées pour deux cas d'intérêt courant, c'est-à-dire l'oxydation à haute température du graphite et du molybdène dans l'air. Les résultats de la théorie sont présentés et discutés de telle façon que leur généralité est mise en valeur aussi bien que les conditions physicochimiques sous-lesquelles des processus simples de calculs sont vraisemblablement acceptables.

Zusammenfassung—Der Einfluss der Trennschichtstoffgeschwindigkeit senkrecht zu Oberflächen mit heterogenen Reaktionen wird quantitativ untersucht. Ein einfaches algebraisches Modell wird entwickelt, das die Ermittlung aller einschlägigen, dimensionslosen Koeffizienten der Reaktionsgeschwindigkeit erlaubt für den gesamten Bereich von reaktionsgeschwindigkeits- ("chemischen") bis diffusionskontrollierten einstufigen, irreversiblen, heterogenen Reaktionen beliebiger kinetischer Ordnung. Anschauliche Beispiele werden angegeben für den Fall turbulenter Grenzschichten an ebenen Oberflächen bei Reaktionen erster Ordnung. Der Einfluss dieser Trennschichtströmung (des Stefan–Nusseltstroms) erweist sich stets dann bedeutsam, wenn die Reaktionsgeschwindigkeit nicht vollständig chemisch kontrolliert wird *und* die Grösse $[\ln(1 + B_{\mathrm{diff}})]/B_{\mathrm{diff}}$ wesentlich von eins abweicht. Dabei ist B_{diff} ein diffusionskontrollierter, dimensionsloser Stofftransportparameter, der *a priori* abhängig vom reagierenden Stoffanteil im Zustrom und der Reaktionsstöchiometrie erhalten werden kann. Es erweist sich, dass der Stefan–Nusseltstrom (i) die hergebrachte Ansicht zerstört, dass Diffusionsbeschränkungen schliesslich alle Oberflächenreaktionen als Reaktionen erster Ordnung erscheinen lassen (ii), eine Verbindung zwischen dem Profilwiderstand an reagierenden Oberflächen und der wirklichen Kinetik der Reaktion herstellt und (iii) die Form einer möglicherweise nützlichen Beziehung zwischen der erforderlichen Energie zur Aufrechterhaltung einer vorgeschriebenen Temperatur an der reagierenden Oberfläche und der wirklichen Kinetik der chemischen Reaktion bei dieser Temperatur unverändert lässt. Anwendungen der Theorie auf spezifische heterogene Reaktionen (z.B. Oxydation, Chlorierung, chemische Dampfplattierung) werden durch die Zusammenstellung repräsentativer Werte des Stoffübergangsparameters B_{diff} erleichtert. Die Fehler, die durch Vernachlässigung des Stefan–Nusseltstromes begangen werden, sind an Hand zweier gegenwärtig interessanter Fälle diskutiert, nämlich der Hochtemperaturoxydation von Grafit und Molybdän in Luft. Die Ergebnisse der Theorie werden so angegeben und diskutiert, dass ihre Allgemeingültigkeit wie auch die physiko-chemischen Bedingungen betont werden, unter denen einfache Rechenverfahren annehmbar erscheinen.

Аннотация—Исследуется влияние массовой скорости на границе раздела фаз, нормальной к поверхности, где протекают гетерогенные реакции, на явную кинетику таких реакций. Создана простая алгебраическая модель, которая позволяет получить все необходимые безразмерные коэффициенты скорости реакции в широком диапазоне от управления скоростью реакции («химической») до управления диффузией для одноступенчатых гетерогенных реакций с кинетикой произвольного порядка. Приводятся результаты исследования турбулентных пограничных слоев на плоской поверхности для случая реакции первого порядка. Установлено значительное влияние потока Стефана–Нуссельта для условий, когда скорость реакции не управляется полностью химически и величина $[\ln(1 + B_{\rm diff})]/B_{\rm diff}$ существенно отличается от единицы. Здесь $B_{\rm diff}$ безразмерный параметр массообмена при управлении диффузией, выраженный *a priori* через массовые концентрации и стехиометрию реакции. Было найдено, что представление о потоке Стефана–Нуссельта позволяет: (1) отказаться от освященного веками взгляда, что диффузионные ограничения, в конце концов, вызывают маскировку всех поверхностных реакций под реакции первого порядка, (2) установить связь между профильным сопротивлением на реагирующих поверхностях и истинной кинетикой реакции и (3) оставить неизменной форму полезного соотношения между энергией, необходимой для поддержания заданной температуры реагирующей поверхности, и истинной кинетикой химической реакции при этой температуре. Применение этой теории к определенным гетерогенным реакциям/например, окислению, хлорированию, нанесению химических паров/облегчено благодаря систематизированным характерным величинам параметра массообмена $B_{\rm diff}$. Разбираются погрешности, обусловленные пренебрежением потоком Стефана–Нуссельта для двух представляющих интерес случаев, а именно, высокотемпературного окисления графита и молибдена в воздухе. Анализ теоретических результатов построен таким образом, чтобы подчеркнуть их общий характер, а также установить физико-химические условия, упрощающие расчеты.