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SHORTER COMMUNICATIONS

STEADY-STATE FIRST-ORDER REACTION AT AN INFINITE PLANE SURFACE TO WHICH REACTANT DIFFUSES FROM A POINT SOURCE*

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NOMENCLATURE

d,	distance of point source from reacting surface [cm];
D,	diffusion coefficient [$\text{cm}^2\,\text{s}^{-1}$];
$E_1(x)$,	exponential integral, equation (19);
I,	integral defined by equation (14);
$J_n(x)$,	Bessel function of first kind and nth order;
k,	rate constant of surface reaction [$\text{cm}\,\text{s}^{-1}$];
$M(\lambda)$,	function defined by equation (12);
p,	parameter in Laplace transform, equation (15);
Q,	strength of point source [$\text{mol}\,\text{s}^{-1}$];
r,	dimensionless radial coordinate, equation (1);
R,	radial coordinate [cm];
s,	fraction of reactant consumed by surface reaction;
t,	integration variable;
w,	dimensionless reaction rate, equation (1);
W,	reaction rate [$\text{mol}\,\text{cm}^{-2}\,\text{s}^{-1}$];
y,	dimensionless concentration, equation (1);
Y,	concentration [$\text{mol}\,\text{cm}^{-3}$];
z,	dimensionless axial coordinate, equation (1);
Z,	axial coordinate [cm].

Greek symbols

κ,	dimensionless rate-constant parameter, equation (4);
λ,	integration variable, equation (9);
ξ,	integration variable, equation (16);
η,	auxiliary variable.

Subscripts

0,	solution for $\kappa = 0$;
∞,	solution for $\kappa = \infty$;
s,	surface;
1,	defined by equation (7).

THE PRESENT analysis was carried out in connection with an experimental study of the heterogeneous reaction of metal vapor and oxygen at the surface of growing metal-oxide deposits [1, 2]. Although the intended application of the analysis to the experimental work was not successful, as discussed briefly later on, the analytical results may be applicable for other experimental situations.

The model adopted for analysis consists of a point source of constant strength Q, from which reactant diffuses to an infinitely extended plane surface at a distance d from the source. The infinite half-space containing the source is filled with inert stagnant gas through which the reactant diffuses with constant diffusivity D. On the surface, reactant is consumed by first-order reaction at the rate $W = kY_s$, where k is the rate constant and Y_s the concentration of reactant at the surface. A steady-state solution for the concentration Y within the half-space, and in particular for Y_s is sought.

For reasons of axial symmetry, it is convenient to introduce a cylindrical coordinate system Z, R, with the point source located at $Z = d$, $R = 0$, and the reacting surface given by $Z = 0$. Furthermore, the following dimensionless variables are substituted:

$$\begin{aligned} z &= Z/d & r &= R/d \\ y &= (4\pi Dd/Q)Y & w &= (4\pi d^2/Q)W. \end{aligned} \tag{1}$$

The problem reduces to finding a solution $y(z, r)$ of Laplace's equation

$$\frac{\partial^2 y}{\partial r^2} + \frac{1}{r}\frac{\partial y}{\partial r} + \frac{\partial^2 y}{\partial z^2} = 0 \tag{2}$$

which has the appropriate singularity at the point (1, 0), remains finite for $r \to \infty$, $z \to \infty$, and satisfies the boundary condition

$$w(r) = (\partial y/\partial z)_{z=0} = \kappa y(0, r). \tag{3}$$

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In dimensionless form, the problem thus depends on the single parameter

$$\kappa = kd/D \tag{4}$$

which determines the relative importance of reaction and diffusion effects on the rate [3]. Solutions for the limiting cases $\kappa = \infty$ (complete diffusion control) and $\kappa = 0$ (complete reaction control) are readily obtained by the method of placing a mirror-image source at $(-1, 0)$. A positive image source yields the solution

$$y_0 = [(z-1)^2 + r^2]^{-\frac{1}{2}} + [(z+1)^2 + r^2]^{-\frac{1}{2}} \tag{5}$$

which satisfies (3) for $\kappa = 0$. With negative image source, one obtains the solution

$$y_\infty = [(z-1)^2 + r^2]^{-\frac{1}{2}} - [(z+1)^2 + r^2]^{-\frac{1}{2}} \tag{6}$$

that vanishes at $z = 0$ and thus satisfies (3) for $\kappa = \infty$. At the surface, these expressions yield $y_0(0, r) = 2(1 + r^2)^{-\frac{1}{2}}$ and $w_\infty(r) = 2(1 + r^2)^{-\frac{3}{2}}$.

The general solution for arbitrary values of κ is most conveniently expressed as the linear superposition

$$y(z, r) = y_0(z, r) + y_1(z, r). \tag{7}$$

Since $y_0(z, r)$ has the required singularity at $(1, 0)$, $y_1(z, r)$ must satisfy Laplace's equation without singularity in the half-space $z \geqslant 0$, subject to the boundary condition

$$(\partial y_1/\partial z)_{z=0} - \kappa y_1(0, r) = \kappa y_0(0, r). \tag{8}$$

Separating variables in (2) and requiring the solution to remain finite for $z \to \infty$ one obtains the general solution

$$y_1(z, r) = \int_0^\infty M(\lambda)\, \mathrm{e}^{-\lambda z} J_0(\lambda r)\, \mathrm{d}\lambda. \tag{9}$$

Substitution of (5) and (9) into the boundary condition (8) yields the expression

$$-\int_0^\infty (\lambda + \kappa)\, M(\lambda)\, J_0(\lambda r)\, \mathrm{d}\lambda = 2\kappa(1 + r^2)^{-\frac{1}{2}} \tag{10}$$

from which $M(\lambda)$ must be determined. Introducing the orthogonality property of the Bessel function

$$\int_0^\infty r\, J_m(\lambda' r)\, J_m(\lambda r)\, \mathrm{d}r = \frac{1}{\lambda}\delta(\lambda' - \lambda)$$

one obtains

$$M(\lambda) = -2\kappa\lambda(\lambda + \kappa)^{-1} \int_0^\infty r(1 + r^2)^{-\frac{1}{2}} J_0(\lambda r)\, \mathrm{d}r. \tag{11}$$

With the use of a tabulated integral transform [4] this expression may be evaluated, with the result

$$M(\lambda) = -2\kappa(\lambda + \kappa)^{-1}\, \mathrm{e}^{-\lambda}. \tag{12}$$

Substitution into (9) yields

$$y(z, r) = y_0(z, r) - 2\kappa I(z, r) \tag{13}$$

where

$$I(z, r) = \int_0^\infty (\lambda + \kappa)^{-1}\, \mathrm{e}^{-\lambda(z+1)} J_0(\lambda r)\, \mathrm{d}\lambda. \tag{14}$$

By making use of the Laplace transform

$$\int_0^\infty \mathrm{e}^{-\lambda p} J_0(\lambda r)\, \mathrm{d}\lambda = (r^2 + p^2)^{-\frac{1}{2}} \tag{15}$$

it can be demonstrated that (13) converges towards the limiting expressions y_0 for $\kappa \to 0$ and y_∞ for $\kappa \to \infty$. These proofs will not be presented here.

The integral $I(z, r)$ may be transformed by substituting the identity

$$(\lambda + \kappa)^{-1} = \int_0^\infty \mathrm{e}^{-(\lambda+\kappa)\xi}\, \mathrm{d}\xi, \tag{16}$$

reversing the order of integration, and using (15). One obtains in this way

$$I(z, r) = \int_0^\infty [r^2 + (1 + z + \xi)^2]^{-\frac{1}{2}}\, \mathrm{e}^{-\kappa\xi}\, \mathrm{d}\xi. \tag{17}$$

A closed-form expression for the general solution (17) has not been found. For the special case $r = 0$, elementary substitutions yield the expression

$$y(z, 0) = -2\kappa\, \mathrm{e}^{\kappa(1+z)} E_1[\kappa(1 + z)] + \begin{cases} 2(1 - z^2)^{-1} & 0 \leqslant z < 1 \\ 2z(z^2 - 1)^{-1} & 1 < z < \infty \end{cases} \tag{18}$$

where $E_1(x)$ is the tabulated exponential integral [5] defined by

$$E_1(x) = \int_x^\infty t^{-1}\, \mathrm{e}^{-t}\, \mathrm{d}t. \tag{19}$$

An asymptotic expansion of $I(0, r)$ for large values of κ was obtained by repeated use of integration by parts. The corresponding expression for the surface concentration is

$$\begin{aligned} y(0, r) = 2\kappa^{-1}(1 + r^2)^{-\frac{3}{2}}[1 &+ \kappa^{-1}(r^2 - 2)(r^2 + 1)^{-1} \\ &- \kappa^{-2}(9r^2 - 6)(r^2 + 1)^{-2} - 0(\kappa^{-3})]. \end{aligned} \tag{20}$$

This expression also converges rapidly for moderately large values of κ and large values of r. Equations (18) and (20) were used as checks on the numerical results presented below.

Numerical evaluations were performed only for the concentration at the surface $y(0, r)$ and the corresponding rate $w(r)$. For $z = 0$, Equations (13) and (17) may be further simplified, by making use of the boundary condition (3) and the relation $(\partial y_0/\partial z)_{z=0} = 0$. One obtains in this manner the expression

$$\begin{aligned} y(0, r) = -2(\partial I/\partial z)_{z=0} = 2 \int_0^\infty (\xi + 1) \\ \times [r^2 + (\xi + 1)^2]^{-\frac{3}{2}}\, \mathrm{e}^{-\kappa\xi}\, \mathrm{d}\xi. \end{aligned} \tag{21}$$

For the numerical evaluation of (21), the differential equation

$$\mathrm{d}\eta/\mathrm{d}x = 2(x + 1)\left[r^2 + (x + 1)^2\right]^{-\frac{3}{2}} \mathrm{e}^{-\kappa x} \qquad (22)$$

was integrated on the Laboratory IBM 7044 computer by the fourth-order Runge–Kutta method. A variable step size was chosen so that the relative increment $\Delta\eta/\eta$ remained smaller than 10^{-4}. The integration was terminated at the upper limit $x = 6{\cdot}9\ \kappa^{-1}$. Since the integrand is always smaller than $\mathrm{e}^{-\kappa x}$, the error due to neglect of the remainder of the integral was less than that incurred by truncating the integral

$$\int_0^\infty \mathrm{e}^{-\kappa x}\,\mathrm{d}x,$$

which, at the same upper limit, is 0·1 per cent.

Results of the computation are presented in Table 1 and in Figs. 1 and 2. The influence of the parameter κ on dimensionless concentration and rate shown in Fig. 1 may be subdivided into the effect on the values for $r = 0$ and that on the dependence on radial distance r. The latter effect is shown separately in Fig. 2 by a plot of relative values $w(r)/w(0)$, which demonstrates the gradual transition from the $(1 + r^2)^{-\frac{1}{2}}$ dependence for reaction control to the $(1 + r^2)^{-\frac{3}{2}}$ dependence for diffusion control.

The division into these two effects was used in a comparison of the analysis with experimental results obtained by the method of [1]. In this manner, two independently determined values of κ were derived for each experiment; one was obtained from the dependence of the reaction rate on radial distance from the center of the oxide deposit, the other from the ratio of actual to completely diffusion-controlled rate at the center. In contrast to earlier measurements at a total pressure of 0·5 torr, which indicated complete diffusion control [1], the results obtained at lower pressures showed that a regime of transition from diffusion to reaction control had been attained. However, the two independently derived values of κ did not agree well with each other, and, moreover, they did not vary with chamber pressure in the theoretically expected manner. In view of these inconsistencies which were attributed to the neglect of the influence of convective transport, this comparison will not be discussed further. The results of the analysis should be useful, however, under experimental conditions for which the neglect of flow effects is justified.

To conclude the discussion of the analytical results, an interesting property of the solution (21) is derived. It is obtained by computing the fraction of reactant issuing from the point source that is consumed by surface reaction. This fraction is given by

$$s = Q^{-1}\int_0^\infty W(R)\,2\pi R\,\mathrm{d}R = \tfrac{1}{2}\kappa\int_0^\infty y(0, r)\,r\,\mathrm{d}r. \qquad (23)$$

Substituting (21), reversing the order of integration, and

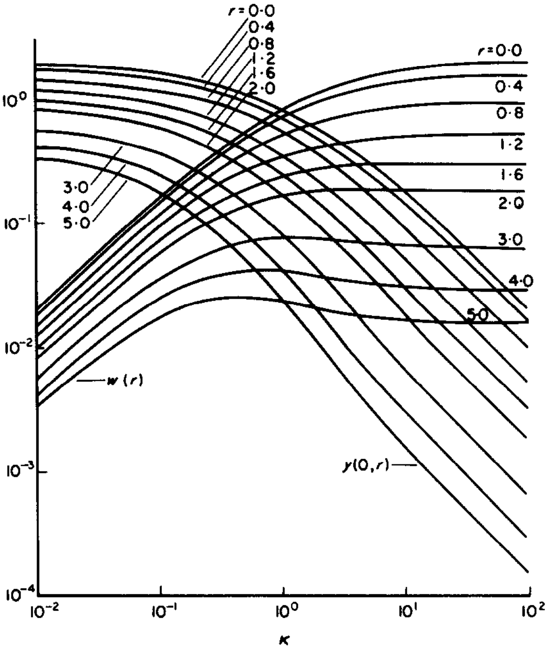

FIG. 1. Dimensionless reactant concentration at the surface and dimensionless reaction rate vs. rate parameter.

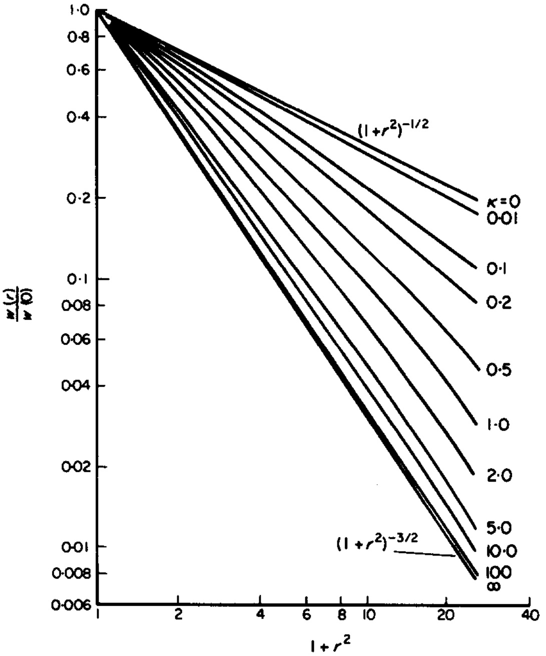

FIG. 2. Influence of rate parameter on radial distribution of reaction rate.

Table 1. *Dimensionless concentration at the surface*

$$y(0, r) = 2\int_0^\infty (\xi + 1)\left[r^2 + (\xi + 1)^2\right]^{-\frac{3}{2}} e^{-\kappa\xi}\, d\xi$$

r	$\kappa = 0{\cdot}01$	0·1	0·2	0·5	1·0	2·0	5·0	10·0	100·0
0·0	1·916	1·596	1·402	1·076	8·070 × 10^{-1}	5·545 × 10^{-1}	2·956 × 10^{-1}	1·687 × 10^{-1}	1·960 × 10^{-2}
0·2	1·878	1·559	1·366	1·045	7·798	5·331	2·823	1·603	1·850
0·4	1·775	1·460	1·272	9·606 × 10^{-1}	7·083	4·772	2·478	1·390	1·575
0·6	1·634	1·326	1·144	8·484	6·140	4·048	2·043	1·126	1·245
0·8	1·482	1·182	1·008	7·308	5·169	3·320	1·621	8·761 × 10^{-2}	9·436 × 10^{-3}
1·0	1·336	1·045	8·792 × 10^{-1}	6·213	4·284	2·674	1·261	6·686	7·029
1·2	1·203	9·214 × 10^{-1}	7·646	5·258	3·530	2·141	9·755 × 10^{-2}	5·080	5·230
1·4	1·086	8·141	6·657	4·452	2·910	1·715	7·567	3·878	3·923
1·6	9·851 × 10^{-1}	7·220	5·817	3·783	2·408	1·380	5·913	2·988	2·979
1·8	8·975	6·432	5·106	3·231	2·003	1·119	4·666	2·330	2·295
2·0	8·218	5·759	4·505	2·774	1·677	9·141 × 10^{-2}	3·721	1·839	1·794
3·0	5·649	3·552	2·590	1·407	7·624 × 10^{-2}	3·762	1·403	6·712 × 10^{-3}	6·362 × 10^{-4}
4·0	4·216	2·397	1·642	8·011 × 10^{-2}	3·988	1·838	6·523 × 10^{-3}	3·070	2·874
5·0	3·322	1·721	1·115	4·966	2·314	1·017	3·503	1·635	1·520

setting $r^2 = \eta$, one obtains

$$s = -\kappa \int_0^\infty e^{-\kappa\xi}(\xi + 1)\left[\eta + (\xi + 1)^2\right]^{-\frac{1}{2}} \Big|_{\eta=0}^{\infty} d\xi = 1. \tag{24}$$

Thus, the reactant is consumed completely at the surface, for any arbitrary value of κ. This result is, of course, meaningless for $\kappa = 0$.

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FURTHER RESULTS FROM USE OF A TRANSCENDENTAL PROFILE FUNCTION IN CONDUCTION AND CONVECTION

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NOMENCLATURE

A,	coefficient;
a,	profile parameter, function of n;
b,	profile parameter, function of n;
C,	coefficient;
c,	specific heat;
$-Ei(-u)$,	exponential integral;
$E_p(u)$,	general exponential integral;
f,	coefficient;
g,	variable;
G_n,	function related to exponential;
$i^m \operatorname{erfc} \eta$,	mth repeated integral of the error function;
J,	coefficient;
K,	coefficient;
k,	thermal conductivity; also, running index;
n,	exponent;
p,	general function; running index;
q_i,	ith generalized coordinate; q_1, surface temperature; q_2, penetration depth;
T,	arbitrary constant temperature;
t,	time;
u,	$\exp(a + b\eta)$;
u_0,	$\exp a$;
x, y, z,	space coordinates;
pro,	dimensionless temperature profile approximation.

Greek symbols

α,	thermal diffusivity;
β,	profile parameter;
$\Gamma(1 + n)$,	gamma function;
ε,	an arbitrary small number; also, profile parameter;
η,	general variable;