

Boundary Conditions for Some Surface-Catalyzed Reactions

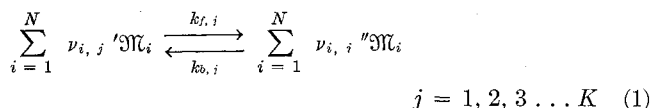
PAUL A. LIBBY* AND FORMAN A. WILLIAMS†

University of California at San Diego, La Jolla, Calif.

THERE has recently been demonstrated in the aerospace literature considerable interest concerning the surface recombination of atoms.¹⁻⁵ The analyses of this phenomenon have been carried out within the framework of boundary-layer theory and have involved a boundary condition at the exposed surface relating the normal gradient of atom mass fraction and the atom mass fraction itself. It is generally stated and/or recognized that these analyses for a binary system apply as well to more complicated systems, provided that the concentration of reactants and products is vanishingly small.^{6,7} It is the purpose of the present note to develop the boundary conditions when this latter assumption is not employed.‡

We want to state at the outset that some of the results presented here are perhaps known to chemical engineers as indicated, for example, by Ref. 9. However, the implications of the condition of steady state and, further, of the condition of local adsorption equilibrium leading to the surface boundary conditions for diffusive flows, appear to be new. In any case, it may be useful to the aerospace community to have readily available the present results.§

For generality, we consider a set of surface-catalyzed reactions of the form



and we make a series of assumptions in order to provide the basis for our treatment. We assume that the surface on which catalysis takes place is nonporous, i.e., has no internal structure, but rather a well-defined interface with the gas. We consider both adsorption of molecules on open sites of the surface and adsorption of molecules of species i at sites already occupied by species j . We differentiate as to the likelihood of this latter adsorption by introducing an adsorption coefficient depending on i and j , but we assume that each open site is equally available to each species. ¶ Denote the number of adsorption sites per unit projected area by γ_0 and the surface concentrations of species i as γ_i , both in moles per square centimeter, for example. We now arrange our identification system such that the species with the subscript $1, 2, \dots, N'$ are present in the gas as well as on the sur-

face, and that the species with the subscripts $N' + 1, N' + 2, \dots, N$ are present on the surface but not in the gas; we thus reflect the possibility that some of the reaction steps of Eq. (1) lead to products that are so strongly adsorbed as to be absent from the gas. Our fluidmechanical interest in such products is, of course, their occupancy of a certain number of sites, which are thus unavailable for adsorption by species present both in the gas and on the surface, and their capacity to alter directly the adsorption properties of the surface itself.

Following previous work, we characterize the interaction of the species in the gas with open sites in terms of two coefficients, α_i and μ_i , where α_i is the fraction of the incident i molecules adhering to open sites and μ_i is the rate (moles per square centimeter-second) at which molecules of species i would leave the surface if all possible sites were populated with species i . These coefficients are to be considered physical parameters depending on the surface temperature, on the nature of the surface, and on the nature of species i .

In order to account for adsorption and desorption at occupied sites, we also introduce coefficients α_{ij} and μ_{ij} ; the first set accounts for the adsorption of a molecule of species i at a site occupied by a molecule of species j , i.e., α_{ij} is the fraction of i molecules incident on a unit projected area which would be adsorbed if all sites were populated with species j . The second set accounts for the desorption of a molecule of species i from a site occupied by a molecule of species j , i.e., μ_{ij} is the rate at which species i would be desorbed in moles per square centimeter-second if all sites were populated with species j . Again these sets of coefficients are to be regarded as physical parameters depending on the same quantities as α_i, μ_i . We assume here that the probability of desorption is the same for a molecule immediately after production on the surface as for the same molecule that has been adsorbed for a long time. In addition, we neglect triple and higher occupancy of each site.

In order to provide the boundary condition for the conservation equations applicable to species in the gas, we seek relations among the net fluxes of each species to the surface, denoted here as b_i in moles per square centimeter-second, the volumetric concentrations at the surface, denoted as c_i in moles per cubic centimeter, and the surface concentrations γ_i . Since the values of γ_i are not known a priori, the N' boundary conditions relating b_i and c_i , $i = 1, 2 \dots N'$ must be found by eliminating the N values of the γ_i 's from $2N' + (N - N')$ equations.

Among the multitude of possible mechanisms for heterogeneous catalysis, two general classes thereof have been identified, although from a particular experiment unequivocal identification of one rather than the other is apparently sometimes difficult. The mechanisms go under the names of Langmuir-Hinshelwood and Rideal-Ely. It is thus convenient to order the reaction steps of Eqs. (1) with one set corresponding to $j = 1, 2 \dots K'$ associated with the L-H mechanism and a second set corresponding to $j = K' + 1, K' + 2, \dots, K$ associated with the R-E mechanism.

We can compactly express the surface creation of species i in moles per square centimeter-second as

$$R_i = \sum_{j=1}^K (\nu_{i,j}'' + \tilde{\nu}_{i,j}'' - \nu_{i,j}' - \tilde{\nu}_{i,j}') \times k_{f,j} \left(\prod_{i=1}^N \gamma_i^{\nu_{i,j}'} \right) \left(\prod_{i=1}^{N'} c_i^{\tilde{\nu}_{i,j}'} \right) \times \left\{ 1 - \left(\frac{k_{b,j}}{k_{f,j}} \right) \left(\prod_{i=1}^N \gamma_i^{\nu_{i,j}'' - \nu_{i,j}'} \right) \left(\prod_{i=1}^{N'} c_i^{\tilde{\nu}_{i,j}'' - \tilde{\nu}_{i,j}'} \right) \right\} \quad (2)$$

where we use the symbols $\tilde{\nu}_{i,j}', \tilde{\nu}_{i,j}''$ to denote the stoichiometric coefficients for species i in the gas in reaction step j , $K' + 1 \leq j \leq K$. Clearly, we need the two sets of co-

Received January 12, 1965. This research was supported under Advanced Research Projects Agency Contract No. DA 31-124-ARO-D-257 with the Institute for Radiation Physics and Aerodynamics at the University of California, San Diego, Calif.

* Professor of Aerospace Engineering. Associate Fellow Member AIAA.

† Associate Professor of Aerospace Engineering. Member AIAA.

‡ The authors are indebted to S. S. Penner for a discussion that aroused their interest in the present problem; to D. E. Rosner, who reviewed an earlier version of this note and who provided important suggestions and relevant references in the chemical literature; and to J. L. Lauer, who made useful comments regarding surface catalysis. We note here that we largely use the notation of Ref. 8.

§ References 9 and 10 may be recommended as entry points to the relevant chemical literature.

¶ There appear to be cases for which this assumption is unsatisfactory; it is readily corrected by introduction of a factor specifying the number of sites required per molecule, by introduction of a site index distinguishing sites that differ in their affinity for a given molecular species, or by some other appropriate procedure.

efficients to account for cases, e.g., atom recombination, where the two reactants are the same but only one is adsorbed. For $j = 1, 2 \dots K'$, clearly $\bar{\nu}_{i,j'} = \bar{\nu}_{i,j''} = 0$ for all i .

Proceeding with the analysis, we express the net flux of species present in the gas in accord with the sets of coefficients just indicated as

$$b_i = \beta_i \left\{ \alpha_i \left[1 - \sum_{j=1}^{N'} \left(\frac{\gamma_j}{\gamma_0} \right) \right] + \sum_{j=1}^{N'} \alpha_{ji} \left(\frac{\gamma_j}{\gamma_0} \right) \right\} - \left\{ \left(\frac{\mu_i \gamma_i}{\gamma_0} \right) + \sum_{j=1}^{N'} \left(\frac{\mu_{ij} \gamma_j}{\gamma_0} \right) \right\} \quad i = 1, 2, \dots, N' \quad (3)$$

where $\beta_i = c_i (k^0 T / 2\pi m_i)^{1/2}$ gives the number of molecules of species i incident upon a unit projected area per unit time, where the factor

$$\left[1 - \sum_{j=1}^{N'} \left(\frac{\gamma_j}{\gamma_0} \right) \right]$$

accounts for the percent of the unit area with open sites, and where the subscript w , applicable to b_i , c_i , T and required to imply values of the variables on the gas side of the gas-solid interface, has been suppressed without ambiguity in the present analysis. Observe that $b_i > 0$ for a net flux into the surface.

We next note that, for steady-state, time-independent flow problems, the conditions

$$R_i = -b_i \quad i = 1, 2, \dots, N' \quad (4)$$

$$R_i = 0 \quad i = N' + 1, \dots, N$$

must hold. Thus Eqs. (2-4) may be looked upon as $2N' + (N - N')$ equations relating b_i , c_i , $i = 1, 2, \dots, N'$ and γ_i , $i = 1, 2, \dots, N$ and permitting N' equations, which relate the b_i 's and c_i 's and which constitute the desired boundary condition, to be developed formally.

The most general case contained in the preceding formalism does not appear to lead to simplification. However, for the case of reactions in accord with the Langmuir-Hinshelwood mechanism and of adsorption only on open sites, interesting and simple results, which are appropriate for boundary-layer flows, can be developed. We thus restrict ourselves to $j = 1, 2, \dots, K'$ and $\alpha_{ij} = \mu_{ij} = 0$ in Eq. (3); we still consider for the moment the possibility of having species on the surface but absent in the gas so that $N' \neq N$.

With these restrictions and with Eqs. (4) imposed, we have the simplified equations

$$\sum_{i=1}^{K'} (\nu_{i,j''} - \nu_{i,j'}) k_{f,j} \left(\prod_{i=1}^{N'} \gamma_i^{\nu_{i,j'}} \right) \times \left\{ 1 - \left(\frac{k_{b,j}}{k_{f,j}} \right) \prod_{i=1}^{N'} \gamma_i^{\nu_{i,j''} - \nu_{i,j'}} \right\} = -b_i \quad i = 1, 2, \dots, N' \quad (5)$$

$$= 0 \quad i = N' + 1, \dots, N \quad (6)$$

$$b_i = \left\{ \alpha_i \beta_i \left[1 - \sum_{j=1}^{N'} \left(\frac{\gamma_j}{\gamma_0} \right) \right] \right\} - \left\{ \mu_i \left(\frac{\gamma_i}{\gamma_0} \right) \right\} \quad i = 1, 2, \dots, N' \quad (7)$$

We now assume that, under the high Reynolds number conditions appropriate for application of boundary-layer theory, the two factors contained in braces in Eq. (7) are each large compared to their difference, i.e., the flux into the surface and the flux from the surface will be much larger than the net flux itself. In this case, the N values of γ_i are obtained from the N' equations that result from setting $b_i \simeq 0$ in Eqs. (7) and the $N - N'$ equations of Eqs. (6). With the values of γ_i so determined, the N' equations (5) yield directly the N' boundary conditions in the form $b_i = b_i(c_1, c_2, \dots, c_{N'})$, $i = 1, 2, \dots, N'$.

This procedure will be recognized as assuming local adsorption equilibrium; it can be made systematic by consider-

ing an expansion of all quantities in terms of a small parameter that represents the ratio of an absorption time to a chemical time. For simplicity, we consider the special case $N' = N$, i.e., the case where all adsorbed species are also present in the gas phase, but it should be noted that the more general case $N' \neq N$ can undoubtedly be put on a firm basis by extending the point of view of the present note. To develop the ideas, select a representative species r with a gas-phase concentration c_r , leading to an incident flux β_r and with surface interaction parameters α_r and μ_r . Select, further, a representative first-order specific reaction rate constant k_r , e.g., in seconds⁻¹.

We now assume that the representative values have been chosen with sufficient wisdom and that the physical and chemical behavior of the system is of such a nature so that $(\alpha_i \beta_i / \alpha_r \beta_r)$, (μ_i / μ_r) ,

$$\left(\frac{\sum_{i=1}^{N'} \nu_{i,j'} - 1}{k_{f,j} \gamma_0} \right) \left(\frac{\sum_{i=1}^{N'} \nu_{i,j''} - \nu_{i,j'}}{k_{f,j}} \right) \quad j = 1, \dots, K'$$

are all of order unity. Furthermore, in accord with the expectation that both fluxes will be large compared to the net flux, we assume $(\mu_r / \alpha_r \beta_r)$ is of order unity. Next define two times

$$\tau_1 \equiv \gamma_0 / \alpha_r \beta_r \quad \tau_2 \equiv k_r^{-1} = \gamma_0 / \gamma_0 k_r \quad (8)$$

where τ_1 may be interpreted physically as a measure of the time required for the representative species to populate all sites, and τ_2 as a measure of the time required by a first-order reaction with a specific rate constant k_r to depopulate all sites. Now assume in accord with the foregoing discussion that

$$\epsilon \equiv \tau_1 / \tau_2 \ll 1 \quad (9)$$

and let

$$\left. \begin{aligned} \gamma_i &\simeq \gamma_i^{(0)} + \epsilon \gamma_i^{(1)} + \dots \\ \beta_i &\simeq \beta_i^{(0)} + \epsilon \beta_i^{(1)} + \dots \\ b_i &\simeq b_i^{(0)} + \epsilon b_i^{(1)} + \dots \end{aligned} \right\} \quad i = 1, 2, \dots, N' = N \quad (10)$$

Substitution of Eqs. (10) into Eqs. (5) and (7) and collection of powers of ϵ , ϵ leads to the following:

$$\frac{b_i^{(0)}}{\alpha_i \beta_i^{(0)}} \simeq \left[1 - \sum_{j=1}^{N'} \left(\frac{\gamma_j^{(0)}}{\gamma_0} \right) \right] - \left(\frac{\mu_i}{\alpha_i \beta_i^{(0)}} \right) \left(\frac{\gamma_i^{(0)}}{\gamma_0} \right) \simeq 0 \quad (11)$$

$$\frac{b_i^{(1)}}{\alpha_r \beta_r} \simeq \sum_{j=1}^{K'} (\nu_{i,j''} - \nu_{i,j'}) \times \left(\frac{\sum_{i=1}^{N'} \nu_{i,j'} - 1}{k_{f,j} \gamma_0} \right) \left(\frac{\sum_{i=1}^{N'} \nu_{i,j''} - \nu_{i,j'}}{k_{f,j}} \right) \prod_{i=1}^{N'} \left(\frac{\gamma_i^{(0)}}{\gamma_0} \right)^{\nu_{i,j''} - \nu_{i,j'}} \times \left\{ 1 - \left(\frac{k_{b,j}}{k_{f,j}} \right) \prod_{i=1}^{N'} \left(\frac{\gamma_i^{(0)}}{\gamma_0} \right)^{\nu_{i,j''} - \nu_{i,j'}} \right\} \quad (12)$$

Equations (11) and (12) represent the formalism for the procedure just presented qualitatively for the special case $N' = N$.

Equation (11) can be used to obtain an explicit relation for $\gamma_i^{(0)}$ in terms of the volumetric concentrations $c_i^{(0)} \sim \beta_i^{(0)}$; note that the second term must be the same for all i 's and denote it as M . Then

$$\gamma_i^{(0)} / \gamma_0 = M \kappa_i c_i^{(0)} \quad (13)$$

where $\kappa_i \equiv (\alpha_i / \mu_i) (k^0 T / 2\pi m_i)^{1/2}$ is a single parameter characterizing the interaction of species i with the surface. But then Eq. (11) yields

$$M = 1 / \left[1 + \sum_{i=1}^N \kappa_i c_i^{(0)} \right] \quad (14)$$

so that

$$\frac{\gamma_i^{(0)}}{\gamma_0} = \kappa_i c_i^{(0)} / \left[1 + \sum_{i=1}^N \kappa_i c_i^{(0)} \right] \quad (15)$$

Substitution of Eq. (15) into Eq. (12) provides the desired boundary condition.

As a special case, consider the unidirectional, surface-catalyzed reaction

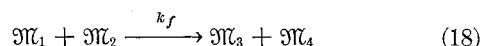


so that $K' = 1$, $N' = 2$; the general relation yields

$$b_1 = \frac{k_f n (\gamma_0 \kappa_1 c_1)^n}{(1 + \kappa_1 c_1 + \kappa_2 c_2)^n} \quad (17)$$

so that for highly dilute reactants and products the frequently employed relation $b_1 \sim c_1^n$ is recovered. However, if $\kappa_1 c_1$ is large compared with $\kappa_2 c_2$ and with unity, then Eq. (17) indicates that b_1 is independent of c_1 , i.e., the reaction is of zero order.¹¹ Especially interesting is the limit $\kappa_2 c_2 \gg 1$, $\kappa_2 c_2 \gg \kappa_1 c_1$, which is more likely to occur downstream, where the reaction has proceeded in the forward direction to a significant extent; in this case $b_1 \sim (c_1/c_2)^n$, thus exhibiting retardation of the reaction rate by the reaction product. Clearly, the effective order of the reaction may change with the streamwise coordinate in a given boundary layer.

It is also interesting to note that for a more complicated unidirectional reaction of the form



the general relation for the flux of species 1, e.g., yields

$$b_1 = \frac{\gamma_0^2 k_f \kappa_1 \kappa_2 c_1 c_2}{(1 + \kappa_1 c_1 + \kappa_2 c_2 + \kappa_3 c_3 + \kappa_4 c_4)^2} \quad (19)$$

Clearly, depending on the magnitudes of each product $\kappa_i c_i$ compared to unity, a range of reaction orders from plus to minus unity can occur.

In conclusion, it is noted that the foregoing considerations apply to turbulent as well as to laminar boundary layers.

References

- Chung, P. M., Liu, S. W., and Mirels, H., "Effect of discontinuity of surface catalytic on boundary layer flow of dissociated gas," *Intern. J. Heat Mass Transfer*, **6**, 193-210 (1963).
- Chung, P. M. and Anderson, A. D., "Heat transfer around blunt bodies with surfaces of finite catalytic efficiency in frozen dissociated hypersonic flow," *Advances in the Astronautical Sciences* (Plenum Press, New York, 1962), Vol. 8.
- Rae, W. J., "A solution for the nonequilibrium flat plate boundary layer," *AIAA J.*, **1**, 2279-2288 (1963).
- Fox, H., "Laminar boundary layers with chemical reactions," Air Force Office of Scientific Research AFOSR 64-1394, Polytechnic Institute of Brooklyn, Aerodynamics Lab. PIBAL Rept. 835 (June 1964).
- Janowitz, G. S. and Libby, P. A., "The effect of variable transport properties on a dissociated boundary layer with surface reaction," *Intern. J. Heat Mass Transfer*, **8**, 7-18 (1965); also Polytechnic Institute of Brooklyn, Aerodynamics Lab. PIBAL Rept. 804 (October 1963).
- Chambre, P. L. and Acrivos, A., "On chemical surface reactions in laminar boundary layer flows," *J. Appl. Phys.*, **27**, 1322-1328 (1956).
- Rosner, D. E., "Convective diffusion as an intruder in kinetic studies of surface catalyzed reactions," *AIAA J.*, **2**, 593-610 (1964).
- Williams, F. A., *Combustion Theory* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965).
- Hougen, O. A. and Watson, K. M., "Solid catalysts and reaction rates," *Ind. Eng. Chem.*, **35**, 529-541 (1943).
- Hayward, D. O. and Trapnell, B. M. W., *Chemisorption* (Butterworths, London, 1964).
- Rosner, D. E., "Effects of convective diffusion on the apparent kinetics of zeroth order surface-catalyzed chemical reactions," *Chem. Eng. Sci.* (to be published).

Generalized Matrix Force and Displacement Methods of Linear Structural Analysis

ALAN L. YETTRAM* AND HUSAIN M. HUSAIN†
University of Leeds, Leeds, England

Nomenclature

Force method

- P = column matrix† of all generalized forces
 P_0, P_1 = column matrices of known and unknown generalized forces, respectively
 b_g, b_{0g}, b_{1g} = rectangular matrices of stress resultants (internal forces) in element g due to unit values of components of P, P_0, P_1 , respectively
 b, b_0, b_1 = rectangular matrices of stress resultants in all elements due to unit values of components of P, P_0, P_1 , respectively
 S_g = column matrix of stress resultants in element g due to P
 S, S_0, S_1 = column matrices of stress resultants in all elements due to P, P_0, P_1 , respectively
 w_g = column matrix of strain resultants (over-all internal deformations) of element g , corresponding to S_g
 w, w_0, w_1 = column matrices of strain resultants of all elements, corresponding to S, S_0, S_1
 p, p_0, p_1 = column matrices of all displacements in the directions of forces P, P_1, P_0 , respectively
 f_g = square matrix describing flexibility of element g
 f = square matrix of flexibilities of all elements (un-assembled)

Displacement method

- r = column matrix of all displacements
 r_0, r_1 = column matrices of known and unknown displacements, respectively
 a_g, a_{0g}, a_{1g} = rectangular matrices of strain resultants (displacements of extremities) of element g due to unit values of components of r, r_0, r_1 , respectively
 a, a_0, a_1 = rectangular matrices of the strain resultants of all elements due to unit values of components of r, r_0, r_1 , respectively
 v_g = column matrix of strain resultants of element g due to r
 v, v_0, v_1 = column matrices of strain resultants of all elements due to r, r_0, r_1 , respectively
 T_g = column matrix of stress resultants (forces at extremities) in element g , corresponding to v_g
 T, T_0, T_1 = column matrices of stress resultants in all elements, corresponding to v, v_0, v_1
 R, R_0, R_1 = column matrices of all forces in the directions of displacements r, r_1, r_0 , respectively
 k_g = square matrix describing stiffness of element g
 k = square matrix of stiffnesses of all elements (un-assembled)

Introduction

THAT there are two related possible approaches to the analysis of structures has long been realized. Ostenfeld,¹ however, first fully outlined the principles that underlie the duality between the force (or flexibility) method and the displacement (or stiffness) method. Argyris² expressed the relationship between the two methods in matrix notation and put forward procedures for the solution of structures under either applied forces or imposed displacements.

Received January 6, 1965.

* Lecturer in Aircraft Structures, Department of Civil Engineering.

† Research Assistant, Department of Civil Engineering.

‡ Column and diagonal matrices, when shown in expanded form, are denoted, respectively, by { } and [].