NASA TECHNICAL NOTE

NASA TN D-7012

NASA TN D-7012

A SEMIEMPIRICAL MODEL FOR BOUNDARY LAYER DIFFUSION IN FORCED CONVECTION FLOW

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • DECEMBER 1970

1. Report No. NASA TN D-7012	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle
A SEMIEMPIRICAL MODEL FOR BOUNDARY LAYER DIFFUSION IN FORCED CONVECTION FLOW

5. Report Date
December 1970

6. Performing Organization Code

7. Author(s)
Alex Vary

8. Performing Organization Report No.
E-4985

9. Performing Organization Name and Address
Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio 44135

10. Work Unit No.
120-27

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D. C. 20546

13. Type of Report and Period Covered
Technical Note

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The relation among the Sherwood, Schmidt, and Reynolds numbers, $Sh = aSc^m Re^n$, is routinely used in liquid metal corrosion studies involving convective diffusion mass transfer from surfaces. A different form of this equation is presented for correlating convective mass flux with hydrodynamic and surface factors in liquid metal flows. A mass transfer coefficient is defined in terms of instantaneous mass flux and axial concentration gradient in the bulk stream. A mathematical model is proposed for the empirical evaluation of this mass transfer coefficient. The model shows that in-line concentration measurements are needed for valid correlations with hydrodynamic and surface factors.

17. Key Words (Suggested by Author(s))
Convective mass transfer; Boundary layer diffusion; Liquid metal corrosion; Nuclear liquid-metal systems; Mass transfer coefficient

18. Distribution Statement
Unclassified - unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	25	$3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

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SUMMARY

This report pertains to mass transfer involving boundary layer convective diffusion as the rate-controlling factor. In this case, hydrodynamic and surface conditions and diffusing specie concentrations in the bulk stream influence the mass transfer rate through their effect on the concentration gradient in the boundary layer. Herein, semiempirically based equations are used to evolve mass transfer relations that depend on the measurement of bulk stream concentration boundary conditions.

It is observed that the instantaneous mass flux $\mathscr{m}$ is related to the axial concentration gradient in the bulk liquid stream: $\mathscr{m} = g'(dc/dx)$, (where c is the concentration and x is distance). The mass transfer coefficient g' is functionally related to the thermophysical properties of the fluid, hydrodynamic factors, and geometric properties of the reaction surface. Herein, g' is expressed explicitly in terms of mean stream velocity and mass flow rate as well as in terms of dimensionless groupings of hydrodynamic and surface properties.

The mass transfer coefficient is evaluated by means of the experimental conditions corresponding to the mathematical model $\mathscr{m}_L = g'(c_L - c_0)/L$, where $\mathscr{m}_L$ is the integrated mass flux $\left[\int_0^L (\mathscr{m}/L)dx\right]$, L is the test section length, and $c_L - c_0$ is the axial concentration change in an isothermal test section. Evaluation of g' then depends on computing mass flux $\mathscr{m}_L$ per unit axial change of bulk stream concentration under conditions in which g' is axially invariant (or essentially invariant).

Using the previously described method, g' can be evaluated for a range of hydrodynamic and surface conditions to establish empirical values for the coefficients and exponents involved in functionally relating g' to hydrodynamic and surface parameters. The procedure requires actual measurements of concentration boundary conditions that have heretofore been circumvented.

INTRODUCTION

Corrosive attack and mass transfer effects are important factors to consider in the design and operation of energy conversion systems using liquid metals as working and heat exchange fluids. Although containment materials that are highly resistant to corrosive attack by liquid metals have been identified and tested, the need to improve our understanding of corrosion and mass transfer processes remains. In high-temperature nuclear applications, more information concerning the influence of hydrodynamic factors on convective transfer of soluble materials is needed. Modes and rates of depletion and accumulation of alloy elements, interstitials, and reaction byproducts are of special interest in the development of reliable, long-life nuclear reactor systems cooled by liquid metals.

Hydrodynamic factors will influence the rate of corrosive attack or deposit formation in liquid metal flows where boundary layer convective diffusion is rate controlling (refs. 1 and 2). The variation of convective mass flux with hydrodynamic factors depends on the relation between momentum and concentration distributions in the boundary layer. However, both theory and experimental experience are incomplete, and neither provides adequate information relating convective mass transfer to momentum transfer. Therefore, liquid metal investigators employ semiempirical relations based on analogies among mass, momentum, and heat transfer (refs. 3 to 6). But this approach requires the accumulation of much more experimental data than have thus far been obtained to verify these relations.

Results of mass transfer experiments involving hydrodynamic variables in high-temperature liquid metals cannot always be unambiguously interpreted or extrapolated to predict long-term convective mass transfer results (ref. 7). This is partly due to complexities involved in conducting suitable experiments and measuring bulk stream concentrations with high-temperature liquid metals under forced flow. Analytical and experimental efforts have generally been directed toward circumventing actual concentration measurements within test sections. The usual procedure also involves making semitheoretically based estimates of mass transfer coefficients. The resultant estimates of mass transfer coefficients are then used to predict mass flux or to compare results with theory. But this method depends on a priori assignment of values to numerical quantities appearing in certain empirical equations (e.g., $Sh = aRe^{n}Sc^{m}$, the Sherwood equation). At best, predicted results can be expected to agree with measured mass fluxes only within an order of magnitude.

This report is concerned with cases in which the aforementioned practice is unsatisfactory. Herein, the experimental techniques currently used with liquid metals are reexamined with a veiw toward securing more accurate convective diffusion mass transfer information. The major objective is to present convective mass transfer equations in a form that will be useful in determining values for mass transfer coefficients empirically. A mathematical model is proposed for the empirical evaluation of mass transfer coefficients and for facilitating the prediction of trends under various forced-flow boundary conditions. Application of the model would necessitate determining actual variations in axial concentration gradients.

CONVECTIVE MASS TRANSFER EQUATIONS

Preliminary Considerations

This report deals with liquid metal corrosion in a conduit under forced flow wherein the rate-controlling process is convective diffusion in the liquid boundary layer. In this case, hydrodynamic variables and boundary conditions will influence the corrosion (or deposition) rates by their effect on convective mass flux from (or to) the conduit surface. The ensuing discussion will apply specifically to situations in which the diffusing substance tends to saturate the liquid at the conduit surface or in which the diffusing substance is precipitating from a supersaturated solution. The diffusing substance, as contemplated herein, may be the major constituent of the containment material, an alloy element, an interstitial specie, or a reaction byproduct.

Hereinafter, for the purpose of the discussion, fully developed turbulent liquid flow through a circular conduit of uniform cross section is considered. The influence of boundary layer temperature gradients, heat flux, and concentration gradients of other components of a mixture on diffusion in the boundary layer are ignored. (It is assumed that the latter conditions do not necessarily limit the applicability of the equations given herein.)

The mass transfer boundary layer (i.e., diffusion sublayer) is the domain within which the concentration gradient (the driving force) primarily resides. For convective mass transfer, both molecular and eddy diffusion affect the mass transfer rate in the diffusion sublayer. It is important to distinguish between the boundary layer associated with mass transfer and that associated with momentum transfer. Each can differ markedly from the other in both thickness and transfer profile. For turbulent flow, there will tend to be a large disparity between the momentum and concentration distributions near the mass transfer surface (ref. 8).

Herein an equation is sought for the instantaneous steady-state mass flux at any given point or station axially along the conduit under fully developed, steady temperature conditions. That is, temperature and, hence, thermophysical properties are constant at any given station. The local mass flux is presumed to depend only on hydrodynamic variables (e.g., velocity, mass flow, and fluid friction), concentrations, and the properties of the conduit surface.

According to the Fick equation, the mass flux will be proportional to the local concentration gradient in the diffusion sublayer:

$$\mathcal{m} = \rho D\left(\frac{\partial c}{\partial y}\right)_{y=0} \tag{1}$$

where $\mathcal{m}$ is the diffusing mass flux, ρ is the bulk stream density, D is the diffusion coefficient, and $\partial c/\partial y$ is the concentration gradient normal to the reaction surface. (All symbols are defined in appendix A.)

The diffusion coefficient D consists of two terms under the turbulent conditions considered herein because eddy effects are superimposed on molecular diffusion in the sublayer (i.e., $D = D_m + D_t$). The molecular diffusion coefficient D_m is a function of concentration and temperature. The turbulent (eddy) diffusion coefficient D_t is a function of eddy velocity and characteristic eddy transport (mixing) length (ref. 8). Therefore, both D and $\partial c/\partial y$ will depend on the momentum transfer rate in the boundary layer, given that D_t is of the order of or greater than D_m.

Under the previously stated conditions, equation (1) is indeterminate unless the mass flux can be mathematically related to the momentum flux. However, both theory and experimental experience are incomplete, and neither provides adequate information relating convective mass transfer to momentum transfer (ref. 9). Therefore, one might rely on some assumed analogy between mass and momentum or energy transfer. Since relevant fluid friction and heat-transfer data have generally been collected for zero mass transfer, the validity of the aforementioned analogies will be taken as essentially limited to dilute concentrations of the diffusing substance. The amount of solute introduced is assumed to have a negligible effect on the density of the bulk liquid even at saturation. These conditions are considered to be satisfied in nuclear liquid metal systems in which the diffusing specie concentrations are generally of the order of 1000 ppm or less.

Correlation of Mass Flux With Hydrodynamic Factors

In this section, an explicit relation is developed for convective mass transfer in terms of the experimental operating variables, such as velocity and mass flow rate, and in terms of nondimensional parametric groupings. The resulting equations will serve to define a mass transfer coefficient in terms of the axial concentration gradient along the flow conduit.

Consider first the widely accepted mass transfer relation based on the following empirical heat-transfer relation for turbulent flow in round tubes (ref. 10):

$$\mathrm{Nu} = a\mathrm{Re}^n\mathrm{Pr}^m \tag{2}$$

The mass transfer analog of equation (2) is formed by substituting appropriate nondimensional mass transfer groupings for the Nusselt Nu and Prandtl Pr numbers:

$$\mathrm{Sh} = a\mathrm{Re}^n\mathrm{Sc}^m \tag{3}$$

The transformation of Pr to Sc is accomplished by substituting ρD for k/c_p. The transformation of Nu to Sh is accomplished by substituting $g/\rho D$ for h/k, where the mass transfer coefficient g is defined as follows (ref. 11):

$$\boldsymbol{m} = g(c_w - c_\delta) \tag{4}$$

Hence, equation (3) becomes

$$\boldsymbol{m} = a\rho D\mathrm{Re}^n\mathrm{Sc}^m\left(\frac{c_w - c_\delta}{d}\right) \tag{5}$$

Since $(c_w - c_\delta)/d$ is clearly an approximation for $\partial c/\partial y$, the term $(a\mathrm{Re}^n\mathrm{Sc}^m)$ must represent an adjustment factor, since $\boldsymbol{m}$ in equation (5) is necessarily identical to $\boldsymbol{m}$ in equation (1). Thus, equation (5) is simply a modified version of the Fick equation.

It is advantageous to relate $\boldsymbol{m}$ to the bulk stream axial concentration gradient instead of to the radial gradient across the boundary layer. An equation that is analogous to equation (5) can be obtained to relate mass flux $\boldsymbol{m}$ to the axial concentration gradient dc/dx in the bulk stream; for example,

$$\boldsymbol{m} = \alpha \frac{M}{\pi \boldsymbol{d}} \frac{dc}{dx} \tag{6}$$

Under the simplifying assumption that the mass $\boldsymbol{m}\pi\boldsymbol{d}\,dx$ is instantaneously distributed in the differential volume $(1/4)\pi\boldsymbol{d}^2dx$, the coefficient α might be taken equal to unity. According to the analysis of appendix B, however, α is a function of Re and Sc; hence,

$$\boldsymbol{m} = a \frac{M}{\pi\boldsymbol{d}} \mathrm{Re}^n\mathrm{Sc}^m \frac{dc}{dx} \tag{7}$$

(Note that the coefficient a and exponents m and n in equations (2), (3), and (7) do not necessarily have the same numerical values.) Mathematically eliminating d between M/d and Re^n in equation (7) results in the desired equation for m, which is explicit in velocity, mass flow rate and axial concentration gradient (note that $\rho U = M/A_s$ and $A_s = (1/4)\pi d^2$):

$$m = a'\mathrm{Sc}^m \rho^{(1-n)/2} \nu^{-n} (MU)^{(n+1)/2} \frac{dc}{dx} \tag{8}$$

The coefficient a' differs from a in equation (7) in that it is a function of the exponent n, since a' includes numerical quantities raised to the nth power.

Equation (8) reduces to an equation for mass flux in terms of a mass transfer coefficient and the axial concentration gradient (note that the axial concentration change is not a driving force in the same sense as is the radial concentration change across the boundary layer):

$$m = g' \frac{dc}{dx} \tag{9}$$

This new mass transfer coefficient g' is expressed explicitly in terms of velocity and mass flow rate:

$$g' = a'\mathrm{Sc}^m \rho^{(1-n)/2} \nu^{-n} (MU)^{(n+1)/2} \tag{10}$$

More generally, the mass transfer coefficient can be expressed in terms of nondimensional groupings that include the Reynolds number (see appendix C):

$$g' = b\rho\nu \mathrm{Sc}^m \mathrm{Re}^n P^e \tag{11}$$

Equation (11) is derived directly from equation (10), and the equations are mutually exclusive with respect to MU and Re. The dimensionless parameter P is related to the geometric properties of the corroding surface. As explained in appendix C, the parameter P can be expressed in different ways (e.g., ϵ/d, L/d, d_1/d_2, etc.).

In either equation (10) or (11), g' is seen to depend on thermophysical properties of the fluid and on hydrodynamic and surface geometry factors. Since surface factors are accounted for through P in equation (11), surface factors must be implicit in a' in equation (10). Obviously, this means that equation (10) applies only to cases with identical surface conditions, if a' is to be taken as constant.

APPLICATION AND INTERPRETATION OF ANALYTICAL RESULTS

Equation (9) is the defining equation for the mass transfer coefficient g'. Equations (10) and (11) are expressions for g' in terms of experimental variables and parameters that influence its value under various conditions. In this section, methods for evaluating g' in a forced-flow test section are considered. A mathematical model suitable for this purpose is proposed and discussed. Subsequently, the variation of g' and, hence, m with hydrodynamic and surface factors is discussed. Particular attention is given to the ambiguities in past liquid metal corrosion experiments. These ambiguities apparently resulted from circumvention of the concentration measurements which are required by the present model.

Evaluation of Mass Transfer Coefficient

In any mass transfer experiment involving a forced-flow circuit, one or more conduit segments or test sections are usually considered. The test section should contain a suitable reaction surface with respect to which mass removal or deposition rates may be determined. It should also provide for meaningful measurement of concentration differences for some predetermined length. It is by these means that the empirical evaluations of the mass transfer coefficient being sought can be obtained.

Therefore, equation (9) is adapted to a conduit segment of length L along which the hydrodynamic and surface factors are constant. Also, for simplicity, let it be given that the conduit segment is isothermal and, hence, that thermophysical properties are constant. Under these conditions, the mass transfer coefficient can be considered a constant; therefore, equation (9) will yield the following expression for the integrated mass flux m_L along the conduit segment L:

$$m_L = \int_0^L \frac{m}{L}\,dx = \frac{g'}{L}(c_L - c_0) \tag{12}$$

where c_0 is the bulk concentration at $x = 0$ and c_L is the bulk concentration at $x = L$. Equation (12) defines g' in terms of quantities that can serve as a basis for correlating mass flux with the hydrodynamic parameters included in equation (10) or (11).

Caution must be exercised in using equation (12), since the net measured mass flux is a time-averaged as well as a space-averaged quantity. As corrosive attack progresses, the mass flux may change because of changes in the nature of the corroding surface. The rate-controlling process may cease being boundary layer convective diffusion because of chemical changes in the substrate or the liquid. Or, surface variations may produce hydrodynamic changes that alter the mass transfer coefficient (see appendix D).

When there are interim changes in the mass transfer rate, there will generally be corresponding changes in $c_L - c_0$. It is apparent from this and the previous considerations that the validity of mass transfer correlations will depend on ascertaining whether there is a variation of the axial concentration gradient with respect to time as well as with respect to hydrodynamic and surface conditions. By analogy, one should remember to consider concentration measurements to be as important in mass transfer as temperature measurements are in heat-transfer investigations.

The previous discussion indicates that the mass transfer coefficient can be accurately evaluated only under rather special conditions, even if concentration measurements are made. Furthermore, it should be apparent that a proper evaluation of g' depends on computing mass flux per unit axial change of bulk stream concentration under conditions in which g' can be taken as being axially invariant. Hereinafter, some data are presented to indicate appropriate values for the exponent n in equations (8) and (10).

Variation of Mass Flux With Reynolds Number

One purpose of equations (9) to (12) is to provide a format for experimentally evaluating the exponents m, n, and e. However, it has been suggested that an appropriate value for n can be assigned on the basis of the heat-transfer analogy (ref. 1). The turbulent heat-transfer exponent of 0.8 has been adopted by many investigators for correlating convective mass transfer with Reynolds number. Although this particular value is not unequivocally confirmed by experimental results obtained heretofore, we will tentatively adopt it herein. The uncertainty with regard to the Reynolds number exponent is illustrated by the case cited below.

The authors of reference 12 obtained mass transfer data for stainless-steel specimens exposed to flowing lithium in a forced-circulation loop. There was mass removal from specimens in a hot-sample section and mass deposition in a cold-sample section. Data were obtained for Reynolds numbers between 1000 and 16 000. Both mass removal and deposition were patently influenced by hydrodynamic factors, which indicated that boundary layer convective diffusion was rate controlling in each instance. The deposition rate increased linearly with $Re^{0.8}$ for each of several temperatures from 328° to 490° C in the cold-sample section. However, mass removal in the hot-sample section increased parabolically with $Re^{0.8}$ for each of several temperatures from 510° to 612° C. The mass removal data indicated a higher power of Re (e.g., approximately twice 0.8). Or, if 0.8 is valid for the Reynolds number exponent, then other variables must have influenced the mass transfer rate. But this question remains open because reference 12 provides no data relative to concentration gradients in the test sections.

Moreover, there is insufficient information concerning the method used for varying Re, which was defined in terms of sample length (i.e., it is not clear whether sample length, velocity, or both were variables).

Variation of Mass Flux With Velocity

Many investigators prefer to correlate mass flux directly with velocity instead of Reynolds number. A common practice has been to adopt the Reynolds number exponent n for the velocity. According to equation (8), however, the velocity exponent equals (n+1)/2. If n has values near 1, the difference between n and (n+1)/2 is small and either value will suffice for practical purposes.

If mass flow rate M is held constant, equation (8) states that mass flux will vary in direct proportion with $U^{(n+1)/2}$, provided that dc/dx and other factors are constant. But note that, in the same conduit (or in conduits with identical diameters or cross sections), the mass flow rate will be directly proportional to velocity (since $M = \rho U A_s$, A_s = constant). In this case, equation (8) states that m varies directly with $U^{(n+1)}$, provided that dc/dx and other factors are constant. If n is 1, then in the former case m varies directly with U, and in the latter case m varies directly with U^2.

Both approximately linear and parabolic variations of mass flux with respect to velocity have been observed. In one investigation involving sodium in forced-flow stainless-steel loops (ref. 13), the mass flow rate was held constant so that the only hydrodynamic variable was velocity. Data were obtained with a number of loops under the aforementioned conditions, and an analysis showed that the mass removal rate varied approximately linearly with velocity. The velocity exponent was computed to be 0.884. This agrees quite well with the velocity exponent of 0.9 obtained in equation (8) if n is assigned the value of 0.8 as is usually done when using equation (5). On the other hand, data reported in reference 14 indicate a parabolic variation of mass removal rate with velocity for nickel alloy conduits. According to equation (8), this result should be expected if n is approximately 1 and M varies directly with U while dc/dx is fixed.

It appears that the foregoing results are consistent with the assumption that variations in the overall axial gradients were negligible relative to the variation in velocity. Otherwise, the results would not agree so well with those predicted by equation (8). But this would imply that changes in velocity produce compensating changes in $c_w - c_\delta$. This would be necessary in order that dc/dx remain essentially fixed (see eq. (B6)). However, neither reference 13 nor 14 provides the concentration information required to support assumptions concerning either the constancy or mode of variation of axial gradients.

Variation of Mass Flux With Mass Flow Rate

Tests have also been performed to determine the effect of variations in mass flux with mass flow rate at some fixed velocity, but the results are inconclusive. Two tests specifically devised for this purpose are reported in references 15 and 16. Special corrosion cartridges were installed in forced-flow stainless-steel loops with sodium. The cartridges contained annular channels that produced different mass flow rates at a fixed velocity. The cartridge design in the loop of reference 15 differed from that in the loop of reference 16. In the former loop, the mass removal rate increased in direct proportion with mass flow rate. In the latter loop the mass removal rate was essentially unaffected by mass flow rates differing by a factor of 2.

Equation (8) states that m should vary directly with M if U and dc/dx are constant, but variations of M might produce inverse variations of dc/dx. From equation (8) it is then possible that under some conditions m will appear to be invariant with respect to M. In the two tests cited, the difference in cartridge geometries could probably partly account for the disagreement in results. Unfortunately, not enough information exists to explain the manner in which dc/dx differed between the two cases.

Variation of Mass Flux With Surface Factors

Convective mass transfer involving eddy diffusion will be influenced by surface roughness and irregularities and the geometric character of the test section or conduit. These factors can influence mass flux independently of the nominal Reynolds number and other parameters included in the mass transfer coefficient g'. However, the exponential relations of mass flux with respect to surface factors have been studied even less than has mass flux with respect to hydrodynamic factors.

Surface geometry effects are represented by the P parameter introduced in equation (11) (see appendix C). Even when not represented explicitly (e.g., eq. (10)), surface geometry effects should nevertheless be considered factors in the mass transfer coefficient g'. The definition of P will vary because it depends on the surface and geometric parameters that characterize the test section type being investigated. Moreover, the P parameter is subject to change if the surface conditions change with time because of mass removal or deposition (e.g., enroughening).

There are many instances where anticipated correlations with Re or Sc have not been realized because surface and geometry variables altered the expected convective mass transfer rate. The authors of reference 3, for example, found appreciably increased convective mass transfer rates due to enroughening of benzoic acid surfaces by the formation of small fissures. In liquid-metal corrosion loops, locations with cracks and crevices show higher rates of attack (ref. 15). Also, higher rates of mass removal or deposition are found on leading (front) surfaces of specimens and in locations with flow disturbances (ref. 17).

The parameter P might correspond to the so-called downstream effect or x/d term included in some definitions of the mass transfer coefficient. In references 4 and 17, for example, this x/d ratio is simply a normalized length against which variations in m are referred. Such a term is unnecessary in an expression for g' if a mathematical model of the form of equation (12) is adopted. Therein, the axial variation of mass flux is already taken into account by the definition of m_L as the integrated average mass flux.

MEASUREMENT AND ANALYSIS OF CONCENTRATION VARIATIONS

Various techniques have been employed to detect impurities and solute concentrations that influence corrosive mass transfer in liquid metals. These include methods for detection and analysis of dissolved or entrained species in the bulk liquid at ppm levels. Devices used include plugging indicators, conductivity meters, cold traps, cover gas chromatographs, and drawn-sample vacuum-distillation apparatuses, and so forth (ref. 17).

However, techniques for in-line monitoring of concentration variations along test sections have not been sufficiently developed. There are two basic methods that could serve this purpose: (1) spaced (periodic) direct sampling and analysis of the bulk stream through openings into the test section conduit, and (2) continuous indirect sensing of relevant physical or radiological changes that correlate well with solute concentrations. New and novel experiment designs and advanced instrumentation would be required. Previous results indicate that the needed probe, instrument, and analytical sensitivities can probably be realized. Suitable in-line techniques and devices are described and discussed in reference 7 for the ppm range. However, future needs will undoubtedly involve sensitivities in the ppb range. The prospects of suitable devices in this range are unknown.

It has been suggested that concentration variations might be deduced from post-test inspection and analysis of mass transfer results. For example, the variations of penetration depth or deposit height with axial distance downstream of the test section inlet might be interpreted as an indication of similar variations in the bulk liquid concentration during testing. However, this technique may be satisfactory only in special and rather simple situations. The inclusion of test specimens or geometric complexities may invalidate assumptions of simple correspondence between dc/dx and mass removal or deposition profiles.

In practical applications and in experimental forced-flow circuits, there will be two extreme temperatures producing thermal gradient mass transfer (refs. 1 and 2). Associated with each temperature is a known (or assumed) equilibrium concentration of the diffusing specie(s). This knowledge is often used to define thermally induced concentration differences that give rise to mass transfer; hence, it is used to circumvent actual measurement of $c_L - c_0$ if one is attempting to evaluate the limiting case. For example, in mass transfer experiments, the difference between the equilibrium concentration for each of the two extreme temperatures can be substituted for $c_L - c_0$ to produce correlations between g' and m provided that the following assumptions are reasonable approximations for the real system. First, liquid entering the test section has a concentration corresponding to saturation at the lower temperature (higher temperature for deposition). Second, the test section is practically isothermal. Third, liquid leaving the test section has a concentration corresponding to saturation at the higher temperature (lower temperature for deposition).

In any test situation meeting the aforementioned conditions, it is desirable to attain essentially equilibrium saturation in the liquid exactly at the end of the test section for all flow conditions. However, no a priori criterion is available for selecting suitable test section lengths for each flow condition. In lieu of making all the appropriate measurements, therefore, there is no totally accurate means of evaluating the mass transfer coefficient.

CONCLUDING REMARKS

Heretofore, liquid-metal corrosion experiments and analyses have circumvented making actual measurements of mass transfer coefficients and concentration boundary conditions. The mathematical model proposed herein requires that convective mass flux be computed with respect to the axial concentration change along the test section. It is suggested that otherwise it is futile to expect valid and consistent correlations between convective mass flux and hydrodynamic (velocity, mass flow rate, and Reynolds number) and surface (roughness and form drag) factors. This situation arises because variations in hydrodynamic and surface factors produce variations in both boundary layer and bulk stream concentration gradients.

Obtaining the needed concentration measurements is difficult with high-temperature liquid-metal systems. However, it is worth considering the adoption of experimental techniques and devising instrumentation that could aid in acquiring the axial concentration data required by the mathematical model proposed herein. If done, this should facilitate more precise prediction of mass transfer rates with respect to variations in hydrodynamic and surface factors.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 4, 1970,
120-27.

APPENDIX A

SYMBOLS

[The symbols are defined in terms of the basic dimensions of mass, M; length, L; time, T; force, F; and temperature, θ.]

A_s	cross-sectional area of conduit, L^2
a, a', a''	dimensionless coefficient
b	dimensionless coefficient
c	point (or bulk stream) concentration, M/M
c_p	specific heat at constant pressure, FL/MT
c_w	concentration at reaction surface (wall), M/M
c_δ	diffusion sublayer concentration at $y = \delta$ (or $y \geq \delta$ for eq. (5)), M/M
D	diffusion coefficient, L^2/T
D_m	molecular diffusion coefficient, L^2/T
D_t	turbulent diffusion coefficient, L^2/T
$\boldsymbol{d}$	conduit diameter, L
e	numerical exponent
f	friction factor
g	mass transfer coefficient, M/L^2T
g'	mass transfer coefficient, M/LT
g_c	gravitational constant, ML/FT^2
h	heat-transfer coefficient, $F/LT\theta$
K	numerical coefficient, M/FT
k	thermal conductivity, $F/T\theta$
L	test section axial length, L
l	specimen length, L
M	mass flow rate, M/T
m	numerical exponent
$\boldsymbol{m}$	mass flux, M/L^2T
Nu	Nusselt number, hd/k
n	numerical exponent
P	dimensionless parameter
Pr	Prandtl number, $c_p\rho\nu/k$
Re	Reynolds number, $\boldsymbol{d}U/\nu$
Sc	Schmidt number, ν/D
Sh	Sherwood number, $g\,\boldsymbol{d}/\rho D$
t	time, T
U	mean stream velocity, L/T
u	point axial velocity, L/T
w	point axial mass flow rate, M/T

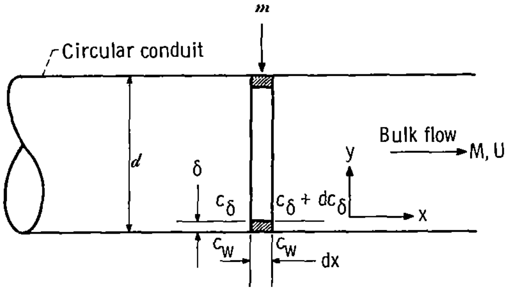
x	axial distance along conduit, L
y	radial (normal) distance from surface, L
δ	diffusion sublayer thickness, L
ϵ	root-mean-square roughness height, L
ν	kinematic viscosity, L^2/T
ν_m	molecular viscosity, L^2/T
ν_t	turbulent viscosity, L^2/T
ρ	density of liquid, M/L^3

APPENDIX B

RELATION OF MASS FLUX TO AXIAL CONCENTRATION GRADIENT

The relation between the mass flux from the conduit wall and mean axial concentration gradient in the liquid stream is derived in this appendix.

Let us consider a segment of a circular conduit with diameter d as illustrated in sketch (a). This analysis will be concerned with the differential annular volume indicated. The concentration at the reaction surface c_w is constant for the entire conduit segment. The diffusion sublayer thickness is δ and the concentration at $y = \delta$ changes from c_δ to $c_\delta + dc_\delta$ over dx.



(a)

The mass balance for a differential annular element within the diffusion sublayer is

$$c\,dw + \pi d m\,dx = \left(c + \frac{\partial c}{\partial x}dx\right)dw + \pi d\left(m - \frac{\partial m}{\partial y}dy\right)dx \tag{B1}$$

where m is the mass flux through the diffusion sublayer into the bulk stream and dw is the mass flow rate in the differential annular element of the diffusion sublayer. The following expression for m is obtained from equation (B1):

$$m = \frac{1}{\pi d}\int_0^\delta \frac{dw}{dy}\frac{\partial c}{\partial x}dy \tag{B2}$$

The variation of mass flow rate w with y in δ, is

$$\frac{dw}{dy} = \rho u\pi(d - y) \approx \rho u\pi d, \qquad 0 \leq y \leq \delta \tag{B3}$$

where $\delta << d$. From reference 10,

$$\left(\frac{du}{dy}\right)_{y=0} = \frac{fU^2}{2\nu} \tag{B4}$$

Let du/dy in the diffusion sublayer equal $(du/dy)_{y=0}$, integrate $u = \int_0^y (fU^2/2\nu)dy$, and substitute for u in equation (B3).

It will be assumed that $\partial c/\partial x$ increases linearly with y in the diffusion sublayer, that is,

$$\frac{\partial c}{\partial x} = \frac{y}{\delta}\frac{dc_\delta}{dx} \tag{B5}$$

It will be further assumed that dc_δ/dx is related to the mean bulk concentration gradient dc/dx through the Reynolds and Schmidt numbers, that is,

$$\frac{dc_\delta}{dx} = \varphi(Re, Sc)\frac{dc}{dx} \tag{B6}$$

Combining equations (B2) to (B6) and integrating yield

$$m = \frac{\rho U^2 f\delta^2}{6\nu}\varphi(Re, Sc)\frac{dc}{dx} \tag{B7}$$

Since $\rho U^2 = (4/\pi d^2)MU$, we have

$$m = \frac{M}{\pi d}\frac{2fU\delta^2}{3\nu d}\varphi(Re, Sc)\frac{dc}{dx} \tag{B8}$$

or,

$$m = \frac{M}{\pi d}\frac{2f}{3}\left(\frac{\delta}{d}\right)^2 Re\ \varphi(Re, Sc)\frac{dc}{dx} \tag{B9}$$

From reference 8, the relation between the diffusion sublayer thickness δ and the viscous sublayer thickness δ_0 is

$$\delta = \delta_0 Sc^{-1/3} \tag{B10}$$

where $\delta_0 \geq \delta$. If the viscous sublayer is assumed to be laminar, then according to reference 10,

$$\frac{\delta_0}{d} = (5\,\mathrm{Re}^{-1})\sqrt{\frac{2}{f}} \tag{B11}$$

Combining equations (B9) to (B11) yields

$$m = \frac{M}{\pi d}\,\frac{100}{3}\,\mathrm{Re}^{-1}\mathrm{Sc}^{-2/3}\,\varphi(\mathrm{Re}, \mathrm{Sc})\frac{dc}{dx} \tag{B12}$$

It is deemed reasonable to assume that $\varphi(\mathrm{Re}, \mathrm{Sc})$ is a simple power function of Re and Sc so that equation (B12) becomes

$$m = a\,\frac{M}{\pi d}\,\mathrm{Re}^{n}\mathrm{Sc}^{m}\,\frac{dc}{dx} \tag{B13}$$

(The exponent n probably ranges from 0 to 1, but we refrain from assigning any particular value for n, or for a or m, at the present stage.)

APPENDIX C

SURFACE GEOMETRY PARAMETER

Examination of equation (B9) shows that the friction factor f and, hence, surface roughness or form drag will influence convective mass transfer. Moreover, for turbulent flow over rough surfaces we should not expect equation (B11) to hold since the viscous sublayer may not be laminar. In general, therefore, f will not cancel out as in equation (B12) and some power of f should be implicit in the coefficient a' of equation (8).

Consider the following equation which is equivalent to equation (8) except for f^e:

$$\mathit{m} = a''f^e Sc^m \rho^{(1-n)/2}\nu^{-n}\mathit{d}^{(n+1)}\left(\frac{MU}{A_s}\right)^{(n+1)/2}\frac{dc}{dx} \tag{C1}$$

The coefficient a'' differs from a' by the factor $(\pi/4)^{(n+1)/2}$ and by the purely numerical coefficient assumed to be associated with f^e. Let us proceed by noting that equation (C1) is unaltered if combined with the factor $(\rho U^2/\rho U^2)^{(n+1)/2}$:

$$\mathit{m} = a''f^e Sc^m \rho\nu\left(\frac{\mathit{d}U}{\nu}\right)^{(n+1)}\left(\frac{MU}{A_s\rho U^2}\right)^{(n+1)/2}\frac{dc}{dx} \tag{C2}$$

Since $\mathit{d}U/\nu$ equals Re and $MU/A_s\rho U^2$ equals unity, equation (C2) may be written as

$$\mathit{m} = a''f^e \rho\nu Sc^m Re^{n+1}\frac{dc}{dx} \tag{C3}$$

The friction factor f may be a simple function of the Reynolds number as in the Blasius equation, $f = 0.079/Re^{0.25}$ which applies to smooth circular tubes. On the other hand, f may be totally independent of Re as in the Hopf equation, $f = 0.01(2\epsilon/\mathit{d})^{0.314}$ which applies to turbulent flow in rough tubes (ref. 10). Clearly, the exponents of f and Re will change as surface conditions are altered. Furthermore, in the case of conduits with in-stream corrosion specimens or other objects, the Reynolds number is usually written in terms of the object's characteristic dimension, say l, so that $Re = lU/\nu$. But we can retain Re in its conventional form by combining it with the factor l/d.

In accordance with the preceding considerations, equation (C3) is rewritten in terms of the parameters Re, Sc, and P:

$$m = b\rho\nu \mathrm{Sc}^m \mathrm{Re}^n P^e \frac{dc}{dx} \tag{C4}$$

The exponent n in equation (C4) is not necessarily the same as n + 1 in equation (C3). Likewise, the coefficient b in equation (C3) will differ from a'' or a' in all the previous equations ((8), (10), (C1), and (C2)). In any case, the exponents and coefficients should be experimentally determined. (See appendix D for further comments concerning the exponents.)

The parameter P is related to surface and conduit geometry particulars that characterize the test section or conduit segment of interest. The surface geometry factors involved in P are those which would affect the boundary layer concentration gradient and, hence, dc/dx. Therefore, P should be differently defined for each type of reaction surface according to roughness, presence of in-stream corrosion specimens, annular conduits, protrusions, corners, and so forth. We can thus account for mass flux variations due to a variety of typical surface geometry factors encountered in practical and experimental situations. For example, given uniform conduits that differ only in surface roughness, P might be taken simply as the roughness factor ϵ/d. If specimen length effects need to be taken into account, then P might be set equal to l/d. If annular channels are used, then diameter ratios d_1/d_2 would be appropriate. Obviously, P may be composed of combinations of suitable terms.

APPENDIX D

VARIATIONS IN MASS TRANSFER EXPONENTS

After any corrosive process has been in progress for a sufficiently long period, the original surface may have been altered by particulate mass removal, leaching, cracking, deposition, and other like processes. Therefore, as the attack goes on, the mass transfer coefficient will change even though the rate-controlling process, velocity, mass flow rate, and thermophysical properties are unchanged.

One mode by which the mass transfer coefficient varies with respect to surface conditions is due to the variabilities of the exponents m, n, and e in equation (D1) with respect to surface conditions:

$$g' = b\rho\nu \mathrm{Sc}^{m}\mathrm{Re}^{n}P^{e} \tag{D1}$$

This situation is analogous to that found in heat-transfer studies where the roughening of an initially smooth surface alters the relation among Nu, Pr, and Re. This is reflected by significant changes in the empirical exponents m and n. Like changes should be expected in the exponents involved in the convective mass transfer coefficient. For example, it can be shown that the Reynolds number exponent may tend to increase (e.g., from 0.8 to 1.0) as the conduit surface is enroughened by mass removal. For the velocity and mass flow rate product MU common to most liquid metal applications, even small changes (e.g., 0.1) in $(n+1)/2$ in equation (D2) can produce significant changes in the mass transfer coefficient:

$$g' = a'\rho^{(n-1)/2}\nu^{-n}\mathrm{Sc}^{m}(MU)^{(n+1)/2} \tag{D2}$$

This would involve changes both in a' and n in the case of equation (D2), since, as stated in Correlation of Mass Flux With Hydrodynamic Factors, a' includes numerical quantities raised to the power n. One would expect, in the case of equation (D1), to discover that e and n remain constant only if P is properly defined with respect to surface factors.

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NASA-Langley, 1970 — 12 E-4985