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A PRELIMINARY STUDY ON THE USE OF REFERENCE STATES IN PREDICTING TRANSPORT RATES IN FLOWS WITH CHEMICAL REACTIONS

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Abstract—High-speed laminar Couette flows with additions, at the stationary surface, of substances capable of reacting with the free-stream gas are examined in a preliminary study on the use of reference states and constant-property solutions in predicting mass-, momentum- and energy-transfer rates in flows with chemical reactions. In order to simplify the analysis, a model in which Fick's Diffusion Law is applicable and in which Prandtl number and Schmidt number equal unity is studied. In general, evaluation of the reference state requires a description of the concentration distributions and, consequently, information concerning the chemical reactions. Since obtaining this information requires, in general, about as much effort as would solving exactly for the transport rates, it appears that the concept of a reference state is of limited practical value for the general problem of flows with chemical reactions. However, if the forward reaction rates are fast and the backward reaction rates are slow (a sufficient condition for diffusion-controlled reaction rates), then the problem of calculating the reference state is reduced to the problem of calculating the fluid velocity at the reaction plane. If, in addition, the reactions occur near either the inner or outer limit of the viscous layer, then calculations of the reference state are straightforward; in a linear approximation, the reference enthalpy is given by an expression including terms involving, as factors, the heat of reaction whereas the reference concentrations are given simply by the arithmetic averages of the concentrations at the two bounding surfaces. In numerical calculations for Couette flows with diffusion-controlled reaction rates, errors introduced in estimates of the location of the reaction zone appear to dominate any other errors which may be introduced when using these approximate methods. Since, for flows with inert-coolant injections, the reference-state expressions developed for laminar Couette flows correlate satisfactorily also the results for laminar and (for limited available data) turbulent boundary layers, it is recommended that a study be made of the possibility of extending these reference-state expressions also to laminar and turbulent boundary-layer flows with reactive-coolant injections.

NOMENCLATURE

B_f, blowing rate for momentum transfer $\equiv \dfrac{(\rho v)_w}{\rho u_\infty}\,\dfrac{2}{c_{fo}}$;

$\dfrac{c_{fo}}{2}$, $\dfrac{1}{2}\times$ friction coefficient for zero blowing rate $\equiv \dfrac{\tau_{wo}}{\rho u_\infty^2}$;

c^k, mass fraction of species k;

c_p, "frozen" specific heat at constant pressure $\equiv \sum_k c^k c_p^k$;

D, diffusion coefficient in Fick's Diffusion Law;

h_s, sensible specific enthalpy $\equiv h - h_o$;

h_o, datum specific enthalpy, including chemical enthalpy (i.e. enthalpy of formation or negative of heat of formation at constant pressure).

Δh_o^r, change in enthalpy for specified reaction, evaluated at datum conditions, per unit mass of reference species r produced in the reaction (i.e. negative of heat of reaction at constant pressure per unit mass of reference species r produced in the reaction)

$$\equiv \sum_k h_o^k\, \nu^k M^k / \nu^r M^r,$$

with ν^k and ν^r negative for reactants, positive for products;

k, thermal conductivity;

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M,	molecular weight;
Ma,	Mach number;
p,	pressure;
Pr,	Prandtl number $\equiv c_p \mu/k$;
q_s,	sensible heat flux $\equiv - k\, \mathrm{d}T/\mathrm{d}y + \sum_k \rho^k V^k h_s^k$;
r_o,	recovery factor for zero blowing rate $\equiv \frac{2\, c_p (T_{ro} - T_\infty)}{u_\infty^2}$;
R,	gas constant;
Sc,	Schmidt number $\equiv \mu/\rho D$;
T,	temperature;
T_{ro},	recovery temperature for zero blowing rate;
u,	velocity parallel to wall;
u_f,	velocity parallel to wall at reaction plane;
v,	velocity normal to wall;
V^k,	diffusion velocity, normal to wall, of species k;
y,	co-ordinate normal to wall;
δ,	thickness of shear layer in Couette flow;
μ,	dynamic viscosity coefficient;
ν^k,	stoichiometric coefficient of species k (negative for reactants, positive for products);
ρ,	density;
τ,	viscous stress;
$\dot{\omega}^k$,	mass rate of production, per unit volume, of species k.

Superscripts

$*$,	reference state;
k,	species k.

Subscripts

w,	stationary surface (or wall);
∞,	moving surface (or free stream);

A tilde over a symbol indicates that the symbol refers to an element, not to a species.

INTRODUCTION

CALCULATING exactly the mass-, momentum-, and energy-transfer rates in high-speed boundary layers is complicated by the dependence of the values of the fluid properties on temperature and composition. Rubesin and Johnson [1], Young and Janssen [2], Eckert [3] and Sommer and Short [4] have noted empirically, however, that the momentum- and energy-transfer rates in boundary layers without mass additions at the wall may be predicted to good approximation by inserting values of fluid properties corresponding to a reference temperature (or enthalpy) into equations developed for fluids with constant properties. Scott [5] obtained a fair correlation of results of several calculations for boundary layers with additions of inert coolants at the wall by supplementing the concept of a reference temperature by the concept of a reference composition and evaluating all fluid properties at a reference coolant concentration of 0·4 times the coolant concentration at the wall (the coolant concentration in the free stream being zero). He side-stepped the problem of calculating a reference temperature for the case with mass additions, however, and evaluated fluid properties, for all flow conditions, at a temperature of 1450°F. Gross *et al.* [6] also correlated empirically these calculated values of heat- and momentum-transfer rates. They evaluated the transfer coefficients at free-stream conditions and the blowing parameters at temperatures calculated using the reference-temperature equation given by Eckert [3] for the case with no mass additions: the effects of molecular-weight differences were handled empirically by multiplying the blowing parameters by the cube root of the ratio of the free-stream-gas molecular weight to the coolant molecular weight. The concept of a reference composition was not used. Romig [7], Eckert and Tewfik [8] and Wilson [9] have shown that use of a reference enthalpy facilitates correlating momentum- and energy-transfer rates in laminar boundary layers with dissociations but with no mass additions. Wilson [9] and Dorrance [10] noted that, for laminar boundary layers without mass additions, the reference temperature is given to good approximation by the velocity-averaged temperature; Burggraf [11] found that, for turbulent flows without mass additions, the reference temperature is given to good approximation by the temperature at the outer edge of the laminar sublayer.

The physical bases for the concepts of reference temperatures and reference compositions were examined by Knuth [12]. In a study of binary high-speed laminar Couette flows, simplifications were realized as a consequence of the nature of the boundary conditions, and information concerning the effects of differences in the heat capacities of the two species and the effects of deviations of Prandtl number, Schmidt number, and Lewis number from unity were obtained. An exact expression for the reference composition was obtained for the case of isothermal flow; a linearized expression for the reference temperature was obtained for the case in which the viscosity is a linear function of temperature and independent of composition. To first order in blowing rates, the reference composition is the arithmetic average of the compositions at the two surfaces, whereas the expression for the reference temperature is a simple extension of Eckert's expression for the reference temperature for a laminar boundary layer with no mass addition at the wall. Basing all fluid properties upon the reference state suggested by this Couette-flow study, mass-, momentum-, and energy-transfer rates and recovery factors for laminar boundary-layer flows of fluids with variable fluid properties were given as functions of blowing rates for several coolants (including hydrogen and iodine) and for several speeds (up to $Ma = 12$) by only two curves to an approximation adequate for many engineering applications.

Since, for flows without mass additions at the wall, the reference-temperature expression used for laminar flows correlates satisfactorily the data for turbulent flows also, Knuth and Dershin [13] attempted then to correlate data for turbulent flows with mass additions using the reference-state expressions developed by Knuth [12] for laminar flows. From examinations of the limited available data, they concluded that, at least for Mach numbers up to 3, the reference-temperature expression developed for laminar flows with mass transfers appears to correlate satisfactorily the data for turbulent flows with mass transfers. Since no data including dependable measurements of foreign-gas concentrations at the surface were available, no conclusions were drawn concerning the applicability of the reference-concentration expression developed for laminar flows to turbulent flows.

None of these references consider, however, the use of reference states and constant-property solutions in predicting transport rates for flows with additions, at a bounding surface, of substances capable of reacting with the free-stream gas. The present paper describes results of a preliminary effort to extend the previous studies to include this technically important (but difficult) case.

LAMINAR COUETTE FLOWS OF REACTING SUBSTANCES

In order to obtain insight into the nature of transport phenomena and thermodynamic conditions existing in high-speed boundary-layer flows involving diffusions of reacting substances, consider laminar Couette flows (requiring only relatively simple mathematics) characterized by the following features (cf. Fig. 1):

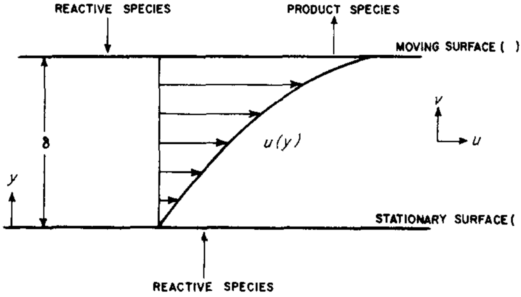

Fig. 1. Couette-flow model with arbitrary chemical reactions.

1. The velocity of the moving surface, as well as the temperature and concentrations at this surface, are uniform and steady, and are specified.
2. Heat and mass may pass readily through the moving surface; a steady force, required to maintain steady motion, acts on this surface in the direction of motion.
3. The momentum flux and the viscous stress in the direction normal to the two surfaces are much smaller than the pressure at some reference plane in the model.
4. The kinetic energy associated with the mass-weighted average velocity in the direction normal to the two surfaces is much smaller than the enthalpy of the fluid at some reference plane in the model.
5. Fick's Diffusion Law describes to good

approximation the diffusion of a given substance relative to the rest of the mixture.†

6. Body force, Dufour, and Soret effects are negligible.
7. The Prandtl and Schmidt numbers (hence, also the Lewis number) are equal to unity.
8. Viscosity of mixture is constant with value fixed by the reference state of the mixture. (It follows from 7 and 8 that the product of density and diffusion coefficient and the ratio of thermal conductivity and specific heat are constants with values fixed by the reference state of the mixture.)

This simple model contains the most important features of high-speed boundary-layer flows involving mass, momentum, and energy transfers, variable specific heats and chemical reactions.

Conservations of mass, *k*th chemical species, momentum, and energy for this model are described by the ordinary differential equations

$$\frac{\mathrm{d}\rho v}{\mathrm{d}y} = 0 \tag{1}$$

$$\rho v \frac{\mathrm{d}c^k}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\, \rho D \frac{\mathrm{d}c^k}{\mathrm{d}y} + \dot{\omega}^k \tag{2}$$

$$\rho v \frac{\mathrm{d}u}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\, \mu \frac{\mathrm{d}u}{\mathrm{d}y} \tag{3}$$

$$\rho v \frac{\mathrm{d}h_s}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\left(k \frac{\mathrm{d}T}{\mathrm{d}y} + \sum_k \rho D h_s^k \frac{\mathrm{d}c^k}{\mathrm{d}y}\right) + \mu \left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)^2 - \sum_k h_o^k\, \dot{\omega}^k. \tag{4}$$

The energy equation, (4), may be placed in a form more similar to the forms of the remaining equations; multiply the momentum equation, (3), by velocity *u* and add the product to the energy equation with the result

$$\rho v \frac{\mathrm{d}(h_s + u^2/2)}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\left(k \frac{\mathrm{d}T}{\mathrm{d}y} + \sum_k \rho D h_s^k \frac{\mathrm{d}c^k}{\mathrm{d}y} + \mu \frac{\mathrm{d}\, u^2/2}{\mathrm{d}y}\right) - \sum_k h_o^k\, \dot{\omega}^k. \tag{5}$$

Then, since Fick's Diffusion Law is applicable and since the Prandtl number equals the Schmidt number, the first two terms on the right-hand side of the energy equation, (5), may be written [15]

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(k \frac{\mathrm{d}T}{\mathrm{d}y} + \sum_k \rho D h_s^k \frac{\mathrm{d}c^k}{\mathrm{d}y}\right)$$
$$= \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{k}{c_p} \frac{\mathrm{d}h_s}{\mathrm{d}y} - \frac{k}{c_p} \sum_k h_s^k \frac{\mathrm{d}c^k}{\mathrm{d}y} + \rho D \sum_k h_s^k \frac{\mathrm{d}c^k}{\mathrm{d}y}\right)$$
$$= \frac{\mathrm{d}}{\mathrm{d}y} \frac{k}{c_p} \frac{\mathrm{d}h_s}{\mathrm{d}y}.$$

Hence the energy equation becomes

$$\rho v \frac{\mathrm{d}(h_s + u^2/2)}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\left[\frac{k}{c_p} \frac{\mathrm{d}h_s}{\mathrm{d}y} + \mu \frac{\mathrm{d}(u^2/2)}{\mathrm{d}y}\right] - \sum_k h_o^k\, \dot{\omega}^k. \tag{6}$$

Now the forms of the several equations of change differ only by terms involving the rate of production of the *k*th chemical species. However, if one uses the stoichiometric relations for the several chemical reactions, then continuity and energy equations having a form like the form of the momentum equation may be written [16]. Consider the chemical reaction for which mass conservation is described by

$$\sum_k \nu^k M^k = 0. \tag{7}$$

For this reaction, the production rates of the *k*th and the *r*th species are related by

$$\frac{\dot{\omega}^k}{\nu^k M^k} = \frac{\dot{\omega}^r}{\nu^r M^r} \tag{8}$$

whereas the production rate of the *k*th element is zero, i.e. the several elements are conserved even if chemical reactions occur.

Treat first the continuity equations. Multiplying the equation of change for the *l*th species, (2), by the ratio of the mass of the *k*th element found in the *l*th species to the mass of the *l*th

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† It has been shown [14] that a sufficient condition for the applicability of Fick's Diffusion Law is that the several binary diffusion coefficients are equal to each other and to the diffusion coefficient in Fick's equation.

species and summing them over all species, one obtains

$$\rho v \frac{\mathrm{d}\tilde{c}^k}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y} \rho D \frac{\mathrm{d}\tilde{c}^k}{\mathrm{d}y}. \tag{9}$$

Here a tilde indicates that the symbol refers to an element, not to a chemical species. This equation applies also to the case in which more than one chemical reaction occurs.

Treat now the energy equation. Writing the production rate $\dot{\omega}^k$ of the kth chemical species in terms of the production rate $\dot{\omega}^r$ of a reference species,

$$\sum_k h_o^k \dot{\omega}^k = \dot{\omega}^r \sum_k h_o^k \frac{\nu^k M^k}{\nu^r M^r} = \dot{\omega}^r \Delta h_o^r. \tag{10}$$

Substituting for $\dot{\omega}^r$ from the equation of change for the reference species, (2), and substituting then for $\sum_k h_o^k \dot{\omega}^k$ in the energy equation, (6) gives

$$\rho v \frac{\mathrm{d}[h_s + (u^2/2) + c^r \Delta h_o^r]}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{k}{c_p}\frac{\mathrm{d}h_s}{\mathrm{d}y} + \mu \frac{\mathrm{d}(u^2/2)}{\mathrm{d}y} + \rho D \frac{\mathrm{d}c^r \Delta h_o^r}{\mathrm{d}y}\right). \tag{11}$$

Extension to the case in which more than one chemical reaction takes place is accomplished by adding more terms of the form $c^r \Delta h_o^r$ to the dependent variable.

Since the Prandtl and Schmidt numbers equal unity, the several equations of change may be integrated now to obtain the following expressions for the Reynolds analogy between transport of mass, momentum, and energy:

$$\frac{(\rho^k \tilde{V}^k)_w}{\rho u (\tilde{c}^k - \tilde{c}^k)} = \frac{\tau_w}{\rho u^2} = \frac{-q_{sw} - (\rho^r V^r)_w \Delta h_o^r}{\rho u [h_s - h_{sw} + (u^2/2) + (c^r - c_w^r)\Delta h_o^r]} \tag{12}$$

and the following symmetrical relations between the several distributions:

$$\frac{\tilde{c}^k - \tilde{c}_w^k}{\tilde{c}_\infty^k - \tilde{c}_w^k} = \frac{u}{u_\infty} = \frac{h_s - h_{sw} + (u^2/2) + (c^r - c_w^r)\Delta h_o^r}{h_{s\infty} - h_{sw} + (u_\infty^2/2) + (c_\infty^r - c_w^r)\Delta h_o^r}. \tag{13}$$

The relation between enthalpy h_s and velocity u given in (13) will be used in the derivation of the reference-enthalpy expression.

Recall that reference values of the fluid properties are desired which, when used in equations for flow with constant fluid properties, give correct values of transport rates at the stationary surface for flow with variable fluid properties. In order to obtain some insight into the manner in which the reference composition is to be computed, consider the equation describing transfer of a chemical element which *is* added at the moving surface but *is not* added at the stationary surface:

$$(\rho v)_w \tilde{c}^a - \rho D \frac{\mathrm{d}\tilde{c}^a}{\mathrm{d}y} = 0. \tag{14}$$

Separating variables and integrating

$$(\rho v)_w \delta = \int_{\ln \tilde{c}_w{}^a}^{\ln \tilde{c}_\infty{}^a} \rho D \, \mathrm{d} \ln \tilde{c}^a. \tag{15}$$

Consider now isothermal flow. Then, to good approximation,

$$\rho D = \frac{pD}{RT} M \tag{16}$$

with pD/RT independent of composition. Hence

$$(\rho v)_w \delta = \frac{pD}{RT} \int_{\ln \tilde{c}_w{}^a}^{\ln \tilde{c}_\infty{}^a} M \, \mathrm{d} \ln \tilde{c}^a. \tag{17}$$

Alternatively, if one sets the molecular weight equal to a constant with value fixed by the reference composition of the mixture, then

$$(\rho v)_w \delta = \frac{pD}{RT} M^* \int_{\ln \tilde{c}_w{}^a}^{\ln \tilde{c}_\infty{}^a} \mathrm{d} \ln \tilde{c}^a. \tag{18}$$

Equating the right-hand sides of (17) and (18)

$$M^* = \frac{\int_{\ln \tilde{c}_w{}^a}^{\ln \tilde{c}_\infty{}^a} M \, \mathrm{d} \ln \tilde{c}^a}{\int_{\ln \tilde{c}_w{}^a}^{\ln \tilde{c}_\infty{}^a} \mathrm{d} \ln \tilde{c}^a}. \tag{19}$$

Similarly, in order to obtain some insight into the manner in which the reference enthalpy is to be computed, consider the equation describing transfer of momentum

$$\tau = \mu \frac{\mathrm{d}u}{\mathrm{d}y}. \tag{20}$$

Separating variables, substituting for u from $\tau = \tau_w + (\rho v)_w u$, and integrating

$$(\rho v)_w \delta = \int_{\ln \tau_w}^{\ln \tau_\infty} \mu \, \mathrm{d} \ln \tau. \tag{21}$$

Alternatively, if one sets the viscosity equal to a constant with value fixed by the reference state of the mixture, then

$$(\rho v)_w \delta = \mu^* \int_{\ln \tau_w}^{\ln \tau_\infty} \mathrm{d} \ln \tau. \tag{22}$$

Equating the right-hand sides of (21) and (22)

$$\mu^* = \frac{\displaystyle\int_{\ln \tau_w}^{\ln \tau_\infty} \mu \, \mathrm{d} \ln \tau}{\displaystyle\int_{\ln \tau_w}^{\ln \tau_\infty} \mathrm{d} \ln \tau}. \tag{23}$$

Since the purpose of the immediate calculations is to obtain insight into the concept of a reference enthalpy, consider the case in which the viscosity is a linear function of sensible enthalpy and its dependence upon composition is handled by evaluation at the reference molecular weight. Then, from (23),

$$\mu^* = \mu \, (M^*, h_s^*) \tag{24}$$

with

$$h_s^* = \frac{\displaystyle\int_{\ln \tau_w}^{\ln \tau_\infty} h_s \, \mathrm{d} \ln \tau}{\displaystyle\int_{\ln \tau_w}^{\ln \tau_\infty} \mathrm{d} \ln \tau}. \tag{25}$$

(If the reference composition is established, then the reference temperature is a known function of the reference enthalpy.) The evaluation of the integral appearing in the numerator of the right-hand side of (25) is facilitated by substituting for the enthalpy h_s from (13) and for the viscous stress τ from $\tau = \tau_w + (\rho v)_w u$. It is seen now that the evaluation of either the reference composition, (19), or the reference enthalpy, (25), requires a description of the concentration distributions and, consequently, information concerning the chemical reactions. Since obtaining this information requires, in general, about as much effort as would solving exactly for the transport rates, it appears that the concept of a reference state is of limited practical value for the general problem of flows with chemical reactions.

However, if the forward chemical-reaction rates are fast and the backward chemical-reaction rates are slow, then the reactions occur in a "reaction plane"; the reaction rates are controlled by the mass-diffusion rates, the reactant supplied at the moving surface does not reach the stationary surface, and one is able to carry out the indicated integrations. In the expression for the reference enthalpy, it is convenient to use sometimes, as the reference species, the reactant supplied at the moving surface. Letting $r = b$, the concentration ratio $(c^r - c_w^r)/(c_\infty^r - c_w^r)$ may be written, using the Reynolds analogy, as a function of velocity ratio

$$\begin{aligned} \frac{c^r - c_w^r}{c_\infty^r - c_w^r} = \frac{c^b}{c_\infty^b} &= 0, & u < u_f \\ &= \frac{u - u_f}{u_\infty - u_f}, & u > u_f. \end{aligned} \tag{26}$$

(Note that, since the chemical reactions are confined to a reaction plane omissions of tildes are justified in this equation.) Substituting from (13) and (26) into (25), expanding in series, retaining only first-order terms in blowing rates, and integrating, one obtains

$$\begin{aligned} h_s^* \approx \frac{1}{2}\left(h_{sw} + h_{s\infty} + \frac{u_f}{u_\infty} c_\infty^b \Delta h_o^b\right) + \frac{1}{6}\,\frac{u_\infty^2}{2} \\ + B_f^* \left[\frac{1}{12}\left(h_{sw} - h_{s\infty} - \frac{u_f}{u_\infty} c_\infty^b \Delta h_o^b\right) \right. \\ \left. + \frac{1}{6}\,\frac{u_f}{u_\infty}\left(1 - \frac{u_f}{u_\infty}\right) c_\infty^b \Delta h_o^b\right]. \end{aligned} \tag{27}$$

At other times, it is convenient to use, as the reference species, the reactant supplied at the stationary surface. Letting $r = c$, the concentration ratio $(c^r - c_w^r)/(c_\infty^r - c_w^r)$ may be written using the Reynolds analogy, as a function of velocity ratio

$$\begin{aligned} \frac{c^r - c_w^r}{c_\infty^r - c_w^r} = \frac{c_w^c - c^c}{c_w^c} &= \frac{u}{u_f}, & u < u_f \\ &= 1, & u > u_f. \end{aligned} \tag{28}$$

Substituting from (13) and (28) into (25), expanding in series, retaining only first-order terms in blowing rates, and integrating, one obtains,

$$h^* \approx \frac{1}{2}\left(h_{sw} + \frac{u_\infty - u_f}{u_\infty} c^c_w \,\Delta h^c_o + h_{s\infty}\right) + \frac{1}{6}\,\frac{u^2_\infty}{2} + B^*_f\left[\frac{1}{12}\left(h_{sw} + \frac{u_\infty - u_f}{u_\infty} c^c_w \,\Delta h^c_o - h_{s\infty}\right) - \frac{1}{6}\,\frac{u_f}{u_\infty}\left(1 - \frac{u_f}{u_\infty}\right) c^c_w \,\Delta h^c_o\right]. \tag{29}$$

Evaluate the expression for the reference molecular weight for the model (cf. Fig. 2) in which the several species may be divided into four groups: (1) inert species ($k = a$) supplied at the moving surface, (2) reactive species ($k = b$) supplied at moving surface, (3) reactive species ($k = c$) supplied at stationary surface, and (4) reaction products ($k = d$). Then the molecular weight may be written as a function of mass fractions

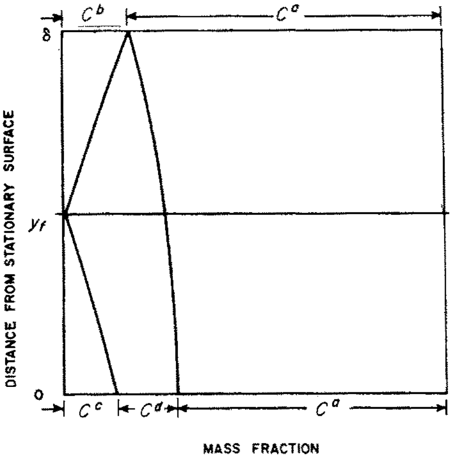

FIG. 2. Couette-flow model with a diffusion-controlled chemical reaction and four groups of chemical species (a = inert species, b = reactive species, c = reactive species, and d = product species).

$$M = \frac{M^a}{\left(1 + \dfrac{M^a - M^b}{M^b} c^b + \dfrac{M^a - M^c}{M^c} c^c + \dfrac{M^a - M^d}{M^d} c^d\right)} \tag{30}$$

and, using the Reynolds analogy, the mass fractions may be written as functions of velocity ratios

$$\frac{c^a - c^a_w}{c^a_\infty - c^a_w} = \frac{u}{u_\infty}$$

$$\frac{c^b}{c^b_\infty} = 0, \qquad u < u_f$$

$$= \frac{u - u_f}{u_\infty - u_f}, \qquad u > u_f$$

$$\frac{c^c_w - c^c}{c^c_w} = \frac{u}{u_f}, \qquad u < u_f$$

$$= 1, \qquad u > u_f$$

$$c^d = 1 - c^a - c^b - c^c. \tag{31}$$

Substituting from (30) and (31) into (19), expanding in series, retaining only first-order terms in $1 - c^a$, c^b, c^c, and c^d, and integrating, one obtains,

$$1 - \frac{M^a - M^b}{M^b} c^{b*} - \frac{M^a - M^c}{M^c} c^{c*} - \frac{M^a - M^d}{M^d} c^{d*} \approx 1 - \frac{M^a - M^b}{M^b}\left(1 - \frac{u_f}{u_\infty}\right)\frac{c^b_\infty}{2} - \frac{M^a - M^c}{M^c}\,\frac{u_f}{u_\infty}\,\frac{c^c_w}{2} - \frac{M^a - M^d}{M^d}\left[1 - \frac{c^a_w + c^a_\infty}{2} - \left(1 - \frac{u_f}{u_\infty}\right)\frac{c^b_\infty}{2} - \frac{u_f}{u_\infty}\,\frac{c^c_w}{2}\right]. \tag{32}$$

Hence, for the present model,

$$c^{a*} \approx \frac{c^a_w + c^a_\infty}{2}$$

$$c^{b*} \approx \left(1 - \frac{u_f}{u_\infty}\right)\frac{c^b_\infty}{2}$$

$$c^{c*} \approx \frac{u_f}{u_\infty}\,\frac{c^c_w}{2}$$

$$c^{d*} = 1 - c^{a*} - c^{b*} - c^{c*}. \tag{33}$$

It is seen that, for the special case in which the chemical reactions occur in a reaction plane, the problem of calculating the reference state is replaced now by the problem of calculating the velocity u_f at the reaction plane. For two special cases, a satisfactory approximate solution is obtained easily.

1. If the mass fraction c^b_∞ is much smaller than the mass fraction c^c_w, then the reactions occur near the moving surface; it is convenient to use, as the reference species, the reactant supplied at the moving surface ($r = b$), and the several reference-state expressions are given to good approximation by

$$h_s^* \approx \frac{1}{2}(h_{sw} + h_{s\infty} + c^b_\infty \Delta h^b_o) + \frac{1}{6}\frac{u^2_\infty}{2}$$

$$+ \frac{1}{12} B_f^*(h_{sw} - h_{s\infty} - c^b_\infty \Delta h^b_o) \tag{34}$$

$$c^{a*} \approx \frac{c^a_w + c^a_\infty}{2}$$

$$c^{b*} \approx 0$$

$$c^{c*} \approx \frac{c^c_w}{2}$$

$$c^{d*} \approx 1 - \frac{c^a_w + c^a_\infty + c^c_w}{2}. \tag{35}$$

2. If the mass fraction c^c_w is much smaller than the mass fraction c^b_∞, then the reactions occur near the stationary surface; it is convenient to use, as the reference species, the reactant supplied at the stationary surface ($r = c$), and the several reference-state expressions are given to good approximation by

$$h_s^* \approx \frac{1}{2}(h_{sw} + c^c_w \Delta h^c_o + h_{s\infty}) + \frac{1}{6}\frac{u^2_\infty}{2}$$

$$+ \frac{1}{12} B_f^*(h_{sw} + c^c_w \Delta h^c_o - h_{s\infty}) \tag{36}$$

$$c^{a*} \approx \frac{c^a_w + c^a_\infty}{2}$$

$$c^{b*} \approx \frac{c^b_\infty}{2}$$

$$c^{c*} \approx 0$$

$$c^{d*} \approx 1 - \frac{c^a_w + c^a_\infty + c^b_\infty}{2}. \tag{37}$$

On the other hand, if no information concerning the location of the reaction plane is available, and if one is required to make an estimate of the reference state, then the most rational procedure would be to set $u_f/u_\infty = 1/2$ with the result

$$h^* \approx \frac{1}{2}(h_{sw} + h_{s\infty}) + \frac{1}{4} c^b_\infty \Delta h^b_o + \frac{1}{6}\frac{u^2_\infty}{2}$$

$$+ \frac{1}{12} B_f^*(h_{sw} - h_{s\infty}) \tag{38}$$

$$c^{a*} \approx \frac{c^a_w + c^a_\infty}{2}$$

$$c^{b*} \approx \frac{c^b_\infty}{4}$$

$$c^{c*} \approx \frac{c^c_w}{4}$$

$$c^{d*} \approx 1 - \frac{c^a_w + c^a_\infty}{2} - \frac{c^b_\infty + c^c_w}{4}. \tag{39}$$

If the coolant is not reactive, then

$$h^* \approx \frac{1}{2}(h_{sw} + h_{s\infty}) + \frac{1}{6}\frac{u^2_\infty}{2}$$

$$+ \frac{1}{12} B_f^*(h_{sw} - h_{s\infty}) \tag{40}$$

$$c^{a*} \approx \frac{c^a_w + c^a_\infty}{2}$$

$$c^{c*} \approx \frac{c^c_w + c^c_\infty}{2}$$

with superscript a referring to species other than those species added at the stationary wall and with superscript c referring to those species added at the stationary wall. Finally, if no coolant is added at the wall, then

$$h^* \approx \frac{1}{2}(h_{sw} + h_{s\infty}) + \frac{1}{6}\frac{u^2_\infty}{2} \tag{42}$$

which for $Pr = 1$, compares favorably with the empirical reference-enthalpy equation used for two-dimensional boundary layers without mass additions [3].

DISCUSSION

Errors introduced using reference states and constant-property solutions may be evaluated by comparing values of mass-, momentum-, and energy transfer rates calculated using this approximate method with values of these transfer rates calculated using an exact method. Such comparisons have been made for several Couette-flow models [17–20], namely (1) tetrafluoroethylene (Teflon) diffusing into air, (2) hydrogen diffusing into air, and (3) no diffusion. In these models, if coolant oxidation occurs, then it takes place in a flame sheet, i.e. the oxidation rate is diffusion controlled; the transport coefficients μ, k/c_p, and ρD vary as the square root of the sensible enthalpy h_s.

For those cases in which no chemical reactions occur, using the reference enthalpy and constant property solutions introduces an error of 2 per cent (cf. Table 1). For those cases in which chemical reactions occur, various errors are introduced depending upon the approximation used. If (27) is used, i.e. if exact values of u_f/u_∞ (0·61 for the hydrogen flame and 0·79 for the tetrafluoroethylene flame) are used, then an error of 4 per cent appears; if (34) is used, i.e. if the value of u_f/u_∞ is approximated by unity, then errors of 16 and 5 per cent are realized; and if (38) is used, i.e. if the value of u_f/u_∞ is approximated by 1/2, then, to the nearest per cent, no error appears. Finally, using (36), i.e. approximating u_f/u_∞ by 0 (an illogical approximation when u_f/u_∞ equals 0·61 and 0·79) leads to errors of 32 and 61 per cent.

Table 1. Errors introduced using approximate calculation methods in several Couette-flow Models†

Coolant gas	Coolant oxidation?	Blowing rate, $B_{f\infty}$	Velocity ratio, u_f/u_∞	Approximation method (equation)	Error‡ (per cent)
None	—	0	—	(42)	2
H_2	No	0·0696	—	(40)	2
C_2F_4	No	3·53	—	(40)	2
H_2	Yes	0·268	0·61	(27)	4
C_2F_4	Yes	4·83	0·79	(27)	4
H_2	Yes	0·268	0·61	(34)	16
C_2F_4	Yes	4·83	0·79	(34)	5
H_2	Yes	0·268	0·61	(38)	0
C_2F_4	Yes	4·83	0·79	(38)	0
H_2	Yes	0·268	0·61	(36)	32
C_2F_4	Yes	4·83	0·79	(36)	61

† In all models, main-stream gas is air, $\rho_\infty u_\infty \delta/\mu_\infty = 3{\cdot}18 \times 10^5$, and $Ma_\infty = 8{\cdot}9$.

‡ Error is based upon difference between values of transfer rates calculated using exact and approximate methods.

In the approximation using (34), the error is greater for the system containing hydrogen than for the system containing tetrafluoroethylene partly because more heat is released by hydrogen oxidation than by tetrafluoroethylene oxidation and partly because the flame sheet is farther from the moving surface for the hydrogen coolant than for the tetrafluoroethylene coolant. The fact that no error appears in the approximation using (38) is due to the presence of compensating errors. The approximation using (36) is included only to illustrate the magnitude of the errors which may be encountered if the improper equations are selected.

These numerical results substantiate the suggestions that one use equation (27) or (29) and (33) if the reaction-zone location is known exactly, equations (34) and (35) if the reaction-zone location is known to be near the outer edge of the boundary layer, equations (36) and (37) if the reaction-zone location is known to be near the wall, and equations (38) and (39) if no information concerning the reaction-zone location is available. If no reactions occur, then the methods of [7] and [8] are preferred.

After the reference state is established, then the several transport rates may be predicted using constant-property relations. For laminar Couette flows, one might compute, e.g. the viscous stress at the wall using

$$\frac{\tau_w \delta}{\mu^* u_\infty} = \frac{(\rho v)_w\, \delta/\mu^*}{\exp\,[(\rho v)_w \delta/\mu^*] - 1} \tag{43}$$

and the mass- and energy-transfer rates from the viscous stress using the Reynolds analogy which, for $Pr = Sc = 1$, is given by equation (12).

CONCLUSIONS

From results of the Couette-flow analyses and calculations, the following conclusions are drawn concerning the use of reference states and constant-property solutions to predict transport rates in flows with additions, at a bounding surface, of substances capable of reacting with the free-stream gas:

1. Evaluation of either the reference composition or the reference enthalpy requires, in general, a description of the concentration distributions, and, consequently, information concerning the chemical reactions. Since obtaining this information requires, in general, about as much effort as would solving exactly for the transport rates, it appears that the concept of a reference state is of limited practical value for the general problem of flows with chemical reactions.
2. However, for the case in which the chemical reactions occur in a reaction plane (so that the reaction rate is diffusion-controlled), one is able to carry out the required integrations; the problem of calculating the reference state is replaced then by the problem of calculating the fluid velocity at the reaction plane.
3. For cases in which the chemical reaction rates are fast and occur near either the inner or the outer limit of the boundary layer, calculations of the reference state are straightforward; in a linear approximation (satisfactory for many engineering applications), the reference enthalpy is given by an expression including terms involving, as factors, the heat of reaction whereas the reference concentrations are given simply by the arithmetic averages of the concentrations at the wall and in the free stream.
4. In the case of diffusion-controlled reaction rates, errors introduced in estimates of the location of the reaction zone appear to dominate any other errors which may be introduced when using these approximate methods.
5. Since, for flows with mass additions but without chemical reactions, the reference-state expressions developed for laminar Couette flows correlate satisfactorily also the results for laminar and (for limited available data) turbulent boundary layers, it is recommended that a study be made of the possibility of extending the reference-state expressions derived here also to laminar and turbulent boundary-layer flows with reactive-coolant injections. For boundary-layer flows with arbitrary Prandtl numbers, one might replace the coefficient of $u_\infty^2/2$ in the reference-enthalpy expressions by $0{\cdot}22r_0^*$ so that, for the case with no mass addition, the reference-enthalpy expression reduces to the expression given by Eckert.

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Résumé—A la suite d'une recherche préliminaire concernant l'utilisation des états de référence et des solutions à propriété constante pour l'évaluation des taux de transport d'énergie, de quantité de mouvement et de masse dans des écoulements avec réactions chimiques, on a étudié les écoulements de Couette laminaires à grande vitesse, avec apports, sur la surface fixe, de substances réagissant avec le fluide en écoulement.

Pour simplifier l'analyse, on a étudié un modèle permettant d'appliquer la loi de diffusion de Fick, les nombres de Prandtl et de Schmidt étant égaux à l'unité. En général, l'évaluation de l'état de référence nécessite une description des distributions de concentration et, par conséquent, une information concernant les réactions chimiques. Comme cette information est, en général, aussi difficile à obtenir que l'évaluation exacte des coefficients de transport, il semble que le concept d'un état de référence ait une valeur pratique limitée pour le problème général des écoulements avec réactions chimiques. Toutefois, si les taux de réactions sont rapides au début et lents à la fin (condition suffisante pour les vitesse de réaction à diffusion contrôlée) le problème du calcul de l'état de référence se réduit au problème du calcul de la vitesse sur fluide sur le plan de réaction. Si, de plus, les réactions se font près de la fontière intérieure ou extérieure de la couche visqueuse, les calculs de l'état de référence sont alors directs; dans une approximation linéaire l'enthalpie de référence est donnée par une expression comprenant des termes contenant, en facteur, la chaleur de réaction tandis que les concentrations de référence sont données simplement par les moyennes arithmétiques des concentrations sur les deux surfaces limites. Dans les calculs numériques relatifs aux écoulement de Couette avec vitesse de réaction à diffusion contrôlée, les erreurs commises dans les estimations de la position de la zone de réaction semblent dominer toutes les autres erreurs qui peuvent s'introduire quand on utilise ces méthodes approchées.

Comme pour des écoulements avec injection de refroidiseur inerte, les expressions d'état de référence développées pour des écoulements de Couette laminaires traduisent de façon satisfaisante les résultats des couches laminaires et (pour un nombre limité de données) des couches limites turbulentes, il est conseillé d'étudier la possibilité d'étendre également ces expressions aux écoulements de couches limites laminaires et turbulentes avec injection de fluide refroidisseur réactif.

Zusammenfassung—Für Laminare Couette-Strömungen von hoher Geschwindigkeit, wobei von der ruhenden Wand ein Zusatz von Substanzen, die mit dem strömenden Gas reagieren, erfolgt, wird vorläufig die Verwendbarkeit von Bezugszuständen und Lösungen für konstante Eigenschaften untersucht, um Stoff-, Impuls- und Energieaustausch in Strömungen mit chemischen Reaktionen zu ermitteln. Zur Vereinfachung der Analyse dient ein Modell, in welchem das Fick'sche Diffusionsgesetz gilt und Prandtl- und Schmidt-Zahl die Grösse eins haben. Im allgemeinen erfordert die Bewertung von Bezugszuständen eine Beschreibung der Konzentrationsverteilungen und damit Kenntnis der chemischen Reaktionen. Da die Erlangung dieser Kenntnis gewöhnlich etwa ebenso aufwendig ist wie die exakte Lösung für die Austauschraten, scheint es, dass das Konzept eines Bezugszustandes von beschränktem praktischen Wert für allgemeine Strömungsprobleme mit chemischen Reaktionen ist. Wenn jedoch die Reaktionsraten in der einen Richtung schnell, in der anderen Richtung langsam sind (eine genügende Bedingung für diffusionskontrollierte Reaktionsraten), reduziert sich die Bestimmung des Bezugszustandes auf die Berechnung der Mediumsgeschwindigkeiten an der Reaktionsebene. Wenn weiterhin die Reaktionen nahe der inneren oder äusseren Grenze der zähen Schicht erfolgen, ergibt eine einfache Rechnung den Bezugszustand; in einer linearen Näherung ist die Bezugsenthalpie durch einen Ausdruck gegeben, mit der Reaktionswärme also Faktor und den Bezugskonzentrationen als arithmetisches Mittel der Konzentrationen an den beiden begrenzenden Flächen. Bei numerischen Berechnungen von Couette-Strömungen mit diffusionskontrollierten Reaktionsraten scheinen Fehler, die auf Schätzungen der Lage der Reaktionszone beruhen, vor allen anderen, durch diese Näherungsmethoden eingeführten Fehlern zu dominieren. Nachdem für Strömungen mit inerter Kühlmitteleinblasung die für laminare Couette-Strömungen entwickelten Ausdrücke für Bezugszustände auch die Ergebnisse für laminare und (für beschränkt verfügbare Daten) turbulente Grenzschichten zufriedenstellend korrelieren, wäre eine Studie einer möglichen Ausdehnung dieser Bezugszustandausdrücke auf laminare und turbulente Grenzschichtströmungen mit reaktiver Kühlmitteleinblasung zu empfehlen.

Аннотация—В предварительном исследовании по использованию характерных состояний и решений при постоянных физических константах для определения скоростей переноса массы, количества движения и энергии для течений при химических реакциях рассматривается ламинарное течение Куэтта при больших скоростях с подачей через неподвижную поверхность веществ, способных вступать в реакцию с газом основного потока. Чтобы упростить анализ, рассматривается модель, к которой применим закон диффузии Фика, при числах Прандтля и Шмидта, равных единице. В общем, для определения характерного состояния необходимо описание распределения концентраций и, следовательно, сведения о химических реакциях. Так как получение этих сведений требует обычно таких же усилий, как и точное определение скоростей переноса, понятие характерного состояния имеет ограниченную практическую ценность для решения общей задачи течений при химических реакциях. Однако, если скорости прямых реакций велики, а скорости обратных реакций малы (достаточное условие для реакций, скорость которых определяется диффузией), задача определения характерного состояния сводится к задаче определения скорости жидкости в плоскости реакции. Если, кроме того реакции имеют место у внутренней или у наружной границы вязкого слоя, определение характерного состояния простое; в линейном приближении характерная энтальпия представлена в виде выражения, в которое члены, содержащие теплоту, входят в качестве коэффициентов, а характерные концентрации определяются просто как средние арифметические концентраций на двух ограничивающих поверхностях. При численных расчётах течений Куэтта для реакций со скоростями, определяемыми диффузией, ошибки в определениях положения области реакции преобладают над другими ошибками, которые могут быть внесены при использовании этих приближённых методов. Так как для течений с вводом инертных охладителей выражения характерного состояния, выведенные для ламинарных течений Куэтта, удовлетворительно согласуются с результатами для ламинарных и турбулентных пограничных слоёв (данные по последним ограничены), рекомендуется исследовать возможности применения этих выражений характерного состояния также и к течениям в ламинарных и турбулентных пограничных слоях с вдувом реагирующих охладителей.