

THE TURBULENT BOUNDARY LAYER IN THE PRESENCE OF SURFACE CHEMICAL REACTIONS
(WITH REFERENCE TO CARBON SURFACES)

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Formulas are obtained for the limiting law of heat transfer when chemical reactions occur at the eroded surface and within the boundary layer. Formulas are derived for the heat content of the wall in the case of mixed heat transfer with due regard to injection of gases due to thermal decomposition of the material.

1. EQUATIONS

For a multicomponent gas mixture in the presence of chemical reactions heat is transferred by conduction and by the diffusion flux of chemical enthalpy [1]

$$q = \lambda \frac{\partial T}{\partial y} + \sum_{i=1}^n \rho V_i K_i h_i, \quad h_i = \int_0^T c_{pi} dT + h_i^0.$$

Neglecting thermo-baro-diffusion and diffusive heat conduction and carrying out simple transformations [1] we obtain for a multicomponent gas mixture an expression for the heat flux in the form

$$q = -\frac{\lambda}{c_p} \left[\left(\frac{\partial h}{\partial y} - \sum_{i=1}^n h_i \frac{\partial K_i}{\partial y} \right) + \frac{\rho D_{12} c_p}{\lambda} \sum_{i=1}^n h_i \frac{\partial K_i}{\partial y} \right],$$

$$h = \sum_{i=1}^n K_i h_i.$$

Here h is the total heat content of the mixture. For the case in which the Lewis-Semenov number $N_{Le} \approx 1$, the total energy flux is

$$q = -\frac{\lambda}{c_p} \frac{\partial h}{\partial y} \quad \left(N_{Le} = \frac{\rho D_{12} c_p}{\lambda} \approx 1 \right). \quad (1.1)$$

In this case the differential energy equation, written for the total heat content of the mixture, will have the form

$$\rho u \frac{\partial h}{\partial x} + \rho v \frac{\partial h}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\lambda}{c_p} \frac{\partial h}{\partial y} \right). \quad (1.2)$$

Integrating this equation with respect to the thickness of the enthalpy boundary layer and introducing the definition of the total energy loss thickness in the usual way

$$\delta_h^{**} = \int_0^{\delta_h} \frac{\rho u}{\rho_0 u_0} \frac{h - h_0}{h_w - h_0} dy,$$

we obtain an integral relationship for the energy of the boundary layer

$$\frac{dR_h^{**}}{dX} + \frac{R_h^{**}}{\Delta h} \frac{d(\Delta h)}{dX} + \frac{R_h}{D} \frac{d(D)}{dX} - R_h \frac{j_w}{\rho_0 u_0} =$$

$$= R_L \frac{q_w}{\rho_0 u_0 \Delta h} \quad (\Delta h = h_w - h_0). \quad (1.3)$$

Here D is the diameter of the channel, R_L and R_h^{**} are characteristic Reynolds numbers, written, respectively, for the characteristic length and total energy thickness δ_h^{**} .

We introduce the Stanton number S , the wall permeability parameter b_1 , and the relative law of heat transfer

$$S_h = \frac{q_w}{\rho_0 u_0 (h_w - h_0)}, \quad b_1 = \frac{j_w}{\rho_0 u_0 S_h}, \quad \Psi_h = \frac{S_h}{S_0}. \quad (1.4)$$

Here S_0 is the Stanton number in standard conditions. In view of definitions (1.4) Eq. (1.3) is converted to the form

$$\frac{dR_h^{**}}{dX} + \frac{R_h^{**}}{\Delta h} \frac{d(\Delta h)}{dX} + \frac{R_h^{**}}{D} \frac{d(D)}{dX} = R_L S_0 (\Psi_h + b_n),$$

$$b_h = \frac{j_w}{\rho_0 u_0 S_0} = b_1 \Psi_n. \quad (1.5)$$

For S_0 we take a power-law approximation [2, 3]

$$S_0 = A R_h^{**m} P^{-0.75} \left(P = \frac{c_p \mu}{\lambda} \right). \quad (1.6)$$

Here P is the Prandtl number; $A = 0.0128$, $m = 0.25$ for R_h^{**} from $10^3 - 10^5$.

2. LAW OF HEAT TRANSFER

The relative law of heat transfer (1.4) in the presence of a transverse material flux (injection of gases, chemical erosion, complex ablation) [3] has the form

$$\Psi_h = \left(\int_0^1 \frac{d\Theta}{\sqrt{(1 + b_1 \Theta) \rho / \rho_0}} \right)^2 \quad \left(\Theta = \frac{h - h_w}{h_0 - h_w} \right). \quad (2.1)$$

Here Θ is the dimensionless enthalpy.

To solve equation (2.1) we need to have a connection between ρ / ρ_0 and Θ .

If we assume that the gas mixture in the boundary layer conforms to ideal-gas laws, then

$$\frac{\rho}{\rho_0} = \frac{MT_0}{M_0 T}, \quad M = \left(\sum_{i=1}^n \frac{K_i}{M_i} \right)^{-1}. \quad (2.2)$$

Here M is the molecular weight of the mixture. We must also find a connection between the profiles of enthalpy and gas concentration.

If we write the equation of continuity for the i -th component of the binary mixture (or for a group of components comprising an effective binary mixture) in terms of the reduced concentrations K_i^0 , as in [1], then it will have the form

$$\rho u \frac{\partial K_i^0}{\partial x} + \rho v \frac{\partial K_i^0}{\partial y} = \frac{\partial}{\partial y} \left(\rho D_{12} \frac{\partial K_i^0}{\partial y} \right).$$

Here K_i^0 is the concentration of the i -th chemical element, irrespective of the chemical compound which contains it.

Then when $N_{Le} = N_{Sc} = P = 1$ there is an analogy between the reduced concentrations and the total enthalpy (N_{Sc} is the Schmidt number)

$$\frac{h - h_w}{h_0 - h_w} = \frac{K_i^0 - (K_i^0)_w}{(K_i^0)_0 - (K_i^0)_w} \quad \left(N_{Sc} = \frac{\mu}{\rho D_{11}} \right). \quad (2.3)$$

From the equation of mass flux of oxidant on the erosion surface and using Eqs. (1.1), (1.4), and (2.3) we find

$$b_1 = \frac{(K_i^0)_0 - (K_i^0)_w}{(K_i^0)_w}. \quad (2.4)$$

Here i indicates a component which cannot penetrate the heat-transfer surface.

Accordingly, for the "injected" component, in this case carbon,

$$b_1 = \frac{K_w^\circ(C)}{1 - K_w^\circ(C)}. \quad (2.5)$$

As an example we consider the case of chemical erosion of carbon in a flow of oxygen according to the reaction $C + O \rightarrow CO$. In this case we have

$$K_w^\circ(C) = \frac{b_1}{1 + b_1} = r_1 K_w^\circ(CO), \quad \text{or} \quad r_1 = \frac{b_1}{1 + b_1}. \quad (2.6)$$

Here r is the weight fraction of carbon in CO; it is assumed in this case that at a wall temperature $> 1800\text{--}2000^\circ\text{K}$ oxidation occurs in the diffusion region and, hence, the erosion rate depends on the rate of delivery of oxidant to the surface (and not on the rate of the chemical reaction); hence, the concentration of oxidant on the surface can be regarded as zero, i.e., $K_w(O) = 0$, $K_w(CO) = 1$.

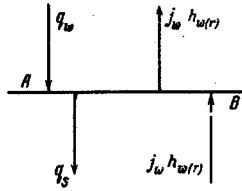


Fig. 1

Using analogy (2.3) we can write

$$K^\circ(C) = r_1 K_w^\circ(CO) = K_w(C)(1 - \Theta). \quad (2.7)$$

It follows from equalities (2.6) and (2.7) that

$$K(CO) = 1 - \Theta. \quad (2.8)$$

Then for a binary mixture of O_2 and CO the ratio of the molecular weights at any point of the boundary layer, in view of equalities (2.2) and (2.8), can be written in the form

$$M = \frac{M_0 M_w}{M_0 + (M_w - M_0)\Theta}. \quad (2.9)$$

Similarly, for the local temperature

$$T = \frac{h}{c_p} = \frac{(h_0 - h_w)\Theta + h_w}{c_p},$$

or

$$T = \frac{h_w + (h_0 - h_w)\Theta}{c_{pw} + (c_{p0} - c_{pw})\Theta}$$

$$(c_p = (c_{p0} - c_{pw})\Theta + c_{pw}). \quad (2.10)$$

In view of (2.9) and (2.10) the first equation of (2.2) takes the form

$$\frac{\rho}{\rho_0} = \frac{[\psi_3 + (1 - \psi_2)\Theta]}{[\psi_1 + (1 - \psi_1)\Theta][\psi_3 + (1 - \psi_3)\Theta]}$$

$$\left(\psi_1 = \frac{h_w}{h_0}, \psi_2 = \frac{c_{pw}}{c_{p0}}, \psi_3 = \frac{M_0}{M_w}\right). \quad (2.11)$$

For gases of equal valency $c_{pw}|c_{p0} = M_0|M_w$. In this case the limiting relative law of heat transfer (2.1) reduces to the following expressions for subsonic flow in the presence of injection [3]:

$$\Psi_h = \frac{4}{(1 - \psi_1)b_1} \left[\ln \frac{\sqrt{(1 - \psi_1)(1 + b_1)} + \sqrt{b_1}}{\sqrt{1 - \psi_1} + \sqrt{\psi_1 b_1}} \right]^2$$

$$(\psi_1 < 1), \quad (2.12)$$

$$\Psi_h = \frac{1}{(\psi_1 - 1)b_1} \left[\text{arc tg} \left(\frac{b_1}{(\psi_1 - 1)(1 + b_1)} \right)^{1/2} - \text{arc tg} \left(\frac{b_1 \psi_1}{\psi_1 - 1} \right)^{1/2} \right]^2 (\psi_1 > 1). \quad (2.13)$$

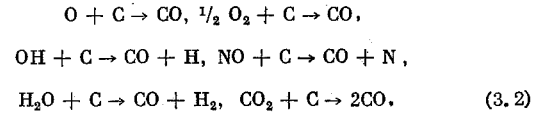
3. ENERGY BALANCE ON SURFACE

A. Case of chemical erosion of carbon surface. According to the balance (Fig. 1), on the eroded surface AB

$$q_w = q_s + j_w h_w' - j_w h_w'', \quad h_\Sigma^\circ = h_w' - h_w''. \quad (3.1)$$

Here q_s is the heat flux used in heating fresh material, h_Σ° is the total heat of chemical formation; the subscript w denotes surface, the subscript w' denotes the surface of the gas, and the subscript w'' denotes the surface of the solid.

The mixture of gases acting on the eroded surface is of complex composition [5]. The chemical erosion of carbon in these conditions is due to a variety of oxidation-reduction reactions at the eroded surface. The most probable reactions (up to $T \approx 4000^\circ\text{K}$) are



The expression for the total heat (3.1) in this case will be

$$h_\Sigma^\circ = \frac{Q_p}{M_w}, \quad Q_p = \sum_{i=1}^n (nQ_2) - \sum_{i=1}^n (nQ_1).$$

Here Q_T is the total heat effect of the reactions occurring on the surface, n is the number of moles of the particular product involved in the reaction, Q_1 is the heat of formation of the initial products involved in the reactions (3.2), and Q_2 is the heat of formation of the final products of the reactions (3.2). After simple transformations of (3.1) and using (1.4) and (3.1) we determine the heat content of the wall

$$h_w = h_0 + b_1 h_\Sigma^\circ + \frac{q_s}{q_w} (h_w - h_0). \quad (3.3)$$

The parameter b_1 is determined from (2.4)

$$(K_i^\circ)_0 = \sum_{j=1}^p \frac{m_j}{M_i} (K_i)_0. \quad (3.4)$$

Here m_j is the weight fraction of the j -th element in the i -th chemical compound. For instance, for a gas of complex composition the reduced concentration $(K_0^\circ)_0$ for oxygen in an undisturbed flow is written as

$$K_0^\circ(O) = K_0(O_2) + 16/17 K_0(OH) + 16/18 K_0(H_2O) +$$

$$+ 16/30 K_0(NO) + 16/44 K_0(CO_2) + \dots \quad (3.5)$$

Here $K(O_2)$, $K(OH)$, $K(H_2O)$, etc. are the weight fractions of chemically active compounds containing oxygen in the undisturbed flow.

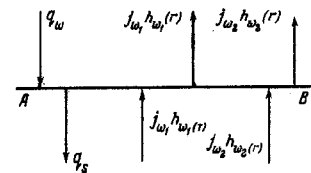


Fig. 2

Using the assumption of the diffusive regime of reaction and the probability of the occurrence of reactions (3.2) for the case of "local equilibrium," we have from equalities (2.4) and (3.4)

$$b_1 = \frac{1}{16/28 K_w(CO)} \left(\sum_{j=1}^p \frac{m_0}{M_j} (K_j)_0 - 16/18 K_w(CO) \right). \quad (3.6)$$

On the other hand, from Eq. (2.5),

$$K_w(\text{CO}) = \frac{16}{28} \frac{b_1}{1 + b_1} \quad (3.7)$$

Substituting Eq. (3.7) in equality (3.6) we obtain a formula for the permeability parameter

$$b_1 = \frac{3}{4} \left[\sum_{j=1}^p \frac{m_0}{M_j} (K_j)_0 \right] \quad (3.8)$$

Here M_0 is the weight fraction of chemically active oxygen, and M_j is the molecular weight of the j -th component containing O_2 .

In Eq. (3.3) in a first approximation we take $q_s = 0$. We find T_w' . By solving the one-dimensional heat-conduction equation for a semi-infinite body with a moving outer boundary for the given T_w' , we find q_s . From Eq. (3.3) we determine the final value of T_w .

Having determined T_w or h_w and assuming it constant over the profile we find ψ_1 . From formula (3.8) we calculate b_1 . We then determine the limiting relative law of heat transfer ψ_h from Eqs. (2.12) or (2.13).

Thus, we have all the necessary data for the solution of (1.5). For a plate

$$R_h^{**} = \frac{D_*}{D} \left[\frac{A(1+m)}{p^{0.75}} R_L (\Psi_h + b_h) x \right]^{0.8} \quad (3.9)$$

for profiles with varying velocity on the outer boundary of the boundary layer (nozzles)

$$R_h^{**} = \frac{D_*}{D} \left[\frac{A(1+m)}{p^{0.75}} (\Psi_h + b_h) R_* \int_0^x \left(\frac{D_*}{D} \right)^{0.75} dx \right]^{0.8},$$

$$X = x/D^*, \quad R_* = 4G/\pi g u_0 D_* \quad (3.10)$$

Here G is the gas flow rate, D_* is the diameter of the critical section of the nozzle, and x is the coordinate along the generatrix of the profile. Substituting (3.9) or (3.10) in (1.6) we find S_0 . Using expression (1.4) we determine S_h . The erosion of carbon is finally found as $j_w = b_1 \rho_0 u_0 S_h$.

B. Case of chemical erosion of carbon surface accompanied by injection of gas due to thermal decomposition of surface. Depending on the composition of the substance the transverse gas flow may vary [7-11]. Some coatings can release up to 70% or more (by weight) of gases. This can greatly reduce the heat transfer and ultimately the burnup of the coke base. In this case we assume

$$q_s = q_{s1} + q_{s2} \quad (3.11)$$

Here q_{s1} is the heat spent on heating the coke residue, q_{s2} is the heat spent on heating the released gases to the wall temperature (for convenience we can include here the heat of transformation h_Σ spent on evaporation of water released due to the decomposition of resins, the further decomposition of resins, the further decomposition of heavy hydrocarbons, and so on).

Thus,

$$q_{s2} = j_{w2} [h_{w'2} + h_\Sigma - h']$$

Then, in view of (3.1) and (3.11) the heat energy balance at the heat-transfer surface AB can be written as (Fig. 2)

$$q_w = j_{w1} h_\Sigma^0 + j_{w2} [h_{w'2} + h_\Sigma - h'] + q_{s1}$$

where h' is the heat content of the gas at the temperature of onset of destruction of the coating material. After similar transformations (see

case A) the heat content of the wall becomes

$$h_w = h_0 + b_1' h_\Sigma^0 + b_1'' [h_{w'2} + h_\Sigma - h'] + \frac{q_{s1}}{q_w} (h_w - h_0) \quad (3.12)$$

Here the wall permeability parameter b_1 depends only on the chemical erosion and is calculated from formula (3.6); the wall permeability parameter b_1'' depends on the injection of gases due to thermal decomposition.

The over-all wall permeability parameter is

$$b_1 = b_1' + b_1''$$

We also determine the heat content h_w of the wall by the method of successive approximations. In the first approximation we neglect the last two terms of Eq. (3.12).

We solve the problem of unsteady heat conduction with a moving outer boundary at temperature T_w' and we find the rate of heating of the material. Knowing the rate of decomposition of the material we determine the amount of injected gas j_{w2} and the flux q_{s1} . Then we finally determine T_w . The rest of the calculation is similar to case A.

The rate of displacement of the outer boundary j_{wy} will depend only on the value of b_1'

$$j_{wy} = b_1' \rho_0 u_0 S_h \quad (3.13)$$

The number S_h is determined with due regard to b_1'' . It is clear from (2.13) that when b_1'' is large the dimensionless heat transfer coefficient will be very small.

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