A simple model of the non-equilibrium dissociation of a gas in Couette and boundary-layer flows

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SUMMARY

At sufficiently high temperature the oxygen and nitrogen molecules in air dissociate into atoms. Energy is required for this decomposition and, furthermore, if the temperature is not uniform, concentration gradients are formed and energy is transferred by the consequent interdiffusion of atoms and molecules. In this paper, a simple model of a gas is formulated to illustrate the effect of these processes on heat transfer in three situations: (1) in a layer of gas at rest between two walls at different temperature, (2) in Couette flow, and (3) in a laminar boundary layer on a flat plate.

In the model, the law for the rate of reaction (dissociation and recombination) is of an especially simple form with the speed of reaction characterized by a single parameter. When the parameter becomes large, the gas approaches chemical equilibrium; at the other extreme, no reaction occurs within the gas.

Two chemical conditions of the walls are considered, one being that the walls are catalytic (the surface reaction rate is assumed sufficiently high to hold the gas at the wall in chemical equilibrium), and the other that the walls have no effect on the reaction, i.e. they are non-catalytic.

The most important of the simplifications made are: (*a*) The reaction rate law is put in a form in which the equilibrium concentration of atoms varies linearly with temperature. Thus, there is only one temperature at which the gas is undissociated instead of the actual range of temperature. (*b*) In problems (1) and (2), μ, k, and ρD are taken to be constant. (*c*) In problem (3) the Lewis number is assumed to be unity. (*d*) Only binary mixtures of atoms and molecules are considered (so that ionization and more complex dissociation processes are not covered). (*e*) Coupling of irreversible flows, such as that causing thermal diffusion, is neglected. (*f*) Only problems in which the pressure is constant are considered.

1. INTRODUCTION

When the temperature of air is raised sufficiently, for instance, by being brought to relative rest in the boundary layer on a body moving at a very high speed, some of the molecules of the constituent gases dissociate into atoms. Energy is 'absorbed' in the dissociation and is transported by the interdiffusing atoms and molecules. Both processes affect the heat transfer through the mixture. This paper describes three instances of heat transfer in a simple model of a dissociating (and recombining) gas. These are: (1) The heat transfer through a layer of the gas at rest between two walls at different temperature. (2) Couette flow. (3) Boundary-layer flow.

Leipmann & Bleviss (1956) and Liepmann & Roshko (1957) have considered the Couette flow of a dissociated gas which is in chemical equilibrium. Their work suggested the present study in which the assumption of equilibrium is dropped but in which other simplifications are introduced.

A paper by Hirschfelder (1957) dealing with heat transfer in a chemically reacting mixture appeared after the present work was essentially complete. There the exact equations governing the heat transfer through a layer of a reacting gas are discussed and an iterative method of solution, applicable when the reaction rates are high, is developed. The similarity between the character of these solutions and those of the present model, when a reaction rate parameter is large, are pointed out below.
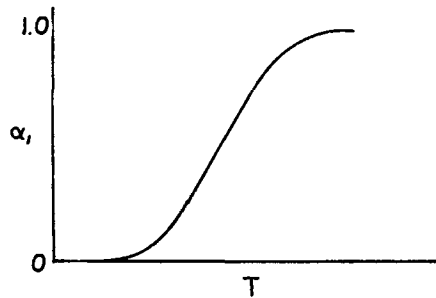

Figure 1. Equilibrium dependence of atom concentration on temperature.

To see how the heat transfer process is modified by the dissociation of the fluid, consider the forward and reverse reactions $O_2 \leftrightarrows 2O$ taking place in a closed vessel. These reactions establish an equilibrium composition that is a function of pressure and temperature. Thus, if the gas is heated slowly and uniformly at constant pressure, the mass fraction, α_1, of atoms varies as shown in figure 1 (see, for example, Lighthill (1957)).

As the atoms appear, the curve of enthalpy *vs* temperature becomes steeper; this is a consequence of the energy required to decompose the molecule.

On the other hand, if the gas is not heated uniformly, spacewise variations in composition as well as in temperature appear. The temperature gradients establish heat fluxes and the concentration gradients give rise to mass flows and diffusion. The diffusing components transport their enthalpy with them, and this transport constitutes an energy flow that may be large compared with that caused by the thermal gradients.

In general then, dissociation (and recombination) directly alters heat transfer processes: firstly by creating 'sources' and 'sinks' of energy, and secondly by providing, through diffusion currents, another energy transport mechanism.

There are, of course, other indirect (but important) consequences, such as the change in viscosity, specific heats, gas constant, and so forth. Let us consider again a gas in an enclosure. Suppose the temperature is suddenly and uniformly increased, then the rate of production of atoms exceeds the rate of disappearance and the mixture approaches the new equilibrium at a finite rate which depends upon the pressure, the temperature, and the concentration of atoms. Now notice that a gas can be kept permanently out of equilibrium by diffusion, even when it is stationary and the heat transfer processes are steady. It is, therefore, of interest and it is one purpose of this paper to study how departure from equilibrium affects the heat transfer mechanism in a dissociating gas.

In this paper only the dissociation of a single diatomic gas into a binary mixture of atoms and molecules is treated. The ionization and dissociation of more complex gases and mixtures of gases is not considered.

In § 2 the equations governing the flow of a reacting gas are given. The simplifications leading to the model gas are discussed in § 3 and its behaviour in the three situations described above is presented in the final sections.

2. GENERAL EQUATIONS

2.1. *Conservation equations*

The equations governing the flow of a mixture of interdiffusing and chemically reacting gases are derived in Hirschfelder, Curtiss & Bird (1954). Before these equations can be stated, however, it is necessary to define the several velocities that arise in such a flow.

Consider a mixture of gases moving relative to some fixed coordinate system. A small plane, perpendicular to the flow of constituent i, and moving so that, on the average, no molecules of i cross it, moves with the velocity of i, γ_i. The mass flow of i per unit area relative to the fixed coordinate system is $n_i m_i \gamma_i$, where n is the number of moles per unit volume and m is the molecular weight. The total mass flow per unit area is $\sum n_i m_i \gamma_i$. Thus, with the mass density ρ given by $\rho = \sum n_i m_i$, the mass average velocity $\mathbf{V}$ is defined by $\mathbf{V} = (1/\rho) \sum n_i m_i \gamma_i$. Finally, the diffusion velocity of the ith component, $\mathbf{V}_i$, is the velocity of that component relative to the mass average velocity; thus $\mathbf{V}_i = \gamma_i - \mathbf{V}$.

H 2

In the following, the conservation equations, taken from Hirschfelder *et al.* (1954), are stated first for a mixture composed of an arbitrary number of components and then for a mixture containing but two. In the problems treated later, these two components will be the atoms and molecules of a dissociated diatomic gas.

Only very simplified forms of these equations are needed in the first two problems treated in this paper. Nevertheless, we give the complete equations here in order to describe more clearly the physical processes involved and because they are needed in the boundary layer problem of § 6.

Conservation of mass

The equation for the conservation of mass of each species can be written

$$\partial n_i / \partial t + \nabla . n_i (\mathbf{V} + \mathbf{V}_i) = K_i, \tag{1}$$

where K_i is the mole rate of production of the ith component per unit volume by chemical reaction.

Note first that the multiplication of this equation by m_i, the summation of the resulting equation over all i, and use of the overall mass conservation condition $\sum m_i K_i = 0$, lead to the usual continuity equation

$$\partial \rho / \partial t + \nabla . (\rho \mathbf{V}) = 0. \tag{2}$$

The variables $\mathbf{V}_i$ and K_i in equation (1) are determined by the thermodynamic properties and their gradients. Consider first the diffusion velocity. In general, diffusion may be caused by gradients in the pressure and temperature as well as in concentration. In many important situations the last-named cause is dominant, and it is the only one considered in the following discussion, i.e. cross-coupling of the fluxes is neglected. If, in addition to this restriction, the mixture consists of only two components, then (see Hirschfelder *et al.* (1954, p. 516))

$$\mathbf{V}_i = - (D/\alpha_i) \nabla \alpha_i, \qquad i = 1, 2, \tag{3}$$

where D is the binary diffusion coefficient and α_i the mass fraction of the ith component defined by

$$\alpha_i = \frac{n_i m_i}{n_1 m_1 + n_2 m_2} = \frac{\rho_i}{\rho}.$$

We turn next to the variable K_i, the net rate of production of species i by chemical reaction. Such a reaction is described by an equation of the form

$$\beta_1 J_1 + \beta_2 J_2 + \dots \rightleftharpoons \nu_1 J_1 + \nu_2 J_2 + \dots .$$
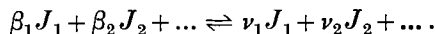
J_i denotes the ith chemical component, and β and ν the stoichiometric coefficients of reactants and products, respectively. The net rate of reaction, r, can be put in the form (see Hirschfelder *et al.* 1954, p. 748)

$$r = K_f(T) n_1^{\beta_1} n_2^{\beta_2} \dots - K_r(T) n_1^{\nu_1} n_2^{\nu_2} \dots,$$

in which K_f and K_r are the rate constants for the forward and reverse reaction. Then

$$K_i = (\nu_i - \beta_i) r.$$

Also, introducing the mole fraction, $X_i = n_i/n$ and with $n = p/(RT)$, we may write

$$r = K_f(T)\left(\frac{p}{RT}\right)^{\Sigma\beta_i} X_1^{\beta_1} X_2^{\beta_2} \ldots - K_r(T)\left(\frac{p}{RT}\right)^{\Sigma\nu_i} X_1^{\nu_1} X_2^{\nu_2} \ldots .$$

As a specific example of a reaction rate law, consider that for the decomposition of oxygen $O_2 \rightleftharpoons 2O$. Hirschfelder (1957) states that in this reaction the net rate of production of atoms, K_1, is given by

$$K_1 = -n^3 K_r[X_1^2 - \{(1 - X_1)/p\}\exp(1 \cdot 58 - 60\,000/T)],$$

where

$$K_r = 1 \cdot 2 \times 10^{16}(T/300)^{5/2} \text{ cm}^6/\text{mole}^2 \text{ sec,}$$

and p is pressure in atmospheres, T the absolute temperature in degrees Kelvin, and X_1 denotes the mole fraction of atoms.

It should be noted that the equation formed by setting K_i equal to zero yields the equilibrium composition of the mixture as a function of the pressure and temperature.

The expression for the reaction rate K_i and the above equation for the diffusion velocity $\mathbf{V}_i$ may now be put in equation (1) to form the mass conservation expression for the ith component. When we have two components we need, in addition to the overall continuity equation (2), a conservation equation for only one of the two, for α_1 say,

$$\rho(\partial\alpha_1/\partial t + \mathbf{V}.\nabla\alpha_1) - \nabla.(\rho D \nabla\alpha_1) = m_1 K_1. \tag{4}$$

This equation comes, with some algebraic manipulation, from equation (1) with the use of equations (2) and (3). The appropriate expressions for K_1 will be inserted later.

Conservation of momentum

In terms of the mass average velocity, $\mathbf{V}$, with components u_α, the equations of motion are the usual ones* :

$$\rho\frac{Du_\alpha}{Dt} = -\frac{\partial p}{\partial x_\alpha} - \frac{2}{3}\frac{\partial}{\partial x_\alpha}\left(\mu\frac{\partial u_\beta}{\partial x_\beta}\right) + \frac{\partial}{\partial x_\beta}\left[\mu\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)\right], \tag{5}$$

in which μ is the viscosity of the mixture and

$$D/Dt = \partial/\partial t + u_\alpha \partial/\partial x_\alpha.$$

Conservation of energy

The energy equation is

$$\rho\frac{Dh}{Dt} - \frac{Dp}{Dt} = \nabla.(k\nabla T - \sum_i \rho_i h_i \mathbf{V}_i) + \Phi, \tag{6}$$

in which Φ is the dissipation function, given by

$$\Phi = \mu\left(\frac{\partial u_\alpha}{\partial x_\beta}\right)\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right) - \frac{2}{3}\mu\left(\frac{\partial u_\alpha}{\partial x_\alpha}\right)^2,$$

* The equation given by Penner (1955) and derived by von Kármán contains additional stress terms arising from diffusion. In general, these would be small compared to the usual stress terms and need not, especially in view of the later approximations, be included here.

and h is the enthalpy per unit mass of mixture. The energy carried by diffusion is $\sum \rho_i h_i \mathbf{V}_i$, in which h_i is the enthalpy per unit mass of component i. The symbol k denotes the thermal conductivity of the mixture with the components treated as non-reacting gases.

2.2. *Thermodynamic properties of the mixture*

The equation of state of a mixture of perfect gases is

$$p = \rho\left(\sum_i R_i \alpha_i\right)T,$$

which for a binary mixture becomes

$$p = \rho\,\frac{R}{m_2}\left[1 + \left(\frac{m_2}{m_1} - 1\right)\alpha_1\right]T.$$

R_i is the gas constant for the ith component.

The enthalpy per unit mass of mixture is given by $h = \sum \alpha_i h_i$, in which

$$h_i = \int_0^T (C_p)_i\,dT + h_i^0,$$

where h_i^0 is the enthalpy of formation extrapolated to absolute zero and C_p the specific heat at constant pressure.

2.3. *Boundary conditions*

The boundary conditions that are to be applied to the temperature and mass average velocity are the usual ones and require no special discussion. They will be stated later for each problem. However, the conditions to be satisfied by the concentrations at solid boundaries may not be equally familiar. They are discussed briefly here.

If the wall has a catalytic effect on a reaction, then there may be a net rate of production of the species involved, *per unit area* of the wall. In steady flow, this production of each species must be balanced by the flux normal to, and at, the wall. In the following, two simple extremes are considered: (1) the wall is not catalytic, and (2) the wall reaction rate is such as to hold the concentrations there in chemical equilibrium at the wall temperature.

When the wall is non-catalytic, the flux of each component normal to the wall must vanish at the wall. Hence, if, as in the problems considered in this paper, the gradients are normal to the wall (or in the boundary-layer case are assumed to be), then

$$n_i m_i \mathbf{V}_i|_{\text{wall}} = -\rho D \nabla \alpha_i|_{\text{wall}} = 0.$$

3. Idealized gas and simplified equations

In this section we state the properties of a simplified model of a gas that approximates, at least qualitatively, the behaviour of the mixture of atoms and molecules formed when a gas, such as oxygen, is subjected to a temperature gradient at temperatures high enough to cause dissociation.

First, the two components are assumed to be perfect gases with constant specific heats. Hence

$$h_1 = (C_p)_1\,T + h_1^0, \qquad h_2 = (C_p)_2\,T + h_2^0,$$

where h^0 is the enthalpy of formation and the subscripts 1 and 2 denote atoms and molecules, respectively. Then

$$h = \alpha_1 h_1 + \alpha_2 h_2$$

or, since $\alpha_1 + \alpha_2 = 1$,

$$h = (C_p)_2\,T + \alpha_1[(C_p)_1 - (C_p)_2]T + \Delta h^0 \alpha_1,$$

where $\Delta h^0 = h_1^0 - h_2^0$. That is, Δh^0 is the enthalpy of dissociation at absolute zero and h_2^0 is taken to be zero. Now $\{(C_p)_1 - (C_p)_2\}/(C_p)_2$ is small; it is of the order of 10^{-1} for oxygen. Further, $[(C_p)_1 - (C_p)_2]T$ is small compared with Δh^0 for temperatures not greatly exceeding those for complete dissociation. Hence, we neglect the second term in comparison with the first and third and drop the subscript on C_p to obtain

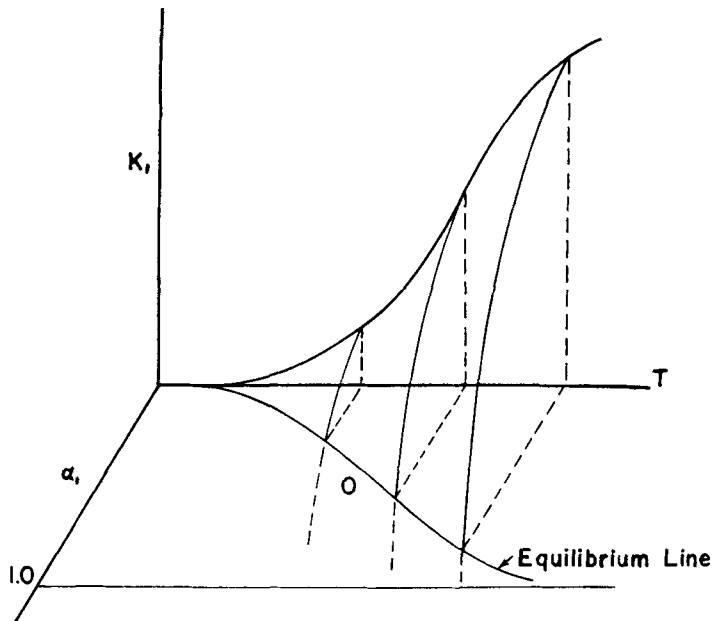$$h = C_p\,T + \Delta h^0 \alpha_1.$$

Figure 2. Reaction rate law.

Consider next the reaction rate law, an example of which was given in §2. When a single gas dissociates or recombines and the pressure is constant, then the net rate of formation of atoms, K_1, is a function of the temperature and the weight fraction of atoms, i.e. $K_1 = K_1(T, \alpha_1)$. The shape of this function depends, of course, on the particular reaction but in general is as sketched in figure 2.

The approximation to the reaction rate law that is to be used in this paper consists of the first-order terms in a Taylor series expansion of K_1 about a point O on the equilibrium line

$$K_1 = \left(\frac{\partial K_1}{\partial T}\right)_0 (T - T_0) + \left(\frac{\partial K_1}{\partial \alpha_1}\right)_0 (\alpha_1 - \alpha_{10}). \tag{7}$$

(In the boundary layer problems, §6, this approximation is slightly modified.) This planar approximation for the surface $K_1 = K_1(T, \alpha_1)$ cannot, of course, be accurate over the entire range of the variables. It requires, for instance, a linear variation of the equilibrium concentration of atoms with temperature, a result that is obviously incorrect near $\alpha_1 = 0$ and $\alpha_1 = 1\cdot0$, and which, of course, makes no sense when the temperature is either below that at which dissociation begins or exceeds that for complete dissociation. Furthermore, in the case of oxygen, while it is true that the equilibrium concentration of atoms is approximately linear with temperature for α_1 not near zero or unity, the slope, $\partial K_1/\partial \alpha_1$, of the surface varies greatly along the equilibrium line. A rate law of the form in equation (7) does, nevertheless, describe qualitatively the dissociation (and recombination) at a finite rate of a gas in a range of temperature between the onset and completion of dissociation.

The stationary gas and the Couette flow problems are further idealized by the assumption that k, μ and ρD are constants.

The conservation equations for a gas with the above properties can then be summarized as follows. The overall continuity equation is unchanged; it is
$$\partial\rho/\partial t + \nabla \cdot (\rho \mathbf{V}) = 0.$$
Equation (4), the conservation equation for the atoms, becomes
$$\rho[\partial\alpha_1/\partial t + \mathbf{V} \cdot \nabla\alpha_1] - \rho D\nabla^2\alpha_1 = b_1\alpha_1 + b_2 T + b_3.$$
The right-hand side, the rate of production of atoms, is temporarily written in the general linear form shown. A non-dimensional temperature will be introduced and the constants prescribed for each particular problem.

When μ is constant the equation of motion is
$$\rho(\partial\mathbf{V}/\partial t + \mathbf{V} \cdot \nabla\mathbf{V}) = -\nabla p + \mu\nabla^2\mathbf{V} + \tfrac{1}{3}\mu\nabla(\nabla \cdot \mathbf{V}). \tag{8}$$
In the energy equation (6), the term $\sum \rho_i h_i \mathbf{V}_i$ can be simplified to
$$\sum_i \rho_i h_i \mathbf{V}_i = -h_1\rho D\nabla\alpha_1 - h_2\rho D\nabla\alpha_2$$
$$= -(h_1 - h_2)\rho D\nabla\alpha_1$$
$$= -\Delta h^0\rho D\nabla\alpha_1,$$
when the term $[(C_p)_1 - (C_p)_2]T$ is neglected. Hence
$$\rho\frac{Dh}{Dt} - \frac{Dp}{Dt} = k\nabla^2 T + \Delta h^0\rho D\nabla^2\alpha_1 + \Phi. \tag{9}$$

4. Gas at rest between two walls

4.1. *Effect of reaction rate*

Before studying the behaviour of the gas described in the preceding section in Couette flow, it is instructive to examine its heat transfer

characteristics in the absence of motion. Consider, then, the case in which the gas is confined between two infinite walls, a distance s apart, at constant temperatures T_s and T_w.

In this situation, the atom conservation equation (4) becomes

$$-\rho D \, d^2\alpha_1/dy^2 = m_1 K_1 = b_1 \alpha_1 + b_2 T + b_3,$$

where y is the coordinate normal to the walls. The energy equation (9) reduces to

$$k \, d^2T/dy^2 + \Delta h^0 \rho D \, d^2\alpha_1/dy^2 = 0.$$

The overall continuity equation and the equations of motion are satisfied by $\mathbf{V} = 0$ and $p = $ constant.

Now write $m_1 K_1$ in the form

$$m_1 K_1 = g(\alpha_{1n} \theta - \alpha_1),$$

where

$$\theta = \frac{T - T_w}{T_s - T_w}$$

and g and α_{1n} are constants. Thus we assume that in chemical equilibrium the mixture would be composed completely of molecules at the temperature of the cold surface, $y = 0$, and that at the temperature of the hot boundary, $y = s$, the ratio of the density of atoms to the density of the mixture would be α_{1n}. The rate of the reaction is characterized by the magnitude of g.

To put the equations in non-dimensional form, let

$$\eta = y/s, \qquad \alpha = \alpha_1/\alpha_{1n}, \qquad G = (gs^2)/(\rho D),$$

$$H = \frac{\rho D \Delta h^0 \alpha_{1n}}{k(T_s - T_w)} = \frac{Le \, \Delta h^0 \alpha_{1n}}{C_p(T_s - T_w)},$$

in which Le is the Lewis number, $\rho D C_p/k$. The dimensionless temperature θ is defined above.

In these terms we have

$$d^2\alpha/d\eta^2 - G(\alpha - \theta) = 0, \tag{10}$$

$$d^2\theta/d\eta^2 + H \, d^2\alpha/d\eta^2 = 0. \tag{11}$$

The first of these equations is a statement of the balance between the atom production in a layer of the gas and the net diffusion out of the layer. The constitution of the parameter G reflects the fact that it is the ratio of the reaction rate to the diffusion rate that determines the degree of departure from chemical equilibrium.

In equation (11), H is a measure of the energy carried by mass diffusion relative to that carried by thermal conduction. The energy transport by diffusion comes about from the dissociation of molecules in the neighbourhood of the hot wall, the diffusion of the resulting atoms towards the cool wall, and their subsequent recombination.

When the walls are not catalytic the boundary conditions on α are

$$\left. \frac{\partial \alpha}{\partial \eta} \right|_{\eta = 0} = \left. \frac{\partial \alpha}{\partial \eta} \right|_{\eta = 1} = 0.$$

From the definition of θ, $\theta(0) = 0$ and $\theta(1) = 1$.

Solutions to equations (10) and (11) satisfying these boundary conditions and for various values of the reaction rate parameter G are given in figure 3. The unbroken line is the atom concentration, and the broken one the temperature profile. Only half the channel is shown in this figure since the solutions are antisymmetric about the centreline. The parameter H has been set equal to 9, an arbitrary value large enough to show plainly the effect of dissociation.
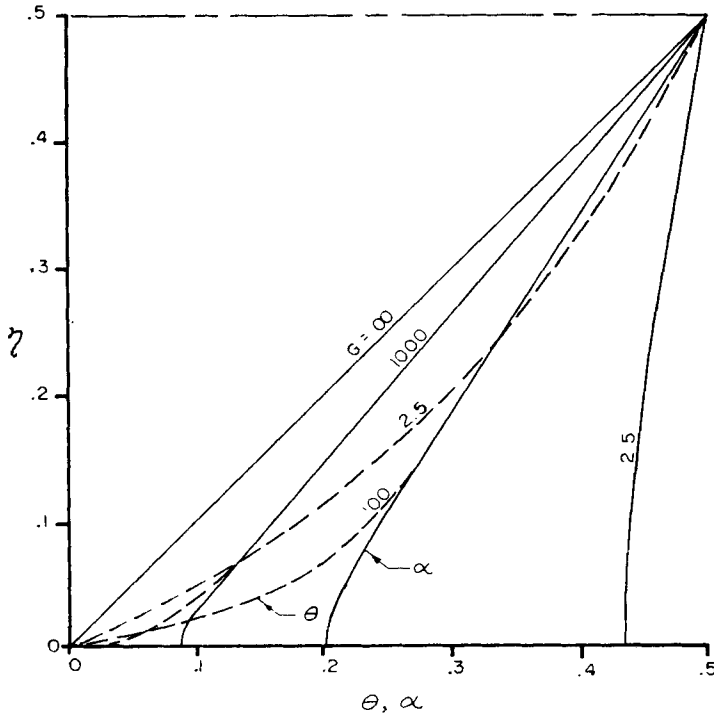

Figure 3. Temperature and atom concentration profiles for non-catalytic walls, $H = 9$. Effect of reaction rate parameter G. Temperature θ given by broken lines, atom concentration α by unbroken lines.

It can be seen from figure 3 that with increasing G a region in which α is almost exactly equal to θ, i.e. a region of chemical equilibrium, spreads from the centre of the channel toward the walls until finally at large G non-equilibrium conditions exist only in thin layers next to the walls. Hirschfelder (1957) observes that these thin regions of large change in temperature and concentration gradients constitute boundary layers. The reason for their existence can be clearly seen in the present simple analysis, since the energy transported by thermal conduction and by diffusion outside the boundary layers must, when the wall is non-catalytic, be transferred to the wall solely by conduction. Thus, the need for a greatly increased temperature gradient at the wall is evident.

In general, boundary layers will appear in the solution whenever the reaction rate is high and the boundary conditions are incompatible with chemical equilibrium.

As $G \to \infty$ the fluid approaches equilibrium throughout the channel. The non-dimensional temperature gradient, $d\theta/d\eta$, approaches unity except at the walls where the limiting value is $(1+H)$. When $G \to 0$ the energy carried by diffusion vanishes (since $d\alpha/d\eta \to 0$) and $d\theta/d\eta \to 1$ everywhere. The concentration of atoms becomes constant across the channel at a value in equilibrium with the average temperature, i.e. $\alpha = 0.5$.

Figure 4 shows the effect of G on the non-dimensional heat transfer, q_w^*, defined by

$$q_w^* = \frac{q_w s}{k(T_s - T_w)},$$

where q_w is the heat flow to the wall $y = 0$ per unit area per unit time. This quantity, equal to $d\theta/d\eta$ at the walls (when, as in this example, the walls are not catalytic), ranges from unity when $G = 0$ to $(1+H)$ as $G \to \infty$.
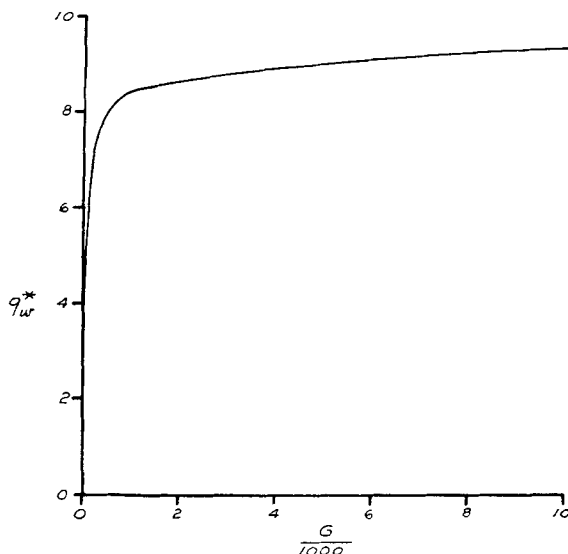

Figure 4. Dependence of heat transfer on reaction rate, no flow, non-catalytic walls.

Now to illustrate the influence of a surface catalytic reaction, let the reaction rate on both walls be such that the mixture there is held in chemical equilibrium. Then the boundary conditions are

$$\alpha(0) = 0, \qquad \alpha(1) = 1,$$
$$\theta(0) = 0, \qquad \theta(1) = 1,$$

and the solution is $\theta = \alpha = \eta$, regardless of the reaction rate. The non-dimensional heat transfer is $(1+H)$, the value at the limit $G = \infty$ in the preceding case. Note that there is a gradient in concentration at the wall and hence a flux of energy by diffusion to the wall.

Notice, also, that chemical equilibrium exists even for zero reaction rate, a result which follows, of course, from the particular boundary conditions that were assumed and from the linear reaction rate law.

4.2. *Chemical equilibrium*

This section on the heat transfer through a dissociating gas will be concluded by consideration of the simplifications which arise when the gas is assumed, at the outset, to be in chemical equilibrium. In this discussion the simplifications introduced in § 3 are not needed.

Consider then the energy equation which comes directly from equations (3) and (6) for a two-component reacting mixture of gases between walls at different temperature

$$\frac{d}{dy}\left[k\frac{dT}{dy} + h_1\rho D\frac{d\alpha_1}{dy} + h_2\rho D\frac{d\alpha_2}{dy}\right] = 0.$$

Integrating once and remembering that $(\alpha_1 + \alpha_2) = 1$, we have

$$k\frac{dT}{dy} + (h_1 - h_2)\rho D\frac{d\alpha_1}{dy} = \text{const.} = q_w.$$

Now in equilibrium, $\alpha_1 = \alpha_1(T,p)$. Then, since the pressure is constant, the above equation can be written

$$k\left[1 + (h_1 - h_2)\frac{\rho D}{k}\frac{d\alpha_1}{dT}\right]\frac{dT}{dy} = q_w,$$

in which the expression in brackets is fixed by the temperature. Thus the expression

$$k\left[1 + (h_1 - h_2)\frac{\rho D}{k}\frac{d\alpha_1}{dT}\right]$$

may be considered to be an effective thermal conductivity, k_{ef}. Hirschfelder (1957) also notes the possibility of such a definition and remarks that the expression is a generalization of the Eucken correction to the coefficient of heat conduction for polyatomic molecules*.

Again regarding the mixture as a single gas, we define the effective specific heat by

$$(C_p)_{ef} = \left(\frac{\partial h}{\partial T}\right)_p = \frac{\partial}{\partial T}(\alpha_1 h_1 + \alpha_2 h_2)$$

$$= (h_1 - h_2)\frac{\partial\alpha_1}{\partial T} + \alpha_1\frac{\partial h_1}{\partial T} + \alpha_2\frac{\partial h_2}{\partial T}.$$

Then since

$$h_i = \int_0^T (C_p)_i\, dT + \Delta h_i^0,$$

$$(C_p)_{ef} = (h_1 - h_2)\frac{\partial\alpha_1}{\partial T} + \overline{C_p},$$

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* H. W. Leipmann also made use of this concept in a series of lectures at the Douglas Aircraft Company, California, in February and March 1955.

where $\overline{C}_p$, equal to $[\alpha_1(C_p)_1 + \alpha_2(C_p)_2]$, is the average specific heat of the mixture when the components are considered to be inert. Now notice that if the viscosity is assumed unchanged by the reaction, then an effective Prandtl number can be defined by

$$(Pr)_{\text{ef}} = \frac{(C_p)_{\text{ef}}\mu}{k_{\text{ef}}} = \frac{\overline{C}_p\mu\left[1 + \dfrac{(h_1-h_2)}{\overline{C}_p}\dfrac{d\alpha_1}{dT}\right]}{k\left[1 + (h_1-h_2)\dfrac{\rho D}{k}\dfrac{d\alpha_1}{dT}\right]}$$

$$= Pr\,\frac{\left[1 + \dfrac{(h_1-h_2)}{\overline{C}_p}\dfrac{d\alpha_1}{dT}\right]}{\left[1 + \dfrac{(h_1-h_2)Le}{\overline{C}_p}\dfrac{d\alpha_1}{dT}\right]},$$

where the Lewis number is $\rho D\overline{C}_p/k$. Hence, when the Lewis number is unity (Lees (1956) estimates that for air $Le = 1\cdot45$), the effective Prandtl number of the dissociating gas is the same as that for an inert mixture of the same composition.

Kuo (1957) introduces a constant effective Prandtl number into his study of the dissociation of air in the boundary layer. It appears, however, that in the transformations of the energy equation which give rise to the parameter, the thermal conductivity itself is interpreted as an effective conductivity. Thus a direct comparison with the variable $(Pr)_{\text{ef}}$ above is difficult.

5. Couette flow

5.1. *Walls at equal temperature*

We turn now to Couette flow, the steady flow between two plane walls. One wall is stationary and the other is in uniform motion in its own plane. The equations describing such a flow become, for the simplified gas,

$$\rho D\,d^2\alpha_1/dy^2 - g(\alpha_1 - \alpha_{1n}\phi) = 0,$$

$$\mu\,d^2u/dy^2 = 0,$$

$$k\,d^2T/dy^2 + \rho D\Delta h^0\,d^2\alpha_1/dy^2 + \mu(du/dy)^2 = 0,$$

where ϕ is a non-dimensional temperature defined below.

Let us restrict our attention first to flows between equal temperature walls and let

$$\eta = \frac{y}{s}, \qquad u^* = \frac{u}{u_s}, \qquad \phi = \frac{T-T_w}{T_w}, \qquad \alpha = \frac{\alpha_1}{\alpha_{1n}},$$

$$U^2 = \frac{u_s^2\,Pr}{C_p\,T_w}, \qquad G = \frac{gs^2}{\rho D}, \qquad H = \frac{\rho D\Delta h^0\alpha_{1n}}{kT_w} = \frac{Le\,\Delta h^0\alpha_{1n}}{C_p\,T_w},$$

where u_s is the velocity of the moving wall, T_w is the wall temperature, s the distance between the walls and Le is, as before, the Lewis number. The reaction rate law has again been put in a form which implies that there would be no atoms in an equilibrium mixture at the wall temperature.

Thus, we have

$$d^2\alpha/d\eta^2 - G(\alpha - \phi) = 0, \tag{12}$$

$$d^2u^*/d\eta^2 = 0, \tag{13}$$

$$d^2\phi/d\eta^2 + H\,d^2\alpha/d\eta^2 + U^2(du^*/d\eta)^2 = 0. \tag{14}$$

The solution to equation (13) satisfying the boundary conditions is

$$u^* = \eta,$$

and the dissipation term in (14) becomes a uniformly distributed heat source of strength U^2. Hence, for a fixed value of U, the energy flux through the walls is independent of G and H and simply equal to the energy
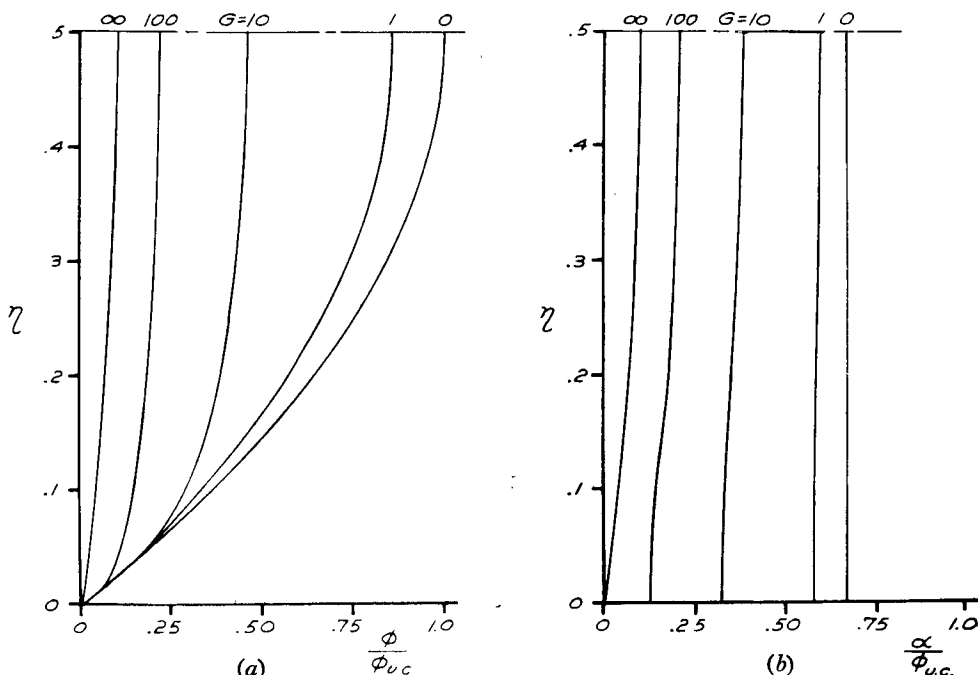

Figure 5. Couette flow, non-catalytic walls at equal temperature, $H = 9$. Effect of reaction rate parameter G. (a) Temperature profile. (b) Atom concentration profile.

flowing from the source. The effect of the diffusion will then be to reduce the temperature gradient (and hence the temperature) required to transfer the energy to the walls.

The boundary conditions are

$$\phi(0) = \phi(1) = 0$$

and, when the walls are not catalytic,

$$\left.\frac{d\alpha}{d\eta}\right|_{\eta=0} = \left.\frac{d\alpha}{d\eta}\right|_{\eta=1} = 0.$$

Solutions to equations (12) and (14) satisfying these conditions with $(1 + H) = 10$, $U = 1$, and for various values of G, are shown in figure 5.

In this figure and in the following, $\phi_{u.c.}$ denotes the non-dimensional temperature at the centre of the channel when the gas does not dissociate; its value is $\frac{1}{8}$. The solutions in this case are symmetrical about the channel centreline, and again only half the channel is shown.

Since $d\alpha/d\eta = 0$ on the walls and the energy flow from the distributed source is given, the temperature gradient on the walls is independent of G. As G increases, again, as in the preceding section, the fluid approaches chemical equilibrium except in the neighbourhood of the walls.

On the other hand, when $G \to 0$ the temperature distribution becomes that for an undissociated gas while α assumes the equilibrium value for the average temperature.
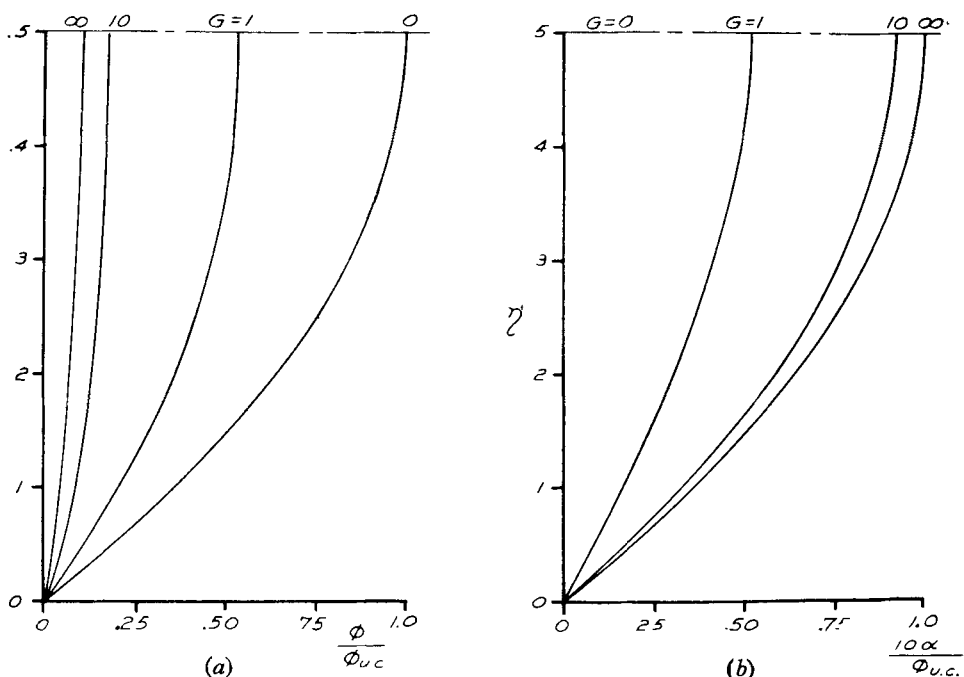

Figure 6. Couette flow, catalytic walls at equal temperature, $H = 9$. Effect of reaction rate parameter G. (*a*) Temperature profile. (*b*) Atom concentration profile.

As in the simple heat transfer analysis, the effect of catalytic reaction at the walls will be illustrated by solutions with $\alpha(0) = \alpha(1) = 0$. Figures 6 (*a*) and 6 (*b*) summarize these solutions. As expected, a large value of G brings the gas to equilibrium. (Note that the α scale in figure 6 (*b*) has been changed.) But now as $G \to 0$ all the atoms disappear while the temperature again becomes that of an undissociated gas. The surface reaction is essentially a sink for the atoms.

The above calculations have dealt with the effects of variation in the net rate of dissociation and recombination. Another important property of the mixture is the diffusion coefficient. This coefficient, D, appears in H

as well as in G. Therefore, a change in G alone should be visualized as a variation in the reaction rate or channel width, not of D. We may vary D alone by holding the product GH constant while we vary H. When there is no diffusion ($H = 0$) and the walls are non-catalytic, the temperature is unaffected by dissociation (see figure 7) even though the mixture is in chemical equilibrium: all the energy is flowing by thermal conduction. As $D \to \infty$ ($H \to \infty$) the atom concentration becomes uniform, as one would expect.
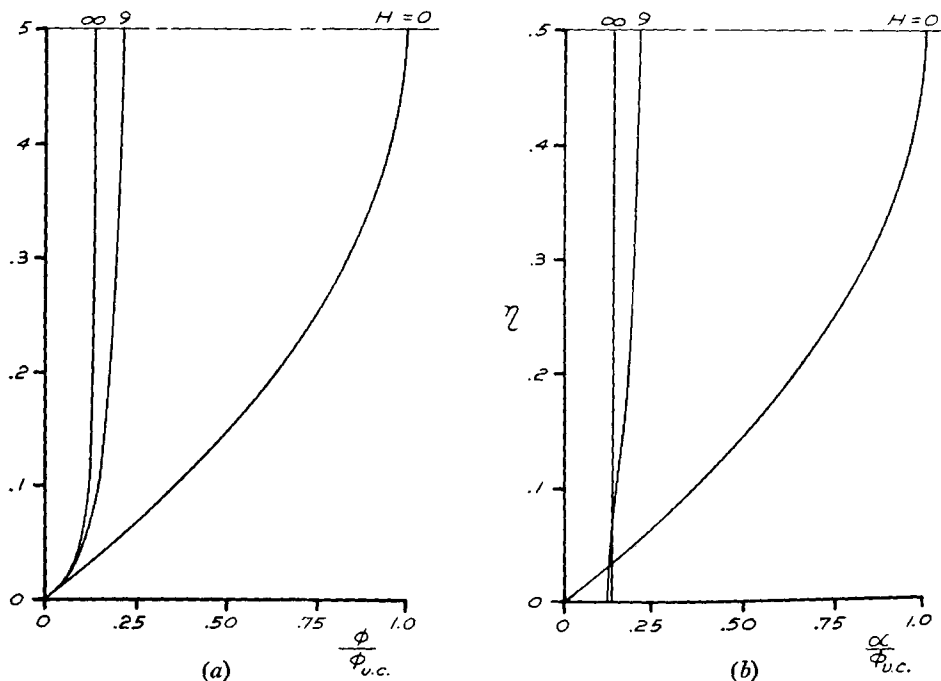

Figure 7.   Couette flow, non-catalytic walls at equal temperature, $GH = 900$.   Effect of diffusion coefficient.   (*a*) Temperature profile.   (*b*) Atom concentration profile.

5.2. *Comparison with the boundary layer*

All the examples just discussed were ones in which the walls were held at equal temperatures. We consider next boundary conditions that are more suggestive of boundary-layer flows. The upper plate, $\eta = 1$, is visualized as the edge of the boundary layer and the lower as the wall. For instance, the conditions

$$\phi(1) = 0, \qquad \alpha(1) = 0,$$

$$\left. \frac{d\phi}{d\eta} \right|_{\eta=0} = 0, \qquad \left. \frac{d\alpha}{d\eta} \right|_{\eta=0} = 0,$$

would correspond to the flow of an undissociated, cool gas past an insulated, non-catalytic wall.

The solution in this case is already contained in figure 6 if the centre-line there, $\eta = 0.5$, is taken to be the insulated wall and the station $\eta = 0$ viewed as the 'free stream'. The fall in the wall 'recovery temperature' as G increases is shown by the values at $\eta = 0.5$. It should be remembered, however, that the reason for the reduction in this case is the enhanced conduction from the fluid of the dissipated energy. In the boundary layer there is an additional effect. The temperature is generally reduced throughout the layer because a large amount of the kinetic energy entering the layer is absorbed in dissociating the new fluid continually entering.

Another case of interest is the flow of a dissociated gas past a cool wall. The corresponding Couette boundary conditions are

$$\theta(1) = 1, \qquad \theta(0) = 0,$$

$$\alpha(1) = 1, \qquad \alpha(0) = 0 \quad \text{or} \quad \frac{d\alpha}{d\eta}\bigg|_{\eta=0} = 0,$$

where we have redefined U^2 and H by

$$U^2 = \frac{u_s^2 \, Pr}{C_p(T_s - T_w)}, \qquad H = \frac{Le \, \Delta h^0 \alpha_{1n}}{C_p(T_s - T_w)},$$

and now

$$\theta = \frac{T - T_w}{T_s - T_w},$$

where T_s is the temperature at $y = s$. Equations (12), (13) and (14) are unaffected by this change.

The non-dimensional heat transfer to the cool wall, the quantity of greatest interest here, is defined by

$$q_w^* = \frac{q_w \, s}{k(T_s - T_w)}$$

and is equal to $d\theta/d\eta$ at $\eta = 0$ when the wall is not catalytic. An approximate expression for this quantity, valid when $\exp\{G(1+H)\}^{1/2} \gg 1$, is

$$\frac{d\theta}{d\eta}\bigg|_{\eta=0} = \frac{1}{1 + H\{G(1+H)\}^{-1/2}} \left[1 + H + \frac{U^2}{2} + \frac{U^2 H}{G(1+H)} \right].$$

The heat transfer increases with G and

$$\lim_{G \to \infty} q_w^* = 1 + H + \tfrac{1}{2}U^2.$$

When the cool wall is catalytic, $\alpha(0) = 0$, and the non-dimensional energy flux to the wall by thermal and diffusive transport is

$$(d\theta/d\eta + H \, d\alpha/d\eta)_{\eta=0},$$

a quantity equal to $1 + H + \tfrac{1}{2}U^2$ whatever the value of G.

If the gas is assumed to be in equilibrium initially, then $\alpha = \theta$, and equation (14) (with ϕ replaced by θ) yields

$$\theta + H\theta = -\tfrac{1}{2}U^2\eta^2 + C_1\eta + C_2.$$

The conditions $\theta(0) = 0$, $\theta(1) = 1$ require

$$C_2 = 0, \qquad C_1 = 1 + H + \tfrac{1}{2}U^2,$$

and thus

$$q_w^* = (1+H) \left. \frac{d\theta}{d\eta} \right|_{\eta = 0} = 1 + H + \tfrac{1}{2} U^2.$$

5.3. *A mechanical analogy*

A mechanical analogy, helpful in visualizing the form of the solutions discussed in this and in the preceding section, can be developed as follows.

Consider two strings, one weightless and under tension H, the other weighing U^2 per unit length and under unit tension. Denote the weightless string displacement by α and the other by θ. Let the strings be connected by a distributed spring, an elastic sheet, with spring constant per unit width equal to GH.

The force balance on the α string requires

$$H \, d^2\alpha/d\eta^2 = -GH(\theta - \alpha),$$

and the θ displacement satisfies

$$d^2\theta/d\eta^2 = -U^2 + GH(\theta - \alpha).$$

A rearrangement yields the Couette flow equations and setting $U^2 = 0$ yields the simple heat transfer case.
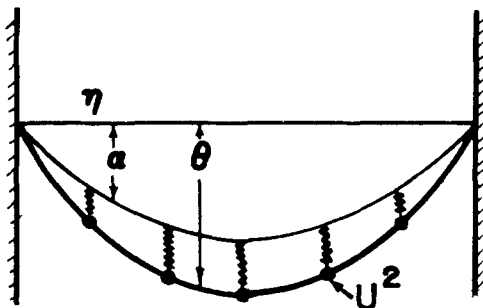
Figure 8. Mechanical analogy.

In the sketch (figure 8) the boundary conditions are those for catalytic walls at equal temperature. We can enforce the non-catalytic condition, $(d\alpha/d\eta)_{\text{wall}} = 0$, by connecting the α string to frictionless sliders on the wall. The vertical component of the force applied to a wall by the strings are $d\theta/d\eta$ and $H \, d\alpha/d\eta$. Thus, these forces are analogous to the energy flowing into the wall by thermal conduction and diffusion, respectively. A variation in the reaction rate constant g corresponds to a change in the spring constant GH with all other parameters (including H) fixed.

6. LAMINAR BOUNDARY LAYER

6.1. *Solution of the energy equation*

In this final section we discuss the flow of a gas past a flat plate in circumstances in which dissociation and/or recombination may occur

within the boundary layer. Three recent papers have dealt with the heat transfer in laminar boundary-layer flows of a dissociated gas. Lees (1956) studied two limiting cases of heat transfer to blunt-nosed bodies at hypersonic speeds, the case of chemical equilibrium, and that of no recombination except possibly at the surface within the boundary layer. Fay & Riddell (1956) obtained affine solutions in the neighbourhood of the stagnation point for those limiting cases and for a finite recombination rate. Kuo (1957) studied the laminar boundary layer of a gas in chemical equilibrium on a flat plate.

We again consider the gas to consist of two components, atoms and molecules. The usual boundary-layer approximations* to equations (2), (4), (5) and (6) in §2 are:

$$\frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial y}(\rho v) = 0,$$ (15)

$$\rho\left(u\frac{\partial \alpha_1}{\partial x} + v\frac{\partial \alpha_1}{\partial y}\right) - \frac{\partial}{\partial y}\left(\rho D\frac{\partial \alpha_1}{\partial y}\right) = m_1 K_1,$$ (16)

$$\rho\left(u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y}\right) = \frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right),$$ (17)

$$\rho\left(u\frac{\partial h}{\partial x} + v\frac{\partial h}{\partial y}\right) = \frac{\partial}{\partial y}\left[k\frac{\partial T}{\partial y} + (h_1 - h_2)\rho D\frac{\partial \alpha_1}{\partial y}\right] + \mu\left(\frac{\partial u}{\partial y}\right)^2.$$ (18)

Here the pressure has been assumed constant, which is, however, a poor approximation near the leading edge of a flat plate at velocities high enough to dissociate air. The equations might be better associated with the flow past a surface shaped to minimize the pressure variation, a wind-tunnel wall, say. In the analysis which follows immediately below, the simplifications introduced in §3 are not necessary, and they will be first introduced in §6.2.

Lees (1956) has shown that the energy equation takes a much simpler form when the Lewis number is unity. To see this, note that

$$h = \alpha_1 h_1 + \alpha_2 h_2$$

with

$$h_i = \int_0^T (C_p)_i\, dT + h_i^0.$$

Then

$$\frac{\partial h}{\partial y} = \overline{C_p}\frac{\partial T}{\partial y} + (h_1 - h_2)\frac{\partial \alpha_1}{\partial y},$$

where $\overline{C_p} = \alpha_1(C_p)_1 + \alpha_2(C_p)_2$. Thus, the first term on the right-hand side

---

* Reaction rates may in many cases be high enough to confine the region of departure from chemical equilibrium to the neighbourhood of the plate leading edge. The use of boundary layer equations to calculate the non-equilibrium flow under these conditions would, of course, be incorrect.

of equation (18) can be written

$$\frac{\partial}{\partial y}\left[\frac{k}{\overline{C_p}}\frac{\partial h}{\partial y} + (h_1 - h_2)\frac{k}{\overline{C_p}}(Le-1)\frac{\partial \alpha_1}{\partial y}\right],$$

where, now, $Le = \rho D\overline{C_p}/k$. Hence, when $Le = 1$, the term

$$\frac{\partial}{\partial y}\left(\frac{k}{\overline{C_p}}\frac{\partial h}{\partial y}\right)$$

contains the energy flux due to diffusion as well as the usual heat flow caused by the thermal gradient. Now the energy equation can be written

$$\rho\left(u\frac{\partial h}{\partial x} + v\frac{\partial h}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{k}{\overline{C_p}}\frac{\partial h}{\partial y}\right) + \mu\left(\frac{\partial u}{\partial y}\right)^2. \tag{19}$$

If we have boundary conditions on h or conditions on T and α_1 that determine the boundary conditions on h, then this equation together with (15) and (17) may be solved by the procedure of Chapman & Rubesin (1949). This solution is obtained without reference to equation (16) and, hence, does not require knowledge of the reaction rate. The individual distributions of temperature and atom concentration, however, would not be known. Interesting flows in which the enthalpy boundary conditions are known at the wall are flow past an insulated and non-catalytic plate, for which

$$\frac{\partial h}{\partial y} = \overline{C_p}\frac{\partial T}{\partial y} + (h_1 - h_2)\frac{\partial \alpha_1}{\partial y} = 0, \qquad \text{on} \quad y = 0;$$

and flow past a wall at known temperature on which a catalytic reaction maintains chemical equilibrium, for which

$$h(x, 0) = \alpha_1(T_w)h_1(T_w) + \alpha_2(T_w)h_2(T_w),$$

in which the α's depend only on temperature since the pressure is constant.

We assume that the properties at the edge of the boundary layer are known and are independent of x. Again this is not a realistic assumption for the flow immediately following a strong leading-edge shock. The Chapman & Rubesin procedure then follows. First introduce the stream function defined by

$$\rho u = \rho_\infty \partial \psi/\partial y, \qquad \rho v = -\rho_\infty \partial \psi/\partial x.$$

Then in x, ψ coordinates the momentum equation becomes

$$\frac{\partial u}{\partial x} = \frac{1}{\rho_\infty}\frac{\partial}{\partial \psi}\left(\mu\frac{\rho}{\rho_\infty}u\frac{\partial u}{\partial \psi}\right).$$

Next we assume $\mu\rho = C\mu_\infty\rho_\infty$, with C a constant, then

$$\frac{\partial u}{\partial x} = \frac{C\mu_\infty}{\rho_\infty}\frac{\partial}{\partial \psi}\left(u\frac{\partial u}{\partial \psi}\right).$$

Lees (1956) and Kuo (1957) justify this approximation for air in chemical equilibrium at high enthalpy levels. Here, where equilibrium does not necessarily exist, the approximation, even if less accurate, has little influence on the nature of the following qualitative results. The energy equation (19)

becomes, when the Prandtl number $\overline{C}_p \mu/k$ is constant,

$$\frac{\partial h}{\partial x} = \frac{\mu_\infty C}{\rho_\infty Pr} \frac{\partial}{\partial \psi} \left(u \frac{\partial h}{\partial \psi} \right) + \frac{C\mu_\infty}{\rho_\infty} u \left(\frac{\partial u}{\partial \psi} \right)^2 .$$

Let

$$u^* = \frac{u}{u_\infty} , \qquad h^* = \frac{h - h_\infty}{h_\infty} , \qquad \mu^* = \frac{\mu}{\mu_\infty} ,$$

$$x^* = \frac{x}{L} , \qquad \rho^* = \frac{\rho}{\rho_\infty} , \qquad \psi^* = \frac{\psi}{[(\mu_\infty/\rho_\infty)u_\infty LC]^{1/2}} ,$$

where L is a reference length and the subscript ∞ denotes free stream conditions. Then we have

$$\frac{\partial u^*}{\partial x^*} = \frac{\partial}{\partial \psi^*} \left(u^* \frac{\partial u^*}{\partial \psi^*} \right) \tag{20}$$

and

$$\frac{\partial h^*}{\partial x^*} = \frac{1}{Pr} \frac{\partial}{\partial \psi^*} \left(u^* \frac{\partial h^*}{\partial \psi^*} \right) + \frac{u_\infty^2}{h_\infty} u^* \left(\frac{\partial u^*}{\partial \psi^*} \right)^2 . \tag{21}$$

The solution of (20) is

$$u^* = \tfrac{1}{2} f'(\eta),$$

where η is defined by $f(\eta) = \psi^*/\sqrt{x^*}$ and f is the Blasius function satisfying

$$ff'' + f''' = 0,$$

$$f'(\infty) = 2, \qquad f'(0) = f(0) = 0.$$

Since u^* is a function only of η, it is convenient to write the energy equation in x^*, η coordinates

$$\frac{\partial^2 h^*}{\partial \eta^2} + Pr f \frac{\partial h^*}{\partial \eta} - 2Pr f' x^* \frac{\partial h^*}{\partial x^*} = -\tfrac{1}{4} Pr \frac{u_\infty^2}{h_\infty} (f'')^2.$$

Chapman & Rubesin find, by separation of variables, a solution of this equation (in their analysis, T is the dependent variable) for a wall temperature that varies with x. The solution will, of course, be applicable here when the wall enthalpy is a given function of x.

When the wall is non-catalytic and insulated, the boundary conditions are $h^*(x^*, \infty) = 0$ and $\partial h^*(x^*, 0)/\partial \eta = 0$. These conditions are satisfied by a solution that depends only on η. This particular solution, denoted by $N(\eta)$, satisfies

$$N'' + Pr f N' = -\tfrac{1}{4} Pr (u_\infty^2/h_\infty)(f'')^2,$$

$$N'(0) = 0, \qquad N(\infty) = 0, \tag{22}$$

from which we get

$$N = \tfrac{1}{2} (u_\infty^2/h_\infty) \sigma(\eta),$$

where

$$\sigma(\eta) = \tfrac{1}{2} Pr \int_\eta^\infty [f''(\xi)]^{Pr} \int_0^\xi [f''(v)]^{2-Pr} \, dv \, d\xi.$$

The function $\sigma(\eta)$ for $Pr = 0{\cdot}72$ is given by Chapman & Rubesin (1949, figure 4).

If the free stream is undissociated and the gas in the boundary layer assumed to be in chemical equilibrium, then the above solution becomes essentially that obtained by Kuo for this case.

6.2. *The temperature and concentration profiles*

As remarked earlier the above solution yields no information about the temperature and concentration profiles when the reaction rate is finite. The qualitative behaviour of these variables can be obtained if we introduce approximations of the kind discussed in § 3. Again let $h = C_p T + \Delta h^0 \alpha_1$, and assume that

$$m_1 K_1 = (\rho/\rho_\infty) g(\alpha_{1n} T^* - \alpha_1),$$

where $T^* = (T - T_\infty)/T_\infty$. Thus we are assuming that there are no atoms in the free stream and that any increase in temperature above the free stream value causes dissociation. The factor ρ/ρ_∞ is introduced into the reaction rate law for convenience; when it is present the energy and concentration equations are linear in the x^*, η coordinates defined above.

With these expressions for h and $m_1 K_1$ and with the help of equation (16), the energy equation becomes, in the x^*, η coordinates,

$$\frac{\partial^2 T^*}{\partial \eta^2} + Prf\frac{\partial T^*}{\partial \eta} - 2Prf'x^*\frac{\partial T^*}{\partial x^*} = -\frac{Pr u_\infty^2}{4C_p T_\infty}(f'')^2 + $$
$$+ \frac{4Pr L\Delta h^0 g(\alpha_{1n} T^* - \alpha_1)x^*}{\rho_\infty u_\infty C_p T_\infty},$$

and the concentration equation is

$$\frac{\partial^2 \alpha_1}{\partial \eta^2} + Scf\frac{\partial \alpha_1}{\partial \eta} - 2Scf'x^*\frac{\partial \alpha_1}{\partial x^*} = -\frac{4Sc L g(\alpha_{1n} T^* - \alpha_1)x^*}{\rho_\infty u_\infty},$$

where $Sc = \mu/\rho D$ is the Schmidt number. We see from these equations that the significant x variable for changes in T^* and α_1 is

$$\frac{x^* Lg}{\rho_\infty u_\infty} = \frac{xg}{\rho_\infty u_\infty}.$$

Calling this quantity x^0 and letting $\alpha = \alpha_1/\alpha_{1n}$, we get

$$\frac{\partial^2 T^*}{\partial \eta^2} + Prf\frac{\partial T^*}{\partial \eta} - 2Prf'x^0\frac{\partial T^*}{\partial x^0}$$
$$= -\frac{Pr u_\infty^2}{4C_p T_\infty}(f'')^2 + \frac{4Pr \Delta h^0 \alpha_{1n} x^0(T^* - \alpha)}{C_p T_\infty}, \quad (23)$$

$$\frac{\partial^2 \alpha}{\partial \eta^2} + Scf\frac{\partial \alpha}{\partial \eta} - 2Scf'x^0\frac{\partial \alpha}{\partial x^0} = -4Sc x^0(T^* - \alpha). \quad (24)$$

Now, following Marble and Adamson (1954)* we could write

$$T^*(x^0, \eta) = T_{\mathrm{I}}^*(\eta) + T_{\mathrm{II}}^*(\eta)x^0 + T_{\mathrm{III}}^*(\eta)x^{0^2} + ...,$$

$$\alpha(x^0, \eta) = \alpha_{\mathrm{I}}(\eta) + \alpha_{\mathrm{II}}(\eta)x^0 + \alpha_{\mathrm{III}}(\eta)x^{0^2} + ...$$

* Equations similar to (23) and (24) arise in a flame propagation problem treated by these authors. Howarth (1938) formulated a series solution of the form shown for an incompressible boundary layer problem.

If these series are substituted in equations (23) and (24) and like powers of x^0 are equated, we get

$$T_I^{*\prime\prime} + Pr f\, T_I^{*\prime} = -\frac{Pr\, u_\infty^2}{4 C_p\, T_\infty}\,(f'')^2$$

...

$$T_n^{*\prime\prime} + Pr f T_n^{*\prime} - 2n\, Pr f'\, T_n^* = \frac{4 Pr\, \Delta h^0 \alpha_{1n}}{C_p\, T_\infty}\,(T_{n-1}^* - \alpha_{n-1}),$$

and

$$\alpha_I'' + Sc f \alpha_I' = 0$$

...

$$\alpha_n'' + Sc f \alpha_n' - 2n\, Sc f' \alpha_n = -4 Sc(T_{n-1}^* - \alpha_{n-1}).$$

Thus, the coefficients could be determined term by term when the boundary conditions depend only on η. Numerical or machine solutions of the successive equations for T_n^* and α_n would be required, however, and in view of the approximation to the reaction rate, are not justified.

We note, however, that for the case of an undissociated gas flowing past an insulated and non-catalytic plate, i.e. when the boundary conditions are

$$T^*(x^0, \infty) = 0, \qquad \frac{\partial T^*(x^0, 0)}{\partial \eta} = 0,$$

$$\alpha(x^0, \infty) = 0, \qquad \frac{\partial \alpha(x^0, 0)}{\partial \eta} = 0,$$

then the leading terms are those that would be obtained for an undissociated gas; α_I is zero and T_I^* is the usual temperature distribution in a perfect gas on an insulated plate. A heuristic argument, given below, suggests that far downstream the temperature profile returns to this shape (but with a lower absolute magnitude). We may expect from this that the change in the temperature profile shape is relatively small and that the use of similar profiles in integrals of the energy and concentration equations would yield approximate equations for the change in magnitude of the temperature and concentration with x.

To see why the temperature may be expected to have the same shape far downstream as at the start, recall that in Couette flow an increase in the channel width increased the reaction rate constant and brought the gas closer to chemical equilibrium. Likewise, here the concentration gradients across the boundary layer which tend to keep the gas out of equilibrium become weaker as the thickness increases. Therefore, since gradients along streamlines also decrease with x, it is reasonable to expect that the gas approaches chemical equilibrium as x increases. We can easily find the temperature and atom concentration at equilibrium if we assume that the Lewis number is unity. First, we have the solution for h^* in this case;

it is the function $N(\eta)$ obtained earlier. Then, since we are assuming that $h = C_p T + \Delta h^0 a_{1n} \alpha$ and (the equilibrium condition) $\alpha = T^*$, we have

$$h^* = \frac{h}{h_\infty} - 1 = \left(1 + \frac{\Delta h^0 \alpha_{1n}}{C_p T_\infty}\right) T^*.$$

Therefore, in equilibrium,

$$T^* = N(\eta) \Big/ \left(1 + \frac{\Delta h^0 \alpha_{1n}}{C_p T_\infty}\right).$$

Now observing that N and T_1^* satisfy the same equation and boundary conditions, we see that the temperature profile has, in equilibrium, the same shape as it has at the leading edge but, of course, is reduced in magnitude. Thus, if, as the above considerations suggest, the gas approaches equilibrium in the boundary layer as it moves downstream, we can describe approximately the approach to equilibrium by setting

$$T^* = N(\eta)\Omega(x^0), \qquad \alpha = N(\eta)\Delta(x^0),$$

in integrals of the energy and diffusion equations (23) and (24) to determine Ω and Δ.

We have then

$$\Omega \int_0^\infty N'' \, d\eta + Pr\,\Omega \int_0^\infty fN' \, d\eta - 2Pr\,x^0\Omega' \int_0^\infty f'N \, d\eta$$

$$= -\frac{Pr\,u_\infty^2}{4C_p T_\infty} \int_0^\infty (f'')^2 \, d\eta + \frac{4Pr\,\Delta h^0 \alpha_{1n} x^0}{C_p T_\infty} (\Omega - \Delta) \int_0^\infty N \, d\eta,$$

and

$$\Delta \int_0^\infty N'' \, d\eta + Sc\,\Delta \int_0^\infty fN' \, d\eta - 2Sc\,x^0\Delta' \int_0^\infty f'N \, d\eta$$

$$= -4Sc\,x^0(\Omega - \Delta) \int_0^\infty N \, d\eta.$$

Let

$$I_1 = \frac{u_\infty^2}{4C_p T_\infty} \int_0^\infty (f'')^2 \, d\eta,$$

and note that since

$$\int_0^\infty N'' \, d\eta = 0$$

equation (22) shows that

$$I_1 = -\int_0^\infty fN' \, d\eta.$$

Further

$$\int_0^\infty fN' \, d\eta = -\int_0^\infty f'N \, d\eta = -I_1.$$

Then, if we let

$$I_2 = 4\int_0^\infty N \, d\eta,$$

we have finally

$$\Omega + 2x^0\Omega' = 1 - \frac{\Delta h^0 \alpha_{1n} I_2}{C_p T_\infty I_1} x^0(\Omega - \Delta) \tag{25}$$

and

$$\Delta + 2x^0 \Delta' = \frac{I_2}{I_1} x^0 (\Omega - \Delta). \tag{26}$$

Eliminating Ω and setting

$$\delta = 2\left(1 + \frac{\Delta h^0 \alpha_{1n}}{C_p T_\infty}\right)\Delta,$$

$$z = \frac{1}{2}\left(1 + \frac{\Delta h^0 \alpha_{1n}}{C_p T_\infty}\right)\frac{I_2}{I_1} x^0,$$

we get

$$z^2 \delta'' + z(1+z)\delta' + \tfrac{1}{2}(z - \tfrac{1}{2})\delta = z, \tag{27}$$

where the derivatives are taken with respect to z. The initial conditions are $\Omega(0) = 1$ and $\Delta(0) = 0$. (It is interesting that any other conditions at $x^0 = 0$ in equations (25) and (26) result in infinite derivatives in Ω and Δ there.) The condition on Ω can be replaced by a second condition on Δ as follows. Differentiation of equation (26) yields

$$\Delta' + 2x^0 \Delta'' + 2\Delta' = (I_2/I_1)[x^0(\Omega' - \Delta') + \Omega - \Delta],$$

from which we get, by the provisional assumption that derivatives at $x^0 = 0$ are finite,

$$\Delta'(0) = \frac{d\Delta}{dx^0}(0) = \frac{1}{3}\frac{I_2}{I_1}.$$

In terms of δ then, the initial conditions are

$$\delta(0) = 0, \qquad \frac{d\delta(0)}{dz} = \delta'(0) = \frac{4}{3}.$$

Solutions to the homogeneous equation corresponding to (27) may be found in Kamke (1948, p. 451). They are $z^{-1/2}$ and $z^{-1/2}e^{-z}$. From these, a particular solution to equation (27) satisfying the required boundary conditions may be found by a formal application of standard methods. The solution is

$$\delta = 2 - z^{-1/2}e^{-z}\int_0^z t^{-1/2}e^t \, dt. \tag{28}$$

An expansion of this expression about $z = 0$, or, better, a series solution of the original differential equation, yields

$$\delta = \sum_{n=0}^{\infty} a_n z^{n+1},$$

with $\alpha_0 = 4/3$ and

$$\alpha_n = -\frac{a_{n-1}}{n + \frac{3}{2}}, \qquad n = 1, 2, \dots.$$

In figure 9, the solid curve extending from $z = 0$ to $z = 4$ is a plot of the first few terms of this series.

The behaviour of the solution at large z also may be determined either from an examination of the integral in equation (28) or from a series

formulation.   Erdélyi (1956, p. 69), states that the integral

$$\int_b^z e^t t^{-\nu} \, dt$$

behaves like

$$e^z \sum_{m=0}^{\infty} (\nu)_m z^{-\nu-m}, \qquad \text{as } z \to \infty,$$

where $(\nu)_0 = 1$, $(\nu)_r = \nu(\nu+1)...(\nu+r-1)$, $r = 1, 2, ...$.
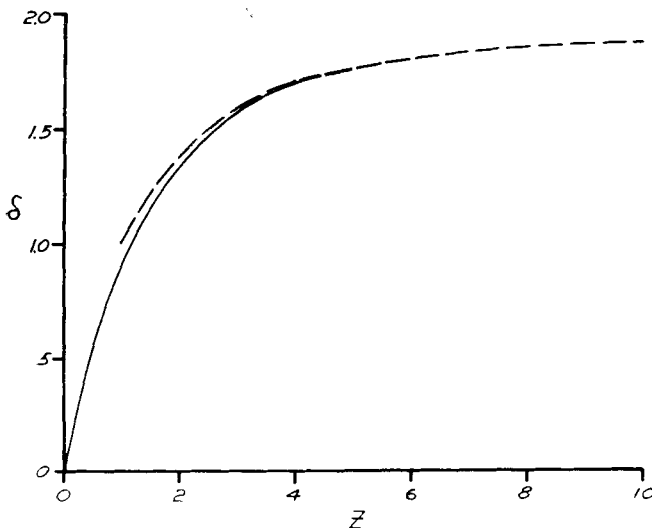

Figure 9. Atom concentration level as a function of distance along the plate.

The use of this asymptotic expansion in the expression for δ in equation (28), or the substitution of a series in inverse powers of z directly into the differential equation yields

$$\delta = \sum_{n=0}^{\infty} b_n z^{-n},$$

where $b_0 = 2$ and

$$b_{n+1} = (n - \tfrac{1}{2}) b_n, \qquad n = 0, 1, 2, ...$$

Thus, as z approaches infinity, δ approaches 2, and since

$$\Delta = \tfrac{1}{2}\delta\left(1 + \frac{\Delta h^0 \alpha_{1n}}{C_p T_\infty}\right)^{-1},$$

we have

$$\lim_{z \to \infty} \Delta = \left(1 + \frac{\Delta h^0 \alpha_{1n}}{C_p T_\infty}\right)^{-1}.$$

Equation (26) shows that Ω approaches this same value.   Remembering that

$$T^* = N(\eta)\Omega(x^0), \qquad \alpha = N(\eta)\Delta(x^0),$$

we see that the fluid approaches a state in which $T^* = \alpha$, i.e. chemical equilibrium.

The above series is divergent. The values of δ shown in the dashed curve in figure 9 were computed by retaining, at each value of z, the term up to but not including the smallest. (See Jeffreys & Jeffreys (1950) for a discussion of this procedure.)

The concentration of atoms, then, rises from zero to

$$N(\eta)\left(1 + \frac{\Delta h^0 \alpha_{1n}}{C_p T_\infty}\right)^{-1}$$

while the non-dimensional temperature falls from $N(\eta)$ to this same quantity.

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