Energy transfer through a dissociated diatomic gas in Couette flow

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SUMMARY

The transfer of energy through a dissociated diatomic gas in Couette flow is considered, taking oxygen as a numerical example. The two extremes of chemical equilibrium flow and chemically frozen flow are dealt with in detail, and it is shown that the surface reaction rate is of prime importance in the latter case. The chemical rate equations in the gas phase are used to estimate the probable chemical state of the gas mixture, this being deduced from the ratio of a characteristic chemical reaction time to a characteristic time for atom diffusion across the layer. The influence of the surface reaction appears to spread outwards through the flow from the wall as gas-phase chemical reaction times decrease. For practical values of the surface reaction rate on a metallic wall, the energy transfer rate may be significantly lower in chemically frozen flow than in chemical equilibrium flow under otherwise similar circumstances.

Similar phenomena to those discussed will arise in the more complicated case of boundary layer flows, so that a treatment of the simpler type of shear layer represented by Couette flow may be of some value in assessing the relative importance of the various parameters.

1. INTRODUCTION

There is at present much interest in the flow of gases at temperatures much greater than those which can be withstood by all known solids and, consequently, it is of some importance to know the rate at which heat will be transferred from the gas to the walls of its container, or those of some body passing through it. In heating the gas to such high temperatures it is highly probable that its polyatomic components will dissociate and absorb a large amount of energy in the process. The dissociation energy then exists as a potential source of heat energy, which may be released following a suitable chemical reaction. The usual heat transfer problem is therefore complicated by the need to consider the rates at which such chemical reactions may occur. In this connection it is necessary to consider both homogeneous reactions (those which occur in the gas phase) and heterogeneous reactions, namely those which occur at a solid surface adjacent to the gas.

The general problem is therefore one of some complexity although practical solutions have been found in some cases. The most comprehensive of these to date is the work of Fay & Riddell (1958), who confine their attention to the forward stagnation region of blunt-nosed bodies. Fay & Riddell's solution represents a more exact analysis of the boundary-layer equations, following along the lines of Lees' (1956) largely heuristic discussion of the same problem. Both references take explicit account of the difference in the rate of transfer of heat energy by thermal conduction and the rate of transfer of dissociation energy, the transport medium in the latter case being simple mass diffusion of atoms. It has been assumed in both cases that air behaves as a single diatomic gas. Previous solutions of the dissociation problem have been given by Moore (1952), Crown (1952) and Beckwith (1953). The first reference deals with the flat plate problem whilst the second two deal with forward stagnation regions, but all assume that the gas is in chemical equilibrium and imply that thermal energy and mass diffuse at identical rates (more strictly, they assume equality of the appropriate diffusion coefficients).

The complexity of the problem is increased in all of these works by the need to consider the boundary layer on a flat plate or at a stagnation point, giving rise to the familiar non-linear differential equations of boundary layer theory. However, much that is characteristic of the boundary layer is reproduced in the simpler viscous flow known as Couette flow. The lack of variation of properties in the direction of flow then creates notable simplifications, a fact which has been exploited by Illingworth (1950) for the case of a fluid of constant chemical composition. Under this restriction, Illingworth's work represents the only solution of the full Navier–Stokes equations valid for all Reynolds and Mach numbers. More recently Liepmann & Bleviss (1956) have used Couette flow to exhibit some of the properties of a shear layer of dissociated gas. Their treatment implies equality of mass and thermal energy diffusion coefficients, however, and only considers flow at chemical equilibrium, but it extends the gas temperatures into the range for which ionization becomes appreciable.

In the following sections we consider the question of energy transfer through a simple dissociated diatomic gas in Couette flow (using some values appropriate to oxygen for numerical illustrations). The energy equation is readily integrated, yielding a relation between enthalpy, atom concentration, and velocity. A simplification of the treatment is achieved following the assumption that the gas behaves as an ideal dissociating gas, a concept introduced by Lighthill (1956). Real gases such as oxygen and nitrogen appear to be very nearly ideal in this sense in a temperature range sufficient to cover problems of practical interest and a simple expression for enthalpy in terms of temperature and concentration results. From here on the problem resolves itself into the determination of atom concentration in terms of either temperature or velocity in any particular set of circumstances. Once this is achieved, the skin friction coefficient and Stanton, or Nusselt, number follows directly from integration of the momentum equations.

In order to determine the atom concentration it is necessary to consider the kinetics of the dissociation and recombination reactions. While not difficult in principle, the treatment results in an unwieldy non-linear differential equation which would require numerical integration. Results are given below for two extreme cases, namely very fast and very slow homogeneous reaction rates, the full rate equations being used only to give an estimate of the conditions under which such assumptions may plausibly be made. The heterogeneous, surface reaction is considered in both cases and is shown to have a controlling influence on energy transfer rate when gas-phase reactions occur very slowly.

It may be permissible to interpolate here some brief remarks on the mechanisms involved in the energy transfer process. All three of the transport phenomena are explicitly concerned in the process, the basic mechanism in the gas phase being thermal conduction. Thermal energy is the sum of the energies contained in the translational, rotational, and vibrational modes of the gas molecules, so that its rate of transport must be a function of the facility with which these energies can be interchanged. When such interchange occurs so rapidly that it is reasonable to assume that each internal mode is in equilibrium at the local temperature, the classical Eucken correction is derived which modifies the monatomic thermal conductivity value to account for the extra degrees of freedom of polyatomic molecules. At the temperatures which we shall consider here, the Eucken correction is probably accurate enough, but, in any case, it will be found that thermal conductivity can be absorbed into certain dimensionless numbers which may reasonably be assumed constant across the gas layer. Energy transfer also arises from the dissipation of ordered kinetic energy of mass motion into random thermal energy due to viscous actions in the gas. The final rate of heat recovery by these means is affected by the ratio of the vorticity and heat energy diffusion coefficients, in other words, the Prandtl number.

When the gas consists of a mixture of molecules and their dissociated atoms a further potential source of heat energy exists. Each atom in the mixture can be visualized as a vehicle for the transport of dissociation energy as it diffuses through the gas layer, the energy being released in the form of heat as a result of a recombination reaction. The rate of heat recovery in this case will be found to be a function of the ratio of the mass diffusion coefficient and the thermal energy diffusion coefficient (the Lewis number) in exact analogy with the viscous dissipation phenomenon. Furthermore, this heat recovery rate depends on the appropriate chemical reaction rates and it will also depend on whether the dissociation energy is released in the gas phase or directly at the solid surface.

2. THE CONSERVATION EQUATIONS

The mass conservation equation for the ith species of a general mixture of reacting gases can be expressed in the form

$$\text{div}[n_i(\mathbf{q}+\mathbf{q}_i)] = \omega_i, \qquad (1)$$

where n_i is the number density of species i and $\mathbf{q}_i$ is its diffusion velocity vector. $\mathbf{q}$ is the mass average velocity vector and ω_i is the 'source' term which results from production of species i due to chemical reactions, the units of ω_i being number of species i produced per unit volume per unit time. If m_i is the mass of a particle of the ith species, the general mass conservation requirement is $\sum m_i \omega_i = 0$. Since $\sum m_i n_i \mathbf{q}_i = 0$ as a result of the definition of diffusion velocity, multiplication of equation (1) by m_i followed by summation over all i leads to

$$\operatorname{div} \rho \mathbf{q} = 0, \tag{2}$$

where $\rho = \sum m_i n_i$, the mixture density. Equation (2) is the usual form of the continuity relation.

The momentum balance is unchanged when chemical reactions occur and is written as

$$\rho(\mathbf{q} \cdot \operatorname{grad})\mathbf{q} + \operatorname{div} \mathbf{p} = 0, \tag{3}$$

where $\mathbf{p}$ is the pressure tensor (see, e.g. Hirschfelder *et al.* 1954, eqns. (7.2–23) *et seq.* for definition).

The energy equation can be derived by considering a particular elemental mass of gas moving with the mass average velocity. In a steady flow this gains internal energy E at a rate $\rho \mathbf{q} \cdot \operatorname{grad} E$ units of energy per unit volume per unit time due to convection. E is the internal energy of the gas mixture per unit mass and is equal to $\rho^{-1} \sum m_i n_i e_i$, where e_i is the internal energy of a particle of the ith species above some arbitrarily determined zero level. For example, for a binary mixture of symmetrical diatomic molecules and their dissociated atoms we can take the internal energy of a molecule, e_m, as zero at the absolute zero of temperature. Then the internal energy of each atom, e_a, at the same temperature will be one-half of the energy required to dissociate the molecule at this temperature. The elemental mass under consideration will also gain kinetic energy of mass motion by convection, but this is accounted for by the action of the stresses exerted by the fluid on the element. In addition these stresses do an amount of work $-p \operatorname{div} \mathbf{q}$ in compressing the element (p is thermodynamic pressure) and dissipate an amount of mechanical energy Φ which appears in the form of heat. Φ is the familiar dissipation function. Finally, the element gains energy from two other sources, namely from thermal conduction and by diffusion of the separate species across its boundaries. Thermal conduction provides a term $\operatorname{div}(\lambda \operatorname{grad} T)$, where T is temperature and λ is the coefficient of thermal conductivity, whilst diffusion results in a rate of gain of energy per unit volume per unit time equal to $-\operatorname{div}(\sum n_i h_i \mathbf{q}_i)$. h_i is the enthalpy of a particle of species i and appears here in preference to internal energy e_i since each component gas in the mixture must perform flow work on the gas of its own species which is in front of it. It should be noted that the additional kinetic energy of each species which arises from the difference between mass average and diffusion velocities has been neglected here, but this is an assumption which is generally made (e.g. Chapman & Cowling 1939, p. 145). The

contributions from thermal conduction and mass diffusion can be combined in a single quantity $\mathbf{q}_0$, the energy flux vector, defined as

$$\mathbf{q}_0 = -\lambda \operatorname{grad} T + \sum n_i\, h_i\, \mathbf{q}_i, \qquad (4)$$

so that the energy conservation requirement can ultimately be written in the form

$$\rho\mathbf{q}\cdot\operatorname{grad} E = -\operatorname{div}\mathbf{q}_0 - p\operatorname{div}\mathbf{q} + \Phi. \qquad (5)$$

We shall neglect the thermal diffusion contribution to diffusion velocity since this is generally negligible, particularly when we have to deal with large concentration gradients. (A description of thermal diffusion is given by von Kármán (1956).) In that case the diffusion velocity of species i is given by

$$\mathbf{q}_i = \frac{n^2}{\rho n_i} \sum_j m_j\, D_{ij}\operatorname{grad}(n_j/n) \qquad (6)$$

(see, e.g. Hirschfelder *et al.* 1954, eqns. (7.4–3)). The quantity n is the total particle density while n_i and n_j are the particle densities of the ith and jth species. m_j is the mass of a particle of the jth species. D_{ij} is the diffusion coefficient for diffusion of species i through species j, the summation being taken over all species except i. We shall confine attention to binary gas mixtures, in which case (6) reduces to

$$\mathbf{q}_1 = \frac{n^2}{\rho n_1}\, m_2\, \mathscr{D}_{12}\operatorname{grad}(n_2/n), \qquad (7)$$

where $\mathscr{D}_{12}$ is now a binary diffusion coefficient. Some simplification of (7) results from the definition of a mass ratio, c_i, such that

$$\rho c_i = m_i n_i. \qquad (8)$$

Plainly $\sum c_i = 1$ and (7) then reduces to

$$c_1\mathbf{q}_1 = -\mathscr{D}_{12}\operatorname{grad} c_1, \qquad (9)$$

with a similar equation for $\mathbf{q}_2$. (Note $\mathscr{D}_{21} = \mathscr{D}_{12}$.)

The conservation equations can also be written in terms of mass fractions, as can the energy flux vector $\mathbf{q}_0$. We may also use enthalpy per unit mass rather than per particle, but, before making these modifications we will simplify the equations to apply to Couette flow.

3. Couette flow

The variation of all properties in the x-direction is zero in Couette flow (see figure 1 for definitions). In order to satisfy the continuity equation, equation (2), $\rho v = \text{const.}$, v being the mass average velocity normal to the walls. But $v = 0$ at $y = 0$ and at $y = \delta$; whence it must be zero everywhere.

With these simplifications and treating only a binary mixture consisting of symmetrical diatomic molecules with their dissociated atoms, the conservation equations are as follows. Equation (1) gives

$$\frac{d}{dy}(\rho c_a v_a) = \omega_a m_a \qquad (10)$$

for continuity of the atomic species. (We now write suffix a to indicate atom, suffix m for molecule.) v_a is the atom diffusion velocity normal to the walls. The momentum equations (3) give

$$\frac{d}{dy}\left(\mu \frac{du}{dy}\right) = 0 = \frac{dp}{dy}, \tag{11}$$

and the energy equation (5) becomes

$$\frac{d}{dy}\left(\lambda \frac{dT}{dy}\right) - \frac{d}{dy}\left(\rho c_a H_a v_a + \rho c_m H_m v_m\right) + \mu\left(\frac{du}{dy}\right)^2 = 0. \tag{12}$$

H_i is enthalpy of the ith species per unit mass and μ is the dynamic coefficient of viscosity. Making use of equation (9) for the diffusion velocities and the fact that $c_a + c_m = 1$, equation (12) can be rewritten

$$\frac{d}{du}\left(\lambda \frac{dT}{dy}\right) + \frac{d}{dy}\left(\rho \mathscr{D}_{am} D \frac{dc_a}{dy}\right) + \mu\left(\frac{du}{dy}\right)^2 = 0, \tag{13}$$
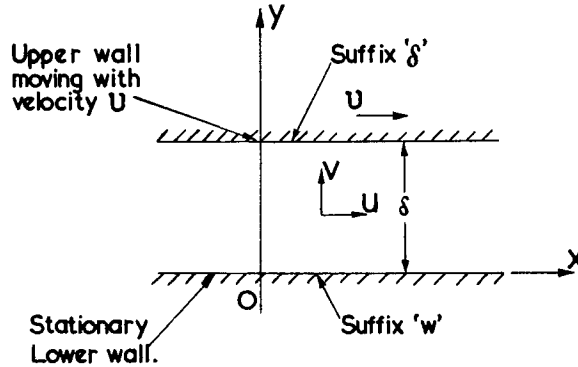
Figure 1. Couette flow.

where the difference $H_a - H_m$ has been set equal to D, the dissociation energy per unit mass at the absolute zero of temperature. This is an approximation which implies equality of the specific heats (per unit mass) of atomic and molecular species. In the present circumstances this is quite a reasonable approximation and will be dealt with further in § 4 below.

Equation (11) can be integrated at once to give $p = $ const. and

$$\mu \frac{du}{dy} = \tau = \text{const.} = \tau_w \tag{14}$$

(τ is the shear stress, suffix w implying evaluation at the lower wall, $y = 0$). Putting equation (14) into equation (13) permits integration of the latter relation, giving

$$\lambda \frac{dT}{dy} + \rho \mathscr{D}_{am} D \frac{dc_a}{dy} + u\tau_w = \text{const.} \tag{15}$$

Evaluating the constant in equation (15) when $y = 0$, it is readily seen with the aid of equation (4) to be equal to $-q_w$, the energy flux into the lower wall. The total enthalpy of the mixture, H, is given by

$$H = c_a H_a + c_m H_m,$$

so that, since p is constant here,

$$\bar{C}_p \frac{dT}{dy} = \frac{dH}{dy} - D \frac{dc_a}{dy} \tag{16}$$

where

$$\bar{C}_p = c_a C_{pa} + c_m C_{pm}. \tag{16a}$$

C_{pa} and C_{pm} are the specific heats of the atomic and molecular species at constant pressure, so that $\bar{C}_p$ is the specific heat of the mixture when its chemical composition is frozen. The approximation $D \simeq H_a - H_m$ has been made in equation (16). Then equation (15) can be written as

$$\frac{\lambda}{\bar{C}_p} \frac{dH}{dy} + D\left(\rho \mathscr{D}_{am} - \frac{\lambda}{\bar{C}_p}\right)\frac{dc_a}{dy} + \frac{\mu}{2} \frac{du^2}{dy} = -q_w. \tag{17}$$

Defining Prandtl number Pr and Lewis number Le as

$$Pr = \mu \bar{C}_p / \lambda, \qquad Le = \rho \bar{C}_p \mathscr{D}_{am} / \lambda, \tag{18}$$

respectively, and assuming that they are constant, integration of equation (17) between $y = 0$ and $y = y$ gives

$$H - H_w + D(Le - 1)(c_a - c_{aw}) + \tfrac{1}{2}Pr\, u^2 = -u\, Pr\, q_w / \tau_w. \tag{19}$$

This result follows from the fact that

$$\int_0^y \frac{dy}{\mu} = \int_0^u \frac{1}{\mu} \frac{dy}{du} du = \frac{u}{\tau_w},$$

u being zero at $y = 0$. When $y = \delta$, then $H = H_\delta$, $c_a = c_{a\delta}$ and $u = U$; equation (19) therefore gives

$$H_\delta - H_w + (Le - 1)D(c_{a\delta} - c_{aw}) + \tfrac{1}{2}Pr\, U^2 = -U\, Pr\, q_w / \tau_w. \tag{20}$$

The recovery enthalpy, H_r, is defined as the value of H_w when $q_w = 0$. Whence

$$H_r = H_\delta + D(Le - 1)(c_{a\delta} - c_{ar}) + \tfrac{1}{2}Pr\, U^2, \tag{21}$$

where c_{ar} is the concentration of atoms at $y = 0$ under zero heat transfer conditions. Equation (20) can now be rewritten

$$-(q_w/\tau_w)U\, Pr = H_r - H_w + D(Le - 1)(c_{ar} - c_{aw}), \tag{22}$$

so that, defining a skin friction coefficient, C_f, and a Stanton number, St, such that

$$\tau_w = \tfrac{1}{2}\rho_w U^2 C_f, \tag{23}$$

$$-q_w = \rho_w U\{H_r - H_w + D(Le - 1)(c_{ar} - c_{aw})\}St, \tag{24}$$

equation (22) shows that

$$St = \frac{1}{2Pr} C_f. \tag{25}$$

This is the form of Reynolds analogy for Couette flow of a dissociating gas mixture, the analogy factor being exactly $1/Pr$ in this case. This result is also given by Liepmann & Bleviss (1956) but is shown to be perfectly general here (provided St and C_f are defined as in equations (23) and (24)), since no mention has so far been made about the chemical state of the gas.

The problem is now reduced to that of finding τ_w (or C_f). Integration of equation (14) gives

$$y\tau_w = \int_0^u \mu\, du,$$

or, in dimensionless form,

$$y' Re_w C_f = 2 \int_0^{u'} \frac{\mu}{\mu_w}\, du', \qquad (26)$$

where $y' = y/\delta$, $u' = u/U$ and $Re_w = \rho_w U\delta/\mu_w$.

The viscosity μ is dependent upon temperature and chemical composition, the value of C_f deduced from equation (26) depending rather critically on this variation. There is some evidence, however, to show that μ for the type of gas mixtures which we are considering continues to obey Sutherlands law quite well up to very high temperatures (e.g. $9000°$ K), and with this in mind we shall assume μ proportional to $T^{1/2}$. While this assumption may not be strictly justifiable, it simplifies the analysis and should enable reasonable comparisons to be made under varying conditions. Noting that Nusselt number, $Nu = StPrRe_w$, equation (25) shows that we now can express equation (26) as

$$y'\, Nu = \int_0^{u'} \sqrt{T'}\, du'; \quad \text{in particular } Nu = \int_0^1 \sqrt{T'}\, du', \qquad (27)$$

where $T' = T/T_w$. Equations (19) and (22) show that

$$H' - H'_w + D'(Le-1)(c_a - c_{aw}) + \tfrac{1}{2}\gamma Pr M_w^2 u'^2$$
$$= u'\{H'_r - H'_w + D'(Le-1)(c_{ar} - c_{aw})\}, \qquad (28)$$

where H', H'_w, H'_r and D' are H, H_w, H_r and D divided by RT_w/W_m. R is the universal gas constant and W_m is the molecular weight of the molecules. $M_w^2 = U^2 W_m/(\gamma RT_w)$ and is similar to a Mach number, based on the speed of sound at the lower plate. This is only strictly true if the gas is undissociated at the lower wall, γ then being the ratio of specific heats, but it is best regarded as simply a convenient non-dimensional group in the present circumstances. The enthalpy is a function of temperature and concentration which is known *a priori*, so that, once c_a is established as a function of either T' or u' (or both), equations (27) and (28) enable us to find Nu and hence velocity, temperature and concentration profiles.

Evaluation of concentration now constitutes the major problem and to this end one is led to consider the kinetics of the dissociation and recombination reactions. Before proceeding with a discussion of this topic we will introduce the concept of the ideal dissociating gas, which is due to Lighthill (1956), and which permits some further simplifications in the treatment of the problem.

4. THE IDEAL DISSOCIATING GAS

It can be shown that the number ratio of the constituents of a dissociating diatomic gas in equilibrium is given by

$$\frac{n_{ae}^2}{n_{me}} = \frac{f_a^2}{f_m} \exp(-d/kT) \tag{29}$$

where suffix e implies equilibrium value. The quantity d is the dissociation energy per molecule and k is Boltzmann's constant. f_a and f_m are partition functions for the atomic and molecular species, and may be taken to be products of the simple partition functions of the appropriate degrees of freedom, provided cross-couplings between different freedoms are negligible (see Moelwyn-Hughes 1947). The mixture density is $\rho = m_a n_a + 2m_a n_m$ and it is readily shown that equation (29) gives

$$\frac{c_{ae}^2}{1 - c_{ae}} = \frac{\rho_d}{\rho} \exp(-d/kT), \tag{30}$$

where $\rho_d = m_a f_a^2 / 2 f_m$: this quantity is a characteristic density (Lighthill 1956), which is found to be roughly constant for oxygen and nitrogen over the temperature range 1000° K to 7000° K, being about 150 gm/cc for O_2 and 130 gm/cc for N_2. The thermal equation of state for the mixture is

$$p = (1 + c_a)\rho(R/W_m)T, \tag{31}$$

assuming that each component gas in the mixture is thermally perfect, so that equation (30) could be rewritten in the form

$$\frac{c_{ae}^2}{1 - c_{ae}^2} = \frac{\rho_d RT}{p W_m} \exp(-W_m D/RT). \tag{32}$$

This is a rather more convenient form for present purposes.

The approximation $\rho_d = $ const. requires f_a^2 to be proportional to f_m and it can be shown (Lighthill 1956) that this is equivalent to fixing the amount of energy stored in the vibrational and rotational modes of the molecules at $\frac{3}{2}kT$. (In fact this energy will vary from kT to $2kT$, depending on the degree to which the vibrational mode is excited.) The enthalpies per unit mass of each species are then

$$H_a = 5RT/W_m + D, \qquad H_m = 4RT/W_m, \tag{33}$$

and so $H_a - H_m = D + RT/W_m$. However, RT/W_m is much smaller than D for the temperatures which are of interest here and $H_a - H_m \simeq D$ is a very reasonable approximation. (In fact, for a real gas, oxygen for example, the vibrational mode of the molecules is very nearly fully excited at such temperatures and H_m is nearer to $\frac{9}{2}(RT/W_m)$, so that the approximation is better than would be suggested by treating oxygen as an ideal dissociating gas.)

The specific enthalpy of the whole mixture is plainly

$$H = (4 + c_a)RT/W_m + c_a D. \tag{34}$$

Equation (34) is used later to eliminate the H' quantities from equation (28), (note that $H' = (4 + c_a)T' + c_a D'$). If it is found reasonable to assume

that the mixture is close to a chemical equilibrium state (i.e. $c_a \simeq c_{ae}$), equation (32) can be used to eliminate c_a from equation (28) in terms of temperature. Otherwise, c_a must be found from the chemical rate equations.

5. REACTION KINETICS

Consider the dissociation reaction of the symmetrical diatomic species, A_2. The stoichiometric equation describing the reaction is

$$A_2 + X \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2A + X \qquad (35)$$

in the usual notation (e.g. Penner 1955). The specific reaction rate constants for forward and reverse reactions, k_f and k_r, are generally expressed in terms of the concentrations of the respective reactants measured in moles/cc, for reactions of order higher than the first. We shall write (A_2) to mean 'concentration of species A_2 in moles/cc' and similarly for the other species. The species X in equation (35) may be either A_2 or A in a pure mixture, so that (X) represents the total number of moles of mixture per cc. Accordingly $(X) = p/RT$, where p is thermodynamic pressure and R the universal gas constant, so long as the individual gases A_2 and A can be treated as thermally perfect.

The net rate of production of the atomic species A, in moles/cc per sec, is

$$\frac{d(A)}{dt} = 2k_f(A_2)(X) - 2k_r(A)^2(X),$$

or, in terms of mole fractions,

$$\frac{d(A)}{dt} = 2k_f(X)^2 x_m - 2k_r(X)^3 x_a. \qquad (36)$$

(The mole fractions are $x_m = (A_2)/(X)$, $x_a = (A)/(X)$.) Under chemical equilibrium conditions, $d(A)/dt = 0$ and equation (36) gives

$$\frac{k_f}{k_r} = \frac{x_{ae}^2}{x_{me}}(X) = (X)K_x. \qquad (37)$$

K_x is the equilibrium constant in terms of mole fractions (or what is equivalent, number density ratios) and can be found from equation (29). Thus, knowing either k_f or k_r, the other can be found from equation (37).

Let us now write equation (36) in the form

$$\frac{d}{dt}[x_a(X)] = -2k_r(X)^3[2x_{ae} - x_{ae}^2 + \Delta x_a - x_{ae}\Delta x_a]\frac{\Delta x_a}{x_{me}},$$

where $\Delta x_a = x_a - x_{ae}$, and assume $\Delta x_a \ll 1$. The reaction will now proceed at very nearly constant p and T, so that (X) and x_{ae} may be assumed constant to all intents and purposes. Then

$$\frac{1}{\Delta x_a}\frac{d\Delta x_a}{dt} \simeq -2k_r(X)^2\left[\frac{2x_{ae} - x_{ae}^2}{1 - x_{ae}}\right] \simeq \text{const.,} \qquad (38)$$

and we can define a characteristic time, t_c, such that

$$\frac{1}{t_c} = \frac{1}{\Delta x_a} \frac{d\Delta x_a}{dt}. \tag{39}$$

Equation (38) shows that t_c is constant under the stated conditions; it is in fact the time taken for a small deviation of atom concentration to fall to $1/e$ of its equilibrium value at conditions p and T. Thus t_c can be used as a measure of the rate at which the chemical reaction proceeds in the direction of equilibrium, and can be compared with some characteristic flow time in order to give an indication of the probable chemical state of the gas. The obvious choice of flow parameter is the time taken for an atom to diffuse across the layer. In Couette flow equation (9) gives

$$v_a = -\frac{\mathscr{D}_{am}}{\delta} \frac{1}{c_a} \frac{dc_a}{dy'},$$

and we can reasonably assume $(c_a^{-1} dc_a/dy')$ to be of order unity. The binary diffusion coefficient, $\mathscr{D}_{am}$, is of order 1 cm²/sec at room temperatures ($\sim 300°$ K) and 1 atmosphere pressure and varies roughly as $T^{3/2}/p$. Thus $v_a \sim (T/300)^{3/2}(p(\text{atm.})\delta)^{-1}$ so that a characteristic time for diffusion of an atom across the layer, t_d, may be defined as

$$\frac{1}{t_d} = \frac{v_a}{\delta} \sim \left(\frac{T}{300}\right)^{3/2} \frac{1}{p\delta^2}. \tag{40}$$

Equations (38), (39) and (40) now give

$$\frac{t_c}{t_d} = \frac{1}{2}\left[\frac{1 - x_{ae}}{2x_{ae} - x_{ae}^2}\right]\left(\frac{RT}{p}\right)^2 \frac{1}{k_r}\left(\frac{T}{300}\right)^{3/2} \frac{1}{p(\text{atm.})\delta^2},$$

or

$$\frac{t_c}{t_d} \sim \left[\frac{1 - x_{ae}}{2x_{ae} - x_{ae}^2}\right]\frac{T^{7/2}}{p^3\delta^2 k_r} \quad (p \text{ in atmospheres}). \tag{41}$$

We can say that if $t_c/t_d \ll 1$ then the flow will effectively be in chemical equilibrium in the gas phase, whilst if $t_c/t_d \gg 1$ then chemical reactions occur so slowly in the gas phase that chemical composition will, effectively, not vary on this account. Plainly the factor in square brackets in equation (41) can exert considerable influence on the ratio of the characteristic times through its influence on t_c. The mole fraction x_{ae} is never either zero or unity in a finite temperature range (see equation (29)), although it may approach these values extremely closely. Equations (38) and (39) merely indicate that any excess or deficiency of atoms above or below the relevant equilibrium value is adjusted extremely rapidly when the mixture is predominantly of the atomic species, whilst the reverse is true when the gas is predominantly composed of molecules. The reasons are that recombination is a three-body process (two atoms plus any other particle) which is therefore relatively improbable when few atoms exist. Dissociation is a two-body process requiring, however, a certain high energy level encounter between the particles concerned and this is a relatively improbable occurrence at the lower temperatures where the mixture is mainly composed

of molecules. Within the range $0 \cdot 1 < x_{ae} < 0 \cdot 9$ the quantity in question varies by less than 10^2 in magnitude.

Before equation (41) can be used to provide an indication of the magnitude of t_c/t_d one must know the magnitude and temperature dependence of k_r. Here the available evidence is rather indecisive. Feldman (1957) suggests that a lower limit for k_r in air (treated as a single diatomic gas) is about 10^{18} cc²/mole²/sec for temperatures up to about 5000° K, the trend being for k_r to decrease with rising temperature. Fay & Riddell (1958) write the reverse specific reaction rate constant as $k_r = K_1 T^{-3/2}$, where K_1 is a constant, and estimate K_1 to be $5 \times 10^{14} (300)^{3/2}$ for oxygen; in other words,

$$k_r \simeq 5 \times 10^{14} (T/300)^{-3/2} \text{ cc}^2/\text{mole}^2/\text{sec}.$$

Hirschfelder (1956), however, quotes a value of

$$k_r \simeq 10^{16} (T/300)^{5/2} \text{ cc}^2/\text{mole}^2/\text{sec}$$

for oxygen, basing this result on the theoretical work of Eyring, Gershinowitz & Sun (1935) for recombination of atomic hydrogen, whilst Camm & Keck (1957), by monitoring the radiative relaxation zone behind a moving normal shock wave, deduce a value $k_r \sim 10^{16}$ cc²/mole²/sec in pure oxygen or nitrogen, which is substantially invariant with temperature. In view of this conflicting evidence it does not seem unreasonable for the present to set $k_r = 10^{17}$ cc²/mole²/sec and ignore its temperature variation. Apart from Fay & Riddell's, the estimates quoted above lie within roughly an order of magnitude of this value either way in the interesting temperature range for dissociation. Therefore we shall write

$$t_c/t_d \sim 10^{-5}/p^3\delta^2 \tag{42}$$

and, remembering that this estimate may vary by one or two orders of magnitude in either direction, use equation (42) to estimate the probable chemical state of the gas mixture.

In particular it can be seen that the flow must be very close to a chemical equilibrium state for pressures of 1 atmosphere or greater, so long as δ is not much less than 1 cm, but that a decrease of pressure, say down to 10^{-2}–10^{-3} atmospheres, combined with shear layer thicknesses around 1 mm will rapidly lead towards the freezing of homogeneous reactions*.

So far we have not considered the influence of surface reactions on the flow pattern. When the t_c/t_d ratio is very small it seems reasonable to suppose that particles remain in a particular flow region for a sufficient time to allow the chemical equilibrium state to be very closely approached there. Consequently, this state would constitute a good first approximation to the true state of affairs and any iterative procedure founded upon it would be expected to converge very rapidly. Under these conditions, the

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* In applying considerations of this sort to an object flying at hypersonic speeds, it must be remembered that pressures in the boundary layer on the object will usually be many times the undisturbed, atmospheric value.

species' concentrations and mass fluxes become functions of temperature and pressure which will not admit the imposition of arbitrary boundary values at the walls $y = 0$ and $y = \delta$. The surface reaction rate which would specify these boundary conditions will vary very widely (for different wall materials, for example) so that it may seem that conditions of chemical equilibrium in the gas phase and arbitrarily fast surface reactions are incompatible.

For the case of heat transfer in a stagnant gas, Hirschfelder (1956) has shown that the two conditions are reconcilable following the introduction of transients in the flow variables which have appreciable values only in a thin gas layer adjacent to the surface. The methods used by Hirschfelder, to evaluate the thickness of this layer are valid for Couette flow. The example quoted there, for energy transfer through oxygen at one atmosphere pressure with no surface reaction, gives the thickness of the layer as less than 10^{-3} cm, the actual thickness decreasing with increase of wall temperature (N.B. temperatures lie in the range 2000–6000° K). For low wall temperature values, the fast homogeneous reaction rates cause the atom concentration to fall to zero (for all practical purposes) some distance from the wall and the problem of surface reactions does not arise. It is interesting to note from equation (42) that with $p = 1$ atmosphere and $\delta < 10^{-3}$ cm, t_c/t_d becomes greater than unity, a fact which would lead one to suspect the equilibrium approximation. Hirschfelder shows that for plate separation distances greater than the distortion layer thickness, energy transfer rate is virtually unaffected by heterogeneous reaction rate.

The continuity requirement for the atomic species can be expressed in the following form, using equations (10) and (36) and writing the diffusion velocity v_a in terms of concentration gradient,

$$\frac{d}{dy}\left[\rho \mathscr{D}_{am}\frac{dc_a}{dy}\right] = \tfrac{1}{2}k_r\, W_m\left(\frac{p}{RT}\right)^3\left[\frac{4c_a^2}{(1+c_a)^2} - K_x\left(\frac{1-c_a}{1+c_a}\right)\right]. \quad (43)$$

K_x is the equilibrium constant in terms of mole fractions and can be found from equations (29) and (37),

$$K_x = \frac{n_{ae}^2}{nn_{me}} = \frac{4RT}{pW_m}\rho_d\exp(-T_d/T), \quad (44)$$

where $T_d = d/k$, the characteristic dissociation temperature. For oxygen $T_d = 59\,000°$ K and $\rho_d = 150$ gm/cc; whence $pK_x = 1540T\exp(-59\,000/T)$, with p measured in atmospheres. Writing k_r as $K_1(T)^\sigma$ cc²/mole²/sec, equation (43) for oxygen becomes

$$\frac{d}{dy}\left[\rho\mathscr{D}_{am}\frac{dc_a}{dy}\right] = 2\cdot9 \times 10^{-5}K_1\,p^3T^{\sigma-3}\left[\frac{4c_a^2}{(1+c_a)^2} - \right.$$

$$\left. - 1540\exp(-59\,000/T)\frac{T}{p}\left(\frac{1-c_a}{1+c_a}\right)\right], \quad (45)$$

p being measured in atmospheres. One could now eliminate T from equation (45) in terms of c_a and u and the y-derivatives could be replaced by u-derivatives, using equations (28) and (27). This would result in a differential equation for c_a in terms of u, but involving the Nusselt number, which is not known *a priori*. The solution would not be seriously influenced by the value of Nu and no doubt some plausible value for this quantity could be employed at the start of an iteration scheme. However, the equation is very unwieldy, and no attempt has been made to solve it here. Instead we shall go on to consider the two extreme cases of $t_c/t_d \ll 1$ and $t_c/t_d \gg 1$, assuming in the first case that atom concentration is equal to the local equilibrium value, and in the second case that no gas phase reactions occur at all. In the latter case it becomes necessary to consider the details of the surface reaction.

6. CHEMICAL EQUILIBRIUM FLOW

When $t_c/t_d \ll 1$ it can be assumed that $c_a \simeq c_{ae}$ everywhere at the local temperature and pressure. It should be observed that this does not imply that the net rate of production of atoms is, or even approaches, zero. Indeed the reverse is true; the rate of production of a particular species can be considered to be 'very fast' in these circumstances. It is just that the chemical reaction can proceed at the required rate with concentrations *not too far removed* from an equilibrium value. Mathematically, it could be said that the coefficient of the term in square brackets on the right-hand side of equation (43) approaches ∞ while $c_a \to c_{ae}$ in such a way as to cause the product to approach a suitable finite, non-zero limit. Then equation (43) is not required and c_a can be found from equation (32). Putting this value into equation (28) provides the required (T', u') relation.

Since we do not seek great accuracy it is simplest to solve equation (28) graphically and, likewise, to integrate equation (27) graphically to find Nu. As a numerical example, some values have been obtained in this way for energy transfer through oxygen at one atmosphere pressure. The temperature at the upper plate has been taken to be $5000°\,K$, the lower plate being maintained at $T_w = 1000°\,K$. The dimensionless dissociation energy per unit mass, D', is therefore equal to 59 in this case, and $\rho_d/\rho_w = 0\cdot39 \times 10^6$. The Prandtl number has been taken to be $0\cdot75$, while γ at the lower wall is equal to $\frac{4}{3}$ for the ideal dissociating gas. These values are reasonable approximations in the circumstances as we are more interested in trends and comparisons than in actual values. The (T', u') relation has been found under these conditions for two M_w values, namely $M_w = 2$ and $M_w = 20$, and several Lewis number values between $1\cdot0$ and $2\cdot0$. The value of Le for oxygen is probably about $1\cdot4$, the other values being included to demonstrate the effects of mass diffusion on the profiles, etc.

Dimensionless velocity, temperature, concentration of atoms and enthalpy profiles are shown in figures 2 to 5 for $M_w = 2$ and figures 6 to 9 for $M_w = 20$. Figure 10 shows the variation of Nusselt number with Lewis number for the two M_w values.

All profiles are, to a greater or lesser extent, affected by the value of the Lewis number, although the variations are so small in the case of velocity distribution when $M_w = 2$ that they do not show up on the scale of figure 2. Similarly Nu depends slightly on Le, although the variation is not detectable when $M_w = 2$. The results of §3 show that the rate of energy transfer into the lower wall is given by

$$-q_w = \frac{Nu}{\delta} \frac{\lambda_w}{\bar{C}_{pw}} [H_\delta - H_w + D(Le-1)(c_{a\delta} - c_{aw}) + \tfrac{1}{2}Pr U^2]. \qquad (46)$$
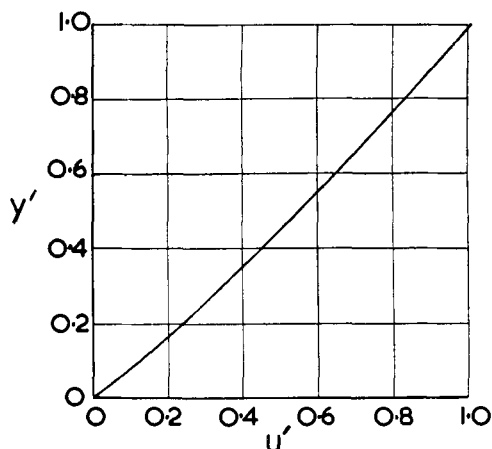
Figure 2. Velocity profile in chemical equilibrium flow. $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere. All values of Le.
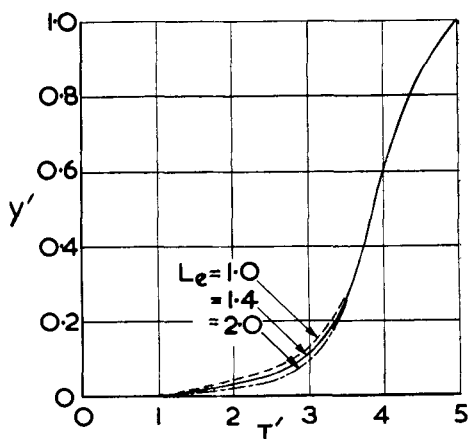
Figure 3. Temperature profiles in chemical equilibrium flow $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere.
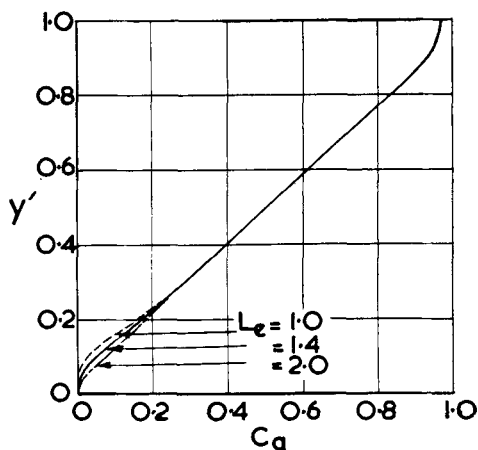
Figure 4. Atom concentration profiles in chemical equilibrium flow. $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere.
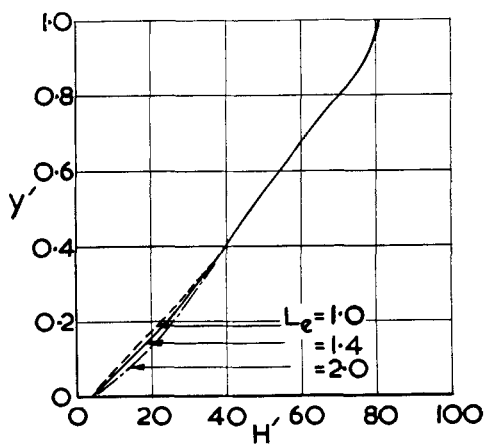
Figure 5. Enthalpy profiles in chemical equilibrium flow. $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere.

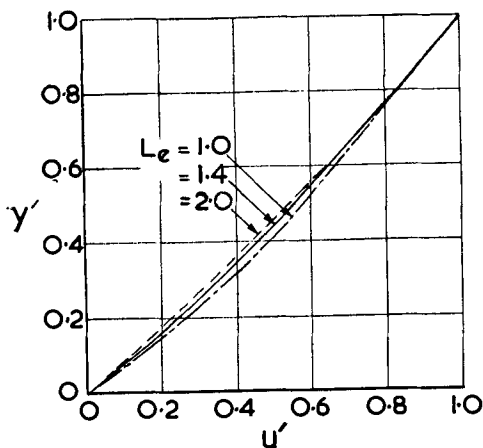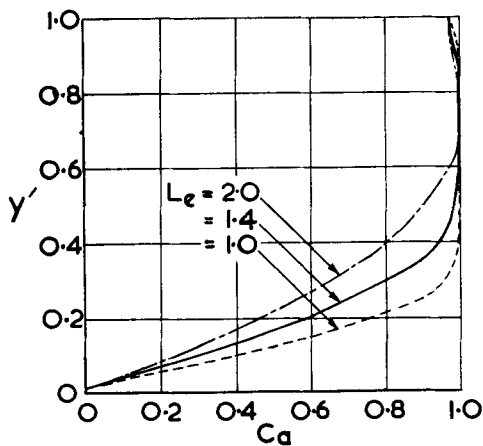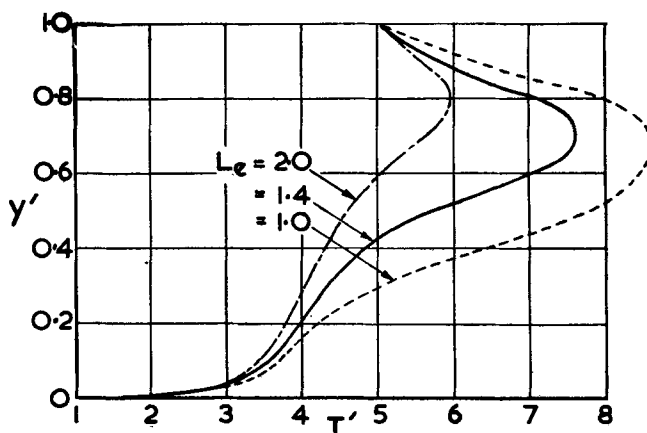Figure 6. Velocity profiles in chemical equilibrium flow. $M_w = 20$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere.

Figure 7. Atom concentration profiles in chemical equilibrium flow. $M_w = 20$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere.

Figure 8. Temperature profiles in chemical equilibrium flow. $M_w = 20$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere.

Since Nu is substantially invariant with Le, the energy transfer rate is almost a linear function of $(Le-1)$, other things being equal. For the examples evaluated here the ratio $q_w(Le = 1\cdot4)/q_w(Le = 1\cdot0)$ is about $1\cdot3$ when $M_w = 2$ and $1\cdot1$ when $M_w = 20$. An analysis which assumes $Le = 1\cdot0$ may therefore give energy transfer rates which are quite significantly low, particularly for the case in which viscous dissipation contributes a relatively small term. (A practical example of such a flow occurs in the region of the forward stagnation point of hypersonic vehicles.)
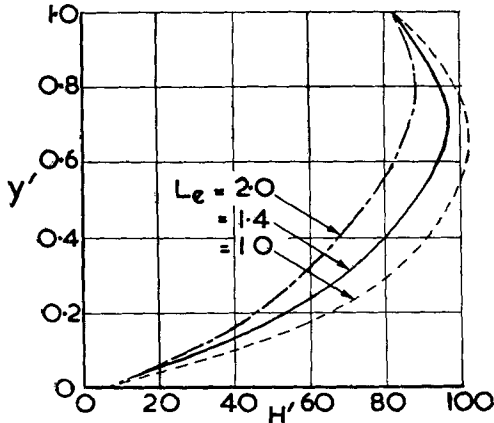

Figure 9. Enthalpy profiles in chemical equilibrium flow. $M_w = 20$, $T_w = 1000°$ K, $T_\delta = 5000°$ K, $p = 1$ atmosphere.
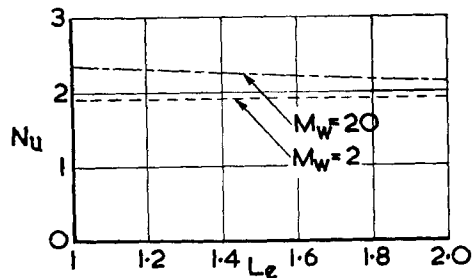
Figure 10. Nusselt number variation with Lewis number for $M_w = 2$, and $M_w = 20$; chemical equilibrium flow.

It should be observed that for all cases considered in this section, $dc_a/dy \simeq dc_{ae}/dy \to 0$ as $y \to 0$. Therefore all the energy is transferred into the lower wall by thermal conduction alone and temperature gradients there should be larger for larger values of Le. This effect can be seen in figure 3, when $M_w = 2$, but does not show up on figure 8. Inspection of the solution in the latter case shows that in fact the (T', y') curves cross over near to $T' = 1$ and the picture is then similar to the lower half of figure 3. · The effect of Lewis number on the profiles may be qualitatively explained as follows, viewing an increase in Lewis number as an increase in the ability of atoms to diffuse through the layer. Then for larger values of Le these particles can penetrate to regions closer to the wall before recombining and giving up their dissociation energy as heat, resulting in the steeper temperature gradients there. In the outer parts of the layer, viscous heating tends to maintain the atom concentration at its upper wall value, indeed when $M_w = 20$ the viscous heating is to intense as to cause an increase in atom concentration (see figure 7; note $c_{a\delta} = 0\cdot965$ in this case) and rapidly leads to virtually complete dissociation. The increased mobility of the atoms (implied by larger Le values), permits them to escape from this region more readily, however, and the viscous heating can only maintain a smaller zone of high concentration when Le is large. The net result is that a greater proportion of the viscous heating is available in the

form of thermal energy when mass diffuses less readily, as exemplified by the very large temperature peak in figure 8 when $Le = 1·0$. The temperature values there will be modified somewhat by ionization of the oxygen atoms, a fact which may well cause Le to be of some importance in magneto-gasdynamic applications.

The effects of variation of wall temperature ratio, T_δ/T_w, on Nu are rather complicated, as can be appreciated from an inspection of equations (27) and (28). The rapid rise of c_{ae} with temperature is an important factor and it has not been found possible to relate Nu to T_δ/T_w in any simple manner. However, in an attempt to obtain a reasonable correlation between these quantities for the single case, $T_w = 1000°$ K, it was found that better results were obtained if the peak value of temperature in the layer, T_p, was used in place of T_δ. This choice affected the high M_w values most since viscous heating gave T_p values in excess of T_δ in all cases. Only for values of T_δ approaching T_w was the effect felt at $M_w = 2$. Some results of plotting Nu against $C = (\rho\mu)_p/(\rho\mu)_w$ are shown in figure 11, suffix p indicating evaluation at peak temperature conditions. The general quantity
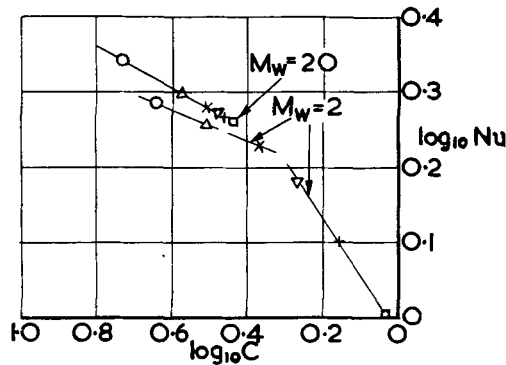

Figure 11. Variation of Nusselt number with wall temperature ratio, T_δ/T_w, in chemical equilibrium flow.

Symbol:—	O	Δ	×	∇	+	□
T_δ/T_w:—	5·0	4·0	3·5	3·0	2·0	1·0

C is important in boundary-layer theory, where it appears as an explicit factor in the boundary-layer equations. Fay & Riddell (1958) have demonstrated its significance in the stagnation region where a factor $[(\rho\mu)_\delta/(\rho\mu)_w]^{0·4}$ appears in the heat transfer rate value, suffix δ implying evaluation at the edge of the boundary layer in this case. It is not too surprising to find that C correlates wall temperature variation quite well in Couette flow, therefore, although it must be stressed that the examples quoted here are for one lower wall temperature value only ($T_w = 1000°$ K). Since flow in a stagnation region is generally one for which viscous dissipation plays only a small part in determining energy transfer rate, it tends to be closer to Couette flow at low M_w values, where T_p is less than, or at most of the same order as, T_δ.. On this basis, wall temperature

ratio effects in boundary-layer flows with large viscous heating terms may perhaps be better correlated using a peak temperature in the layer, as is so for the $M_w = 20$ case in Couette flow. The small amount of evidence which has been derived here to support this suggestion is in no way conclusive, but may perhaps be borne in mind in future studies.

The values of C used here are equal to $[(1 + c_{ae})_p (T_p/T_w)^{1/2}]^{-1}$, since c_{aew} is zero for all practical purposes when $T_w = 1000°$ K. It appears from figure 11 that Nu varies as some power of C which differs in different ranges. When $M_w = 20$, the lowest value of T_p is about $3800°$ K, so that a fair degree of dissociation still exists there ($c_{ae} \simeq 0.47$ at $T = 3800°$ K, $p = 1$ atmosphere). The same is true of the first three values of C when $M_w = 2$ (see figure 11), but at $C \simeq 0.5$ (where $T_p \simeq 3250°$ K and $c_{ae} \simeq 0.1$) the slope alters abruptly. It must be concluded that peak temperature and degree of dissociation have a significant effect on Nusselt number.

7. Chemically frozen flow

Having considered some aspects of chemical equilibrium flow ($t_c/t_d \ll 1$) attention will now be directed towards flows at the other extreme, for which $t_c/t_d \gg 1$. In this case, chemical reactions occur so slowly in the gas phase that they can reasonably be neglected altogether in a first approximation and the term ω_a in equation (10) put equal to zero. This state will be called chemically frozen flow and § 5 has indicated that it may be a valid concept at low pressures and/or small values of δ.

To solve this problem it is necessary to consider the details of the surface reaction which may take place. The heterogeneous recombination reaction occurs between a gas atom and an atom adsorbed (or chemisorbed) by the wall. Observations (for example Shuler & Laidler (1949)) have shown this to be a first-order process, requiring the surface to be fully covered with adsorbed particles. The efficiency of the wall as a catalyst for the recombination reaction can be defined as the ratio of the number of gas atoms being converted into molecules to the total number of gas atoms striking the wall per unit area per unit time, and will be denoted by Γ. For the type of flow represented here by Couette flow, the microscopical system is not too far removed from its equilibrium state and for present purposes it can be assumed that the actual distribution of molecular velocities is Maxwellian. The Maxwellian distribution function, F, is expressed in terms of the peculiar velocities of the particles of a particular species (vector $\mathbf{q}_i'$ with components u_i', v_i' and w_i'), this velocity being defined as the velocity of random, thermal motion of a particle relative to the local mass average velocity. The mean of $\mathbf{q}_i'$ over all particles of species i is the diffusion velocity, $\mathbf{q}_i$. The distribution function F is given by

$$F = n_i \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp(-m_i \mathbf{q}_i'^2/2kT),$$ (47)

where n_i is the number density of species i, m_i is the mass of a particle and k is Boltzmann's constant. The number of particles whose velocities lie

in the range $\mathbf{q}_i'$ to $\mathbf{q}_i' + d\mathbf{q}_i'$ is $F \, du_i' \, dv_i' \, dw_i'$. Since the mass average velocity at the wall is zero in both Couette and boundary-layer flows, the number of particles of the ith kind striking the wall per unit area per unit time will be

$$s_{iw} = \int_{-\infty}^{\infty} du_i' \int_{-\infty}^{\infty} dw_i' \int_{-\infty}^{0} v_i' F \, dv_i' = n_{iw} k T_w (2\pi m_i k T_w)^{-1/2},$$

or

$$s_{iw} = x_{iw} p (2\pi m_i k T_w)^{-1/2}, \tag{48}$$

where x_{iw} is the mole fraction $(= n_{iw}/n_w)$ and p is the thermodynamic pressure $(= n_w k T_w)$. Equation (48) now provides an estimate of the rate at which gas atoms strike the wall and from the definition of recombination coefficient Γ, the mass flux of atoms into the wall is seen to be $\Gamma m_a s_{aw}$. With no reactions occurring in the gas phase, the continuity requirement (equation (10)) becomes simply

$$\rho \mathscr{D}_{am} \frac{dc_a}{dy} = \left(\frac{2c_{aw}}{1 + c_{aw}}\right) \frac{\Gamma p m_a}{(2\pi m_a k T_w)^{1/2}} ; \tag{49}$$

in particular, for oxygen,

$$\rho \mathscr{D}_{am} \frac{dc_a}{dy} = \frac{350}{\sqrt{T_w}} \Gamma p \left(\frac{c_{aw}}{1 + c_{aw}}\right). \tag{50}$$

We will only deal in detail with the lower wall, assuming that conditions at $y = \delta$ correspond to the equilibrium state at the appropriate temperature and pressure. The quantity $\rho \mathscr{D}_{am}$ in equation (49) can be written as μ/Sc, where Sc is the Schmidt number $(Sc = Pr/Le)$. Sc is constant through the layer since both Le and Pr have been assumed constant, so that writing μ proportional to $\sqrt{T}$ as before, equation (49) assumes the dimensionless form

$$\frac{dc_a}{dy'} = \frac{1}{\sqrt{T'}} \frac{\delta Sc \Gamma p}{\mu_w (2\pi m_a k T_w)^{1/2}} \left(\frac{2c_{aw}}{1 + c_{aw}}\right). \tag{51}$$

But

$$(dc_a/dy') = (dc_a/du')(du'/dy') = (dc_a/du')(Nu/\sqrt{T'})$$

from equation (27), so that equation (51) can be written

$$\frac{dc_a}{du'} = A, \tag{52}$$

where A is a constant. Integration of equation (52) yields

$$c_a = (c_{a\delta} - c_{aw})u' + c_{aw}, \tag{53}$$

since $c_a = c_{a\delta}$ when $u' = 1$ and $c_a = c_{aw}$ when $u' = 0$. The constant A is given by

$$A = (c_{a\delta} - c_{aw}) = \frac{\delta Sc \Gamma p}{\mu_w (2\pi m_a k T_w)^{1/2}} \frac{1}{Nu} \left(\frac{2c_{aw}}{1 + c_{aw}}\right). \tag{54}$$

The concentration of atoms at the lower wall can now be determined as a function of recombination coefficient in any particular circumstances, once the Nusselt number has been found. By writing the dimensionless

enthalpy values appearing in equation (28) in terms of T' and c_a (see §4), equation (53) can be used to eliminate c_a in terms of u'. Then the (T', u') relation required for evaluation of Nu is found to be

$$T' = \frac{[(4+c_{a\delta})(T_\delta/T_w) - (4+c_{aw}) + \tfrac{1}{2}\gamma Pr M_w^2]u' - \tfrac{1}{2}\gamma Pr M_w^2 u'^2}{(4+c_{aw}) + (c_{a\delta} - c_{aw})u'}. \quad (55)$$

Since the (T', u') relation is a function of c_{aw} it would be possible to use equation (55) to find Nu for some chosen c_{aw} value and then to use equation (54) to find the value of Γ appropriate to the chosen conditions. (Values of T_δ, T_w, M_w, p, etc. would be known since they are required to specify the problem.) However, it is found that the (T', u') relation does not depend very critically on the value of c_{aw}, so that Nu is substantially invariant with this quantity for any chosen T_δ/T_w, $c_{a\delta}$, M_w, etc. Lewis number does not appear in equation (55), except through its influence on c_{aw}, whence it can be inferred that Nu is independent of Le for all practical purposes.

The energy flux into the lower wall is

$$-q_w = \lambda_w \left(\frac{dT}{dy}\right)_{y=0} + \rho_w \mathscr{D}_{am} D \left(\frac{dc_a}{dy}\right)_{y=0} \quad (56)$$

and is in part due to thermal conduction, in part due to atom diffusion with release of dissociation energy directly at the wall. Since the (T', u') relation is independent of c_{aw} it can be seen that the (T', y') relation is likewise independent of this quantity; therefore, for any given values of T_δ, T_w, δ, $c_{a\delta}$ and M_w, heat transfer by thermal conduction takes place at the same rate for all values of Γ in chemically frozen flow. In other words, the temperature profile through the layer does not depend on the surface reaction rate. The remaining mechanism of energy transfer, however, depends critically on the value of Γ. The second term on the right-hand side of (56) can be rewritten as $(\rho_w \mathscr{D}_{am} D Nu/\delta)(dc_a/du')_{u'=0}$, since $T' = 1$ when $y' = 0$, and (53) shows that $(dc_a/du')_{u'=0} = c_{a\delta} - c_{aw}$, where c_{aw} is found as a function of Γ from (54). It can be seen from (54) that c_{aw} is a minimum when Γ has its maximum value of unity and furthermore that c_{aw} can never be equal to zero. (It is, of course, always less than $c_{a\delta}$ unless Γ is negative. This would imply that the surface reaction was a dissociation rather than a recombination reaction, however, requiring T_w values higher than would be practically possible.) From this result, the conclusion can be drawn that it is not possible to recover all the dissociation energy in chemically frozen flow that may otherwise be recovered in chemical equilibrium flow under similar conditions, provided that the T_w value is not too high. (It seems unlikely that T_w could be allowed to go much above 1000–1500° K in a practical case.)

For comparison with the previous, chemical equilibrium case some values have been calculated for $T_\delta = 5000°$ K, $T_w = 1000°$ K and $M_w = 2$, the gas being oxygen as before. The value of $c_{a\delta}$ has been set equal to 1·0 and the Schmidt number $Sc = 0·75/1·4$. A reasonable estimate of μ for the mixture is $\mu = 5 \times 10^{-4}(T/1000)^{1/2}$ gm/cm sec (being roughly the value

for molecular oxygen at high temperatures), bearing in mind the assumptions previously made with regard to this quantity. The Nusselt number, calculated graphically, has the value 1·76 and equation (54) gives

$$1 - c_{aw} = \frac{10^4}{1\cdot5} p\Gamma\delta\left(\frac{c_{aw}}{1+c_{aw}}\right). \tag{57}$$

(In the event that $\Gamma = 0$, equation (54) gives $c_{aw} = c_{a\delta} = 1\cdot0$, and Nu can be evaluated analytically using (55). For the example quoted here, $Nu = 1\cdot73$, in good agreement with the graphical evaluation for $c_{aw} < c_{a\delta}$.) Figures 12 and 13 compare the velocity and temperature profiles in the two cases (N.B. $Le = 1\cdot4$ for the equilibrium flow), the profiles being independent of δ so long as it is not too small in the chemical equilibrium case. The curves marked 'chemically frozen flow' are good approximations for all surface reaction rates. The filling out of the equilibrium state temperature profile due to gas phase recombination reactions is apparent in figure 13. Figure 14 compares the ('dimensionless') concentration profiles.

When the product $p\delta = 10^{-3}$, equation (57) gives $0\cdot15(1 - c_{aw}^2) = \Gamma c_{aw}$ and this relation is shown plotted in figure 15. The least value of c_{aw} in this case is almost equal to $0\cdot15$. It can be seen that $p\delta = 10^{-3}$ is consistent with the requirement for chemically frozen flow, since equation (42) could be written as $t_c/t_d \sim 10/p$, and frozen flow would in all probability occur for $p < 10^{-1}$ to 10^{-2} atmospheres. (In passing, it appears to be quite possible that frozen flow conditions may be realized on a model in a conventional shock tube, provided the low pressure end can be sucked down sufficiently far. Such conditions may also arise during satellite re-entry into the earth's atmosphere.)
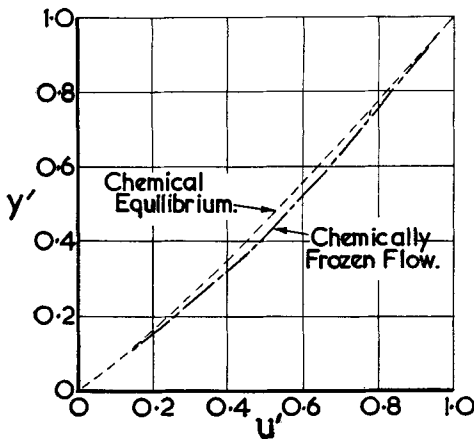
Figure 12. Comparison of velocity profiles. $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K.

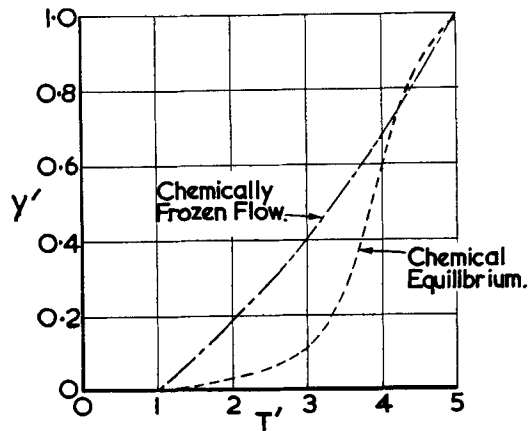Figure 13. Comparison of temperature profiles. $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K.

When $\Gamma = 1\cdot0$, the rate of energy transfer is a maximum and it is interesting to compare it with the chemical equilibrium value in otherwise similar circumstances. Denoting final energy transfer rate in chemically frozen flow by q_{wf}, and in chemical equilibrium flow by q_{we}, the ratio
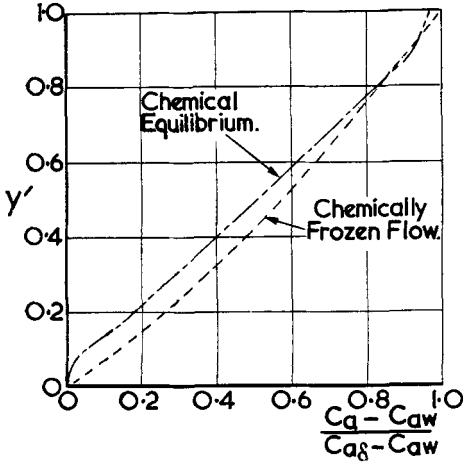
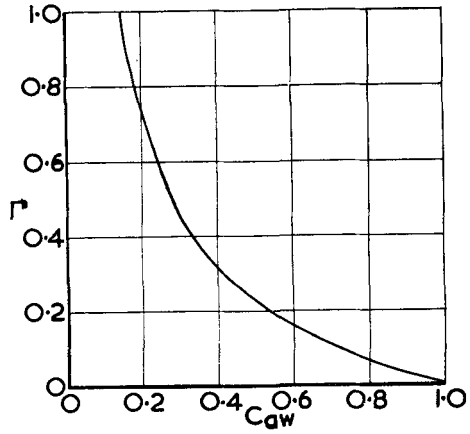Figure 14. Comparison of atom concentration profiles. $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K.

Figure 15. Surface recombination coefficient *vs* atom concentration at the wall. $M_w = 2$, $T_w = 1000°$ K, $T_\delta = 5000°$ K. $p\delta = 10^{-3}$ atm. cm.

$q_{wf}/q_{we} \simeq 0.85$ for the examples quoted here. Thus it would appear that the 'fully catalytic wall' is a less effective means in these particular circumstances of recovering dissociation energy than gas phase recombination.

Couette flow can be interpreted as a crude approximation to a laminar boundary-layer flow in which the effects of convection have been neglected compared with those of diffusion, the Couette flow thickness δ being regarded as a local boundary-layer thickness. It is therefore interesting to compare the present theory with that of Fay & Riddell (1958), bearing in mind that actual numerical values may be widely different, whilst the general effects of the various parameters on the final result are in all probability similar.

For the heat transfer rate, $-q_w$, in the stagnation region of a blunt-nosed body Fay & Riddell give

$$-q_w = \frac{\lambda_w}{x\bar{C}_{pw}} Nu_s(H_\delta + \tfrac{1}{2}U^2 - H_w),$$

where x = distance measured round the nose from the stagnation point, suffix w refers to the wall, and suffix δ to the edge of the boundary layer. U is velocity at the edge of the boundary layer, so that $H_\delta + \tfrac{1}{2}U^2 = H_s$, the stagnation enthalpy. Nu_s is a Nusselt number found to be given by

$$Nu_s = 0.67Re^{1/2}\left(\frac{\rho_\delta\mu_\delta}{\rho_w\mu_w}\right)^{0.4}\{1 + A(Le-1)(D/H_s)c_{a\delta}\},$$

where Re is a Reynolds number, $Re = Ux\rho_w/\mu_w$ and $Dc_{a\delta}$ is the amount of energy per unit mass in the flow outside the boundary layer which is stored as dissociation energy. A is a constant almost equal to 0.5 which varies somewhat according as the flow is in chemical equilibrium or is chemically frozen. (In their later paper, $A = 1$ and the Lewis number

is raised to a power equal to roughly 0·6, which also varies somewhat with the chemical state of the flow. The numerical differences are very small, however, when $Le \sim 1$.)

The general result is seen to be very similar to the Couette flow result

$$-q_w = \frac{Nu}{\delta} \frac{\lambda_w}{\bar{C}_{pw}} \{H_\delta - H_w + D(Le-1)(c_{a\delta} - c_{aw}) + \tfrac{1}{2}PrU^2\},$$

when allowance is made for the difference in definition of Nusselt number in the two cases and for the interpretation of δ. (The $\rho\mu$ ratio dependence is not so clear cut, but this is hardly surprising since boundary-layer thickness is directly affected by the values of ρ and μ whereas δ in Couette flow is not.) The two solutions compare well in general shape when the flow is in chemical equilibrium and the wall is 'cool', for then $c_{aw} \simeq 0$ and $H_\delta \gg H_w$, $H_\delta + \tfrac{1}{2}PrU^2 \gg H_w$, in each case. An important difference arises when the flow is chemically frozen, however, as a result of differences in the interpretation of a fully catalytic wall. Fay & Riddell (in their later paper) remark that when the wall is catalytic, "the atom concentration will be reduced to its equilibrium value at the wall temperature". In particular, if T_w is low enough, c_{aw} would approach zero on this hypothesis, whereas it is clear from the present work that this can never occur since it would require an infinite value of the recombination coefficient Γ. When comparing q_{wf} and q_{we} values for Couette flow, the consequences of assuming $c_{aw} = 0$ in place of putting $\Gamma = 1$ are not too serious (in fact q_{wf}/q_{we} for $c_{aw} = 0$ is roughly 0·9 in place of 0·85 when $\Gamma = 1$). But Hirschfelder (1956) suggests that Γ for recombination of oxygen atoms on a metal surface is roughly equal to $2/T_w$, so that it is never greater than 10^{-2} in a practical case. For the examples quoted here, $\Gamma \sim 10^{-3}$ when $T_w = 1000° K$ and the lower wall is metallic, whence it can be seen from equation (57) that $c_{aw} \simeq c_{a\delta} = 1·0$. Thus only a very small fraction of the dissociation energy is recovered and $q_{wf}/q_{we} \simeq 0·21$, representing a considerable reduction in the frozen flow heat transfer rate.

8. CONCLUSIONS

It has been shown how the homogeneous chemical reaction rate exercises considerable control over the detailed properties of a layer of shear flow. When these reaction rates are fast compared with the rate of diffusion of the various chemical species in the mixture, local chemical equilibrium composition is closely approached and the nature of the surface reaction is is unimportant in the majority of the flow. In particular, energy transfer rate is effectively uninfluenced by the surface reaction rate. When the lower wall is sufficiently cool, as it may have to be in practice, the atom concentration falls to zero some distance above the surface and energy is finally transferred to the wall by thermal conduction alone.

When homogeneous reaction rates become very slow compared with atom diffusion rates, the picture changes considerably. Energy transfer into the wall occurs through both possible mechanisms (even when the wall is cool), the thermal conduction contribution remaining sensibly

independent of surface reaction rate, whilst the atom diffusion contribution depends critically on the value of surface recombination coefficient. If the wall is a very effective catalyst for the recombination reaction, almost all the atoms which strike it will recombine and give up their dissociation energy to it directly. Thus a large 'atom sink' is set up at the wall, which requires large concentration gradients to provide the necessary rate of atom diffusion. For any given value of the 'external' concentration $(c_{a\delta})$ an increase in the value of Γ will therefore result in lower atom concentrations at the wall, and hence in higher rates of final energy transfer. By the nature of the surface reaction, c_{aw} can never be zero there since, if it was zero, there would be no atoms present to take part in the reaction.

It is suggested that even for quite high surface reaction rates (e.g. one atom in every 100–1000 atoms which strike the wall recombining) energy transfer occurs significantly more slowly in chemically frozen flow than in otherwise comparable circumstances with chemical equilibrium flow. It seems reasonable to suppose that the influence of the surface reaction spreads out into the shear layer as homogeneous reaction rates decrease.

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