The linearized flow of a dissociating gas

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The equations for planar two-dimensional steady flow of an ideal dissociating gas are linearized, assuming small disturbances to a free stream in chemical equilibrium.

As an example of their solution, the flow past a sharp corner in a supersonic stream is evaluated and the variations of flow properties in the relaxation zone are found. Numerical illustrations are provided using an 'oxygen-like' ideal gas and comparisons made with a characteristics solution. The flow past a sharp corner can be studied in a conventional shock tube and it may be possible to verify the present theory experimentally. In particular it may prove feasible to use the results to obtain a measure of the reaction rates in the gas mixture.

1. Introduction

When the chemical composition of a gas changes by chemical reaction a further source of dissipation is present in the flow field. The reactions are natural, thermodynamically irreversible, processes and as such lead to the production of entropy. The important difference between this type of entropy production and that associated with the transport phenomena is that it does not depend explicitly on the gradients of velocity, temperature and concentration. Thus its influence is not necessarily confined to the interior of boundary layers or shock waves, but may spread over the entire flow field.

The equations governing the flow of a chemically reacting gas mixture have been derived previously, for example, Kirkwood & Wood (1957), and Clarke (1958a). In the present paper an attempt is made to consider flows with small perturbations, dealing only with the two-dimensional steady problem. The treatment is simplified by considering the dissociation reaction in a symmetrical diatomic gas A_2, each A_2 molecule being made up from two A_1 atoms. In the pure gas the reaction is

$$A_2 + A_3 \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2A_1 + A_3. \tag{1}$$

The species A_3 can be either A_2 or A_1, either is assumed to be equally effective, and k_f and k_r are the overall specific reaction rate constants for the forward and reverse reactions.

Further simplification is obtained by assuming that A_2 is an ideal dissociating gas (Lighthill 1957). In that case, writing c_e for the equilibrium atom mass fraction of A_1 atoms in the mixture, we have

$$c_e^2/(1 - c_e^2) = (\rho_d RT/pW_2) \exp(-DW_2/RT) \tag{2}$$

(R is the universal gas constant, T the absolute temperature, p the pressure, W_2 the molecular weight of the molecules and D the dissociation energy per unit mass). ρ_d is a characteristic dissociation density which, for the ideal gas, is assumed to be constant.

The flow equations are linearized, assuming small perturbations to the mean flow. Explicit solutions for the variation of pressure, density, atom concentration and temperature on the wall behind a sharp corner in supersonic flow are found as an example. It is found that the zone of influence of the corner is bounded upstream by the 'frozen flow' Mach line and also that the flow is not of the simple wave type as it would be in an ordinary inert gas flow.

2. Two-dimensional steady flow

In the particular case of two-dimensional steady flow, with velocity components u and v directed along the x- and y-axes, respectively, the equations for a dissociating diatomic gas become*

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} + \frac{\partial p}{\partial x} = 0, \tag{3}$$

$$\rho u \frac{\partial v}{\partial x} + \rho v \frac{\partial v}{\partial y} + \frac{\partial p}{\partial y} = 0, \tag{4}$$

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} - \frac{1}{\tau} \{K(1-c) - c^2\} = 0, \tag{5}$$

$$u \frac{\partial p}{\partial x} + v \frac{\partial p}{\partial y} + \rho a_f^2 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + \frac{\rho a_f^2 \sigma}{\tau} \{K(1-c) - c^2\} = 0, \tag{6}$$

$$T u \frac{\partial s}{\partial x} + T v \frac{\partial s}{\partial y} + \frac{1}{\tau} \{K(1-c) - c^2\} (\mu_1 - \mu_2) = 0. \tag{7}$$

Equations (3) and (4) are the momentum equations (ρ is the mixture density) and equation (5) is the continuity equation for the atomic species (mass fraction c). τ is a characteristic reaction time, defined in terms of the specific reaction rate constant for recombination, k_r, as

$$\tau = W_2^2 / 4 k_r \rho^2 (1+c), \tag{8}$$

(k_r is measured in (mole/unit volume)$^{-2}$ per unit time). The quantity K is defined as

$$K = (W_2 k_f / 4 \rho k_r), \tag{9}$$

and can be related to the atom mass fraction under equilibrium conditions in some circumstances. For example, if we choose to evaluate an equilibrium composition c_e at local values of p and T then it can be shown that $K = (1+c) c_e^2 / (1 - c_e^2)$, c being the *actual* concentration of atoms under these conditions (Clarke 1958a). This form will be found useful below, but is discarded in the linear theory in favour of evaluation of c_e at local pressure p and entropy s.

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* A brief account of the equations (5), (6) and (7) is given in Appendix A.

Equation (6) is a rearranged form of the overall mass conservation equation (Kirkwood & Wood 1957). σ is a function of the thermodynamic variables only. In the present case

$$\sigma = \frac{\rho\beta_f}{C_{pf}}\left(\frac{\partial h}{\partial c}\right)_{p,T} + \frac{1}{\rho}\left(\frac{\partial \rho}{\partial c}\right)_{p,T}, \tag{10}$$

where

$$\beta_f = -\rho^{-2}\left(\frac{\partial \rho}{\partial T}\right)_{p,c}; \quad C_{pf} = \left(\frac{\partial h}{\partial T}\right)_{p,c}. \tag{10a}$$

(β_f is the volume expansion coefficient and C_{pf} the specific heat at constant pressure, both for the mixture in a chemically frozen state.)

The thermal and caloric equations of state for the ideal dissociating gas are given by

$$p = \rho(1+c)\,(R/W_2)\,T, \tag{11}$$

$$h = (4+c)\,(R/W_2)\,T + cD, \tag{12}$$

respectively. h is the specific enthalpy and D is the dissociation energy per unit mass.* σ can be evaluated via equations (10a), (11), (12). In the present case

$$\sigma = [(DW_2/RT)+1]\,[4+c]^{-1} - [1+c]^{-1}. \tag{13}$$

Equation (7) is the entropy equation, derived from the energy equation

$$\rho u \frac{\partial h}{\partial x} + \rho v \frac{\partial h}{\partial y} - u \frac{\partial p}{\partial x} - v \frac{\partial p}{\partial y} = 0, \tag{14}$$

and the thermodynamic equation

$$T\,ds = dh - \rho^{-1}\,dp - (\mu_1 - \mu_2)\,dc. \tag{15}$$

μ_1 and μ_2 are the chemical potentials of atoms and molecules, respectively. It can be shown (Clarke 1958a) that

$$\mu_1 - \mu_2 = \frac{RT}{W_2}\log\left\{\left(\frac{c}{c_e}\right)^2 \frac{1-c_e^2}{1-c^2}\right\}, \tag{15a}$$

if c_e is evaluated at the local p and T values.

Two important results follow from the above set of equations. First, eliminating p between equations (3), (4) and (14) shows that

$$h + \tfrac{1}{2}(u^2 + v^2) = \text{const.} = h_0 \tag{16}$$

along streamlines, as in the inert gas-flow case. Secondly, defining the vorticity ζ as

$$\zeta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}, \tag{17}$$

equations (3), (4) and (15) show that

$$(u^2 + v^2)^{\frac{1}{2}}\,\zeta = -\frac{\partial h_0}{\partial n} + T\frac{\partial s}{\partial n} + (\mu_1 - \mu_2)\frac{\partial c}{\partial n}. \tag{18}$$

* Other authors have made use of the dissociation energy per molecule, written as d usually. The relation between D above and d is $D = N_0 d/W_2$ where N_0 is Avogadro's number. The quantities $W_2 D/R = d/k$ (k = Boltzmann's constant) have the dimensions of temperature and are sometimes written as T_d. For oxygen $T_d = 59,000\ °K$.

The operator $\partial/\partial n$ is equal to $(u/q)\,\partial/\partial y - (v/q)\,\partial/\partial x$, where $q^2 = u^2 + v^2$, and denotes differentiation normal to the streamlines. Equation (18) is Crocco's theorem in two dimensions, generalized to include the case of chemical reactions within the flow field (see Hayes & Wu 1958). h_0 will be assumed constant everywhere (the flow is assumed to originate in a region of constant stagnation enthalpy). Using equation (15a), equation (18) in these circumstances becomes

$$(u^2+v^2)^{\frac{1}{2}}\,\zeta = T\frac{\partial s}{\partial n} + \frac{RT}{W_2}\log\left\{\left(\frac{c}{c_e}\right)^2\frac{1-c_e^2}{1-c^2}\right\}\frac{\partial c}{\partial n}. \tag{19}$$

It follows that ζ is only zero when the flow is in complete chemical equilibrium ($c = c_e$) or when the flow is chemically frozen ($c = $ const.). (Note that equations (7) and (15a) show that $s = $ const. everywhere in these cases.)

Suppose now that the actual atom concentration c differs but little from the local equilibrium value evaluated at local p and T, i.e. put

$$c = c_e + \bar{c}, \quad \bar{c} \ll c_e.$$

If we assume in addition that $\bar{c} \ll 1 - c_e$, the entropy equation (equation (7)) with the aid of equation (15a) can be written approximately as

$$u\frac{\partial s}{\partial x} + v\frac{\partial s}{\partial y} \simeq \frac{2R}{W_2}\frac{\bar{c}^2}{c_e(1-c_e^2)\,\tau_e}, \tag{20}$$

where $\tau_e = W_2^2(1-c_e)/8k_r\rho_e^2 c_e$. ($\rho_e$ is the density which would occur at the local values of p and T if the local atom concentration was equal to the equilibrium value c_e.) This result indicates that the entropy rise along streamlines is of second order in the deviation of concentration from its equilibrium value at local values of p and T. We now make a slight but decisive change in the interpretation of the local equilibrium state. It is assumed that c_e *from now on* refers to an equilibrium composition at the local pressure and *entropy* values, and that c differs from this c_e by an amount c', i.e. we put

$$c = c_e + c'. \tag{21}$$

By analogy with the case for which c_e is evaluated at local p and T, we now write the chemical reaction rate term as

$$(1/\tau)\{K(1-c) - c^2\} \simeq -c'/\tau', \tag{22}$$

thereby defining τ'. (It does not seem possible to evaluate τ' *a priori* in the same way as with τ_e above, since with c_e evaluated at local p and s, K in equation (9) no longer becomes a simple function of concentrations.) Then equations (5) and (6) can be written in approximate form,

$$u\frac{\partial c_e}{\partial x} + v\frac{\partial c_e}{\partial y} + u\frac{\partial c'}{\partial x} + v\frac{\partial c'}{\partial y} + \frac{c'}{\tau'} = 0, \tag{23}$$

$$u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y} + \rho a_f^2\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) - \rho a_f^2\,\sigma\frac{c'}{\tau'} = 0, \tag{24}$$

and by comparison with equation (20) we write

$$u\frac{\partial s}{\partial x} + v\frac{\partial s}{\partial y} \sim O\left(\frac{R}{W_2}\frac{c'^2}{\tau'}\right). \tag{25}$$

Since c_e now refers to equilibrium at local p and s values,

$$dc_e = \left(\frac{\partial c_e}{\partial p}\right)_s dp + \left(\frac{\partial c_e}{\partial s}\right)_p ds. \tag{26}$$

Writing in future $\qquad\qquad (\partial c_e/\partial p)_s = \lambda, \tag{26a}$

for brevity, equations (25) and (26) give

$$u\frac{\partial c_e}{\partial x} + v\frac{\partial c_e}{\partial y} = \lambda\left(u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y}\right) + O\left[\frac{R}{W_2}\frac{c'^2}{\tau'}\left(\frac{\partial c_e}{\partial s}\right)_p\right]. \tag{27a}$$

Equation (23) can now be written approximately as

$$\lambda\left(u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y}\right) + u\frac{\partial c'}{\partial x} + v\frac{\partial c'}{\partial y} + \frac{c'}{\tau'} = 0, \tag{27}$$

since the term in c'^2/τ' is of a smaller order of magnitude than c'/τ'. (We show below that $(\partial c_e/\partial s)_p$ is less than order unity.)

In order to find the quantity λ we proceed as follows. We can write

$$\lambda = \left(\frac{\partial c_e}{\partial p}\right)_T + \left(\frac{\partial c_e}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_{s,e}, \tag{28}$$

where the subscript e is added to the last partial derivative to emphasize that it is to be evaluated with c following its equilibrium composition. Under conditions of chemical equilibrium $\mu_1 = \mu_2$ and equation (15) becomes

$$T\,ds = dh - \rho^{-1}\,dp.$$

At constant entropy, therefore,

$$\left(\frac{\partial h}{\partial T}\right)_{p,e} dT + \left(\frac{\partial h}{\partial p}\right)_{T,e} dp - \frac{1}{\rho}dp = 0$$

and so $\qquad \left(\frac{\partial T}{\partial p}\right)_{s,e} = \left[\rho^{-1} - \left(\frac{\partial h}{\partial p}\right)_{T,e}\right] \Big/ \left(\frac{\partial h}{\partial T}\right)_{p,e}. \tag{29}$

λ can now be found via equations (28), (29), (11), (12) and (2). For the ideal dissociating gas equation (2) shows that

$$\left(\frac{\partial c_e}{\partial p}\right)_T = -\frac{c_e(1-c_e^2)}{2p}; \quad \left(\frac{\partial c_e}{\partial T}\right)_p = \frac{c_e(1-c_e^2)(D'+1)}{2T},$$

where we now write D' for $W_2 D/RT$, and equation (12) shows that

$$\left(\frac{\partial h}{\partial p}\right)_{T,e} = \frac{RT}{W_2}(D'+1)\left(\frac{\partial c_e}{\partial p}\right)_T,$$

$$\left(\frac{\partial h}{\partial T}\right)_{p,e} = (4+c_e)\frac{R}{W_2} + \frac{RT}{W_2}(D'+1)\left(\frac{\partial c_e}{\partial T}\right)_p.$$

The final result for the ideal gas is therefore

$$p\lambda = c_e(1-c_e^2)\left\{\frac{(D'+1)(1+c_e)-(4+c_e)}{(D'+1)^2 c_e(1-c_e^2)+2(4+c_e)}\right\}. \tag{30}$$

In order to find $(\partial c_e/\partial s)_p$ we first write it in the form

$$\left(\frac{\partial c_e}{\partial s}\right)_p = \left(\frac{\partial c_e}{\partial T}\right)_p \left(\frac{\partial T}{\partial s}\right)_{p,e};$$

whence it follows, since $(\partial s/\partial T)_{p,e} = (\partial h/\partial T)_{p,e}/T$ from the thermodynamic equation above, that

$$\left(\frac{\partial c_e}{\partial s}\right)_p = \left(\frac{\partial c_e}{\partial T}\right)_p T \Big/ \left(\frac{\partial h}{\partial T}\right)_{p,e}. \tag{31}$$

From the results given above, the value of the derivative in the ideal dissociating gas is

$$\frac{R}{W_2}\left(\frac{\partial c_e}{\partial s}\right)_p = \frac{c_e(1-c_e^2)(D'+1)}{2(4+c_e)+(D'+1)^2 c_e(1-c_e^2)}. \tag{32}$$

It can be seen that $R(\partial c_e/\partial s)_p/W_2$ is roughly of order D'^{-1}. For an oxygen-like ideal gas $D' = 59,000/T$ so that D' is roughly of order 10 in the interesting range of dissociation.

3. Small disturbance approximations

The assumption will now be made that disturbances to the free stream are small. The free stream is taken to be a gas whose velocity is U, parallel to the x-axis, and whose pressure, density and temperature are given by p_∞, ρ_∞ and T_∞. The degree of dissociation in the free stream is c_∞ and this is necessarily an equilibrium value.

Furthermore, we assume that c_e differs but little from c_∞, an assumption which is justifiable provided both p and s do not change appreciably from their free-stream values. The (dimensionless) disturbance quantities are defined as follows,

$$\left.\begin{aligned}
p &= p_\infty(1+p'), \\
T &= T_\infty(1+T'), \\
\rho &= \rho_\infty(1+\rho'), \\
u &= U(1+u'), \\
v &= Uv', \\
c &= c_e+c', \\
c_e &= c_\infty+c'_e,
\end{aligned}\right\} \tag{33}$$

where all the primed quantities are very much less than unity. Choosing some suitable characteristic length* L, and writing

$$x = L\xi, \quad y = L\eta, \tag{34}$$

the flow equations can now be expressed in dimensionless form. In writing down these equations we assume that squares and products of disturbance quantities are negligible to a first order of approximation. Equations (3) and (4) become

$$\rho_\infty U^2 \frac{\partial u'}{\partial \xi} + p_\infty \frac{\partial p'}{\partial \xi} = 0, \tag{35}$$

$$\rho_\infty U^2 \frac{\partial v'}{\partial \xi} + p_\infty \frac{\partial p'}{\partial \eta} = 0. \tag{36}$$

* There is no *geometric* length characteristic of the flow round a sharp corner. L is entirely arbitrary and is introduced here solely for convenience so that the equations can be written in dimensionless form.

Since λ will not differ markedly from its free-stream value, equation (27) becomes

$$p_\infty \lambda_\infty \frac{\partial p'}{\partial \xi} + \frac{\partial c'}{\partial \xi} + \frac{c'}{\Gamma} = 0, \tag{37}$$

where suffix ∞ indicates evaluation at free-stream conditions and we write

$$\Gamma = \tau_\infty U/L, \tag{38}$$

where τ_∞ is taken as the mean value of τ', i.e.

$$\tau_\infty = \mathrm{Av}\left(-c'\tau\{K(1-c)-c^2\}^{-1}\right). \tag{39}$$

(Γ is the ratio of a characteristic reaction time to a characteristic flow time.)
Likewise equation (24) reduces approximately to

$$p_\infty \frac{\partial p'}{\partial \xi} + \rho_\infty a_f^2 \left(\frac{\partial u'}{\partial \xi} + \frac{\partial v'}{\partial \eta}\right) - \rho_\infty a_{f\infty}^2 \sigma_\infty \frac{c'}{\Gamma} = 0. \tag{40}$$

We may remark here that a_f, the frozen sound speed, is defined as

$$a_f^2 = \left(\frac{\partial p}{\partial \rho}\right)_{s,c},$$

(suffixes s and c indicating that entropy and concentration are held constant during the differentiation). It readily follows from equation (15), which may also be written as
$$T\,ds = de + p\,d(\rho^{-1}) - (\mu_1 - \mu_2)\,dc$$
(e is the specific internal energy $= 3(R/W_2)\,T + cD$ for the ideal gas), that*

$$a_f^2 = \frac{(\partial h/\partial T)_{p,c}}{(\partial e/\partial T)_{\rho,c}}\frac{p}{\rho} = \frac{4+c}{3}\frac{p}{\rho}. \tag{41}$$

Differentiating equation (40) with respect to η, the terms in $\partial^2 p'/\partial\xi\,\partial\eta$ and $\partial^2 u'/\partial\xi\,\partial\eta$ can be eliminated in terms of derivatives of v' by using equations (35) and (36). The result is

$$-U^2 \frac{\partial^2 v'}{\partial \xi^2} + a_{f\infty}^2 \left(\frac{\partial^2 v'}{\partial \xi^2} + \frac{\partial^2 v'}{\partial \eta^2}\right) - a_{f\infty}^2 \sigma_\infty \Gamma^{-1}\frac{\partial c'}{\partial \eta} = 0. \tag{42}$$

The c' term in equation (42) can be eliminated by using equation (37) differentiated with respect to η and the result is

$$\Gamma\frac{\partial}{\partial \xi}\left\{(a_{f\infty}^2 - U^2)\frac{\partial^2 v'}{\partial \xi^2} + a_{f\infty}^2 \frac{\partial^2 v'}{\partial \eta^2}\right\} + (a_{f\infty}^2 - U^2)\frac{\partial^2 v'}{\partial \xi^2} + a_{f\infty}^2 \frac{\partial^2 v'}{\partial \eta^2}$$
$$-\rho_\infty U^2 a_{f\infty}^2 \sigma_\infty \lambda_\infty \frac{\partial^2 v'}{\partial \xi^2} = 0. \tag{43}$$

* At constant s and c the thermodynamic equation gives
$$[1-\rho(\partial h/\partial p)_{T,c}]\,dp = \rho(\partial h/\partial T)_{p,c},$$
$$[1-\rho^2 p^{-1}(\partial e/\partial p)_{T,c}]\,d\rho = \rho^2 p^{-1}(\partial e/\partial T)_{\rho,c}.$$
But for the ideal gas h is not a function of p and e is not a function of ρ under present circumstances. The result given in equation (41) follows at once.

But it has been shown by Clarke (1958a) that

$$1 + \rho_\infty a_{f\infty}^2 \, \sigma_\infty \lambda_\infty = (a_{f\infty}/a_{e\infty})^2, \qquad (44)$$

where $a_{e\infty}$ is the equilibrium speed of sound in the free stream. Defining the frozen and equilibrium Mach numbers

$$M_f = U/a_{f\infty}, \quad M_e = U/a_{e\infty} \qquad (45)$$

it follows that equation (43) can be rewritten as

$$\Gamma \frac{\partial}{\partial \xi} \left\{ (1 - M_f^2) \frac{\partial^2 v'}{\partial \xi^2} + \frac{\partial^2 v'}{\partial \eta^2} \right\} + (1 - M_e^2) \frac{\partial^2 v'}{\partial \xi^2} + \frac{\partial^2 v'}{\partial \eta^2} = 0. \qquad (46)^*$$

In order to find the equation satisfied by the pressure perturbation, the process of elimination of the variables can now be repeated in precisely the same way as that outlined above, only this time a start is made by differentiating equation (40) with respect to ξ, and it then readily follows that p' satisfies an equation identical in all respects with equation (46).

The two equations will now be used to find the flow behind a sharp corner in a supersonic stream. Before doing so, however, it is interesting to note that in the limiting cases of $\Gamma = 0$ and $\Gamma = \infty$, equation (46) reduces to the ordinary wave equation for sound propagation at the equilibrium and frozen sound speeds, respectively. In practice $0 < \Gamma < \infty$, and it is with these conditions that we will deal below.

4. Supersonic flow round a sharp corner

The flow is assumed to be supersonic in the sense that both M_f and M_e are greater than unity. Figure 1 is a sketch of the general configuration. At point O the flow turns through a *small* angle $-\theta$, so that the equations for v' and p' derived
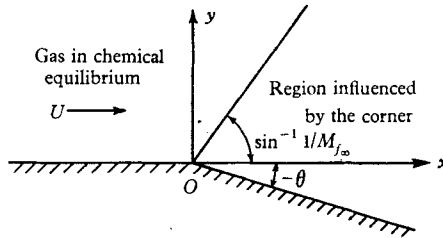

FIGURE 1. Supersonic flow round a sharp corner.

above can be assumed valid descriptions of the field. The flow from $\xi = -\infty$ to $\xi = 0$ is uniform and quantities there will be denoted by suffix ∞.

The boundary condition at the wall is given by

$$v' = -\tan\theta(1 + u'), \quad \text{when} \quad \eta = -\xi \tan\theta,$$

but to the present order of approximation this can be replaced by

$$v' \simeq -\theta, \quad \text{when} \quad \eta \simeq 0. \qquad (47)$$

* The writer's attention has been drawn to a recent paper by Moore & Gibson (1959) in which a similar equation is derived by a different approach. These authors solve a similar problem to that treated below by approximating equation (46) in the form of the telegraph equation via a suitable co-ordinate transformation.

Since the flow is supersonic, all the disturbance quantities are identically zero upstream of the corner* and, accordingly, we define the Laplace transform of a disturbance quantity by

$$\bar{\delta}(z, \eta) = \int_0^\infty \delta'(\xi, \eta) \exp(-z\xi) \, d\xi, \tag{48}$$

(where δ' is any disturbance variable).

It follows that $\bar{v}$ satisfies the equation

$$\frac{d^2\bar{v}}{d\eta^2} - (zB_f)^2 \left[\frac{B^2 + z\Gamma}{1 + z\Gamma} \right] \bar{v} = 0, \tag{49}$$

where z is the Laplace operator (see equation (48)) and $\bar{p}$ satisfies a similar equation. In equation (49)

$$B_f^2 = M_f^2 - 1, \quad B_e^2 = M_e^2 - 1, \quad B^2 = B_e^2/B_f^2 > 1. \tag{50}$$

We choose the following solution for $\bar{v}$,

$$\bar{v} = \text{const. } \exp\left(-zB_f \left[\frac{B^2 + \Gamma z}{1 + \Gamma z} \right]^{\frac{1}{2}} \eta \right),$$

since it represents an outgoing wave motion. The transformed boundary condition, equation (47), is

$$\bar{v}(z, 0) = -\theta/z,$$

whence
$$\bar{v} = -(\theta/z) \exp\left(-zB_f \left[\frac{B^2 + \Gamma z}{1 + \Gamma z} \right]^{\frac{1}{2}} \eta \right). \tag{51}$$

Since equation (49) is also satisfied by $\bar{p}$ we can write (where A is a constant to be determined),

$$\bar{p} = A \exp\left(-zB_f \left[\frac{B^2 + \Gamma z}{1 + \Gamma z} \right]^{\frac{1}{2}} \eta \right).$$

The transformed version of equation (36), however, is

$$\frac{p_\infty}{\rho_\infty U^2} \frac{\partial \bar{p}}{\partial \eta} = -z\bar{v}$$

and it readily follows from equation (51) that

$$\bar{p} = -\left(\frac{\rho_\infty U^2}{p_\infty} \right) \frac{\theta}{zB_f} \left[\frac{1 + \Gamma z}{B^2 + \Gamma z} \right]^{\frac{1}{2}} \exp\left(-zB_f \left[\frac{B^2 + \Gamma z}{1 + \Gamma z} \right]^{\frac{1}{2}} \eta \right). \tag{52}$$

Defining a pressure coefficient C_p as

$$C_p = 2p_\infty p'/\rho_\infty U^2, \tag{53}$$

the value of this quantity on the wall ($\eta = 0$ to a sufficient order of accuracy) can be found from

$$\bar{C}_{pw} = -\frac{2\theta}{zB_f} \left[\frac{1 + \Gamma z}{B^2 + \Gamma z} \right]^{\frac{1}{2}}. \tag{54}$$

* See remarks made in §5 below.

The transform on the right-hand side of equation (54) can be inverted (Erdélyi, Magnus, Oberhettinger & Tricomi 1954) and we find that

$$C_{pw} = -(2\theta/B_f)\left\{\exp\left[-(B^2+1)\,\xi/2\Gamma\right]I_0[(B^2-1)\,\xi/2\Gamma]\right.$$

$$\left. + \int_0^{\xi/\Gamma}\exp\left[-\tfrac{1}{2}(B^2+1)\,W\right]I_0[\tfrac{1}{2}(B^2-1)\,W]dW\right\}. \qquad (55)$$

I_0 is the zero-order modified Bessel function of the first kind. Figure 2 shows $(B_fC_{pw}/2\theta)+1$ plotted against $x/\tau_\infty U(=\xi/\Gamma)$ for a typical value of B^2, namely 1·5. With this value for B^2, $M_e = 2\cdot12$ and $M_f = 1\cdot83$, respectively, if

$$(a_{f\infty}/a_{e\infty})^2 = 1\cdot35.$$

This value of the speeds of sound ratio can arise, for example, at a pressure of one atmosphere and temperature of 4,250 °K in an 'oxygen-like' ideal dissociating gas (see Clarke 1958a).
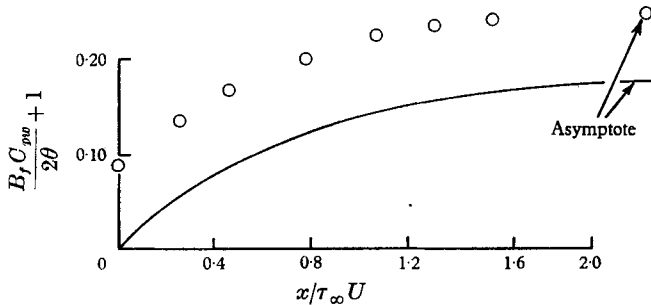

FIGURE 2. Variation of pressure on the wall; $B^2 = 1\cdot5$. $\bigcirc$ = characteristics solution.

It can be seen from figure 2 that, in contrast to the inert gas Prandtl–Meyer flow round a corner, the pressure is not constant on the wall downstream of the point O, but rises steadily as x increases. It can be shown that $C_{pw} \to -2\theta/B_e$ as $\xi/\Gamma \to \infty$. The integral in equation (55) can be rewritten* as

$$B^{-1} - \int_{\xi/\Gamma}^{\infty}\exp\left[-\tfrac{1}{2}(B^2+1)W\right]I_0[\tfrac{1}{2}(B^2-1)W]dW.$$

When $\xi/\Gamma \to \infty$ the asymptotic form of I_0 can be used both in the first term of equation (55) and in the integral above (i.e. $I_0(\alpha) \sim (2\pi\alpha)^{-\frac{1}{2}}\exp\alpha$). The asymptotic form of C_{pw} is then given by

$$-B_fC_{pw}/2\theta \sim [\pi(B^2-1)\,\xi/\Gamma]^{-\frac{1}{2}}\exp(-\xi/\Gamma)+B^{-1}-(B^2-1)^{-\frac{1}{2}}\mathrm{erfc}\,(\xi/\Gamma)^{\frac{1}{2}}, \qquad (56)$$

where erfc is the complementary error function. The result quoted above follows in the limit as $\xi/\Gamma \to \infty$, and $(B_fC_{pw}/2\theta)+1$ tends asymptotically to the value 0·183 in figure 2. The percentage variation of pressure behind the corner is quite significant therefore.

As remarked in §2, the flow is not irrotational for $0 < \Gamma < \infty$. It seems reasonable to suppose that the continuous pressure rise behind the corner results

$$* \;\textit{Note:}\int_0^{\infty}\exp(-\alpha\xi)I_0(\beta\xi)\,d\xi = (\alpha^2-\beta^2)^{-\frac{1}{2}}.$$

from the reflexion of the primary (expansive) disturbances from the vortex sheets as compression waves. The vorticity arises as a direct consequence of the (thermodynamically irreversible) chemical reactions.

In order to find the density variations in the flow it is observed that the mass conservation equation in its more familiar form, namely

$$\frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} = 0, \tag{57a}$$

reduces to

$$\frac{\partial \rho'}{\partial \xi} = -\frac{\partial u'}{\partial \xi} - \frac{\partial v'}{\partial \eta}$$

in the present approximation. Using equation (35) it follows that

$$\frac{\partial \rho'}{\partial \xi} = \frac{p_\infty}{\rho_\infty U^2} \frac{\partial p'}{\partial \xi} - \frac{\partial v'}{\partial \eta}.$$
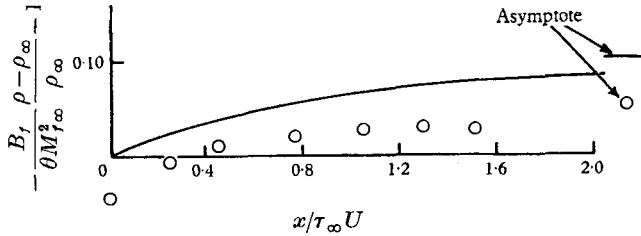

FIGURE 3. Variation of density on the wall; $B^2 = 1.5$, $(a_{f\infty}/a_{e\infty})^2 = 1.35$.
$\circ$ = characteristics solution.

The transform of the density increment, $\bar{\rho}$, is therefore (using equation (58))

$$\bar{\rho} = \tfrac{1}{2}\bar{C}_p - z^{-1}(\partial \bar{v}/\partial \eta).$$

In particular it is found from equations (54) and (51) that, on the wall,

$$\bar{\rho}_w = -\frac{\theta}{zB_f}\left[\frac{1+\Gamma z}{B^2+\Gamma z}\right]^{\frac{1}{2}}\left\{M_f^2 + B_f^2\frac{(B^2-1)}{(1+\Gamma z)}\right\}. \tag{57}$$

The first term here is simply $(\tfrac{1}{2}M_f^2)$ times the pressure coefficient transform. Noting that $1 + \Gamma z$ is the transform of $\Gamma^{-1}\exp(-\xi/\Gamma)$ and making use of the convolution theorem, it can eventually be shown (see Appendix B) that

$$-B_f\rho_w'/\theta M_f^2 = \exp\left[-(B^2+1)\xi/2\Gamma\right]I_0[(B^2-1)\xi/2\Gamma]$$

$$+ (a_{f\infty}/a_{e\infty})^2\int_0^{\xi/\Gamma}\exp\left[-\tfrac{1}{2}(B^2+1)W\right]I_0[\tfrac{1}{2}(B^2-1)W]dW. \tag{58}$$

The value of $-(B_f\rho_w'/\theta M_f^2) - 1$ is shown plotted against $x/\tau_\infty U$ in figure 3 for $B^2 = 1.5$ and $(a_{f\infty}/a_{e\infty})^2 = 1.35$. By similar methods to those used for C_{pw} we can show that $\rho_w' \to -\theta M_e^2/B_e$ as $x/\tau_\infty U \to \infty$. It is observed that the variation of density behind the corner is smaller than that of the pressure in the present case and that ρ_w' decreases continuously along the wall.

The values of atom concentration on the wall can be found as follows. Equation (37) can be rewritten in the form

$$\frac{\partial}{\partial \xi}(c'\exp \xi/\Gamma) = -p_\infty\lambda_\infty\exp(\xi/\Gamma)\frac{\partial p'}{\partial \xi}$$

and it follows after an integration by parts that c' on the wall is given by

$$c'_w = -(\rho_\infty U^2 \lambda_\infty / 2) \left\{ C_{pw}(\xi) - \exp(-\xi/\Gamma) \int_0^{\xi/\Gamma} C_{pw}(W) e^W \, dW \right\}. \quad (59a)$$

Making use of the expression for C_{pw} (equation (55)) the expression for c'_w reduces to (see Appendix B),

$$c'_w = (\rho_\infty U^2 \lambda_\infty \theta / B_f) \exp[-(B^2+1)\xi/2\Gamma] I_0[(B^2-1)\xi/2\Gamma]. \quad (59)$$

The asymptotic value of c'_w as $\xi/\Gamma \to \infty$ is therefore

$$c'_w \sim (\rho_\infty U^2 \lambda_\infty \theta / B_f) [\pi(B^2-1)\xi/\Gamma]^{-\frac{1}{2}} \exp(-\xi/\Gamma), \quad (60)$$

showing, as we might expect, that $c'_w \to 0$ and the concentration approaches a new equilibrium value.

The 'small disturbance' version of equation (27a) can be written as

$$\frac{\partial c'_e}{\partial \xi} = p_\infty \lambda_\infty \frac{\partial p'}{\partial \xi},$$

where it can now be verified (using equation (59)) that the last term there can be neglected in a first approximation, at least near the wall. (There seems to be no reason why it should not be negligible everywhere, but equation (59) verifies that it is so only near the wall.) Then

$$c'_{ew} = p_\infty \lambda_\infty p'_w = \tfrac{1}{2} \rho_\infty U^2 \lambda_\infty C_{pw}. \quad (61)$$

From the definitions of c'_e and c' (note $c - c_\infty = c'_e + c'$) and using the results equations (60) and (61), it now follows that

$$c_w - c_\infty = -(p_\infty \lambda_\infty M_f^2 \theta(4+c_\infty)/3B_f)$$
$$\times \int_0^{\xi/\Gamma} \exp[-\tfrac{1}{2}(B^2+1)W] I_0[\tfrac{1}{2}(B^2-1)W] dW. \quad (62)$$

c_w is the actual atom concentration at the wall and use has been made of the definition of $a_{f\infty}^2$ from equation (41). $p_\infty \lambda_\infty$ can be found from equation (30).

From the previous results the temperature variation along the wall can be found, using the thermal equation of state (equation (11)) for the mixture. The dimensionless temperature increment is given to a sufficient degree of accuracy by

$$T'_w = p'_w - \rho'_w - \frac{c_w - c_\infty}{1 + c_\infty}. \quad (63)$$

As an illustration figures 4 and 5 show $(c_w - c_\infty)$ and $(T_w - T_\infty)$ $(= T_\infty T'_w)$ plotted against $x/\tau_\infty U$ for a θ of $5°$. The values of p_∞ and T_∞ are taken to be one atmosphere and $4250 °K$, and the gas is an 'oxygen-like' ideal dissociating one. In that case D' in equation (30) is equal to $59,000/T_\infty = 13 \cdot 68$ and with $\rho_d = 150 \, \mathrm{g/ml.}$, $c_\infty = 0 \cdot 78$. Thus $p_\infty \lambda_\infty = 0 \cdot 086$.

The temperature rises steadily behind the corner (after the abrupt drop at the corner), approaching the asymptotic value shown in figure 5. The rise in temperature is a direct result of the fall in atom concentration. The recombination reaction results in the liberation of dissociation energy which reappears in the gas as random, thermal energy.

The energy equation (equation (14)) in the small disturbance approximation shows that

$$h_w - h_\infty = \tfrac{1}{2}U^2 C_{pw}. \tag{64}$$

(N.B. C_{pw} = pressure coefficient at the wall.) Thus the enthalpy on the wall rises continuously after its abrupt fall at the corner and, in conformity with the adverse pressure gradient, the velocity must decrease as $x/\tau_\infty U$ increases (see equation (16)). The velocity on the wall behind the corner is always greater than U, however.
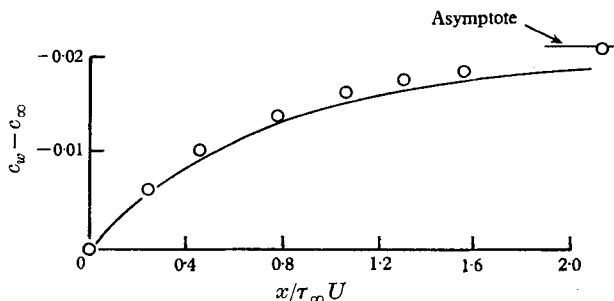

FIGURE 4. Variation of atom mass fraction on the wall; $B^2 = 1\cdot5$, $(a_{f\infty}/a_{e\infty})^2 = 1\cdot35$, $p_\infty = 1$ atm., $T_\infty = 4250$ °K, $c_\infty = 0\cdot780$. $\bigcirc$ = characteristics solution.
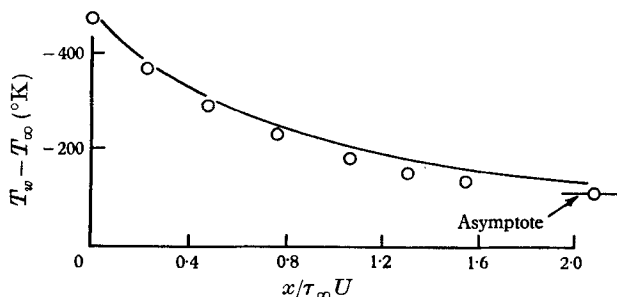

FIGURE 5. Variation of temperature on the wall; $B^2 = 1\cdot5$, $(a_{f\infty}/a_{e\infty})^2 = 1\cdot35$, $p_\infty = 1$ atm., $T_\infty = 4250$ °K, $c_\infty = 0\cdot780$. $\bigcirc$ = characteristics solution.

From the values of p, T and c computed above, the value of τ_∞ from equation (39) can be calculated. In the present case it is found that $\tau_\infty = 3\cdot85 \times 10^9/k_{r\infty}$. (It is found that τ', of which τ_∞ is the mean value, varies by about $\pm 10\%$ for $0 \leqslant x/\tau_\infty U \leqslant 2$.) Since k_r may be anywhere in the range 10^{14}–10^{17}ml.^{2}/mole^{2}sec, τ_∞ may be anywhere in the range $40\,\mu$sec to $0\cdot04\,\mu$sec. For the example quoted $U \sim 3 \times 10^5$ cm/sec, so that $x/\tau_\infty U = 1$ corresponds to an x of between 12 to $0\cdot012$ cm. The length scale of the relaxation zone is seen to depend quite critically therefore on the value of $k_{r\infty}$. Thus if the density increment ρ'_w could be measured (with an interferometer, for example) it should be possible to obtain a reasonable estimate of the magnitude of $k_{r\infty}$.

Conditions like those adopted to illustrate the present theory could be achieved in the zone of equilibrium flow behind the primary shock wave in a shock tube. The feasibility of checking the theory by these means is being investigated.

The linearizations which have been made in §3 would appear to be justified by the results obtained in the present section, provided both Mach numbers, M_f and

M_e, are neither too large nor too near unity. However, as τ_∞ becomes very small the gradients of velocity, temperature, etc., become very large in the streamwise (roughly, the x-wise) direction and it seems highly probable that it would be necessary in such cases to take account of the transport phenomena in the very short relaxation zone behind the corner. This question is, however, outside the scope of the present work. It should be reiterated that no account has been taken of the energy interchanges which occur in the internal modes of the molecules. The effects of these internal relaxations are ordinarily assumed to be negligible in the region of appreciable dissociation, but the present simple theory may be modified to take account of their presence and so provide a check on their relative importance.

5. Further remarks on the flow round a corner

The previous section has been almost entirely devoted to a discussion of the variations of p, ρ, T, etc., on the wall. This is primarily because it is much easier to evaluate these quantities analytically there, but solutions for the whole flow field can be obtained. In particular, the inversion of the exponential term in the transform of $\bar{v}$ and $\bar{p}$ can be accomplished (Morrison 1956). Reference to Morrison's paper will show that the final (physical plane) values for the disturbance variables would, however, be in the form of very intractable expressions. It is hoped that the simpler discussion of flow at (and hence, as can be seen from the form of the equations, also near) the wall will be of some interest.

Finally, we may note some general results from the solutions obtained. The Laplace inversion theorem shows that

$$v'(\xi, \eta) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \frac{\theta}{zB_f} \exp\left[\xi z - zB_f \left(\frac{B^2 + \Gamma z}{1 + \Gamma z}\right)^{\frac{1}{2}} \eta\right] dz.$$

(a is a real number greater than the real part of the singularities in the integrand.) Closing the straight line contour with an infinite semicircle to the right, it can be seen that integration along the semicircle is equivalent to that on the original contour. The index of the exponential on the new contour tends to

$$|z| \exp\left[(i \arg z)(\xi - B_f \eta)\right]$$

as $|z| \to \infty$. Since $-\frac{1}{2}\pi < \arg z < \frac{1}{2}\pi$, the integral approaches zero, therefore, if $\xi - B_f \eta < 0$.

It follows that the effect of the corner is first felt along a line through the corner inclined at an angle $\sin^{-1}(M_f^{-1})$ to the free stream (i.e. the 'frozen' Mach angle). In contrast to the inert (or equilibrium) cases, it also follows from the integral above that the disturbance is not constant among characteristic lines passing through the corner (Kirkwood & Wood 1957, have shown that the characteristic directions are defined by the local values of M_f in a reacting system). This result is in line with the general result, quoted by the above-named authors, that simple wave flow does not exist in a reacting gas mixture. A possible physical explanation of this phenomenon in two-dimensional flow has been given after equation (56) above.

In order to investigate the flow in the vicinity of the equilibrium Mach line through the corner we may proceed as follows. Let us consider the pressure coefficient, which, from equations (52) and (53), is given by

$$-\frac{C_p B_f}{2\theta} = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \sqrt{\left(\frac{1+\omega}{B^2+\omega}\right)} \exp\left\{\omega\xi' - \omega\eta' B_f \sqrt{\left(\frac{B^2+\omega}{1+\omega}\right)}\right\} \frac{d\omega}{\omega}, \quad (65)$$

where we have written $\Gamma z = \omega$, $\xi/\Gamma = \xi'$ and $\eta/\Gamma = \eta'$. Then it is convenient to put

$$\xi' - \eta' B_f B = \xi' - \eta' B_e = \delta \quad (66)$$

and to rewrite the integral in equation (65) as

$$-\frac{C_p B_f}{2\theta} = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \sqrt{\left(\frac{1+\omega}{B^2+\omega}\right)} \exp\left\{\frac{\delta\omega}{B} \sqrt{\left(\frac{B^2+\omega}{1+\omega}\right)}\right\}$$

$$\times \exp\left[\omega\xi'\left\{1 - \frac{1}{B}\sqrt{\left(\frac{B^2+\omega}{1+\omega}\right)}\right\}\right] \frac{d\omega}{\omega}. \quad (67)$$

In this form a solution valid for large values of ξ' and small values of δ can be obtained by the method of steepest descents. The index of the second exponential term in equation (67) is not a particularly manageable function of ω but fortunately it turns out that $\omega = 0$ is a saddle point. The appropriate steepest path comes from $\mathrm{Rl}\,\omega = -\infty$ below the real axis, approaches and leaves $\omega = 0$ along an approximately parabolic curve given by $\mathrm{Im}\,\omega = \pm(-\mathrm{Rl}\,\omega)^{\frac{1}{2}}$ and proceeds towards $\mathrm{Rl}\,\omega = -\infty$ above the real axis. It includes a semicircular indentation to the right of the simple pole at $\omega = 0$ and can be reconciled with the original inversion contour. Then we can write

$$\omega\{1 - B^{-1}\sqrt{[(B^2+\omega)/(1+\omega)]}\} = -\tfrac{1}{2}s^2,$$

where s is a real quantity, and it follows that

$$-\frac{C_p B_f}{2\theta} \sim \frac{1}{2B} + \frac{1}{2\pi i}\int_{-\infty}^{\infty} \exp\left(-\tfrac{1}{2}\xi's^2\right)\left\{\exp\left[\frac{\delta\omega}{B}\sqrt{\left(\frac{B^2+\omega}{1+\omega}\right)}\right]\sqrt{\left(\frac{1+\omega}{B^2+\omega}\right)}\frac{1}{\omega}\frac{d\omega}{ds}\right\}ds. \quad (68)$$

The term in braces in this integral must be expanded as a power series in the real variable s. A solution which is physically significant can be obtained from equation (68) when it is recognized that the expansion of the term

$$\omega\sqrt{\{(B^2+\omega)/(1+\omega)\}}$$

in the second exponential begins $(isB^2)/\sqrt{(B^2-1)}$. Then the leading term of the integral in equation (68) can be written as

$$\frac{1}{2\pi i}\int_{-\infty}^{\infty} \exp\left\{-\tfrac{1}{2}\xi's^2 + is\delta B/\sqrt{(B^2-1)}\right\}(sB)^{-1}ds$$

$$= \frac{1}{\pi B}\int_{0}^{\infty} \exp\left(-\tfrac{1}{2}\xi's^2\right)\sin\left\{s\delta B/\sqrt{(B^2-1)}\right\}s^{-1}ds$$

$$= \frac{1}{2B}\operatorname{erf}[\delta/\sqrt{\{2\xi'(1-B^{-2})\}}].$$

The final solution for C_p can be written out in terms of x, y, τ_∞, etc., and is

$$C_p \sim -\frac{2\theta}{B_e}\left\{\tfrac{1}{2} + \tfrac{1}{2}\operatorname{erf}\left(\frac{x - yB_e}{\sqrt{\{2x\tau_\infty U(1-B^{-2})\}}}\right)\right\}. \quad (69)$$

Recalling the definitions of ξ', Γ, etc., equation (69) may be expected to give an indication of the variation of C_p on either side of the equilibrium Mach line, provided that $x \gg \tau_\infty U$. (The writer is indebted to Prof. Lighthill for suggesting this approach to the problem.)

It should also be noted that the contour in equation (65) can be deformed into a single circuit embracing the branch points at $\omega = -1$ and $-B^2$, plus a single circuit surrounding the pole at $\omega = 0$. Then it follows that the latter circuit gives rise to the dominant contribution (namely B^{-1}), since any contribution from the former must be $O(\exp(-\xi'))$, when η' is appreciably smaller than ξ'/B_e, and this is negligible when $\xi' \gg 1$.

It follows from equation (69) that at distances from the corner large compared with the characteristic chemical length $\tau_\infty U$, a smooth but quite rapid fall of pressure occurs across the equilibrium Mach line. The pressure coefficient would appear to reach its ultimate, equilibrium, value of $-2\theta/B_e$ without falling markedly below this, in contrast to the situation occurring on and near the wall. There, it will be recalled, the pressure drops discontinuously across the frozen Mach line to its frozen flow value, $C_p = -2\theta/B_f$, thereafter rising steadily until the final equilibrium value is reached some way downstream. Equation (69) suggests that less and less pressure drop occurs across the frozen Mach line as distance from the corner increases, the majority of the decrease arising in the region centred about the equilibrium Mach line. The sharpness of this latter pressure drop for any given x and y is increased by a reduction of τ_∞ and it seems that the passage towards the full equilibrium flow limit of $\tau_\infty \to 0$ occurs quite smoothly. The centring of the pressure drop about the equilibrium line will, however, occur for any value of τ_∞, provided one is far enough away from the corner.

It is interesting to note that the dissipative effect of the chemical reactions in the gas smears the pressure drop over a wider and wider region around $x = yB_e$ as x increases, under any given conditions. Thus, far from the corner, the flow *appears* to be expanding through a fan of waves, even without the non-linear flattening effects which would be present in practice. One may conclude that such non-linear, convective terms will act to flatten out the pressure drop still further in these regions. The present analysis is the two-dimensional analogue of Chu's (1957) treatment of the one-dimensional unsteady piston problem and the conclusions are in agreement with those found in that case.

6. Comparison with characteristics solutions

Since the appearance of the first version of the present work (Clarke 1958*b*) some characteristics solutions of the flow round a corner have become available (Cleaver 1959). The results of this investigation are shown on figures 2 to 5 for comparison with the predictions of the linear theory. The characteristics solution was carried out for an identical set of free-stream conditions to those used in the linear theory example, and in fact constitutes an exact numerical solution of the equations 3 to 7 inclusive in § 2 above for the 'oxygen-like' ideal dissociating gas. k_r was assumed to be a constant, however, since no reliable information exists at present of its temperature (and possibly also concentration) dependence. In view of the relatively small percentage changes in T and c in the present example,

this is perhaps not a serious objection, particularly since k_r is unlikely to be a very strong function of either variable.

The agreement between the exact and linear theories is seen to be quite reasonable, particularly when it is recalled that the linear theory will in any case overestimate the pressure drop at the corner even when the gas is chemically inert. The *variation* of pressure in the relaxation zone is predicted quite well by the present linear theory, as can be seen from figure 6 which shows the ratio p_w/p_{w0} plotted against $x/\tau_\infty U$ for the two solutions (p_w = pressure on the wall, p_{w0} = pressure on the wall immediately behind the corner). With allowances for the classical defects in the linear theory, it would appear to give an adequate description of the relaxation zone behind the corner.
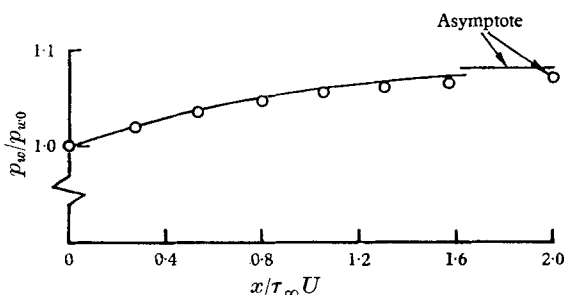

FIGURE 6. Ratio of pressure on the wall p_w to pressure immediately behind the corner p_{w0}. O = characteristics solution.

Appendix A

The term $\tau^{-1}\{K(1-c)-c^2\}$ which appears in equations (5), (6) and (7) in the text expresses the mass rate of production of atoms per unit mass of mixture due to the chemical reaction described in equation (1). It is derived as follows. The net rate of production of atoms measured in moles per unit volume per unit time is equal to $2\{k_f$ (concentration of A_2) (concentration of A_3) $- k_r$ (concentration of $A_1)^2$ (concentration of A_3)$\}$, the concentration being measured here in moles per unit volume. To write this result in terms of mass fractions, it is observed that the mass fraction of $A_2 = 1-c$, and the mass fraction of $A_3 = 1$. The molecular weight of A_3 is the mean molecular weight of the mixture, namely $W_2/1+c$. The net rate of atom production measured in terms of mass of atoms per unit mass of mixture per unit time is, therefore,

$$\frac{W_2}{\rho}\left\{k_f(1-c)\frac{\rho}{W_2}(1+c)\frac{\rho}{W_2} - k_r c^2 \frac{4\rho^2}{W_2^2}(1+c)\frac{\rho}{W_2}\right\}$$
$$= \left(4k_r\rho^2\frac{1+c}{W_2^2}\right)\left\{\frac{k_f}{4k_r}\frac{W_2}{\rho}(1-c) - c^2\right\}. \tag{A1}$$

At equilibrium there is no net rate of atom production, and so

$$(W_2 k_f/4\rho k_r)_e = c_e^2/1-c_e,$$

suffix e implying equilibrium. Choosing c_e to be the equilibrium value at the actual local p and T values and making use of equation (11) to relate ρ_e to ρ, it can be seen that $k_f W_2/4\rho k_r$ reduces to K as given above (equation (9)). The term in parentheses on the right side of equation (A1) is τ^{-1} as defined in equation (8).

The entropy equation (equation (7)) is derived from equations (14) and (15) giving

$$Tu\frac{\partial s}{\partial x} + Tv\frac{\partial s}{\partial y} = -(\mu_1 - \mu_2)\left(u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y}\right).$$ (A 2)

The last term in parentheses in equation (A 2) can be replaced by

$$\tau^{-1}\{K(1-c) - c^2\}$$

by equation (5) and it can be shown that

$$\mu_1 - \mu_2 = (R/W_2)\log\{c^2(1-c_e^2)/c_e^2(1-c^2)\};$$

whence the form of equation (7) follows.

The continuity equation in the present case can be written (see equation (57a))

$$u\frac{\partial\rho}{\partial x} + v\frac{\partial\rho}{\partial y} + \rho\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) = 0.$$ (A 3)

Writing density as a function of p, s and c,

$$d\rho = \left(\frac{\partial\rho}{\partial p}\right)_{s,c}dp + \left(\frac{\partial\rho}{\partial s}\right)_{p,c}ds + \left(\frac{\partial\rho}{\partial c}\right)_{p,s}dc.$$ (A 4)

$(\partial p/\partial\rho)_{s,c} = a_f^2$, the frozen sound speed. Using (A 4) and (A 3) we can now write

$$u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y} + \rho a_f^2\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial x}\right) + a_f^2\left(\frac{\partial\rho}{\partial s}\right)_{p,c}\left\{u\frac{\partial s}{\partial x} + v\frac{\partial s}{\partial y} - \left(\frac{\partial s}{\partial c}\right)_{p,\rho}\left(u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y}\right)\right\} = 0.$$ (A 5)

Making use of equations (5) and (7), it follows that the last term in (A 5) can be expressed as

$$-a_f^2\left(\frac{\partial\rho}{\partial s}\right)_{p,c}T^{-1}\left\{\mu_1 - \mu_2 + T\left(\frac{\partial s}{\partial c}\right)_{p,\rho}\right\}\frac{1}{\tau}\{K(1-c) - c^2\}.$$ (A 6)

The quantity $T^{-1}(\partial\rho/\partial s)_{p,c}\{\mu_1 - \mu_2 + T(\partial s/\partial c)_{p,\rho}\}$ in (A 6) is written as $-\rho\sigma$ in equation (6) in the text. The value of σ given in equation (10) can be obtained from manipulation of the thermodynamic equation. It is then in a suitable form for evaluation from the thermal and caloric equations of state. Details of the derivation are given by Clarke (1958a) but the equation of continuity was first given in this form by Kirkwood & Wood (1957).

Appendix B

The derivation of equation (58) from equation (57) proceeds as follows. Noting that

$$\bar{C}_{pw} = -\frac{\theta}{zB_f}\left[\frac{1+\Gamma z}{B^2+\Gamma z}\right]^{\frac{1}{2}}$$

we can write equation (57) as

$$\bar{\rho}_w = \frac{M_f^2}{2}\bar{C}_{pw} + \frac{B_f^2}{2}\frac{(B^2-1)}{1+\Gamma z}\bar{C}_{pw}.$$ (B 1)

Thus

$$\rho_w = \frac{M_f^2}{2}C_{pw} + B_f^2\frac{(B^2-1)}{2\Gamma}\int_0^\xi\exp\left(-\frac{\xi-\xi'}{\Gamma}\right)C_{pw}\left(\frac{\xi'}{\Gamma}\right)d\xi'.$$ (B 2)

Putting the value of C_{pw} from equation (55) into the integral in equation (B 2) gives a term proportional to

$$\int_0^\xi\exp\left(-\frac{\xi-\xi'}{\Gamma}\right)\exp\left[-\frac{(B^2+1)\xi'}{2\Gamma}\right]I_0\left[\frac{(B^2-1)\xi'}{2\Gamma}\right]d\xi'$$

$$+\int_0^\xi\exp\left(-\frac{\xi-\xi'}{\Gamma}\right)\int_0^{\xi'/\Gamma}\exp\left[-\frac{(B^2+1)W}{2}\right]I_0\left[\frac{(B^2-1)W}{2}\right]dW\,d\xi'.$$ (B 3)

Integrating the last term above by parts yields the terms

$$\Gamma \int_0^{\xi/\Gamma} \exp\left[-\frac{(B^2+1)W}{2}\right] I_0\left[\frac{(B^2-1)W}{2}\right] dW - \int_0^\xi \exp\left(-\frac{\xi-\xi'}{\Gamma}\right)$$
$$\times \exp\left[-\frac{(B^2+1)\xi'}{2\Gamma}\right] I_0\left[\frac{(B^2-1)\xi'}{2\Gamma}\right] d\xi'. \quad (B\,4)$$

The last integral in expression (B4) cancels with the first integral in expression (B3). It follows from equation (B2) and equation (55) that

$$\rho_w = -\frac{\theta M_f^2}{B_f}\left\{\exp\left[-\frac{(B^2+1)\xi}{2\Gamma}\right] I_0\left[\frac{(B^2-1)\xi}{2\Gamma}\right]\right\}$$
$$-\frac{\theta M_f^2}{B_f}\left(1 + B_f^2 \frac{(B^2-1)}{M_f^2}\right) \int_0^{\xi/\Gamma} \exp\left[-\frac{(B^2+1)W}{2}\right] I_0\left[\frac{(B^2-1)W}{2}\right] dW.$$
$$(B\,5)$$

The result quoted in equation (58) follows from reorganization of the terms in equation (B5).

Equation (59a) for the concentration increment can be reduced in a similar way to that outlined above. Thus, from equation (55) we can write the last term in equation (59a) as

$$\exp\left(-\xi/\Gamma\right) \int_0^{\xi/\Gamma} C_{pw}(W) e^W dW = -\frac{2\theta}{B_f} \exp\left(-\xi/\Gamma\right)$$
$$\times \left\{\int_0^{\xi/\Gamma} \exp\left[-\tfrac{1}{2}(B^2-1)W\right] I_0[\tfrac{1}{2}(B^2-1)W] dW\right.$$
$$+ \int_0^{\xi/\Gamma} e^W \int_0^W \exp\left[-\tfrac{1}{2}(B^2+1)u\right] I_0[\tfrac{1}{2}(B^2-1)u] du\, dW\right\}.$$

Integration of the last integral by parts shows that

$$\exp\left(-\xi/\Gamma\right) \int_0^{\xi/\Gamma} C_{pw}(W) e^W dW$$
$$= -\frac{2\theta}{B_f} \int_0^{\xi/\Gamma} \exp\left[-\tfrac{1}{2}(B^2+1)W\right] I_0[\tfrac{1}{2}(B^2-1)W] dW$$

and the result quoted in equation (59) follows at once.

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