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The Two-Dimensional Flow of an Ideal
Dissociating Gas*

- by -

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S U M M A R Y

By neglecting viscosity, heat conduction and diffusion, a method for investigating the effect of dissociation on the two dimensional flow of a high temperature supersonic gas stream has been examined. The ideal 'oxygen-like' gas introduced by Lighthill (1957) has been used and in all cases the internal modes of the molecules are assumed to be instantaneously adjusted to be in equilibrium with each other.

A brief introduction to the ideal dissociating gas and the rate equation is given and then the partial differential equations governing the motion of this ideal gas are treated by a standard characteristic method. Due to the entropy production associated with the chemical reactions, analytical solutions are not possible, and a numerical step-by-step method is used to obtain a solution.

As an application of the method developed the flow field around a sharp corner of an ideal dissociating gas is examined and a limited investigation of the free stream conditions and expansion angle on the resulting relaxation zone has been given.

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LIST OF SYMBOLS

a_f	Frozen speed of sound
a_e	Equilibrium speed of sound
A	Atom
A_2	Molecule
c	Concentration of atomic species, in mass fractions
D	Dissociation energy per unit mass
e	Internal energy per unit mass
h	Enthalpy per unit mass of molecule
k_D	Specific reaction rate coefficient for dissociation
k_R	Specific reaction rate coefficient for recombination
K_e	Equilibrium constant
κ	Net mass rate of production of atomic species
m	Mass of atomic species
M_e	Equilibrium Mach Number
M_f	Frozen Mach Number
n	Normal co-ordinate in natural co-ordinate system
p	Pressure
R	Gas constant for molecular species
s	Streamwise co-ordinate in natural co-ordinate system
\tilde{S}	Entropy per unit mass
T	Temperature
T_D	Characteristic temperature
t	Time
x	Space co-ordinate
u	Velocity in streamwise direction

List of Symbols (Continued)

ρ	Density
ρ_D	Characteristic density for dissociation
τ	Characteristic chemical time
θ	Direction of velocity in natural co-ordinate system
μ_a	Chemical potential of atomic species
μ_m	Chemical potential of molecular species
ξ	Parameter of characteristic curve measured along the curve
$\Delta\xi_{\pm}$	Increments of length along characteristic lines
σ	Thermodynamic variable defined in equation (21)
l	Distance measured from corner of the wall
$\bar{P}_r \bar{P}_s$	Distance between the r^{th} and s^{th} points

Subscripts

o	Free stream conditions
e	Equilibrium conditions
$(1, 2, 3 \text{ etc})$	Points in flow field
W	Conditions at the wall
a	atomic species
m	molecular species

1. Introduction

In the hypersonic flight regime high stagnation enthalpies are realised which are sufficient to dissociate the diatomic constituents of air. Generally the problem of including the high energy changes associated with dissociation into aerodynamic problems is difficult owing to the complexity of the thermodynamics. However by postulating an idealised diatomic gas, Lighthill was able to formulate the equations governing such a gas in a simple form, and yet still retain the main characteristics which a real diatomic gas would exhibit at high temperatures. This ideal gas provides an excellent means of investigating the effect of dissociation in high temperature gas flows.

If the reaction rate of the chemical process is finite then for any deviation from a state of equilibrium there will elapse a finite period of time before a new state of equilibrium is achieved. When the time to reach equilibrium is comparable with the time it takes for a particle to pass through the flow, then areas of the flow field will arise in which non-equilibrium states are encountered. The object of this work is to investigate these non-equilibrium regions or relaxation zones, which arise when a high temperature reacting gas is expanded round a sharp corner. To do this, plane flow has been considered.

The problem has been simplified by neglecting viscosity, heat conduction and diffusion, and by assuming that the translational, rotational and vibrational degrees of freedom are always adjusted to be in thermal equilibrium with each other. The equations of motion governing the flow of an ideal 'oxygen like' dissociating gas have been formulated and treated in a manner similar to that suggested by Chu (1957). Due to the entropy production associated with the chemical reactions analytical solutions are not possible and thus a numerical step-by-step solution similar to that encountered in the familiar method of characteristics has to be employed.

2. The Ideal Dissociating Gas

The dissociating gas is considered to be composed of symmetrical diatomic molecules and is 'ideal' in the sense that for a specified temperature range the thermodynamics can be simplified greatly by noting that a group of temperature dependent terms arising in the law of mass action may conveniently be taken as a constant. Lighthill (Ref.11) first noticed this and found that, for a diatomic gas which is in chemical equilibrium, the law of mass action may be written as

$$\frac{c_e^2}{1 - c_e} = \frac{\rho}{\rho_e} \exp \left(- \frac{D}{R T_e} \right), \quad (1)$$

where c_e is the concentration by mass of the atomic species, D is the dissociation energy per unit mass, R the gas constant for the molecular species, the suffix 'e' implying that a state of equilibrium exists.

The characteristic density ρ_D , see Ref.11, is strictly a function of temperature, but for the temperature range $3000^\circ\text{K} < T < 7000^\circ\text{K}$ the variation of ρ_D is small for oxygen and thus may be considered to have a constant value of 150 gm/cc.

Implicit in the assumption that ρ_D is a constant is the requirement that the vibrational degrees of freedom of the molecule are always just half excited even at low temperatures. This enable the internal energy to be written in the following simple form,

$$e = 3RT + Dc \quad (2)$$

and thus the enthalpy is

$$h = (4 + c) RT + Dc. \quad (3)$$

Finally, the equation of state may be deduced by considering the partially dissociated gas to be an assembly of two independent perfect gases and is

$$p = \rho(1 + c)RT \quad (4)$$

As Lighthill points out, this ideal associating gas will only be representative over the temperature range $3000^\circ\text{K} < T < 7000^\circ\text{K}$. Outside these limits ionisation and vibrational excitation will become important and this has not been allowed for. However in the examples presented below, since only small expansion angles are considered, the Lighthill approximations are adequate.

3. The Rate Equation

By assuming that the molecular and atomic states of the assembly are independent, the equation describing the reaction may be written formally as,



where X represents a third body, which in collision with a molecule or an atom may act as an heat sink or source. For a pure diatomic gas this third body may be an atom or a molecule. k_D and k_R are the specific reaction rate coefficients for dissociation and recombination; both being dependent on local temperature and concentration in general. They may be obtained from statistical considerations, or from experiment,

From Ref.14 the net rate of production of the atomic species may be written as,

$$\frac{d(A)}{dt} = 2 k_D (A_2)(X) - 2 k_R (A)^2 (X) \quad (6)$$

where brackets represent the concentration of the species in mol./cc.

It is more convenient to express the concentration in mass fractions.

Noting that $(A) = \frac{\rho c}{m}$, $(A_2) = \frac{\rho(1-c)}{2m}$ and that $(X) = \frac{\rho(1+c)}{2m}$ then equation (6) becomes

$$\frac{dc}{dt} = \frac{k_D}{2} \left(\frac{\rho}{m}\right) (1-c^2) - k_R \left(\frac{\rho}{m}\right)^2 (1+c)c^2 \quad (7)$$

At equilibrium $\frac{dc}{dt} = 0$ and therefore

$$\frac{k_D}{k_R} = 2 \left(\frac{\rho_e}{m}\right) \left(\frac{c_e^2}{1-c_e}\right) = K_e \quad (8)$$

K_e , being the equilibrium constant.

As the flows discussed later are of an expansive nature it is convenient to express the rate equation in terms of k_R rather than k_D . Thus if the concentration c_e is evaluated at local p and T , equation (7) becomes

$$\frac{dc}{dt} = \frac{\rho^2 k_R (1+c)}{m^2} \left[\left(\frac{1-c^2}{1-c_e^2}\right) c_e^2 - c^2 \right] \quad (9)$$

It may be noticed that $\tau = m^2 / \rho^2 k_R (1+c)$ has the dimensions of time and may be taken as a characteristic chemical time. By considering a small deviation from equilibrium under conditions of almost constant pressure and temperature then equation (9) may be written in the following approximate form,

$$\frac{1}{c'} \cdot \frac{dc'}{dt} = - \frac{1}{\tau_c} \left(\frac{2c_e}{1-c_e^2} \right) = \text{const.} \quad (10)$$

Here c' is a small deviation from the initial equilibrium conditions c_e . Thus it is seen that τ can be taken as proportional to the time which it takes for a small deviation of the concentration to return to its initial equilibrium value and may thus be used as a measure of the rate at which the chemical reaction proceeds towards equilibrium.

When $\tau \rightarrow 0$ then $c \rightarrow c_e$ and equilibrium flow exists and as $\tau \rightarrow \infty$ c will remain constant and the flow is called frozen.

The recombination rate coefficients are difficult to determine and published results suggest that it lies within the range $10^{14} < k_R < 10^{17}$ for oxygen (k_R measured in mole⁻². cm⁶. sec⁻¹).

Recent investigations Ref.13, give $k_R = 0.8 \times 10^{15}$ at a temperature of $3,500^\circ\text{K}$ which is in close agreement with Ref.2.

4. The Two Dimensional Flow of an Ideal Dissociating Gas

By making the simplifying assumption that viscosity, heat conduction and diffusion may be neglected, the general equations governing the supersonic flow of a reacting gas are reduced to a hyperbolic system of differential equations. By utilising the method of characteristics Ref.4, a numerical solution may thus be obtained.

To obtain a numerical solution it was found advantageous to work in the natural co-ordinate system. In this curvilinear system s is measured along a streamline in the direction of the velocity vector \underline{u} and n is measured normal to it. θ is the inclination of the velocity \underline{u} to some arbitrarily chosen datum. It should be noticed however, that although this co-ordinate system is convenient it has the disadvantage of not automatically revealing all the characteristic directions in the subsequent analysis.

The overall or global continuity equation may then be written as

$$\frac{u}{\rho} \cdot \frac{\partial \rho}{\partial s} + \frac{\partial u}{\partial s} + u \frac{\partial \theta}{\partial n} = 0 \quad (11)$$

and the continuity of the atomic species is

$$u \frac{\partial c}{\partial s} - \frac{\kappa}{\rho} = 0 \quad (12)$$

where κ is the rate of mass production of the atomic species c per unit volume.

The momentum equations are

$$u \frac{\partial u}{\partial s} + \frac{1}{\rho} \frac{\partial p}{\partial s} = 0 \quad (13)$$

and

$$u^2 \frac{\partial \theta}{\partial s} + \frac{1}{\rho} \frac{\partial p}{\partial n} = 0 \quad (14)$$

By considering the thermodynamics of the mixture the energy equations may be used to express the entropy change along a streamline in the form

$$u \frac{\partial \tilde{S}}{\partial s} + \frac{1}{\rho T} (\mu_a - \mu_m) \kappa = 0 \quad (15)$$

where \tilde{S} is the specific entropy and μ is the chemical potential.

Finally, the equation of state is specified by expressing the density as a function of pressure, entropy and concentration

$$d\rho = \rho_{\tilde{S}} d\tilde{S} + \rho_c dc + \frac{1}{\alpha^2} dp. \quad (16)$$

where $\rho_{\tilde{S}} = \left(\frac{\partial \rho}{\partial \tilde{S}} \right)_{p,c}$, and $\rho_c = \left(\frac{\partial \rho}{\partial c} \right)_{\tilde{S},p}$ and the subscripts indicating

which variables are held constant during differentiation.

Writing the equation of state with the density as the dependent variable enables the results obtained in Ref.4 to be included in the following analysis.

Equations (11 - 16) constitute six quasi-linear partial differential equations in six unknown dependent variables u, p, ρ, c, \tilde{S} , and in the two independent variables s and n of the form

$$L_j = a_{ij} \frac{\partial u_i}{\partial s} + b_{ij} \frac{\partial u_i}{\partial n} + c_j = i, j = 1, \dots, 6. \quad (17)$$

In this equation the cartesian tensor notation has been employed and thus to obtain the values of the coefficients and dependent variables in the six equations (17), the subscripts (i,j) must be taken over all possible combinations of i,j, each of which may take any of the values 1,2,...,6.

As the equations (17) stand the dependent variables appear differentiated in the directions 's' or 'n'. To obtain a solution, Ref.4, it is necessary to have the dependent variables differentiated in directions along which the normal derivatives are not necessarily continuous. These directions are called characteristic directions and the curve which they describe is called the characteristic curve. To find these directions a system of multipliers λ_j dependent on (s,n) is specified such that in a linear combination $L = \lambda_j L_j$ all the dependent variables u_i appear differentiated in the same direction given by $\frac{dn}{ds} = \alpha$ (say).

If the curve specified by $\frac{du}{ds} = \alpha$ is given by $s(\xi), n(\xi)$ where ξ is a parameter associated with the characteristic curve $\alpha = \frac{\partial n}{\partial \xi} / \frac{\partial s}{\partial \xi}$.

The condition that all the variables in $L = \lambda_j L_j$ are differentiated in the same direction α is thus given by

$$(\lambda_j b_{ij}) : (\lambda_j a_{ij}) = \frac{\partial n}{\partial \xi} : \frac{\partial s}{\partial \xi} \quad (18)$$

If the six equations given by equation (17) are compatible, i.e if a characteristic direction exists, then the λ_j may be eliminated to yield a characteristic determinantal relation which defines the directions of the tangents to the characteristics curves at the point (s,n) for specific values of the dependent variable, i.e.

$$\frac{\partial n}{\partial \xi} / \frac{\partial s}{\partial \xi} = \pm \frac{1}{\sqrt{M_f^2 - 1}} \quad (19)$$

where M_f is the Mach number based on the frozen speed of sound.

A third characteristic direction exists and is coincident with the streamline.

The dependent variables u_i will also satisfy the equation $L = \lambda_j L_j = 0$ at the point (s,n) . Thus by eliminating first $\frac{\partial u_i}{\partial s}$ and then $\frac{\partial u_i}{\partial n}$ from $L = \lambda_j L_j = 0$ with the aid of equations (18) two more equations will result. These combined with equations (17) yield several determinantal equations which gives relationships between the variables u_i along characteristic directions. One relationship of importance which results is the following

$$\sqrt{\frac{M_f^2 - 1}{\rho u^2}} \cdot dp \pm d\theta + \frac{1}{M_f} \left(\frac{\kappa \sigma}{\rho u} \right) d\xi \pm = 0 \quad (20)$$

where $d\xi \pm$ are increments of length along characteristic lines corresponding to the characteristic directions $\frac{dn}{ds} = \pm 1 / \sqrt{M_f^2 - 1}$

and

$$\sigma = - \frac{1}{\rho T} \left(\frac{\partial \rho}{\partial \tilde{S}} \right)_{p,c} \left[\mu_a - \mu_m + T \left(\frac{\partial \tilde{S}}{\partial c} \right)_{p,\rho} \right] \quad (21)$$

is a variable which provides a convenient grouping of the thermodynamic variables involved and was first introduced by Kirkwood and Wood Ref.15. Three other characteristic relations (equations 12, 13, 15) are obtained and all hold along the streamlines.

Thus provided the kinetics of the reacting gas are known and provided suitable initial data are given then equations (12)(13)(15) and (19) and (20), enable all the unknown dependent variables to be calculated at all points in the flow field.

4.1. Integration of the characteristic equations

The equations are non-linear and are not reducible in the sense of Courant and Friedrich Ref. 4, and therefore in order to obtain a solution a numerical step-by-step method must be employed. To facilitate numerical computation it is convenient to express all the equations in terms of finite differences.

Assuming that conditions are known at two points p_1 and p_2 , then provided P_1, P_2 are sufficiently close together the point p_3 at which the two characteristic lines through P_1 and P_2 intersect may be found by letting the tangents to the frozen Mach lines at P_1 and P_2 represent the characteristic lines in a first approximation. This will of course introduce an error which can be reduced by iteration; the convergence of this iteration depending on the size of the interval chosen for $p_1 p_2$. This has not been analysed analytically, but trial and error revealed that for the cases discussed in this report, it is desirable that $P_1 P_2$ should not be greater than 0.01 of a dimensionless unit. Here length has been non-dimensionalised by $u_0 \tau_0$.

After non-dimensionalising the variables with free stream conditions, i.e. $p = \frac{p}{p_0}$ etc. equations (19) may be written

$$\frac{p_0}{\rho_0 u_0^2} \sqrt{\frac{M_{F1}^2 - 1}{\rho_1 u_1^2}} \Delta p_1 + \Delta \theta_1 + \frac{1}{M_F} \left(\frac{\kappa_1 \sigma_1}{\rho_1 u_1} \right) \Delta \xi_1 + \dots = 0 \quad (21)$$

and

$$\frac{p_0}{\rho_0 u_0^2} \sqrt{\frac{M_{F2}^2 - 1}{\rho_2 u_2^2}} \Delta p_2 - \Delta \theta_2 + \frac{1}{M_F} \left(\frac{\kappa_2 \sigma_2}{\rho_2 u_2} \right) \Delta \xi_2 - \dots = 0 \quad (22)$$

where subscripts (1) (2) represent the values of the variables at the points P_1 and P_2 ,. The finite differences $\Delta p_1, \Delta p_2, \Delta \theta_1$ etc. are defined by

$$\Delta p_1 = p_3 - p_1 \quad (23)$$

$$\Delta p_2 = \Delta p_1 + p_1 - p_2 \quad (24)$$

$$\Delta \theta_1 = \theta_3 - \theta_1 \quad (25)$$

$$\Delta \theta_2 = \Delta \theta_1 + \theta_1 - \theta_2 \quad (26)$$

This of course, is only a first order approximation since it has been assumed that the coefficients in the differential equations (21, 22) are constant along the characteristic lines joining the points (P_1, P_3) and (P_2, P_3) , their values being taken at the points 1 and 2 respectively. To obtain a better approximation an iteration process must be used, i.e. values obtained at the point 3 are used to obtain a mean value for the coefficients and the slope of the characteristic lines, and the procedure is repeated. Once again trial and error revealed that only one iteration need be used when examination is carried out along the characteristic

$$\text{lines } \frac{dn}{ds} = \pm \frac{1}{\sqrt{M_F - 1}}$$

From equations (21 - 26) expressions can be found for the change in p and θ from points P_1 to P_3 , i.e.

$$\begin{aligned} \frac{P_0}{\rho_0 u_0^2} \left[\frac{\sqrt{M_{F1}^2 - 1}}{\rho_1 u_1^2} + \frac{\sqrt{M_{F2}^2 - 1}}{\rho_2 u_2^2} \right] \Delta p_1 &= (\theta_1 - \theta_2) - \frac{P_0}{\rho_0 u_0^2} \frac{\sqrt{M_{F2}^2 - 1}}{\rho_2 u_2^2} (p_1 - p_2) \\ &- \frac{(\widetilde{P_1 P_3})}{M_{F1}} \left(\frac{\kappa \sigma}{\rho_1 u_1} \right) - \frac{(\widetilde{P_2 P_3})}{M_{F2}} \left(\frac{\kappa \sigma}{\rho_2 u_2} \right), \quad (27) \end{aligned}$$

and

$$\begin{aligned} \left[\frac{\sqrt{M_{F1}^2 - 1}}{\rho_1 u_1^2} + \frac{\sqrt{M_{F2}^2 - 1}}{\rho_2 u_2^2} \right] \Delta \theta &= \frac{P_0}{\rho_0 u_0^2} \frac{\sqrt{M_{F1}^2 - 1}}{\rho_1 u_1^2} \cdot \frac{\sqrt{M_{F2}^2 - 1}}{\rho_2 u_2^2} \cdot (p_1 - p_2) \\ &- \frac{\sqrt{M_{F1}^2 - 1}}{\rho_1 u_1^2} (\theta_1 - \theta_2) - \frac{\sqrt{M_{F2}^2 - 1}}{\rho_2 u_2^2} \frac{(\widetilde{P_1 P_2})}{M_{F1}} \left(\frac{\kappa \sigma}{\rho_1 u_1} \right) + \frac{\sqrt{M_{F1}^2 - 1}}{\rho_1 u_1^2} \\ &\quad \frac{(\widetilde{P_2 P_3})}{M_{F2}} \left(\frac{\kappa \sigma}{\rho_2 u_2} \right). \quad (28) \end{aligned}$$

where $\widetilde{P_r P_s}$ (say) is the distance between the r^{th} point and s^{th} point.

Thus the flow inclination and pressure are known at P_3 . Before the other variables can be found the relations holding along the streamlines must be used. Knowing the flow inclination at P_3 a first approximation may be obtained by projecting the tangent to the streamline at P_3 to intersect the line $\widetilde{P_1 P_2}$ at $P_{(1,2)}$ (say). Then by assuming that a linear variation of the variables exists over the segment $\widetilde{P_1 P_2}$ conditions at $P_{(1,2)}$ may be found. Once $P_{(1,2)}$ has been located and the values of the dependent variables are known at that point then the following relations hold along the streamline.

$$\rho_0 u_0^2 \Delta u_{(1,2)} + \rho_{(1,2)} u_{(1,2)} + p_0 \Delta p_{(1,2)} = 0 \quad (29)$$

$$u_{(1,2)} \Delta c_{(1,2)} - \frac{\kappa_{(1,2)}}{\rho_{(1,2)}} \cdot (\overline{P_{(1,2)} P_3}) = 0, \quad (30)$$

$$\rho_0 h_0 + \rho_{(1,2)} \Delta h_{(1,2)} - p_0 \Delta p_{(1,2)} = 0, \quad (31)$$

where $\Delta u_{(1,2)} = u_3 - u_{(1,2)}$; $\Delta p_{(1,2)} = p_3 - p_{(1,2)}$; $\Delta c_{(1,2)} = c_3 - c_{(1,2)}$,

$$\Delta h_{(1,2)} = h_3 - h_{(1,2)}$$

and $u_{(1,2)}$ etc define values of the dependent variables at the point $P_{(1,2)}$.

In order that this approximation shall be useful it is necessary to locate the point $P_{(1,2)}$ fairly accurately. It was found that at least one iteration was needed in order that the values of the dependent variables at $P_{(1,2)}$ were located to the same order of accuracy as the increments Δc , Δu , Δh and Δp . At this stage p , θ , u , c , h are known at P_3 and now the other variables may be calculated.

The caloric equation of state for an ideal dissociating gas may be written in terms of finite differences to give -

$$\frac{\Delta h}{h_1} = \frac{\Delta T}{T_1 + \left(\frac{c_1}{4 + c_1}\right) T_D} + \frac{\Delta c}{c_1 + \frac{4 T_1}{T_1 + T_D}} \quad (32)$$

and the thermal equation of state becomes

$$\frac{\Delta p}{p_1} = \frac{\Delta \rho}{\rho_1} + \frac{\Delta c_1}{1 + c_1} + \frac{\Delta T}{T_1} \quad (33)$$

To evaluate the slope of the characteristic line at P_3 the frozen Mach number is needed and may be evaluated (Appendix A) from the following finite difference equation

$$\frac{\Delta a_{f,1}^2}{a_{f,1}^2} = \frac{\Delta T}{T_1} + \frac{(5 + 2c_1)}{(1 + c_1)(4 + c_1)} \cdot \Delta c_1 \quad (34)$$

If the equilibrium composition is evaluated at local pressure and temperature, then c_0 at the point P_3 may be obtained from the law of mass action, i.e.

$$\frac{c_{e_3}^2}{1 - c_{e_3}^2} = \frac{\rho_D}{\rho_3(1 + c_3)} \exp \left\{ - \frac{T_D}{T_3} \right\} \quad (35)$$

The reaction rate is

$$\left(\frac{dc}{dt} \right)_3 = \frac{\kappa_3}{\rho_3} = \frac{1}{\tau_3} \left[\frac{(1 - c_3^2)c_{e_3}^2}{(1 - c_{e_3}^2)} - c_3^2 \right] \quad (36)$$

where

$$\tau_3 = \frac{1}{\tau_0 k_R \rho_3^2 (1 + c_3)} \quad (37)$$

The thermodynamic variables σ may be written, Appendix B,

$$\sigma = \frac{(1 + c_3)(1 + \frac{T_D}{T_3}) - (4 + c_3)}{(1 + c_3)(4 + c_3)} \quad (38)$$

for an ideal dissociating gas.

Thus all the flow and thermodynamic variables are known at P_3 . In a like manner the whole flow field may be calculated by constructing a characteristic net, see Fig. 1 for example.

Two relatively simple solutions arise when the flow is considered to be frozen or in equilibrium.

(i) Frozen Flow :

For frozen flow the characteristic chemical time τ becomes infinite and thus all the terms involving the chemical reactions disappear. Equation (20) becomes

$$\frac{\sqrt{M_F^2 - 1}}{\rho u^2} \Delta p \pm \Delta \theta = 0 \quad (39)$$

and thus it is seen that the flow will occur isentropically. This type of flow occurs at the apex of a Prandtl-Meyer expansion in a reactive fluid and its solution is easily constructed.

(ii) Equilibrium Flow:

For the other extreme when $\tau = 0$ the flow is in equilibrium and for this ideal case it is found that the disturbance front propagates with a_e . The equations of motion governing the equilibrium flow are :

$$\frac{u_e}{\rho_e} \frac{\partial \rho_e}{\partial s} + \frac{\partial u_e}{\partial s} + u_e \frac{\partial \theta_e}{\partial n} = 0 \quad (41)$$

$$\rho_e u_e \frac{\partial u_e}{\partial s} + \frac{\partial p_e}{\partial s} = 0 \quad (42)$$

$$u_e^2 \frac{\partial \theta_e}{\partial s} + \frac{1}{\rho_e} \frac{\partial p_e}{\partial n} = 0 \quad (43)$$

$$u_e \frac{\partial \tilde{S}_e}{\partial s} = 0 \quad (44)$$

$$d\rho_e = \frac{1}{a_e^2} dp_e + \left(\frac{\partial p_e}{\partial c_e} \right)_{p, \tilde{S}_e} dc_e + \left(\frac{\partial p_e}{\partial \tilde{S}_e} \right)_{p, c_e} d\tilde{S}_e \quad (45)$$

Note that the equilibrium concentration $c_e(\tilde{S}, p)$ has been evaluated at local pressure and entropy and is only the same as $c_e(p, T)$ when equilibrium exists.

Once again equations (41 - 45) constitute a quasi-linear system of differential equations and may be solved in much the same manner as before. It is now found however that the characteristic directions are defined by

$$\frac{dn}{ds} = \pm \frac{1}{\sqrt{M_e^2 - 1}}, \quad (46)$$

where M_e is based on the equilibrium speed of sound. As pointed out by Chu Ref.³ it is interesting to note that for a reacting gas, although the order of the equations is reduced when $\tau = 0$ the system still remains hyperbolic.

The numerical solution is analogous to that of section (5.2.) and as before it is convenient to write the relations holding along the characteristics in terms of finite differences, i.e.

$$\frac{\sqrt{M_e^2 - 1}}{\rho_e u_e} \Delta p_e \pm \Delta \theta_e = 0 \quad (47)$$

$$\rho_e u_e \Delta u_e - \Delta p_e = 0 \quad (48)$$

$$\rho_e \Delta h_e + \Delta p_e = 0. \quad (49)$$

The thermal and caloric equation of state becomes

$$p_e = \rho_e (1 + c_e) R T_e, \quad (50)$$

$$h_e = (4 + c_e) R T_e + C_e D. \quad (51)$$

At this stage p_e , h_e , u_e are known and in order to evaluate c_e , ρ_e , and T_e the equilibrium concentration is first found from

$$\frac{c_e^2}{1 - c_e^2} = \frac{\rho_D}{p_e} \frac{(h_e - c_e D)}{(4 + c_e)} \exp \left\{ - \frac{T_D R(4 + c_e)}{(h_e - c_e D)} \right\}, \quad (52)$$

thus giving the temperature and density from equations (50, 51).

To evaluate the characteristics directions the equilibrium sound speed must be used and may be obtained from the ratio in Ref. 5

$$\left(\frac{a_F}{a_e} \right)^2 = 1 + \frac{c_e (1 - c_e)}{3} \frac{\left[(1 + \frac{T_D}{T})(1 + c_e) - (4 + c_e) \right]^2}{(1 + \frac{T_D}{T})^2 c_e (1 - c_e^2) + 8 + 2 c_e}$$

where it has been tabulated for varying temperature and pressure.

For the small expansion angles which have been used to illustrate the characteristic method the equilibrium conditions appear to provide an asymptotic value for the dependent variables behind the corner. Further examples considering larger expansion angles and other initial conditions are required however to see the true significance of those 'asymptotic' values.

The frozen and equilibrium cases (or expansive flows have also been discussed by Heims, Ref. 9. In the latter the conditions behind the corner are found by considering Prandtl-Meyer flow in which allowance has been made for the chemical composition of the gas by integrating, step-by-step, along isentropes with the aid of a Mollier chart.

5. The Application of the Two Dimensional Theory to the expansion of an Ideal Dissociating Gas

For a high temperature reacting gas the flow round a corner will no longer occur isentropically and marked differences from the classical Prandtl-Meyer flow will arise. Thus in order to investigate the flow field for such an expansion the theory and method given in section (4) has been applied to three specific examples. The three cases for which the flow field has been examined are

- (i) $p_0 = 1 \text{ atm.}$, $T_0 = 4250^\circ\text{K.}$, $c = 0.78$ and expansion angle = 5° .
 - (ii) $p_0 = 0.1 \text{ atm.}$, $T_0 = 3750^\circ\text{K.}$, $c = 0.83$ and expansion angle = 5° .
 - (iii) $p_0 = 0.1 \text{ atm.}$, $T_0 = 3750^\circ\text{K.}$, $c = 0.83$ and expansion angle = 10° .
- all at a Mach No. of 1.83.

As the flow round wedge sections are likely to be of more importance in the laboratory, the above conditions were chosen to correspond to those conditions likely to be encountered in shock tubes. The conditions of the wall are generally those of interest and so the wall temperature, pressure, concentration and Mach number have been plotted against the non-dimensional length measured from the corner of the wall. Further to obtain a more general visual picture of the overall flow field behind the expansion isobar plots have been made of cases (i) and (iii).

The transit time through the apex of the expansion fan is vanishingly small so in the region very close to the corner there will be a lag in the inert degrees of freedom. Generally, the inert degrees of freedom will include vibration as well as dissociation but in this report however only the relaxation effects due to dissociation are considered. The vibrational degree of freedom is taken to be always excited to just half its classical value. For the cases discussed here the degree of dissociation is fairly high ($c \sim 0.8$) and the energy stored in the vibrational modes of the remaining molecules will be small compared with that of dissociation. Thus, the assumption that the vibrational mode is instantaneously adjusted to be in local equilibrium with the translational and rotational modes should not affect the results appreciably. At the apex of the fan then, the isentropic temperature drop will cause the atoms to be no longer in chemical equilibrium with the molecules. Thus a transition region must exist in which the system has time to approach a new equilibrium value. In this region the atoms recombine and supply the flow with some of its dissociative energy. This process continues until a balance is achieved between the concentrations of the atoms and molecules. This relaxation to a new equilibrium level is an irreversible one and is accompanied by an increase in entropy.

The zone over which this relaxation occurs is very dependent on the free stream conditions ahead of the corner and the expansion angle. As the

method of solution for such flows is necessarily a lengthy process only a limited investigation of these effects has been obtained. Of the cases solved, the most pronounced variation occurred with the reduction of free stream pressure. By reducing the pressure from one atmosphere to one tenth of an atmosphere for the same expansion angle the relaxation zone at the wall increased from approximately 0.026 cms to approximately 1.735 cms. This is because the recombination of the atoms requires a three body collision. Thus, as the density becomes smaller the probability of such collisions is less, and so the time to reach a new equilibrium level will be longer. Variation of the expansion angle from 5° to 10° in cases (ii, iii) showed that the relaxation zone at the wall increased by approximately 0.9 cms.

A further influence on the relaxation zone arises from the recombination rate coefficient. Owing to the lack of data concerning the recombination rate coefficient for oxygen, in the cases discussed an arbitrary value of 10^{17} cc²/mol²sec was used. Recent evidence however Ref.13 would suggest that a value of $-k_R = 10^{15}$ cc²/mol²sec would be a better estimate. It would appear that due to this arbitrary choice of k_R the length of the relaxation zones are underestimated by a factor of one hundred in this report. Also k_R has been assumed constant throughout. Over the temperature range which these examples cover Ref. 13 suggests that k_R would only change from $0.78 \cdot 10^{15}$ cc²/mol²sec to 0.69×10^{15} cc²/mol²sec and so the assumption $k_R = \text{const.}$ throughout the expansion appears to be satisfactory.

In Ref. 7, Feldman reports the existence of a recombination shock out in the flow field due to the relaxation. In the cases discussed, the relaxation along the wall caused a steepening of the Mach lines at the wall but due to the relaxation effects occurring through the expansion, away from the corner, it is unlikely that the Mach lines will coalesce even at great distances from the wall. To investigate such recombination shocks it suggests that much larger expansion angles must be considered.

In a recent paper by Clarke, Ref.16, the linearised flow of an Ideal Dissociating gas is discussed. For the small expansion angles considered the variation of the non-dimensional dependent variables in the relaxation zone are in good agreement with the non-linear solutions presented in figures 3 - 8.

6. Conclusions

The method presented in this report provides a means of investigating the effect of dissociation on the flow field of a high temperature reacting gas. The method is successful in so far that results can be obtained, but the number of computing hours required for each solution makes it impracticable for extensive investigations to be made without the aid of a digital computer or the further possibility of a numerical graphical procedure being developed.

Of the cases examined for expansive flows of an ideal 'oxygen-like' dissociating gas round a sharp corner it was found that the relaxation zones were considerably influenced by the free stream conditions, and for the small expansion angles considered the flow will quickly be adjusted to new equilibrium conditions.

7. Acknowledgement

The author wishes to express his appreciation to Dr. J. F. Clarke, for his supervision and encouragement during the course of this work.

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APPENDIX A

The speeds of sound for an ideal dissociating gas

(i) Frozen Sound Speed

To write the frozen speed of sound in a form which is suitable for numerical computation it is convenient to consider the following energy relation, i.e.

$$T d\tilde{S} = du - \frac{dp}{\rho} - (\mu_a - \mu_m) dc \quad (A1)$$

Taking the enthalpy and internal energy 'e' of the gas to be functions of the pressure, temperature and concentration, together with the fact that the relation $h = e + \frac{p}{\rho}$ holds, then the following expression may be obtained.

$$\frac{dp}{d\rho} = \frac{p}{\rho} \left\{ \frac{\left(\frac{\partial h}{\partial p} \right)_{T,c} dp + \left(\frac{\partial h}{\partial T} \right)_{p,c} dT + \left(\frac{\partial h}{\partial c} \right)_{p,T} - Td\tilde{S} - (\mu_a - \mu_m) dc}{\left(\frac{\partial \rho}{\partial p} \right)_{T,c} dp + \left(\frac{\partial \rho}{\partial T} \right)_{p,c} dT + \left(\frac{\partial \rho}{\partial c} \right)_{p,T} - Td\tilde{S} - (\mu_a - \mu_m) dc} \right\} \quad (A2)$$

For dissociating gas, the pressure does not appear explicitly in the energy relation, thus if the above expression is evaluated for constant local values of entropy and concentration it is reduced to,

$$\left(\frac{\partial p}{\partial \rho} \right)_{\tilde{S},c} = \frac{p}{\rho} \frac{\left(\frac{\partial h}{\partial T} \right)_{p,c}}{\left(\frac{\partial \rho}{\partial T} \right)_{p,c}} = \frac{p}{\rho} \frac{C_{pf}}{C_{vf}} \quad (A3)$$

where C_{pf} is the frozen specific heat at constant pressure, and C_{vf} is the frozen specific heat at constant volume. For an ideal dissociating gas equation (A3) is readily shown to be

$$a_f^2 = \left(\frac{\partial p}{\partial \rho} \right)_{\tilde{S},c} = \frac{(1+c)(4+c)RT}{3} \quad (A4)$$

(ii) Equilibrium Sound Speed

The equilibrium speed of sound can, in principle, be evaluated in a like manner but unfortunately the right hand side of equation (A2) becomes unwieldy and thus the best method is to evaluate a_e by considering a ratio of the sound speeds.

Considering the density as a function of pressure, entropy and concentration, we have

$$d\rho = \frac{1}{a_f^2} dp + \left(\frac{\partial \rho}{\partial \tilde{S}} \right)_{p,c} d\tilde{S} + \left(\frac{\partial \rho}{\partial c} \right)_{p,\tilde{S}} dc \quad (A5)$$

Now for a gas which is in equilibrium, and whose local entropy values are considered constant, this last equation may be written

$$\left(\frac{\partial \rho}{\partial p} \right)_{\tilde{S},c_e} = \frac{1}{s_e^2} = \frac{1}{a_f^2} + \left(\frac{\partial \rho}{\partial c} \right)_{p,\tilde{S}} \frac{c_e}{p} \quad (A6)$$

Rather than evaluate $\left(\frac{\partial \rho}{\partial c} \right)_{p,\tilde{S}}$, $\left(\frac{\partial c_e}{\partial p} \right)_{\tilde{S}}$ in detail, reference is made to

Clarke (1958) where this has been evaluated for the ideal dissociating gas, and is

$$\left(\frac{a_f}{a_e} \right)^2 = 1 + \frac{c_e(1-c_e)}{3} \frac{\left[\left(1 + \frac{T_D}{T} \right) (1+c) - (4+c_e) \right]^2}{\left(1 + \frac{T_D}{T} \right)^2 c_e(1-c_e^2) + 8 + 2c_e} \quad (A7)$$

This has been evaluated for varying temperature and pressure, and the results presented therein are used in this report when the flow field has been evaluated for equilibrium conditions.

APPENDIX B

The thermodynamic variable $\tilde{\sigma}$

In the general analysis of chemically reacting flows Ref. 5, the variable $\tilde{\sigma}$ provides a convenient grouping of the thermodynamic variables involved, and is defined as

$$\tilde{\sigma} = - \frac{1}{\rho T} \left(\frac{\partial \rho}{\partial \tilde{\sigma}} \right)_{p,c} \left[\mu_a - \mu_m + T \left(\frac{\partial s}{\partial c} \right)_{p,\rho} \right]$$

As pointed out in Ref. 5, this is not the most convenient form for evaluation and it may be written as

$$\tilde{\sigma} = - \frac{\left(\frac{\partial \rho}{\partial T} \right)_{p,c}}{\rho \left(\frac{\partial h}{\partial T} \right)_{p,c}} \left(\frac{\partial h}{\partial c} \right)_{p,T} + \frac{1}{\rho} \left(\frac{\partial \rho}{\partial c} \right)_{p,T}$$

For the ideal dissociating gas

$$\left(\frac{\partial \rho}{\partial T} \right)_{p,c} = \frac{\rho}{T} \quad \left(\frac{\partial h}{\partial c} \right)_{p,T} = (RT + D)$$

$$\left(\frac{\partial h}{\partial T} \right)_{p,c} = (4 + c)R \quad \left(\frac{\partial \rho}{\partial c} \right)_{p,T} = - \frac{\rho}{1+c}$$

thus

$$\tilde{\sigma} = \frac{(1+c) \left(1 + \frac{T D}{T} \right) - (4+c)}{(1+c)(4+c)}$$

and

$$\mu_a - \mu_m = - \frac{RT}{W_m} \log_e \left[\frac{\rho_D}{\rho} \frac{(1-c)}{c^2} \exp - \frac{T D}{T} \right]$$

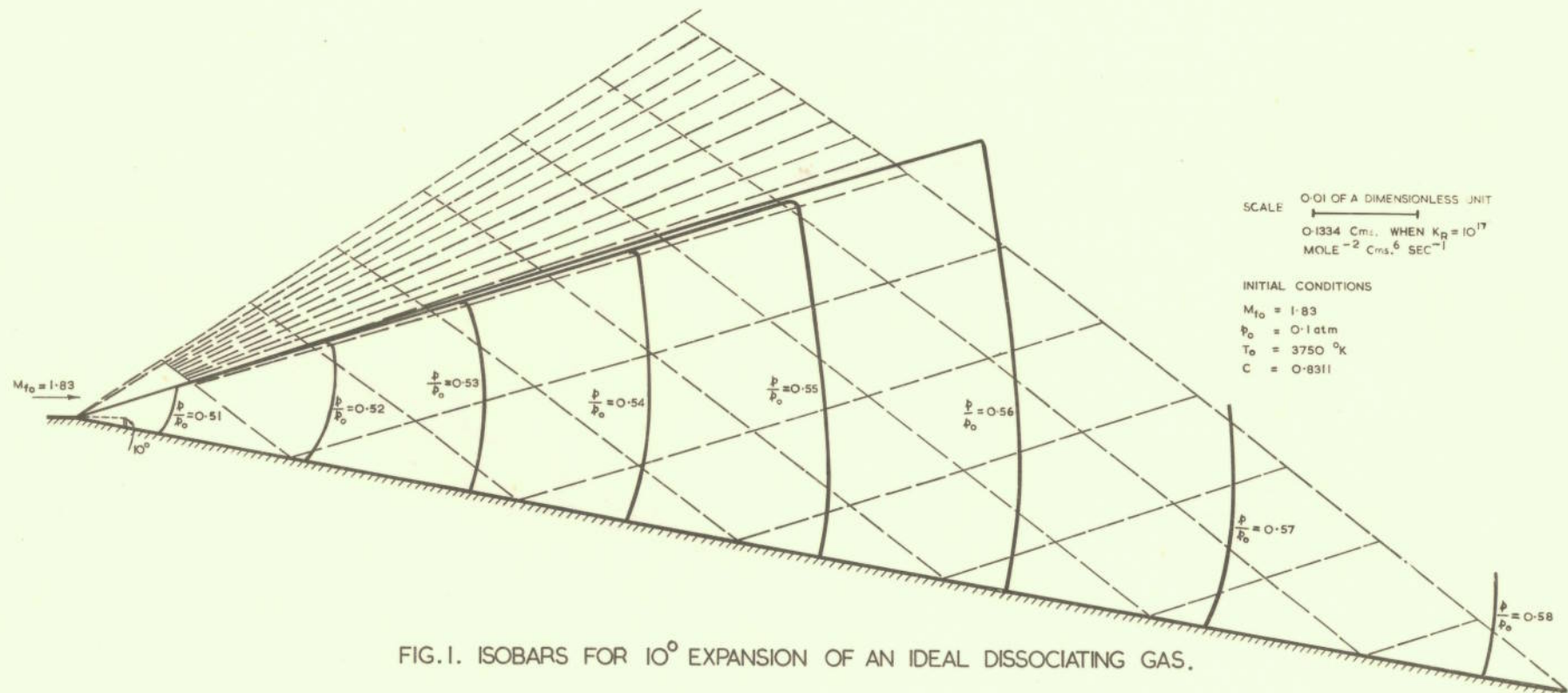


FIG.1. ISOBARS FOR 10° EXPANSION OF AN IDEAL DISSOCIATING GAS.

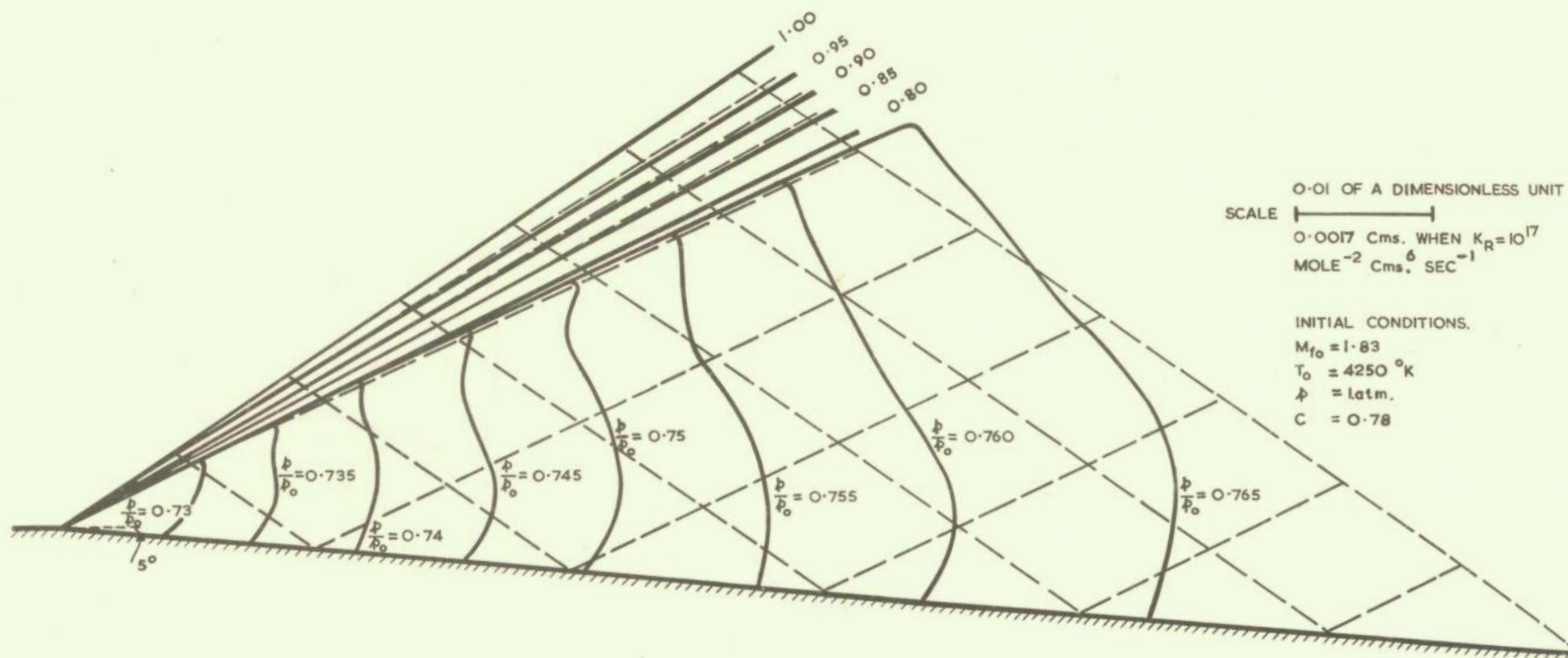


FIG. 2. ISOBARS FOR 5° EXPANSION OF AN IDEAL DISSOCIATING GAS

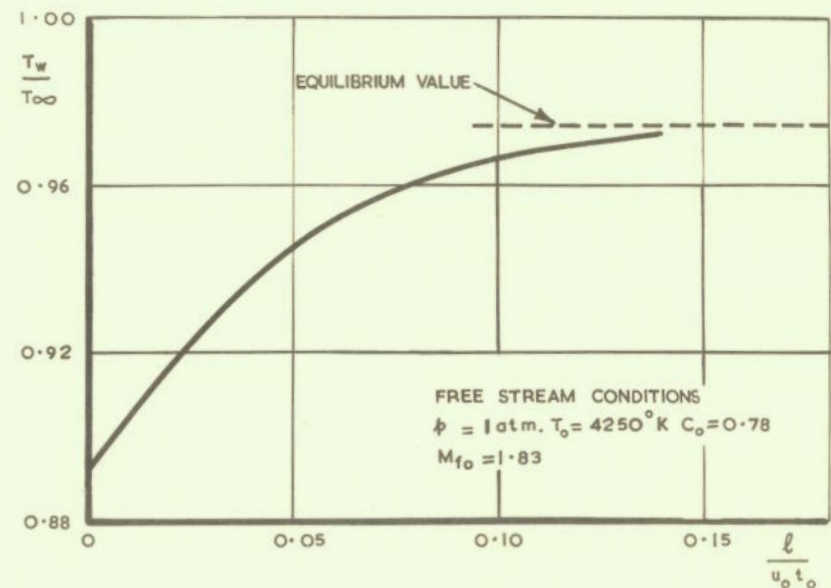
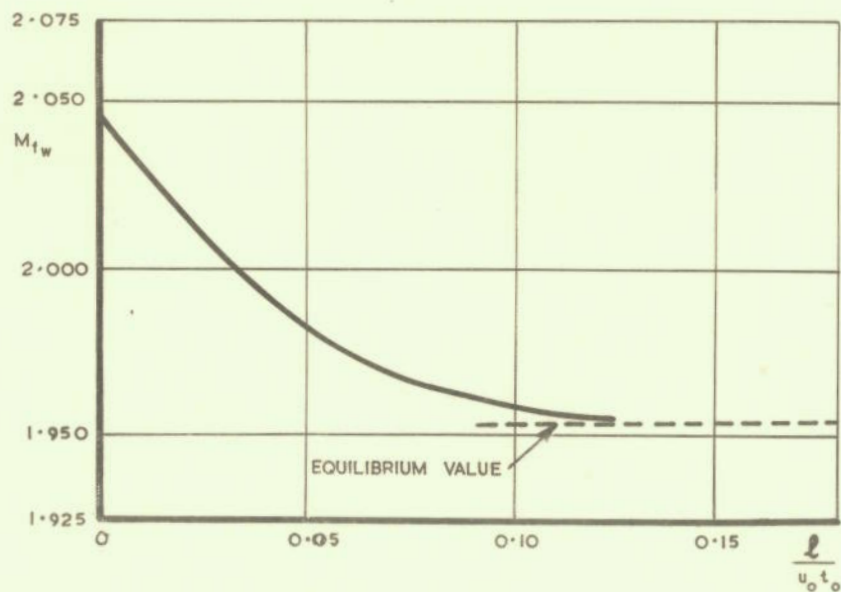
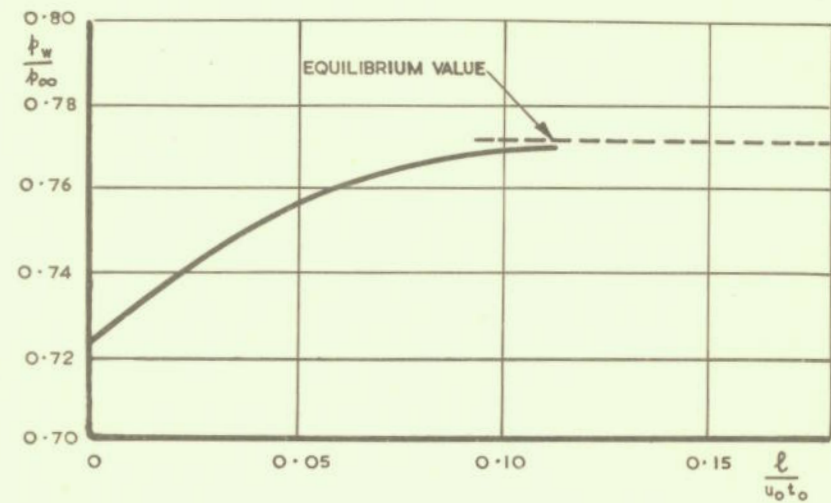
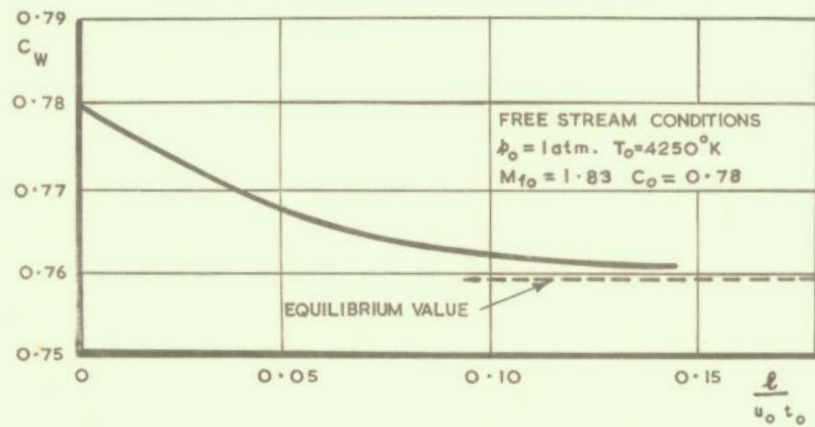


FIG. 3. CONDITIONS AT WALL FOR 5° EXPANSION

FIG. 4. CONDITIONS AT WALL FOR 5° EXPANSION.

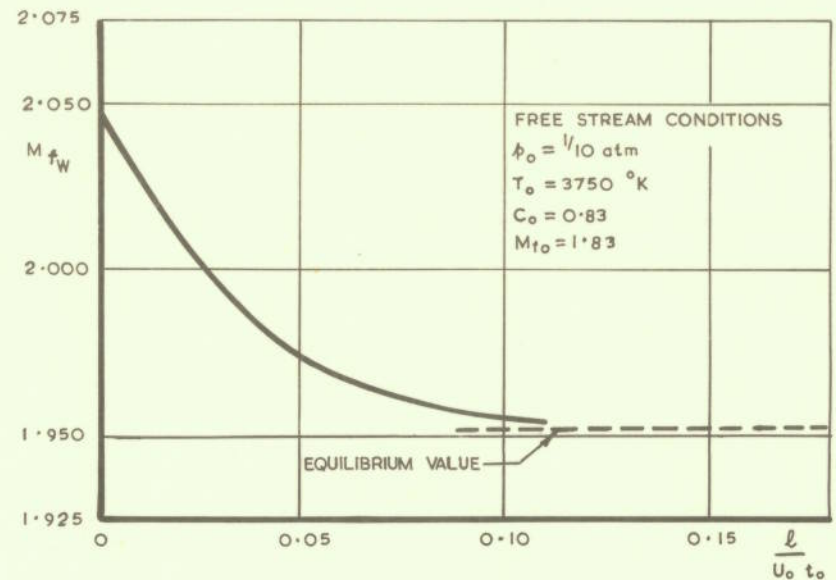
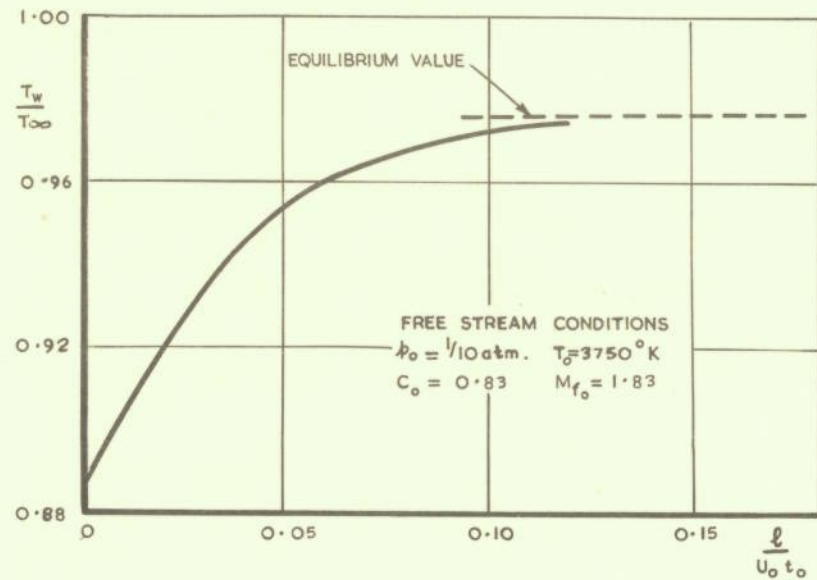
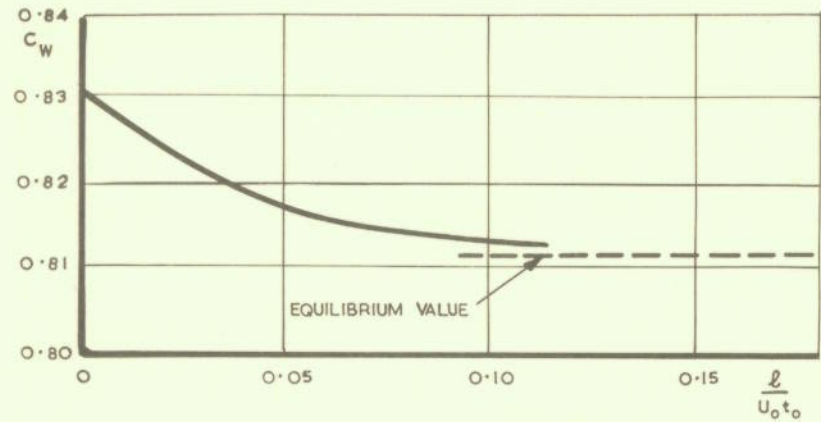
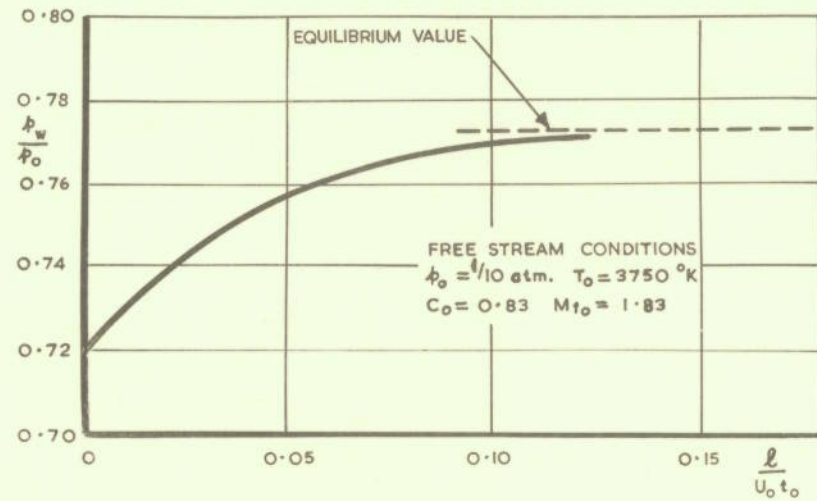


FIG. 5. CONDITIONS AT WALL FOR 5° EXPANSION.

FIG. 6. CONDITIONS AT WALL FOR 5° EXPANSION.

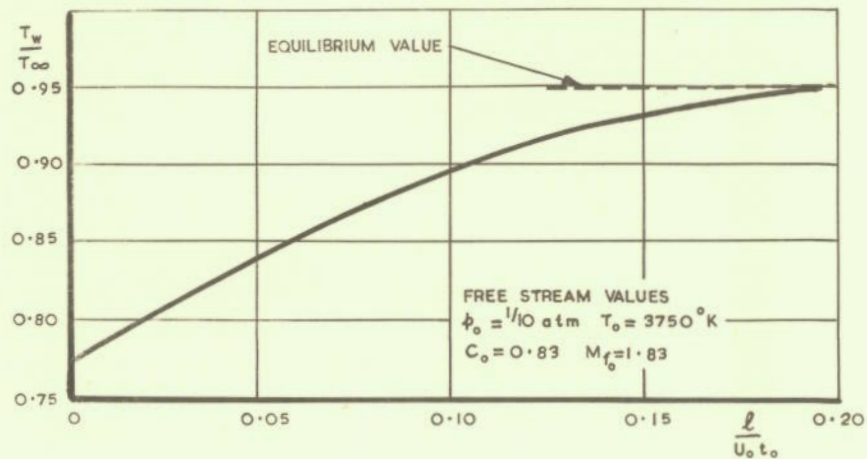
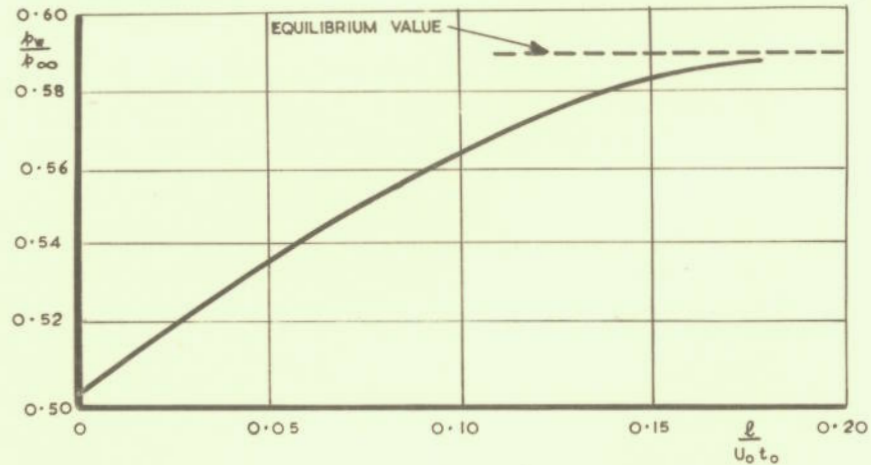


FIG. 7. CONDITIONS AT WALL FOR 10° EXPANSION.

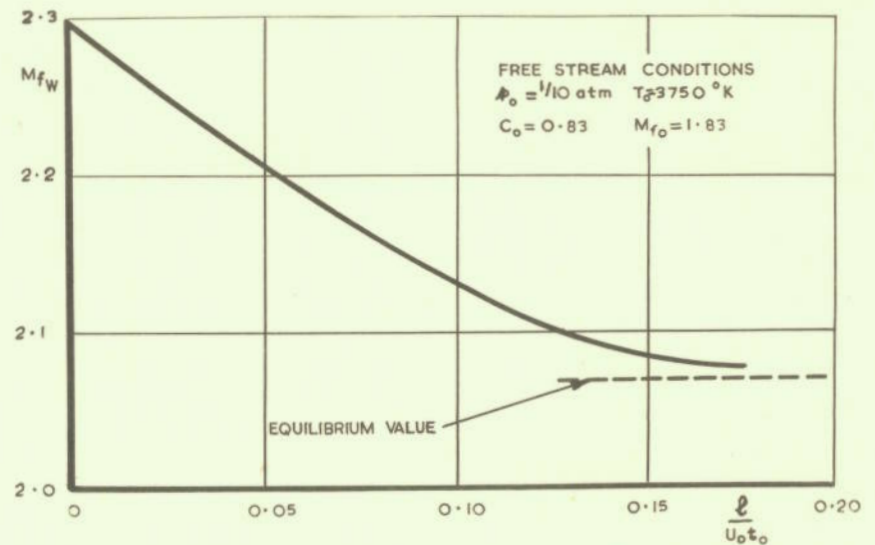
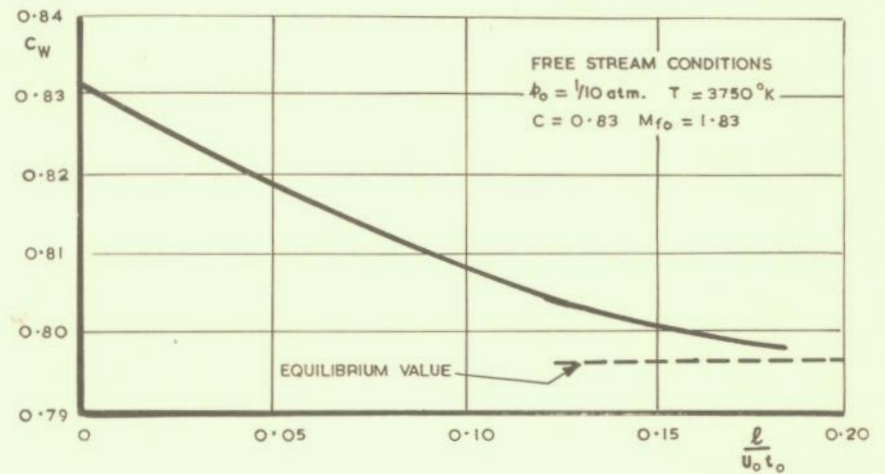


FIG. 8. CONDITIONS AT WALL FOR 10° EXPANSION