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The Two-Dimensional Flow of an Ideal
Dissociating Gas*

- by -

J. W. Cleaver, B.A., D.C.Ae.

SUMMARY

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 $\text{mole}^{-2} \cdot \text{cm}^6 \cdot \text{sec}^{-1}$).

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.

