Non-equilibrium flow of an ideal dissociating gas

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SUMMARY

The theory of an 'ideal dissociating' gas developed by Lighthill (1957) for conditions of thermodynamic equilibrium is extended to non-equilibrium conditions by postulating a simple rate equation for the dissociation process (including the effects of recombination). This equation contains the 'equilibrium' parameters of the Lighthill theory plus a further 'non-equilibrium' parameter which determines the time scale of the dissociation phenomena.

The behaviour of this gas is investigated in flow through a strong normal shock wave and past a bluff body. The assumption is made that the gas receives complete excitation of its rotational and vibrational degrees of freedom in an infinitesimally thin region according to the familiar Rankine–Hugoniot shock wave relations before dissociation begins. The variation of the relevant thermodynamic variables downstream of this region is then computed in a few particular cases. The method used in the latter case is an extension of the 'Newtonian' theory of hypersonic inviscid flow. In particular, the case of a sphere is treated in some detail. The variation of the shock shape and the 'stand-off' distance with the coefficient Λ, which is the ratio of the sphere diameter to the length scale of the dissociation process, is exhibited for conditions extending from completely undissociated flow to dissociated flow in thermal equilibrium. Results would indicate that significant and observable changes from the undissociated values occur, although values for the non-equilibrium parameter are not, at present, available.

1. INTRODUCTION

Lighthill (1957) has considered the fluid dynamical problems associated with a dissociating gas under conditions of thermodynamic equilibrium, while referring to papers in preparation on the quasi-equilibrium and non-equilibrium conditions. In order to make the problem tractable an idealized gas was postulated which exhibits, during dissociation, the main features of a real dissociating gas such as nitrogen or oxygen. This gas was called 'an ideal dissociating gas'. In this paper, two problems will be considered in which the behaviour of this gas is studied under non-equilibrium thermodynamic conditions. Thus, we attack the problem originally proposed (Lighthill 1957) for part III of the series of which that paper was part I. To do this, it is necessary to postulate the rate of dissociation of the molecules into atoms, under conditions far removed from equilibrium. At present the form of such a relation and the values of the relevant parameters concerned with its non-equilibrium behaviour are not known, although attempts have been made to deduce such a relation (see, for example, Wood 1956 and Evans 1956). In view of this uncertainty a somewhat simplified form of the dissociation rate has been assumed which gives the correct equilibrium conditions, as well as the most important features of the non-equilibrium ones. This relation is discussed in §2. It will be seen in the later sections of this paper, however, that the exact form of this relation may not give results which differ very much from the present one, owing to the predominance of one factor over all others. This is the exponential factor in the Maxwellian distribution of the energy in the molecules and atoms.

The two problems here considered are, first, the flow of an ideal dissociating gas, assumed initially undissociated, through a strong normal shock wave and, secondly, the flow of the same gas past a bluff body. The latter problem involves a further generalization of the author's theory of flow past bluff bodies on the so-called 'Newtonian' assumptions.

The gas is assumed in both cases to have its rotational and vibrational modes fully excited by passing through an infinitesimally thin shock wave behind which the gas begins to dissociate. In other words we assume the time scale for the changes in the rotational and vibrational energy of the molecules is small compared with that for changes in the amount of dissociation in the gas. When undissociated, the Lighthill ideal dissociating gas behaves like a perfect diatomic gas with constant specific heats but with only half the vibrational energy as given by the principle of equipartition of energy. Thus the ratio of specific heats when undissociated is $\frac{4}{3}$. If initially, the flow has a velocity U and density ρ_0, passage through a normal shock wave, in the absence of dissociation, reduces the velocity to $\frac{1}{7}U$, and increases the density and pressure to $7\rho_0$ and $\frac{6}{7}\rho_0 U^2$ respectively. The effect of dissociation is then to absorb some of the energy associated with the translational, rotational and vibrational modes of the molecule, thereby reducing the temperature of the gas. The pressure itself can change very little since the maximum it can reach is $\rho_0 U^2$. Hence, the main effect of dissociation is to further increase the density behind a normal shock wave. In the above argument 'temperature' is used to mean that associated with the energy in the translational modes of the molecules and atoms.

On the assumption that the normal shock is strong, the main parameter that describes the flow through the initial shock wave is the energy per unit mass of gas, which is conserved through it. The amount of dissociation which is going to take place behind the shock then depends solely on the physical constants of the gas itself and this energy. In particular, only the ratio of this energy to the energy required to dissociate the gas and the ratio of a characteristic density of dissociation ρ_D to the free stream density ρ_0

appear. These constants will be referred to as the 'equilibrium constants' since their values can be determined from equilibrium considerations alone. The rate at which equilibrium behind the shock wave is achieved is determined by a constant C. The value $(\rho_0 C)^{-1}$ gives the time scale of the dissociation process behind the shock wave.

In a similar way, the changes normal to the bow shock wave of a bluff body take place according to the Rankine–Hugoniot relations. Momentum tangential to the shock wave, and hence tangential velocity, is conserved. Since the density behind the shock wave increases from a value $7\rho_0$ to higher values due to dissociation, the approximation of large density behind the shock used by the author (1956) and others (Chester 1956; Ivey, Klunker & Bowen 1948) and called the 'Newtonian approximation' is especially relevant. By using such an approximation it is possible to predict some of the geometrical properties of the flow, such as bow shock wave and streamline positions. In theory it is also possible to predict the pressure variation corrected from the crude 'Newtonian' value. In practice such a derivation proves rather laborious. But as the present investigation is based on qualitative rather than quantitative assumptions about the gas itself, the theory is regarded as sufficiently justified if it can predict a qualitative picture of the flow.

The relevant non-equilibrium parameter in this case is denoted by Λ and is the ratio of the body size to the length scale of the dissociation phenomenon. For the normal shock wave the time scale of the dissociation process is $(C\rho_0)^{-1}$ and hence the length scale of the whole flow is $U/C\rho_0$ where U is the free-stream velocity. Thus $\Lambda = lC\rho_0/U$ where l is the characteristic length of the body. For small Λ the body is small compared with the distance dissociation requires and thus for $\Lambda = 0$ we have the undissociated flow of a perfect gas with a constant ratio of specific heats $\gamma = \frac{4}{3}$. For large Λ, however, the main dissociation takes place at the bow shock wave, and dissociative equilibrium is maintained throughout the region between the shock wave and the body. Quite generally, we can make further predictions about the flow between shock and body by considering a 'local' value of Λ which we will denote by λ. The local length scale of the dissociation is $u/C\rho_0$, where u is the local velocity and hence $\lambda = lC\rho_0/u$. Near the stagnation point, λ is large and hence dissociative equilibrium is achieved in this region. Also, on the basis of the approximation of the present theory, changes in the velocity along the streamlines are negligible and hence, near the body, where the streamlines all originate in the region near the stagnation point, the velocity is small. Thus, near the body, λ is also large and we have dissociative equilibrium. Proceeding outwards along the normal to the body surface therefore, we have dissociative equilibrium at the surface whence the amount of dissociation decreases until it is zero on the shock wave itself. From the theory, dissociation profiles between the shock and body can be computed, showing in detail the amount of dissociation across the 'shock layer' at various stations on the body.

The amount of dissociation between the shock and the body, since it increases the density of the fluid in this region, will tend to decrease the distance between shock and body due to the contraction of stream tubes. Schwarz & Eckermann (1956) infer the amount of excitation of the vibrational modes of the molecules of polyatomic gases from measurements of the 'stand-off' distance of the shock wave from the stagnation point. This adds interest to the discussion (§4) of the variation of this length with the rate of dissociation.

2. Rates of dissociation

The ideal dissociating gas has been discussed by Lighthill (1957) and the laws governing its equilibrium behaviour deduced. When thermodynamic equilibrium is not attained, however, it is necessary to consider the actual processes of molecular dissociation and atomic recombination. Equilibrium is achieved when the rate of dissociation of the molecules into atoms is equal to the rate of production of new molecules by the recombination of atoms. Thus, the net rate of dissociation

$$\frac{d\alpha}{dt} = r_D - r_R, \tag{2.1}$$

where α is the ratio by weight of atoms dissociated to weight of atoms and molecules at a point and r_D and r_R denote the rates of dissociation and recombination respectively. In equilibrium, $r_D = r_R$ and hence if we know either r_D or r_R, using the equilibrium theory (Lighthill 1957), we can deduce a relation between r_D and r_R for the ideal dissociating gas. In particular we shall attempt to find a value for r_D. Now dissociation of a gas molecule is accomplished by increasing the energy in the internal degrees of freedom to a point which is sufficient to overcome the binding forces holding the atoms together. The necessary increase in internal energy is achieved by transfer from other forms of energy during a collision. If the collisions are sufficiently violent dissociation ensues. Hence, the rate of dissociation r_D will be to a first approximation proportional to the number of binary collisions of a molecule with another molecule or free atom such that the total energy available in the collision is sufficient to cause dissociation. We can therefore write

$$r_D = C_1(\alpha, T)\rho(1-\alpha)e^{-D/kT}, \tag{2.2}$$

where ρ is the density, T the temperature, D is the energy of dissociation and k is Boltzmann's constant. $C_1(\alpha, T)$ is a function yet to be determined. The factor $\rho(1-\alpha)$ gives the number of molecules per unit volume of the gas. Since we are primarily interested in binary collisions C_1 will, in general, consist of a sum of two terms, one corresponding to collisions between the molecules themselves and another for the collisions between atoms and molecules. At constant temperature the former will be proportional to $(1-\alpha)$ and the latter to α. The factors of proportionality will depend on the respective collision cross-sections. An attempt to evaluate these has been made by Wood (1956) and also Evans (1956) on the basis of simple kinetic theory. In view of the uncertainty attached to these values however the assumption will be made in this paper that C_1 is independent of α. The main variation in C_1, it is thought, will come from the dependence on temperature, which we shall assume to follow an inverse-power law. Such a variation is expected since the energy in many degrees of freedom (the rotational and vibrational energy of each colliding molecule, and their relative translational energy) may combine to make dissociation possible if their total exceeds D. The inference of an inverse-power law in such a case (Hinshelwood 1940) rests on the fact that the proportion of states of a system in which the energy, made up of n 'independent square terms', exceeds a value D, large compared with $\frac{1}{2}nkT$, is

$$e^{-D/kT}(D/kT)^{\frac{1}{2}n-1}/(\tfrac{1}{2}n-1)!.$$

However, the precise value of n which is appropriate is unknown, although it will be shown not to be crucial. The value $n = 7$, used below, includes the relative translational energy but the rotational and vibrational energies of only one colliding molecule, on the grounds that the vibrational energies are not fully excited, that the molecules sometimes collide with free atoms, and that it is uncertain whether any mode of collision could use all the available energy. We therefore assume the expression for the rate of dissociation to be

$$r_D = C_p(1-\alpha)T^{-s}e^{-D/kT}, \tag{2.3}$$

where C and s are constants. The dependence of the results obtained from this formula on the exponent s can be exhibited by choosing different values for s in the computation (in practice, 0 and 2·5).

From equilibrium theory (Lighthill 1956), we note that for the ideal dissociating gas

$$\frac{\alpha^2}{1-\alpha} = \frac{\rho_D}{\rho}e^{-D/kT} \tag{2.4}$$

in conditions of thermodynamic equilibrium, where ρ_D is a constant characteristic of the gas. This is therefore the condition $r_D = r_R$. Hence an expression for r_R of the form

$$r_R = \frac{CT^{-s}}{\rho_D}\rho^2\alpha^2 \tag{2.5}$$

will satisfy equilibrium conditions. Further, an expression of this form might be expected since recombination requires a three-body collision of either three atoms or two atoms and a molecule and occurs, therefore, at a rate proportional to the square of the density $\rho\alpha$ of free atoms. The net rate of dissociation therefore becomes

$$\frac{d\alpha}{dt} = C_p T^{-s}\left\{(1-\alpha)e^{-D/kT} - \frac{\rho}{\rho_D}\alpha^2\right\}. \tag{2.6}$$

Comparison of expression (2.6) with the results of Wood (1956) and Evans (1956) shows that the main features agree. In these two papers different expressions of the dissociation rates are deduced. Different values of s are obtained and also the variation of C with α is included. The latter variation is however simply linear. Recombination is neglected in most of the work of Wood and Evans.

The relation (2.6) will be used throughout this paper. The variations of C from its constant value are probably small when compared with the variation of the exponential factor in (2.6) for any cases of interest. This, it is hoped to predict a qualitative picture of the flow in non-equilibrium thermodynamic conditions.

3. FLOW THROUGH A NORMAL SHOCK WAVE

(i) *Equations of one-dimensional motion*

In the region behind the Rankine–Hugoniot shock wave, the rate of dissociation is given by (2.6) with d/dt as the total rate of change with time. Since the flow is steady, however, the changes are purely convective and we can write (2.6) in the form

$$u\frac{d\alpha}{dx} = C_1 \rho T^{-s}\left\{(1-\alpha)e^{-D/kT} - \alpha^2\frac{\rho}{\rho_D}\right\}, \tag{3.1}$$

where x is the coordinate measured normal to the shock wave in a downstream direction and u is the velocity of the gas in this direction.

In the region behind the Rankine–Hugoniot shock wave the gas is assumed inviscid and without heat conduction. The equation of state for the ideal dissociating gas is then

$$\frac{p}{\rho} = RT(1+\alpha). \tag{3.2}$$

Continuity of mass and momentum for strong shock waves requires

$$\left.\begin{aligned} \rho u &= \rho_0 U, \\ p+\rho u^2 &= \rho_0 U^2, \end{aligned}\right\} \tag{3.3}$$

where p is the pressure. The constant on the right-hand side of these equations takes the value in front of the Rankine–Hugoniot shock since these quantities are conserved through it too. Finally the total energy of the gas is conserved and thus

$$i + \tfrac{1}{2}u^2 = \tfrac{1}{2}U^2, \tag{3.4}$$

where i is the enthalpy of the gas. The five equations (3.1)–(3.4) then determine the problem completely provided that i is known in terms of the other variables. For an ideal dissociating gas the internal energy e per unit mass is of the form

$$e = 3RT + \frac{D}{2m}\alpha, \tag{3.5}$$

where m is the atomic mass. The first term is the contribution to the energy from the various degrees of freedom (R is the gas constant for the undissociated gas) which is the same for both atoms and molecules. This arises from the fact that although the atoms have only three degrees of freedom, their mass is only half that of the molecules. Also the molecules of an ideal dissociating gas have only half the energy in their vibrational degrees of freedom (and hence have effectively six degrees of freedom). The second term is the energy absorbed by dissociation. By use of (3.2) and (3.5), equation (3.4) yields

$$(4+\alpha)RT+\tfrac{1}{2}u^2+\frac{D\alpha}{2m} = \tfrac{1}{2}U^2. \tag{3.6}$$

Furthermore, equations (3.2), (3.3) and (3.6) give

$$\frac{u}{U}=\frac{\rho_0}{\rho}=\left(\frac{4+\alpha}{7+\alpha}\right)\left\{1-\sqrt{\left(1-\frac{(7+\alpha)(1+\alpha)(\mu-\alpha)}{\mu(4+\alpha)^2}\right)}\right\}, \tag{3.7}$$

$$\frac{RT}{U^2}=\frac{1}{7+\alpha}\left\{1-\frac{\alpha}{\mu}-\frac{4+\alpha}{7+\alpha}\left[1-\sqrt{\left(1-\frac{(7+\alpha)(1+\alpha)(\mu-\alpha)}{\mu(4+\alpha)^2}\right)}\right]\right\}, \tag{3.8}$$

where a new variable $\mu = mU^2/D$ (the ratio of the kinetic energy of undisturbed gas to its dissociation energy) has been introduced. Equations (3.7) and (3.8) together with (3.1) then give

$$\frac{d\alpha}{dx} = F(\alpha) \tag{3.9}$$

for a certain complicated function $F(\alpha)$, and the variation of α with x is given by

$$x = \int_0^{\alpha}\frac{d\alpha}{F(\alpha)}. \tag{3.10}$$

The thickness of the dissociation region can conveniently be defined as

$$x = \int_0^{0\cdot 95\alpha_e}\frac{d\alpha}{F(\alpha)} \tag{3.11}$$

where α_e is the equilibrium value of the dissociation obtained from $F(\alpha) = 0$, this being the distance required to reach 95% of the equilibrium value. Once the function $x = x(\alpha)$ is known from (3.10), it is then possible to obtain, by direct substitution, the values of all the other physical variables from (3.7), (3.8) and (3.2).

Before the integral can be evaluated, however, it is necessary to determine the range of values of interest for the various parameters. The equilibrium constants D and ρ_D are known and hence typical values of μ and ρ_D/ρ_0 can be chosen. The values $\mu = 1$ and $\frac{1}{2}$, and $\rho_D/\rho_0 = 10^6$ and 10^7, are used in the computations. The latter values are typical of the part of the atmosphere where the density is from a tenth to a hundredth of its sea-level value. Due to the exponential factor in (2.6) it is effectively only the logarithm of ρ_D/ρ_0 which is important.

The values of C and s are concerned with essentially the non-equilibrium conditions. C, which is unknown, determines the length scale of the dissociation process. Conversely, the thickness of the dissociation region, as observed in any experimental work, would determine the value of C

which could then be used in further computations—as those in the latter part of this paper. The parameter s is given the values 0 and 2·5 as discussed above.

(ii) *Computed results*

In the figures 1 to 4 various combinations of the parameters μ, ρ_D/ρ_0 and s are used in the integration of (3.11) and the results are plotted for the different flow variables against a non-dimensional length scale $x_1 = (x\rho_0 C/R^s U^{1-2s})$. Table 1 is designed to give a key to the curves in figures 1 to 6. In figures 1 and 2, $s = 0$ and the variation of α (figure 1) and the density and temperature (figure 2) are exhibited for (a) $\mu = 1$, $\rho_0/\rho_D = 10^{-6}$; (b) $\mu = \frac{1}{2}$, $\rho_0/\rho_D = 10^{-6}$; (c) $\mu = 1$, $\rho_0/\rho_D = 10^{-7}$. In figure 3, $s = 2\cdot 5$ and the other variables are as in (a) and (b). The most characteristic feature of all these curves is the rapid variation near the Rankine–Hugoniot shock wave and the much slower variation near equilibrium. This is almost entirely due to the exponential form of the energy distribution in the gas, as can be shown by replacing all the other factors by suitable constant values and repeating the integration. This is most conveniently done by considering the temperature variation. This procedure was adopted for result (a) and in figure 2 (b) the result obtained is plotted as curve (d). Curve (d) represents

Curve	μ	ρ_0/ρ_D	s	α_e	Δ
(a)	1	10^{-6}	0	0·591	51
(b)	$\frac{1}{2}$	10^{-6}	0	0·204	570
(c)	1	10^{-7}	0	0·645	106
(d)	1	10^{-6}	0	0·591	—
(e)	1	10^{-6}	2·5	0·591	0·025
(f)	1	10^{-6}	2·5	0·591	0·85

Table 1. Key to figures 1 to 6.

$$\frac{dT_1}{dx_0} = -0\cdot 0952\left\{e^{-1/T_1} - e^{-1/T_{1e}}\right\} \tag{3.12}$$

where $T_1 = 2RT/U^2$ and T_{1e} is the value of T_1 for equilibrium under the conditions of (a).

An estimate of the distance required to reach equilibrium can be obtained by considering the distance required for the dissociation to reach 95% of its equilibrium value. This value is denoted by Δ. A change in the total energy of the gas from the dissociation energy ($\mu = 1$) to half that value ($\mu = \frac{1}{2}$) causes an increase in Δ by a factor of the order of 10. An interesting feature of the flow in this region is the only slight variation of the pressure there (figure 4).

The effect of variation of the parameter s can best be seen in figure 5, where the ratio of α to its equilibrium value α_e is plotted against x_1/Δ. It will be seen that the increase in s tends to decrease the rapidity of the rise in α. In order to contrast the difference of the results of the present investigation with the results observed in the absence of chemical changes the local length scale $(\alpha-\alpha_e)/(d\alpha/dx_1)$ is plotted in figure 6. The rapid variation just behind the shock wave is again evident, whereas such length scales are approximately constant in vibrational relaxation behind shock waves.

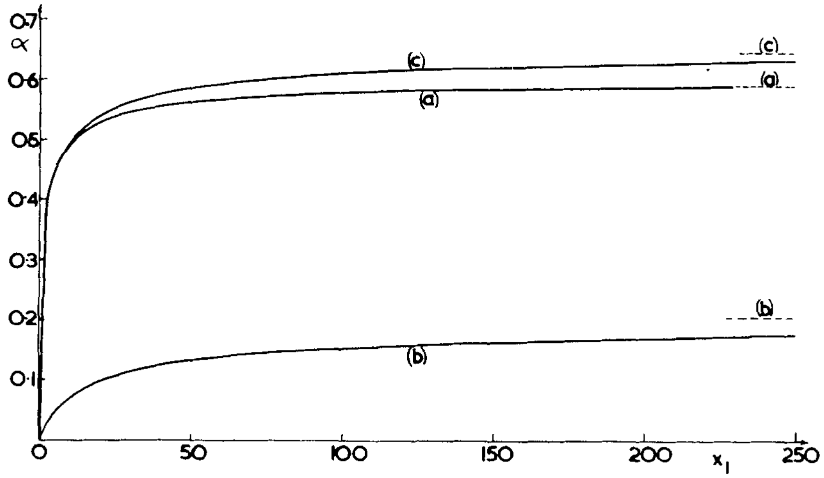


Figure 1. Amount of dissociation α behind a normal shock wave ($s = 0$).

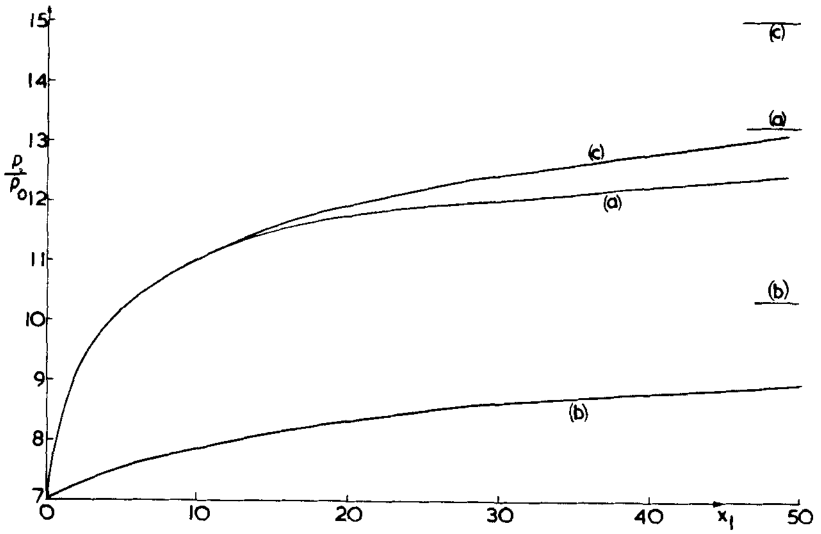


Figure 2 (*a*). The variation of density behind a normal shock wave ($s = 0$).

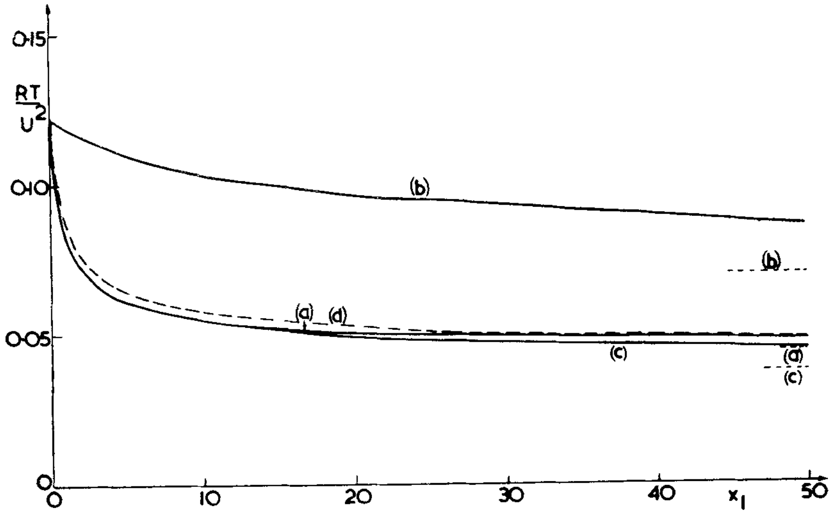


Figure 2 (*b*). The variation of temperature behind a normal shock wave ($s = 0$).

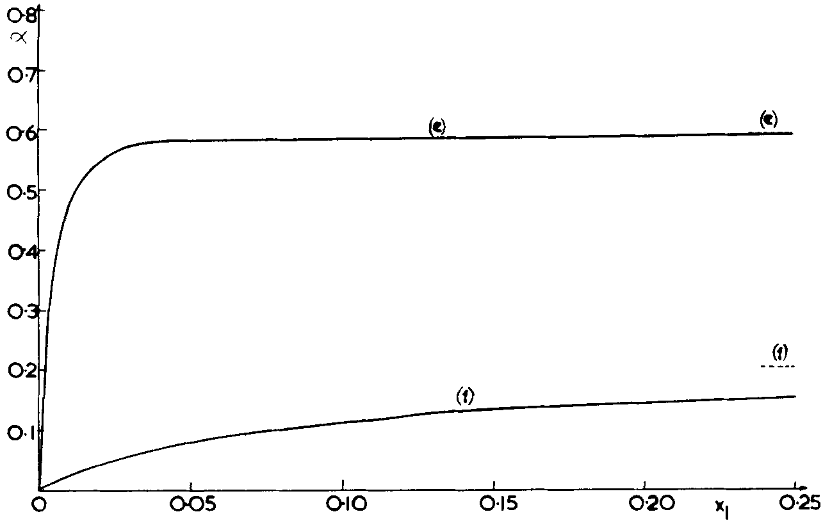


Figure 3. Amount of dissociation α behind a normal shock wave ($s = 2·5$).

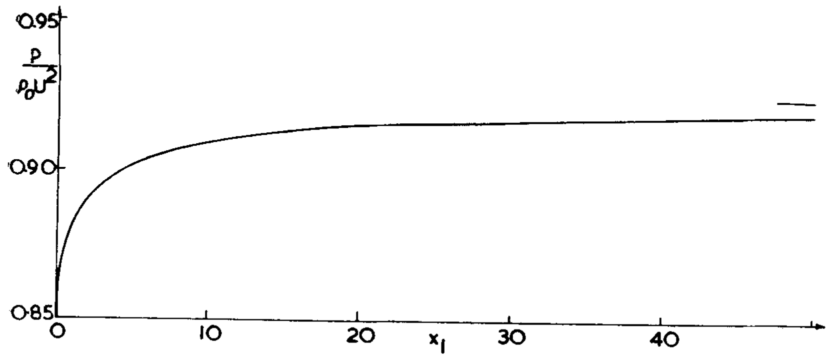


Figure 4. Pressure variation behind a normal shock wave ($s = 0$).

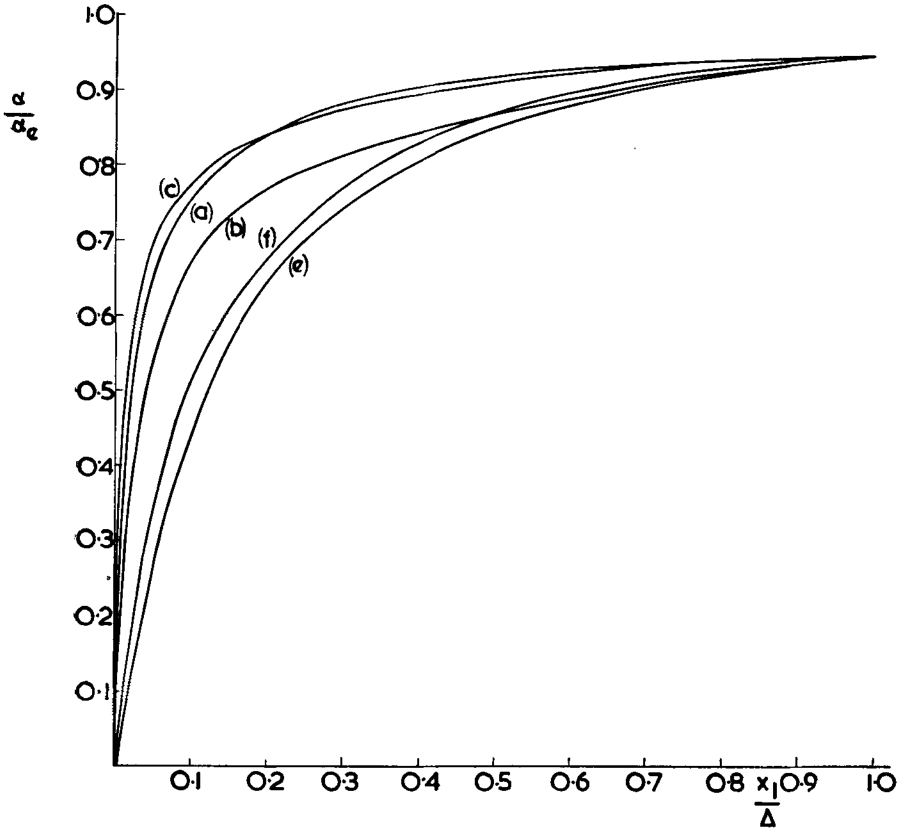


Figure 5. Comparison of the shapes of the dissociation curves.

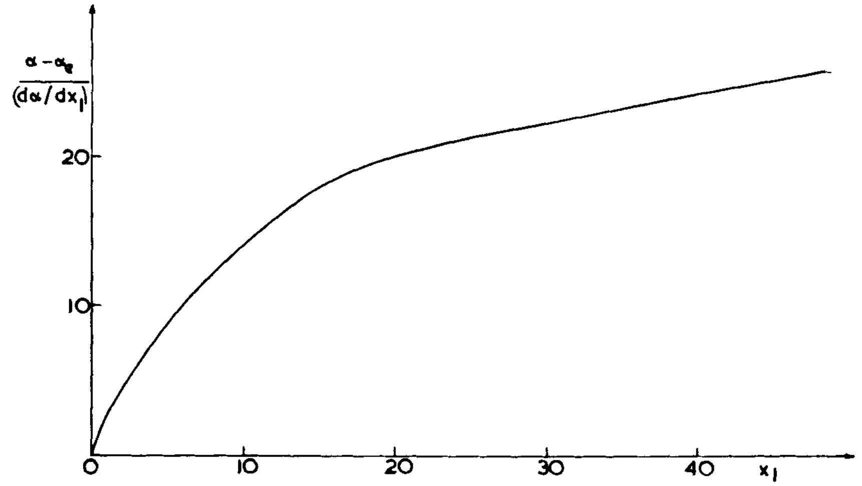


Figure 6. The length scale of the dissociation process behind a normal shock wave.

4. FLOW PAST BLUFF BODIES

Having discussed the behaviour of flow through a normal shock wave in a uniform flow, we can now proceed further and consider the flow behind the bow shock wave of a bluff body. In the previous work it was noted that the density behind a strong shock wave was large and that the effect of dissociation was to increase it still further. The theory developed by Busemann (1933, pp. 275–277), Ivey *et al.* (1948), and re-derived by the author (1956) makes use of the approximation of γ near unity for a perfect gas with constant specific heats. Alternatively, this may be stated as requiring the density to be large—and, in general, this is the more correct statement. Since, therefore, in the dissociating gas this condition is satisfied more nearly than for a perfect gas, this type of approximation would seem to be a natural one to adopt. If therefore we use boundary layer coordinates x and y along and perpendicular to the body, the equations of motion, with viscosity and heat conduction neglected, are

$$\left.\begin{aligned} \frac{u}{h}\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}+\frac{uv}{r}+\frac{1}{\rho h}\frac{\partial p}{\partial x} &= 0,\\ \frac{u}{h}\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y}-\frac{u^2}{r}+\frac{1}{\rho}\frac{\partial p}{\partial y} &= 0,\\ \frac{\partial}{\partial x}(\rho uk)+\frac{\partial}{\partial y}(\rho vhk) &= 0,\\ \frac{Di}{Dt}-\frac{1}{\rho}\frac{Dp}{Dt} &= 0, \end{aligned}\right\} \qquad (4.1)$$

where u and v are the components of velocity in the x- and y-directions respectively, $h\,dx$ and $k\,dz$ are the elements of length in the x- and z-directions respectively and $D/Dt = (u/h)(\partial/\partial x) + v(\partial/\partial y)$. For an ideal dissociating gas (Lighthill 1957),

$$i = (4+\alpha)RT + \frac{D}{2m}\alpha. \tag{4.2}$$

With use of the approximation (as in Freeman 1956) that the density is large throughout the region, (4.1) becomes

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = 0, \tag{4.3}$$

$$\frac{1}{\rho}\frac{\partial p}{\partial y} - \frac{u^2}{r} = 0, \tag{4.4}$$

$$\frac{\partial}{\partial x}(\rho uk) + \frac{\partial}{\partial y}(\rho vhk) = 0, \tag{4.5}$$

$$u\frac{\partial i}{\partial x} + v\frac{\partial i}{\partial y} = 0, \tag{4.6}$$

since changes between the shock and the body are large compared with those along the body. In terms of the stream function ψ, for which $\rho uk = \partial\psi/\partial y$, $\rho vhk = -\partial\psi/\partial x$, we have

$$u = u(\psi), \qquad \frac{\partial p}{\partial \psi} = \frac{u}{rk}, \qquad i = I(\psi). \tag{4.7}$$

If, as assumed in the previous paper, the streamlines and shock lie close to the body, (4.7) gives p (the Newtonian plus centrifugal value as in Freeman 1956) in terms x and ψ. From (4.2),

$$RT = \left\{I(\psi) - \frac{D}{2m}\alpha\right\}\frac{1}{4+\alpha}, \tag{4.8}$$

and, by the equation of state of the gas (3.2),

$$\rho = \frac{p(x,\psi)}{\{I(\psi) - (D/2m)\alpha\}}\left(\frac{4+\alpha}{1+\alpha}\right), \tag{4.9}$$

where $I(\psi)$ is the value of the enthalpy on the streamline $\psi = \text{const.}$

Finally, using the equation (2.6) for the rate of dissociation, we obtain

$$\frac{\partial \alpha}{\partial x} = \frac{C\rho hT^{-s}}{u(\psi)}\left\{(1-\alpha)e^{-D/kT} - \frac{\rho}{\rho_D}\alpha^2\right\}, \tag{4.10}$$

where $h = h(x)$ in this approximation. The equation (4.10) together with (4.7), (4.8) and (4.9) becomes a first-order differential equation which can be solved along each streamline, i.e. for each value of ψ. The values of $u(\psi)$ and $I(\psi)$ can be deduced from their values on the shock wave where the streamline ψ crosses it. For this purpose, the shock wave can be assumed to lie along the body itself.

Having in this way obtained the amount of dissociation along each streamline we then find it possible to obtain the positions of the shock wave and streamlines from the formula

$$y = \int_0^{\psi} \frac{1}{kpu}\, d\psi \tag{4.11}$$

for x constant. This may be written

$$y = \int_0^{\psi} \frac{\{I(\psi)-(D/2m)\alpha\}(1+\alpha)}{k(x).p(x,\psi).(4+\alpha).u(\psi)}\, d\psi, \tag{4.12}$$

which can be evaluated when the solutions of (4.10) are known. The theory will again break down in regions where ρ becomes small, or p becomes small, as noted in the previous paper (Freeman 1956). This occurs at some point on most bodies, since the centrifugal forces tend to decrease the pressure at the body surface.

Near the body, the velocity u is small due to the fact that the streamlines there originate at the stagnation point. In the case of two-dimensional flow this requires a higher approximation to u to be found to make (4.12) converge, although this is not necessary (see Freeman 1956) in the three-dimensional case. Since the condition $u \to 0$ at the body requires that the terms in the curly bracket of (4.10) should vanish, we infer that dissociative equilibrium is achieved in this region. Thus along the body itself the amount of dissociation is determined by

$$\frac{\alpha^2}{1-\alpha} = \frac{\rho_D}{\rho} e^{-D/kT}. \tag{4.13}$$

Physically this means that the time scale of the flow is so large that the gas has time to adjust itself to equilibrium. If this is the case, it is possible to obtain α along $\psi = 0$, as the variation of $p(x,\psi)$ is already known. Hence it is relatively easy to obtain a second approximation to u near the wall by retaining the pressure term in the first equation of (4.1) to a first approximation and putting $\psi = 0$. Hence

$$u = u(\psi) - \int_0^{x} \frac{1}{\rho h} \frac{\partial p}{\partial x}\, dx, \tag{4.14}$$

where ρ is determined by (4.9). It is possible to develop the theory for the two-dimensional flow provided the above higher approximation is introduced.

In the following, however, we concern ourselves solely with axially symmetric bluff bodies since these are likely to be the most important from a practical viewpoint. Further, we shall consider the particular case of a sphere. This is the simplest type of body and will give the behaviour in regions near the stagnation point correctly for all bluff bodies with the same local radius of curvature. The approximation does however break down (Freeman 1956) before the streamlines reach an angle of 60° from the front stagnation point due to the decrease in pressure along the body.

For a sphere of radius a, we introduce the new variable ξ defined by $\psi = \frac{1}{2}\rho_0 U a^2 \sin^2\xi$. This gives $u = U\sin\xi$, $I = \frac{1}{2}U^2\cos^2\xi$ and

$$p = \left\{\frac{\sin 3\theta + \sin^3\xi}{3\sin\theta}\right\}\rho_0 U^2 \tag{4.15}$$

(see Freeman 1956), where θ is the angle measured from the front stagnation point. Equation (4.10) may then be written in the form

$$\frac{\partial\alpha}{\partial\Theta} = \frac{4+\alpha}{(1+\alpha)(1-[\alpha/\mu_1])}\left\{(1-\alpha)e^{-(4+\alpha)/(\mu_1-\alpha)} - \right.$$
$$\left. - \frac{2\rho_0}{\rho_D}\left(\frac{\sin 3\theta + \sin^3\xi}{3\sin\theta\cos^2\xi}\right)\frac{(4+\alpha)\alpha^2}{(1+\alpha)(1-[\alpha/\mu_1])}\right\} \tag{4.16}$$

where

$$\Theta = \frac{2aC\rho_0}{U}\int_\xi^\theta \left\{\frac{\sin 3\theta + \sin^3\xi}{3\sin\theta\sin\xi\cos^2\xi}\right\} d\theta.$$

Here, we have assumed that $s = 0$ and written $\mu_1 = \mu\cos^2\xi$. The latter integral can be evaluated to give

$$\Theta = \frac{2aC\rho_0}{U}\frac{[\theta - \xi + \sin 2\theta - \sin 2\xi + \sin^3\xi\log(\tan\frac{1}{2}\theta/\tan\frac{1}{2}\xi)]}{3\sin\xi\cos^2\xi}. \tag{4.17}$$

Substituting in (4.16) the value of θ from (4.17), we obtain a differential equation in α and Θ along the streamline ξ = constant. This must be solved numerically however since (4.17) gives only an implicit relation for θ and equation (4.16) is extremely complex. When (4.16) is solved, the position of the streamlines may be obtained from

$$y = \frac{3}{2}\int_0^\xi \frac{\cos^3\xi(1+\alpha)(1-[\alpha/\mu_1])}{(\sin 3\theta + \sin^3\xi)(4+\alpha)}, \tag{4.18}$$

and the position of the shock is then derived by putting $\xi = \theta$ in (4.18). Near the front stagnation point, it is possible to extend the theory a little further. In this region, since $\sin\xi \sim \xi$ and $\cos\xi \sim 1$, (4.16) may be written

$$\frac{\partial\alpha}{\partial\Theta} = \frac{4+\alpha}{(1+\alpha)(1-[\alpha/\mu])}\left\{(1-\alpha)e^{-(4+\alpha)/(\mu-\alpha)} - \frac{2\rho_0}{\rho_D}\frac{\alpha^2(4+\alpha)}{(1+\alpha)(1-[\alpha/\mu])}\right\}, \tag{4.19}$$

where
$$\Theta = \Lambda\left(\frac{\theta-\xi}{\xi}\right) \quad \text{with} \quad \Lambda = \frac{2aC\rho_0}{U},$$

and (4.18) simply becomes

$$\frac{y}{a} = \frac{1}{2\theta}\int_0^\xi \frac{(1+\alpha)(1-[\alpha/\mu])}{(4+\alpha)}\,d\xi. \tag{4.20}$$

Assuming that α is a function of Θ only, we then have

$$\frac{d\alpha}{d\Theta} = \frac{(4+\alpha)}{(1+\alpha)(1-[\alpha/\mu])}\left\{(1-\alpha)e^{-(4+\alpha)/(\mu-\alpha)} - \frac{2\rho_0}{\rho_D}\frac{\alpha^2(4+\alpha)}{(1+\alpha)(1-[\alpha/\mu])}\right\}, \tag{4.21}$$

and from (4.20)

$$\frac{y}{a} = \frac{1}{2\Lambda}\int_{\Lambda(\theta-\xi)/\xi}^{\infty} \frac{(1+\alpha)(1-[\alpha/\mu])\,d\Theta}{(4+\alpha)(1+[\Theta/\Lambda])^2}. \tag{4.22}$$

The stand-off distance, δ, is then given by putting $\theta = \xi$ in (4.22), and hence we obtain

$$\frac{\delta}{a} = \frac{1}{2\Lambda}\int_0^\infty \frac{(1+\alpha)(1-[\alpha/\mu])\,d\Theta}{(4+\alpha)(1+[\Theta/\Lambda])^2}, \tag{4.23}$$

where

$$\Theta = \int_0^\alpha \frac{(1+\alpha)(1-[\alpha/\mu])}{(4+\alpha)}\left\{(1-\alpha)e^{-(4+\alpha)/(\mu-\alpha)} - \frac{2\rho_0}{\rho_D}\frac{\alpha^2(4+\alpha)}{(1+\alpha)(1-[\alpha/\mu])}\right\}^{-1} d\alpha.$$

5. NUMERICAL COMPUTATIONS

In the preceding section, a theory has been developed to give the flow pattern for a uniform stream of an ideal dissociating gas past a sphere. In view of the complex nature of the equations, however, it was not possible to state explicitly any results. It is necessary therefore to continue by adopting numerical methods and restricting consideration to particular cases. In view of the fact that probably most of the variation is determined by the exponential factor, it was decided to take one particular flow (with $\mu = 1$, $\rho_0/\rho_D = 10^{-6}$) and attempt to exhibit the dependence on the coefficient Λ which determines the effective time scale of the dissociative process. The results obtained are exhibited in figures 7 to 11. Figure 7 shows a typical result for the dissociation along a streamline ($\xi = 5°$). It will be noticed that the variation along each streamline is similar to that behind a normal shock wave. The rate at which dissociation takes place however depends very much on the value of the time scale factor Λ. For $\Lambda = 0$, we obtain the solution for a perfect gas with $\gamma = \frac{4}{3}$, whereas for large Λ we approach the solution for a gas in dissociative equilibrium.

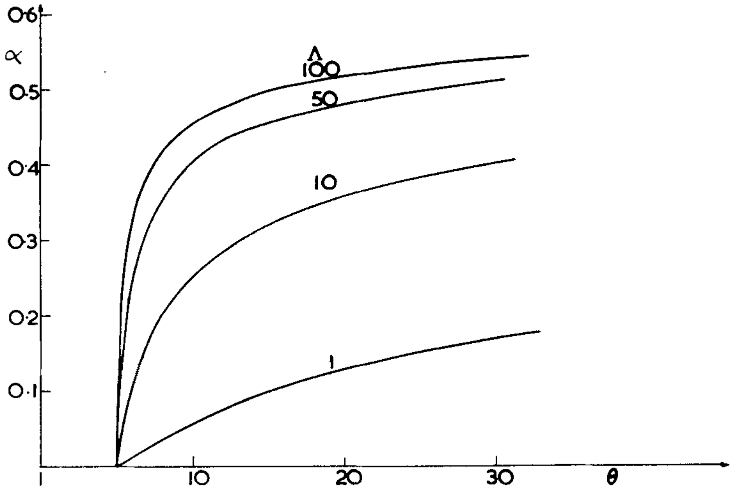
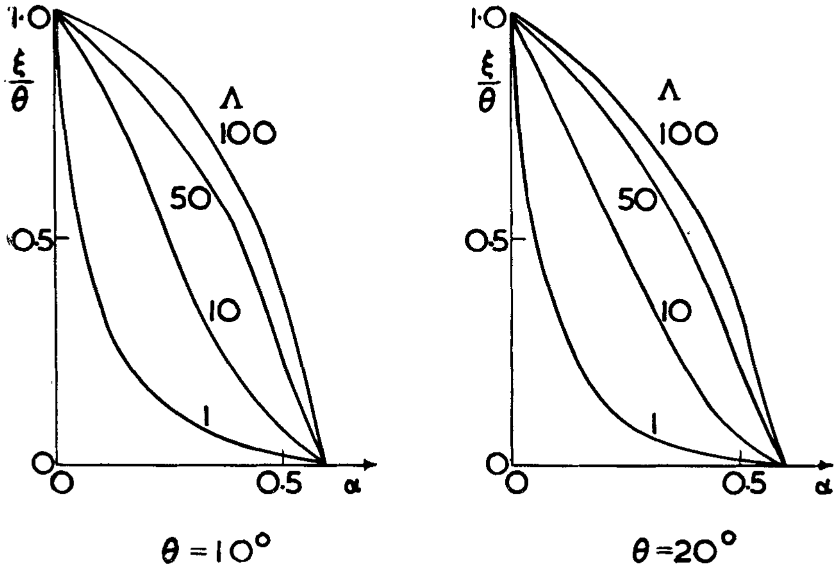


Figure 7. The amount of dissociation along the streamline $\xi = 5°$ for various values of Λ in flow past a sphere ($\mu = 1$, $\rho_0/\rho_D = 10^{-6}$).



(*a*) (*b*)

Figure 8. The dissociation profiles between the shock wave and the surface of the sphere ($\mu = 1$, $\rho_0/\rho_D = 10^{-6}$).

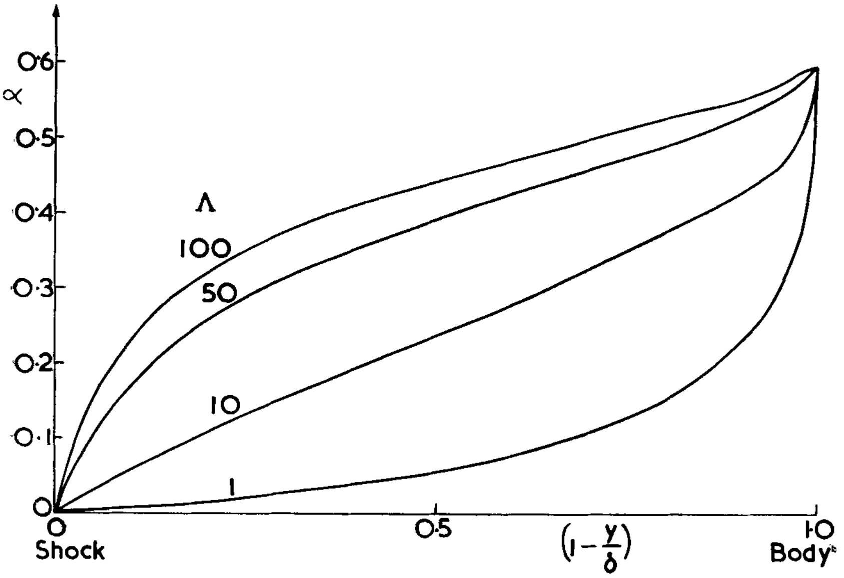


Figure 9. The amount of dissociation α along the dividing streamline between the shock wave and the stagnation point for various values of $\Lambda(\mu = 1, \rho_0/\rho_D = 10^{-6})$.

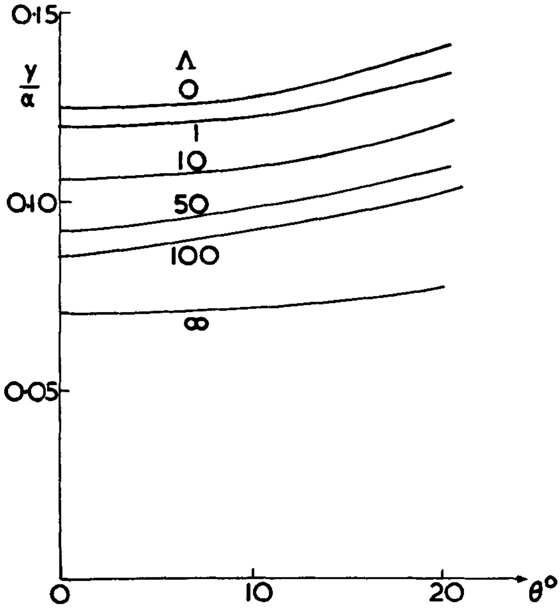


Figure 10. The shock shape for various values of $\Lambda(\mu = 1, \rho_0/\rho_D = 10^{-6})$.

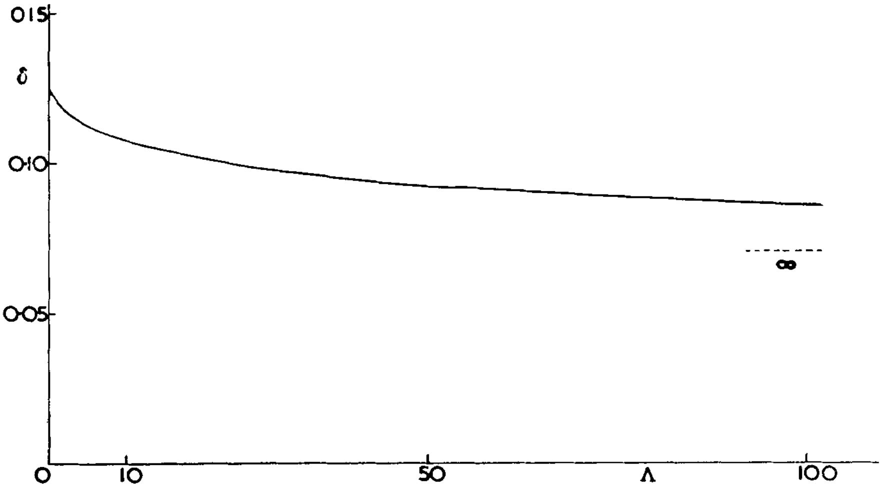


Figure 11. The ' stand-off ' distance δ as a function of $\Lambda(\mu = 1, \rho_0/\rho_D = 10^{-6})$.

Figure 8 shows the dissociation profiles at $\theta = 10^\circ$ and 20°. The dissociation begins to be important closer and closer to the shock wave ($\xi = \theta$) as Λ is increased. For the smaller values of Λ (< 1) the dissociation takes place almost completely in the region near the body where the velocities are small. In figure 9, the results obtained at the stagnation point from equations (4.21), and (4.22) are plotted to show the variation along the dividing streamline of α, the amount of dissociation. The rapid rise of α in the regions of low velocity when Λ is small is again evident. From a physical viewpoint however, figures 10 and 11 probably give the most useful information. The distance of the shock wave from the body can be easily measured from Schlieren or shadow photographs and consequently any variation with dissociation observed. In figure 10, the distance of the shock wave away from the body for various values of Λ is shown, and in figure 11 the stand-off distance itself is plotted as a function of Λ. It will be seen that between the limits of a gas with constant specific heats and a dissociated gas in thermodynamic equilibrium the distance of the shock wave away from the body can change by as much as 50%. It is hoped that these results, although only of limited application since they are obtained in this one particular case, are of value in showing that appreciable changes in the geometry of the flow field may be expected.

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