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Non-equilibrium Theory of an Ideal-dissociating Gas through a Conical Nozzle

by

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Corrections and addenda C.P. No.438

Page 1, line 28

Insert "at conditions" and "at hypersonic speed"

line 40

Insert "and a cause of concern to the aerodynamicist who is interested in making tests within such nozzles"

Page 2, line 24

Make new paragraph and insert "one dimensional".

line 26

Delete "normal to the axis may only" and insert "in area"

Page 6, line 37

Delete "The amount .... parameter"

line 39

Insert "The author would refer the reader to the former work for a more detailed discussion of this problem".

line 20

Delete "The form of" and "looks promising since it would"

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Non-equilibrium Theory of an Ideal-dissociating Gas through a Conical Nozzle

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N. C. Freeman, Ph.D.
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5th August, 1958

SUMMARY

The one-dimensional flow of an ideal-dissociating gas in non-equilibrium flow through a conical nozzle is investigated using the simple rate equation of Freeman (1958). The effect of the rate parameter Λ (the ratio of the time scale of the motion to that of dissociation) on the flow is investigated for one set of initial conditions. It is shown that thermodynamic equilibrium cannot be achieved in the conical section if Λ is finite. The composition of the gas becomes frozen at some point in the nozzle and further expansion causes no further recombination.

Similar results have been obtained by Bray (1958) and Heims (1958).

Introduction

In a recent paper the author considered the effect of dissociation away from thermodynamic equilibrium in a gas flowing through a plane shock wave and past a bluff body (Freeman, 1958). A simple rate equation was postulated depending on the collision theory of the dissociation process to predict the relative rates of dissociation and recombination in the gas.

In this paper this rate equation is used to compute the flow obtained in a conical nozzle. This type of flow occurs in a hypersonic shock tunnel when the hot gas generated behind the shock wave is expanded through a nozzle to obtain higher Mach numbers in the working section. The hot gas (at a sufficient distance behind the shock wave which produces it) will be in thermodynamic equilibrium, but this equilibrium will be disturbed again as the flow expands in the nozzle. The resulting effect is well known to chemical engineers (Penner, 1955). If the expansion is sufficiently rapid, the cooling in the nozzle occurs at a rate which is much faster than the dissociation process itself which is in this case mostly confined to the recombination of atoms into molecules. Consequently the density of the atoms and molecules in the nozzle falls to such a level that the heat recovered from recombination collisions is insufficient to combat the large loss of heat in expansion. In fact, a position is eventually reached where the composition of the

gas/

gas 'freezes' out with a certain amount of dissociated gas still existing at temperatures much below the equilibrium values for the gas.

Thus the air in the working section of the tunnel will not be in thermodynamic equilibrium. The amount by which the gas is out of equilibrium depends on the rate at which the dissociation takes place in the nozzle and, in particular, on a parameter Λ which is the ratio of the time scale for the flow through the nozzle to the time scale of the dissociation process. If Λ is small, the changes due to dissociation take place much slower than the time the gas takes to move through the nozzle. Consequently, the gas remains frozen at a level close to its initial dissociation level. However, if Λ is large, the dissociation rate is rapid compared to the time scale of the flow, and the gas is near thermodynamic equilibrium. Between these two extremes lies the correct value for the particular gas with which we are concerned. At present, values of the rate parameter are not available for direct comparison, although the general indication is that the recombination may take place very rapidly.

The procedure adopted for the calculations in the present paper is to consider the flow in the nozzle to be one-dimensional and inviscid. A stream of air in thermodynamic equilibrium of velocity u_o, density ρ_o, pressure p_o, temperature T_o and an amount of dissociation α_o enters the nozzle at the point $x = 0$. The amount of dissociation is the ratio of the weight of atoms per unit volume to the weight of atoms and molecules. This approximation may be quite reasonable for the case of nozzles in hypersonic flow where the nozzle angle is usually quite small and hence changes normal to the axis may only occur slowly. The area of the nozzle is specified in terms of the initial area A_o and a length scale x_o in the form $A = A_o(1 + [x/x_o])^2$. x_o is then the distance of the initial section from the apex of the cone, and x is the distance along the cone axis from the initial section.

2. Equations of Motion

The gas in the nozzle is specified in terms of variables α, ρ, p, u and T which denote the amount of dissociation, density, pressure, velocity and temperature respectively. As the gas flows through the nozzle, mass, momentum and energy are conserved. These requirements may be written for the ideal dissociating gas postulated by Lighthill (1957) and used in the previous paper (Freeman, 1958) in the form

$$\rho u A = \rho_o u_o A_o, \qquad \ldots(2.1)$$

$$\frac{di}{dx} = -\frac{1}{\rho}\frac{dp}{dx}, \qquad \ldots(2.2)$$

and

$$i + \tfrac{1}{2}u^2 = i_o + \tfrac{1}{2}u_o^2 \qquad \ldots(2.3)$$

where $i = \dfrac{(4+\alpha)}{(1+\alpha)}\dfrac{p}{\rho} + \dfrac{D}{2m}\alpha$ is the enthalpy of the dissociating gas.

D is the energy of dissociation and m the mass of one atom. The rate of dissociation is then postulated to take the form

u/

$$u \frac{d\alpha}{dx} = \frac{C}{T^s} \left\{ \rho(1 - \alpha)\, e^{-\frac{D}{kT}} - \frac{\rho^2}{\rho_D} \alpha^2 \right\} \qquad \ldots(2.4)$$

where k = Boltzmann's constant and C, s and ρ_D are constants. ρ_D is a characteristic density for the gas and may be obtained from equilibrium considerations. C governs the rate of the dissociation process. The exponent s was inserted in the equation to take account of the distribution of energy in the various degrees of freedom during the collisions, and was discussed in a previous paper (Freeman 1958). In view of the dependence of the behaviour on the exponential term, the effect of this factor is likely to be small, and in the following work it is assumed zero. It should be noted, however, that the behaviour of the gas when governed by the recombination process is likely to be influenced by this factor. Equation (2.4) together with (2.1), (2.2), (2.3) and the equation of state for the gas, which is

$$\frac{p}{\rho} = RT(1 + \alpha) \qquad \ldots(2.5)$$

where $R = k/2m$ is the gas constant for the undissociated gas, then specify the problem completely.

After a little algebra, these equations may be reduced to two simultaneous non-linear ordinary first order differential equations. These are

$$\frac{d\alpha}{dx}\left[3\mu\left\{1 - \frac{1}{\rho^2(1+x)^4}\right\}\frac{1}{(1+\alpha)(4+\alpha)} - \frac{\alpha^2 + 8\alpha + 4 - 3\alpha_o}{(1+\alpha)(4+\alpha)} + \frac{3\beta}{(4+\alpha)(1+\alpha)}\right]$$
$$+ \frac{1}{\rho}\frac{d\rho}{dx}\left\{\mu\left(1 - \frac{1}{\rho^2(1+x)^4}\right) + \beta + \alpha_o - \alpha - \frac{6\mu}{\rho^2(1+\alpha)(1+x)^4}\right\}$$
$$- \frac{12\mu}{(1+\alpha)\rho^2(1+x)^5} = 0 \qquad \ldots(2.6)$$

and

$$\frac{d\alpha}{dx} = \rho(1+x)^2\Lambda\left\{\rho(1-\alpha)\exp\left[-\frac{4+\alpha}{\alpha_o - \alpha + \beta + \mu(1 - \rho^{-2}(1+x)^{-4})}\right] - \frac{\rho^2\alpha^2}{\rho_D/\rho_o}\right\} \qquad \ldots(2.7)$$

where we have non-dimensionalised the variables by writing x for x/x_o, ρ for ρ/ρ_o. β and μ correspond to the ratios of the initial thermal energy to the dissociation energy $i_o/[D/2m]$ and the initial kinetic energy to the dissociation energy $\frac{1}{2}u_o^2/[D/2m]$. The rate process is

governed/

governed by the value of the parameter $\Lambda = C\rho_o x_o/u_o$ which is the ratio of the time scale of the flow through the nozzle x_o/u_o to that for the dissociation $[C\rho_o]^{-1}$. The equations (2.6) and (2.7) must then be solved with the boundary conditions

$$\alpha = \alpha_o, \quad \rho = 1 \quad \text{at} \quad x = 0. \qquad \ldots(2.8)$$

It will be observed that in general it is difficult to obtain a solution to (2.6) and (2.7) without resort to numerical methods. Particular solutions are known for $\Lambda = 0$, $\Lambda = \infty$. For $\Lambda = 0$, we have

$$\alpha = \alpha_o, \quad \beta\rho^{\frac{1+\alpha_o}{3}} = \beta + \mu\left(1 - \frac{1}{\rho^2(1+x)^4}\right) \qquad \ldots(2.9)$$

which corresponds to completely frozen flow and is the solution for an ideal gas of constant specific heats $c_p = (4 + \alpha_o)R$, $c_v = (3 + \alpha_o)R$. For $\Lambda = \infty$, we have thermodynamic equilibrium for which

$$\frac{\alpha^2}{1-\alpha} = \frac{[\rho_D/\rho_o]}{\rho} \exp\left[-\frac{1}{T}\right] \qquad \ldots(2.10)$$

$$\log T^3 + \frac{1+\alpha}{T} + \alpha + 2\log\frac{\alpha}{1-\alpha}$$

$$= \log\left[\frac{4+\alpha_o}{\beta}\right]^3 + \left(\frac{1+\alpha_o}{4+\alpha_o}\right)(\beta) + \alpha_o + 2\log\frac{\alpha_o}{1-\alpha_o}$$

$$\ldots(2.11)$$

and

$$T = \frac{1}{4+\alpha}\left\{\beta + \alpha_o - \alpha + \mu\left(1 - \frac{1}{\rho^2(1+x)^4}\right)\right\}. \qquad \ldots(2.12)$$

The first equation is obtained directly from (2.7) by letting $\Lambda \to \infty$. The remaining system of algebraic equations is obtained by integrating a combination of equations (2.1) - (2.4) with $\Lambda = \infty$. The integrable equation corresponds to the entropy of the flow which is conserved when $\Lambda = \infty$. Since it is not possible to obtain explicit solution from equations (2.6) and (2.7) it was decided to compute numerically solutions corresponding to one set of conditions behind a shock wave and attempt to find the variation of the resulting solution with the rate parameter Λ. The solution chosen was for a shock of Mach number approximately 18 moving into air at a pressure of approximately 10 mm of Hg. The equilibrium relations across a shock wave for the ideal dissociating gas given in Lighthill's paper (1957) were used. The corresponding values of α_o, β and μ are 0·40, 0·29 and 0·60 respectively with $\rho_D/\rho_o = 10^6$.

The resulting solution for α as a function of x at various values of Λ are plotted in Fig. 1. It will be seen that the dissociation

in/

in the nozzle takes place at first near the equilibrium value and then breaks away very quickly to assume a constant value which we will denote by α_∞. A plot of the density shows that the density differs very little for the extreme cases of completely frozen and equilibrium flow (Fig. 2). The freeze of α at the value α_∞ takes place when the rate of dissociation becomes small which occurs rapidly and almost discontinuously due to the exponential form of the term. Fig. 3 shows how α_∞ varies with Λ. It will be seen that the change from completely frozen to equilibrium flow in which $\alpha_\infty = \infty$ takes place over the range $4 < \log_{10} \Lambda < 13$. For a nozzle of half-angle θ and initial area A_o, the parameter Λ may be written

$$\frac{[C\rho_o]}{\tan\theta}\sqrt{\frac{A_o}{\pi}} \qquad \text{...(2.13)}$$

and thus it should be possible by varying the geometry of the nozzle and the density conditions at the beginning to obtain the range of values of Λ to check the theory. The parameter $[C\rho_o]$ may be determined from a detailed study of the density variation in the flow behind a shock wave.

Mathematically the equations (2.6) and (2.7) are interesting due to the rapid variation of the solution in the neighbourhood of the point of divergence from the 'equilibrium' value. Even numerical solution of the equations is difficult if the solution is required over the complete range of Λ due to the severe form of the behaviour at the 'divergence' point. As was mentioned in the Introduction the solution is not entirely independent of the power of T originally introduced in the rate equation (2.4), since the form of the recombination rate after the departure from the equilibrium curve will be dependent upon it. The equation (2.4) may then be written in the form

$$u\frac{d\alpha}{dx} = -\frac{C}{T^{-s}}\frac{\rho^2}{\rho_D}\alpha^2 \qquad \text{...(2.14)}$$

since ρ and u very quickly tend to their limiting asymptotic forms where $\rho \sim x^{-2}$ and $u \sim u_1$ (constant) as $x \to \infty$. The form of this equation becomes

$$\frac{d\alpha}{dx} = -B\frac{\alpha^2}{x^4}.\frac{1}{T^{+s}}. \qquad \text{...(2.15)}$$

Thus it is not possible in this application to ignore the variation with T^{-s} as was confidently done in the previous paper (Freeman 1958). It is not thought however that the exponent s could be sufficiently large to invalidate the results completely.

3. Discussion and Conclusion

It would seem fruitful to try to explore analytically the solution of the set of equations (2.6) and (2.7). It does not seem possible to do this by any systematic approach, although a certain amount of information can be deduced from studying a simple equation which may be

regarded/

regarded as a model of the equations. This equation is derived from equation (2.7) by noting that ρ does not differ greatly from its equilibrium value ρ_e. Equation (2.7) may be written

$$\frac{d\alpha}{dx} \approx \frac{\rho_e^3(1+x)^2\Lambda}{[\rho_D/\rho_o]}\left\{\frac{\rho_D}{\rho_o}\cdot\frac{(1-\alpha)}{\rho_e}\exp\left[-\frac{(4+\alpha)}{\alpha_o-\alpha+\beta+\mu[1-\rho_e^{-2}(1+x)^{-4}}\right]-\alpha^2\right\}. \quad ...(3.1)$$

The first term can then be approximated by its value at equilibrium and we obtain

$$\frac{d\alpha}{dx} = \Lambda_D\, F(x)\, \{\alpha_e^2 - \alpha^2\} \quad ...(3.2)$$

where

$$F(x) = \rho_e^3\,(1+x)^2$$

$$...(3.3)$$

and

$$\Lambda_D = \frac{\Lambda}{\rho_D/\rho_o}.$$

Equation (3.2) is then a Riccati equation, and may be reduced to a second-order linear differential equation in the usual way by writing

$$\alpha = \frac{1}{\Lambda,F}\,\frac{1}{\beta}\,\frac{d\beta}{dx}$$

from which (3.2) becomes

$$\frac{d^2\beta}{dx^2} - \frac{F'}{F}\frac{d\beta}{dx} - \Lambda_D^2\, F^2\, \alpha_e^2\, \beta = 0. \quad ...(3.4)$$

The form of this equation looks promising since it would appear at first sight to be directly amenable to asymptotic estimation for Λ_D large. However, the form of the function α_e makes this very difficult since it behaves like xe^{-kx^ν} with $\nu > 0$ as $x \to \infty$. In fact, consideration of equation (3.4) shows that the function β depends on the Bessel functions of imaginary argument of the function $\Lambda\alpha_e$, and its rapid variation results from the variation of α_e near infinity, i.e., due to the singular behaviour of one of them at the origin. The form of equation (3.2) shows clearly however how the form of solution of the equations will change as x becomes large.

In the previous sections therefore we have considered the flow of an ideal dissociating gas through a conical nozzle, and the particular case computed shows that attainment of thermodynamic equilibrium is not possible within the nozzle. Any extension to the nozzle, such as for example, a constant area working section would restore equilibrium only comparatively slowly since the process would be governed by the recombination rate term. The amount by which the conditions differ from equilibrium depends, however, on the rate parameter.

Similar results to those obtained above have been obtained by Bray (1958) using the same rate equation and Heims (1958).

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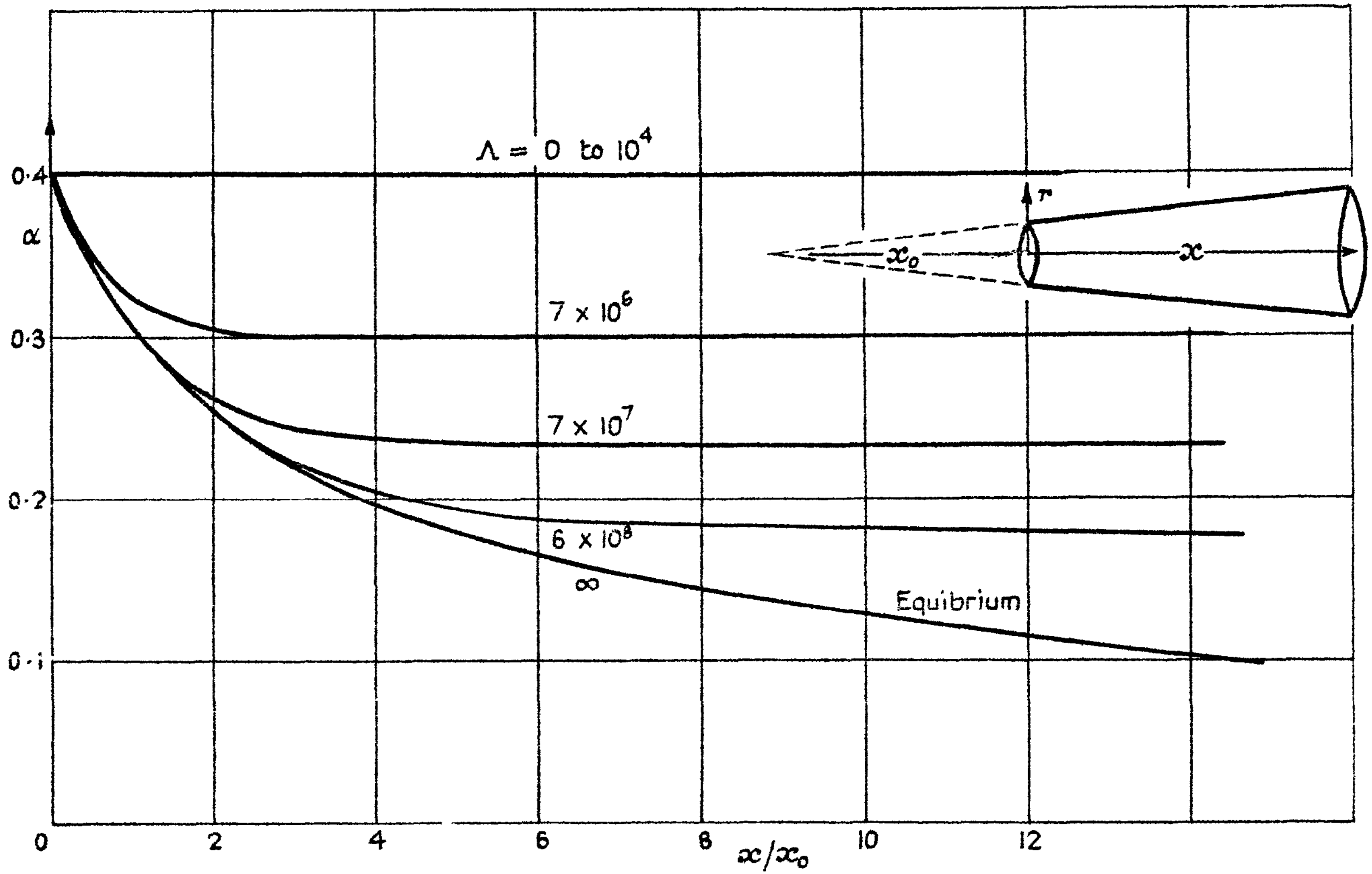
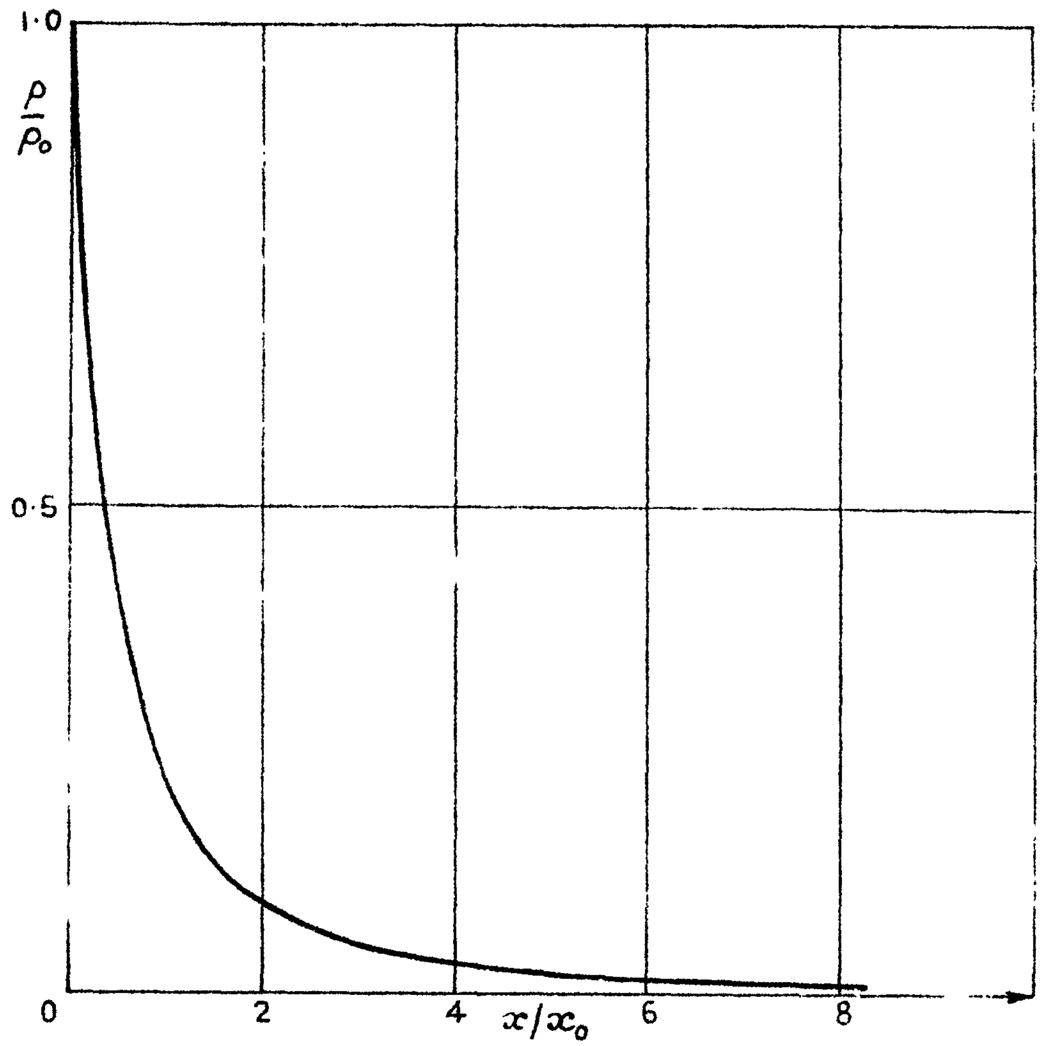


Variation of amount of dissociation, α, along the nozzle for various values of the dissociation rate parameter Λ

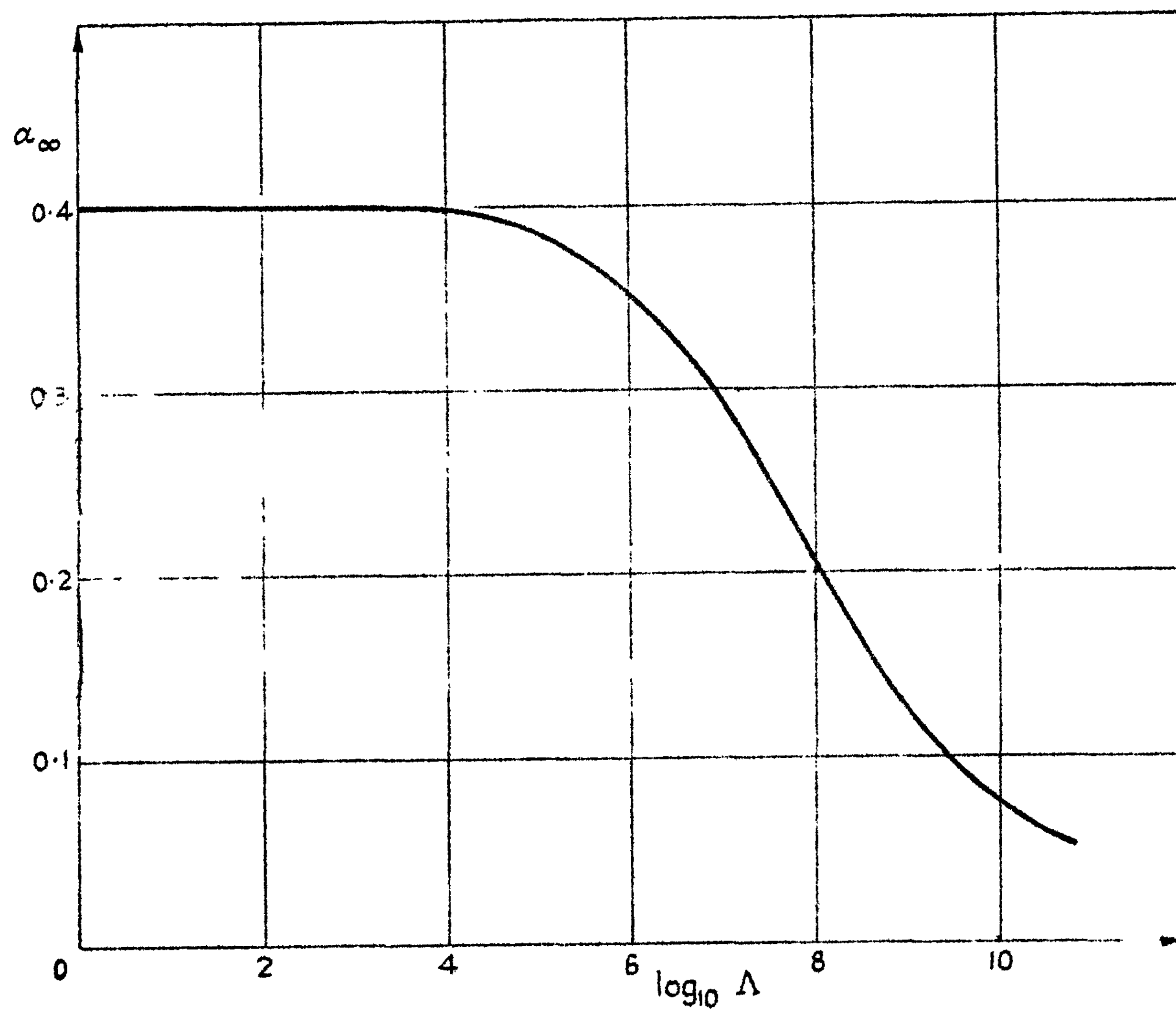
FIG. 1.

FIG 2



Variation of density along the nozzle. (Dependence on Λ cannot be shown on this scale which is identical with that of Fig 1)

FIG. 3



The variation of α_∞ with Λ

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