Dr. S. Ananthakrishnan who is now in Brazil was closely associated with this work in its early stages. I am thankful to the Ministry of Education and the Department of Atomic Energy, Government of India, for the award of a scholarship.

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THE STRUCTURE OF STRONG SHOCK WAVES USING THE FOKKER-PLANCK MODEL

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ABSTRACT

The structure of strong shock waves in monatomic gases is studied using the Fokker-Planck model to represent the particle collisions and the Mott-Smith distribution to describe the distribution function within the shock front. The differential equation governing the variation of the density within the shock is derived by using the variational principle. The thickness of the shock front is evaluated numerically for various monatomic gases for Mach numbers varying from 2 to 20, and besides, the variation of the shock thickness with viscosity is also studied for different gases. Several parameters of physical interest within the shock, such as density, temperature and mean velocity of flow are evaluated numerically and detailed curves showing their variation within the shock are presented for different Mach numbers. It is found that the temperature rises very steeply, reaches a maximum within a distance less than half the thickness of the shock and then diminishes slowly to attain its asymptotic downstream values. The variation of the mean velocity is slow for weak shocks, but for higher Mach numbers, the mean velocity diminishes steeply and reaches the downstream values within half the thickness of the shock.

1. INTRODUCTION

IN recent years, the study of the structure of strong shock waves has attracted the attention of a large number of workers. The bibliography[1-3] on the subject is too vast to be reviewed here but a perspective of the recent work in the field could be obtained from the several volumes on the Advances in Applied Mechanics. A large number of investigations on the subject have started with the BGK model for the collision in the gas at the shock. Narasimha and collaborators[4] have computed the profiles for the density and

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temperature distribution within the shock for a range of Mach numbers and have also studied the development of the complete distribution function within the shock. Besides the BGK model, the Boltzmann expression[5] for the collision integral has also served as the starting point for several investigators to study the structure of strong shock waves and the flow field near the shock.

An important technique that has been used abundantly in the literature is the method of least errors,[5,6] in which the best expression for the distribution function, usually a Mott-Smith Ansatz[7] is derived by applying the minimum error criterion on the distribution function. Using the Boltzmann equation and the Mott-Smith Ansatz for the distribution function within the shock, Narasimha and Deshpande have obtained the best solution for the distribution function by minimising the total error and have plotted the profiles for parameters of interest within the shock for a few monatomic gases.

A well-known expression for the collision integral in the Boltzmann transport equation is the Fokker-Planck term,[8] but surprisingly enough, very little work seems to have been carried out for determining the shock structure using this model for collision processes in gases. Both the Boltzmann collision integral as well as the Fokker-Planck expression are derived from probability considerations and must be equally suitable for describing the thermodynamic as well as the statistical properties of the gas within the shock front. One should also expect that both the expressions should be more accurate to describe the shock structure than the simple BGK model. A reason why the Fokker-Planck collision term was not used extensively in the literature is its supposed complexity but it is nevertheless a practicable model for studying shock structure not only for simple monatomic gases but for complicated molecules where vibrational, rotational and electronic relaxation effects are present. It is the object of the present paper to study both analytically and numerically the structure of strong shock waves in monatomic gases like argon using this model.

2. THE FOKKER-PLANCK TERM

The Boltzmann transport equation for a gas is given by

$$\frac{\partial f}{\partial t} + \underline{v}\cdot\nabla f + \frac{\mathbf{F}}{m}\cdot\nabla_v f = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}. \tag{1}$$

where m, v and F denote respectively the mass of the atom, its thermal velocity and the force acting on it. As mentioned in the Introduction, various

expressions are available for the collision operator $(\partial f/\partial t)_c$. In this paper, we use the Fokker-Planck expression for the collision which is given by

$$\begin{aligned}\triangle t\left(\frac{\partial f}{\partial t}\right) = &-\sum_i \frac{\partial}{\partial v_i}(f\langle\triangle v_i\rangle)\\ &+\frac{1}{2}\sum_i \frac{\partial^2}{\partial v_i^2}(f\langle\triangle v_i^2\rangle)\\ &+\sum_{i<j}\frac{\partial^2}{\partial v_i\partial v_j}(f\langle\triangle v_i\triangle v_j\rangle) + 0(\triangle t)^2.\end{aligned} \tag{2}$$

Here $\triangle v_i$ denotes the increment in the velocity as a result of collision during a time interval $\triangle t$. The Fokker-Planck term involves the averages $\langle\triangle v_i\rangle$; $\langle\triangle v_i\triangle v_j\rangle$ and to evaluate these, it is necessary to know the distribution function $\psi(v_0, v, t)$ which gives the probability that the velocity of an atom jumps to v from an initial value v_0 during an interval of time t as a result of collision. For gases in which the change in momentum of a particle due to collisions occurs stochastically, the distribution function ψ is well known[8] and is given by

$$\begin{aligned}\psi(v, v_0, t) = &\left[\frac{m}{2\pi kT}(1-e^{-2t/\tau})\right]^{3/2}\\ &\times\exp.\left\{-\frac{(v-v_0e^{-t/\tau})^2}{\frac{2kT}{m}(1-e^{-2t/\tau})}\right\}.\end{aligned} \tag{3}$$

For large values of t, the above function tends to a Maxwellian distribution, and its time dependence is significant for values of t of the order of the frictional parameter τ. This is again related to the coefficient of viscosity and is given by

$$\beta = \frac{1}{\tau} = \frac{6\pi a\eta}{m} \tag{4}$$

where a is the radius of the atom, m its mass and η is the coefficient of viscosity. Evaluating the averages using the distribution function (3), we find that

$$\begin{aligned}\langle\triangle v_i\rangle &= \int \triangle v_i\,\psi(v_0, v, t)\,d(\triangle v)\\ &= -b_i\end{aligned} \tag{5}$$

$$\langle\triangle v_i\triangle v_j\rangle = a^2\delta_{ij} + b_ib_j \tag{6}$$

where

$$a^2 = \frac{kT}{m}(1 - e^{-2t/\tau}) \tag{7 a}$$

and

$$b_i = v_i(1 - e^{-t/\tau}). \tag{7 b}$$

Since τ is small, we shall set $t = \triangle t$ and evaluate by passing on to the limit when $\triangle t \to 0$. Later, we shall consider the case when this approximation is not made, and Δt is taken to be some characteristic time for the problem, *i.e.*, collision interval or the time taken for a molecule in the upstream gas to pass through a distance of the order of the shock thickness. If we pass on to the limit when $\triangle t \to 0$, we obtain the well-known formula

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \beta \operatorname{div} f \underset{\sim}{v} + q \triangle_v f \tag{8}$$

where,

$$q = \frac{\beta k T}{m}. \tag{9}$$

3. THE SHOCK STRUCTURE

We shall consider the steady one-dimensional flow of a gas through a plane shock layer. In a frame of reference fixed with respect to the shock, the Boltzmann equation reduces to

$$v_x \frac{d}{dx} f(v, x) = \beta \operatorname{div} f \underset{\sim}{v} + q \triangle_v f$$

$$= G(v, f) \tag{10}$$

Here $G(v, f)$ represents the collision term. We denote by (n_1, u_1, T_1, p_1) and (n_2, u_2, T_2, p_2) respectively the density, mean velocity of flow, temperature and pressure in front of and behind the shock. The distribution function is a function of x at or near the shock, and attains the free stream values far away from the shock on either side and the boundary conditions are

$$f(v, -\infty) = F_1(v) \; ; \; f(v, +\infty) = F_2(v) \tag{11}$$

where F denotes the equilibrium Maxwellian distribution. The subscripts 1 and 2 refer in general to the far upstream and downstream sides of the shock.

For the distribution function f_0 within the shock, we assume a Mott-Smith function and write

$$f_0(v, x) = [1 - \gamma(x)] F_1(v) + \gamma(x) F_2(v) \tag{12}$$

where

$$F_i(v) = n_i \left(\frac{\beta_i}{2\pi}\right)^{3/2} \exp. [-\beta_i (v - u_i)^2], \; i = 1, 2. \tag{13}$$

where the parameters n_i, u_i and β_i denote respectively the number density, gas velocity and the inverse square of the most probable thermal speed for the distribution.

The density function $\gamma(x)$ in (12) is unknown for the present and we determine it by the method of minimum errors following Narasimha and Deshpande.[5] We define the residual and total errors by means of the equations

$$e(\underset{\sim}{v}, x) = v_x \frac{df_0}{dx} - G(v, f_0) \tag{14}$$

and

$$E(x) = \int e^2(\underset{\sim}{v}, x)\, d\underset{\sim}{v} \tag{15}$$

where the integration extends over the whole of the velocity space. We further write

$$J = \int E(x)\, dx \tag{16}$$

where the integration extends over the thickness of the shock. J then gives the total error. A simple calculation now shows that

$$G(v, f_0) = 3\beta f_0 + \beta v \cdot \nabla_v f_0$$
$$+ q\gamma_1 \triangle_v F_1(v) + q\gamma_2 \triangle_v F_2(v) \tag{17}$$

where for the sake of convenience we write

$$\gamma_1 = [1 - \gamma(x)] \; ; \; \gamma_2 = \gamma(x) \tag{18}$$

Further

$$E(x) = \int d\underset{\sim}{v} \{\gamma'^2 v_x^2 (F_1 - F_2)^2 + [3\beta(\gamma_1 F_1 + \gamma_2 F_2)$$
$$+ \beta v \cdot \nabla_v (\gamma_1 F_1 + \gamma_2 F_2) + q\gamma_1 \triangle_v F_1 + q\gamma_2 \triangle_v F_2]^2$$

$$- 2v_x\gamma' (F_2 - F_1) [3\beta (\gamma_1 F_1 + \gamma_2 F_2) + \beta \cdot \nabla v$$

$$\times (\gamma_1 F_1 + \gamma_2 F_2) + q\,\gamma_1 \,\Delta v\, F_1 + q\,\gamma_2 \,\Delta v\, F_2]\} \tag{19}$$

$$= P\gamma'^2 + \gamma' (T\gamma + U) + Q\gamma^2 + R\gamma + S \tag{20}$$

where the coefficients P, Q, R, S, T and U can easily be written as integrals by comparison of (19) with (20). For example,

$$P = \int v_x^2 (F_2 - F_1)^2 \, d\underline{v} \tag{21}$$

Writing

$$T\gamma + U = Z$$

$$Q\gamma^2 + R\gamma + S = Y \tag{22}$$

we can rewrite (20) as

$$E(\gamma, \gamma', x) = P\gamma'^2 + Z\gamma' + Y \tag{23}$$

where P, Z and Y are functions of γ and hence of x. The integrals occurring in P, Z and Y can be evaluated by direct integration. These can in fact be expressed as a sum of certain simple integrals, whose values are tabulated in *Appendix I*. After heavy algebraic work, we find that P, Y and Z are given by the following expressions:

$$P = \int v_x^2 (F_2 - F_1)^2 \, d\underline{v}$$

$$= \left[n_1^2 \left(\frac{\beta_1}{2\pi}\right)^{3/2} \left\{\frac{1}{4\beta_1} + u_1^2\right\} + n_2^2 \left(\frac{\beta_2}{2\pi}\right)^{3/2} \left\{\frac{1}{4\beta_2} + u_2^2\right\} \right.$$

$$\left. - 2n_1 n_2 \left(\frac{\beta_1\beta_2}{2\pi}\right)^{3/2} \frac{1}{(\beta_1 + \beta_2)^{3/2}} e^{-\delta} \left\{\frac{1}{2} + \frac{(\beta_1 u_1 + \beta_2 u_2)^2}{\beta_1 + \beta_2}\right\} \right] \tag{24}$$

where

$$\delta = \frac{\beta_1\beta_2}{(\beta_1 + \beta_2)} (u_1 - u_2)^2$$

It is to be noted that P is independent of x. Next

$$Z = n_1^2 \left(\frac{\beta_1}{2\pi}\right)^{3/2} [-\beta\gamma_1 u_1 + 2u_1 (3\beta\gamma_1 - 6q\beta_1\gamma_1) + 3u_1 (2q\gamma_1\beta_1 - \beta\gamma_1)]$$

$$- n_2^2 \left(\frac{\beta_2}{2\pi}\right)^{3/2} [-\beta\gamma_2 u_2 + 2u_2 (3\beta\gamma_2 - 6q\beta_2\gamma_2)$$

$$+ 3u_2 (2q\gamma_2\beta_2 - \beta\gamma_2)] + 2n_1 n_2 \left(\frac{\beta_1\beta_2}{\pi}\right)^{3/2} e^{-\delta}$$

$$\left\{ [3\beta a (\gamma_2 - \gamma_1) + a^2 \beta_2\gamma_2 (a - u_2) - a^2 \beta_1\gamma_1 (a - u_1) \right.$$

$$+ 4\gamma_2\beta_2^2 aq (a - u_2)^2 - 4\gamma_1\beta_1^2 qa (a - u_1^2)$$

$$- 6qa (\gamma_2\beta_2 - \gamma_1\beta_1)] \frac{1}{(\beta_1 + \beta_2)^{3/2}} + [-2\beta\beta_2\gamma_2 (2a - u_2)$$

$$+ 2\beta\beta_1\gamma_1 (2a - u_1) + 8q \{\gamma_2\beta_2^2 (a - u_2) - \gamma_1\beta_1^2 (a - u_1)\}]$$

$$\times \frac{3}{2(\beta_1 + \beta_2)^{5/2}} + [-2a\beta (\beta_2\gamma_2 - \beta_1\gamma_1) + 4qa (\gamma_2\beta_2^2 - \gamma_1\beta_1^2)]$$

$$\left. \times \frac{3}{2(\beta_1 + \beta_2)^{5/2}} \right\} \tag{25}$$

where

$$a = \frac{(\beta_1 u_1 + \beta_2 u_2)}{\beta_1 + \beta_2} \tag{26}$$

and

$$\delta = \frac{\beta_1\beta_2}{\beta_1 + \beta_2} (u_1 - u_2)^2. \tag{27}$$

Finally

$$Y = n_1^2 \left(\frac{\beta_1}{2\pi}\right)^{3/2} \left[9\gamma_1^2 (\beta - 2\beta_1 q)^2 + \frac{15}{4} (2q\gamma_1\beta_1 - \beta)^2 + \beta_1^3 u_1^2 \right.$$

$$\left. + 9\gamma_1^2 n_1^2 (\beta - 2\beta_1 q)(2q\gamma_1\beta_1 - \beta) \right] + n_2^2 \left(\frac{\beta_2}{2\pi}\right)^{3/2}$$

$$\times \left[9\gamma_2^2 (\beta - 2\beta_2 q)^2 + \frac{15}{4} (2q\gamma_2\beta_2 - \beta)^2 + \beta_2^3 u_2^2 + 9\gamma_2^2 n_2^2 \right.$$

$$\left. \times (\beta - 2\beta_2 q)(2q\gamma_2\beta_2 - \beta) \right] + n_1 n_2 \left[\frac{\beta_1\beta_2}{\pi(\beta_1 + \beta_2)}\right]^{3/2} e^{-\delta}$$

$$[18\gamma_1\gamma_2 (\beta - 2\beta_1 q)(\beta - 2\beta_2 q) + 8\beta_1\beta_2 (2q\gamma_1\beta_1 - \beta)(2q\gamma_2\beta_2 - \beta)$$

$$\times \left\{ \frac{23}{8(\beta_1 + \beta_2)^2} + \frac{5}{8(\beta_1 + \beta_2)} [(a - u_1)^2 + (a - u_2)^2] \right.$$

$$\times \left[1 + \frac{1}{8(\beta_1 + \beta_2)} \right] + \frac{(2a - u_1 - u_2)^2}{2(\beta_1 + \beta_2)} + \frac{(a - u_1)(a - u_2)}{(\beta_1 + \beta_2)} \Big\}$$

$$- \beta\beta_1\beta_2 u_2 (2q\beta_1\gamma_1 - \beta) \left\{ \frac{5(a-u_2)}{(\beta_1+\beta_2)} + \frac{8(a-u_1)}{(\beta_1+\beta_2)} \right.$$

$$\left. + 8(a-u_1)^2 (a-u_2) \right\} - \beta\beta_1\beta_2 u_1 (2q\beta_2\gamma_2 - \beta)$$

$$\times \left\{ \frac{5(a-u_1)}{(\beta_1+\beta_2)} + \frac{8(a-u_2)}{(\beta_1+\beta_1)} + 8(a-u_2)^2 (a-u_1) \right\}$$

$$+ 8\beta^2 \beta_1\beta_2 u_1 u_2 \left\{ (a-u_1)(a-u_2) + \frac{1}{2(\beta_1+\beta_2)} \right\}$$

$$+ 12\gamma_1\beta_2 (\beta - 2q\beta_1)(2q\beta_2\gamma_2 - \beta) \left\{ \frac{3}{2(\beta_1+\beta_2)} + (a-u_2)^2 \right\}$$

$$- 12\beta_1\beta_2 u_2\gamma_1 (\beta - 2\beta_1 q)(a-u_2) - 12\beta\beta_1 u_1\gamma_2 (\beta - 2\beta_2 q)(a-u_1)$$

$$\left. + 12\gamma_2\beta_1 (\beta - 2\beta_2 q)(2q\gamma_1\beta_1 - \beta) \left\{ \frac{3}{2(\beta_1+\beta_2)} + (a-u_1)^2 \right\} \right]. \tag{28}$$

The expressions for T, U, Q, R and S may similarly be found, but for lack of space, we do not reproduce them here.

The 'best' value of γ can be obtained by minimising the local error E, by regarding it as a function of the variables γ and γ' and using then the theory of maxima and minima. It can alternatively be obtained from the calculus of variations by minimizing the total error

$$J = \int E(x)\, dx = \int E(\gamma, \gamma', x)\, dx$$

by regarding J as a functional of γ and γ'. Both the methods lead to the identical set of equations. For example, differentiating (20) with respect to γ and γ', we get

$$\frac{\partial E}{\partial \gamma'} = 2P\gamma' + T\gamma + U = 0 \tag{29}$$

or

$$\gamma' = -\frac{(T\gamma + U)}{2P}. \tag{30}$$

$$\frac{\partial E}{\partial \gamma} = T\gamma' + 2Q\gamma + R = 0 \tag{31}$$

or

$$\gamma' = -\frac{(2Q\gamma + R)}{T}. \tag{32}$$

By differentiating (30) with respect to x and substituting for γ' from (32) one gets

$$2P\gamma'' = 2Q\gamma + R. \tag{33}$$

Equation (33) is the differential equation satisfied by the density function and should be solved for γ along with the boundary conditions

$$\gamma(-\infty) = 0 \quad \text{and} \quad \gamma(+\infty) = 1. \tag{34}$$

One can verify that the Euler equation for the variational principle

$$\delta J = 0 \tag{35}$$

also leads to an identical differential equation.

It was found during our calculations that a slight rearrangement of equation (33), as obtained by using the form (23) instead of (20) facilitates the numerical computations substantially.

We have now

$$\delta J = \delta \int E(\gamma, \gamma', x)\, dx = \delta \int (P\gamma'^2 + Z\gamma' + Y)\, dx = 0.$$

Here Z and Y are functions of γ. We have then

$$F_{\gamma'} = 2P\gamma' + Z\,; \quad F_\gamma = \gamma' Z_\gamma + Y_\gamma \tag{36}$$

and

$$\frac{d}{dx} F_{\gamma'} = 2P\gamma'' + Z' = 2P\gamma'' + Z_\gamma \gamma'. \tag{37}$$

Hence the Euler differential equation becomes

$$2P\gamma'' = Y_\gamma. \tag{38}$$

This equation can be integrated at once. Multiplying both sides by γ' and integrating, we get

$$P\gamma'^2 = Y + C \tag{39}$$

where C is an integration constant whose value can be determined from the boundary conditions ahead of the shock.

The thickness of the shock is now given by

$$\delta = \int dx = \int_0^1 \left(\frac{P}{Y+C}\right)^{\frac{1}{2}} dy. \tag{40}$$

4. Numerical Calculations and Discussion of Results

Numerical calculations were made for different Mach numbers varying from 2 to 20 for the thickness of the shock front, the function $\gamma(x)$, the variation of the density $n(x)$, the mean velocity $\bar{u}(x)$ and the temperature $T(x)$ within the shock front for argon. These were evaluated from the following definition for these parameters:

$$n = n_1\gamma_1 + n_2\gamma_2 = n_1 + \gamma(n_2 - n_1) \tag{41}$$

$$\bar{u} = \int \underset{\sim}{v} f(\underset{\sim}{v}, x)\, d\underset{\sim}{v} = \frac{n_1 u_1}{n} \tag{42}$$

$$p(x) = nkT(x) = \int v^2 f(\underset{\sim}{v}, x)\, d\underset{\sim}{v}$$

$$= \frac{1}{n}\sum_i n_i\gamma_i T_i + \frac{m}{kn}\sum n_i\gamma_i (u - \bar{u})^2 \tag{43}$$

where m is the mass of the atom in the gas.

The differential equation satisfied by γ involves the parameter β, which is proportional to the coefficient of viscosity. Since viscosity changes with temperature, β is a function of temperature and we chose the power law

$$\beta = \beta_0 T^S$$

with $S = \frac{1}{2}$ for the calculations. This choice was made essentially for the simplicity that it brings into the calculations but we have made some preliminary computations with the value $S = 0{\cdot}816$, which is the accepted value for argon. The parameters n_2, T_2 and M_2 downstream of the shock were calculated using the Rankine-Hugoniot relations. When the power law for β and the Rankine-Hugoniot equations were substituted in equation (39), the differential equation for γ assumes a form

$$\frac{d\gamma}{dx} = f(\gamma, x) \tag{44}$$

where

$$f = \left(\frac{Y+C}{P}\right)^{\frac{1}{2}}$$

and is a long expression. This equation was programmed for a Ferranti-Sirius digital computer and integrated directly. The curves given in Fig. 1 plot the variation of the density with respect to the distance which is given by the formula (41), for the Mach numbers $M = 3, 5$ and 10 respectively. The distance is measured in units of the upstream mean free path λ_1, and the curves were plotted for the thin layer within the shock. The curves steadily increase from their upstream values to their downstream values as determined by the jump conditions. The increase is steeper for stronger shocks represented by higher Mach numbers and takes place within a few mean free paths.

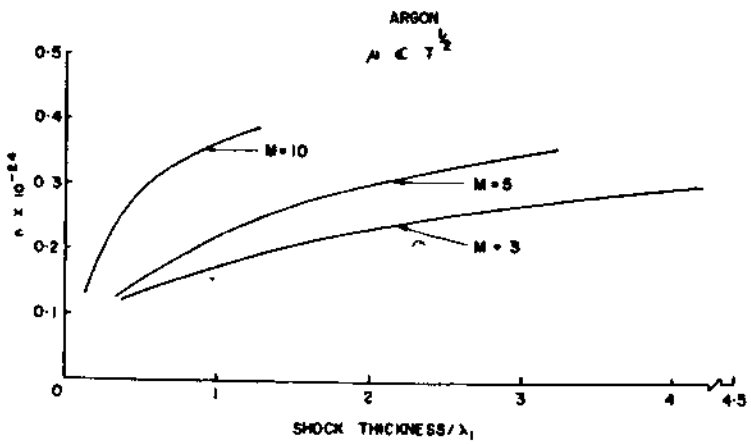

FIG. 1. Variation of n *Vs.* Shock Thickness.

The equation (40) for the thickness of the shock was integrated by Simpson's rule using the Ferranti-Sirius digital computer and the thickness of the shock was evaluated for Argon, Neon, Helium, Xenon, Krypton, for Mach numbers 2 to 20. Some typical values obtained from the output of the computer are tabulated in Table I. One may notice that the shock thickness generally decreases with strength.

In Figs. 2, 3 and 4, we have plotted $n - n_1/n_2 - n_1$ against distance within the shock. The nature of the variation of the density as shown by

TABLE I

Mach No.	Shock Thickness/λ_i				
	Helium $\mu = 200 \times 10^{-6}$ poise	Argon $\mu = 210 \times 10^{-6}$ poise	Xenon $\mu = 234 \times 10^{-6}$ poise	Krypton $\mu = 253 \times 10^{-6}$ poise	Neon μ 317·9×1 poise
2·0	1·8807995	3·8402297	19·99091	7·470854	118·94582
3·0	1·3989681	4·1824679	16·768553	7·6210040	123·20981
5·0	1·0700610	3·2400536	7·878238	4·1874116	110·6004
6·0	0·9149048	2·6452942	5·884421	3·2298241	95·06452
8·0	0·64277760	1·791395	3·902652	2·1090419	67·27930
10·0	0·45829669	1·2803399	2·813898	1·502969	50·2785
12·0	0·36511886	0·9612694	2·1397391	1·1605656	36·04286
20·0	0·13828939	0·4118914	1·0208368	0·50310960	15·27532

these curves is similar to the experimental curves given by Schultz, Grunow and Frohn[9] and others though we have not made a comparison, as the parameters in our calculations are not entirely the same as those used by these authors.

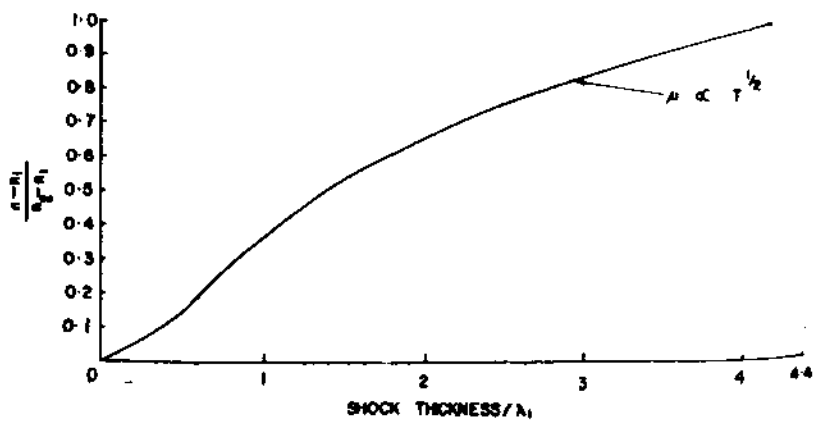

FIG. 2. Shock Profile at M = 3 (Argon)

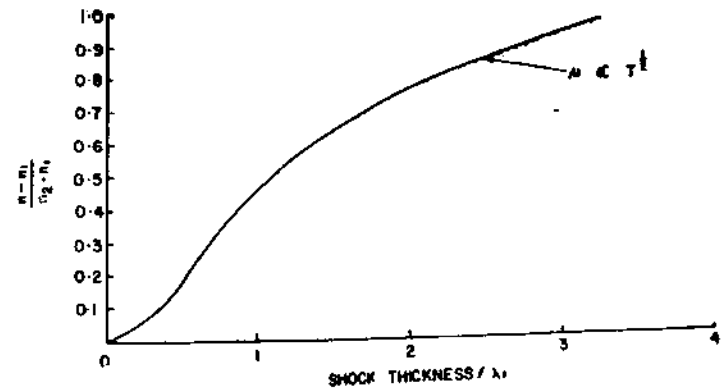

FIG. 3. Shock Profile at M = 5 (Argon).

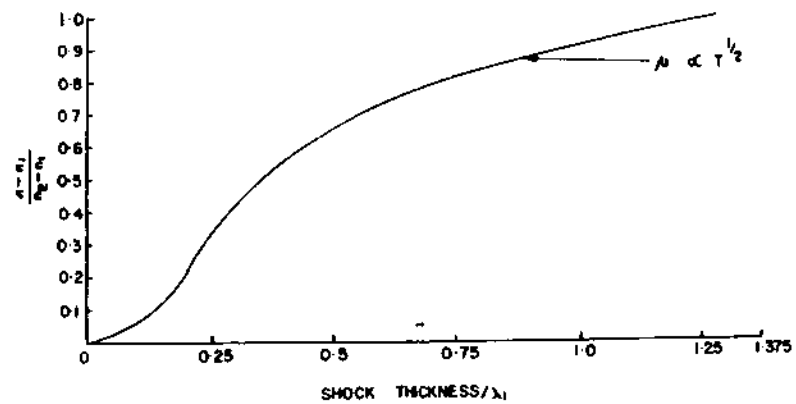

FIG. 4. Shock Profile at M = 10 (Argon).

Figures 5 and 6 plot the variations of the mean velocity U and the temperature as defined by the parameter $(T - T_1/T_2 - T_1)$ within the shock front. It can be seen that the variation in the mean velocity is slow for weak shocks, but as the Mach number increases, the mean velocity of flow diminishes steeply and reaches its downstream values within half the thickness of the shock. The curves for the temperature variation are very interesting. They show that the temperature variation is very steep, has a maximum which occurs at a distance of less than half the thickness of the shock and

then diminishes slowly to attain its asymptotic downstream values. They also show that the maximum temperature of the gas is reached within the shock and the value behind the shock as given by the Rankine-Hugoniot equations is much smaller than this. This is an important fact emerging from our studies using the Fokker-Planck model and it is worthwhile to conduct experiments to verify this kind of behaviour of the temperature within the shock front.

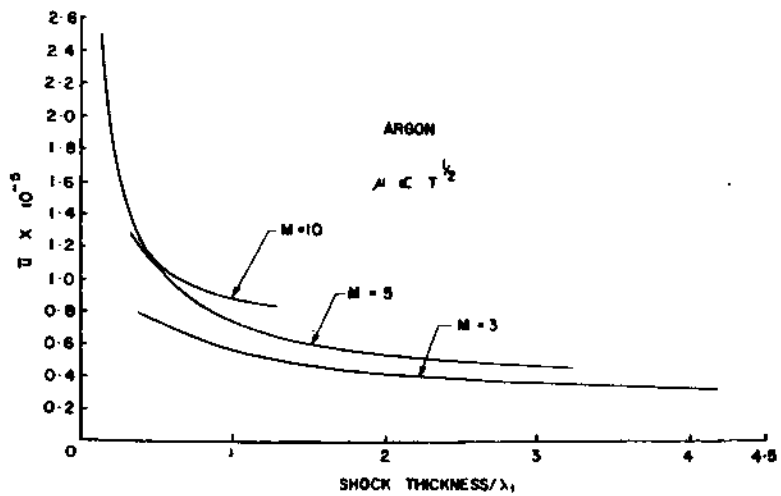

FIG. 5. Variation of $\bar{u}$ *Vs.* Shock Thickness.

Since the differential equation for γ depends on the coefficient of viscosity it is possible to study the dependence of the shock structure on the coefficient of viscosity or in other words, to find out how the thickness and other related parameters vary for different gases having almost the same atomic radius. The shock thickness was calculated, for five-different gases, namely, Helium, Argon, Xenon, Krypton and Neon. The plot of δ with respect to the coefficient of viscosity is given in Fig. 7 for a range of Mach numbers. The calculations were made for the case wherein the upstream value of the temperature of all the gases is reduced to the room temperature and for Mach number varying from 5 to 20. It can be seen that within the range of viscosity values calculated, the shock thickness increases first. The curves become steeper for smaller Mach numbers and in fact they become so steep for Mach numbers less than five that they could not be reproduced in the same figure on the same scale. It will be again worthwhile to

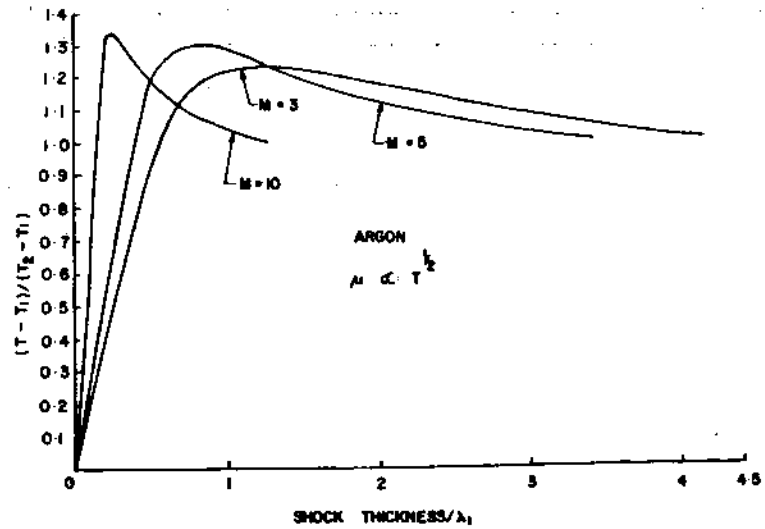

FIG. 6. Variation of Temperature *Vs.* Shock Thickness.

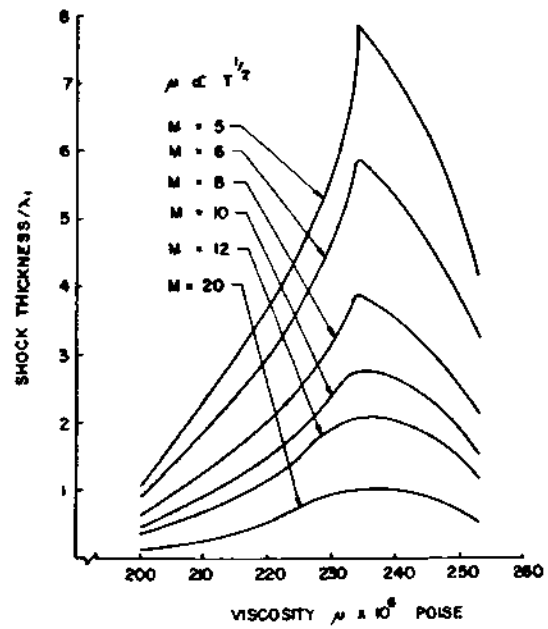

FIG. 7. Variation of Shock Thickness *Vs.* Viscosity.

study experimentally the variation of the shock thickness with viscosity coefficient to verify the nature of the variation as predicted by the theoretical curves or Table I.

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APPENDIX

(1) $$J_0^{(1)} = \int F_1^2\, d\underset{\sim}{v} = n_1^2 \left(\frac{\beta_1}{2\pi}\right)^{3/2}$$

(2) $$J_1^{(1)} = \int (v_y^2 + v_z^2)\, F_1^2\, d\underset{\sim}{v} = \frac{n_1^2}{\pi^{3/2}\, \beta_1^{1/2}\, 2^{5/2}}$$

(3) $$J_2^{(1)} = \int [4q\, \beta_1^2\, \gamma_1\, (v_x - u_1)^2 - 2\beta\beta_1 v_x\, (v_x - u_1)]^2\, F_1^2\, d\underset{\sim}{v}$$

$$= \frac{3}{4}\, n_1^2 \left(\frac{\beta_1}{2\pi}\right)^{3/2} (2q\, \gamma_1\beta_1 - \beta)^2 + \frac{n_1^2\, \beta^2\, u_1^2\, \beta_1^{5/2}}{2\sqrt{2}\, \pi^{3/2}}$$

(4) $$J_3^{(1)} = \int (v_y^2 + v_z^2)\, F_1^2\, d\underset{\sim}{v} = \frac{n_1^2\, \beta_1^{1/2}}{4\sqrt{2}\, \pi^{3/2}}$$

(5) $$J_4^{(1)} = \int [4q\, \beta_1^2\, \gamma_1\, (v_x - u_1)^2 - 2\beta\beta_1 v_x\, (v_x - u_1)]\, F_1^2 d\underset{\sim}{v}$$

$$= \frac{(2q\, \gamma_1\beta_1 - \beta)}{4\sqrt{2}}\, n_1^2 \left(\frac{\beta_1}{\pi}\right)^{3/2}$$

(6) $$J_5^{(1)} = \int (v_y^2 + v_z^2)\, [4q\, \beta_1^2\, \gamma_1\, (v_x - u_1)^2 - 2\beta\beta_1 v_x\, (v_x - u_1)]\, F_1^2\, d\underset{\sim}{v}$$

$$= \frac{(2q\, \beta_1\gamma_1 - \beta)}{8\sqrt{2}}\, \frac{n_1^2\, \beta_1^{1/2}}{\pi^{3/2}}$$

(7) $$K_0 = \int F_1 F_2 dv$$

$$= n_1 n_2 \left[\frac{\beta_1\beta_2}{\pi\, (\beta_1 + \beta_2)}\right]^{3/2} e^{-\delta}.$$

In what follows α is defined as

$$\alpha = \frac{\beta_1 u_1 + \beta_2 u_2}{\beta_1 + \beta_2}$$

(8) $$L_1^{(1)} = \int (v_x - u_1)\, e^{-(\beta_1+\beta_2)(v_x-\alpha)^2}\, dv_x$$

$$= (\alpha - u_1) \left[\frac{\pi}{(\beta_1 + \beta_2)}\right]^{1/2}$$

(9) $$L_2^{(1)} = \int (v_x - u_1)^2 \exp. [-(\beta_1 + \beta_2)(v_x - \alpha)^2]\, dv_x$$

$$= \sqrt{\frac{\pi}{(\beta_1 + \beta_2)}} \left[\frac{1}{2(\beta_1 + \beta_2)} + (\alpha - u_1)^2\right]$$

$$(10)\ L_{12} = \int (v_x - u_1)(v_x - u_2)^2 e^{-(\beta_1+\beta_2)(v_x-a)^2} dv_x$$

$$= \sqrt{\frac{\pi}{(\beta_1+\beta_2)}} \left[\frac{(a-u_1)}{2(\beta_1+\beta_2)} + \frac{(a-u_2)}{(\beta_1+\beta_2)} + (a-u_1)(a-u_2)^2\right]$$

$$(11)\ L_{21} = \int (v_x - u_1)^2 (v_x - u_2) e^{-(\beta_1+\beta_2)(v_x-a)^2} dv_x$$

$$= \sqrt{\frac{\pi}{(\beta_1+\beta_2)}} \left[\frac{(a-u_2)}{2(\beta_1+\beta_2)} + \frac{(a-u_1)}{(\beta_1+\beta_2)} + (a-u_2)(a-u_1)^2\right]$$

$$(12)\ L_{22} = \int (v_x - u_1)^2 (v_x - u_2)^2 e^{-(\beta_1+\beta_2)(v_x-a)^2} dv_x$$

$$= \sqrt{\frac{\pi}{(\beta_1+\beta_2)}} \left\{\frac{3}{4(\beta_1+\beta_2)^2} + \frac{1}{2(\beta_1+\beta_2)}[(2a-u_1-u_2)^2 + 2(a-u_1)(a-u_2)] + (a-u_1)^2 + (a-u_2)^2\right\}.$$

POLAROGRAPHY OF EUROPIUM IN AQUEOUS AND AQUEOUS METHANOLIC SOLUTIONS

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ABSTRACT

The standard rate constants for the reduction of europium in perchlorate and chloride media and the formal rate constants in sulphate, acetate and lactate solutions are reported. The rate increases in the order of increasing polarisability of the anion or the increasing stability of the complex, *viz.*, perchlorate < sulphate < lactate ≈ acetate.

The effect of methanol on the polarography of europium has been studied. In perchlorate and chloride media, the half-wave potential shifts to negative values and then to positive values as the methanol content is increased. In acetate solutions, the shift is continuously to negative potentials. This is attributed to the effect of complex formation in acetate media and ion-pairing in perchlorate and chloride media. The effect of viscosity on the diffusion current was found to obey the Stokes-Einstein equation.

INTRODUCTION

THE reduction of europium (III) to europium (II) involves a change in the inner $4f$ shell. The reduction is therefore expected to be irreversible.[1] The chemical composition of the supporting electrolyte should have little effect on the nature of the electrode process since the outermost shell would remain unaltered in the reduction. It is interesting, however, to note that the rate of the electrode process is altered by the kind and concentration of the anion in the supporting electrolyte. The effect of the solvent is also considerable, the electrode process being reversible in acetonitrile,[2] quasi-reversible in aqueous ethanol[3] and irreversible in acetone.[4] A study of the polarography of europium in complexing and non-complexing media in aqueous and methanolic solutions is reported here.

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