Shock-wave structure in binary mixtures of chemically inert perfect gases

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Starting with expressions for viscous stress, heat flux and diffusion flux, we formulate a continuum theory for steady flow of a binary mixture of chemically inert perfect gases through a normal shock of arbitrary strength. For shocks of vanishing strength, a solution by series expansion in Grad's (1952) shock-strength parameter gives a result essentially the same as found previously by Dyakov (1954). For stronger shocks a straightforward numerical integration, quite analogous to that useful in the simpler pure-gas problem, is laid out.

The resulting problem has eight parameters: shock strength, ratio of specific heats, ratio of bulk viscosity to shear viscosity, Prandtl number, Schmidt number, thermal diffusion factor, molecular mass ratio, and initial mixture concentration. A dozen examples were worked out on a simple desk calculator to exhibit the influence of some of these parameters. They involve the gas pairs argon^{40}–argon^{36}, argon–neon, argon–helium, and xenon–helium.

In discussing the results, special attention is paid to the degree of success with which the weak-shock theory may be extrapolated to arbitrary shock strength, and to the question of the accuracy of the Navier–Stokes approximation for a mixture of gases of very different molecular weights.

1. Introduction

A shock wave in a pure gas is broadened into a continuous transition zone by viscosity and thermal conduction, in the view of the continuum theory of gases. From this same viewpoint, a shock in a gas mixture is further broadened by dissipative species-diffusion processes, and a partial separation of the mixture is caused by the gradients within the shock.

Previous theoretical studies of shock waves and sound waves in binary gas mixtures have been made, notably by Cowling (1942), Dyakov (1954), and Kohler (1949), and the essential results for very weak waves have found their way into important reference works by Herzfeld (1955) and Hirschfelder, Curtiss & Bird (1954). Interesting and somewhat related papers on shocks in dusty or ionized gases have recently been contributed by Carrier (1958), Jukes (1957), and Tidman (1958). The present paper is primarily an extension and elaboration of the works of Cowling and Dyakov. Whereas Cowling neglected viscosity, thermal conduction and thermal diffusion in order to gain a preliminary insight into diffusion effects in shocks, and Dyakov limited his treatment to waves of sufficient weakness so that the separation of the mixture could be neglected as a higher order effect at the first stage of calculation, we make a direct frontal attack by numerical integration, to find the structure of a shock of arbitrary strength in a binary mixture of chemically inert perfect gases, including effects of viscosity, thermal conduction, ordinary-, baro-, and thermal-diffusion.

Of course, even accurate numerical integrations do not make the present theory (based on the Navier–Stokes approximations to viscous stress, heat flux, and diffusion flux) valid for arbitrary shock strength. Indeed one might intuitively expect that the maximum shock strength for which these calculations will give realistic predictions would be reduced as the molecular mass ratio of the mixture increases, due to the difficulty of maintaining thermal equilibrium between the light and the heavy constituents. Thus experiment may prove someday that the more 'interesting' features of the present results, which mostly appear when the mass ratio is fairly large and the shock strength is finite, are not realistic at all. Nevertheless, it has been interesting and instructive to the author to see just what the Navier–Stokes approximation says about this rather complicated problem.

2. Diffusion velocity and conservation of mass

We take as our starting point the results of Chapman and Enskog for the diffusion velocities of a binary mixture of perfect gases, obtained by kinetic theory. Equations 8.4, 7 and 8.3, 7 of Chapman & Cowling (1939) may be combined with the definitions of the total density and mass velocity of the mixture,

$$\rho = \rho_1 + \rho_2, \tag{1}$$

$$\rho u = \rho_1 u_1 + \rho_2 u_2, \tag{2}$$

to give, in our present nomenclature,

$$u_1 - u = \frac{\rho M_1 M_2}{\rho_1 M^2} D_{12} \left\{ f(1-f) \left[\frac{M_1 - M_2}{M} \frac{d}{dx}(\ln p) - \alpha \frac{d}{dx}(\ln T) \right] - \frac{df}{dx} \right\}. \tag{3}$$

Subscript 1 refers to the heavier molecular species and f is the mole-fraction of that species

$$f = \rho_1 M / \rho M_1. \tag{4}$$

The mean molecular mass M of the mixture depends on f, being given by

$$M = f M_1 + (1-f) M_2. \tag{5}$$

The binary diffusion coefficient D_{12} and the thermal-diffusion factor α are positive quantities, except in some exceptional gas pairs for which α may be slightly negative.

The qualitative nature of the separation of species within a normal shock can be seen directly from (3). If we view the shock as fixed in space, with steady flow from left to right so that $u > 0$, we then expect $dp/dx > 0$ and $dT/dx > 0$ within the shock (unless the situation varies drastically from that in a pure gas). The driving forces tending to separate the mixture are $d(\ln p)/dx$ and $d(\ln T)/dx$, leading respectively to baro-diffusion and thermal diffusion. From (2) we see that *baro-diffusion speeds up the heavier component*, $M_1 - M_2 > 0$, and slows down the lighter component relative to the mass velocity of the mixture. If $\alpha > 0$, which we would normally expect for M_1 not too close to M_2 (cf. Chapman & Cowling

1952, p. 254), then *thermal diffusion slows down the heavier component* and speeds up the lighter. (This is consistent with the sign convention for α, namely, that it is positive when the heavier molecules seek the colder regions.) Thus under most cirumstances thermal diffusion will partially counteract baro-diffusion within a shock wave. This same conclusion was reached by Dyakov (1954) and, in the related acoustic problem, by Kohler (1949). Of course, once any separation has taken place, ordinary diffusion, with driving potential df/dx, will tend to homogenize the mixture.

In the absence of chemical reactions each component of the mixture is subject to a simple continuity equation,

$$\rho_1 u_1 = m_1 \text{ (constant)}, \tag{6}$$

$$\rho_2 u_2 = m_2 \text{ (constant)}. \tag{7}$$

Equation (2) gives

$$\rho u = m_1 + m_2 = m \text{ (constant)} \tag{8}$$

as the continuity equation of the mixture. These equations make it clear that slowing down a component relative to the mixture velocity increases the concentration of that component relative to its value outside the shock wave. Thus, if baro-diffusion dominates thermal diffusion, the lighter molecules will be concentrated in the shock. This is usually the case. The degree of concentration would be expected to be greatest about where $d(\ln p)/dx$ is maximum. For very weak shocks this proves to be at the centre of the shock, and the concentration profile is symmetric about this point (Dyakov 1954). For stronger shocks, the maximum $d(\ln p)/dx$ will be upstream of the maximum of dp/dx, so we expect a peak concentration of the light species upstream of the centre of the shock. This upstream shift of the separation maximum is reinforced by ordinary diffusion, which accelerates the heavier molecules relative to the mixture when they are upstream of the separation maximum and decelerates them after they pass it.

Note that equations (3), (6) and (8) do not suggest that the relative scarcity of heavy molecules in the upstream portion of the shock is compensated by an equal enrichment of this species at some other position in $-\infty < x < \infty$, unless dp/dx should ever change sign. It does not in any of the examples worked out here. The tempting intuitive notion that conservation of mass prohibits a net deficiency of either species relative to the proportions of the mixture at infinity is not applicable to steady-state analysis, and usually arises when we include in our thinking the essentially transient idea of shock generation in a mixture of initially homogeneous composition.

An accurate analysis of transient shock formation in a mixture is outside our present scope. However, a qualitative description is suggested now in hopes of clarifying the relation between the following strictly steady-state results and the corresponding 'long-time' behaviour of a particular shock-formation problem. Suppose that a piston is impulsively accelerated to constant velocity in a tube containing a mixture initially homogeneous and at rest. The author supposes that in the initial instant (less than a mean molecular collision time) of that piston motion, the light molecules struck by the piston fly away from it more rapidly than their heavy neighbours. In the course of subsequent collisions, which transmit the impulse of the piston out into the gas, this behaviour is reproduced at the front of the column of gas which has started to move with a mean velocity equal to that of the piston, and becomes a characteristic feature of the structure of this front (the shock wave). After a sufficient number of collisions, the motion and structure of this shock front become locally stationary if viewed by an observer moving with the shock speed.

In the meantime, the heavy molecules which move away slowly from the piston during the initial instant produce a local surplus of this species in the immediate vicinity of the piston. This surplus is embedded in a region of gas which soon has the mean motion of the piston and redistributes itself by ordinary diffusion. The region throughout which this original surplus is subsequently spread thus grows out from the piston face in proportion to $\surd$(time), while the shock front moves away from the piston in proportion to time. Between the shock and the region of redistribution of the heavy molecules which are 'left behind' during shock formation, there appears an ever-lengthening column of homogeneous mixture having the velocity of the piston and the composition of the undisturbed gas. In the steady-flow analysis of the shock structure, the properties of this column are those supposed to exist at $x = +\infty$, so that the residual effects of shock formation, including the local enrichment of heavy molecules which compensates for the local depletion in the shock, are specifically excluded from the steady-state theory.

3. Conservation of momentum

The diffusion equation (1) results from the momentum conservation principle applied to the relative motion of the constituents of the mixture. The momentum equation for the mixture moving as a whole is

$$\rho u^2 + p - (\tfrac{4}{3}\mu + \kappa)\frac{du}{dx} = P = \rho_0 u_0^2 + p_0, \tag{9}$$

which differs from that for a pure gas only through the dependence of μ and κ on f in the present case. In fact, virtually nothing is known about the bulk viscosity coefficient κ for gas mixtures, since this additional dissipative mechanism is hard to separate experimentally from ordinary viscosity, heat conduction, and diffusion. We carry the symbol κ in this analysis just to be open-minded, although the subsequent calculation will assume κ/μ to be constant, with no particular physical justification.

4. Conservation of energy

The differential equation of conservation of energy for the mixture may be integrated to give

$$\rho u(h + \tfrac{1}{2}u^2) - u(\tfrac{4}{3}\mu + \kappa)\frac{du}{dx} + q_x = \tfrac{1}{2}Q = m(h_0 + \tfrac{1}{2}u_0^2). \tag{10}$$

The specific enthalpy in (10) is given by the rule for mixtures of chemically inert perfect gases

$$\rho h = \rho_1 h_1 + \rho_2 h_2 = (\rho_1 c_{p1} + \rho_2 c_{p2})T. \tag{11}$$

In (11) explicit use is made of the important assumption that both components of the mixture share the same temperature.

The heat flux q_x in (10) contains two terms in addition to the ordinary Fourier conduction, one a simple convection of partial enthalpies at the diffusion velocity, the other due to the diffusion thermo-effect (Chapman & Cowling 1952, equation 8.41, 3),

$$q_x = -\lambda\frac{dT}{dx} + \rho_1(u_1-u)\left(h_1-h_2+\frac{M^2}{M_1M_2}\frac{p}{\rho}\alpha\right). \tag{12}$$

When (12) is substituted in (10), it proves convenient to group together all the enthalpy terms. One easily shows that

$$\begin{aligned}\rho uh+\rho_1(u_1-u)(h_1-h_2) &= m_1h_1+m_2h_2\\ &= (m_1c_{p1}+m_2c_{p2})T\\ &\equiv mc_pT,\end{aligned}$$

where c_p denotes not the local and variable specific heat of the mixture, but the specific heat of the mixture outside the shock (hence a constant for any given shock problem). The last step above follows directly from the basic definition of specific heat of an inert perfect gas mixture

$$\rho c_p = \rho_1c_{p1}+\rho_2c_{p2}$$

and the observation that outside the shock $u_1 = u_2 = u$.

Equation (10) is thus rewritten as

$$\rho u(\tfrac{1}{2}u^2+c_pT) - u(\tfrac{4}{3}\mu+\kappa)\frac{du}{dx} - \lambda\frac{dT}{dx} + \frac{\rho_1M^2}{\rho M_1M_2}(u_1-u)p\alpha = \tfrac{1}{2}Q. \tag{13}$$

5. Equation of state

If we define a gas constant for the mixture outside the shock wave by

$$R \equiv p_0/\rho_0T_0,$$

then inside the shock, where the mean molecular mass is variable, we have

$$p = \frac{M_0}{M}\rho RT. \tag{14}$$

6. Dimensionless variables and boundary conditions

Equations (1) through (7), (9), (13) and (14) give ten independent relations for the ten unknowns ρ, ρ_1, ρ_2, u, u_1, u_2, f, M, p, and T. They can be reduced to three coupled first-order differential equations for u, T and f. These, together with a sufficiency of transport property data and the boundary conditions

$$\frac{du}{dx} = \frac{dT}{dx} = \frac{df}{dx} = 0 \quad \text{at} \quad x = \pm\infty \tag{15}$$

define the problem.

We introduce dimensionless variables and parameters as follows:

$v = mu/P$ (velocity),
$\tau = m^2RT/P^2$ (temperature),
$a = mQ/P^2$ (shock strength),
$\gamma = c_p/(c_p - R)$ (specific heats ratio),
$X = \frac{4}{3} + \frac{\kappa}{\mu}$,
$\theta = M_1/M_2$ (molecular mass ratio),
f_0 = mole fraction of heavy molecules outside the shock,

and the reference length $L = \mu/m$.

The three equations for v, τ and f can be arranged as autonomous equations for dv/dx, $d\tau/dx$ and df/dx as follows

$$L\frac{dv}{dx} = \frac{1}{X}\left\{v + \frac{1+(\theta-1)f_0}{1+(\theta-1)f}\frac{\tau}{v} - 1\right\}, \tag{16}$$

$$L\frac{d\tau}{dx} = \frac{\gamma-1}{2\gamma}\left(\frac{\mu c_p}{\lambda}\right)\left\{2v - v^2 - a + 2\tau\left[\frac{\gamma}{\gamma-1} - \frac{1+(\theta-1)f_0}{1+(\theta-1)f} + (f_0 - f)\alpha\right]\right\}, \tag{17}$$

$$L\frac{df}{dx} = -\left(\frac{\mu}{\rho D_{12}}\right)\frac{(f_0-f)[1+(\theta-1)f]^3}{[1+(\theta^2-1)f][1+(\theta-1)f_0]} - L\frac{f(1-f)[1+(\theta-1)f]}{1+(\theta^2-1)f}$$
$$\times\left\{(\theta-1)\frac{d}{dx}(\ln v) - [(\theta-1) - \alpha\{1+(\theta-1)f\}]\frac{d}{dx}(\ln \tau)\right\}. \tag{18}$$

7. Method of solution

The method used to solve (16)–(18) numerically is quite commonplace in the shock-wave literature (e.g. Grad 1952, Gilbarg & Paolucci 1953, or Talbot & Sherman 1959) and will only be described in principle here.*

The independent variable x can be easily eliminated by dividing (17) and (18) by (16). This yields two 'direction field' equations for $d\tau/dv$ and df/dv, for which we seek a particular solution joining the upstream and downstream states of the gas. The co-ordinates of these states (v, τ, f at $x = \pm\infty$) are easily found by setting $dv/dx = d\tau/dx = df/dx = 0$ in (16), (17) and (18).

Since these state points are obviously singular points of the direction-field equations, a preliminary investigation of the direction field in their vicinity must be made to determine the end-slopes of the desired solution curve and the correct point from which to start the numerical integration. This analysis shows in the present case that the downstream singular point is almost invariably a saddle point and the upstream singular point a node, just as they are for the Navier–Stokes equations in a pure gas. The integration must be started from the downstream singular point and this guarantees the existence of a unique solution.

After the solution curve is found in v–τ–f space, the spatial distribution of v is found by a numerical quadrature of (16).

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* Readers interested in these details are invited to communicate directly with the author.

8. Concentration dependence of transport properties

The numerical integration of the direction-field equations and the quadrature of (16) require a knowledge of the concentration and temperature dependence of viscosity μ, thermal diffusion factor α, and the ratios μ/λ and $\mu/\rho D_{12}$. Numerical data could of course be used directly, but for the present sample calculations simple analytic approximations were introduced after a study of data for argon–helium mixtures (cf. figure 1; Chapman & Cowling 1952, pp. 232, 243, 248; Hirschfelder *et al.* 1954, p. 584). These approximations provide a local fit to the empirical transport property behaviour in the vicinity of the known mixture state ahead of the shock. They are

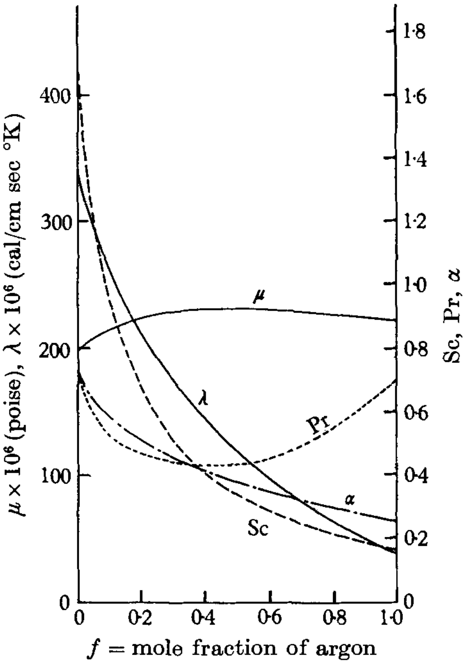

FIGURE 1. Properties of argon–helium mixtures.

$$\mu \propto T^{\frac{3}{4}}, \text{ independent of } f,$$

$$\mu/\lambda \propto M, \text{ independent of } T,$$

$$\mu/\rho D_{12} \propto 1/M, \text{ independent of } T,$$

$$\alpha \propto 1/M, \text{ independent of } T.$$

While some of these are certainly inaccurate if applied to large variations of f and T, they are entirely adequate for the purpose at hand, since f actually does not vary widely in a given shock, and the assumed temperature dependence is fairly realistic except in the case of α. Thermal diffusion is fortunately a sufficiently small effect so that sizeable errors in α produce much reduced errors in the shock profiles.

If we introduce the Prandtl number, Schmidt number, and thermal-diffusion factor of the mixture ahead of the shock as basic parameters of the shock-structure problem, the approximations above state that

$$\mu c_p/\lambda = Pr\,(M/M_0) = Pr\,[1+(\theta-1)f]/[1+(\theta-1)f_0]$$

(remember that c_p already refers to the mixture outside the shock),

$$\mu/\rho D_{12} = Sc\,(M_0/M)$$

and

$$\alpha = \alpha_0(M_0/M).$$

9. Series solution for weak shocks

In the limit of vanishing shock strength, $\mathscr{M} \to 1$, a series-expansion solution of (16), (17) and (18) is appropriate, and the first terms have been found by Dyakov (1954), albeit in a nomenclature quite different from ours. We proceed a little differently here, expanding in terms of the shock-strength parameter proposed by Grad (1952) instead of the pressure ratio, Dyakov's choice. One hopes that the former expansion parameter, which remains finite as $\mathscr{M} \to \infty$, would lead to quicker convergence, or at least better approximation by the first term of the series, at moderate Mach numbers. In fact, this seems to be the case.

Grad's parameter ϵ is introduced by

$$v_0 = \frac{1}{2}\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{2\gamma}{\gamma-1} \pm \epsilon\right), \tag{19}$$

where the + sign gives $v_0(x = -\infty)$ and the − sign $v_0(x = +\infty)$. It is related to our earlier parameter a by

$$a = \frac{1}{4}\left(\frac{\gamma-1}{\gamma+1}\right)\left[\left(\frac{2\gamma}{\gamma-1}\right)^2 - \epsilon^2\right], \tag{20}$$

and to the shock Mach number by

$$\epsilon = \frac{2\gamma}{\gamma-1}\left(\frac{\mathscr{M}^2-1}{\gamma\mathscr{M}^2+1}\right). \tag{21}$$

Next we define new dimensionless velocity and temperature variables, which vary from −1 to +1 through the shock, whatever the value of ϵ. These are w and t, given by

$$v = \frac{1}{2}\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{2\gamma}{\gamma-1} + \epsilon w\right), \tag{22}$$

$$\tau = \frac{1}{4}\left(\frac{\gamma-1}{\gamma+1}\right)^2\left\{\frac{4\gamma}{(\gamma-1)^2} + 2\epsilon t - \epsilon^2\right\}. \tag{23}$$

A new concentration variable may be introduced by

$$f_0 - f = \epsilon^2\phi. \tag{24}$$

We now expand w, t and ϕ in ϵ, i.e.,

$$\left.\begin{aligned} w &= w^{(0)} + \epsilon w^{(1)} + \epsilon^2 w^{(2)} + \ldots, \\ t &= t^{(0)} + \epsilon t^{(1)} + \epsilon^2 t^{(2)} + \ldots, \\ \phi &= \phi^{(0)} + \epsilon\phi^{(1)} + \epsilon^2\phi^{(2)} + \ldots, \end{aligned}\right\} \tag{25}$$

and substitute these series into (16), (17) and (18). Grouping terms of like order in ϵ, and solving the resulting simple differential equation for $w^{(0)}$, we get

$$w^{(0)} = -\tanh\left\{\frac{\gamma^2-1}{4\gamma}\frac{\epsilon}{\left[X+\frac{\gamma-1}{Pr}+\frac{\gamma f_0(1-f_0)}{Sc}\left(\frac{M_1-M_2}{M_0}-\frac{\gamma-1}{\gamma}\alpha_0\right)^2\right]}\frac{\rho u x}{\mu}\right\}, \tag{26}$$

$$t^{(0)} = -w^{(0)}, \tag{27}$$

$$\phi^{(0)} = \frac{(\gamma+1)(\gamma-1)^2 f_0(1-f_0)}{8\gamma\quad Sc} \times\left\{\frac{\frac{M_1-M_2}{M_0}-\frac{\gamma-1}{\gamma}\alpha_0}{X+\frac{\gamma-1}{Pr}+\frac{\gamma f_0(1-f_0)}{Sc}\left(\frac{M_1-M_2}{M_0}-\frac{\gamma-1}{\gamma}\alpha_0\right)^2}\right\}\{(1-(w^{(0)})^2\}, \tag{28}$$

for the lowest-order non-vanishing terms in w, t and ϕ. The corresponding result for shock thickness based on maximum slope,

$$\delta_m = 2/|dw/dx|_{\max}, \tag{29}$$

is

$$\frac{\rho u \delta_m}{\mu} = \frac{8\gamma}{\gamma^2-1}\left(\frac{1}{\epsilon}\right)\left\{X+\frac{\gamma-1}{Pr}+\frac{\gamma f_0(1-f_0)}{Sc}\left(\frac{M_1-M_2}{M_0}-\frac{\gamma-1}{\gamma}\alpha_0\right)^2\right\}. \tag{30}$$

When our nomenclature is brought into agreement with that of Dyakov (1954), these last four results agree perfectly with his. The quantity in braces in (30) is also identical with the corresponding factor in the sound-attenuation coefficient, found by Kohler (1949), and cited by Hirschfelder *et al.* (1954, p. 732, equations 11.4–20). It may be noted in passing that, in Herzfeld (1955, p. 691, equations 18–3), the last term in this brace is cited incorrectly by omission of the factor $f_0(1-f_0)$ which makes that term vanish for a pure gas.

Besides giving a check on the correctness of (16), (17) and (18), equations (28) and (30), when boldly extrapolated to finite shock strengths, give a very useful approximate survey of the results which are obtained more accurately by numerical integrations.

10. Sample numerical calculations

The dozen examples shown here were picked to exhibit the following.

(*a*) The effect of shock strength on the concentration-versus-velocity integrals for a single initial gas mixture (argon–helium, equal parts by moles). The Mach numbers chosen were 1·34 ($\epsilon = 1$), 2·05 ($\epsilon = 2$), 4·84 ($\epsilon = 2{\cdot}8$) and ∞ ($\epsilon = 3$), the last obviously just for fun. These results are shown in figure 2, where they are compared with the approximation given by equations (24) and (28). As might have been expected, the weak-shock approximation is quite accurate at $\epsilon = 1$, and discrepancies between it and the numerical results increase continually with increasing ϵ. The merit of the series solutions in terms of the parameter ϵ, which remains finite as $\mathscr{M} \to \infty$, is seen from the fair approximation given by its first term even at very large shock strengths.

(*b*) The effect of initial mixture ratio on various shock properties, for a particular gas-pair (argon–helium) and shock strength ($\epsilon = 2$). Thus figure 3 shows concentration-velocity integrals on a semi-logarithmic scale (to emphasize percentage changes in concentration). Note that these are decidedly more symmetrical about the mid-velocity, and thus agree better qualitatively with the weak-shock theory when f_0 is small, than when it is large. This is a coincidence brought about by the superposition of two effects, the first being the general movement of the maximum separation towards the upstream side of the shock (towards the right in figure 3) in response to ordinary diffusion and the fact that the separating potential is $\ln p$ rather than p (as discussed in §2). The second effect is intuitively rather obvious, and well illustrated by figures 4 and 5. When the initial mixture contains just a little of the lighter gas, the separation is brought about by the light molecules of the shocked gas running out ahead of the main shock or mean-velocity transition of the entire mixture. This evidently shifts the maximum separation even farther upstream relative to the main shock and leads to the very asymmetrical f–v curves in figure 3a. When the initial mixture contains just a little heavy gas, the heavier molecules lag behind the main shock, thus shifting the maximum separation downstream and partially cancelling the first effect mentioned above.

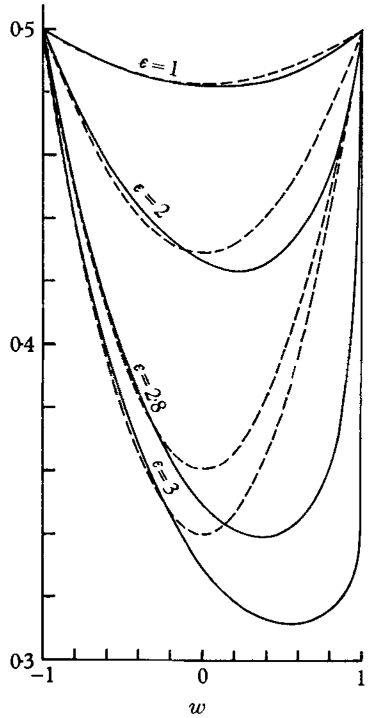

FIGURE 2. Concentration-velocity integrals for various shock strengths; $f_0 = 0·5$.

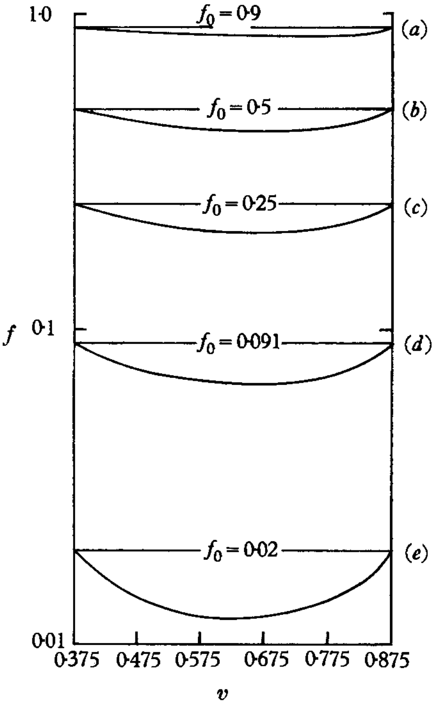

FIGURE 3. Concentration-velocity integrals for various initial mixture ratios; $\epsilon = 2$.

If the reader has been distracted from the foregoing argument by the rather odd appearance of the argon velocity profile in figure 5, he is forgiven forthwith. The behaviour of that curve, which indicates that the argon is momentarily accelerated, rather than slowed down, upon entry into the shock, is the single most intriguing—and perhaps unbelievable—result of the present study. It implies, upon transformation of co-ordinates to a frame at rest in the unshocked gas, that upon arrival of the shock the argon first jumps backwards, then turns and runs fast to catch up with the shock. The same prediction is inherent in Dyakov's weak-shock theory, which incidentally predicts a corresponding undershoot of the helium velocity in figure 4. It is interesting to note that the latter prediction is one

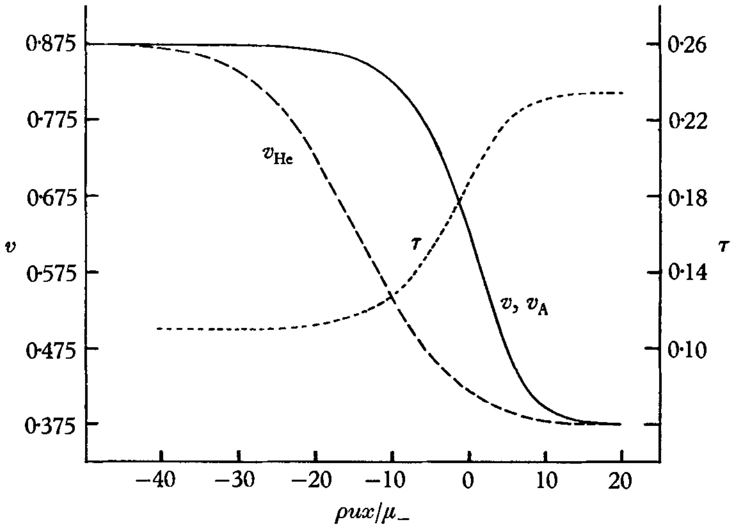

FIGURE 4. Shock profiles with very little light gas; $f_0 = 0\cdot9$, $\epsilon = 2$.

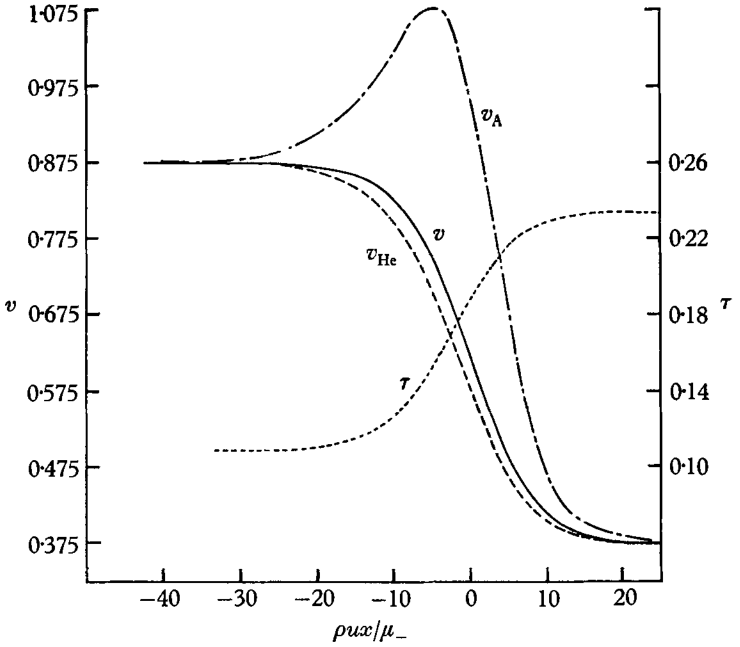

FIGURE 5. Shock profiles with very little heavy gas; $f_0 = 0\cdot02$, $\epsilon = 2$.

qualitative implication of the weak-shock theory which is refuted by the accurate numerical integrations. Regarding the physical plausibility of this effect, the author has no very fixed opinion as yet. It is certainly hard to imagine the source of the effect from a molecular viewpoint and no corresponding effect is found in Carrier's dusty-gas analysis, if the latter may be considered to give an indication of proper physical behaviour in a limit of very large mass ratio. A mass ratio of 10 (argon–helium) and shock Mach number of 2·05 may simply carry the present analysis beyond the valid range of the Navier–Stokes approximation although that approximation would still be quite accurate for a Mach 2·05 shock in a pure monatomic gas (cf. Talbot & Sherman 1959).

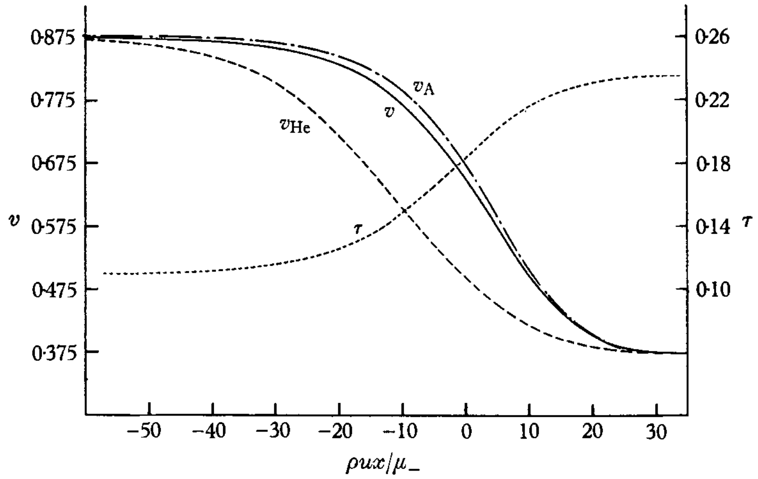

FIGURE 6. Shock profiles with equal initial proportions of light and heavy gases; $f_0 = 0{\cdot}5$, $\epsilon = 2$.

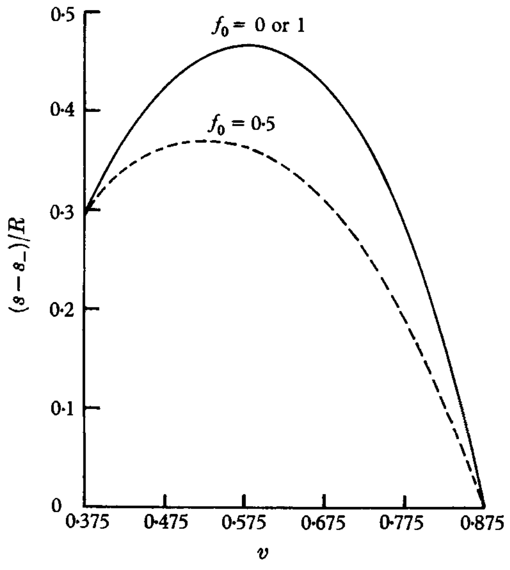

FIGURE 7. Entropy-velocity integrals; $\epsilon = 2$.

Figures 4, 5 and 6 (the last showing velocity profiles for the intermediate case $f_0 = 0{\cdot}5$) emphasize that a shock wave in a mixture may be quite complicated compared to that in a pure gas, and that it may actually extend over a distance which is quite large compared with the conventionally defined shock thickness (cf. equation (29)). They also suggest that experimentalists interested in this problem should take care to know exactly to what flow properties their instruments respond.

Figure 7 shows the effect of initial mixture ratio on the entropy-velocity relationship within the shock. Actually, the quantity labelled s here is not strictly the entropy of the actual non-equilibrium state of the gas at a point inside the shock, but the entropy of the equilibrium state having the same pressure, temperature and concentration. This is a quantity easy to calculate—in our case from the formula

$$\frac{S-S_-}{R} = f\ln\left[\left(\frac{T}{T_-}\right)^{1/(\gamma_1-1)}\frac{u_1}{u_-}\right] + (1-f)\ln\left[\left(\frac{T}{T_-}\right)^{1/(\gamma_2-1)}\frac{u_2}{u_-}\right]. \tag{31}$$

It is presumably slightly larger than the entropy of the true non-equilibrium state, since a bit of fluid, if isolated in the latter condition, would spontaneously tend to the condition whose entropy we calculate.

Setting aside this rather fine point, we see in figure 7 just what we expect. While the mixture is being separated in the upstream portion of the shock, entropy rises at a rate smaller than in a pure gas shock of the same strength. While remixing is taking place farther downstream, entropy rises faster (or falls more slowly) than in the pure gas.

Figure 8 shows some over-all or extreme properties of the shock transition as functions of f_0. From 8*a* we see both that diffusion effects broaden a shock in A–He quite spectacularly, and that the weak-shock theory, equation (30), gives a very good idea of the dependence of this broadening upon initial mixture ratio. From 8*b* we see that the maximum ratio of diffusion velocity to mixture velocity, $(u_1 - u_2)/u$, is smallest when diffusive broadening of the shock is largest, and that the highest diffusion velocities appear when there is only a trace of one gas or the other present. The quantity plotted is simply related to f by use of equations (5), (6) and (7), i.e.

$$\frac{u_1-u_2}{u} = \frac{f_0-f}{f(1-f)}\frac{1+(\theta-1)f}{1+(\theta-1)f_0}. \tag{32}$$

The weak-shock approximation to this result is

$$\frac{u_1-u_2}{u} = \epsilon^2\frac{(\gamma+1)(\gamma-1)^2}{8\gamma Sc}\left\{\frac{\dfrac{M_1-M_2}{M_0}-\dfrac{\gamma-1}{\gamma}\alpha_0}{X+\dfrac{\gamma-1}{Pr}+\dfrac{\gamma f_0(1-f_0)}{Sc}\left(\dfrac{M_1-M_2}{M_0}-\dfrac{\gamma-1}{\gamma}\alpha_0\right)^2}\right\}(1-w^{(0)^2}). \tag{33}$$

This equation gives a fairly true image of the numerical results, particularly for small f_0, but is considerably worse at large f_0 for reasons reviewed at the beginning of this subsection.

(*c*) The effect of mass ratios (and accompanying mixture properties) at constant f_0 and shock strength. Instead of making an artificial parameter study by changing θ alone, we deemed it more interesting to treat real mixtures of various gases, to attain a wide range of θ along with the associated changes in α, Pr, and Sc which nature provides. Thus calculations were made for $f_0 = 0\cdot5$ and $\epsilon = 2$ in the mixtures ^{40}A–^{36}A ($\theta = 10/9$), A–Ne ($\theta = 2$), A–He ($\theta = 10$) and Xe–He ($\theta = 32\cdot8$). Table 1 shows the variation of shock thickness and maximum diffusion velocity with θ in these mixtures, all of which have $\gamma = 5/3$ and $X = 4/3$.

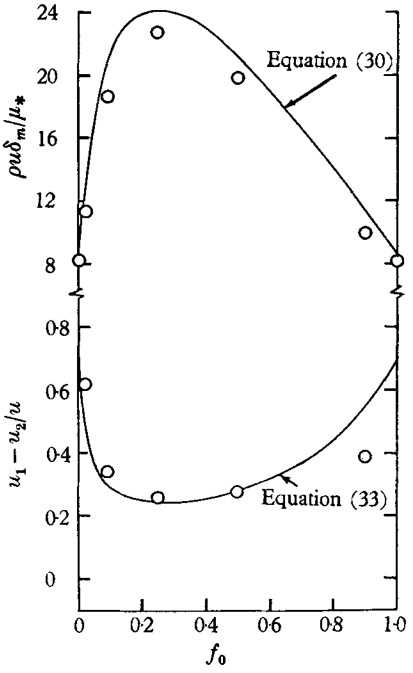

FIGURE 8. Shock thickness and maximum diffusion velocity; $\epsilon = 2$. ○, Numerical results.

Gas pair	θ	$\dfrac{M_1 - M_2}{M_0}$	α_0	Pr	Sc	$\dfrac{\rho u\delta_m}{\mu_*}$ Numerical integration	Equation 49	$\left(\dfrac{u_1-u_2}{u}\right)_{\max}$ Numerical integration	Equation 52
Pure argon	1	0	0	0·704	—	8·15	8·55	—	—
^{40}A–^{36}A	10/9	0·10526	0·013	0·704	0·784	8·18	8·58	0·0209	0·0198
A–Ne	2	0·66667	0·17	0·667	0·750	8·99	9·49	0·116	0·112
A–He	10	1·6364	0·37	0·440	0·330	19·84	21·15	0·273	0·284
Xe–He	32·8	1·8817	0·434	0·250	0·200	35·8	37·8	0·276	0·301

TABLE 1. Effect of θ on shock thickness and maximum diffusion velocity. $f_0 = 0\cdot5$, $\mathcal{M} = 2\cdot05$, $\gamma = 5/3$, $X = 4/3$ for all cases; μ_* = viscosity at point of maximum $\mu\, du/dx$.

We see again that the weak-shock theory is very useful for rough predictions at finite shock strength. Note that quite refined experimentation would be required to detect either the minute separation of the isotopic mixture ^{40}A–^{36}A, or the broadening of the shock due to diffusion in this case. A similar result is found for shocks in atmospheric air, in which the importance of θ is emphasized by the fact that the diffusive shock broadening due to the 0·94 % of argon present is about 80 % as much as that due to the diffusion of the oxygen and nitrogen.

11. Criticism of the theory when θ is large

As mentioned several times above, the present theory seems deficient in the case of large θ, when it insists that both mixture components always share the same temperature. This has led to some intuitively implausible results in the examples worked out here for argon–helium mixtures. For example, figure 4 shows the mean-velocity change of the helium almost half-way accomplished before the random velocity (temperature) of this constituent has been appreciably influenced. One might intuitively expect these two quantities to start changing at about the same time.

To get a better picture of actual events during shock passage through a mixture with large θ, one might try at least two theoretical approaches. The first is to devise some supplementary 'relaxation' equation to account for the difficulty of maintaining thermal equilibrium between light and heavy constituents, and to couple this equation to the present set, modifying the latter somewhat to admit the existence of two different temperatures. An example of this approach is given by Jukes (1957) who discusses shock structure in a mixture of protons and electrons. Jukes's calculation shows a significant difference between electron and ion temperatures throughout a wide zone ahead of the 'velocity shock' but sheds no direct light on the present problem, since diffusive separation of electrons and ions was taken to be negligible in view of the intense electric field which this would produce. Regarding this technique it may be noted pessimistically that the coupling of the ordinary sort of relaxation equation (cf. Jukes 1957) to the Navier–Stokes equations leads to very nasty singular-point behaviour of the resulting equations, which precludes straightforward numerical integration from one side of the shock to the other.

The second possibly profitable approach would be an extension of the method of Mott-Smith (1951) to treat a gas mixture. Again, this approach has been applied to a hydrogen plasma (Tidman 1958), but not to a mixture in which diffusive separation is unrestrained by electric fields.

Finally, of course, one might attempt an experimental determination of the true state of affairs with shocks in, say, A–He mixtures. In fact, some early work along this line, by Professor D. F. Hornig of Brown University (now of Princeton) gave the author his first inclination to study this problem.

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