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The structure of shock-waves in gas mixtures

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The structure of shock-waves in gas mixtures is studied. The separation of component velocities and temperatures is described. Velocity overshoot is never found to exist. Other effects, namely, temperature overshoot and undershoot and velocity undershoot are shown to exist in a manner which is self-consistent with the derivation of the governing equations.

1. Introduction

In an early investigation Cowling (1942) considers shock structure in a binary mixture by employing the Chapman–Enskog mixture equations (Chapman & Cowling 1939). Viscous and heat conducting effects are neglected so that diffusion is the only dissipative mechanism. A notable feature of this study is that Cowling finds a smooth transition between the up- and downstream states, provided that the shock strength is sufficiently weak. Later Dyakov (1954) included the remaining dissipative effects and was able to find an analytical description of weak shock-waves. (Dyakov's equations, although of the same form as the Chapman–Enskog mixture equations, have their origin in a macroscopic derivation, Landau & Lifshitz (1959), and hence in principle have a more general application.) Sherman (1960) also considered the structure of weak shock-waves, and in the process brought to light certain new and peculiar effects. Among these is the possibility of a trace element of heavy gas having a velocity above its upstream value. This is the, by now, controversial velocity overshoot effect. Sherman also numerically integrated the exact Chapman–Enskog mixture equations for various mixture and shock parameters. More recently Oberai (1965, 1966), using Mott-Smith's bimodal distributions (Mott-Smith 1951), also considered the mixture shock-wave problem.

As is well known this last approach is best applied to strong shock-waves. Our approach is aimed more at weak shock-waves, so for this reason we will not have occasion to discuss Oberai's work. Finally, we mention two recent experimental investigations, Center (1967) and Rothe (1966), which bear strongly on the overshoot controversy.

In addition to describing the gross transition from the upstream to the downstream equilibrium points, a shock analysis of mixtures must describe the separation of the components of the mixture. The components separate in the sense that the component velocities differ (and hence density ratios vary). Also the random energies of the components about their own velocities, i.e. their temperatures, differ. A further complication is the fact that these effects occur on different scales. Both velocity and temperature differences can linger long after the shock transition. As a rule, however, the latter is the persistent effect in most cases. In order to describe shock structure the two fluid mixture equations will be used (Goldman & Sirovich 1967, 1969). We now briefly describe these in comparison with the Chapman–Enskog mixture equations.

Both the mixture and simple gas theories of Chapman–Enskog (Chapman & Cowling 1939) follow from the expansion of the distribution function in a small parameter ϵ. This quantity can generally be associated with the ratio of microscopic to macroscopic scales. Denoting the mean-free-path by l and a typical macroscopic scale by Δ the small parameter in a simple gas theory is

$$\epsilon_0 = l/\Delta. \tag{1}$$

An examination of the comparable mixture development (Goldman & Sirovich 1967, 1969) shows that instead of (1) the small parameter becomes

$$\epsilon_1 = l/C\Delta, \tag{2}$$

where C is related to the Schmidt number Sc, through

$$C = \frac{2\tilde{\rho} Sc}{\tilde{n}(m_\alpha + m_\beta)}$$

($\tilde{\rho}$ is mass density, $\tilde{n}$ number density, m_α and m_β the molecular masses). Unlike Sc, C is relatively insensitive to concentration changes (Goldman & Sirovich 1967). Since C can be quite small (for argon–helium mixtures, $C \approx 0{\cdot}3$ and xenon–helium mixtures $C \approx 0{\cdot}15$) small ϵ_1, see (2), can be quite restrictive.

In Goldman & Sirovich (1967, 1969) the Boltzmann equations for mixtures are investigated under the milder condition that ϵ_0, see (1), be small. It is shown there that a macroscopic theory still follows. This theory, which reduces to the Chapman–Enskog theory when $C = O(1)$, contains component temperature and velocity differences. A new equation describes the former and a generalized diffusion equation describes the latter.

One of the main consequences of the shock-wave solution of the two-fluid equations is the elimination of the Sherman anomaly. Another interesting aspect of the calculation is the description of temperature separation even when $C = O(1)$ and this is a higher order effect from the point of view of the Chapman–Enskog theory. Although velocity overshoot is eliminated a number of curious new effects appear. These are: velocity undershoot, temperature overshoot, temperature undershoot. The circumstances under which these occur and their description are clear from the figures.

In view of these effects we give a relatively detailed discussion of the validity of the shock solutions. For the shock structure problem it is more appropriate to use instead of mean-free-path the closely connected quantity

$$l = \tilde{\mu}/\overline{m} \tag{3}$$

($\tilde{\mu}$ is the mixture viscosity). $\overline{m}$ denotes the total mass flux

$$\overline{m} = \tilde{\rho}\tilde{U} \tag{4}$$

($\tilde{U}$ is the macroscopic velocity). The macroscopic scale Δ then is the shock thickness. One restriction on the validity of a solution is that $\epsilon_0 \ll 1$ since higher order derivatives are neglected in a Chapman–Enskog type derivation. A second type of approximation comes in the neglect of quadratic and higher degree products of component velocity and temperature differences. A plausible condition for the validity of a solution is that when the solution is substituted into the neglected terms these are small compared to the terms which have been retained. When this is true and also $\epsilon_0 \ll 1$ we will say that the solution is self-consistent. The already mentioned peculiar effects can all be found to occur in a self-consistent manner. It is of interest to note that in those régimes in which the Sherman anomaly occurs, it fails to be self-consistent with the derivation of the mixture equations in the above sense.

2. The two fluid shock equations

For a steady one-dimensional flow the two fluid equations (Goldman & Sirovich 1967, 1969) are:

$$\frac{d}{d\tilde{x}}\tilde{\rho}_\alpha \tilde{U}_\alpha = 0, \quad \frac{d}{d\tilde{x}}\tilde{\rho}_\beta \tilde{U}_\beta = 0, \tag{5}$$

$$\begin{aligned}(\tilde{U}_\alpha - \tilde{U}_\beta) = {} & -\frac{\tilde{n}^2}{\tilde{n}_\alpha \tilde{n}_\beta}\tilde{D}_{\alpha\beta}\left[\frac{d}{d\tilde{x}}\left(\frac{\tilde{n}_\alpha}{\tilde{n}}\right) + \frac{\tilde{n}_\alpha \tilde{n}_\beta}{\tilde{\rho}\tilde{n}}(m_\beta - m_\alpha)\frac{d}{d\tilde{x}}\ln\tilde{p}\right. \\ & \left. + \frac{1}{\tilde{p}}\frac{d}{d\tilde{x}}\frac{\tilde{n}_\alpha \tilde{n}_\beta k(\tilde{T}_\alpha - \tilde{T}_\beta)}{\tilde{n}} - \frac{\tilde{n}_\alpha \tilde{n}_\beta}{\tilde{T}\tilde{n}^2}\eta\frac{d\tilde{T}}{d\tilde{x}}\right] - \frac{1}{\lambda_U}\frac{d}{d\tilde{x}}\tilde{U}(\tilde{U}_\alpha - \tilde{U}_\beta);\end{aligned} \tag{6}$$

$$\begin{aligned}& (\tilde{U}_\alpha - \tilde{U}_\beta)\frac{d}{d\tilde{x}}\tilde{T} + \tilde{U}\frac{d}{d\tilde{x}}(\tilde{T}_\alpha - \tilde{T}_\beta) + \left[\tilde{T}\frac{d}{d\tilde{x}}(\tilde{U}_\alpha - \tilde{U}_\beta) + (\tilde{T}_\alpha - \tilde{T}_\beta)\frac{d}{d\tilde{x}}\tilde{U}\right. \\ & \qquad \left. - \tilde{n}_\alpha k\frac{d}{d\tilde{x}}\tilde{\kappa}_\alpha\frac{d}{d\tilde{x}}\tilde{T} + \tilde{n}_\beta k\frac{d}{d\tilde{x}}\tilde{\kappa}_\beta\frac{d}{d\tilde{x}}\tilde{T} - k\left(\frac{\tilde{\mu}_\alpha}{\tilde{n}_\alpha} - \frac{\tilde{\mu}_\beta}{\tilde{n}_\beta}\right)\left(\frac{d\tilde{U}}{d\tilde{x}}\right)^2\right](\gamma - 1) \\ & = -\lambda_T(\tilde{T}_\alpha - \tilde{T}_\beta),\end{aligned} \tag{7}$$

$$\frac{d}{d\tilde{x}}(\tilde{\rho}\tilde{U}) = 0, \tag{8}$$

$$\frac{d}{d\tilde{x}}(\tilde{\rho}\tilde{U}^2 + \tilde{P}) = 0, \tag{9}$$

$$\frac{d}{d\tilde{x}}\left(\frac{\tilde{n}k\tilde{T}\tilde{U}}{\gamma - 1} + \frac{\tilde{\rho}\tilde{U}^3}{2} + \tilde{P}\tilde{U} + \tilde{Q}\right) = 0. \tag{10}$$

In the above and in what follows we take $m_\beta \geqslant m_\alpha$. $\tilde{n}$, $\tilde{\rho}$, $\tilde{p}$, $\tilde{U}$, $\tilde{T}$, $\tilde{P}$ and $\tilde{Q}$ are, respectively, the number density, mass density, pressure, velocity, temperature, total stress and heat conduction of the composite gas. Subscripted quantities represent analogous component variables. $\tilde{D}_{\alpha\beta}$, $\tilde{\mu}_\alpha$, λ_T, $\tilde{\kappa}_\alpha$, $\tilde{\eta}$, as well as other transport coefficients and 'cross-sections', are defined in appendix A. γ, a constant, is the ratio of specific heat of each of the component gases, and in all calculations will be taken to be $\frac{5}{3}$.

The above set of equations are terminated by the 'constitutive' relations:†

$$\tilde{P} = -\tfrac{4}{3}\tilde{\mu}\frac{d\tilde{U}}{d\tilde{x}} + \tilde{n}k\tilde{T}; \tag{11}$$

$$\tilde{Q} = -\tilde{\kappa}\frac{d\tilde{T}}{d\tilde{x}} + \frac{\gamma}{\gamma-1}k\tilde{T}\frac{\tilde{n}_\alpha\tilde{n}_\beta}{\tilde{\rho}}(m_\beta - m_\alpha)(\tilde{U}_\alpha - \tilde{U}_\beta) + \frac{\tilde{n}_\alpha\tilde{n}_\beta}{\tilde{n}^2}\eta\tilde{p}(\tilde{U}_\beta - \tilde{U}_\alpha). \tag{12}$$

It is important for a number of reasons to have explicit conditions under which the above equations are valid. For example, when examining the shock solutions we will then be able to verify which solutions are self-consistant with the derivation of the above equations. Quadratic expressions in temperature and velocity differences have been neglected in a number of places. Typical conditions for the neglect of these terms are given by

$$\left|\tfrac{4}{3}\tilde{\mu}\frac{d\tilde{U}}{d\tilde{x}}\right| + |\tilde{n}k\tilde{T}| \gg \left|\frac{\tilde{\rho}_\alpha\tilde{\rho}_\beta}{\tilde{\rho}}(\tilde{U}_\alpha - \tilde{U}_\beta)^2\right|, \tag{13}$$

$$\left|\tilde{\kappa}\frac{d\tilde{T}}{d\tilde{x}}\right| + \left|\frac{\gamma k\tilde{T}\tilde{n}_\alpha\tilde{n}_\beta}{(\gamma-1)\tilde{\rho}}(m_\beta - m_\alpha)(\tilde{U}_\alpha - \tilde{U}_\beta)\right| \gg \left|\frac{\gamma\tilde{n}_\alpha\tilde{n}_\beta k}{(\gamma-1)\tilde{n}}(\tilde{T}_\alpha - \tilde{T}_\beta)(\tilde{U}_\alpha - \tilde{U}_\beta)\right|. \tag{14}$$

(13) arises out of the stress equation (11) and (14) out of heat flow equation (12). In addition the derivation of (5)–(12) depends on scale variations being smooth with respect the 'mean-free-path', (3).

The composite continuity, momentum and energy equations (8), (9) and (10), as well as the component continuity equations, are immediately integrable.

$$\tilde{\rho}_\alpha\tilde{U}_\alpha = \overline{m}_\alpha, \tag{15}$$

$$\tilde{\rho}_\beta\tilde{U}_\beta = \overline{m}_\beta, \tag{16}$$

$$\tilde{\rho}\tilde{U} = \tilde{\rho}_\alpha\tilde{U}_\alpha + \tilde{\rho}_\beta\tilde{U}_\beta = \overline{m}, \tag{17}$$

$$\tilde{\rho}\tilde{U}^2 + \tilde{P} = \mathscr{P}, \tag{18}$$

$$\frac{\tilde{n}k\tilde{T}\tilde{U}}{\gamma-1} + \frac{\tilde{\rho}\tilde{U}^3}{2} + \tilde{P}\tilde{U} + \tilde{Q} = \frac{\mathscr{Q}}{2}. \tag{19}$$

The constants of integration in (15)–(18) are, respectively, the α, β and total mass fluxes, the total momentum flux and the total energy flux. Using these, the component and composite quantities are related by

$$\tilde{U}_\beta = \tilde{U} - (\tilde{\rho}_\alpha/\tilde{\rho})(\tilde{U}_\alpha - \tilde{U}_\beta), \tag{20}$$

$$\tilde{T}_\beta = \tilde{T} - (\tilde{n}_\alpha/\tilde{n})(\tilde{T}_\alpha - \tilde{T}_\beta). \tag{21}$$

For later purposes it is convenient to define the number density averaged mass,

$$\tilde{m}_T = \tilde{\rho}/\tilde{n}; \tag{22}$$

$\tilde{m}_T$ is not a constant, but on multiplying numerator and denominator by $\tilde{U}$, we see that

$$\tilde{m}_T(-\infty) = \tilde{m}_T(\infty) = \tilde{m}_{T_0}.$$

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† It is clear that bulk viscosity may be included by a trivial redefinition of $\tilde{\mu}$.

In analogy with simple gas shock structure (Becker 1922), it proves convenient to introduce the following normalization:

$$\left.\begin{aligned} &U = \frac{\overline{m}\tilde{U}}{\mathscr{P}}, \quad U_\alpha = \frac{\overline{m}\tilde{U}_\alpha}{\mathscr{P}}, \quad T = \frac{\overline{m}^2 k\tilde{T}}{\mathscr{P}^2\tilde{m}_{T_0}}, \quad T_\alpha = \frac{\overline{m}^2 k\tilde{T}_\alpha}{\mathscr{P}^2\tilde{m}_{T_0}}, \\ &m_T = \frac{\tilde{m}_T}{\tilde{m}_{T_0}}, \quad x = \frac{\overline{m}\tilde{x}}{\tilde{\mu}_0}, \quad n_{\alpha 0} = \frac{\tilde{n}_{\alpha_0}}{\tilde{n}_0}, \quad \delta = \frac{\overline{m}\mathscr{Q}}{\mathscr{P}^2}. \end{aligned}\right\} \tag{23}$$

The zero subscript denotes upstream quantities, and $\tilde{\mu}_0$ is the upstream value of viscosity.

Introducing this normalization into the above relations and eliminating the densities through the flux relations (15), (16), we obtain the following dimensionless equations:

Composite momentum:

$$U + \frac{1}{m_T}\frac{T}{U} - \tfrac{4}{3}\mu\frac{dU}{dx} = 1. \tag{24}$$

Composite energy:

$$\frac{\gamma}{\gamma-1}\frac{T}{m_T} + \frac{U^2}{2} - \tfrac{4}{3}\mu U\frac{dU}{dx} - \kappa\frac{dT}{dx} + \tau UT\left(\frac{1}{U_\alpha} - \frac{1}{U_\beta}\right) = \frac{\overline{m}\mathscr{Q}}{2\mathscr{P}^2} = \frac{\delta}{2}. \tag{25}$$

Diffusion:

$$\begin{aligned} U_\alpha - U_\beta = -D\frac{U_\alpha U_\beta}{U^2}\bigg[&\frac{d_1}{m_T^2}\frac{d}{dx}\left(\frac{m_T U}{U_\alpha}\right) - \eta\frac{U^2}{U_\alpha U_\beta T}\frac{dT}{dx} \\ &+ d_2\frac{U^3}{TU_\alpha U_\beta}\frac{d}{dx}\left(\frac{T}{Um_T}\right) + \frac{1}{m_T}\frac{U}{T}\frac{d}{dx}\left(\frac{m_T U(T_\alpha - T_\beta)}{U_\alpha U_\beta}\right)\bigg] - \frac{2m_{\alpha\beta}}{\Lambda\tilde{m}_T}\frac{d}{dx}U(U_\alpha - U_\beta). \end{aligned} \tag{26}$$

Temperature diffusion:

$$\begin{aligned} &(U_\alpha - U_\beta)\frac{dT}{dx} + U\frac{d}{dx}(T_\alpha - T_\beta) + \tfrac{2}{3}T\frac{d}{dx}(U_\alpha - U_\beta) \\ &\quad + \tfrac{2}{3}(T_\alpha - T_\beta)\frac{dU}{dx} - \frac{2}{3}\left(\frac{m_\alpha}{\tilde{m}_{T_0}}\frac{\overline{m}}{\overline{m}_\alpha}\right)U\frac{d}{dx}\left(\kappa_\alpha\frac{dT}{dx}\right) \\ &\quad + \frac{2}{3}\left(\frac{m_\beta}{\tilde{m}_{T_0}}\frac{\overline{m}}{\overline{m}_\beta}\right)U\frac{d}{dx}\left(\kappa_\beta\frac{dT}{dx}\right) - \tfrac{2}{3}(\mu_\alpha U_\alpha - \mu_\beta U_\beta)\left(\frac{dU}{dx}\right)^2 = -\Lambda(T_\alpha - T_\beta). \end{aligned} \tag{27}$$

The coefficients d_1 and d_2 are constants but the coefficients m_T, μ, κ, κ_α, κ_β, D, τ, Λ, μ_α, μ_β are functions of the dependent variables. Explicit forms for the coefficients are given in appendix A.

Apart from the parameters which specify the gas properties, the flow is characterized by three parameters, the mass ratio, the density ratio and the composite Mach number. The last is defined as

$$M_0^2 = \tilde{m}_{T_0}\tilde{U}_0^2/\gamma k\tilde{T}_0. \tag{28}$$

Since gradients and differences of velocity and temperature must vanish at ± ∞, and since m_T has been shown to have the same value at $\pm\infty$ ($m_T(\pm\infty) = 1$), the composite momentum and energy equations, (20) and (21), yield the classical Rankine–Hugoniot relations for composite velocity and temperature.

A seeming paradox occurs in this connexion. If, for example, we allow m_α to vanish and hold n_α fixed, the Rankine–Hugoniot relations of a simple gas are not obtained. For in this case (24) becomes $(m_\beta \tilde{U}_0^2/\gamma k\tilde{T}_0)(\eta_\beta/n)$ instead of $m_\beta \tilde{U}_0^2/\gamma k\tilde{T}_0$. This paradox is resolved when one recognizes that the α-gas, although of zero mass density, still has a pressure $\tilde{n}_\alpha k\tilde{T}$ and an energy per unit volume,

$$\tilde{n}_\alpha k\tilde{T}/(\gamma-1).$$

(The average speed of α-particles is infinite.) An interpretation of this limit might be that it gives a mixture of β-particles and photons. However, the basic equations themselves become suspect in this limit.

The velocities and temperatures upstream and downstream can be expressed in terms of δ:

$$U_\alpha(\mp\infty) = U(\mp\infty) = \frac{1}{\gamma+1}[\gamma \pm (\gamma^2(1-\delta)+\delta)^{\frac{1}{2}}], \tag{29}$$

$$T_\alpha(\mp\infty) = T(\mp\infty) = \frac{1}{(1+\gamma)^2}[\gamma \pm (1-\gamma)(\gamma^2(1-\delta)+\delta)^{\frac{1}{2}} - \gamma^2(1-\delta)+\delta]. \tag{30}$$

δ is related to the Mach number by

$$\delta = \frac{1}{4}\left(\frac{\gamma-1}{\gamma+1}\right)\left\{\left(\frac{2\gamma}{\gamma-1}\right)^2 - \left[\frac{2\gamma}{\gamma-1}\left(\frac{M_0^2-1}{\gamma M_0^2+1}\right)\right]^2\right\}.$$

We also introduce the shock strength parameter, ϵ, by

$$\epsilon = [\gamma^2(1-\delta)+\delta]^{\frac{1}{2}} \tag{31}$$

(this differs from the ϵ used by Sherman (1960), see appendix B). Inverting (31),

$$\delta = \frac{\gamma}{\gamma^2-1} + \frac{\epsilon^2}{1-\gamma^2}. \tag{32}$$

In terms of the Mach number

$$\epsilon = \gamma\left(\frac{M_0^2-1}{\gamma M_0^2+1}\right) \tag{33}$$

and

$$M_0^2 = \frac{\gamma+\epsilon}{\gamma(1-\epsilon)}, \tag{34}$$

so that ϵ varies between zero and unity as the Mach number varies from one to infinity.

We introduce new velocity and temperature variables through (Grad 1952)

$$U = \frac{1}{1+\gamma}(\gamma+\epsilon\omega), \tag{35}$$

$$U_{\alpha,\beta} = \frac{1}{1+\gamma}(\gamma+\epsilon\omega_{\alpha,\beta}), \tag{36}$$

$$T = \frac{1}{(1+\gamma)^2}[\gamma+(1-\gamma)\epsilon t-\epsilon^2], \tag{37}$$

$$T_{\alpha,\beta} = \frac{1}{(1+\gamma)^2}[\gamma+(1-\gamma)\epsilon t_{\alpha,\beta}-\epsilon^2], \tag{38}$$

so that on comparison with (29), (30) we have

$$\omega(\mp\infty) = \omega_{\alpha,\beta}(\mp\infty) = \pm 1, \tag{39}$$

$$t(\mp\infty) = t_{\alpha,\beta}(\mp\infty) = \pm 1. \tag{40}$$

Since the governing differential equations are autonomous, we may introduce

$$\omega(x=0) = 0 \tag{41}$$

which is sufficient to fix the origin.

3. Perturbation method for weak shock-waves

We now restrict attention to weak shock-waves, i.e. the shock parameter, see (31), ϵ small. To do this we adapt a method, due to Grad (1952), used in the study of simple gases.

Inspection of (24)–(27) shows that the component variables frequently occur in the form of a velocity diffusion

$$U_\alpha - U_\beta = \frac{\epsilon}{\gamma+1}(\omega_\alpha - \omega_\beta) = \frac{\epsilon\Delta\omega}{\gamma+1} \tag{42}$$

and a temperature diffusion

$$T_\alpha - T_\beta = \frac{\epsilon(1-\gamma)}{(\gamma+1)^2}(t_\alpha - t_\beta) = \frac{\epsilon(1-\gamma)}{(\gamma+1)^2}\Delta t. \tag{43}$$

For this reason, in addition to the velocity and temperature, ω and t, we take $\Delta\omega$ and Δt as dependent variables.

Assuming the monotonicity of ω, we can regard t, $\Delta\omega$ and Δt as functions of ω, and expand

$$\left.\begin{aligned} t &= t_0(\omega) + \epsilon t_1(\omega) + \epsilon^2 t_2(\omega) + O(\epsilon^3), \\ \Delta\omega &= \Delta_0\omega + \epsilon\Delta_1\omega + \epsilon^2\Delta_2\omega + O(\epsilon^3), \\ \Delta t &= \Delta_0 t + \epsilon\Delta_1 t + \epsilon^2\Delta_2 t + O(\epsilon^3). \end{aligned}\right\} \tag{44}$$

Substituting into (22), we easily have

$$m_T = 1 + \epsilon m_T^{(1)}\Delta_0\omega + \epsilon^2\{m_T^{(1)}\Delta_1\omega + m_T^{(2)}\Delta_0\omega + \overline{m}_T^{(2)}(\Delta_0\omega)^2\} + O(\epsilon^3), \tag{45}$$

with

$$m_T^{(1)} = \frac{n_{\alpha0}(1-n_{\alpha0})}{\gamma}\left(\frac{m_\beta - m_\alpha}{\tilde{m}_{T_0}}\right). \tag{46}$$

Since we will shortly show that $\Delta_0\omega = 0$, the explicit forms of $m_T^{(2)}$ and $\overline{m}_T^{(2)}$ are unnecessary. Lastly, since l/ϵ is a measure of the scale variation in weak shocks, we renormalize the spatial variable by

$$y = \epsilon x. \tag{47}$$

Introducing (42)–(47), (35), (38) and (32) into (24)–(27), we find that the equations are identically satisfied to the zeroth order in ϵ. To the first order in ϵ we find

$$\left.\begin{aligned} \Delta_0\omega &= 0, \\ t_0 &= \omega, \\ \Delta_0 t &= 0. \end{aligned}\right\} \tag{48}$$

Going to the second order in ϵ, the composite momentum, composite energy and diffusion equations lead respectively to

$$\tfrac{4}{3}\gamma(d\omega/dy)+(\gamma-1)t_1+(1-\omega^2)+m_T^{(1)}\gamma\Delta_1\omega = 0, \tag{49}$$

$$-t_1+\kappa^0(\gamma-1)(d\omega/dy)+\{\gamma m_T^{(1)}-\eta_0 n_{\alpha 0}n_{\beta 0}\}\Delta_1\omega+\tfrac{1}{2}(1-\omega^2) = 0, \tag{50}$$

$$(\gamma+1)D^0\left(d_2-\frac{\gamma-1}{\gamma}\eta_0\right)\frac{d\omega}{dy}-\Delta_1\omega = \frac{2\epsilon\gamma m_{\alpha\beta}d\Delta_1\omega}{C^0\tilde{m}_{T_0}\,dy}, \tag{51}$$

where C^0 is the upstream value of the modified Schmidt number (see appendix A). It should be noted that in (51) a term of $O(\epsilon)$ has been retained. We have done this because C^0 can be small for some gas mixtures. Figures 1 and 2 display transport coefficient data for argon–helium and xenon–helium mixtures. In both cases C^0 is relatively small. It is the retention of this term which distinguishes (7) from the classical diffusion equation and it is because of the possible smallness of C^0 that it must be retained. We notice also the factor $m_{\alpha\beta}/\tilde{m}_{T_0}$ in the last term of (51). This is always less than unity as can be seen from

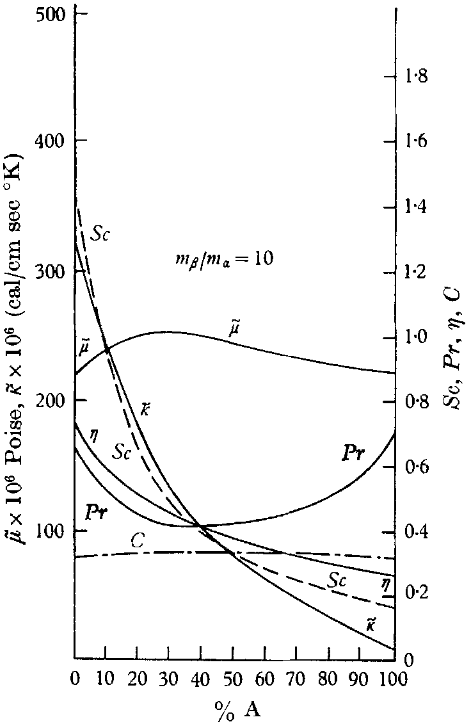

FIGURE 1. A–He data at NTP.

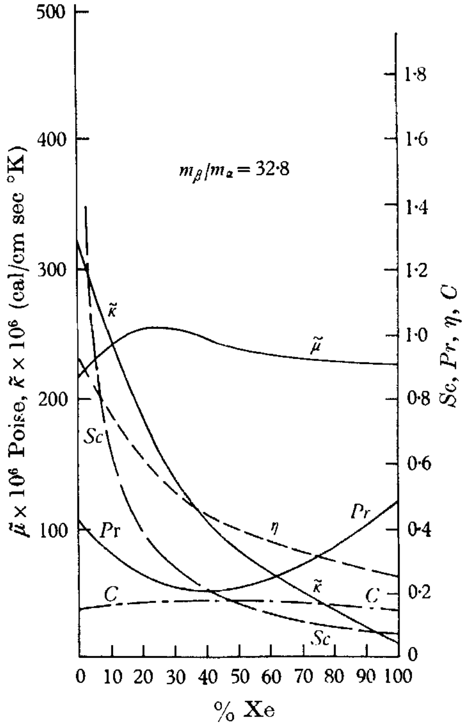

FIGURE 2. Xe–He data at NTP.

$$\frac{m_{\alpha\beta}}{\tilde{m}_{T_0}} = \frac{1}{(m_\alpha/m_\beta)+1}\,\frac{n_\alpha+n_\beta}{n_\alpha+(m_\beta/m_\alpha)n_\beta} < 1. \tag{52}$$

The possible smallness of C^0 also plays a role in determining the temperature difference. It is now convenient to introduce

$$t_\Delta = \Delta_1 t+\epsilon\Delta_2 t. \tag{53}$$

Then the first non-zero order in Δt is governed by

$$\frac{d}{dy}t_\Delta - \frac{2}{3(\gamma-1)}\frac{d}{dy}\Delta_1\omega - \frac{2\overline{m}}{3\tilde{m}_{T_0}}\left[\frac{m_\alpha\kappa_\alpha^0}{\overline{m}_\alpha} - \frac{m_\beta\kappa_\beta^0}{\overline{m}_\beta}\right]\frac{d^2\omega}{dy^2} = -\frac{C^0}{\epsilon\gamma}t_\Delta. \tag{54}$$

In this case it is seen that the smallness of C^0 permits a $\Delta_1 t \neq 0$.

Equations (49), (50), (51) and (54) are only weakly connected. Using (50) we can eliminate t_1 from (49) to obtain

$$[\tfrac{4}{3}\gamma + \kappa^0(\gamma-1)^2]\frac{d\omega}{dy} = \{(\gamma-1)\eta_0 n_{\alpha0}(1-n_{\alpha0}) - \gamma^2 m_T^{(1)}\}\Delta_1\omega + \frac{\gamma+1}{2}(\omega^2-1). \tag{55}$$

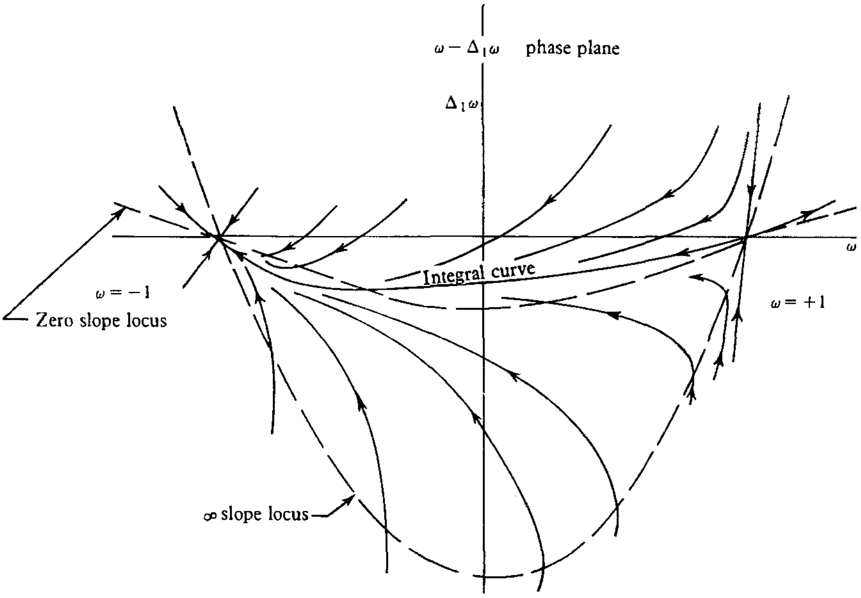

FIGURE 3. Direction field and integral curve for two fluid shock wave.

Then using (55) in (51) we get

$$\frac{2\gamma\epsilon m_{\alpha\beta}}{C^0\tilde{m}_{T_0}}\frac{d}{dy}\Delta_1\omega = -\frac{(\gamma+1)^2 D^0(d_2 - [(\gamma-1)/\gamma]\eta_0)}{\frac{8}{3}\gamma + 2\kappa^0(\gamma-1)^2}(1-\omega^2)$$
$$-\Delta_1\omega\left(1 + \frac{(\gamma+1)D^0(d_2 - [(\gamma-1)/\gamma]\eta_0)[\gamma^2 m_T^{(1)} - (\gamma-1)\eta_0 n_{\alpha0} n_{\beta0}]}{\frac{4}{3}\gamma + \kappa^0(\gamma-1)^2}\right). \tag{56}$$

On dividing (56) by (55) we obtain the first-order equation in the $\Delta_1\omega - \omega$ phase plane which governs the shock structure. The phase plane analysis is standard and we do not go into details. Figure 3 contains a sketch of a typical case. It should be noted that a node (stable) is always obtained upstream and a saddle is always obtained downstream. This is just the reverse of the Navier–Stokes situation (Hayes 1958).

In order to integrate (55) and (56) in the phase plane we must resort to machine computation. Due to the topology of the directional field this is easily carried out by integrating from the saddle to the node. From this the integration in the physical plane as well as the determination of t_1 and t_Δ directly follow also by numerical means. The results of this computation will be discussed in the following section.

To complete the picture note that from (37) and (48)

$$T \sim \frac{\gamma+(1-\gamma)\epsilon(\omega+\epsilon t_1)-\epsilon^2}{(1+\gamma)^2}$$

and from (21) and (43) the component temperatures are

$$\begin{bmatrix} T_\alpha \\ T_\beta \end{bmatrix} \sim T \pm \frac{\epsilon^2(1-\gamma)}{(1+\gamma)^2}\begin{bmatrix} n_{\beta_0} \\ n_{\alpha_0} \end{bmatrix} t_\Delta.$$

Two-temperature theory

If

$$\frac{2\gamma m_{\alpha\beta}}{C^0 \tilde{m}_{T_0}} = O(1) \tag{57}$$

(or smaller) the theory is considerably simplified and analytical results can be obtained. In this case we have

$$(\gamma+1)D^0\left(d_2-\frac{\gamma-1}{\gamma}\eta_0\right)\frac{d\omega}{dy}-\Delta_1\omega = 0 \tag{58}$$

instead of (51). Equations (49), (50), (54) and (58) result from the two temperature equations discussed in Goldman & Sirovich (1967). Equations (49), (50) and (58) easily lead to

$$\left.\begin{aligned} d\omega/dy &= -z_1(1-\omega^2), \\ t_1 &= z_2(1-\omega^2), \\ \Delta_1\omega &= z_3(1-\omega^2), \end{aligned}\right\} \tag{59}$$

where

$$\left.\begin{aligned} z_1 &= (\gamma+1)/2\mathscr{D}, \\ z_2 &= \frac{1}{\mathscr{D}}\left[\frac{2\gamma}{3}-\frac{\gamma}{Pr}-\frac{\gamma}{Sc}n_{\alpha0}(1-n_{\alpha0})\left(\frac{m_\beta-m_\alpha}{\tilde{m}_{T_0}}-\frac{\gamma-1}{\gamma}\eta_0\right)\left(\frac{m_\beta-m_\alpha}{2m_{T_0}}-\eta_0\right)\right], \\ z_3 &= \frac{\gamma z_1}{Sc}\left[\frac{\gamma-1}{\gamma}\eta_0-\frac{m_\beta-m_\alpha}{\tilde{m}_{T_0}}\right], \end{aligned}\right\} \tag{60}$$

with

$$\mathscr{D} = \gamma\left[\tfrac{4}{3}+\frac{\gamma-1}{Pr}+\frac{\gamma}{Sc}n_{\alpha0}(1-n_{\alpha0})\left\{\frac{m_\beta-m_\alpha}{\tilde{m}_{T_0}}-\frac{\gamma-1}{\gamma}\eta_0\right\}^2\right]. \tag{61}$$

In these we have introduced the Prandtl number and Schmidt number which are defined in appendix A.

Solving for ω in (59) we have

$$\omega = -\tanh z_1 y, \tag{62}$$

where we have taken $\omega(0) = 0$, see (41).

The velocity of the component gas is obtained from (20) and to the above order is given by

$$U_\beta = \frac{\gamma+\epsilon}{\gamma+1}+\frac{\epsilon(\omega-1)}{\gamma+1}-\frac{m_\alpha n_{\alpha0}\epsilon^2}{m_\alpha n_{\alpha0}+m_\beta n_{\beta0}}\frac{\Delta_1\omega}{\gamma+1}+O(\epsilon^3). \tag{63}$$

The above results, up to differences in normalization, are the same as those obtained by Dyakov (1954) and Sherman (1960) (see appendix B). It is straightforward, and in fact simple, to find the higher orders in ϵ of the above development. But at the next order the procedure is no longer self-consistent with the Boltzmann equations for mixtures. In fact, the structure of weak shock-waves can be considered directly from the Boltzmann equations. Expanding in ϵ we obtain the same results to the above order. At the next order the results diverge from those which would be obtained from the two-temperature equations. We therefore halt the perturbation expansion at the above order.

Turning next to the calculation of t_Δ, we first note that (57) does not imply that C^0 is large (see (52)). Introducing (59) into (54) we have after some manipulation

$$\frac{dt_\Delta}{dy} - a(1-\omega^2)\omega = -\frac{C^0}{\epsilon\gamma} t_\Delta \tag{64}$$

with
$$a = \frac{4z_1^2}{3}\left[\frac{(\gamma+1)D^0}{1-\gamma}\left(d_2 - \frac{\gamma-1}{\gamma}\eta_0\right) - \frac{\overline{m}}{\tilde{m}_{T_0}}\left(\frac{m_\alpha \kappa_\alpha^0}{\overline{m}_\alpha} - \frac{m_\beta \kappa_\beta^0}{\overline{m}_\beta}\right)\right].$$

Then noting that

$$\frac{dt_\Delta}{dy} = \frac{dt_\Delta}{d\omega}\frac{d\omega}{dy} = -z_1(1-\omega^2)\frac{dt_\Delta}{d\omega},$$

we can rewrite (64) as
$$\frac{dt_\Delta}{d\omega} - \frac{bt_\Delta}{1-\omega^2} = -\frac{a}{z_1}\omega \tag{65}$$

with
$$b = \frac{C^0}{z_1 \epsilon\gamma}.$$

Integrating (65) we obtain

$$t_\Delta = \frac{a}{2z_1^2}\left[(1-\omega^2) + \frac{C_0}{\epsilon\gamma}\left(\frac{1+\omega}{1-\omega}\right)^2 I_b(\omega)\right] \tag{66}$$

with
$$I_b(\omega) = \int_\omega^1 \left(\frac{1-x}{1+x}\right)^b dx.$$

For integer b, one has

$$b = 2n, \quad n \geqslant 1, \quad I_{2n} = -\left(\frac{1-\omega}{1+\omega}\right)^n \left(\frac{1+\omega}{2}\right)$$
$$+ n\sum_{k=0}^{n-1} \frac{(-)^k}{n-k}\binom{n}{k}\left[\left(\frac{2}{1+\omega}\right)^{n-k} - 1\right] + (-)^n n \ln\left(\frac{2}{1+\omega}\right),$$

$$b = 2m+1, \quad m \geqslant 0, \quad I_{2m+1} = -\tfrac{1}{2}(1-\omega^2)^{\frac{1}{2}}\left(\frac{1-\omega}{1+\omega}\right)^m$$
$$+ (-)^m(2m+1)\tan^{-1}\left(\frac{1-\omega}{1+\omega}\right)^{\frac{1}{2}} + (2m+1)$$
$$+ (2m+1)\sum_{k=0}^{m-1}\sum_{l=0}^{m-k-1} \frac{(-)^k}{2m-2k-2l+1}\binom{m}{k}\binom{m-k-1}{l}\left(\frac{1-\omega}{1+\omega}\right)^{m-k-l-\frac{1}{2}}.$$

For non-integer b, $I_b(\omega)$ may be easily evaluated by machine computation. (We note in passing that since $dt_\Delta/d\omega$ vanishes at $\omega = \pm 1$, we have that $(dt/d\omega) + a\omega$ passes through zero as ω passes from -1 to $+1$. Therefore t_Δ changes sign.)

Classical Chapman–Enskog theory

As already pointed out the velocity field through the shock in the above two temperature régimes is the same as that found using the Chapman–Enskog equations for mixtures. Two temperature effects are only weakly coupled to the velocity field. If the modified Schmidt number C^0 is not relatively small, then (53) and (54) tell us that

$$\Delta_1 t = 0$$

which is in keeping with the Chapman–Enskog theory. In fact, if C^0 is not relatively small the two-fluid equations reduce to the Chapman–Enskog mixture equations.

The temperature diffusion equation (7), or its present form (64), is still capable of describing the now higher order temperature separation. From (54) we obtain

$$\Delta_2 t = (\gamma a/C^0)\,\omega(1-\omega^2). \tag{67}$$

That the individual temperatures cross over in this case is clear from (67).

4. Discussion of the results

In discussing the shock-wave solutions it is necessary to consider the ratio of the shock-wave thickness, Δ, to the 'mean-free-path', l. For simplicity we use the maximum slope definition of shock thickness, and we therefore have

$$\frac{\Delta}{l} = \frac{|U(\infty)-U(-\infty)|}{|dU/dx|_{\max}}. \tag{68}$$

If the condition (57) for the two-temperature equations is valid an *a priori* estimate for (68) can be obtained from (59) and (60)

$$\frac{\Delta}{l} \approx \frac{4\gamma}{\epsilon(\gamma+1)}\left[\tfrac{4}{3}+\frac{\gamma-1}{Pr}+\frac{\gamma}{Sc}\left(\frac{m_\beta-m_\alpha}{\tilde{m}_{T_0}}-\frac{\gamma-1}{\gamma}\eta_0\right)^2 n_{\alpha 0}(1-n_{\alpha 0})\right]. \tag{69}$$

The same result holds for the classical Chapman–Enskog equations. This was obtained by Dyakov (1954) and confirmed by Sherman (1960). [The earlier sound propagation work of Kohler (1949) also produces this scaling.] We note that (69) predicts shock-wave thicknesses which may be markedly greater than the predictions of simple gas theory. This effect has been observed in the recent experiments of Center (1967).

Figure 4 contains a plot of shock thickness ratios for argon–helium mixtures at $M_\infty^2 = 4{\cdot}2$. (69) predicts slightly thicker shock-waves, however the difference is always less than 5 %. For weak shocks, at least, the various equations lead to shocks of roughly equal thicknesses.

In order to facilitate comparison with experiment we have considered real gases in our calculations. By this we mean that the transport coefficients which appear in the theory are based on experimental values for real gases. Figures 1, 2, 5 and 6 contain plots of the various transport coefficients necessary for the study of argon–helium and xenon–helium mixtures. Also we have chosen

$M_\infty^2 = 4{\cdot}2$ in all our calculations for A–He mixtures since this corresponds to the case discussed by Sherman (1960) and to the experiments of Center (1967).

A variety of cases were considered and a selection of the results are shown in figures 7–14. While a number of curious effects can be observed on these plots, it should be noted that the velocity overshoot first discussed by Sherman (1960) is

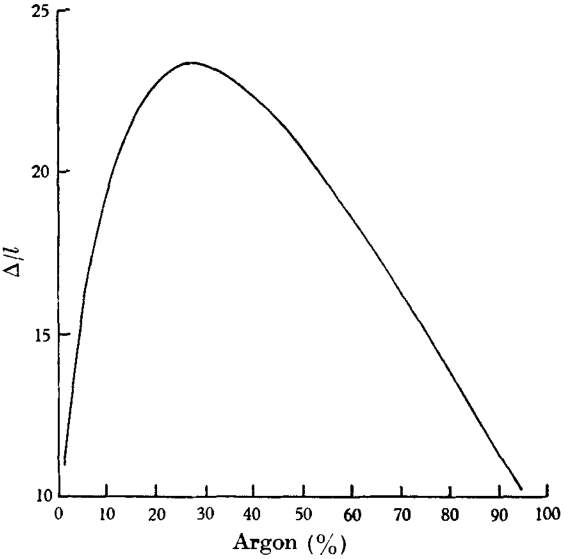

FIGURE 4. Two-fluid shock thickness ratios for A–He mixtures at $M^2 = 4{\cdot}2$.

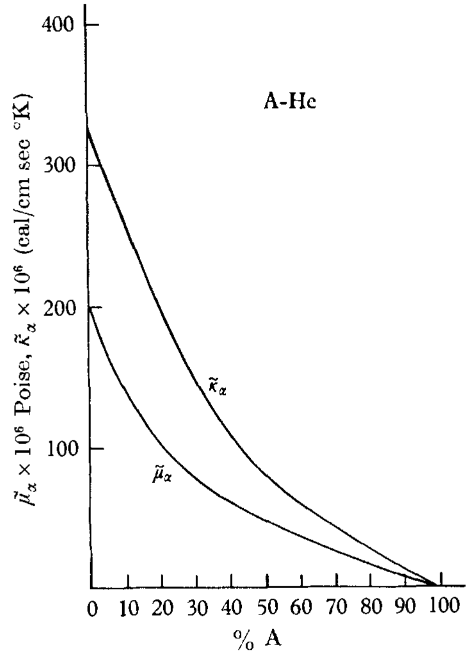

FIGURE 5. $\tilde{\mu}_\alpha$ and $\tilde{\kappa}_\alpha$ (α refers to helium gas).

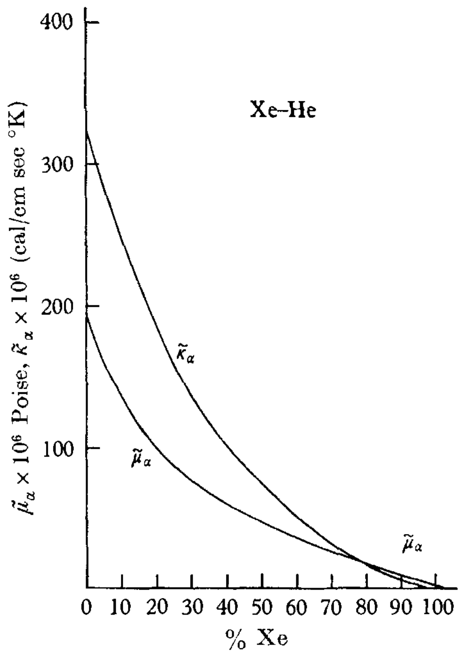

FIGURE 6. $\tilde{\mu}_\alpha$ and $\tilde{\kappa}_\alpha$ (α refers to helium gas).

entirely absent. It will be recalled that this effect predicts that if a binary mixture contains a trace of heavy gas this component first accelerates on entering the shock.

The source of the overshoot effect can be traced to the baro-diffusion term in the diffusion equation. (The diffusion equation is obtained by neglecting the last term in (6), and setting $T_\alpha - T_\beta = 0$.) As is well known (Chapman & Cowling 1939) this term implies that in a gas mixture the heavier component drifts in the direction of the pressure gradient. In passing through a shock the pressure increases and the heavy component experiences a tendency to move faster than the lighter components. For a trace of heavy gas both the Chapman–Enskog and two-temperature solutions given in the last section predict that the heavy component velocity rises above the upstream velocity before finally being retarded by the slower moving lighter components. We mention in passing that Mott-Smith (1966) has given a very persuasive physical argument for the non-existence of an overshoot effect in strong shock-waves. Our discussion however will apply only to the theory of weak shock-waves.

The reason for the disappearance of overshoot in the two-fluid description can also be explained in terms of the governing equations. Equation (51) is the normalized form of equation (6) in the limit of weak shocks. In the comparable limit using the Chapman–Enskog mixture equations one obtains (6) but with the right-hand side absent. But it is precisely for the case of a trace of heavy gas that the right-hand side becomes important. In this limit $m_{\alpha\beta}/\tilde{m}_{T_0}$ approaches unity and, for example, for A–He, $C_0 \approx 0{\cdot}3$ and for Xe–He, $C_0 \approx 0{\cdot}15$. Therefore even though ϵ appears as a coefficient of this term it is only for the weakest shocks, $\epsilon \to 0$, that this term can be neglected. The term in question is clearly a relaxation term and acts against velocity separation and hence prevents overshoot.

An analytical criteria for the onset of overshoot can be given. First, recognizing that velocity overshoot is an upstream phenomena, we expand U_α in the neighbourhood of $\omega = 1$, i.e.

$$U_\beta(\omega) - U_\beta(1) = (\omega - 1)\left.\frac{\partial U_\beta}{\partial w}\right|_1 + O((\omega-1)^2)$$

and hence velocity overshoot is obtained if

$$\left.\frac{\partial U_\beta}{\partial \omega}\right|_{\omega=+1} < 0.$$

On differentiating (36) with respect to ω, to the lowest order this condition is

$$\frac{m_\alpha}{\tilde{m}_{T_0}}\eta_{\alpha 0}\epsilon\left.\frac{d\Delta_1\omega}{d\omega}\right|_{\omega=+1} > 1. \tag{70}$$

An explicit expression for (70) may be obtained from the analysis of the saddle-point at $\omega = 1$. ($d\Delta_1\omega/d\omega$ is the slope associated with the unstable root at $\omega = 1$.) This expression is quite long and we do not include it here. The quantity in (70) has been evaluated under a wide set of conditions and in no case were we able to find overshoot. A direct proof of this non-existence of overshoot has so far eluded us.

Before remarking on the various peculiar effects to be found in figures 7–14 we briefly discuss the notion of a self-consistent solution.

In the derivation of fluid-like equations from the Boltzmann equation a number of approximations are made. If the solution of the fluid-like equations does indeed show that neglected terms are small compared to those retained the solution is said to be self-consistent. There are two types of terms which are neglected in the derivation of fluid-like equations from kinetic theory. The most wide spread approximation is the neglect of high order derivatives and products of low order derivatives. In fact the symbol ϵ in the Chapman–Enskog theory should be interpreted as the ratio of molecular to macroscopic scales. For our problem this requirement is met if $l/\Delta \ll 1$. As can be seen from the information given in figures 7–14, in all the computed cases this condition is fulfilled. As already mentioned the classical Chapman–Enskog mixture equations actually places the more stringent condition

$$l/C^0\Delta \ll 1$$

on a solution. In the régime in which Sherman (1960) found overshoot this condition is violated and the failure of these equations is thereby signalled.

The second type of neglected term involves terms which are quadratic and higher in velocity and temperature diffusion. The precise conditions are given by (13) and (14). Normalizing (13) and (14) and reducing these to lowest order we obtain

$$1 \gg R = \max\left[\frac{\overline{m}_\alpha \overline{m}_\beta \epsilon^4 (\Delta_1 \omega)^2}{\gamma \overline{m}^2 (1 + \epsilon^2 \frac{4}{3} |d\omega/dy|)}\right],$$

$$1 \gg S = \max\left[\frac{\epsilon^2 n_{\alpha 0} n_{\beta 0} P_{r_0} |\Delta_1 t|\, |\Delta_1 \omega|}{\gamma |d\omega/dy| + [(m_\beta - m_\alpha)/\tilde{m}_{T_0}] n_{\alpha 0} n_{\beta 0} P_{r_0} [\gamma/(\gamma-1)] |\Delta_1 \omega|}\right].$$

The use of the maximum value is due to the fact that (13) and (14) must hold pointwise throughout the flow. The values of S and R are given on each of the figures and it is seen that in each case these parameters are small.

Figure 7 contains the shock profile under the same conditions for which Sherman found a more than 20 % velocity overshoot in the heavy gas velocity. For reasons already given we now find no trace of velocity overshoot. It might be mentioned that the Chapman–Enskog mixture equations violate the condition $\epsilon_1 \ll 1$, see (2), if used in this case. Figure 8 gives the accompanying temperature profiles which show temperature separation. This last effect is relatively mild in this case. Figures 9 and 10 are again for an A–He mixture at $M_\infty^2 = 4{\cdot}2$ with roughly equal numbers of A and He atoms.

Figures 11 and 12 also at the same conditions but with a trace of He, exhibit pronounced velocity and temperature separation. For the former undershoot is seen to exist. The temperature oscillation for the He is quite sharp and the condition $\epsilon_0 \ll 1$, see (1), might now be too mild for self-consistency, although all other self-consistency conditions are met. Figures 13 and 14 show shock profiles at $M_\infty^2 = 2{\cdot}5$ and for a 95 % Xe–He mixture. All the same effects as appear in the 95 % A–He case also appear now. Now, however, ϵ_0 is smaller and there does not seem to be any reason to doubt self-consistency in this case.

Sherman (1960) also noted a case (99 % A–He at $M_0^2 = 4{\cdot}2$) for which the weak shock solution possesses a velocity undershoot. But he showed that in this case an exact numerical integration of the Chapman–Enskog mixture equations eliminates the undershoot. This certainly casts doubt on the presence of a velocity undershoot. In fact we have carried out the exact numerical integration of the Chapman–Enskog mixture equations for the conditions stated in figures 11 and 13. In both cases the velocity undershoot is eliminated by these equations. However, in these cases as well as that considered by Sherman the Chapman–

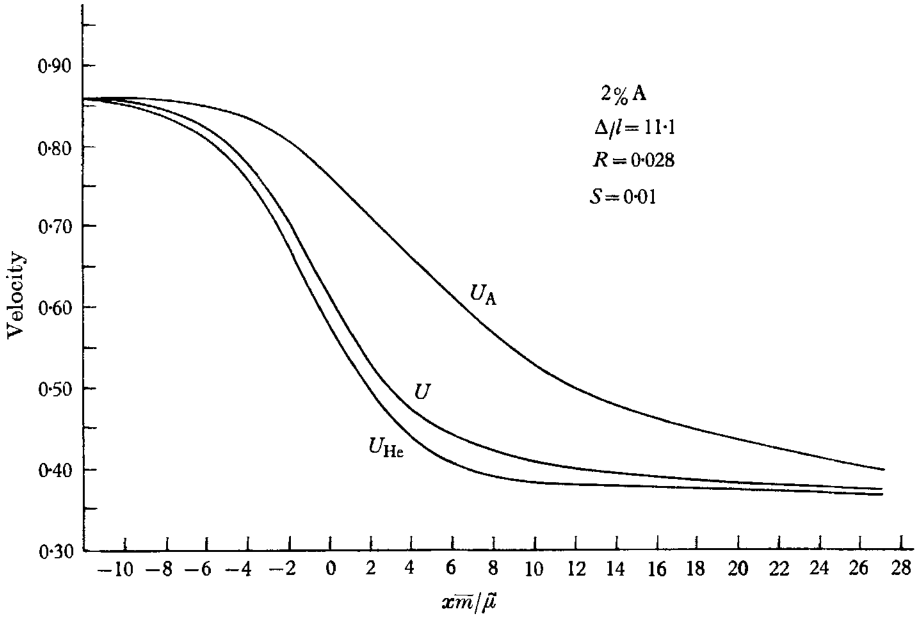

FIGURE 7. Velocity profiles for 2 % A–He mixture at $M_\infty^2 = 4{\cdot}2$.

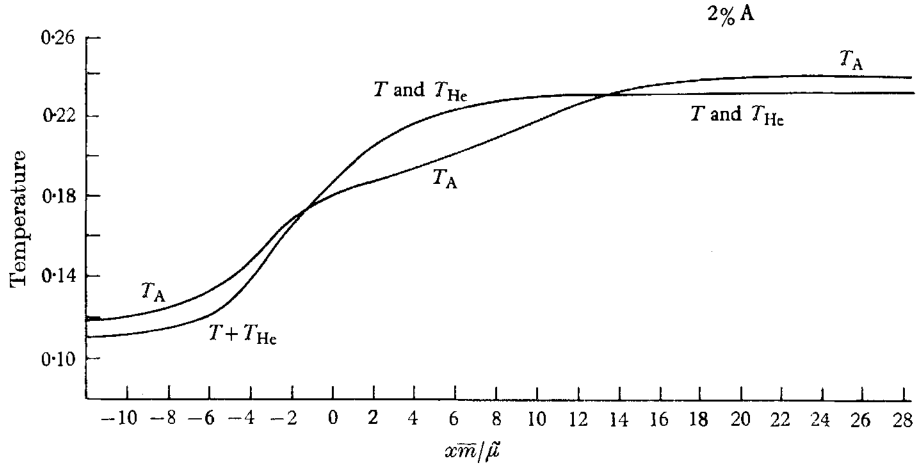

FIGURE 8. Temperature profiles for 2 % A–He mixture at $M_\infty^2 = 4{\cdot}2$.

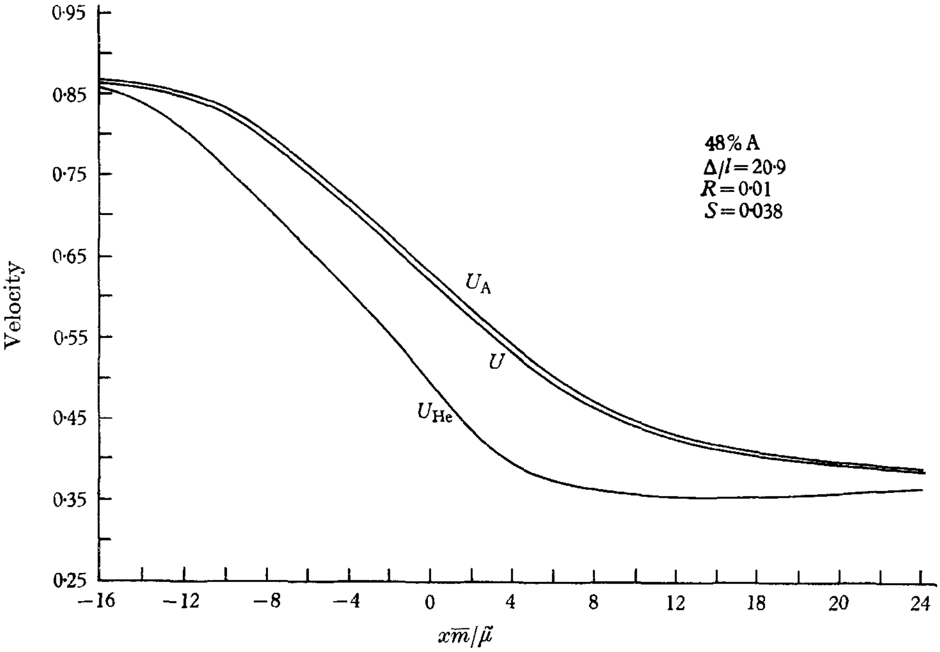

FIGURE 9. Velocity profiles for 48 % A–He mixture at $M_\infty^2 = 4{\cdot}2$.

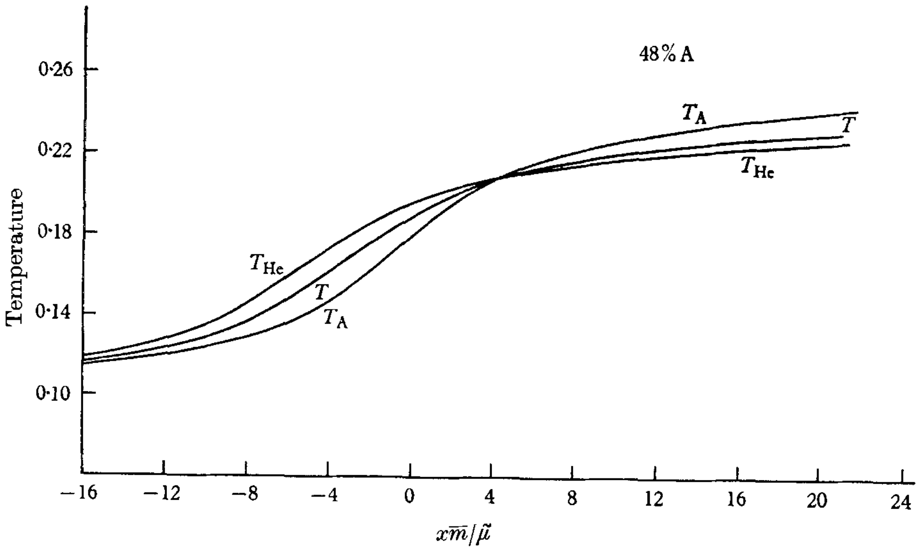

FIGURE 10. Temperature profiles for 48 % A–He mixture at $M_\infty^2 = 4{\cdot}2$.

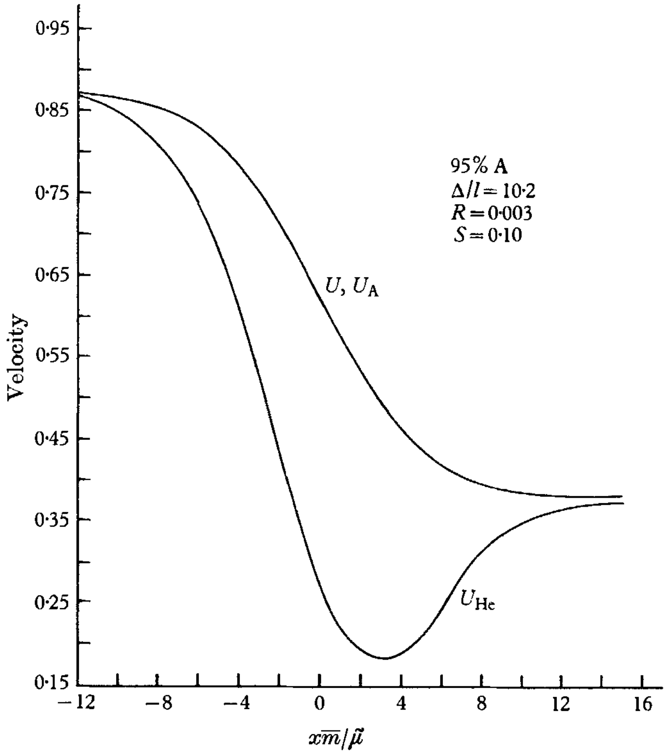

FIGURE 11. Velocity profiles for 95 % A–He mixture at $M_\infty^2 = 4·2$.

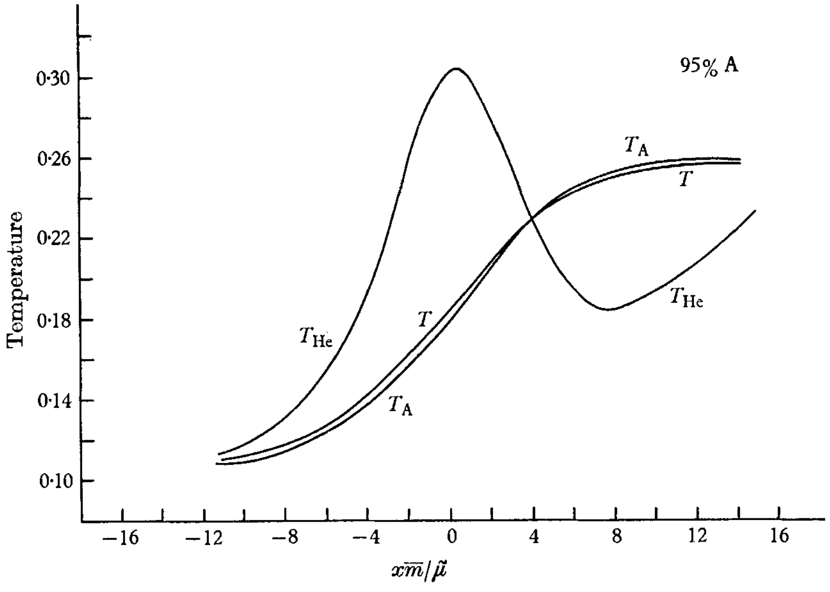

FIGURE 12. Temperature profiles for 95 % A–He mixture at $M_\infty^2 = 4·2$.

Enskog mixture equations violate the condition that $\epsilon_1 \gg 1$. We have in fact found cases for which the Chapman–Enskog mixture equations do not eliminate the velocity undershoot. Such a case is a 95 % Xe–He mixture and $M_0^2 = 3{\cdot}7$. Therefore, there seems to be no reason to doubt the appearance of a velocity undershoot under appropriate conditions.

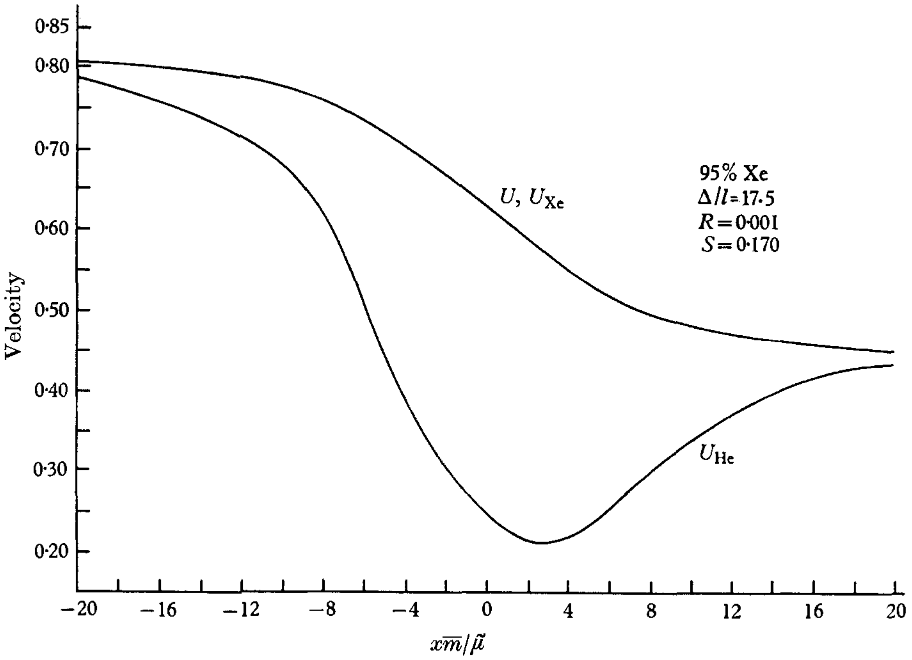

FIGURE 13. Velocity profiles for 95 % Xe–He mixture at $M_\infty^2 = 2{\cdot}5$.

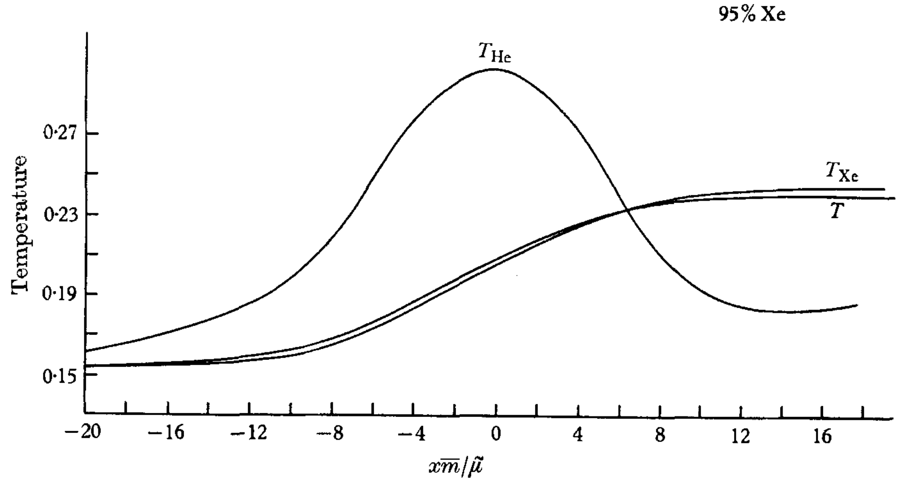

FIGURE 14. Temperature profiles for 95 % Xe–He mixture at $M_\infty^2 = 2{\cdot}5$.

The results presented in this paper were obtained in the course of research sponsored by the Office of Naval Research under Contract Nonr 562(39) with Brown University, Providence, Rhode Island. One of us (E.B.G.) is grateful for additional support from his present department.

Appendix A. Notation for transport coefficients

m_α	Molecular mass of the α-gas.
$\tilde{\mu}_\alpha$	The contribution of the α-gas to the viscosity. ($\tilde{\mu}_\alpha$ is not the viscosity of the α-gas alone.)
$\tilde{\mu} = \tilde{\mu}_\alpha + \tilde{\mu}_\beta$	The viscosity of the mixture.
$\tilde{\kappa}_\alpha$	The contribution of the α-gas to the heat conductivity. ($\tilde{\kappa}_\alpha$ is not the heat conductivity of the α-gas alone.)
$\tilde{\kappa} = \tilde{\kappa}_\alpha + \tilde{\kappa}_\beta$	The heat conduction coefficient of the mixture.
η	The thermal diffusion factor (dimensionless).
$\tilde{D}_{\alpha\beta}$	The diffusion coefficient.
$\lambda_T = \dfrac{2k\tilde{T}}{m_\alpha + m_\beta} \dfrac{1}{\tilde{D}_{\alpha\beta}}$	The relative temperature relaxation frequency.
$\lambda_U = \dfrac{\tilde{m}_T}{2m_{\alpha\beta}} \lambda_T$	The relative velocity relaxation frequency.

Explicit forms for $\tilde{\mu}_\alpha$, $\tilde{\kappa}_\alpha$, $\tilde{\mu}$, $\tilde{\kappa}$, $\tilde{D}_{\alpha\beta}$ are given in Goldman & Sirovich (1967). Due to their length these will not be repeated here.

The normalized coefficients and their leading terms are:

$$\mu = \frac{\tilde{\mu}_\alpha + \tilde{\mu}_\beta}{\tilde{\mu}_0} = 1 + O(\epsilon).$$

$$\mu_\alpha = \frac{\tilde{\mu}_\alpha}{\tilde{\mu}_0} = \frac{\tilde{\mu}_{\alpha 0}}{\tilde{\mu}_0} + O(\epsilon) = \mu_\alpha^0 + O(\epsilon).$$

$$\kappa = \frac{\tilde{\kappa}\tilde{m}_{T0}}{\tilde{\mu}_0 k} = \frac{\gamma}{(\gamma - 1) Pr_0} + O(\epsilon) = \kappa^0 + O(\epsilon).$$

Pr_0 denotes the upstream Prandtl number.

$$\kappa_\alpha = \frac{\tilde{\kappa}\tilde{m}_{T0}}{\tilde{\mu}_0 k} = \frac{\tilde{\kappa}_{\alpha 0}\tilde{m}_{T_0}}{\tilde{\mu}_0 k} + O(\epsilon) = \kappa_\alpha^0 + O(\epsilon).$$

$$\eta = \eta_0 + O(\epsilon).$$

$$\tau = \frac{\gamma}{\gamma - 1} n_{\alpha_0}(1 - n_{\alpha_0}) \left(\frac{m_\beta - m_\alpha}{\tilde{m}_{T_0}}\right) - \eta n_{\alpha 0}(1 - n_{\alpha 0}) m_{T0}.$$

$$D = \frac{\overline{m}^2 \tilde{D}_{\alpha\beta}}{\mathscr{P}\tilde{\mu}_0} = \frac{\overline{m}^2 \tilde{D}_{\alpha\beta}^0}{\mathscr{P}\tilde{\mu}_0} + O(\epsilon) = D^0 + O(\epsilon).$$

$$d_1 = \frac{\overline{m}}{\overline{m}_\beta} \frac{m_\beta}{\tilde{m}_{T_0}}.$$

$$d_2 = (m_\beta - m_\alpha)/\tilde{m}_{T_0}.$$

$$\Lambda = \frac{\mu_0 \lambda_T}{\mathscr{P}} = \frac{2\gamma}{(1 + \gamma)^2} \frac{\tilde{m}_{T_0}}{m_\alpha + m_\beta} \frac{1}{D^0} + O(\epsilon) = \Lambda^0 + O(\epsilon).$$

A related parameter is the modified Schmidt number C,

$$C = \frac{2\tilde{\mu}\tilde{m}_T}{(m_\alpha + m_\beta)\tilde{\rho}\tilde{D}_{\alpha\beta}} = C^0 + O(\epsilon) = \frac{2\gamma\tilde{m}_{T0}}{(m_\alpha + m_\beta) D^0(\gamma + 1)} + O(\epsilon).$$

The Schmidt number itself is

$$Sc = \frac{\tilde{\mu}}{\tilde{\rho}\tilde{D}_{\alpha\beta}} = Sc^0 + O(\epsilon)$$

and

$$D^0 = \frac{\gamma}{(\gamma+1)Sc^0}.$$

Appendix B

To facilitate comparison with the work of Dyakov (1954) and Sherman (1960) we briefly discuss some of the terminology found in these papers.

The governing equations adopted by Dyakov result from a macroscopic derivation of the mixture equations (Landau & Lifshitz 1959). Therefore, they are placed in a more general framework than the mixture equations of the Chapman–Enskog procedure. The equations of both theories, however, have the same form. Instead of individual mass densities, Dyakov considers the mass concentration†

$$c = \frac{\rho_\beta}{\rho}$$

and instead of velocity diffusion he considers the mass diffusion of the β-gas,

$$i = \rho_\beta(U_\beta - U).$$

Instead of (6) and (12) Dyakov uses

$$i = -\rho D_{\alpha\beta}\left[\frac{dc}{dx} + b\frac{dp}{dx} + \lambda\frac{dT}{dx}\right], \tag{B 1}$$

$$Q = \left[\lambda T\left(\frac{\partial\mu}{\partial c}\right)_{p,T} - T\left(\frac{\partial\mu}{\partial T}\right)_{c,p} + \mu\right] i - \kappa\frac{dT}{dx}, \tag{B 2}$$

with

$$b = \left(\frac{\partial\mu}{\partial p}\right)_{c,T} \bigg/ \left(\frac{\partial\mu}{\partial c}\right)_{p,T}.$$

μ denotes the chemical potential. One may show that for the gas considered in this paper

$$\mu = \frac{m_\alpha - m_\beta}{m_\alpha m_\beta} kT\left[\frac{\gamma}{\gamma-1} + \ln p - \frac{\gamma}{\gamma-1}\ln T - \frac{m_\alpha}{m_\alpha - m_\beta}\ln c + \frac{m_\beta}{m_\alpha - m_\beta}\ln(1-c) \right. \\ \left. + \ln\{m_\alpha c + m_\beta(1-c)\}\right]. \tag{B 3}$$

Other quantities of interest are the enthalpy, h, which in our case is

$$h = \frac{\gamma}{\gamma-1}\frac{p}{\rho} \tag{B 4}$$

and the entropy S, which in our case is

$$S = \left(\frac{c}{m_\beta} + \frac{1-c}{m_\alpha}\right)\left(\frac{k}{\gamma-1}\ln T - k\ln p\right) + k\left[\frac{m_\alpha}{m_\alpha - m_\beta}c\ln c + \frac{m_\beta}{m_\alpha - m_\beta}(1-c)\ln(1-c) \right. \\ \left. - \frac{m_\alpha c + m_\beta(1-c)}{m_\alpha - m_\beta}\ln\{m_\alpha c + m_\beta(1-c)\}\right]. \tag{B 5}$$

---

† In this appendix we drop the tildes which were used earlier to denote dimensional quantities.

We note in passing that (B 3), (B 4) and (B 5) satisfy the first law

$$dh = T\,dS + (1/\rho)\,dp + \mu\,dc.$$

Finally, we point out that the energy equation (10) is now

$$(d/dx)\{\rho U(h + \tfrac{1}{2}U^2) + (P - p)\,U + Q\} = 0 \tag{B 6}$$

and that instead of individual component mass conservation, one uses the equivalent

$$i = \rho U(c_0 - c).$$

Since Dyakov only considers a one-temperature theory, the temperature difference term does not appear in (B 1) and of course Dyakov does not consider a temperature difference equation, (7).

The equations used by Sherman (1960) are, with minor modifications, those obtained by the Chapman–Enskog procedure for gas mixtures (Chapman & Cowling 1939) and are therefore more closely related to our work. Sherman introduces the number density concentration

$$f = (n_\beta/n)$$

in terms of which the averaged mass is

$$m_T = f m_\beta + (1 - f)\,m_\alpha$$

(M instead of m_T and M_0 instead of m_{T_0} is used.)

He also uses the energy equation in the form given above, (B 6), and with h such that

$$\rho h = \rho_\alpha h_\alpha + \rho_\beta h_\beta = (\rho_\alpha C_{p\alpha} + \rho_\beta C_{p\beta})\,T$$

where the $C_{p\alpha}$ and $C_{p\beta}$ are the heat capacities of the corresponding components, Sherman defines

$$C_p = \frac{\rho_{\alpha 0} C_{p\alpha} + \rho_{\beta 0} C_{p\beta}}{\rho_0},$$

so that

$$\rho U h + \rho_\beta(u_\beta - u)\,(h_\beta - h_\alpha) = m C_p T.$$

For the gas studied by us

$$C_{p\alpha} = \frac{\gamma}{\gamma - 1}\frac{k}{m_\alpha},$$

so that

$$C_p = \frac{\gamma}{\gamma - 1}\frac{k}{m_{T_0}}.$$

For comparison purposes it is useful to observe that

$$\frac{m_{T_0}}{m_T} = \frac{1 + f_0(\theta - 1)}{1 + f(\theta - 1)},$$

where

$$\theta = m_\beta/m_\alpha.$$

Also Sherman's definition of the ratio of specific heats γ_s is

$$\gamma_s = \frac{C_p}{C_p - (k/m_{T_0})} = \gamma.$$

Finally the connexion between Sherman's shock parameter ϵ_s and ours is

$$\epsilon_s = \frac{2}{\gamma - 1}\,\epsilon.$$

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