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The spherical-droplet problem of evaporation and condensation in a vapour–gas mixture

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The behaviour of a binary mixture of a vapour and an inert gas around the spherical condensed-phase droplet is studied analytically using kinetic theory. By the singular-perturbation method, the linearized Boltzmann equation of B–G–K type is first solved for problems with spherical symmetry under the diffusive boundary condition when the Knudsen number of the problem is small. The macroscopic equations and the appropriate boundary conditions in the form of the temperature and partial-pressure jumps on the interface between the droplet and the gas phase, which enable us to treat the problems at the level of ordinary fluid dynamics, are derived together with the Knudsen-layer structure formed near the interface. Then the velocity, temperature and pressure fields around the droplet are explicitly obtained, as well as the mass, heat and energy flows from it. The results obtained are capable of describing the transition from the diffusion-control to the kinetic-control mechanism in the mass-transfer process. The negative-temperature-gradient phenomenon, a common phenomenon for pure-vapour cases (absence of inert gas), is also possible, manifesting itself more easily as the kinetic-control mechanism becomes prevalent and the critical condition for its existence is given. The present analysis could be applied to other problems with spherical symmetry as well.

1. Introduction

Evaporation and condensation processes occurring at the interface between a condensed phase and its vapour, regardless of whether or not an inert gas exists, involve a non-equilibrium region of the dimension of the molecular mean free path adjacent to the interface. Within this region, collisions between molecules are scarce, and the behaviour of the vapour may be considered to deviate significantly from that predicted or predictable by continuum theory under empirical adhesive (no-slip and jump) boundary conditions at the interface. In the absence of inert gas, a typical behaviour found by kinetic-theory analysis is that even in the continuum limit the temperature and pressure of a vapour at the interface are different from the temperature of the interface and the corresponding saturated-vapour pressure; actually they take larger or smaller values than the corresponding ones associated with the interface, depending upon whether a condensation or evaporation process is taking place (Pao 1971*a*, *b*; Siewert & Thomas 1973; Sone & Onishi 1973, 1978). These jumps are related uniquely to the rate of evaporation or condensation at the interface, providing the appropriate boundary conditions for the treatment of problems at the fluid-dynamics level. These jumps are also responsible for the existence of the negative-temperature-gradient phenomenon first noted by Pao (1971*a*) and later studied by various authors analytically (Thomas, Chang & Siewert 1974; Onishi 1977; Sone & Onishi 1978) and numerically (Matsushita 1976). The mass transfer in this case may be said to be controlled by the kinetic effect. The situation may, however, be quite different when an inert gas is present. For systems with small Knudsen numbers (molecular mean free path divided by the characteristic length), evaporation and condensation of the vapour will be affected by the molecular collisions between the component gases. Especially when the concentration of the inert gas is small, the inert gas molecules may be driven toward the condensing surface and away from the evaporating surface by the collisions with molecules of the vapour, forming a fairly large partial-pressure gradient, and consequently hindering the vapour mass flow. As the concentration increases, this hindrance effect due to the collisions may become large and eventually the vapour mass transfer against this effect will depend on its ability to diffuse through the inert gas or the diffusion coefficient of the mixture, which is a small quantity of the order of the Knudsen number of the system. The mass transfer, therefore, would be very small in this diffusion-control case, compared with that by the kinetic effect.

The estimation of the effect of inert gas on the mass transfer from a droplet of a vapour is of basic importance not only from the theoretical standpoint but also in various technological applications having a close relation to dehydration, combustion, dust removal, etc. (see Fuchs 1959). The present study is concerned mainly with this. Now consider the following steady problem: a spherical condensed-phase droplet of radius L is placed in an infinite expanse of a binary mixture of a vapour and an inert gas, say gas A and gas B respectively. At a great distance from the droplet, the temperature is T_∞ and the partial pressures are P^A_∞ and P^B_∞ respectively. The droplet is kept at a constant temperature T_W, at which the saturated-vapour number density is N^A_W and its pressure is P^A_W, where $P^A_W = N^A_W \mathrm{k} T_W$, k being the Boltzmann constant. It should be noted that the stipulation that the droplet's temperature is held constant and that the problem is steady is not unrealistic but is a good approximation to real physical systems in which weak evaporation or condensation is taking place around relatively large droplets (this is within the limits of the present analysis).

This problem was studied first by Maxwell in 1877 (see his scientific papers 1965) within the framework of continuum theory. Fuchs (1959) discusses the details of this theory and its extensions, citing various related references. The main defect of the continuum theory lies in the fact that it cannot describe at all the transition of mass transfer from diffusion control to kinetic control as the concentration of inert gas becomes smaller. The cause of this defect stems from the empirical (not kinetic-theory-based) boundary conditions taken at the interface of the droplet, which are not dependent on the concentration. The appropriate boundary conditions based on kinetic theory, however, are strongly dependent upon this concentration, and this dependence is crucial in describing the transition from diffusion-control to kinetic-control mass transfer (see §§4 and 6). A kinetic-theory approach, therefore, is needed for the proper description of the behaviour of component gases. Sampson & Springer (1969) treated the problem for the case $P^B_\infty \gg P^A_\infty$ by the application of Lees' moment method (Lees 1959; Lees & Liu 1962) to the Boltzmann equation, and obtained the mass flux, which becomes exactly coincident with Maxwell's result (see Fuchs 1959; Davies 1978) in the continuum limit. Shankar (1970) also studied the same problem based on the same method but for all concentrations, and obtained an expression for the mass flux which seems to describe fairly correctly the qualitative aspect of the transition from diffusion-control to kinetic-control mass transfer. His expression in the limit to continuum reduces to that of Maxwell with a correction factor $(P^A_\infty + P^B_\infty)/P^B_\infty$ due to the mass motion when diffusion control is prevailing, and the present analysis confirms this (see §6). There are, however, at least two drawbacks to the above work: one is that although the moment method may be quite effective in obtaining the gross quantities, e.g. the mass and heat transfers, it may fail to give accurately the local behaviour of the mixture and its component gases especially for small-Knudsen-number cases (the local behaviour is not given explicitly in the above work); the second is that the above authors assumed *a priori* that the temperatures of the component gases are the same at any point in the field, which is not valid within the Knudsen layer (see §4) and may affect the proper values of the temperature and partial-pressure jumps of the component gases and hence the mass and heat transfers. A more rigorous analysis is therefore required for this problem and for its understanding.

To carry out the present analysis, the following assumptions are made: (i) the behaviour of each component gas is governed by the Boltzmann equation of the B–G–K type proposed by Hamel (1965) (governing equation); (ii) gas molecules leaving the interface (of the condensed phase) have a Maxwellian velocity distribution characterized by its temperature T_{W} and velocity (zero here), the number density of gas A $N_{\mathrm{W}}^{\mathrm{A}}$ being given as the saturated-vapour number density at that temperature T_{W}, while that of gas B $N_{\mathrm{W}}^{\mathrm{B}}$ is determined by the condition of no net mass flow across the interface (kinetic boundary condition); (iii) at least one of the component gases is dense, and hence the mean free path of that component is small compared with the characteristic length of the problem, e.g. L (i.e. the Knudsen number $\mathbb{K} \leqslant 1$); and (iv) the deviation ϵ of the system from a stationary equilibrium reference state is small, and the governing Boltzmann equation and its kinetic boundary condition can be linearized about the reference state (i.e. ϵ^2 is neglected compared with $\mathbb{K}^N$ for any positive integer N). Since the analysis in the Knudsen layer is the most difficult and laborious part and furthermore has a universal nature, to some extent, regardless of the problems, it may be worthwhile to give the analysis in as general terms as possible so that it may be applicable to various other problems of spherical symmetry (applicable also to problems of axial symmetry with slight modification), and then proceed to the present concrete problem of the spherical droplet. By assuming that the concentration of inert gas has a moderate or large value, the actual analysis has been worked out to the second order of the Knudsen number in its expansion form, where the effect of curvature of the boundary first enters in the macroscopic jump conditions. As the concentration becomes smaller than a certain threshold value (see §6), however, the smallness of the concentration shifts some of the terms in the expansion to lower order (e.g. from the third order of the Knudsen number, which is neglected here, to its second order, and from second order to first order, etc.), invalidating the whole analysis. By reconsidering the expansion, or equivalently by reverting to the original unexpanded quantities, we could allow for this shifting in the analysis, obtaining a final result whose validity changes consistently from the second order of the Knudsen number to its first order as the concentration decreases and becomes eventually smaller than the threshold value.

2. Kinetic equations and the boundary conditions

For problems with spherical symmetry, the linearized version of the Boltzmann equation of B–G–K type (Hamel 1965) in the spherical coordinate system may be written for steady states as follows:

$$k\mathscr{D}[\varphi^{\mathrm{A}}] = -\varphi^{\mathrm{A}} + n^{\mathrm{A}} + 2\xi_r v^{\mathrm{A}} + (\xi^2 - \tfrac{3}{2})\,\tau^{\mathrm{A}} + 2\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}[\xi_r(v^{\mathrm{B}} - v^{\mathrm{A}}) + \mu_{\mathrm{A}}(\xi^2 - \tfrac{3}{2})(\tau^{\mathrm{B}} - \tau^{\mathrm{A}})], \quad (2.1)$$

$$\frac{M^{\frac{1}{2}}}{\alpha}k\mathscr{D}[\varphi^{\mathrm{B}}] = -\varphi^{\mathrm{B}}+n^{\mathrm{B}}+2M\xi_r v^{\mathrm{B}}+(M\xi^2-\tfrac{3}{2})\tau^{\mathrm{B}}$$

$$+2\mu_{\mathrm{A}}\frac{a_{21}}{a_{22}+a_{21}}[M\xi_r(v^{\mathrm{A}}-v^{\mathrm{B}})+\mu_{\mathrm{B}}(M\xi^2-\tfrac{3}{2})(\tau^{\mathrm{A}}-\tau^{\mathrm{B}})], \quad (2.2)$$

$$\begin{bmatrix} n^{\mathrm{A}} \\ v^{\mathrm{A}} \\ \tau^{\mathrm{A}} \end{bmatrix} = \int \begin{bmatrix} 1 \\ \xi_r \\ \frac{2}{3}\xi^2-1 \end{bmatrix} \varphi^{\mathrm{A}} E \,\mathrm{d}\boldsymbol{\xi} \quad (2.3)$$

$$\begin{bmatrix} n^{\mathrm{B}} \\ v^{\mathrm{B}} \\ \tau^{\mathrm{B}} \end{bmatrix} = \int \begin{bmatrix} 1 \\ \xi_r \\ \frac{2}{3}M\xi^2-1 \end{bmatrix} \varphi^{\mathrm{B}} \tilde{E} \,\mathrm{d}\boldsymbol{\xi}, \quad (2.4)$$

$$p^{\mathrm{A}} = n^{\mathrm{A}}+\tau^{\mathrm{A}}, \quad (2.5)$$

$$p^{\mathrm{B}} = n^{\mathrm{B}}+\tau^{\mathrm{B}}, \quad (2.6)$$

$$\mathscr{D}[\varphi^{\mathrm{S}}] \equiv \xi_r\frac{\partial\varphi^{\mathrm{S}}}{\partial r}+\frac{1}{r}\left\{(\xi^2-\xi_r^2)\frac{\partial\varphi^{\mathrm{S}}}{\partial\xi_r}+(\xi_\varphi^2\cot\theta-\xi_r\xi_\theta)\frac{\partial\varphi^{\mathrm{S}}}{\partial\xi_\theta}-(\xi_\theta\xi_\varphi\cot\theta+\xi_r\xi_\varphi)\frac{\partial\varphi^{\mathrm{S}}}{\partial\xi_\varphi}\right\},$$

$$E = \pi^{-\frac{3}{2}}\exp(-\xi^2), \quad \tilde{E} = \left(\frac{\pi}{M}\right)^{-\frac{3}{2}}\exp(-M\xi^2), \quad \xi^2 = \xi_r^2+\xi_\theta^2+\xi_\varphi^2, \quad \mathrm{d}\boldsymbol{\xi} = \mathrm{d}\xi_r\,\mathrm{d}\xi_\theta\,\mathrm{d}\xi_\varphi,$$

$$M = \frac{m_{\mathrm{B}}}{m_{\mathrm{A}}}, \quad \mu_{\mathrm{A}} = \frac{m_{\mathrm{A}}}{m_{\mathrm{A}}+m_{\mathrm{B}}}, \quad \mu_{\mathrm{B}} = \frac{m_{\mathrm{B}}}{m_{\mathrm{A}}+m_{\mathrm{B}}},$$

and

$$\left.\begin{aligned} k &= \frac{(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}}{(N_0^{\mathrm{A}}\kappa_{\mathrm{AA}}+N_0^{\mathrm{B}}\kappa_{\mathrm{AB}})L}, \quad a_{12} = \frac{N_0^{\mathrm{B}}\kappa_{\mathrm{AB}}}{N_0^{\mathrm{A}}\kappa_{\mathrm{AA}}}, \quad a_{21} = \frac{\kappa_{\mathrm{AB}}}{\kappa_{\mathrm{AA}}}, \\ a_{22} &= \frac{N_0^{\mathrm{B}}\kappa_{\mathrm{BB}}}{N_0^{\mathrm{A}}\kappa_{\mathrm{AA}}}, \quad \alpha = \frac{M^{\frac{1}{2}}(a_{22}+a_{21})}{1+a_{12}}, \end{aligned}\right\} \quad (2.7)$$

where (Lr, θ, φ) is the spherical coordinate system with its origin at the centre of the droplet, $\mathscr{D}$ the Boltzmann differential operator in this coordinate system (Kogan 1969), $N_0^{\mathrm{A}}(2R_{\mathrm{A}}T_0)^{-\frac{3}{2}}E(1+\varphi^{\mathrm{A}})$ and $N_0^{\mathrm{B}}(2R_{\mathrm{A}}T_0)^{-\frac{3}{2}}\tilde{E}(1+\varphi^{\mathrm{B}})$ the molecular-velocity-distribution functions of gas A and gas B respectively, $(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}(\xi_r, \xi_\theta, \xi_\varphi)$ the molecular-velocity vector, $(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}v^{\mathrm{S}}$ the r-component of the mean flow velocity V^{S}, $N_0^{\mathrm{S}}(1+n^{\mathrm{S}})$ the number density N^{S}, $T_0(1+\tau^{\mathrm{S}})$ the temperature T^{S}, $P_0^{\mathrm{S}}(1+p^{\mathrm{S}})$ the partial pressure $P^{\mathrm{S}}(=N^{\mathrm{S}}\mathrm{k}T^{\mathrm{S}})$, m_{A} and m_{B} the molecular masses of gas A and gas B respectively, and R_{A} the gas constant per unit mass of gas A. S appearing as superscript refers to A or B. Here L, T_0, N_0^{S} and $P_0^{\mathrm{S}}(=N_0^{\mathrm{S}}\mathrm{k}T_0)$ are taken, respectively, as a reference length, a reference temperature, a reference number density and a reference pressure of the problem. $N_0^{\mathrm{A}}\kappa_{\mathrm{AA}}$ and $N_0^{\mathrm{B}}\kappa_{\mathrm{AB}}$ represent respectively the number of collisions per unit time of a gas-A molecule with the other gas-A molecules and with gas-B molecules at the reference state, and thus $N_0^{\mathrm{A}}\kappa_{\mathrm{AA}}+N_0^{\mathrm{B}}\kappa_{\mathrm{AB}}$ is the average collision frequency for a gas-A molecule irrespective of its collision partners, being related to the mean free path l^{A} of gas-A molecules by $l^{\mathrm{A}} = (8R_{\mathrm{A}}T_0/\pi)^{\frac{1}{2}}/(N_0^{\mathrm{A}}\kappa_{\mathrm{AA}}+N_0^{\mathrm{B}}\kappa_{\mathrm{AB}})$. It therefore follows that k in (2.7) is equal to $k = (\frac{1}{2}\pi^{\frac{1}{2}})\,\mathbb{K}$, $\mathbb{K}$ $(=l^{\mathrm{A}}/L)$ being the Knudsen number at the reference state. Similarly, since $N_0^{\mathrm{A}}\kappa_{\mathrm{AB}}+N_0^{\mathrm{B}}\kappa_{\mathrm{BB}}$ is related to the mean free path l^{B} of gas-B molecules, we know that $\alpha = l^{\mathrm{A}}/l^{\mathrm{B}}$. κ_{AA}, κ_{BB} and $\kappa_{\mathrm{AB}}(=\kappa_{\mathrm{BA}})$, which are assumed to be constant, are associated with the transport coefficients of the mixture and of its component gases (Hamel 1965):

$$\left.\begin{aligned} \eta^{\mathrm{M}} &= \frac{P_0^{\mathrm{A}}}{N_0^{\mathrm{A}}\kappa_{\mathrm{AA}}+N_0^{\mathrm{B}}\kappa_{\mathrm{AB}}}+\frac{P_0^{\mathrm{B}}}{N_0^{\mathrm{A}}\kappa_{\mathrm{AB}}+N_0^{\mathrm{B}}\kappa_{\mathrm{BB}}} = \frac{\eta^{\mathrm{A}}}{1+a_{12}}+\frac{a_{22}\eta^{\mathrm{B}}}{a_{22}+a_{21}}, \\ D_{\mathrm{AB}} &= \frac{m_{\mathrm{A}}+m_{\mathrm{B}}\,\mathrm{k}T_0}{m_{\mathrm{A}}\,m_{\mathrm{B}}(N_0^{\mathrm{A}}+N_0^{\mathrm{B}})\,\kappa_{\mathrm{AB}}}, \end{aligned}\right\} \tag{2.8}$$

where η^{M} and D_{AB} are respectively the viscosity and diffusion coefficients of the mixture at the reference state, η^{A} and η^{B} being the viscosities of the component gases, defined by $\eta^{\mathrm{A}} = P_0^{\mathrm{A}}/(N_0^{\mathrm{A}}\kappa_{\mathrm{AA}})$ and $\eta^{\mathrm{B}} = P_0^{\mathrm{B}}/(N_0^{\mathrm{B}}\kappa_{\mathrm{BB}})$ (see e.g. Vincenti & Kruger 1965).

The kinetic boundary conditions for φ^{A} and φ^{B} on the interface (at $r = 1$) are given in the linearized form as

$$\varphi^{\mathrm{A}} = \varphi_{\mathrm{W}}^{\mathrm{A}} \equiv n_{\mathrm{W}}^{\mathrm{A}}+(\xi^2-\tfrac{3}{2})\,\tau_{\mathrm{W}}, \quad = p_{\mathrm{W}}^{\mathrm{A}}+(\xi^2-\tfrac{5}{2})\,\tau_{\mathrm{W}}, \quad \text{for } \xi_r > 0, \tag{2.9}$$

$$\varphi^{\mathrm{B}} = \varphi_{\mathrm{W}}^{\mathrm{B}} \equiv n_{\mathrm{W}}^{\mathrm{B}}+(M\xi^2-\tfrac{3}{2})\,\tau_{\mathrm{W}}, \quad = p_{\mathrm{W}}^{\mathrm{B}}+(M\xi^2-\tfrac{5}{2})\,\tau_{\mathrm{W}}, \quad \text{for } \xi_r > 0, \tag{2.10}$$

where $\tau_{\mathrm{W}} = (T_{\mathrm{W}}-T_0)/T_0$ is the perturbed temperature of the interface from the reference state, $n_{\mathrm{W}}^{\mathrm{S}} = (N_{\mathrm{W}}^{\mathrm{S}}-N_0^{\mathrm{S}})/N_0^{\mathrm{S}}$ and $p_{\mathrm{W}}^{\mathrm{S}} = (P_{\mathrm{W}}^{\mathrm{S}}-P_0^{\mathrm{S}})/P_0^{\mathrm{S}}$ are respectively the perturbed number density and pressure of the molecules of gas S leaving the surface after the interaction with it, and $p_{\mathrm{W}}^{\mathrm{S}} = n_{\mathrm{W}}^{\mathrm{S}}+\tau_{\mathrm{W}}$ since $P_{\mathrm{W}}^{\mathrm{S}} = N_{\mathrm{W}}^{\mathrm{S}}\,\mathrm{k}T_{\mathrm{W}}$ holds. $n_{\mathrm{W}}^{\mathrm{A}}$ (or $p_{\mathrm{W}}^{\mathrm{A}}$) is a unique function of τ_{W}, and its explicit functional form is obtained from the Clapeyron–Clausius relation (see e.g. Landau & Lifshitz 1969), while $n_{\mathrm{W}}^{\mathrm{B}}$ (or $p_{\mathrm{W}}^{\mathrm{B}}$) is as yet an unknown constant, to be determined as part of the solution from the no-net-mass-flow condition at the interface (at $r = 1$), i.e.

$$v^{\mathrm{B}} = \int \xi_r\,\varphi^{\mathrm{B}}\tilde{E}\,\mathrm{d}\boldsymbol{\xi} = 0 \quad \text{or} \quad n_{\mathrm{W}}^{\mathrm{B}} = -\tfrac{1}{2}\tau_{\mathrm{W}}-2(\pi M)^{\frac{1}{2}}\int_{\xi_r<0}\xi_r\,\varphi^{\mathrm{B}}\tilde{E}\,\mathrm{d}\boldsymbol{\xi}. \tag{2.11}$$

If N_0^{A} (or P_0^{A}) is chosen so as to be the saturated-vapour number density (or pressure) corresponding to T_0, we then have

$$n_{\mathrm{W}}^{\mathrm{A}} = (\gamma-1)\,\tau_{\mathrm{W}} \quad \text{or} \quad p_{\mathrm{W}}^{\mathrm{A}} = \gamma\tau_{\mathrm{W}}, \tag{2.12}$$

where $\gamma = h_L/(R_{\mathrm{A}}T_0)$, h_L being the latent heat of vapourization per unit mass of gas A (e.g. Onishi 1977).

Multiplying (2.1) by E, $\xi_r E$, and $(\xi^2-\frac{3}{2})\,E$ and integrating the resultant equations over the whole molecular-velocity space, we obtain the important and useful equations, known as transport equations, for gas A. In a similar manner, the corresponding equations for gas B are also obtained. They are:

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}(r^2v^{\mathrm{A}}) = 0, \tag{2.13a}$$

$$\frac{1}{r^3}\frac{\partial}{\partial r}\left(r^3\int\xi_r^2\,\varphi^{\mathrm{A}}\,E\,\mathrm{d}\boldsymbol{\xi}\right)-\frac{3}{2}\frac{p^{\mathrm{A}}}{r} = \frac{1}{k}\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}(v^{\mathrm{B}}-v^{\mathrm{A}}), \tag{2.13b}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\int\xi_r(\xi^2-\tfrac{3}{2})\,\varphi^{\mathrm{A}}E\,\mathrm{d}\boldsymbol{\xi}\right) = \frac{1}{k}3\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}(\tau^{\mathrm{B}}-\tau^{\mathrm{A}}), \tag{2.13c}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}(r^2v^{\mathrm{B}}) = 0, \tag{2.14a}$$

$$\frac{1}{r^3}\frac{\partial}{\partial r}\left(r^3\int M\xi_r^2\varphi^{\mathrm{B}}\tilde{E}\,\mathrm{d}\xi\right)-\frac{3}{2}\frac{p^{\mathrm{B}}}{r}=\frac{1}{k}\mu_{\mathrm{B}}\frac{a_{21}}{1+a_{12}}(v^{\mathrm{A}}-v^{\mathrm{B}}), \tag{2.14b}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\int \xi_r(M\xi^2-\tfrac{3}{2})\,\varphi^{\mathrm{B}}\tilde{E}\,\mathrm{d}\xi\right)=\frac{1}{k}3\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{21}}{1+a_{12}}(\tau^{\mathrm{A}}-\tau^{\mathrm{B}}). \tag{2.14c}$$

A direct consequence of (2.14*a*) and the condition (2.11) is that

$$v^{\mathrm{B}}(r)\equiv 0. \tag{2.15}$$

It may be preferable, and more natural for the description of the behaviour of the gas phase, to use the fluid-dynamic quantities associated with the mixture, the perturbed quantities of which are obtained from the relations

$$\left.\begin{aligned} v&=\frac{m_{\mathrm{A}}N_0^{\mathrm{A}}v^{\mathrm{A}}+m_{\mathrm{B}}N_0^{\mathrm{B}}v^{\mathrm{B}}}{\rho_0}, & n&=\frac{N_0^{\mathrm{A}}n^{\mathrm{A}}+N_0^{\mathrm{B}}n^{\mathrm{B}}}{N_0},\\ \tau&=\frac{N_0^{\mathrm{A}}\tau^{\mathrm{A}}+N_0^{\mathrm{B}}\tau^{\mathrm{B}}}{N_0}, & p&=\frac{N_0^{\mathrm{A}}p^{\mathrm{A}}+N_0^{\mathrm{B}}p^{\mathrm{B}}}{N_0},\end{aligned}\right\} \tag{2.16}$$

where $(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}v$, $N_0(1+n)$, $T_0(1+\tau)$ and $P_0(1+p)$ are respectively the *mean mass-flow* velocity, the number density, the temperature and the pressure of the mixture, and $\rho_0=m_{\mathrm{A}}N_0^{\mathrm{A}}+m_{\mathrm{B}}N_0^{\mathrm{B}}$, $N_0=N_0^{\mathrm{A}}+N_0^{\mathrm{B}}$ and $P_0=P_0^{\mathrm{A}}+P_0^{\mathrm{B}}$.

3. Derivation of macroscopic equations

Equations (2.1) and (2.2) involve two lengthscales L and l^{A} over which the solution may change. First we shall be concerned with the solution which varies over a length of the order of L, i.e. $\partial\varphi^{\mathrm{S}}/\partial r\sim O(\varphi^{\mathrm{S}})$. We call this part of solution the fluid-dynamic part or the Hilbert part (with suffix H attached), and try to find it in an expansion form in k:

$$\varphi^{\mathrm{S}}\equiv\varphi_{\mathrm{H}}^{\mathrm{S}}=\varphi_{\mathrm{H}0}^{\mathrm{S}}+k\varphi_{\mathrm{H}1}^{\mathrm{S}}+k^2\varphi_{\mathrm{H}2}^{\mathrm{S}}+\dots. \tag{3.1}$$

Substituting the expansion into the original equations, with (2.15) being taken into account, and equating like powers of k, we obtain for $m\geqslant 0$

$$\begin{aligned}\varphi_{\mathrm{H}m}^{\mathrm{A}}&=n_{\mathrm{H}m}^{\mathrm{A}}+2\xi_r v_{\mathrm{H}m}^{\mathrm{A}}+(\xi^2-\tfrac{3}{2})\,\tau_{\mathrm{H}m}^{\mathrm{A}}\\ &\quad+2\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}[-\xi_r v_{\mathrm{H}m}^{\mathrm{A}}+\mu_{\mathrm{A}}(\xi^2-\tfrac{3}{2})\,(\tau_{\mathrm{H}m}^{\mathrm{B}}-\tau_{\mathrm{H}m}^{\mathrm{A}})]-\mathscr{D}[\varphi_{\mathrm{H}m-1}^{\mathrm{A}}],\end{aligned} \tag{3.2}$$

$$\begin{aligned}\varphi_{\mathrm{H}m}^{\mathrm{B}}&=n_{\mathrm{H}m}^{\mathrm{B}}+(M\xi^2-\tfrac{3}{2})\,\tau_{\mathrm{H}m}^{\mathrm{B}}\\ &\quad+2\mu_{\mathrm{A}}\frac{a_{21}}{a_{22}+a_{21}}[M\xi_r v_{\mathrm{H}m}^{\mathrm{A}}+\mu_{\mathrm{B}}(M\xi^2-\tfrac{3}{2})\,(\tau_{\mathrm{H}m}^{\mathrm{A}}-\tau_{\mathrm{H}m}^{\mathrm{B}})]-\frac{M^{\frac{1}{2}}}{\alpha}\mathscr{D}[\varphi_{\mathrm{H}m-1}^{\mathrm{B}}],\end{aligned} \tag{3.3}$$

where n_{Hm}^{S}, $v_{\mathrm{H}m}^{\mathrm{S}}$ and $\tau_{\mathrm{H}m}^{\mathrm{S}}$ are defined by (2.3) and (2.4) with $\varphi^{\mathrm{S}}=\varphi_{\mathrm{H}m}^{\mathrm{S}}$, with the understanding that any quantity $f_{\mathrm{H}n}$ for $n<0$ becomes identically zero. Direct substitution of (3.2) and (3.3) into the transport equations (2.13) and (2.14) with φ^{S} replaced by $\varphi_{\mathrm{H}m}^{\mathrm{S}}$ leads us to the following set of equations to be satisfied by the fluid-dynamic quantities $p_{\mathrm{H}m}^{\mathrm{S}}$, $v_{\mathrm{H}m}^{\mathrm{A}}$ and $\tau_{\mathrm{H}m}^{\mathrm{S}}$ (with $m\geqslant 0$),

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}(r^2 v_{\mathrm{H}m}^{\mathrm{A}})=0,\quad v_{\mathrm{H}0}^{\mathrm{A}}=0,\quad \frac{\mathrm{d}p_{\mathrm{H}m}^{\mathrm{A}}}{\mathrm{d}r}=-2\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}v_{\mathrm{H}m+1}^{\mathrm{A}}, \tag{3.4a, b, c}$$

$$\frac{\mathrm{d}}{\mathrm{d}r}(a_{21}p_{\mathrm{H}m}^{\mathrm{A}}+a_{12}p_{\mathrm{H}m}^{\mathrm{B}})=0,\quad \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\tau_{\mathrm{H}m}^{\mathrm{A}}}{\mathrm{d}r}\right)=0,\quad \tau_{\mathrm{H}m}^{\mathrm{A}}=\tau_{\mathrm{H}m}^{\mathrm{B}}, \tag{3.4d, e, f}$$

which holds at least up to $m = 2$. Taking into account (3.4), we can now have the explicit expressions for $\varphi_{\mathrm{H}}^{\mathrm{A}}$ and $\varphi_{\mathrm{H}}^{\mathrm{B}}$ from (3.2) and (3.3). For example, for $\varphi_{\mathrm{H}m}^{\mathrm{A}}$

$$\varphi_{\mathrm{H}m}^{\mathrm{A}} = n_{\mathrm{H}m}^{\mathrm{A}} + 2\xi_r v_{\mathrm{H}m}^{\mathrm{A}} + (\xi^2 - \tfrac{3}{2})\,\tau_{\mathrm{H}m}^{\mathrm{A}} - \xi_r(\xi^2 - \tfrac{5}{2})\frac{\mathrm{d}\tau_{\mathrm{H}m-1}^{\mathrm{A}}}{\mathrm{d}r} - (3\xi_r^2 - \xi^2)\frac{\mathrm{d}v_{\mathrm{H}m-1}^{\mathrm{A}}}{\mathrm{d}r}$$
$$+ (\xi^2 - 3\xi_r^2)\,(\xi^2 - \tfrac{5}{2})\,\frac{1}{r}\frac{\mathrm{d}\tau_{\mathrm{H}m-2}^{\mathrm{A}}}{\mathrm{d}r} \quad (m = 0,\ 1,\ 2). \quad (3.5)$$

Comparing (3.5) and the corresponding expression for $\varphi_{\mathrm{H}m}^{\mathrm{B}}$ with (2.9) and (2.10), respectively we find that $\varphi_{\mathrm{H}0}^{\mathrm{S}}$ can satisfy the boundary condition if $p_{\mathrm{H}0}^{\mathrm{S}}$ and $\tau_{\mathrm{H}0}^{\mathrm{A}}$ are set equal to the corresponding boundary data on the interface ($r = 1$), i.e.

$$p_{\mathrm{H}0}^{\mathrm{A}} = p_{\mathrm{W}0}^{\mathrm{A}}, \quad \tau_{\mathrm{H}0}^{\mathrm{A}} = \tau_{\mathrm{W}0}, \quad p_{\mathrm{H}0}^{\mathrm{B}} = p_{\mathrm{W}0}^{\mathrm{B}}, \qquad (3.6a, b, c)$$

where $p_{\mathrm{W}0}^{\mathrm{S}}$ and $\tau_{\mathrm{W}0}$ are respectively the first terms in the following expansions of $p_{\mathrm{W}}^{\mathrm{S}}$ and τ_{W},

$$p_{\mathrm{W}}^{\mathrm{S}} = p_{\mathrm{W}0}^{\mathrm{S}} + kp_{\mathrm{W}1}^{\mathrm{S}} + k^2 p_{\mathrm{W}2}^{\mathrm{S}} + \dots, \quad \tau_{\mathrm{W}} = \tau_{\mathrm{W}0} + k\tau_{\mathrm{W}1} + k^2\tau_{\mathrm{W}2} + \dots. \qquad (3.7)$$

Conditions (3.6*a*) and (3.6*b*) now provide the boundary conditions for the system of equations (3.4) with $m = 0$ (continuum limit) at the interface. It may be noted, however, that (3.6*c*) does not specify the value for $p_{\mathrm{H}0}^{\mathrm{B}}$ at $r = 1$, but does determine $p_{\mathrm{W}0}^{\mathrm{B}}$ when the value of $p_{\mathrm{H}0}^{\mathrm{B}}$ has been known at $r = 1$, since $p_{\mathrm{W}}^{\mathrm{B}}$ is to be determined as part of the solution from (2.11) (no-net-mass-flow condition). It is clear, however, that $\varphi_{\mathrm{H}m}^{\mathrm{S}}$ with $m \geqslant 1$ cannot satisfy the boundary condition, and this situation is ascribed to the singular character of (2.1) and (2.2) for small values of k. Therefore, we need to reconsider the behaviour of the component gases in the close vicinity of the interface, and seek the solution satisfying the given boundary value at the interface and merging eventually into the one given by the fluid-dynamic part just discussed above (e.g. Sone 1969, 1971; Sone & Onishi 1978). This change of behaviour may be expected to occur over a small distance, of the order of the molecular mean free path, and hence is called rapidly changing behaviour (in contrast to the moderate one of the fluid-dynamic part). A small region where such behaviour occurs is called the Knudsen layer, the details of which will be discussed in the next section as a form of correction to the fluid-dynamic part.

Before proceeding to the Knudsen-layer analysis, we must examine the expansion of the solution in k. So far we have tacitly assumed that the concentration ratio $N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$ be of order unity. However, when it becomes small or large compared with $O(1)$, it may shift down or shift up terms of the expansion at a certain order of k to lower or higher order [because $a_{12} \sim O(N_0^{\mathrm{B}}/N_0^{\mathrm{A}})$, $a_{21} \sim O(1)$], which leads to complete destruction of the present expansion. Actually when $N_0^{\mathrm{B}}/N_0^{\mathrm{A}} \sim O(k)$, $\mathrm{d}p_{\mathrm{H}m}^{\mathrm{A}}/\mathrm{d}r$ must balance $v_{\mathrm{H}m}^{\mathrm{A}}$, not $v_{\mathrm{H}m+1}^{\mathrm{A}}$ as in (3.4*c*) ($v_{\mathrm{H}0}^{\mathrm{A}}$ becomes no longer zero). The solution in this case must be expanded in terms of two parameters, k and $N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$, or in terms of k with the magnitude of $N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$ relative to k being fully taken into account. However, in view of the fact that the original equations are linear and homogeneous, we do not have to re-expand the solution in the two parameters but have only to revert to the original unexpanded quantities. This is done by multiplying (3.4*a*), (3.4*d*) and (3.4*e*) by k^m and (3.4*c*) by k^{m+1} respectively, and then summing with respect to m. As a result of this, we obtain the following final set of macroscopic equations

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}p_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r}\right) = 0, \quad \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r}\right) = 0, \qquad (3.8a, b)$$

$$p_{\mathrm{H}} = \text{const.}, \quad v_{\mathrm{H}}^{\mathrm{A}} = -k\frac{1 + a_{12}}{2\mu_{\mathrm{B}}\,a_{12}}\frac{\mathrm{d}p_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r}, \qquad (3.8c, d)$$

and
$$p_{\mathrm{H}}^{\mathrm{B}} = -\frac{N_0^{\mathrm{A}}}{N_0^{\mathrm{B}}} p_{\mathrm{H}}^{\mathrm{A}} + \frac{N_0}{N_0^{\mathrm{B}}} p_{\mathrm{H}}, \quad \tau_{\mathrm{H}}^{\mathrm{B}} = \tau_{\mathrm{H}}^{\mathrm{A}}, \quad n_{\mathrm{H}}^{\mathrm{S}} = p_{\mathrm{H}}^{\mathrm{S}} - \tau_{\mathrm{H}}^{\mathrm{S}}, \tag{3.9}$$

which are valid up to $O(k^2)$ for practically all concentrations [$v_{\mathrm{H}}^{\mathrm{A}}$ up to $O(k^3)$ for moderate and large values of $N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$]. These equations are so arranged as to be of an appropriate form with respect to the boundary conditions for them at the interface, to be given later in the next section. Equation (3.8*d*) expresses that a vapour flows down its partial-pressure gradient when the concentration ratio is of order unity or larger, but this will not precisely be the case when the ratio becomes smaller and smaller, as will be seen in §6 (see also Onishi 1984). Note also that $\tau_{\mathrm{H}} = \tau_{\mathrm{H}}^{\mathrm{A}} = \tau_{\mathrm{H}}^{\mathrm{B}}$, at least up to the present stage of approximation.

It should be noted that the well-posedness of the system of differential equations is in general lost in the reduction such as the one from (3.4) to (3.8) when the system involves higher-order derivatives in its inhomogeneous terms (see e.g. Cercignani 1975; Sone 1984). The present linearized system of equations, however, is clearly not such a case.

4. Knudsen-layer analysis and macroscopic jump conditions

Now we shall consider the rapidly changing part of the solution within the Knudsen layer near the interface so that we can obtain the complete solution to the present boundary-value problem. This part of the solution is called the Knudsen-layer (correction) part, and will be sought in the form of a correction to the fluid-dynamic part, i.e.

$$f = f_{\mathrm{H}}(r) + f_{\mathrm{K}}(\eta) \quad \text{with} \quad \eta = \frac{r - r_*}{k}, \tag{4.1}$$

where f stands for any one of the perturbed quantities of interest, and the fluid-dynamic part f_{H} has already been worked out in §3. $r_*(\equiv 1)$ appearing in a stretched coordinate η is introduced to indicate explicitly the terms associated with the curvature of the interface. Since f_{K} has the nature of a correction to f_{H} within the Knudsen layer, we must demand that

$$f_{\mathrm{K}} \to 0 \quad \text{(sufficiently rapidly)} \quad \text{as } \eta \to \infty. \tag{4.2}$$

At this stage, we immediately find that $\mathrm{d}[(r_* + k\eta)^2 v_{\mathrm{K}}^{\mathrm{A}}]/\mathrm{d}\eta = 0$ from (2.13*a*), and the unique solution subject to (4.2) is

$$v_{\mathrm{K}}^{\mathrm{A}}(\eta) \equiv 0. \tag{4.3}$$

Now assuming again that $N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$ is of order unity, we also seek the Knudsen-layer-correction part in the expansion form in k,

$$f_{\mathrm{K}} = f_{\mathrm{K}0} + k f_{\mathrm{K}1} + k^2 f_{\mathrm{K}2} + \dots, \quad \text{with} \quad f_{\mathrm{K}0} \equiv 0. \tag{4.4}$$

The above expansion starts from $O(k)$, because, to order k^0, the fluid-dynamic part of the solution $f_{\mathrm{H}0}$ can satisfy the given boundary condition and therefore the Knudsen-layer-correction part of this order, $f_{\mathrm{K}0}$, does not exist.

Direct substitution of (4.1) with (4.3) and (4.4) into the original equations (2.1) and (2.2) yields the following equations for $\varphi_{\mathrm{K}m}^{\mathrm{S}}$ ($m = 1, 2, \dots$),

$$\xi_r \frac{\partial \varphi_{\mathrm{K}m}^{\mathrm{A}}}{\partial \eta} + \varphi_{\mathrm{K}m}^{\mathrm{A}} = n_{\mathrm{K}m}^{\mathrm{A}} + (\xi^2 - \tfrac{3}{2})\left(\tau_{\mathrm{K}m}^{\mathrm{A}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}} \frac{a_{12}}{1 + a_{12}} (\tau_{\mathrm{K}m}^{\mathrm{B}} - \tau_{\mathrm{K}m}^{\mathrm{A}})\right)$$
$$- \frac{1}{r_*} \sum_{l=0}^{m-1} (-1)^l \left(\frac{\eta}{r_*}\right)^l \mathscr{D}^*[\varphi_{\mathrm{K}m-l-1}^{\mathrm{A}}], \tag{4.5}$$

$$\frac{M^{\frac{1}{2}}}{\alpha}\xi_r\frac{\partial\varphi^{\mathrm{B}}_{\mathrm{K}m}}{\partial\eta}+\varphi^{\mathrm{B}}_{\mathrm{K}m} = n^{\mathrm{B}}_{\mathrm{K}m}+(M\xi^2-\tfrac{3}{2})\left(\tau^{\mathrm{B}}_{\mathrm{K}m}+2\mu_{\mathrm{A}}\,\mu_{\mathrm{B}}\frac{a_{21}}{a_{22}+a_{21}}(\tau^{\mathrm{A}}_{\mathrm{K}m}-\tau^{\mathrm{B}}_{\mathrm{K}m})\right)$$
$$-\frac{M^{\frac{1}{2}}}{\alpha}\frac{1}{r_*}\sum_{l=0}^{m-1}(-1)^l\left(\frac{\eta}{r_*}\right)^l\mathscr{D}^*[\varphi^{\mathrm{B}}_{\mathrm{K}m-l-1}], \qquad (4.6)$$

where $\mathscr{D}^*[\varphi^{\mathrm{S}}_{\mathrm{K}}] \equiv (\xi^2-\xi_r^2)\dfrac{\partial\varphi^{\mathrm{S}}_{\mathrm{K}}}{\partial\xi_r}+(\xi_\varphi^2\cot\theta-\xi_r\,\xi_\theta)\dfrac{\partial\varphi^{\mathrm{S}}_{\mathrm{K}}}{\partial\xi_\theta}-(\xi_\theta\,\xi_\varphi\cot\theta+\xi_r\,\xi_\varphi)\dfrac{\partial\varphi^{\mathrm{S}}_{\mathrm{K}}}{\partial\xi_\varphi}.$

Now the conditions at $\eta = 0$ for $\varphi^{\mathrm{S}}_{\mathrm{K}m}$ up to $m = 2$ become, for $\xi_r > 0$,

$$\varphi^{\mathrm{A}}_{\mathrm{K}m} = \varphi^{\mathrm{A}}_{\mathrm{W}m}-\varphi^{\mathrm{A}}_{\mathrm{H}m}$$
$$\equiv (p^{\mathrm{A}}_{\mathrm{W}m}-p^{\mathrm{A}}_{\mathrm{H}m})-2\xi_r\,v^{\mathrm{A}}_{\mathrm{H}m}+(\xi^2-\tfrac{5}{2})(\tau_{\mathrm{W}m}-\tau^{\mathrm{A}}_{\mathrm{H}m})+\xi_r(\xi^2-\tfrac{5}{2})\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}m-1}}{\mathrm{d}r}$$
$$+(3\xi_r^2-\xi^2)\frac{\mathrm{d}v^{\mathrm{A}}_{\mathrm{H}m-1}}{\mathrm{d}r}-(\xi^2-3\xi_r^2)(\xi^2-\tfrac{5}{2})\left(\frac{1}{r}\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}m-2}}{\mathrm{d}r}\right), \qquad (4.7)$$

$$\varphi^{\mathrm{B}}_{\mathrm{K}m} = \varphi^{\mathrm{B}}_{\mathrm{W}m}-\varphi^{\mathrm{B}}_{\mathrm{H}m}$$
$$\equiv (p^{\mathrm{B}}_{\mathrm{W}m}-p^{\mathrm{B}}_{\mathrm{H}m})+(M\xi^2-\tfrac{5}{2})(\tau_{\mathrm{W}m}-\tau^{\mathrm{A}}_{\mathrm{H}m})+\frac{M^{\frac{1}{2}}}{\alpha}\,\xi_r(M\xi^2-\tfrac{5}{2})\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}m-1}}{\mathrm{d}r}$$
$$-\frac{M}{\alpha^2}(\xi^2-3\xi_r^2)(M\xi^2-\tfrac{5}{2})\left(\frac{1}{r}\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}m-2}}{\mathrm{d}r}\right), \qquad (4.8)$$

with
$$p^{\mathrm{B}}_{\mathrm{W}m} = \tfrac{1}{2}\tau_{\mathrm{W}m}-2(\pi M)^{\frac{1}{2}}\int_{\xi_r<0}\xi_r(\varphi^{\mathrm{B}}_{\mathrm{H}m}+\varphi^{\mathrm{B}}_{\mathrm{K}m})\,\tilde{E}\,\mathrm{d}\boldsymbol{\xi}. \qquad (4.9)$$

Since equations (4.5) and (4.6) are one-dimensional ordinary differential equations with respect to η, we may be able to solve them for $\varphi^{\mathrm{S}}_{\mathrm{K}m}$ formally in terms of $n^{\mathrm{S}}_{\mathrm{K}m}$, $\tau^{\mathrm{S}}_{\mathrm{K}m}$ and $\varphi^{\mathrm{S}}_{\mathrm{K}l}$ $(l < m)$ subject to (4.2), (4.7) and (4.8). Elimination of $\varphi^{\mathrm{S}}_{\mathrm{K}m}$ by substitution of the resulting expressions for $\varphi^{\mathrm{S}}_{\mathrm{K}m}$ into (2.3) and (2.4) with $\varphi^{\mathrm{S}} = \varphi^{\mathrm{S}}_{\mathrm{K}m}$ gives rise to simultaneous linear integral equations for $n^{\mathrm{S}}_{\mathrm{K}m}$, $v^{\mathrm{S}}_{\mathrm{K}m}(\equiv 0)$ and $\tau^{\mathrm{S}}_{\mathrm{K}m}$. For $m = 1$, these integral equations are

$$\pi^{\frac{1}{2}}n^{\mathrm{A}}_{\mathrm{K}1} = \mathrm{L}_1\left[n^{\mathrm{A}}_{\mathrm{K}1},\tau^{\mathrm{A}}_{\mathrm{K}1}+2\mu_{\mathrm{A}}\,\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}(\tau^{\mathrm{B}}_{\mathrm{K}1}-\tau^{\mathrm{A}}_{\mathrm{K}1})\right]-(\tau^{\mathrm{A}}_{\mathrm{H}1}-\tau_{\mathrm{W}1})[J_2(\eta)-J_0(\eta)]$$
$$+v^{\mathrm{A}}_{\mathrm{H}1}[\pi^{\frac{1}{2}}J_0(\eta)-2J_1(\eta)]+\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}0}}{\mathrm{d}r}[J_3(\eta)-\tfrac{3}{2}J_1(\eta)], \qquad (4.10a)$$

$$\tfrac{3}{2}\pi^{\frac{1}{2}}\tau^{\mathrm{A}}_{\mathrm{K}1} = \mathrm{L}_2\left[n^{\mathrm{A}}_{\mathrm{K}1},\tau^{\mathrm{A}}_{\mathrm{K}1}+2\mu_{\mathrm{A}}\,\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}(\tau^{\mathrm{B}}_{\mathrm{K}1}-\tau^{\mathrm{A}}_{\mathrm{K}1})\right]-(\tau^{\mathrm{A}}_{\mathrm{H}1}-\tau_{\mathrm{W}1})[J_4(\eta)-\tfrac{3}{2}J_2(\eta)+\tfrac{3}{2}J_0(\eta)]$$
$$+v^{\mathrm{A}}_{\mathrm{H}1}\{\pi^{\frac{1}{2}}[J_2(\eta)-\tfrac{1}{2}J_0(\eta)]-2J_3(\eta)+J_1(\eta)\}+\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}0}}{\mathrm{d}r}[J_5(\eta)-2J_3(\eta)+\tfrac{7}{4}J_1(\eta)],$$
$$(4.10b)$$

$$\pi^{\frac{1}{2}}n^{\mathrm{B}}_{\mathrm{K}1} = \mathrm{L}_1\left[n^{\mathrm{B}}_{\mathrm{K}1},\tau^{\mathrm{B}}_{\mathrm{K}1}+2\mu_{\mathrm{A}}\,\mu_{\mathrm{B}}\frac{a_{21}}{a_{22}+a_{21}}(\tau^{\mathrm{A}}_{\mathrm{K}1}-\tau^{\mathrm{B}}_{\mathrm{K}1})\right]$$
$$-(\tau^{\mathrm{A}}_{\mathrm{H}1}-\tau_{\mathrm{W}1})[J_2(\zeta)-J_0(\zeta)]+\frac{1}{\alpha}\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}0}}{\mathrm{d}r}[J_3(\zeta)-\tfrac{3}{2}J_1(\zeta)], \qquad (4.10c)$$

$$\tfrac{3}{2}\pi^{\frac{1}{2}}\tau^{\mathrm{B}}_{\mathrm{K}1} = \mathrm{L}_2\left[n^{\mathrm{B}}_{\mathrm{K}1},\ \tau^{\mathrm{B}}_{\mathrm{K}1}+2\mu_{\mathrm{A}}\,\mu_{\mathrm{B}}\frac{a_{21}}{a_{22}+a_{21}}(\tau^{\mathrm{A}}_{\mathrm{K}1}-\tau^{\mathrm{B}}_{\mathrm{K}1})\right]$$
$$-(\tau^{\mathrm{A}}_{\mathrm{H}1}-\tau_{\mathrm{W}1})[J_4(\zeta)-\tfrac{3}{2}J_2(\zeta)+\tfrac{3}{2}J_0(\zeta)]+\frac{1}{\alpha}\frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H}0}}{\mathrm{d}r}[J_5(\zeta)-2J_3(\zeta)+\tfrac{7}{4}J_1(\zeta)],$$
$$(4.10d)$$

where $\zeta = \alpha\eta$, and

$$p^{\mathrm{A}}_{\mathrm{H1}} - p^{\mathrm{A}}_{\mathrm{W1}} = \tfrac{1}{2}(\tau^{\mathrm{A}}_{\mathrm{H1}} - \tau_{\mathrm{W1}}) - \pi^{\frac{1}{2}} v^{\mathrm{A}}_{\mathrm{H1}} - 2\mathscr{I}_1\left[n^{\mathrm{A}}_{\mathrm{K1}}, \tau^{\mathrm{A}}_{\mathrm{K1}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}(\tau^{\mathrm{B}}_{\mathrm{K1}} - \tau^{\mathrm{A}}_{\mathrm{K1}})\right], \tag{4.11a}$$

$$p^{\mathrm{B}}_{\mathrm{H1}} - p^{\mathrm{B}}_{\mathrm{W1}} = \tfrac{1}{2}(\tau^{\mathrm{A}}_{\mathrm{H1}} - \tau_{\mathrm{W1}}) - 2\mathscr{I}_1\left[n^{\mathrm{B}}_{\mathrm{K1}}, \tau^{\mathrm{B}}_{\mathrm{K1}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{21}}{a_{22}+a_{21}}(\tau^{\mathrm{A}}_{\mathrm{K1}} - \tau^{\mathrm{B}}_{\mathrm{K1}})\right]. \tag{4.11b}$$

The fluid-dynamic parts, which entered into the above equations through (4.7) and (4.8), are all evaluated at $r = r_*$ (or $\eta = 0$). L_1, L_2 and $\mathscr{I}_1$ are integral operators defined by

$$\mathrm{L}_1[n, \tau] = \int_0^\infty \{nJ_{-1}(|\eta-\eta_0|) + \tau[J_1(|\eta-\eta_0|) - \tfrac{1}{2}J_{-1}(|\eta-\eta_0|)]\}\,\mathrm{d}\eta_0 + 2J_0(\eta)\,\mathscr{I}_1[n, \tau], \tag{4.12a}$$

$$\begin{aligned}\mathrm{L}_2[n, \tau] = \int_0^\infty \{&n[J_1(|\eta-\eta_0|) - \tfrac{1}{2}J_{-1}(|\eta-\eta_0|)] + \tau[J_3(|\eta-\eta_0|)\\ &- J_1(|\eta-\eta_0|) + \tfrac{5}{4}J_{-1}(|\eta-\eta_0|)]\}\,\mathrm{d}\eta_0 + 2[J_2(\eta) - \tfrac{1}{2}J_0(\eta)]\,\mathscr{I}_1[n, \tau],\end{aligned} \tag{4.12b}$$

and

$$\mathscr{I}_1[n, \tau] = \int_0^\infty \{nJ_0(\eta_0) + \tau[J_2(\eta_0) - \tfrac{1}{2}J_0(\eta_0)]\}\,\mathrm{d}\eta_0, \tag{4.12c}$$

where J_n is the Abramowitz function (Abramowitz & Stegun 1970; Sone 1964)

$$J_n(\eta) = \int_0^\infty t^n \exp\left(-t^2 - \frac{\eta}{t}\right)\mathrm{d}t.$$

It should be understood that, when the integral operators are applied to (4.10*c*), (4.10*d*) and (4.11*b*), the argument η and the integral variable η_0 are replaced by ζ and ζ_0 respectively. Equations (4.11*a*) and (4.11*b*) are related to the integral equations for $v^{\mathrm{A}}_{\mathrm{K1}}$ and $v^{\mathrm{B}}_{\mathrm{K1}}$, which in the present case are identically zero, and are the consequences of these integral equations evaluated at $\eta = 0$ [(4.11*b*) can also be derived from (4.9)]. These two equations have been used in the derivation of the set of integral equations in (4.10). $\tau^{\mathrm{A}}_{\mathrm{H1}}$ (evaluated at $r = r_*$) is an as yet unknown constant to be determined simultaneously with the set of functions $n^{\mathrm{A}}_{\mathrm{K1}}$, $\tau^{\mathrm{A}}_{\mathrm{K1}}$, $n^{\mathrm{B}}_{\mathrm{K1}}$ and $\tau^{\mathrm{B}}_{\mathrm{K1}}$ (actually, $\tau^{\mathrm{A}}_{\mathrm{H1}}$ is so determined that these functions vanish as $\eta \to \infty$). It is noted that two types of small lengthscale over which the Knudsen-layer part varies are involved in the above integral equations: l^{A} and l^{B}, which lead to η and ζ respectively.

The set of solutions $[(\tau^{\mathrm{A}}_{\mathrm{H1}} - \tau_{\mathrm{W1}}), n^{\mathrm{A}}_{\mathrm{K1}}, \tau^{\mathrm{A}}_{\mathrm{K1}}, n^{\mathrm{B}}_{\mathrm{K1}}, \tau^{\mathrm{B}}_{\mathrm{K1}}]$ together with $(p^{\mathrm{A}}_{\mathrm{H1}} - p^{\mathrm{A}}_{\mathrm{W1}})$ and $(p^{\mathrm{B}}_{\mathrm{H1}} - p^{\mathrm{B}}_{\mathrm{W1}})$ may conveniently be expressed in the form

$$\begin{bmatrix} n^{\mathrm{A}}_{\mathrm{K1}} \\ \tau^{\mathrm{A}}_{\mathrm{K1}} \\ n^{\mathrm{B}}_{\mathrm{K1}} \\ \tau^{\mathrm{B}}_{\mathrm{K1}} \end{bmatrix} = v^{\mathrm{A}}_{\mathrm{H1}} \begin{bmatrix} \Omega^{\mathrm{A}}_4 \\ \Theta^{\mathrm{A}}_4 \\ \Omega^{\mathrm{B}}_4 \\ \Theta^{\mathrm{B}}_4 \end{bmatrix} + \frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H0}}}{\mathrm{d}r} \begin{bmatrix} \Omega^{\mathrm{A}}_1 \\ \Theta^{\mathrm{A}}_1 \\ \Omega^{\mathrm{B}}_1 \\ \Theta^{\mathrm{B}}_1 \end{bmatrix}, \tag{4.13}$$

$$\tau^{\mathrm{A}}_{\mathrm{H1}} - \tau_{\mathrm{W1}} = v^{\mathrm{A}}_{\mathrm{H1}} d^{\mathrm{M}}_4 + \frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H0}}}{\mathrm{d}r} d^{\mathrm{M}}_1, \tag{4.14}$$

and

$$p^{\mathrm{A}}_{\mathrm{H1}} - p^{\mathrm{A}}_{\mathrm{W1}} = v^{\mathrm{A}}_{\mathrm{H1}} C^{\mathrm{A}}_4 + \frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H0}}}{\mathrm{d}r} C^{\mathrm{A}}_1, \tag{4.15}$$

$$p^{\mathrm{B}}_{\mathrm{H1}} - p^{\mathrm{B}}_{\mathrm{W1}} = v^{\mathrm{A}}_{\mathrm{H1}} C^{\mathrm{B}}_4 + \frac{\mathrm{d}\tau^{\mathrm{A}}_{\mathrm{H0}}}{\mathrm{d}r} C^{\mathrm{B}}_1, \tag{4.16}$$

$m_{\mathrm{B}}/m_{\mathrm{A}}$	$N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$	$-d_4^{\mathrm{M}}$	d_1^{M}	d_6^{M}	d_7^{M}	d_5^{M}
0.5	0.1	0.37962	1.38491	0.27987	−0.09508	1.02943
	1.0	0.16248	1.64828	0.11843	−0.01526	1.45812
	10.0	0.02434	1.81344	0.01758	0.00024	1.76436
1.0	0.1	0.40614	1.30272	0.30031	−0.12103	0.91049
	1.0	0.22337	1.30272	0.16517	−0.06656	0.91050
	10.0	0.04061	1.30272	0.03003	−0.01208	0.91051
2.0	0.1	0.42243	1.28230	0.31287	−0.13147	0.88222
	1.0	0.28436	1.16551	0.21236	−0.10957	0.72909
	10.0	0.06718	0.97928	0.05070	−0.03350	0.51473

TABLE 1. $\kappa_{\mathrm{AA}} = \kappa_{\mathrm{BB}} = \kappa_{\mathrm{AB}}$

with

$$C_4^{\mathrm{A}} = \tfrac{1}{2}d_4^{\mathrm{M}} - \pi^{\frac{1}{2}} - 2\mathscr{I}_1\left[\Omega_4^{\mathrm{A}},\, \Theta_4^{\mathrm{A}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}(\Theta_4^{\mathrm{B}} - \Theta_4^{\mathrm{A}})\right],$$

$$C_4^{\mathrm{B}} = \tfrac{1}{2}d_4^{\mathrm{M}} - 2\mathscr{I}_1\left[\Omega_4^{\mathrm{B}},\, \Theta_4^{\mathrm{B}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{21}}{a_{22}+a_{21}}(\Theta_4^{\mathrm{A}} - \Theta_4^{\mathrm{B}})\right],$$

$$C_1^{\mathrm{A}} = \tfrac{1}{2}d_1^{\mathrm{M}} - 2\mathscr{I}_1\left[\Omega_1^{\mathrm{A}},\, \Theta_1^{\mathrm{A}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{12}}{1+a_{12}}(\Theta_1^{\mathrm{B}} - \Theta_1^{\mathrm{A}})\right],$$

$$C_1^{\mathrm{B}} = \tfrac{1}{2}d_1^{\mathrm{M}} - 2\mathscr{I}_1\left[\Omega_1^{\mathrm{B}},\, \Theta_1^{\mathrm{B}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}}\frac{a_{21}}{a_{22}+a_{21}}(\Theta_1^{\mathrm{A}} - \Theta_1^{\mathrm{B}})\right],$$

where Ω_i^{S} and Θ_i^{S} $(i = 4, 1)$ are rapidly decreasing functions of η, and d_i^{M} and C_i^{S} are constant, d_i^{M} being determined simultaneously with Ω_i^{S} and Θ_i^{S}. The set $[d_i^{\mathrm{M}}, \Omega_i^{\mathrm{A}}, \Theta_i^{\mathrm{A}}, \Omega_i^{\mathrm{B}}, \Theta_i^{\mathrm{B}}]$ of course satisfies the set of equations (4.10*a*)–(4.10*d*), with inhomogeneous terms proportional to $v_{\mathrm{H}1}^{\mathrm{A}}$ for $i = 4$ and to $\mathrm{d}\tau_{\mathrm{H}0}^{\mathrm{A}}/\mathrm{d}r$ for $i = 1$ in each equation of (4.10). These functions and constants depend only on the concentration ratio and the kind of substance of the two component gases, i.e.

$$\frac{m_{\mathrm{B}}}{m_{\mathrm{A}}},\quad \frac{N_0^{\mathrm{B}}}{N_0^{\mathrm{A}}},\quad \frac{\kappa_{\mathrm{AB}}}{\kappa_{\mathrm{AA}}},\quad \frac{\kappa_{\mathrm{BB}}}{\kappa_{\mathrm{AA}}}. \tag{4.17}$$

The solution $[d_i^{\mathrm{M}}, \Omega_i^{\mathrm{A}}, \Theta_i^{\mathrm{A}}, \Omega_i^{\mathrm{B}}, \Theta_i^{\mathrm{B}}]$ can be obtained fairly accurately by the refined-moment method of Sone & Onishi (1973) [see also Sone & Onishi 1978 for the correction of the misprints]. In applying the method, we have expressed each function in a series expansion in J_n of the following form

$$[\Omega_i^{\mathrm{A}}, \Theta_i^{\mathrm{A}}, \Omega_i^{\mathrm{B}}, \Theta_i^{\mathrm{B}}] = \sum_{n=0}^{N} [A_n, B_n, C_n, D_n]\, J_n(z) \tag{4.18}$$

with

$$z = \begin{cases} \eta & \text{for } \alpha > 1, \\ \alpha\eta & \text{for } \alpha < 1, \end{cases} \tag{4.19}$$

where A_n, B_n, C_n and D_n are constants which depend on the four parameters above. The convergence of the solutions with N was good and we could obtain the solutions correct to 5 or 6 significant figures for d_i^{M}, and to 4 or 5 significant figures for both the functions and C_i^{S}. Some numerical values of $(d_i^{\mathrm{M}}, C_i^{\mathrm{A}}, C_i^{\mathrm{B}})$ for $N = 13$ are listed in

m_B/m_A	N_0^B/N_0^A	$-C_4^A$	C_1^A	C_6^A	$-C_7^A$	C_5^A
0.5	0.1	2.12144	0.56943	0.81445	0.38900	0.70068
	1.0	2.08244	0.60929	0.79152	0.44144	0.83392
	10.0	2.05290	0.63892	0.77486	0.47976	0.92988
1.0	0.1	2.12412	0.55844	0.81631	0.38466	0.66303
	1.0	2.08851	0.55844	0.79585	0.43086	0.66304
	10.0	2.05289	0.55844	0.77539	0.47705	0.66305
2.0	0.1	2.12652	0.55444	0.81782	0.38152	0.65243
	1.0	2.09747	0.53318	0.80145	0.41948	0.59516
	10.0	2.05812	0.50384	0.77832	0.47218	0.51372

TABLE 2. $\kappa_{AA} = \kappa_{BB} = \kappa_{AB}$

m_B/m_A	N_0^B/N_0^A	$-C_4^B$	C_1^B	C_6^B	C_7^B	C_5^B
0.5	0.1	0.07444	0.71254	0.04500	0.13572	1.02732
	1.0	0.03482	0.75403	0.02059	0.06221	1.19018
	10.0	0.00556	0.78410	0.00323	0.00977	1.30475
1.0	0.1	0.07915	0.55844	0.04547	0.10261	0.66295
	1.0	0.04353	0.55844	0.02501	0.05643	0.66295
	10.0	0.00792	0.55844	0.00455	0.01025	0.66296
2.0	0.1	0.07856	0.45178	0.04323	0.07753	0.46474
	1.0	0.04924	0.43084	0.02763	0.04905	0.41682
	10.0	0.01053	0.40264	0.00605	0.01063	0.35026

TABLE 3. $\kappa_{AA} = \kappa_{BB} = \kappa_{AB}$

tables 1–3, and a graph of $(\Omega_i^A, \Theta_i^A, \Omega_i^B, \Theta_i^B)$ is shown in figure 1 for $M = 2.0$, $N_0^B/N_0^A = 0.1$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$. d_i^M and C_i^S may be called the jump coefficients of temperature and partial pressure respectively. Conditions (4.14) and (4.15) give the appropriate boundary conditions for the set of equations in (3.4) with $m = 1$ at the interface for a not so small concentration N_0^B/N_0^A. v_{H1}^A in these conditions may be replaced by $-[(1+a_{12})/(2\mu_B a_{12})]\,(\mathrm{d}p_{H0}^A/\mathrm{d}r)$, from (3.4c). Note that $[d_i^M, C_i^A, \Omega_i^A, \Theta_i^A, \Omega_i^B, \Theta_i^B]$ here corresponds to $[d_i, C_i, \Omega_i, \Theta_i]$ for the pure-vapour case (Sone & Onishi 1978, where the superscript $*$ is attached for $i = 4$), and in the limit $N_0^B/N_0^A \to 0$ $[d_i^M, C_i^A, \Omega_i^A, \Theta_i^A]$ becomes identical to $[d_i, C_i, \Omega_i, \Theta_i]$. In addition, Ω_i^B and Θ_i^B in this limit are not zero, but satisfy a set of integral equations of a different type having inhomogeneous terms involving d_i^M and Θ_i^A. It must be mentioned that exactly the same type of integral equations occurred at any order of k in the two-surface problem of evaporation and condensation studied by Onishi (1984), although the details are omitted there owing to the limited space. Some values of d_i^M and C_i^A ($= C_i^M$ in his notation) and the graphs of Ω_i^S and Θ_i^S are also found there (for $N = 9$).

Now we proceed to the next-order approximation in k ($m = 2$). We have actually obtained the integral equations for the set $[(\tau_{H2}^A - \tau_{W2}), n_{K2}^A, \tau_{K2}^A, n_{K2}^B, \tau_{K2}^B]$ and the two expressions determining $(p_{H2}^A - p_{W2}^A)$ and $(p_{H2}^B - p_{W2}^B)$ respectively. This set of integral equations is extremely complex in that, although the homogeneous parts are exactly the same as in (4.10), the inhomogeneous parts involve various types of integrals of the functions $(\Omega_i^A, \Theta_i^A, \Omega_i^B, \Theta_i^B)$ studied earlier in addition to simple J_n functions. Therefore, we have to omit these equations, jumping directly to their solutions. As was done for the first-order approximation ($m = 1$), the present

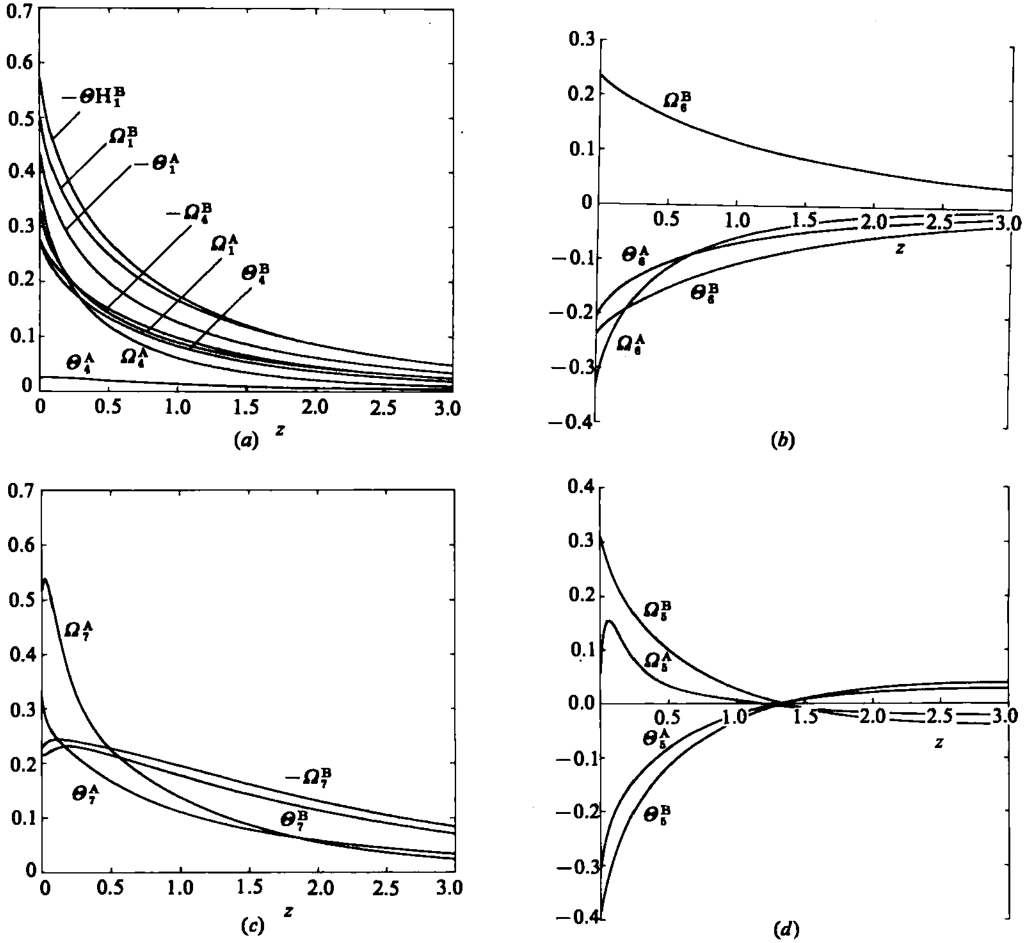

FIGURE 1. Knudsen-layer-correction functions. $m_B/m_A = 2.0$, $N_0^B/N_0^A = 0.1$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$. (*a*) Ω_i^A, Θ_i^A, Ω_i^B, Θ_i^B $(i = 4, 1)$ versus z. (*b*) Ω_6^A, Θ_6^A, Ω_6^B, Θ_6^B versus z. (*c*) Ω_7^A, Θ_7^A, Ω_7^B, Θ_7^B versus z. (*d*) Ω_5^A, Θ_5^A, Ω_5^B, Θ_5^B versus z.

solutions are decomposed as

$$\begin{bmatrix} n_{K2}^A \\ \tau_{K2}^A \\ n_{K2}^B \\ \tau_{K2}^B \end{bmatrix} = v_{H2}^A \begin{bmatrix} \Omega_4^A \\ \Theta_4^A \\ \Omega_4^B \\ \Theta_4^B \end{bmatrix} + \frac{d\tau_{H1}^A}{dr} \begin{bmatrix} \Omega_1^A \\ \Theta_1^A \\ \Omega_1^B \\ \Theta_1^B \end{bmatrix} + 2\frac{dv_{H1}^A}{dr} \begin{bmatrix} \Omega_6^A \\ \Theta_6^A \\ \Omega_6^B \\ \Theta_6^B \end{bmatrix} - \frac{2}{r_*} v_{H1}^A \begin{bmatrix} \Omega_7^A \\ \Theta_7^A \\ \Omega_7^B \\ \Theta_7^B \end{bmatrix} + \frac{2}{r_*}\frac{d\tau_{H0}^A}{dr} \begin{bmatrix} \Omega_5^A \\ \Theta_5^A \\ \Omega_5^B \\ \Theta_5^B \end{bmatrix}, \tag{4.20}$$

$$\tau_{H2}^A - \tau_{W2} = v_{H2}^A d_4^M + \frac{d\tau_{H1}^A}{dr} d_1^M + 2\frac{dv_{H1}^A}{dr} d_6^M - \frac{2}{r_*} v_{H1}^A d_7^M + \frac{2}{r_*}\frac{d\tau_{H0}^A}{dr} d_5^M, \tag{4.21}$$

and

$$p_{H2}^A - p_{W2}^A = v_{H2}^A C_4^A + \frac{d\tau_{H1}^A}{dr} C_1^A + 2\frac{dv_{H1}^A}{dr} C_6^A - \frac{2}{r_*} v_{H1}^A C_7^A + \frac{2}{r_*}\frac{d\tau_{H0}^A}{dr} C_5^A, \tag{4.22}$$

$$p_{H2}^B - p_{W2}^B = v_{H2}^A C_4^B + \frac{d\tau_{H1}^A}{dr} C_1^B + 2\frac{dv_{H1}^A}{dr} C_6^B - \frac{2}{r_*} v_{H1}^A C_7^B + \frac{2}{r_*}\frac{d\tau_{H0}^A}{dr} C_5^B, \tag{4.23}$$

where C_i^{S} ($i = 5, 6, 7$) are constants to be determined by the present set of solutions (d_i^{M}, Ω_i^{A}, Θ_i^{A}, Ω_i^{B}, Θ_i^{B}) ($i = 5, 6, 7$) together with the solutions studied at the first-order approximation.

We could obtain a solution for [d_6^{M}, C_6^{A}, C_6^{B}, Ω_6^{A}, Θ_6^{A}, Ω_6^{B}, Θ_6^{B}] as accurate as those studied earlier. For the remaining two sets, the convergence was not so good because of the complex structure of the inhomogeneous terms involving integrals of the solutions in the previous stage of approximation. However, as far as the temperature-jump coefficients d_i^{M} ($i = 7, 5$) are concerned, 3 significant figures are reliable. We have also listed some of the numerical values of ($d_i^{\mathrm{M}}, C_i^{\mathrm{A}}, C_i^{\mathrm{B}}$) ($i = 6, 7, 5$) in tables 1–3 and plotted the Knudsen-layer-correction functions [Ω_i^{A}, Θ_i^{A}, Ω_i^{B}, Θ_i^{B}] ($i = 6, 7, 5$) in figure 1. The appropriate boundary conditions for (3.4) with $m = 2$ are now given by (4.21) and (4.22) for not so small $N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$. It may be noted that the decomposition in (4.20)–(4.23) is not unique; actually the term proportional to $\mathrm{d}v_{\mathrm{H1}}^{\mathrm{A}}/\mathrm{d}r$ can be incorporated in the term $v_{\mathrm{H1}}^{\mathrm{A}}/r_*$ through (3.4*a*). However, we leave it as it is because it corresponds to [d_6, C_6, Ω_6, Θ_6] for the pure-vapour case (Sone & Onishi 1978). In addition, [d_7^{M}, C_7^{A}, Ω_7^{A}, Θ_7^{A}, Ω_7^{B}, Θ_7^{B}] corresponds to [d_7, C_7, Ω_7, Θ_7] for the pure-vapour case studied by the same authors, and [d_5^{M}, Ω_5^{A}, Θ_5^{A}, Ω_5^{B}, Θ_5^{B}] to [d_5, Ω_5, Θ_5] for the heat-conduction problem of a single gas (Sone & Onishi 1977; Onishi 1979).

Now multiplying (3.6) by k^0, (4.13)–(4.16) by k and (4.20)–(4.23) by k^2, and then summing, we finally obtain the appropriate boundary conditions for the macroscopic equations in (3.8) at the interface and the Knudsen-layer corrections near it. Some rearrangements of these expressions then give as the boundary conditions appropriate for (3.8*a*) and (3.8*b*):

$$\begin{bmatrix} p_{\mathrm{H}}^{\mathrm{A}} - p_{\mathrm{W}}^{\mathrm{A}} \\ \tau_{\mathrm{H}}^{\mathrm{A}} - \tau_{\mathrm{W}} \end{bmatrix} = v_{\mathrm{H}}^{\mathrm{A}} \begin{bmatrix} C_4^{\mathrm{A}} \\ d_4^{\mathrm{M}} \end{bmatrix} + k \frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} \begin{bmatrix} C_1^{\mathrm{A}} \\ d_1^{\mathrm{M}} \end{bmatrix} + 2k \frac{\mathrm{d}v_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} \begin{bmatrix} C_6^{\mathrm{A}} \\ d_6^{\mathrm{M}} \end{bmatrix} - k \frac{2}{r_*} v_{\mathrm{H}}^{\mathrm{A}} \begin{bmatrix} C_7^{\mathrm{A}} \\ d_7^{\mathrm{M}} \end{bmatrix} + k^2 \frac{2}{r_*} \frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} \begin{bmatrix} C_5^{\mathrm{A}} \\ d_5^{\mathrm{M}} \end{bmatrix} \tag{4.24}$$

at the interface ($r = r_* \equiv 1$), and as the Knudsen-layer corrections

$$\begin{bmatrix} n_{\mathrm{K}}^{\mathrm{A}} \\ \tau_{\mathrm{K}}^{\mathrm{A}} \\ p_{\mathrm{K}}^{\mathrm{A}} \\ n_{\mathrm{K}}^{\mathrm{B}} \\ \tau_{\mathrm{K}}^{\mathrm{B}} \\ p_{\mathrm{K}}^{\mathrm{B}} \end{bmatrix} = v_{\mathrm{H}}^{\mathrm{A}} \begin{bmatrix} \Omega_4^{\mathrm{A}} \\ \Theta_4^{\mathrm{A}} \\ \Pi_4^{\mathrm{A}} \\ \Omega_4^{\mathrm{B}} \\ \Theta_4^{\mathrm{B}} \\ \Pi_4^{\mathrm{B}} \end{bmatrix} + k \frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} \begin{bmatrix} \Omega_1^{\mathrm{A}} \\ \Theta_1^{\mathrm{A}} \\ \Pi_1^{\mathrm{A}} \\ \Omega_1^{\mathrm{B}} \\ \Theta_1^{\mathrm{B}} \\ \Pi_1^{\mathrm{B}} \end{bmatrix} + 2k \frac{\mathrm{d}v_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} \begin{bmatrix} \Omega_6^{\mathrm{A}} \\ \Theta_6^{\mathrm{A}} \\ \Pi_6^{\mathrm{A}} \\ \Omega_6^{\mathrm{B}} \\ \Theta_6^{\mathrm{B}} \\ \Pi_6^{\mathrm{B}} \end{bmatrix} - k \frac{2}{r_*} v_{\mathrm{H}}^{\mathrm{A}} \begin{bmatrix} \Omega_7^{\mathrm{A}} \\ \Theta_7^{\mathrm{A}} \\ \Pi_7^{\mathrm{A}} \\ \Omega_7^{\mathrm{B}} \\ \Theta_7^{\mathrm{B}} \\ \Pi_7^{\mathrm{B}} \end{bmatrix} + k^2 \frac{2}{r_*} \frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} \begin{bmatrix} \Omega_5^{\mathrm{A}} \\ \Theta_5^{\mathrm{A}} \\ \Pi_5^{\mathrm{A}} \\ \Omega_5^{\mathrm{B}} \\ \Theta_5^{\mathrm{B}} \\ \Pi_5^{\mathrm{B}} \end{bmatrix}, \tag{4.25}$$

near the interface, where $p_{\mathrm{K}}^{\mathrm{S}} (= n_{\mathrm{K}}^{\mathrm{S}} + \tau_{\mathrm{K}}^{\mathrm{S}})$ has been included for possible later use, and $\Pi_i^{\mathrm{S}} = \Omega_i^{\mathrm{S}} + \Theta_i^{\mathrm{S}}$ ($i = 4, 1, 6, 7, 5$). The partial pressure $p_{\mathrm{W}}^{\mathrm{B}}$ due to the molecules of gas B reflected from the interface is to be determined from the condition

$$p_{\mathrm{W}}^{\mathrm{B}} = p_{\mathrm{H}}^{\mathrm{B}} - v_{\mathrm{H}}^{\mathrm{A}} C_4^{\mathrm{B}} - k \frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} C_1^{\mathrm{B}} - 2k \frac{\mathrm{d}v_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} C_6^{\mathrm{B}} + k \frac{2}{r_*} v_{\mathrm{H}}^{\mathrm{A}} C_7^{\mathrm{B}} - k^2 \frac{2}{r_*} \frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r} C_5^{\mathrm{B}}, \tag{4.26}$$

after the fluid-dynamic part of the solutions has been found. It is noted that $v_{\mathrm{H}}^{\mathrm{A}}$ in (4.24)–(4.26) may be replaced by $-k[(1+a_{12})/(2\mu_{\mathrm{B}} a_{12})]\,(\mathrm{d}p_{\mathrm{H}}^{\mathrm{A}}/\mathrm{d}r)|_{r=1}$ from (3.8*d*). When the concentration ratio $N_0^{\mathrm{B}}/N_0^{\mathrm{A}}$ becomes small, smaller than $O(k)$, the above expressions become no longer valid up to order k^2, because terms of order k^3 associated with higher-order derivatives of $v_{\mathrm{H}}^{\mathrm{A}}$, which were neglected in the present analysis, may come up to order k^2. In this case, the temperature and partial-pressure jumps and the Knudsen-layer structures appear at order k^0 (continuum limit) (cf. (3.6) and (4.4)). In the limit $N_0^{\mathrm{B}}/N_0^{\mathrm{A}} \to 0$, the above expressions coincide exactly with the results for spherically symmetric cases derived from the general theory for the pure-vapour case (Sone & Onishi 1978).

So far we have derived the set of the macroscopic equations (3.8) and (3.9) and the appropriate boundary conditions (4.24) (see (5.6) for the continuity condition of energy flow across the interface, if required) together with the Knudsen-layer corrections (4.25) from the kinetic-theory analysis.

5. Heat and energy fluxes

In addition to the results in §3 and §4, it will become necessary to have available the formulas for the heat and energy fluxes. Let $q^{\mathrm{S}} = P_0^{\mathrm{S}}(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}Q^{\mathrm{S}}$ and $q = P_0(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}Q$ be the heat fluxes for component-S gas and for the mixture respectively. Then Q^{A}, Q^{B} and Q are defined as

$$Q^{\mathrm{A}} = \int \xi_r(\xi^2-\tfrac{5}{2})\varphi^{\mathrm{A}} E\,\mathrm{d}\boldsymbol{\xi}, \quad Q^{\mathrm{B}} = \int \xi_r(M\xi^2-\tfrac{5}{2})\varphi^{\mathrm{B}} \tilde{E}\,\mathrm{d}\boldsymbol{\xi}, \quad Q = \frac{N_0^{\mathrm{A}}}{N_0}Q^{\mathrm{A}} + \frac{N_0^{\mathrm{B}}}{N_0}Q^{\mathrm{B}}. \tag{5.1}$$

The fluid-dynamic parts of Q^{A} and Q^{B} are derived from the application of (3.2) and (3.3) to the above definitions with $\varphi^{\mathrm{S}} = \varphi_{\mathrm{H}m}^{\mathrm{S}}$. Summing all the contributions, we obtain for $Q_{\mathrm{H}}^{\mathrm{A}}$ and $Q_{\mathrm{H}}^{\mathrm{B}}$, and then for Q_{H}:

$$Q_{\mathrm{H}}^{\mathrm{A}} = -\tfrac{5}{4}k\frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r}, \quad Q_{\mathrm{H}}^{\mathrm{B}} = -\tfrac{5}{4}k\frac{1}{\alpha M^{\frac{1}{2}}}\frac{\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}}{\mathrm{d}r}, \tag{5.2}$$

$$Q_{\mathrm{H}} = -\tfrac{5}{4}k\left(\frac{N_0^{\mathrm{A}}}{N_0}+\frac{N_0^{\mathrm{B}}}{N_0}\frac{1}{\alpha M^{\frac{1}{2}}}\right)\frac{\mathrm{d}\tau_{\mathrm{H}}}{\mathrm{d}r} = -\frac{T_0}{L}\frac{\lambda^{\mathrm{M}}}{P_0(2R_A T_0)^{\frac{1}{2}}}\frac{\mathrm{d}\tau_{\mathrm{H}}}{\mathrm{d}r}, \tag{5.3}$$

which are all valid up to $O(k^3)$, where λ^{M} is the thermal conductivity of the mixture. Note that the above formulas are simply the Fourier formulas for heat conduction. The Knudsen-layer-correction parts, on the other hand, can be calculated with the use of (2.13*c*) and (2.14*c*) with $\varphi^{\mathrm{S}} = \varphi_{\mathrm{K}}^{\mathrm{S}}$, and here is listed only Q_{K}, the heat flux for the mixture,

$$Q_{\mathrm{K}1} = 0, \quad Q_{\mathrm{K}2} = 0, \quad Q_{\mathrm{K}3} = 0, \quad \dots . \tag{5.4}$$

With these quantities, the energy fluxes are readily obtained as

$$H^{\mathrm{S}} = Q^{\mathrm{S}} + \tfrac{5}{2}v^{\mathrm{S}}, \quad H = \frac{N_0^{\mathrm{A}}}{N_0}H^{\mathrm{A}} + \frac{N_0^{\mathrm{B}}}{N_0}H^{\mathrm{B}} = Q + \frac{5}{2}\frac{N_0^{\mathrm{A}}}{N_0}v^{\mathrm{A}}, \tag{5.5}$$

where $h^{\mathrm{S}} = P_0^{\mathrm{S}}(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}H^{\mathrm{S}}$ represents the energy flux for component-S gas, and $h = P_0(2R_{\mathrm{A}}T_0)^{\frac{1}{2}}H$ for the mixture.

Incidentally, we note that the condition of continuity of energy flow across the interface is expressed as

$$-\tfrac{5}{4}k\left[\frac{N_0^{\mathrm{A}}}{N_0}+\frac{N_0^{\mathrm{B}}}{N_0}\frac{1}{\alpha M^{\frac{1}{2}}}\right]\left[\frac{\lambda^{\mathrm{C}}}{\lambda^{\mathrm{M}}}\frac{\mathrm{d}\tilde{\tau}}{\mathrm{d}r}-\frac{\mathrm{d}\tau_{\mathrm{H}}}{\mathrm{d}r}\right] = \frac{N_0^{\mathrm{A}}}{N_0}\gamma v^{\mathrm{A}} = \frac{\rho_0}{m_{\mathrm{A}}N_0}\gamma v, \quad \text{at } r = r_*(\equiv 1), \tag{5.6}$$

where $\tilde{T} = T_0(1+\tilde{\tau})$ denotes the temperature field inside the condensed phase and λ^{C} its thermal conductivity. In some problems, when the temperature of the condensed phase cannot be considered constant but a function of r, the above condition should be supplemented in the analysis in addition to (4.24). Note that $h_L = \gamma R_A T_0$ is the difference between the enthalpy $\frac{5}{2}R_A T_0$ (per unit mass) in the vapour phase and that in the condensed phase.

6. Results for the droplet problem

We now consider the spherical-droplet problem posed in the introduction, and find explicitly the velocity, temperature, pressure and number-density fields. Let the state at infinity be taken as the reference state. Then

$$T_0 = T_\infty, \quad P_0^S = P_\infty^S, \quad N_0^S = N_\infty^S, \tag{6.1}$$

where $N_\infty^S = P_\infty^S/(kT_\infty)$. With this choice, the conditions at infinity now become

$$p^A \to 0, \quad \tau^A \to 0, \quad p \to 0, \quad \text{as } r \to \infty, \tag{6.2}$$

which supplement the boundary conditions (4.24) at $r = 1$. The fluid-dynamic part subject to (4.24) and (6.2) is immediately obtained from (3.8) as

$$p_H^A = \frac{F}{r} p_W^A, \quad \tau_H^A = \frac{G}{r}\tau_W, \quad p_H = 0, \quad v_H^A = k\Lambda \frac{F}{r^2} p_W^A, \tag{6.3}$$

other relevant quantities being given from (3.9) and (2.16), where $\Lambda = (1+a_{12})/(2\mu_B a_{12})$, and F and G satisfy the following relations

$$\begin{bmatrix} F-1 \\ G-1 \end{bmatrix} = -k\Lambda F \begin{bmatrix} S_1 \\ S_3 \end{bmatrix} - kG \begin{bmatrix} S_2 \\ S_4 \end{bmatrix}, \tag{6.4}$$

with

$$S_1 = -C_4^A + 2k(2C_6^A + C_7^A), \qquad S_2 = \frac{C_1^A + 2kC_5^A}{\Gamma},$$

$$S_3 = \Gamma[-d_4^M + 2k(2d_6^M + d_7^M)], \quad S_4 = d_1^M + 2kd_5^M,$$

$$\Gamma = \frac{p_W^A}{\tau_W} = \frac{T_\infty}{P_\infty^A}\frac{P_W^A - P_\infty^A}{T_W - T_\infty}.$$

If P_∞^A is the saturated-vapour pressure at T_∞, Γ becomes equal to $\gamma[= h_L/(R_A T_\infty)]$, a material constant of gas A (see (2.12)). From (6.4) the explicit expressions for F and G become

$$F = \frac{1 + k(S_4 - S_2)}{1 + k(\Lambda S_1 + S_4) + k^2\Lambda(S_1 S_4 - S_2 S_3)}, \quad G = \frac{1 + k\Lambda(S_1 - S_3)}{1 + k(\Lambda S_1 + S_4) + k^2\Lambda(S_1 S_4 - S_2 S_3)}, \tag{6.5}$$

valid up to $O(k^2)$ for moderate and large values of N_0^B/N_0^A and up to $O(k)$ for its smaller values.

The distributions of various quantities around the droplet after the Knudsen-layer correction has been made are:

$$v^A = v_H^A = k\Lambda \frac{F}{r^2} p_W^A, \tag{6.6}$$

$$v = \frac{m_A N_\infty^A}{\rho_\infty} v^A, \tag{6.7}$$

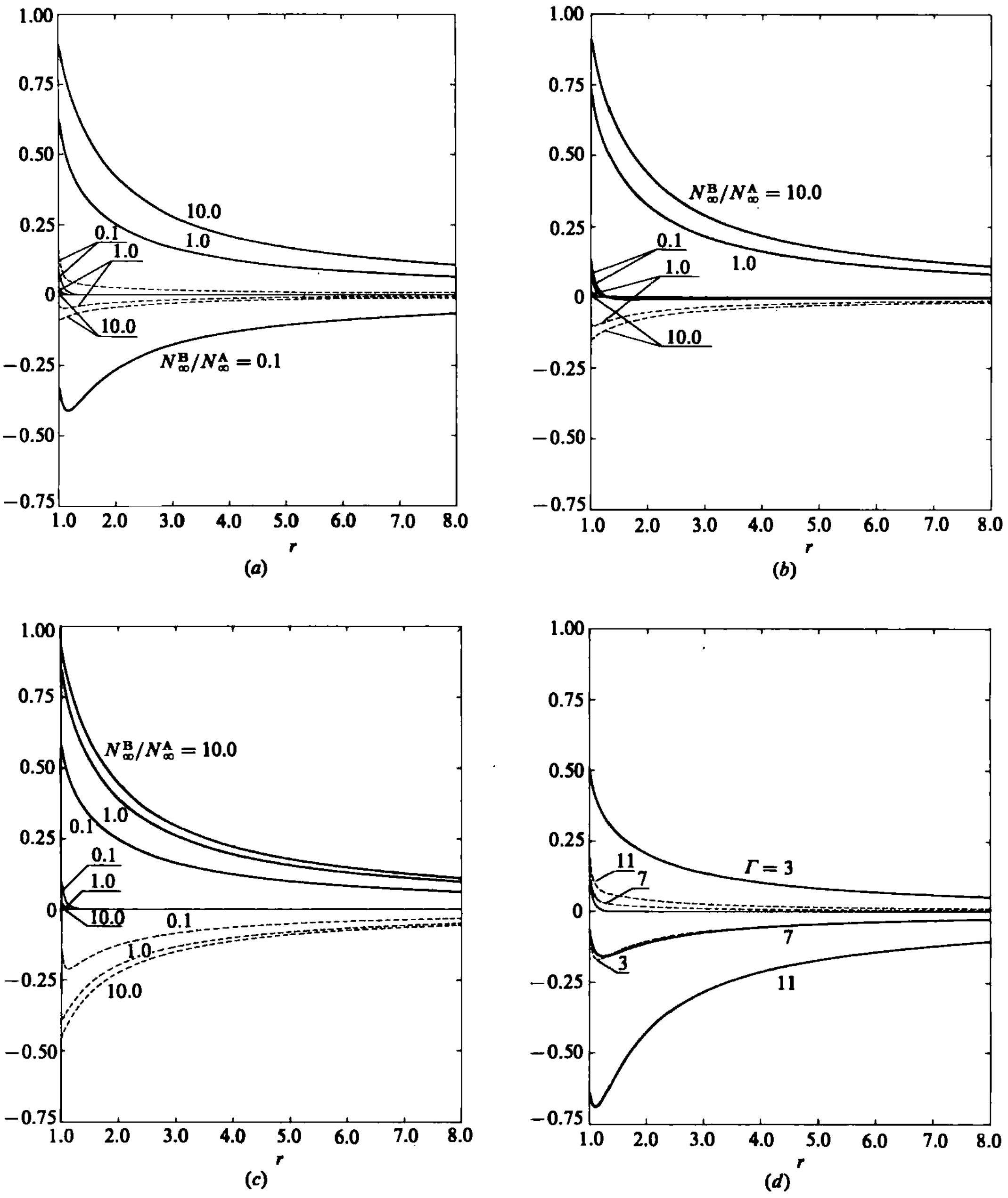

FIGURE 2. Temperature, pressure and number-density distributions of the mixture. $m_B/m_A = 2.0$, $k = 0.1$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$.

——, $\dfrac{T-T_\infty}{T_W-T_\infty}$; - - - - -, $\dfrac{N^A_\infty}{N_\infty}\dfrac{N-N_\infty}{N^A_W-N^A_\infty}$; ——, $\dfrac{P^A_\infty}{P_\infty}\dfrac{P-P_\infty}{P^A_W-P^A_\infty}$.

(*a*) $\Gamma = 11$, (*b*) $\Gamma = 7$, (*c*) $\Gamma = 3$, (*d*) $N^B_\infty/N^A_\infty = 0.05$.

$$\frac{\tau}{\tau_{\mathrm{W}}} = \frac{G}{r} - k\Lambda F\Gamma\{-\Theta_4^{\mathrm{M}}(z) + 2k[2\Theta_6^{\mathrm{M}}(z) + \Theta_7^{\mathrm{M}}(z)]\} - kG\{\Theta_1^{\mathrm{M}}(z) + 2k\Theta_5^{\mathrm{M}}(z)\}, \tag{6.8}$$

$$\frac{p^{\mathrm{A}}}{p_{\mathrm{W}}^{\mathrm{A}}} = \frac{F}{r} - k\Lambda F\{-\Pi_4^{\mathrm{A}}(z) + 2k[2\Pi_6^{\mathrm{A}}(z) + \Pi_7^{\mathrm{A}}(z)]\} - kG\frac{1}{\Gamma}\{\Pi_1^{\mathrm{A}}(z) + 2k\Pi_5^{\mathrm{A}}(z)\}, \tag{6.9}$$

$$\frac{p^{\mathrm{B}}}{p_{\mathrm{W}}^{\mathrm{A}}} = -\frac{P_\infty^{\mathrm{A}}}{P_\infty^{\mathrm{B}}}\frac{F}{r} - k\Lambda F\{-\Pi_4^{\mathrm{B}}(z) + 2k[2\Pi_6^{\mathrm{B}}(z) + \Pi_7^{\mathrm{B}}(z)]\} - kG\frac{1}{\Gamma}\{\Pi_1^{\mathrm{B}}(z) + 2k\Pi_5^{\mathrm{B}}(z)\}, \tag{6.10}$$

$$\frac{p}{p_{\mathrm{W}}^{\mathrm{A}}} = \frac{N_\infty^{\mathrm{A}}}{N_\infty}\frac{p^{\mathrm{A}}}{p_{\mathrm{W}}^{\mathrm{A}}} + \frac{N_\infty^{\mathrm{B}}}{N_\infty}\frac{p^{\mathrm{B}}}{p_{\mathrm{W}}^{\mathrm{A}}}, \tag{6.11}$$

$$\frac{n^{\mathrm{A}}}{n_{\mathrm{W}}^{\mathrm{A}}} = \frac{1}{\Gamma - 1}\left(\Gamma\frac{p^{\mathrm{A}}}{p_{\mathrm{W}}^{\mathrm{A}}} - \frac{\tau^{\mathrm{A}}}{\tau_{\mathrm{W}}}\right), \tag{6.12}$$

$$\frac{n^{\mathrm{B}}}{n_{\mathrm{W}}^{\mathrm{A}}} = \frac{1}{\Gamma - 1}\left(\Gamma\frac{p^{\mathrm{B}}}{p_{\mathrm{W}}^{\mathrm{A}}} - \frac{\tau^{\mathrm{B}}}{\tau_{\mathrm{W}}}\right), \tag{6.13}$$

$$\frac{n}{n_{\mathrm{W}}^{\mathrm{A}}} = \frac{N_\infty^{\mathrm{A}}}{N_\infty}\frac{n^{\mathrm{A}}}{n_{\mathrm{W}}^{\mathrm{A}}} + \frac{N_\infty^{\mathrm{B}}}{N_\infty}\frac{n^{\mathrm{B}}}{n_{\mathrm{W}}^{\mathrm{A}}}, \tag{6.14}$$

where z is defined in (4.19), and

$$\rho_\infty = m_{\mathrm{A}} N_\infty^{\mathrm{A}} + m_{\mathrm{B}} N_\infty^{\mathrm{B}} \quad \text{and} \quad \Theta_i^{\mathrm{M}} = (N_\infty^{\mathrm{A}}\Theta_i^{\mathrm{A}} + N_\infty^{\mathrm{B}}\Theta_i^{\mathrm{B}})/N_\infty.$$

$\tau^{\mathrm{S}}/\tau_{\mathrm{W}}$ is obtained from (6.8) with the replacement of Θ_i^{M} by Θ_i^{S}. Samples of the temperature, pressure, and number-density distributions of the mixture are shown in figure 2, and the partial pressure and number density of gas B in figure 3. As can be seen, the pressure of the mixture is uniform except in the Knudsen layer, which is also apparent from (6.11). In figures 2(a,b), the negative-temperature-gradient phenomenon is observed for small concentrations. The critical condition for this phenomenon to appear is given by the value of Γ, and is obtained by setting $\mathrm{d}\tau_{\mathrm{H}}^{\mathrm{A}}/\mathrm{d}r$ or G equal to zero as

$$\Gamma_{\mathrm{c}} = \frac{1 + k\Lambda[-C_4^{\mathrm{A}} + 2k(2C_6^{\mathrm{A}} + C_7^{\mathrm{A}})]}{k\Lambda[-d_4^{\mathrm{M}} + 2k(2d_6^{\mathrm{M}} + d_7^{\mathrm{M}})]}. \tag{6.15}$$

For Γ larger than Γ_{c}, the temperature gradient of the mixture (and its component gases) is always negative in the sense that it is opposite to the gradient which would be established by the maintained temperature difference between the droplet and at infinity. In the limit $N_\infty^{\mathrm{B}}/N_\infty^{\mathrm{A}} \to 0$ (pure-vapour case), Γ_{c} becomes

$$\Gamma_{\mathrm{c}} = \frac{C_4^{\mathrm{A}}}{d_4^{\mathrm{M}}}\left\{1 - k\left(\frac{4C_6^{\mathrm{A}} + 2C_7^{\mathrm{A}}}{C_4^{\mathrm{A}}} - \frac{4d_6^{\mathrm{M}} + 2d_7^{\mathrm{M}}}{d_4^{\mathrm{M}}}\right) + O(k^2)\right\}, \tag{6.16}$$

which is identical to that calculated from the result of Sone & Onishi (1978). We notice in figure 3 that, as $N_\infty^{\mathrm{B}}/N_\infty^{\mathrm{A}}$ becomes small, the inert gas forms large pressure and (number-)density gradients because its molecules are driven away from the droplet for evaporation ($p_{\mathrm{W}}^{\mathrm{A}} > 0$) and driven toward it for condensation ($p_{\mathrm{W}}^{\mathrm{A}} < 0$) owing to the collisions with vapour molecules. It should be mentioned at this point that the dependence of the pressures of the mixture and its component gases on Γ is insignificant, and practically zero in the graphs.

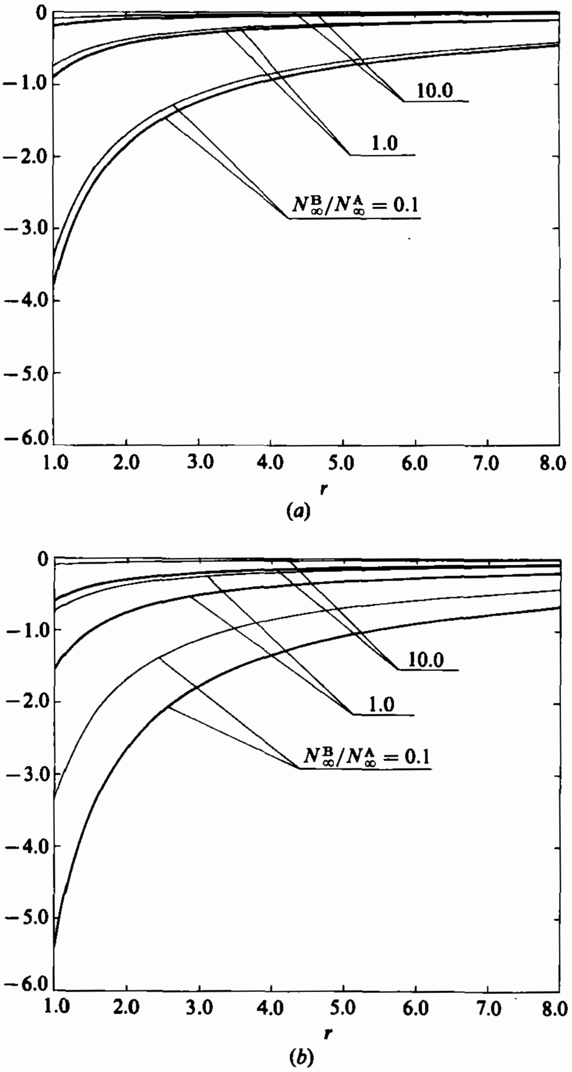

FIGURE 3. Partial pressure and number-density distributions of inert gas B. $m_B/m_A = 2.0$, $k = 0.1$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$. ——, $\dfrac{N^A_\infty}{N^B_\infty}\dfrac{N^B - N^B_\infty}{N^A_W - N^A_\infty}$; ——, $\dfrac{P^A_\infty}{P^B_\infty}\dfrac{P^B - P^B_\infty}{P^A_W - P^A_\infty}$. (*a*) $\Gamma = 11$. (*b*) $\Gamma = 3$.

Now, with the above results, the mass flow $\dot{m}$, heat flow $\hat{q}$ and energy flow $\hat{H}$ from the droplet are given as follows:

$$\frac{\dot{m}}{4\pi L^2} = m_A N^A_\infty (2R_A T_\infty)^{\frac{1}{2}} \frac{P^A_W - P^A_\infty}{P^A_\infty} kAF, \tag{6.17}$$

$$\frac{\hat{q}}{4\pi L^2} = \lambda^M \frac{T_W - T_\infty}{L} G, \tag{6.18}$$

$$\frac{\hat{H}}{4\pi L^2} = \frac{\hat{q}}{4\pi L^2} + \tfrac{5}{2}(2R_A T_\infty)^{\frac{1}{2}} (P^A_W - P^A_\infty) kAF, \tag{6.19}$$

where the formulas for heat and energy fluxes in §5 are used.

We shall examine now F and G for various concentrations. First let $N^{\mathrm{B}}_{\infty}/N^{\mathrm{A}}_{\infty} \sim O(k^n)$ with $n = 1, 2, 3, \ldots$; then $\Lambda \sim O(k^{-n})$, $F \sim O(k^{n-1})$, $G \sim O(1)$ and $k\Lambda F \sim O(1)$. We see from (6.17) that the mass flow is directly proportional to the difference between the saturated-vapour pressure at T_{W} and the vapour pressure at infinity. This is qualitatively the same as in the pure-vapour case, and the present mass transfer may be said to be controlled by the kinetic effect. In the limit $N^{\mathrm{B}}_{\infty}/N^{\mathrm{A}}_{\infty} \to 0$, we obtain from (6.5)

$$k\Lambda F = a_0 - k\left(a_3 + \frac{a_2}{\Gamma}\right) + \ldots, \quad G = 1 - \Gamma a_1 - k(a_4 + \Gamma a_5) + \ldots, \tag{6.20}$$

with

$$a_0 = -\frac{1}{C^{\mathrm{A}}_4} = 0.469035, \quad a_3 = \frac{4C^{\mathrm{A}}_6 + 2C^{\mathrm{A}}_7 + C^{\mathrm{A}}_1 d^{\mathrm{M}}_4}{(C^{\mathrm{A}}_4)^2} = 0.50,$$

$$a_2 = -\frac{C^{\mathrm{A}}_1}{C^{\mathrm{A}}_4} = 0.261\,926, \quad a_1 = \frac{d^{\mathrm{M}}_4}{C^{\mathrm{A}}_4} = 0.209\,541,$$

$$a_4 = d^{\mathrm{M}}_1 + a_2 d^{\mathrm{M}}_4 = 1.185700, \quad a_5 = a_3 d^{\mathrm{M}}_4 - a_1 d^{\mathrm{M}}_1 + a_0(4d^{\mathrm{M}}_6 + 2d^{\mathrm{M}}_7) = 0.$$

The solution in this limit reduces to that given by Sone & Onishi (1978) for the pure-vapour case, where the definition of the a_i's is the same. For later use in the graphs, we write explicitly the mass and heat flows for this limiting case:

$$\frac{\dot{m}_p}{4\pi L^2} = m_{\mathrm{A}} N^{\mathrm{A}}_{\infty}(2R_{\mathrm{A}} T_{\infty})^{\frac{1}{2}} \frac{P^{\mathrm{A}}_{\mathrm{W}} - P^{\mathrm{A}}_{\infty}}{P^{\mathrm{A}}_{\infty}} \left[a_0 - k\left(a_3 + \frac{a_2}{\Gamma}\right)\right], \tag{6.21}$$

$$\frac{\hat{q}_p}{4\pi L^2} = \lambda^{\mathrm{M}} \frac{T_{\mathrm{W}} - T_{\infty}}{L} [1 - \Gamma a_1 - k(a_4 + \Gamma a_5)]. \tag{6.22}$$

Next let $N^{\mathrm{B}}_{\infty}/N^{\mathrm{A}}_{\infty} \sim O(1/k^n)$ with $n = 0, 1, 2, \ldots$. Then $\Lambda \sim O(1)$, and F and G are also of order unity, reducing to

$$F = 1 - kC^{(1)}_p - k^2 C^{(2)}_p + \ldots, \quad G = 1 - kC^{(1)}_T - k^2 C^{(2)}_T + \ldots, \tag{6.23}$$

with

$$C^{(1)}_p = -\Lambda C^{\mathrm{A}}_4 + \frac{C^{\mathrm{A}}_1}{\Gamma}, \quad C^{(2)}_p = \Lambda C^{\mathrm{A}}_4 C^{(1)}_p - \left(\frac{C^{\mathrm{A}}_1}{\Gamma}\right) C^{(1)}_T + \Lambda(4C^{\mathrm{A}}_6 + 2C^{\mathrm{A}}_7) + \frac{2C^{\mathrm{A}}_5}{\Gamma},$$

$$C^{(1)}_T = -\Lambda\Gamma d^{\mathrm{M}}_4 + d^{\mathrm{M}}_1, \quad C^{(2)}_T = \Lambda\Gamma d^{\mathrm{M}}_4 C^{(1)}_p - d^{\mathrm{M}}_1 C^{(1)}_T + \Lambda\Gamma(4d^{\mathrm{M}}_6 + 2d^{\mathrm{M}}_7) + 2d^{\mathrm{M}}_5.$$

Since $k\Lambda F \sim O(k)$, we note that the mass flow in this case is smaller than that in the previous case by a factor of k, and we may express (6.17) as

$$\frac{\dot{m}}{4\pi L^2} = \frac{D_{\mathrm{AB}}}{R_{\mathrm{A}} T_{\infty}} \frac{N_{\infty}}{N^{\mathrm{B}}_{\infty}} \frac{P^{\mathrm{A}}_{\mathrm{W}} - P^{\mathrm{A}}_{\infty}}{L} [1 - kC^{(1)}_p - k^2 C^{(2)}_p + \ldots], \tag{6.24}$$

by the use of the relation $(2R_{\mathrm{A}} T_{\infty})^{\frac{1}{2}} Lk\Lambda = (N_{\infty}/N^{\mathrm{B}}_{\infty}) D_{\mathrm{AB}}$. The mass transfer in this case is proportional to the gradient of vapour pressure and depends on the diffusion coefficient, the ability of the vapour to diffuse through the inert gas. In the continuum limit ($k \to 0$), (6.24) agrees with the one given by Shankar (1970), and this gives Maxwell's result modified by a factor $N_{\infty}/N^{\mathrm{B}}_{\infty}$. It is noted that the solutions with (6.23) are also obtained from (3.4) subject to the boundary conditions (3.6a), (3.6b), (4.14), (4.15), (4.21), (4.22) on the interface and (6.2) at infinity.

Figures 4 and 5 show the graphs of $\dot{m}/\dot{m}_p$ and $\hat{q}/\hat{q}_p$, respectively, for practically

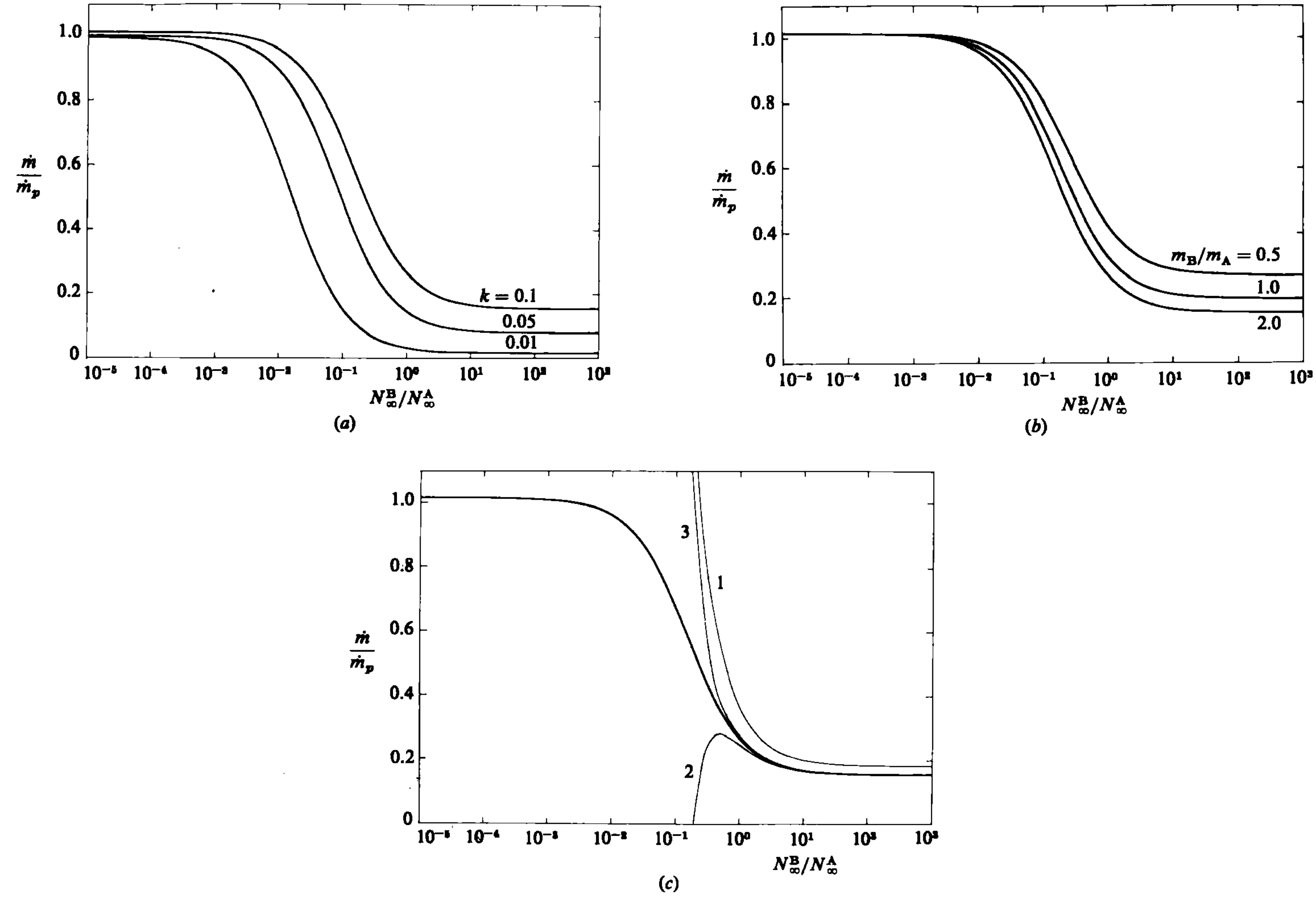

FIGURE 4. (*a*) Mass flow versus concentration. $m_B/m_A = 2.0$, $\Gamma = 11$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$. (*b*) Mass flow versus concentration. $k = 0.1$, $\Gamma = 11$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$. (*c*) Mass flow versus concentration. $m_B/m_A = 2.0$, $\Gamma = 11$, $k = 0.1$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$. ——, equation (6.17); 1, the first term of equation (6.24); 2, up to the second term of (6.24); 3, up to the third term of (6.24).

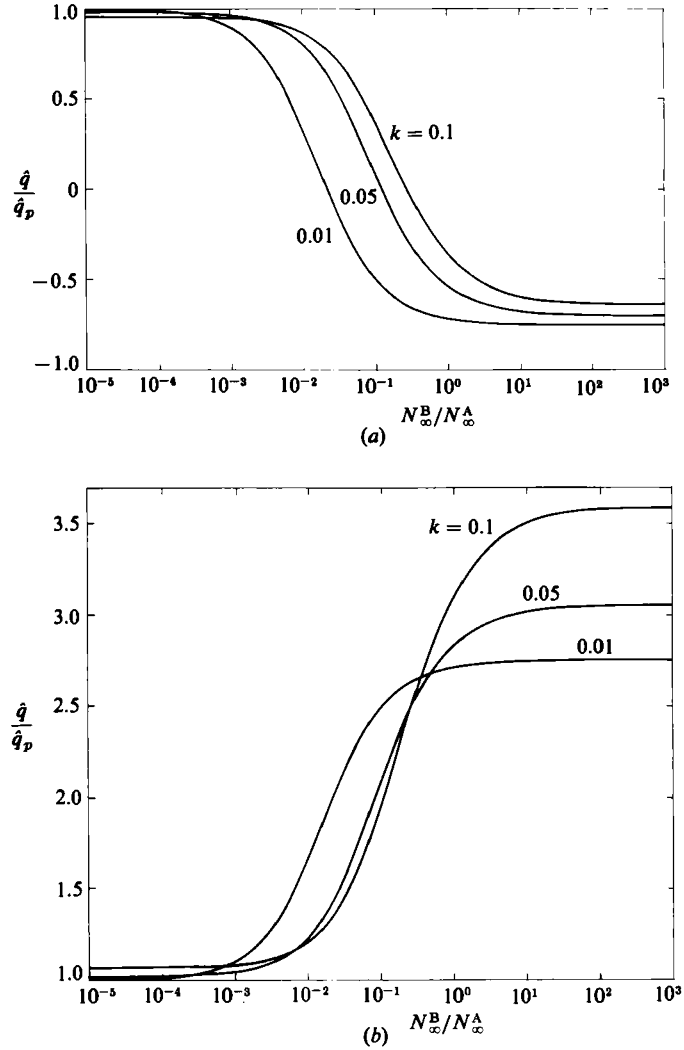

FIGURE 5. Heat flow versus concentration. $m_B/m_A = 2.0$, $\kappa_{AA} = \kappa_{AB} = \kappa_{BB}$. (a) $\Gamma = 11$. (b) $\Gamma = 3$.

all concentrations. It is clearly seen that figure 4 confirms what is stated above. In particular, figure 4(*a*) shows that when N^B_∞/N^A_∞ increases from $O(k)$ to $O(1)$, the mass transfer, or $\dot{m}/\dot{m}_p$, drops sharply from $O(1)$ to $O(k)$. In the limit $N^B_\infty/N^A_\infty \to \infty$,† vapour flow is determined by frequent collisions with inert gas and is less affected by them when the vapour molecules are heavier (see figure 4*b*). In figure 4(*c*) $\dot{m}/\dot{m}_p$, with $\dot{m}$ given in (6.24), is plotted to show how the solution at each stage of approximation in its expansion form of k behaves as the concentration of inert gas decreases. Note that the discrepancy in figure 4 between unity and the value of $\dot{m}/\dot{m}_p$ in the limit $N^B_\infty/N^A_\infty \to 0$ is of order k^2 because $\dot{m}_p$ is valid to order k and so also $\dot{m}$ in this limiting case. As for the heat flow, it is negative for Γ larger than Γ_c since it is proportional to the temperature gradient (see (5.3)). Figure 5(*a*) is one of these cases, and $\hat{q}$ changes

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† This does not mean the complete absence of vapour gas. Vapour gas may exist (enough to satisfy the Boltzmann equation) but if so it does not affect the behaviour of the inert gas at all.

from positive to negative as a result of the change of sign of the temperature gradient as N^B_∞/N^A_∞ decreases (note that $\hat{q}_p$ in this case is always negative). Figure 5(*b*), on the other hand, is a case in which the negative temperature gradient never occurs at any concentration.

Finally, we note that the present problem reduces to a simple heat-conduction problem for a sphere immersed in an inert gas mixture by formally putting $F = 0$. Then from (6.4) we have

$$G = \frac{1}{1+kS_4}, \quad \Gamma = \frac{k(C_1^A + 2kC_5^A)}{1+kS_4}, \tag{6.25}$$

the latter now determining p^A_W, the pressure for inert gas-A molecules reflected from the surface of the sphere (this corresponds to (4.26)).

REFERENCES

ABRAMOWITZ, M. & STEGUN, I. A. 1970 *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, pp. 1001–1003. U.S. Department of Commerce, National Bureau of Standards.

CERCIGNANI, C. 1975 *Theory and Application of the Boltzmann Equation*, pp. 245–248. Scottish Academic Press.

DAVIES, C. N. 1978 Evaporation of airborne droplets. In *Fundamentals of Aerosol Science* (ed. D. T. Shaw), pp. 135–164. John Wiley.

FUCHS, N. A. 1959 *Evaporation and Droplet Growth in Gaseous Media*. Pergamon.

HAMEL, B. B. 1965 Kinetic model for binary gas mixtures. *Phys. Fluids* **8**, 418–425.

KOGAN, M. N. 1969 *Rarefied Gas Dynamics*, pp. 501–502. Plenum Press.

LANDAU, L. D. & LIFSHITZ, E. M. 1969 *Statistical Physics*, §82. Pergamon.

LEES, L. 1959 A kinetic theory description of rarefied gas flows. *Memorandum No.* 51, Guggenheim Aero. Lab., C.I.T.

LEES, L. & LIU, C. Y. 1962 Kinetic-theory description of conductive heat transfer from a fine wire. *Phys. Fluids* **5**, 1137–1148.

MATSUSHITA, T. 1976 Kinetic analysis of the problem of evaporation and condensation. *Phys. Fluids* **19**, 1712–1715.

MAXWELL, J. C. 1965 *The Scientific Papers of James Clerk Maxwell*, vol. II, pp. 625–646. Dover.

ONISHI, Y. 1977 Kinetic theory of evaporation and condensation of a vapor gas between concentric cylinders and spheres. *J. Phys. Soc. Japan* **42**, 2023–2032.

ONISHI, Y. 1979 Asymptotic theory for heat transfer problems of a slightly rarefied gas between coaxial cylinders – hydrodynamic equations and jump conditions. *Trans. Japan Soc. Aero. Space Sci.* **22**, 16–30.

ONISHI, Y. 1984 A two-surface problem of evaporation and condensation in a vapor–gas mixture. In *Rarefied Gas Dynamics* (ed. H. Oguchi), vol. II, pp. 875–884. University of Tokyo Press.

PAO, Y. P. 1971*a* Application of kinetic theory to the problem of evaporation and condensation. *Phys. Fluids* **14**, 306–312.

PAO, Y. P. 1971*b* Temperature and density jumps in the kinetic theory of gases and vapors. *Phys. Fluids* **14**, 1340–1346 [Erratum: 1973 *Phys. Fluids* **16**, 1560].

SAMPSON, R. E. & SPRINGER, G. S. 1969 Condensation on and evaporation from droplets by a moment method. *J. Fluid Mech.* **36**, 577–584.

SHANKAR, P. N. 1970 A kinetic theory of steady condensation. *J. Fluid Mech.* **40**, 385–400.

SIEWERT, C. E. & THOMAS, J. R. 1973 Half-space problems in the kinetic theory of gases. *Phys. Fluids* **16**, 1557–1559.

SONE, Y. 1964 Kinetic theory analysis of linearized Rayleigh problem. *J. Phys. Soc. Japan* **19**, 1463–1473.

SONE, Y. 1969 Asymptotic theory of flow of rarefied gas over a smooth boundary I. In *Rarefied Gas Dynamics* (ed. L. Trilling & H. Y. Wachman), vol. I, pp. 243–253. Academic.

SONE, Y. 1971 Asymptotic theory of flow of rarefied gas over a smooth boundary II. In *Rarefied Gas Dynamics* (ed. D. Dini), vol. II, pp. 737–749, Editrice Tecnico Scientifica.

SONE, Y. 1984 Analytical studies in rarefied gas dynamics. In *Rarefied Gas Dynamics* (ed. H. Oguchi), vol. I, pp. 71–87. University of Tokyo Press.

SONE, Y. & ONISHI, Y. 1973 Kinetic theory of evaporation and condensation. *J. Phys. Soc. Japan* **35**, 1773–1776.

SONE, Y. & ONISHI, Y. 1977 Heat transfer through a rarefied gas between coaxial circular cylinders with large temperature difference. In *Rarefied Gas Dynamics* (*Prog. in Astronaut. and Aeronaut.* vol. 51, (ed. J. L. Potter), part 1, pp. 295–310. AIAA.

SONE, Y. & ONISHI, Y. 1978 Kinetic theory of evaporation and condensation – Hydrodynamic equation and slip boundary condition. *J. Phys. Soc. Japan* **44**, 1981–1994. (See also *Research Rep. No.* 31, Section of Fluid Dynamics, Department of Aeronautical Engineering, Kyoto Univ. 1977, p. 1.)

THOMAS, J. R., CHANG, T. S. & SIEWERT, C. E. 1974 Reverse temperature gradient in the kinetic theory of evaporation. *Phys. Rev. Letters* **33**, 680–682.

VINCENTI, W. G. & KRUGER, C. H. 1965 *Introduction to Physical Gas Dynamics*, Chap. X. John Wiley.