

# The concentration-jump coefficient in a rarefied binary gas mixture

By C. SHEN

Institute of Mechanics, Chinese Academy of Sciences, Beijing, China

(Received 31 March 1983 and in revised form 17 August 1983)

In this paper we consider the problem of the concentration jump of a vapour in the vicinity of a plane wall, which consists of the condensed phase of the vapour, in a rarefied gas mixture of that vapour (*A*) and another 'inert' gas (*B*). The general formulation of the problem of determining the concentration-jump coefficient  $C_{dA}$  is given. In the Knudsen layer the simplest model of Boley–Yip theory is used to simplify the Boltzmann equations for the binary gas mixture. The numerical calculation of the concentration jump coefficient  $C_{dA}$  for various values of evaporation coefficient  $\alpha_A$  is illustrated for the case of  $n_B \gg n_A$ , for which experimental data are available.

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## 1. Introduction

The evaporation and condensation of liquid droplets are among the important contents of aerosol behaviour investigations and are of great practical significance. When the radius  $a$  of the spherical droplets is so small that it is comparable with the mean free path  $\lambda$  of the surrounding gas, the effect of the discrete molecular structure must be taken into account. In the region  $0 < K < 0.1$  ( $K = \lambda/2a$ ), the methods of the slip-flow regime can be used, i.e. the Navier–Stokes equations are used as the controlling equations, and the conditions on the solid boundary under continuum assumptions are modified with various jumps present there. In the case of momentum transfer and energy transfer, when there are velocity and temperature gradients at the wall, there must be discontinuities in the velocities and temperatures of the gas and of the boundary (Maxwell 1879; Kennard 1938). The slip-velocity and temperature-jump boundary conditions have been investigated in detail (Welander 1954; Cercignani 1975; Sone 1966*a, b*), and the dependences of slip coefficient, temperature-jump coefficient and thermal-creep coefficient on the accommodation coefficient have been estimated numerically with fair accuracy (Loyalka 1968; Loyalka & Cipolla 1971; Ivchenko & Yalamov 1971; Onishi 1973; Shen 1983). In the mass-transfer problem of evaporation and condensation of liquid droplets, when a concentration gradient is present at the wall, there must be discontinuity of the vapour concentration, and the concentration-jump boundary condition and concentration-jump coefficient have to be introduced, the investigation of which has been far from complete (see Hidy & Brock 1970). There have been several works (e.g. Pao 1970; Sone & Onishi 1973, 1978) concerning the evaporation and condensation of one-component gas onto its condensed phase. The purpose of this paper is to investigate the concentration-jump boundary condition in the slip flow regime in the case where there exists two species of gases and where one of them may condense on or evaporate from a solid wall of its condensed phase and diffuse through another, and to determine the dependence of the concentration-jump coefficient on the evaporation coefficient.

When a vapour gas (component  $A$ ) evaporates from its condensed phase and diffuses through another gas (component  $B$ ), the concentration of component  $A$  in the gas, under the continuum assumption, satisfies the following equation:

$$\frac{\partial n_A}{\partial t} + \mathbf{u} \cdot \nabla n_A = D_{AB} \nabla^2 n_A, \quad (1)$$

where  $\mathbf{u}$  is the local velocity of the gas,  $D_{AB}$  is the mutual diffusion coefficient between component  $A$  and component  $B$ . In the case of a spherical particle with radius  $a$ , the following boundary conditions are imposed in continuum flow:

$$n_A = n_{A1} \quad (r = a), \quad (2)$$

$$n_A = n_{A0} \quad (r \rightarrow \infty), \quad (3)$$

where  $n_{A1}$  is the equilibrium concentration of component  $A$  at the particle surface. For the simplest case of quiescent fluid and a quasi-stationary process ((1) becomes  $\nabla^2 n_A = 0$ ) the rate of condensation or evaporation is found to be

$$\frac{Q_C}{4\pi a^2} = \frac{D_{AB}(n_{A1} - n_{A0})}{a}, \quad (4)$$

where  $Q_C$  is the total rate of transfer of component  $A$  from the particle surface. The expression (4) in the limit  $a \rightarrow 0$  is incorrect, for, physically speaking,  $Q_C/4\pi a^2$  must be finite, but the right-hand side would lead to  $Q_C/4\pi a^2 \rightarrow \infty$  as  $a \rightarrow 0$ . When  $a \rightarrow 0$  the discrete structure of the gas must be taken into account.

In the slip regime the concentration jump can be postulated at the surface, i.e. in place of (2) the following slip-flow boundary condition can be postulated:

$$n_A - n_{A1} = C_{dA(A)} \lambda_A \frac{dn_A}{dr}, \quad (2)'$$

where  $\lambda_A$  is the mean free path of  $A$  in the gas mixture,† and  $C_{dA}$  is the concentration-jump coefficient. The rate of evaporation is

$$\frac{Q_{SL}}{4\pi a^2} = \frac{D_{AB}(n_{A1} - n_{A0})/a}{1 + C_{dA(A)} \lambda_A/a}. \quad (5)$$

This result can be used in the region  $0 < \mathcal{K} < 0.1$ . The crux of the matter remaining is how to determine  $C_{dA}$ .

In this paper an attempt is made to determine  $C_{dA}$  on the basis of kinetic theory for a binary gas mixture. For simplicity we shall consider the plane-boundary problem. The model Boltzmann equations are solved in the Knudsen layer, and far from the surface the normal gradient of concentration is assumed to approach a constant. At the surface the fraction  $\alpha_A$  of incident molecules of component  $A$  is supposed to be re-emitted from the surface in a Maxwellian distribution with the temperature of the wall, and the remaining  $(1 - \alpha_A)$  portion only changes the direction of the normal component of velocity. Here  $\alpha_A$  is the evaporation or condensation coefficient of  $A$ .

† In a gas mixture consisting of two components, the notion of the mean free path must be further clarified. The size and mass of the vapour molecules and air molecules may differ from each other greatly, so the mean free path  $\lambda_B$  of the air molecules in the mixture and that  $\lambda_A$  of the vapour molecules must be distinguished. The numerical coefficient  $C_{dA}$  in the concentration-jump condition will vary in accordance with which of the different mean free paths is meant. When  $\lambda_A$  is meant,  $C_{dA}$  will be written as  $C_{dA(A)}$ , and when  $\lambda_B$  is meant  $C_{dA}$  will be written as  $C_{dA(B)}$ . Obviously  $C_{dA(A)} = (\lambda_B/\lambda_A) C_{dA(B)}$ .

In §2 the general formulation of the problem will be given. Then the simplifying model Boltzmann equations for a binary gas mixture will be discussed. Finally, for the specific case of  $n_B \gg n_A$ , the calculation of the coefficient  $C_{dA}$  is given, and the result is compared with experimental data.

## 2. The formulation of the problem

The case of an infinite plane wall ( $y = 0$ ) will be considered. Far from the wall (outside Knudsen layer) the vapour concentration has constant normal gradient, and it evaporates from the wall of its condensed phase or condenses on it. We consider the distribution of the vapour concentration in the Knudsen layer near the wall in the presence of another gas.

As far as the two-component gas mixture is concerned, the governing equations are binary-component Boltzmann equations (see e.g. Chapman & Cowling 1970):

$$\left. \begin{aligned} \mathbf{v} \cdot \nabla f_A &= J_A(f_A) + J_{AB}(f_A, f_B), \\ \mathbf{v} \cdot \nabla f_B &= J_B(f_B) + J_{BA}(f_B, f_A), \end{aligned} \right\} \quad (6)$$

where  $\mathbf{v}$  denotes the molecular velocity,  $f_A, f_B$  are the distribution functions of condensable vapour (component  $A$ ) and of the other gas (component  $B$ , say air), the right-hand sides are the collision integral operators,  $J_A$  is the self-collision operator of component  $A$ ,  $J_{AB}$  is the cross-collision operator of components  $A$  and  $B$ , etc.

The air molecules satisfy the Maxwellian boundary condition at the wall

$$f_B(v_x, v_y, v_z)|_{y=0} = \alpha_B \frac{n_B}{(\pi^{\frac{1}{2}} C_{mB})^3} \exp\left(-\frac{v^2}{C_{mB}^2}\right) + (1 - \alpha_B) f_B(v_x, -v_y, v_z), \quad (7)$$

where  $\alpha_B$  is the accommodation coefficient of air at the wall,  $C_{mB} = (2kT/m_B)^{\frac{1}{2}}$  the most-probable speed of the air molecules,  $k$  is Boltzmann's constant, and  $m_B$  is the molecular weight of component  $B$ ; obviously the air molecules also satisfy the condition of no absorption and condensation

$$\int v_y f_B d\mathbf{v} = 0. \quad (8)$$

The vapour molecules satisfy the Maxwellian boundary condition at the wall

$$f_A(v_x, v_y, v_z)|_{y=0} = \alpha_A \frac{n_A}{(\pi^{\frac{1}{2}} C_{mA})^3} \exp\left(-\frac{v^2}{C_{mA}^2}\right) + (1 - \alpha_A) f_A(v_x, -v_y, v_z), \quad (9)$$

where  $\alpha_A$  is the evaporation or condensation coefficient,  $C_{mA} = (2kT/m_A)^{\frac{1}{2}}$  is the most-probable speed of the vapour molecules, and  $m_A$  is the molecular weight of component  $A$ . As component  $A$  evaporates or condenses at the surface, its normal velocity does not vanish, and is determined by the behaviour of solution at infinity. The procedure of determination of normal velocity is shown for the example of small  $n_A$ .

We consider the case of small deviations from equilibrium, when the Boltzmann equations can be linearized and simplifying models can be invoked (see §3). The vapour concentration  $n_A = \int f_A d\mathbf{v}$  can be written as

$$n_A = n_{A1}(1 + \nu_A), \quad (10)$$

and  $\nu_A$  is small (for the definition of  $\nu_A$  through disturbed distribution function  $\phi_A$

see (24)). For our purposes we should consider the case of finite constant concentration gradient far from the wall. One can suppose  $\nu_A$  to have the form

$$\nu_A = cy + b + \nu_{AK}, \quad (11)$$

where  $c$  and  $b$  are constants,  $c = (1/n_{A1}) dn_A/dy$  characterizes the value of the concentration gradient,  $b$  characterizes the value of concentration jump ( $b/c = C_{dA} \lambda$ ), and  $\nu_{AK}$  is a function vanishing at  $\infty$ .

The deviation  $\tau_A$  of the temperature of component  $A$  from its equilibrium value (for the definition of  $\tau_A$  see (26)) can be supposed to be of the form

$$\tau_A = ay + d + \tau_{AK}, \quad (12)$$

with  $\tau_{AK}$  vanishing at  $\infty$ .

Similarly, the small deviations of concentration and temperature of component  $B$  from their equilibrium values have the form

$$\left. \begin{aligned} \nu_B &= \gamma y + \beta + \nu_{BK}, \\ \tau_B &= \alpha y + \delta + \tau_{BK}, \end{aligned} \right\} \quad (13)$$

where  $\nu_{BK}, \tau_{BK}$  vanish at  $\infty$ . Certain constraints imposed on  $a, b, c, d, \alpha, \beta, \gamma, \delta$  can be obtained from the behaviour of the solution at  $\infty$ . We shall show this in the particular case of small concentration of evaporating gas.

Thus, supposing the disturbed concentrations and temperatures to have the form (11)–(13), and to satisfy the boundary conditions (7)–(9), and determining the normal velocity of component  $A$  from a constraint at  $\infty$ , we can solve the linearized form of (6) or its model version in the Knudsen layer and determine the value of  $b$  in particular. We thereby prove that there is a concentration jump and find the concentration-jump coefficient  $C_{dA}$  as  $b/c\lambda$ .

### 3. The modelling of the collision operators in the linearized Boltzmann equations for a binary gas mixture

In rarefied gas dynamics the investigation of the Knudsen layer has been carried out quite extensively, many works have been based on the model Boltzmann equations, among which the most frequently used is the simplest model proposed originally by Bhatnagar, Gross & Krook (1954) and Welander (1954) (referred to as the BKW or BGK equation for simplicity).

What we need to solve are the Boltzmann equations (6) for a binary gas mixture. For the case of small departure from equilibrium, the distribution functions  $f_A, f_B$  can be linearized:

$$f_i(\mathbf{v}, \mathbf{r}, t) = \frac{n_i F_i(\mathbf{v})}{C_{mi}^3} [1 + \phi_i(\mathbf{v}, \mathbf{r}, t)] \quad (i = A, B), \quad (14)$$

where  $F_i = \pi^{-\frac{3}{2}} \exp\left(-\frac{v^2}{C_{mi}^2}\right)$  ( $i = A, B$ ).

And (6) can be written in the form

$$\mathbf{v} \cdot \nabla \begin{pmatrix} \phi_A \\ \phi_B \end{pmatrix} = \left[ \begin{pmatrix} n_A \mathbf{K}_A & 0 \\ 0 & n_B \mathbf{K}_B \end{pmatrix} + \begin{pmatrix} n_B & 0 \\ 0 & n_A \end{pmatrix} \begin{pmatrix} L_{AA} & L_{AB} \\ L_{BA} & L_{BB} \end{pmatrix} \right] \begin{pmatrix} \phi_A \\ \phi_B \end{pmatrix}, \quad (15)$$

where  $\mathbf{K}_A, \mathbf{K}_B$  are the linearized one-component collision operators for  $A$  and  $B$  respectively, which can be modelled with the BKW model;

$$\mathbf{L} \equiv \begin{pmatrix} L_{AA} & L_{AB} \\ L_{BA} & L_{BB} \end{pmatrix}$$

is the linearized cross-collision matrix. Boley & Yip (1972*a, b*) proposed a modelling theory for it with the help of the eigentheory of the cross-collision operators. According to their theory, the simplest model is the one which is obtained in the expansion of  $\mathbf{L}$  in terms of its eigenfunctions and eigenvalues with all conservation eigenfunctions and a relaxation frequency  $\gamma$  (the corresponding eigenvalue being  $-\gamma$ ,  $\gamma$  positive) retained and with all other eigenvalues replaced by this frequency (with negative sign). The conservation laws in collision are thus satisfied, and the eigenfunction corresponding to that relaxation frequency is also properly taken into account. This simplest model can be written

$$\mathbf{L}^{(0)} \begin{pmatrix} \phi_A \\ \phi_B \end{pmatrix} = \left(\frac{k_{AB}}{\mu}\right)^{\frac{1}{2}} \gamma \left[ \begin{pmatrix} \nu_A \\ \nu_B \end{pmatrix} + 2 \begin{pmatrix} \xi_A \cdot \mathbf{U}_A \\ \xi_B \cdot \mathbf{U}_B \end{pmatrix} + \frac{1}{2} (\tau_A + \tau_B) \begin{pmatrix} \xi_A^2 - \frac{3}{2} \\ \xi_B^2 - \frac{3}{2} \end{pmatrix} \right] - \left(\frac{k_{AB}}{\mu}\right)^{\frac{1}{2}} \gamma \begin{pmatrix} \phi_A \\ \phi_B \end{pmatrix}, \quad (16)$$

where  $k_{AB}$  is the coefficient of proportion of the force potential between components  $A$  and  $B$ ,  $\mu = m_A m_B / (m_A + m_B)$  is the reduced mass,

$$\xi_A = \mathbf{v} / C_{mA}, \quad \xi_B = \mathbf{v} / C_{mB}, \quad \mathbf{U}_A = (z_A \mathbf{u}_A + z_B \mathbf{u}_B) / C_{mA},$$

$$\mathbf{U}_B = (z_A \mathbf{u}_A + z_B \mathbf{u}_B) / C_{mB}, \quad z_A = m_A / (m_A + m_B)$$

and

$$z_B = m_B / (m_A + m_B).$$

$\nu_A, \mathbf{u}_A$  and  $\tau_A$  are the departures of local density, velocity and temperature of component  $A$  from equilibrium:

$$\begin{pmatrix} \nu_A \\ \mathbf{u}_A \\ \tau_A \end{pmatrix} = \int F_A \phi_A \begin{pmatrix} 1 \\ \mathbf{v} \\ \frac{3}{2} \xi_A^2 - 1 \end{pmatrix} d\xi_A; \quad (17)$$

$\nu_B, \mathbf{u}_B, \tau_B$  have a similar meaning. In a binary gas mixture the diffusion coefficient  $D_{AB}$  and the eigenvalue  $|A_{01}^{-1}|$  have the following relationship (Boley & Yip 1972*b*):

$$D_{AB} = \left[ \frac{\mu n}{kT} \left(\frac{k_{AB}}{\mu}\right)^{\frac{1}{2}} / |A_{01}^{-1}| \right]^{-1}. \quad (18)$$

Taking  $|A_{01}^{-1}|$  as the relaxation frequency retained (thus we have taken into account the eigenfunction related to the diffusion process) we find the coefficient in (16) to be

$$\left(\frac{k_{AB}}{\mu}\right)^{\frac{1}{2}} \gamma = \frac{kT}{n D_{AB} \mu} \equiv \gamma'. \quad (19)$$

It is well known, in the case of a one-component gas, that making use of the BKW model, when the value of the relaxation frequency is chosen to lead to the correct expressions of viscosity (or conductivity), the correct values of the slip-velocity coefficient  $C_m$  (or the temperature jump coefficient  $C_t$  and the thermal creep coefficient  $C_s$ ) can be obtained (Cercignani 1975; Welander 1954; Sone 1966*a, b*; Loyalka 1968, 1971; Ivchenko *et al.* 1971; Shen 1983). Therefore, when  $\gamma$  is chosen as in (19), the simplest model of the cross-correlation operator is expected to depict the process where mutual diffusion predominates.

#### 4. Example of numerical calculation of the concentration-jump coefficient: the case $n_B \gg n_A$

Under the general formulation of the problem,  $C_{0A}$  depends on the condensation coefficient  $\alpha_A$  and other dimensionless parameters such as  $n_B/n_A, m_B/m_A, S_{AB}/S_{BB}$  ( $S_{AB}$  being the collision cross-section between the vapour and air molecules, and  $S_{BB}$

that between air molecules), so it is rather lengthy and tedious to give the value of  $C_{dA}$  under various values of the various parameters. Here we are confined to giving the detailed calculation in a case when experimental data are available, and the equations can be greatly simplified.

The experiment of Birks & Bradley (1949) on the evaporation of a spherical liquid droplet in quiescent gas seems to be the most exact one under the condition of small  $\mathcal{K}$ . They investigated the evaporation of a dibutyl phthalate ( $C_6H_4(CO \cdot OC_4H_9)_2$ ,  $M = 278$ ) droplet ( $a \approx 0.5$  mm) in low-pressure air. The evaporation pressure of dibutyl phthalate (component  $A$ ) is approximately  $10^{-5}$  mmHg and the air pressure in the experiment was 0.1–200 mmHg. We see from the experimental condition that  $n_B \gg n_A$ , and this can simplify the linearized model (15) greatly.

In the case of a plane wall, when the simplest linearized model of Boley & Yip is used with the eigenfunction related to the diffusion process taken into account ((16) and (19)) (15) can be written as

$$v_y \frac{\partial \phi_A}{\partial y} = n_A K_A \phi_A + n_B \gamma' [\nu_A - \phi_A + 2\xi_{Ay} U_{Ay} + \frac{1}{2}(\tau_A + \tau_B) (\xi_A^2 - \frac{3}{2})], \quad (20)$$

$$v_y \frac{\partial \phi_B}{\partial y} = n_B K_B \phi_B + n_A \gamma' [\nu_B - \phi_B + 2\xi_{By} U_{By} - \frac{1}{2}(\tau_A + \tau_B) (\xi_B^2 - \frac{3}{2})], \quad (21)$$

In general (20) and (21) are to be solved simultaneously. But with  $n_A \ll n_B$  and hence  $u_B \ll u_A$  (20) and (21) can be simplified:

$$v_y \frac{\partial \phi_A}{\partial y} = n_B \gamma' [\nu_A - \phi_A + 2\xi_y U_y + \frac{1}{2}(\tau_A + \tau_B) (\xi^2 - \frac{3}{2})], \quad (22)$$

$$v_y \frac{\partial \phi_B}{\partial y} = n_B K_B \phi_B, \quad (23)$$

with

$$\nu_A = \int F_A \phi_A d\xi, \quad (24)$$

$$U_y = \frac{m_A}{m_A + m_B} \int F_A \phi_A \xi_y d\xi, \quad (25)$$

$$\frac{3}{2}(\nu_A + \tau_A) = \int F_A \phi_A \xi^2 d\xi, \quad (26)$$

and we have dropped the suffix  $A$  in  $\xi_A$  and  $U_A$ . The distribution function of component  $A$  is controlled by cross-collision and that of component  $B$  by self-collision of air molecules. In the state of equilibrium the distribution of air molecules is Maxwellian,  $\phi_B = 0$ , and  $\phi_A$  can be found by solving (22) independently.

Making use of expressions for the mutual diffusion coefficient  $D_{AB}$  and the mean free path of component  $A$  (Kennard 1938; Chapman & Cowling 1960), and introducing the new variable

$$\eta = \frac{8}{3\pi^{\frac{1}{2}}} \frac{y}{\lambda_A}, \quad (27)$$

we can rewrite (22) as

$$\xi_y \frac{\partial \phi_A}{\partial \eta} = \nu_A - \phi_A + 2\xi_y U_y + \frac{1}{2}\tau_A (\xi^2 - \frac{3}{2}), \quad (28)$$

where  $\nu_A$ ,  $U_y$  and  $\tau_A$  satisfy conditions (24), (25) and (26).

The boundary condition (19) at the wall, when linearized, can be written

$$\phi_A(\xi_x, \xi_y, \xi_z) = \alpha[\nu_w + (\xi^2 - \frac{3}{2})\tau_w] + (1 - \alpha)\phi_A(\xi_x, -\xi_y, \xi_z).$$

When the equilibrium concentration at the wall and the wall temperature are taken as reference values, we can simplify the boundary condition further as

$$\phi_A(\xi_x, \xi_y, \xi_z) = (1 - \alpha_A) \phi_A(\xi_x, -\xi_y, \xi_z). \quad (29)$$

The solution of (28) satisfying (29) can be written

$$\left. \begin{aligned} \phi_{A\xi_y > 0} &= \frac{1 - \alpha_A}{\xi_y} \int_0^\infty [-2\xi_y U_y(\zeta) + \nu_A(\zeta) + \frac{1}{2}(\xi^2 - \frac{3}{2})\tau_A(\zeta)] \exp\left(-\frac{\zeta}{\xi_y}\right) d\zeta \exp\left(-\frac{\eta}{\xi_y}\right) \\ &\quad + \frac{1}{\xi_y} \int_0^\eta [2\xi_y U_y(\zeta) + \nu_A(\zeta) + \frac{1}{2}(\xi^2 - \frac{3}{2})\tau_A(\zeta)] \exp\left(-\frac{\eta - \zeta}{\xi_y}\right) d\zeta, \\ \phi_{A\xi_y < 0} &= \frac{1}{|\xi_y|} \int_\eta^\infty [2\xi_y U_y(\zeta) + \nu_A(\zeta) + \frac{1}{2}(\xi^2 - \frac{3}{2})\tau_A(\zeta)] \exp\left(-\frac{|\eta - \zeta|}{|\xi_y|}\right) d\zeta. \end{aligned} \right\} \quad (30)$$

It is easily seen from (28) that  $U_y = \text{const}$ . In fact, multiplying both sides of (28) by  $F_A d\xi$  and integrating, we have

$$\frac{\partial}{\partial \eta} \int \xi_y F_A \phi_A d\xi = 0,$$

i.e. 
$$U_y = \text{const}. \quad (31)$$

From (11) and (12) we see that  $\nu_A$  and  $\tau_A$  have the following forms at  $\infty$ :

$$\left. \begin{aligned} \nu_A &= c'\eta + b, \\ \tau_A &= a'\eta + d, \end{aligned} \right\} \quad (32)$$

where  $c/c' = a/a' = 8/3\pi^{1/2}\lambda_A$ . From (31), (32) and the basic equation (28) one can obtain the form of the solution  $\phi$  at  $\infty$ . Substituting this expression for  $\phi$  into the macroscopic conditions (24)–(26), one obtains the following constraints on  $a'$ ,  $d$  and  $U_y$ :

$$a' = d = 0, \quad (33)$$

$$U_y = -\frac{c' m_A}{2 m_B}. \quad (34)$$

Equation (33) is an isothermal requirement outside the Knudsen layer for component  $A$  in the case  $n_B \gg n_A$ . Equation (34) is a kinetic derivation of the requirement that the normal velocity is determined by the diffusive flux caused by the presence of the concentration gradient at infinity. Substituting (11) and (12) into (30) with (33) and (34) in mind, and substituting the solution into the macroscopic conditions (24)–(26), we obtain, with subscript  $A$  omitted from  $\nu_{AK}, \tau_{AK}$ :

$$b = \frac{\pi^{1/2}}{2\alpha_A} \sigma c' - 2L_0(\nu_K \tau_K), \quad (35)$$

$$\pi^{1/2} \nu_K - 2\alpha_A J_0(\eta) L_0(\nu_K, \tau_K) - L_1(\nu_K, \tau_K) - (1 - \alpha_A) L_1^*(\nu_K, \tau_K) = [J_1(\eta) - \frac{1}{2}\pi^{1/2} J_0(\eta)] \sigma c', \quad (36)$$

$$\begin{aligned} \frac{3}{2}\pi^{1/2}(\nu_K + \tau_K) - 2\alpha_A(J_2(\eta) + J_0(\eta)) L_0(\nu_K, \tau_K) - L_2(\nu_K, \tau_K) - (1 - \alpha_A) L_2^*(\nu_K, \tau_K) \\ = [J_3(\eta) - J_1(\eta) - \frac{1}{2}\pi^{1/2}(J_2(\eta) + J_0(\eta))] \sigma c', \end{aligned} \quad (37)$$

where 
$$\sigma = (2 - \alpha_A) \left(1 + \frac{m_A}{m_B}\right), \quad (38)$$

$$L_0(\nu_K, \tau_K) = \int_0^\infty \{\nu_K J_0(\zeta) + \frac{1}{2}\tau_K [J_2(\zeta) - \frac{1}{2}J_0(\zeta)]\} d\zeta, \quad (39)$$

$\alpha_A$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$b^0$	9.017	4.584	3.104	2.364	1.918	1.621	1.408	1.248	1.123	1.011

TABLE 1. Values of  $b^0$  for various  $\alpha_A$ 

$\alpha_A$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$C_{dA(A)}$	120.6	58.06	37.01	26.61	20.24	15.97	12.88	10.54	8.69	7.19

TABLE 2. Values of  $C_{dA(A)}$  for dibutyl phthalate  $m_B/m_A = 0.1043$ 

$$L_1(\nu_K, \tau_K) = \int_0^\infty [\nu_K J_{-1} + \frac{1}{2}\tau_K(J_1 - \frac{1}{2}J_{-1})] d\zeta, \quad (40)$$

$$L_1^*(\nu_K, \tau_K) = \int_0^\infty [\nu_K J_{-1}^* + \frac{1}{2}\tau_K(J_1^* - \frac{1}{2}J_{-1}^*)] d\zeta, \quad (41)$$

$$L_2(\nu_K, \tau_K) = \int_0^\infty [\nu_K(J_1 + J_{-1}) + \frac{1}{2}\tau_K(J_3 + \frac{1}{2}J_1 + \frac{1}{2}J_{-1})] d\zeta, \quad (42)$$

$$L_2^*(\nu_K, \tau_K) = \int_0^\infty [\nu_K(J_1^* + J_{-1}^*) + \frac{1}{2}\tau_K(J_3^* + \frac{1}{2}J_1^* + \frac{1}{2}J_{-1}^*)] d\zeta, \quad (43)$$

$$J_n(\eta) = \int_0^\infty t^n \exp\left(-t^2 - \frac{\eta}{t}\right) dt, \quad (44)$$

$$J_n \equiv J_n(|\eta - \zeta|), \quad (45)$$

$$J_n^* \equiv J_n(\eta + \zeta). \quad (46)$$

The integral equations (36) and (37) are to be solved simultaneously to give the values of functions  $\nu_K$  and  $\tau_K$ . As there seems no analytic method to solve the coupled Wiener-Hopf equations (36) and (37), one resorts to solving them numerically (see Appendix). Since the left-hand sides of (36) and (37) are linear and homogeneous relative to  $\nu_K, \tau_K$ , one can solve these equations once and for all for  $\sigma c' = 1$  and get  $\nu_K^0 = \nu_K|_{\sigma c'=1}, \tau_K^0 = \tau_K|_{\sigma c'=1}$ , then from (35) one also gets  $b^0 = b|_{\sigma c'=1}$ . A numerical calculation has been done for specific magnitudes of  $\alpha_A$ . The result for  $b^0$  is given in table 1.

$\nu_K, \tau_K$  and  $b$  for arbitrary  $\sigma c'$  can be obtained by multiplying  $\nu_K^0, \tau_K^0$  and  $b^0$  by  $\sigma c'$ , in particular

$$b = \sigma c' b^0 = (2 - \alpha_A) \left(1 + \frac{m_A}{m_B}\right) c' b^0. \quad (47)$$

The concentration-jump coefficient  $C_{dA}$  for specific values of  $\alpha_A$  and mass ratios  $m_A/m_B$  can be found from  $b^0$  given in table 1 and the following formula

$$C_{dA(A)} = \frac{b}{c\lambda_A} = \frac{3\pi^{\frac{1}{2}} b}{8 c'} = \frac{3\pi^{\frac{1}{2}}}{8} (2 - \alpha_A) \left(1 + \frac{m_A}{m_B}\right) b^0. \quad (48)$$

For a binary mixture of dibutyl phthalate and air,  $m_B/m_A = 29/278 = 0.1043$ ; the result for  $C_{dA(A)}$  is given in table 2.



### 5. Comparison with experimental results, and discussion

Birks & Bradley (1949) in their experiment obtained the evaporation rate of a dibutyl phthalate spherical droplet suspended in a capsule of absorbing wall in the continuum regime ( $K = 0$ ) and the slip regime (small  $K$ ). Simple analysis shows that, for a spherical droplet evaporating in a capsule, the radius of which is sufficiently large in comparison with that of the droplet, (4) and (5) are valid with high accuracy in the continuum and slip-flow regimes. So  $Q_C/Q_{SL}$  is linear in  $\lambda_A/a$  for  $\lambda_A/a$  small. One can easily find from the data of Birks & Bradley (1949) that  $C_{dA(B)} = 1.2$  (see also Hidy & Brock 1970). At the same time Birks & Bradley directly measured the rate of mass transfer by evaporating a flat surface of dibutyl phthalate under high vacuum conditions and found  $\alpha_A = 0.69$ .

The calculation in the previous section has given the values of  $C_{dA(A)}$ . To compare with the experiment we have the relationship between  $C_{dA(A)}$  and  $C_{dA(B)}$

$$C_{dA(A)} = \frac{\lambda_B}{\lambda_A} C_{dA(B)}. \tag{49}$$

For the case  $n_B \gg n_A$  we have

$$\lambda_B = \frac{1}{2^{1/2} n_B S_{BB}}, \quad \lambda_A = \frac{1}{n_B S_{AB} (m_A/\mu)^{1/2}}.$$

So  $C_{dA(A)}$  and  $C_{dA(B)}$  are related as

$$C_{dA(A)} = \left( \frac{m_A + m_B}{2m_B} \right)^{1/2} \frac{S_{AB}}{S_{BB}} C_{dA(B)} = \left( \frac{m_A + m_B}{2m_B} \right)^{1/2} \left( \frac{r_A + r_B}{2r_B} \right)^2 C_{dA(B)},$$

where  $r_A$  and  $r_B$  are collision radii for dibutyl phthalate and air respectively. The values of  $r_A$  found by Birks & Bradley (1949) vary from 4.45 Å to 5.44 Å depending on with which partner the collision radius of dibutyl phthalate is determined. Using the result  $C_{dA(B)} = 1.2$  derived from the data of Birks & Bradley, we have  $C_{dA(A)} = 7.88-10.55$  and according to our calculation we ought to put  $\alpha_A = 0.954-0.799$  (see table 2). The lower value agrees fairly well with  $\alpha_A = 0.69$  obtained from the direct measurement of the evaporation rate of dibutyl phthalate in vacuum. It should be pointed out that Birks & Bradley made their direct measurement of  $\alpha_A (= 0.69)$  only in passing to show that  $\alpha_A$  is near unity. The latter conclusion they drew from the measurement of  $Q_C/Q_{SL}$  from which we derived  $C_{dA(B)} = 1.2$ . So it would be incautious to draw definite conclusions about the accuracy of the above calculation from comparison with just one experimental result by Birks & Bradley. It seems to us appropriate to conduct more-direct measurement of  $C_{dA}$  and  $\alpha_A$  for dibutyl phthalate and other substances.

Our analysis of the concentration-jump coefficient for a rarefied binary gas mixture is preliminary. The kinetic model used here does not take into account the internal degrees of freedom, so in comparing theoretical results with experimental data for polyatomic gases, one ought to have some caution. It is of interest to have experimental data for cases of not small  $n_A$  and to compare them with theory.

This work was initiated at the Institute of Mechanics, Chinese Academy of Sciences, and was completed and revised during a stay at the Department of Applied Mathematics and Theoretical Physics, University of Cambridge. The author expresses his thanks to Professor G. K. Batchelor for his kind invitation and hospitality and also for useful discussion. Thanks are due also to Professor C. Cercignani, Professor

Y. Sone and Dr K. Aoki for useful discussions when the author presented this paper at the Euromech Colloquium 169 held at Trondheim, Norway, 20–23 June 1983. He also wishes to acknowledge The Royal Society and British Petroleum for their support during his period of stay at Cambridge.

## Appendix

Expanding  $\nu_K, \tau_K$  as polynomials of  $J_n(\eta)$  (Sone 1964)

$$\nu_K = \sum_{n=0}^m a_n J_n(\eta),$$

$$\tau_K = \sum_{n=0}^m b_n J_n(\eta),$$

substituting into (36) and (37), multiplying the obtained equations by  $\eta^l$  for  $l = 0, 1, \dots, m$  (the moment equations for  $l = m + 1$  are unnecessary in our case, as  $a'$  and  $d$  have been determined to be zero from (24) and (26), which lead to (36) and (37)) and integrating over  $\eta$  from 0 to  $\infty$ , one obtains the following algebraic equations for  $a_n, b_n$  ( $n = 0, \dots, m$ ):

$$\begin{aligned} & \sum_{n=0}^m [\pi^{\frac{1}{2}} I_{l_0} - 2\alpha_A I_{l_0} J_{n+2}(0) E_{0n}^{-1} - H_{ln}^{-1} - (1 - \alpha_A) G_{ln}^{-1}] a_n \\ & + \sum_{n=0}^m [-\alpha_A I_{l_0} (J_{n+4}(0) E_{2n}^{-1} - \frac{1}{2} J_{n+2}(0) E_{0n}^{-1}) - \frac{1}{2} (H_{ln}^1 - \frac{1}{2} H_{ln}^{-1}) - \frac{1}{2} (1 - \alpha_A) (G_{ln}^1 - \frac{1}{2} G_{ln}^{-1})] b_n \\ & = (I_{l_0} - \frac{1}{2} \pi^{\frac{1}{2}} J_{l_0}) \sigma c' \quad (l = 0, 1, \dots, m), \quad (\text{A } 1) \end{aligned}$$

$$\begin{aligned} & \sum_{n=0}^m [\frac{3}{2} \pi^{\frac{1}{2}} I_{ln} - 2\alpha_A (I_{l_2} + I_{l_0}) J_{n+2}(0) E_{0n}^{-1} - (H_{ln}^1 + H_{ln}^{-1}) - (1 - \alpha_A) (G_{ln}^1 + G_{ln}^{-1})] a_n \\ & + \sum_{n=0}^m [\frac{3}{2} \pi^{\frac{1}{2}} I_{ln} - \alpha_A (I_{l_2} + I_{l_0}) (I_{n+4}(0) E_{2n}^{-1} - \frac{1}{2} J_{n+2}(0) E_{0n}^{-1}) \\ & - \frac{1}{2} (H_{ln}^3 + \frac{1}{2} H_{ln}^1 + \frac{1}{2} H_{ln}^{-1}) - \frac{1}{2} (1 - \alpha_A) (G_{ln}^3 + \frac{1}{2} G_{ln}^1 + \frac{1}{2} G_{ln}^{-1})] b_n \\ & = [I_{l_3} + I_{l_1} - \frac{1}{2} \pi^{\frac{1}{2}} (I_{l_2} + I_{l_0})] \sigma c' \quad (l = 0, 1, \dots, m), \quad (\text{A } 2) \end{aligned}$$

where  $I_{ln}, E_{ln}^k, H_{ln}^k, G_{ln}^k$  are definite integrals (Shen 1981):

$$\begin{aligned} I_{ln} &= \int_0^\infty \eta^l J_n(\eta) d\eta = l! J_{l+n+1}(0), \\ H_{ln}^k &= \int_0^\infty \eta^l d\eta \int_0^\infty J_n(\zeta) J_k d\zeta = I_{l, n+k+2} F_{ln}^k, \\ G_{ln}^k &= \int_0^\infty \eta^l d\eta \int_0^\infty J_n(\zeta) J_k^* d\zeta = I_{l, n+k+2} E_{ln}^k, \\ F_{ln}^k &= \int_0^1 \frac{c^n s^{k+1} [2c^{l+2} - (c+s) s^{l+1}]}{c^2 - s^2} ds, \quad c = (1 - s^2)^{\frac{1}{2}}, \\ E_{ln}^k &= \int_0^1 \frac{c^n s^{k+l+2}}{c+s} ds, \quad c = (1 - s^2)^{\frac{1}{2}}. \end{aligned}$$

The set of linear algebraic equations (A 1), (A 2) can easily be solved numerically; the accuracy of calculation can be achieved simply by using fine regions of integration

in the quadrature of  $F_{i_n}^k$  and  $E_{i_n}^k$  by a Gaussian method. The present numerical procedure has been tested for a one-component gas, and the result agrees with that obtained by a refined method in Sone & Onishi (1973) with five-figure accuracy (for  $m = 7$ ).

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