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Approximate theories of thermal diffusion

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Abstract. It is shown why any elementary theory of thermal diffusion must be inadequate if based solely on simple free-path ideas. A fairly elementary alternative theory is given, based on the assumption of a collision frequency that depends on the velocity.

1. Introduction

Approximate theories of viscosity, heat conduction and diffusion in gases appear in many text-books. They are normally based on the concept of the free path or (less often) the collision frequency; the one or the other is taken to have the same value for all molecules of a given gas or (what is roughly equivalent) a mean value of the quantity is used. The transport coefficients are found to be proportional to the mean free paths, or (in the case of a gas mixture) to a linear combination of them. Such approximate theories are useful because they give a simple illustration of the physical processes involved. However, their simplicity has its dangers as well as its advantages.

One danger is because the molecules enjoy a dual role. On the one hand, they are 'carrier' molecules; their velocity distribution is somewhat different from that in a uniform gas, because of the property they are transporting (number of molecules, momentum or energy). On the other hand, they are regarded as forming a background of 'field' molecules, which impede the transport by the 'carrier' molecules. When they are viewed as field molecules, the deviation of their velocity distribution from the steady state (Maxwellian) value is ignored; the collisions of carrier molecules with them are supposed to result simply in the surrender to them of the quantity being transported by the carriers.† So far as heat conduction and viscosity are concerned, this leads to no very great error. For diffusion the errors are more serious; conservation of momentum ensures that collisions between like particles do not destroy any common diffusion velocity possessed by both the carrier and the field particles. Thus collisions between like particles should be neglected in considering diffusion. A similar, but less obvious, correction is required if one is not to find that, starting with a gas at rest, one finishes one's calculations with a gas which is moving bodily as a result of diffusion.

More far-reaching difficulties are met in considering thermal diffusion. Whereas with the other transport phenomena a particular effect is due to a cause similar in nature (e.g. heat conduction is due to a temperature gradient), here the cause (temperature gradient) and the effect (diffusion) are different in nature. Thus, though one can argue that there is no reason why any macroscopic vector cause should *not* lead to any other vector effect, an approximate theory indicating how it happens is strictly desirable. Numerous attempts have been made to construct such a theory (Gillespie 1939, Fürth 1942, Rai and Kothari 1943, Whalley and Winter 1950, Laranjeira 1960, together with others like Frankel 1940, Cacciapuoti 1943, Furry 1948,

† For a Lorentzian gas, the heavy molecules do in fact behave as 'field' molecules in the sense indicated: see Wright (1970 b).

Wright 1970 a,b, which go beyond simple free-path ideas). None of the theories based purely on free-path ideas has proved adequate. This is shown not only by a comparison with exact general theory, but also by Frankel's (1940) brief argument indicating why thermal diffusion depends essentially on the exact laws of interaction between unlike molecules.

2. The formulae of exact theory

Exact theory for a binary monatomic mixture shows that to a first approximation the thermal diffusion ratio k_T is given, in terms of readily identifiable physical quantities, by the equation

$$k_T = \frac{(C-1)(x_1 m_1 \lambda_2 - x_2 m_2 \lambda_1)}{nkD_{12}(m_1 + m_2)} \quad (1)$$

(Chapman and Cowling 1952—equations 9.8, **10**, **11**; 9.81, **1**; and the equations for $[\lambda]_1$ and $[k_T]_1$ at the top of pp. 166 and 167). In this, D_{12} , λ_1 , λ_2 denote first approximations to the diffusion coefficient and to the contributions by the two gases to the thermal conductivity; k is Boltzmann's constant; m_1 , m_2 are the molecular masses, and x_1 , x_2 the molar fractions n_1/n , n_2/n of the two gases (n_1 , n_2 , n are the number densities of the two gases and of the mixture). Finally, C is a pure number whose value depends only on the temperature and the law of interaction between unlike molecules; it is connected with D_{12} by

$$\frac{5}{2}(C-1) = 2 - T \frac{\partial}{\partial T} \ln(pD_{12}) \quad (2)$$

where p is the pressure and T the temperature. We may write

$$D_{12} = \frac{kT}{m_{12}n\bar{\nu}} \quad (3)$$

where m_{12} denotes the reduced mass $m_1 m_2 / (m_1 + m_2)$ and $n\bar{\nu}$ represents a (so far undefined) mean collision frequency. Then (2) becomes

$$\frac{5}{2}(C-1) = T \frac{\partial}{\partial T} \ln \bar{\nu}. \quad (4)$$

Monchick *et al.* (1966) suggested that the first approximation (1) also applies to diatomic and polyatomic gases, provided that λ_1 and λ_2 refer to the conduction of translational energy only. In a later paper, Monchick *et al.* (1968) found that small terms proportional to the conductivities for internal energy needed to be added; they also pointed out that for such gases C is no longer given exactly by equation (2).

In (1), k_T has to be found by proceeding to a higher order of approximation than is required to determine the first approximation D_{12} . Ignoring this discrepancy, we take $D_{12}k_T$ as giving the thermal diffusion coefficient D_T . Then from (1)

$$D_T = \frac{(C-1)T}{p} \frac{x_1 m_1 \lambda_2 - x_2 m_2 \lambda_1}{(m_1 + m_2)}. \quad (5)$$

Any really satisfactory approximate theory of thermal diffusion must yield an equation which mimics (5).

The form of (5) clearly shows that no theory depending purely on the simple free-path ideas can be satisfactory. Such a theory attempts to express D_T as a linear

function of free paths. However, though λ_1 and λ_2 can be taken as roughly proportional to free paths for the two gases, the factor $(C-1)$ introduces a completely different effect. It is possible to express C as the ratio of two different mean free paths, each involving only the collisions of unlike molecules. Such an extra complication is not envisaged in simple free-path theories.

The relative velocity V of thermal diffusion arising from a temperature gradient ∇T is given by

$$V = -\frac{D_T \nabla T}{x_1 x_2 T} = \frac{(C-1)(n_1 m_1 \mathbf{q}_2 - n_2 m_2 \mathbf{q}_1)}{n_1 n_2 k T (m_1 + m_2)} \quad (6)$$

where $\mathbf{q}_1, \mathbf{q}_2$ are the thermal fluxes $-\lambda_1 \nabla T, -\lambda_2 \nabla T$ transported by the two gases. Thus V can be interpreted as arising from the fluxes $\mathbf{q}_1, \mathbf{q}_2$, which are the direct consequence of the temperature gradient. These fluxes are processed, at the collisions of unlike molecules, to lead to relative diffusion (by the conservation of momentum, collisions of like particles cannot create a diffusion velocity). The value of the constant C is determined by the details of the processing mechanism. Equation (6), like those which precede it, represents a first approximation only; however, the same indication of a processing at the collisions of unlike molecules runs through the complicated formulae giving higher approximations.

3. An elementary interpretation of exact theory

The mechanism which processes $\mathbf{q}_1, \mathbf{q}_2$ to yield diffusion velocities is roughly as follows. Consider a mixture in which $m_1 > m_2$; this normally means that λ_1/n_1 , the conductivity of the first gas per particle, is less than λ_2/n_2 . Heat conduction occurs because at any point the molecules of either gas coming from the hot side include more fast (energetic) particles and fewer slow ones than those coming from the cold side. A collision between molecules tends, on an average, to equalize their velocities. In collisions between unlike molecules, if the probability of collisions is independent of the relative velocity, colliding molecules are simply a random selection of the whole; the mean velocity of molecules m_1 and m_2 before collision is zero, and collisions produce zero transfer of momentum from one gas to the other.

However, the probability of collisions may increase or decrease with the relative velocity g of the colliding molecules. For rigid spherical molecules it is proportional to g ; for inverse-square interaction the effective cross section is proportional to g^{-4} , and the collision probability to g^{-3} . If the probability increases with g , the colliding molecules are no longer a random selection but are weighted towards large values of g , and so towards large velocities of the colliding molecules. Since heat conduction requires that more fast molecules are moving down the temperature gradient than up it, the weighting implies that there is an unbalanced transfer of total momentum from each gas to the other at collisions. As a consequence of the heat flux \mathbf{q}_1/n_1 per molecule m_1 , the first gas exerts a force $\kappa_1 \mathbf{q}_1/n_1$ per unit volume on the second through collisions, and experiences an equal and opposite force $-\kappa_1 \mathbf{q}_1/n_1$; similar forces $\pm \kappa_2 \mathbf{q}_2/n_2$ arise from \mathbf{q}_2/n_2 , the heat flux per particle carried by the second gas. The total force per unit volume acting on the first gas is

$$\frac{\kappa_2}{n_2} \mathbf{q}_2 - \frac{\kappa_1}{n_1} \mathbf{q}_1 \quad (7)$$

and that on the second gas is equal and opposite.

The quantities κ_1, κ_2 in (7) are proportional to the number N_{12} of collisions between unlike molecules per unit volume and time, and also to the efficiency of the process which converts heat flux into momentum transfer. This efficiency is greater for \mathbf{q}_2 than for \mathbf{q}_1 , since it depends on g , which is determined predominantly by the larger velocities of the lighter molecules; thus $\kappa_1 < \kappa_2$. The forces on the gases produce a diffusion velocity V of the first gas relative to the second, which increases up to the point when the resistances $\mp \kappa'V$ (say), acting on the gases because of the collisions of unlike molecules, balance these forces. Thus the final V is given by

$$\kappa'V = \frac{\kappa_2}{n_2}\mathbf{q}_2 - \frac{\kappa_1}{n_1}\mathbf{q}_1. \quad (8)$$

Equation (8) agrees in form with (6); since $\kappa_2 > \kappa_1$ and $\lambda_2/n_2 > \lambda_1/n_1$, it correctly indicates that the heavy gas tends to diffuse towards the cooler regions. If m_1 and m_2 are nearly equal, the same is true of κ_1 and κ_2 ; in this case the gas diffusing towards the cooler regions is that corresponding to the lesser of λ_1/n_1 and λ_2/n_2 , which is the gas with the larger molecules. Since κ' , like κ_1 and κ_2 , is proportional to N_{12} , (8) indicates that V is proportional to the ratio of two quantities each proportional to the frequency of collisions between unlike particles, like the $(C-1)$ in (6). Thus we have been able to derive an approximate formulae which does indeed mimic (6).

In deriving (8) we assumed that the probability of collision increases with increasing g . If the reverse is the case, the signs of κ_1 and κ_2 in (8) are reversed; this still agrees with (6), since then, by equation (4), $(C-1)$ is negative.

The argument set out in this section is similar to that of Frankel (1940). However, whereas Frankel asserted that thermal diffusion occurs (in the case $C-1 > 0$) because the lighter molecules are held back from diffusing into the cooler regions, here we ascribe it to the lighter molecules actively pushing the heavy ones into the cooler parts.

4. A semi-elementary theory: heat conduction and diffusion

A theory leading to the actual formulae (4) and (6) requires some knowledge of the velocity distribution functions of the gases. Such a theory is no longer an elementary theory in the sense so far used; it demands integrations similar to those used in the general theory. It may, however, be of some interest to indicate, in as elementary a way as possible, how such a theory can be constructed.

In large measure the notation of Chapman and Cowling (1952) will be used; in particular, $\mathbf{c}_1, \mathbf{c}_2$ denote molecular velocities, $\partial/\partial\mathbf{c}_1$ denotes a gradient in velocity-space and $d\mathbf{c}_1$ a volume-element in velocity-space. However, somewhat modifying that notation, the velocity distribution functions for the two gases will be denoted by n_1f_1, n_2f_2 . Thus, for example, the Maxwellian velocity distribution for the first gas at rest is $n_1f_1^{(0)}$, where

$$f_1^{(0)} = \left(\frac{m_1}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_1\mathbf{c}_1^2}{2kT}\right). \quad (9)$$

For simplicity we shall use the collision interval rather than the free path. In discussing heat conduction it is sufficient to regard the collision intervals τ_1, τ_2 for molecules of the two gases as independent of the velocity. (They are 'ideal' collision intervals, adjusted to take account not only of the frequency of collisions but also of their efficiency in obstructing the transport of heat). Thus a molecule m_1 reaching the point r with velocity \mathbf{c}_1 can be regarded as having undergone its last collision, on

an average, at the point $\mathbf{r} - \mathbf{c}_1\tau_1$, and to have properties characteristic of that point. This means that the velocity distribution in a gas at non-uniform temperature (but uniform composition and pressure) is given to the first order in τ_1 by

$$\begin{aligned} n_1(\mathbf{r})f_1(\mathbf{c}_1, \mathbf{r}) &= n_1(\mathbf{r} - \mathbf{c}_1\tau_1)f_1^{(0)}(\mathbf{c}_1, \mathbf{r} - \mathbf{c}_1\tau_1) \\ &= n_1(\mathbf{r})f_1^{(0)}(\mathbf{c}_1, \mathbf{r}_1) - \mathbf{c}_1\tau_1 \cdot \nabla \{n_1(\mathbf{r})f_1^{(0)}(\mathbf{c}_1, \mathbf{r})\} \end{aligned}$$

or, since the partial pressure $p_1 (\equiv n_1kT)$ is uniform,

$$f_1 = f_1^{(0)} - kT(\mathbf{c}_1\tau_1 \cdot \nabla T) \frac{\partial}{\partial T} \left(\frac{f_1^{(0)}}{kT} \right). \quad (10)$$

The heat flux corresponding to this is

$$\begin{aligned} \mathbf{q}_1 &= \int \frac{1}{2} m_1 c_1^2 \mathbf{c}_1 n_1 f_1 d\mathbf{c}_1 \\ &= -p_1\tau_1 \int \frac{1}{2} m_1 c_1^2 \mathbf{c}_1 (\mathbf{c}_1 \cdot \nabla T) \frac{\partial}{\partial T} \left(\frac{f_1^{(0)}}{kT} \right) d\mathbf{c}_1 \\ &= -\frac{1}{3} p_1\tau_1 \nabla T \frac{\partial}{\partial T} \left(\frac{1}{kT} \int \frac{1}{2} m_1 c_1^4 f_1^{(0)} d\mathbf{c}_1 \right) \\ &= -\frac{5}{2} p_1\tau_1 \nabla T \frac{\partial}{\partial T} \left(\frac{kT}{m_1} \right) = -\frac{5}{2} \frac{p_1\tau_1 k}{m_1} \nabla T. \end{aligned} \quad (11)$$

Hence $\lambda_1 = \frac{5}{2} p_1\tau_1 k/m_1$, and (10) can be written

$$f_1 = f_1^{(0)} - \frac{2\lambda_1}{5kn_1} (\mathbf{c}_1 \cdot \nabla T) \frac{\partial}{\partial T} \left(\frac{m_1 f_1^{(0)}}{kT} \right). \quad (12)$$

The form of the relation connecting λ_1 and τ_1 is unimportant; the important feature is the expression (12) for f_1 . This agrees with the first approximation of Chapman and Cowling (1952), adjusted to give the conductivity λ_1 .

In discussing diffusion we no longer assume a constant collision interval, because of the need to derive an equation like (4). We introduce a quantity $\nu(\mathbf{g})$, such that if a uniform stream n_1' per unit volume of molecules m_1 with velocity \mathbf{c}_1 is moving through a similar stream, n_2' per unit volume, of molecules m_2 with velocity \mathbf{c}_2 , the number of collisions between molecules of the two streams per unit volume and time is $n_1'n_2'\nu(\mathbf{g})$, where $\mathbf{g} = \mathbf{c}_2 - \mathbf{c}_1$. The collisions again are ideal collisions; they cannot alter the total momentum of the colliding molecules but are supposed to change their velocities to values which, for each molecule, are supposed randomly about a mean value equal to the velocity \mathbf{G} of their common mass-centre, given by

$$(m_1 + m_2)\mathbf{G} = m_1\mathbf{c}_1 + m_2\mathbf{c}_2. \quad (13)$$

This means that at each collision the molecule m_1 receives, on an average, the momentum $m_1(\mathbf{G} - \mathbf{c}_1) \equiv m_{12}\mathbf{g}$, where m_{12} again denotes the reduced mass $m_1m_2/(m_1 + m_2)$. Similarly the molecule m_2 loses this momentum.

The velocity-distribution functions during diffusion are taken to be Maxwellian functions relative to the diffusion velocities \mathbf{c}_1' , \mathbf{c}_2' as means. Thus now

$$f_1(\mathbf{c}_1) = f_1^{(0)}(\mathbf{c}_1 - \mathbf{c}_1') \simeq f_1^{(0)}(\mathbf{c}_1) - \mathbf{c}_1' \cdot \frac{\partial f_1^{(0)}}{\partial \mathbf{c}_1} = f_1^{(0)} \left(1 + \frac{m_1 \mathbf{c}_1' \cdot \mathbf{c}_1}{kT} \right) \quad (14)$$

and similarly for f_2 . The total rate of transfer of momentum per unit volume from the second gas to the first at collisions accordingly is

$$n_1 n_2 \iint f_1(\mathbf{c}_1) f_2(\mathbf{c}_2) m_{12} \mathbf{g} \nu(\mathbf{g}) d\mathbf{c}_1 d\mathbf{c}_2 \simeq n_1 n_2 \iint f_1^{(0)} f_2^{(0)} \left(1 + \frac{m_1 \mathbf{c}_1' \cdot \mathbf{c}_1 + m_2 \mathbf{c}_2' \cdot \mathbf{c}_2}{kT} \right) m_{12} \mathbf{g} \nu(\mathbf{g}) d\mathbf{c}_1 d\mathbf{c}_2. \quad (15)$$

The part of (15) arising from unity in the bracket is the integral of an odd function of the velocities, and so vanishes. The remaining part is evaluated by expressing $\mathbf{c}_1, \mathbf{c}_2$ in terms of \mathbf{G}, \mathbf{g} by the relations

$$\mathbf{c}_1 = \mathbf{G} - \frac{m_2 \mathbf{g}}{m_1 + m_2}, \quad \mathbf{c}_2 = \mathbf{G} + \frac{m_1 \mathbf{g}}{m_1 + m_2}. \quad (16)$$

At the same time $d\mathbf{c}_1 d\mathbf{c}_2$ can be replaced by $d\mathbf{G} d\mathbf{g}$, and $f_1^{(0)} f_2^{(0)}$ by $F^{(0)} f^{(0)}$, where $F^{(0)}, f^{(0)}$ are Maxwellian functions similar to $f_1^{(0)}, f_2^{(0)}$, but involving \mathbf{G}, \mathbf{g} as velocities, and $m_1 + m_2, m_{12}$ as masses. Then on carrying out the integration with respect to \mathbf{G} , (15) becomes

$$n_1 n_2 \int f^{(0)} \frac{m_{12}}{kT} \left\{ (\mathbf{c}_2' - \mathbf{c}_1') \cdot \mathbf{g} \right\} m_{12} \mathbf{g} \nu(\mathbf{g}) d\mathbf{g} = -\frac{1}{3} n_1 n_2 V \int f^{(0)} \frac{m_{12}^2 g^2}{kT} \nu(\mathbf{g}) d\mathbf{g} \quad (17)$$

where V is the velocity of relative diffusion, $\mathbf{c}_1' - \mathbf{c}_2'$. We define a mean value $\bar{\nu}$ of $\nu(\mathbf{g})$ by the equation

$$\int f^{(0)} \frac{m_{12} g^2}{kT} \nu(\mathbf{g}) d\mathbf{g} = \bar{\nu} \int f^{(0)} \frac{m_{12} g^2}{kT} d\mathbf{g} = 3\bar{\nu}. \quad (18)$$

Then the momentum transfer (17) becomes

$$-n_1 n_2 \bar{\nu} m_{12} V. \quad (19)$$

If the molecules m_1, m_2 were set diffusing by total forces $\mathbf{P}, -\mathbf{P}$ per unit volume acting on them, \mathbf{P} would have to balance the rate (19) of transfer of momentum. Thus the velocity of diffusion V due to forces $\pm \mathbf{P}$ is found to be given by

$$\mathbf{P} = n_1 n_2 \bar{\nu} m_{12} V. \quad (20)$$

According to the general theory of diffusion, this is equivalent to

$$nD_{12}\mathbf{P} = n_1 n_2 kTV.$$

Hence

$$nD_{12}\bar{\nu} = kT/m_{12} \quad (21)$$

showing that $\bar{\nu}$ is identical with the $\bar{\nu}$ of equation (3). By the definition (18), $n_2 \bar{\nu}, n_1 \bar{\nu}$ denote the mean collision frequencies of molecules m_1, m_2 respectively, and the collision frequency $n\bar{\nu}$ of § 2 is the sum of these.

5. A semi-elementary theory: thermal diffusion

The discussion of thermal diffusion proceeds in much the same way, taking f_1 and f_2 to be given by (12) and a similar equation. There is a transfer of momentum \mathbf{P} per

unit volume and time from the second gas to the first at collisions, given by

$$\begin{aligned} \mathbf{P} &= n_1 n_2 \iint f_1 f_2 m_{12} \mathbf{g} \nu(g) d\mathbf{c}_1 d\mathbf{c}_2 \\ &\simeq -\frac{2m_{12}}{5k} \iint \left\{ n_2 f_2^{(0)} \lambda_1(\mathbf{c}_1 \cdot \nabla T) \frac{\partial}{\partial T} \left(\frac{m_1}{kT} f_1^{(0)} \right) \right. \\ &\quad \left. + n_1 f_1^{(0)} \lambda_2(\mathbf{c}_2 \cdot \nabla T) \frac{\partial}{\partial T} \left(\frac{m_2}{kT} f_2^{(0)} \right) \right\} \mathbf{g} \nu(g) d\mathbf{c}_1 d\mathbf{c}_2 \end{aligned} \quad (22)$$

the part of the integral involving $f_1^{(0)} f_2^{(0)}$ vanishing as before.

Since, by equation (9), $m_1 f_1^{(0)}/kT$ involves m_1 and T only in the combination m_1/kT ,

$$T \frac{\partial}{\partial T} \left(\frac{m_1}{kT} f_1^{(0)} \right) = -m_1 \frac{\partial}{\partial m_1} \left(\frac{m_1}{kT} f_1^{(0)} \right).$$

Hence in (22), if we regard $\nu(g)$ as independent of m_1 ,

$$\begin{aligned} &\iint n_2 f_2^{(0)} \lambda_1(\mathbf{c}_1 \cdot \nabla T) \frac{\partial}{\partial T} \left(\frac{m_1}{kT} f_1^{(0)} \right) \mathbf{g} \nu(g) d\mathbf{c}_1 d\mathbf{c}_2 \\ &= -\frac{\lambda_1 m_1 n_2}{T} \frac{\partial}{\partial m_1} \left(\frac{m_1}{kT} \int \int f_1^{(0)} f_2^{(0)}(\mathbf{c}_1 \cdot \nabla T) \mathbf{g} \nu(g) d\mathbf{c}_1 d\mathbf{c}_2 \right). \end{aligned}$$

The integral in this, like the corresponding integral in (15), is evaluated by changing the variables of integration to \mathbf{G} and \mathbf{g} . The resulting expression is

$$\frac{\lambda_1 m_1 n_2}{3T} \nabla T \frac{\partial}{\partial m_1} \left\{ \frac{m_{12}}{kT} \int f^{(0)} g^2 \nu(g) d\mathbf{g} \right\}.$$

Here $m_{12} f^{(0)}/kT$ involves m_{12} and T only in the combination m_{12}/kT ; hence, by an argument inverse to that just used, this expression is equivalent to

$$-\frac{\lambda_1 m_1 n_2}{3T} \nabla T \frac{\partial m_{12}}{\partial m_1} \frac{T}{m_{12}} \frac{\partial}{\partial T} \left\{ \int f^{(0)} \frac{m_{12} g^2}{kT} \nu(g) d\mathbf{g} \right\} = -\frac{m_2 n_2}{(m_1 + m_2)} \lambda_1 \nabla T \frac{\partial \bar{v}}{\partial T} \quad (23)$$

using equation (18).

The part of (22) involving λ_2 can be similarly evaluated. Thus (22) becomes

$$\mathbf{P} = \frac{2m_{12}}{5k(m_1 + m_2)} \frac{\partial \bar{v}}{\partial T} (n_2 m_2 \lambda_1 - n_1 m_1 \lambda_2) \nabla T. \quad (24)$$

Since \mathbf{P} , $-\mathbf{P}$ are to be regarded as forces acting on the two gases per unit volume, by equation (20) they produce a diffusion velocity \mathbf{V} given by

$$\mathbf{V} = \frac{2}{5kn_1 n_2} \left(\frac{n_2 m_2 \mathbf{Q}_1 - n_1 m_1 \mathbf{Q}_2}{m_1 + m_2} \right) \frac{\partial}{\partial T} (\ln \bar{v}). \quad (25)$$

The expressions for f_1 and f_2 given by (12) and a similar relation strictly need to be modified to allow for this diffusion velocity.

Equation (25) is identical with that derived from (4) and (6). The identity is not surprising. The integrations carried out here are equivalent to those of Chapman and Cowling (1952), though more simply expressed. Also the approximations made are those required to give agreement with the first approximation to exact theory. Seen by

themselves, they are not always consistent, e.g. in discussing diffusion the collision probability is supposed to depend on g , whereas the form (14) for f_1 strictly requires no such dependence.

Laranjeira (1960) found by approximate theory that if m_1/m_2 is large the thermal diffusion factor $\alpha_{12} \equiv k_T/x_1x_2$ varies roughly inversely as a linear function of the proportions x_1, x_2 . This result is also directly deducible by the present method. If m_1/m_2 is large, λ_2/λ_1 is in general large also; hence from (1), approximately

$$\alpha_{12}^{-1} \equiv \frac{x_1x_2}{k_T} = \frac{nkD_{12}}{(C-1)\lambda_2} = \frac{2nm_2D_{12}}{5(C-1)p}\tau_2^{-1}$$

since $\lambda_2 = \frac{5}{2}p x_2 \tau_2 k/m_2$. In this, nD_{12} is to a first approximation independent of density and composition; τ_2^{-1} is a collision frequency, which is a linear function of n_1 and n_2 . Hence α_{12}^{-1} is a linear function of x_1 and x_2 , which is Laranjeira's result. Laranjeira found that experimental results often suggest a similar linear dependence even when m_1/m_2 is not very different from unity; this is to be expected only if τ_1/τ_2 is nearly independent of the composition.

By inverting the steps of the argument of this and the preceding section, a theory of the diffusion thermo-effect can be given. As is to be expected, it agrees with the exact theory to a first approximation; if the total number-flow of molecules is zero ($n_1c_1' + n_2c_2' = 0$), a diffusion velocity V is found to lead to a heat flux equal to $p k_T V$, or

$$\frac{2}{5} \frac{m_{12}}{k} \frac{(n_1 m_1 \lambda_2 - n_2 m_2 \lambda_1)}{(m_1 + m_2)} T \frac{d\bar{v}}{dT} V \tag{26}$$

(cf. equations (1), (3) and (5)).

6. Conclusions

The theory given above strictly applies only to monatomic gases, and needs modification when applied to gases whose molecules possess internal energy. In § 4 the 'ideal' collision interval τ_1 was assumed to be adjusted to take account of the efficiency of collisions in obstructing the flux of energy. Since the efficiency is different for translational and internal energy, two different collision intervals τ_1, τ_1' must now be introduced, referring respectively to the translational and internal energies: corresponding to these, there are contributions λ_1, λ_1' and q_1, q_1' to the thermal conductivity and heat flux. If $\nu(g)$ is still regarded as depending only on g , and not on the internal energies of the colliding molecules, the translational and internal energies are effectively uncoupled, and equations of the form (1), (2) and (25) remain valid, the quantities λ_1, λ_2 and q_1, q_2 referring to the transport of translational energy only.

More correctly, $\nu(g)$ should be replaced by a quantity depending on the internal motions as well as on g . In this case, small terms involving the internal-energy fluxes q_1', q_2' appear in the equation (6) for the diffusion velocity; also the constant $(C-1)$ in the translational term is no longer given exactly by (2). The equation (1) can still be used as an approximation, taking λ_1 and λ_2 as referring to the translational conductivities, but some disagreement with (2) is then to be expected. Results given by Monchick *et al.* (1966) suggest that the experimental values of $(C-1)$ then found are often smaller than the values given by (2), and I have found similar results. A decreased value of $(C-1)$ would presumably imply a decreased efficiency in the conversion of heat fluxes into diffusion velocities through collisions. I have not been able to obtain a general proof that a decrease is to be expected.

Clearly the observed dependence of k_T on the distribution of mass in isotopic molecules (Becker and Beyrich 1952, de Vries *et al.* 1956, Schirdewahn *et al.* 1961) is to be explained as an effect of the internal energy of the molecules. Another effect which may have a similar explanation is the anomalous temperature variation in mixtures containing carbon dioxide, which appears to imply that $(C-1)$ passes through a positive minimum at relatively ordinary temperatures (Cozens and Grew 1964). The simple theory given here is able to indicate these possibilities, but it cannot fill in the details.

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