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HEAT CONDUCTION THROUGH A GAS WITH ONE INERT INTERNAL MODE

by

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Heat Conduction through a Gas with One Inert Internal Mode

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SUMMARY

The rate of energy transfer between parallel flat plates is evaluated when the (stagnant) gas between them is polyatomic with one inert internal mode. Deviations of the thermal conductivity from the complete equilibrium (Eucken) value are expressed in terms of the inert mode relaxation time and the effectiveness of the walls in exciting or de-exciting this mode. The results are obtained via a linear theory consistent with small temperature differences between the plates.

It is found that the Eucken-value of conductivity could be exceeded if the relaxation times are non-zero and the plates very effective in exciting the inert mode. When relaxation times are very short the effect of the walls on the energy transfer rate is small, but the walls make their presence felt by distorting the temperature profiles in "boundary layers" adjacent to the walls which are of order $\sqrt{D\tau}$ in thickness (D = diffusion coefficient, τ = relaxation time). This result is analogous to Hirschfelder's (1956) for the case of chemical reactions.

For experimental measurement of conductivity in a hot wire cell type of apparatus it is shown that extrapolation of measured reciprocal conductivities to zero reciprocal pressure should lead to the full Eucken value. It is also shown that the slope of reciprocal apparent (measured) conductivity versus reciprocal pressure curves is a function of relaxation time as well as of the accommodation coefficients. It is quite possible that the relaxation effect here is comparable with the temperature jump effects, even for rotation in diatomic molecules.

CONTENTS

NOTATION

$c^{(a)}$	Specific heat of active internal modes
$c^{(i)}$	Specific heat of inert internal mode
c_{vt}	Specific heat of translational mode
D	Diffusion coefficient
$e^{(int)}$	Mean internal energy per molecule
$e_j^{(int)}$	Internal energy of a molecule in j- th quantum state
$e^{(a)}$	Mean internal energy per molecule in active modes
$e^{(i)}$	Mean internal energy per molecule in inert modes
h_j	Enthalpy per molecule in j- th state
k	Boltzmann's Constant
$Le^{(a)}$	Lewis number based on $c^{(a)}$ (Eq. 11)
$Le^{(i)}$	Lewis number based on $c^{(i)}$ (Eq. 22)
ℓ	Mean free path
m	Mass of a molecule
n	Number of molecules per unit volume
n_j	Number of molecules in j- th state per unit volume
N	Number of collisions to excite inert modes
p	Pressure
$\dot{q}$	Energy flux
$r^{(i)}$	Inert mode accommodation coefficient
r	Translational temperature accommodation coefficient

Notation (Continued)

T	Translational temperature
$T^{(i)}$	Inert mode temperature
ΔT	Translational temperature jump
u_j	Diffusion velocity of molecules in j-th state
y	Co-ordinate perpendicular to plates
α	Defined in Eq. 29)
δ	Plate separation distance
λ	"Monatomic" thermal conductivity
$\lambda^{(a)}$	λ corrected to account for active modes
τ	Relaxation time for inert mode
Ω	Mean molecular velocity

Suffixes

w	Value at y = 0
δ	Value at y = δ
o	Mean value in gas layer

Other symbols are defined in the text.

1. Introduction

Heat conduction through polyatomic gases is complicated by the interchanges of energy which take place between the internal and translational modes of motion of the gas molecules. So far, the cross-sections for these inelastic collisions have not been estimated for realistic molecular models (Hirschfelder, Curtiss and Bird, 1954), so that although the formal kinetic theory for polyatomic molecules exists (Wang Chang and Uhlenbeck, 1951) no practical use can yet be made of it.

In the event that excitation of the internal modes is very easy, implying a very short time lag for adjustment of the mode to a full equilibrium state, it is reasonable to assume, at least in a first approximation, that equilibrium prevails throughout. This is the basis of the Eucken correction to thermal conductivity to account for the participation of the internal modes (see Hirschfelder et al, loc. cit.). However, not all internal modes of motion have relaxation times short enough to be treated in this way and it is of interest to enquire how so-called "inert" internal modes will affect rates of heat conduction.

We consider the simple problem of the evaluation of heat transfer rate between two horizontal, parallel flat plates, the upper being the hotter of the two, when the intervening space between them is filled with a pure gas whose molecules have one inert internal mode. For example, the gas may be nitrogen at a temperature such that both rotations and vibrations of the molecules are excited but no dissociation or electronic excitation is present. In that case we would assume that the rotations were in equilibrium with the translational modes and count vibration as the inert mode. (Rotations in nitrogen are excited in a few collisions whilst vibrations may require several thousand collisions). For such a set up one may reasonably neglect changes of hydrostatic pressure across the gas layer and, with the hot plate uppermost, natural convection is absent. (The system is entirely the same as the one used by Hirschfelder (1956) to study heat conduction in chemically reacting gas mixtures).

2. The Equations

Once a steady state has been established, the energy equation yields the simple solution

$$- \dot{q} = \text{constant} = - \dot{q}_w \ , \tag{1}$$

where $\dot{q}$ is the energy flux vector (with but one component, in the y-direction, in the present instance) and $- \dot{q}_w$ is the energy transfer rate into the lower wall. In a pure gas all molecules are of the same mass, m, and consequently there is no thermal diffusion present. However, each molecule will not be in the same internal quantum state and we can use the set of quantum numbers which define an internal state to distinguish one molecule from another. That is, we may regard the mixture as made up of a number of different "chemical species". In that event kinetic theory relates the energy flux vector to the temperature gradients and the appropriate diffusion velocities as follows ,

$$- \dot{q} = \lambda \frac{dT}{dy} - \sum_j h_j n_j u_j \tag{2}$$

In Eq.2 T refers to the temperature of the translational modes and λ is a coefficient of thermal conductivity evaluated on the assumption that the molecules behave as monatomic particles (i.e. their internal degrees of freedom play no part in its evaluation). The summation term represents the energy flux arising from interdiffusion of the different "species". h_j is the average enthalpy per molecule in the j-th quantum state, n_j the relevant number density and u_j the diffusion velocity of this particular "species".

h_j can be written as

$$h_j = \frac{5}{2} kT + e_j^{(int)} \tag{3}$$

where $e_j^{(int)}$ represents the energy of the internal modes in quantum state j, per molecule. (k is Boltzmann's Constant). It follows that

$$\sum_j h_j n_j u_j = \sum e_j^{(int)} n_j u_j \ , \tag{4}$$

since all particles have the same mass m, and $\sum_j m n_j u_j = 0$ by definition of the diffusion velocities.

The force field surrounding a molecule is, strictly, dependent on its internal quantum state, so that a different diffusion coefficient will arise for each of the different "species" in the mixture. However, the differences are usually very small and in the present treatment we will assume that diffusion of all molecules is adequately described in terms of the appropriate "monatomic" self-diffusion coefficient D, since we are dealing with a pure gas here. Following Hirschfelder et al (1954) we can then write

$$- n_j u_j = n D \frac{d}{dy} (n_j/n) , \qquad (5)$$

n being the total number of molecules per unit volume. Since the $e_j^{(int)}$ quantities are constants it follows from eqs. 4 and 5 that

$$- \dot{q} = \lambda \frac{dT}{dy} + n D \frac{de^{(int)}}{dy} , \qquad (6)$$

where

$$e^{(int)} = n^{-1} \sum_j n_j e_j^{(int)} \qquad (7)$$

is the mean internal energy per molecule. This quantity is now separated into parts which arise from the active and inert degrees of freedom,

$$e^{(int)} = e^{(a)} + e^{(i)} \qquad (8)$$

respectively. For simplicity the number of inert modes is restricted to one: no such restriction need be placed on the active degrees of freedom although in thinking of, say, diatomic molecules, only one such mode will arise. $e^{(a)}$ can be written as $\sum_j e_j^{(a)} (n_j/n)$ and it will be assumed that the distribution numbers n_j correspond to a Boltzmann arrangement of energies among the allowed levels which is specified by the translational temperature T. Consequently we can write

$$\frac{de^{(a)}}{dy} = \frac{de^{(a)}}{dT} \cdot \frac{dT}{dy} = c^{(a)} \frac{dT}{dy} . \qquad (9)$$

$c^{(a)}$ (which equals $\sum_j e_j^{(a)} d(n_j/n)/dT$) is the specific heat of the active modes, and it follows at once that eq. 6 can be re-expressed as follows,

$$- \dot{q} = \lambda (1 + Le^{(a)}) \frac{dT}{dy} + n D \frac{de^{(i)}}{dy} \qquad (10)$$

where

$$Le^{(a)} = \frac{n D c^{(a)}}{\lambda} \tag{11}$$

is a Lewis number based on the active mode's internal specific heat. Then

$$\lambda^{(a)} = \lambda(1 + Le^{(a)}) \tag{12}$$

is the Eucken-corrected value of conductivity to account for the instantaneous excitation of the active internal degrees of freedom.

Each "species" in the gas has its own continuity equation which, in the present simple case, has the form

$$\frac{d}{dy}(n_j u_j) = \omega_j . \tag{13}$$

ω_j is the volume rate of production of molecules in the j-th state as a result of purely gas phase encounters between molecules. With eqs. 5 and 7 it follows, on multiplication of eq. 13 by $e_j^{(int)}$ and summation over all quantum states j, that

$$-\frac{d}{dy}\left(n D \frac{de^{(int)}}{dy}\right) = \sum_j e_j^{(int)} \omega_j . \tag{14}$$

The term on the right hand side of eq. 14 represents the net rate at which energy enters the internal states per unit volume, and it will be a function of the population of all the states j, the transition probabilities between them and the rate at which molecules collide. In writing eq. 9 we have already dealt with the active modes, albeit approximately, so that eq. 14 must be reduced to an equation involving only excitation of the remaining, inert mode. Thus we write

$$-\frac{d}{dy}\left(n D \frac{de^{(i)}}{dy}\right) = R^{(i)} \tag{15}$$

where $R^{(i)}$ represents the rate of production of energy in the inert mode per unit volume. It should be noted that the treatment of internal energy from the assumption of eq. 8 onwards implies no cross-coupling between the active and inert internal motions. In general, if such coupling did exist, a part of the energy in the active mode would be a function of the population of the inert states. Insofar as we are assuming that the inert modes are not instantaneously excited, then at least a part of $e^{(a)}$ could not be represented as being in equilibrium with the translational temperature T. This requirement of no cross coupling is not necessary for eq. 15 as it stands, however, since $R^{(i)}$ could well include such effects.

The treatment of $R^{(i)}$ in terms of the appropriate transition probabilities, etc. would in general be very complicated, since transitions between any permitted levels for the mode are possible. Instead we shall assume that

$$R^{(i)} = -\frac{n}{\tau}\left(e^{(i)} - e_{eq}^{(i)}\right) . \qquad (16)$$

That is to say, we assume that excitation of the inert mode is directly proportional to the difference between the actual mean energy per molecule $e^{(i)}$ and the mean energy which a molecule would possess if the inert mode were in equilibrium with the actual local translational temperature, namely $e_{eq}^{(i)}$. This latter is therefore a function of T only. τ is a suitable relaxation time, determined by the transition probability values, etc. and the minus sign is necessary since, if $e^{(i)} > e_{eq}^{(i)}$, the natural process is one of de-excitation. τ is essentially positive. That results of the form 16 are valid approximations for small departures from equilibrium has been demonstrated by Herzfeld (1955) for the case of but two quantum states in the inert mode and also in the Landau and Teller case of the harmonic oscillator. In the latter event the mode is a multi-state one but transitions only occur between immediately adjacent levels. The validity of eq. 16 as an approximation in more general kinds of multi-state systems has recently been demonstrated by Shuler (1959).

Using the results 1, 10, 12, 15 and 16 the equations governing energy transfer rate between the two plates can now be written as

$$\lambda^{(a)} \frac{dT}{dy} + n D \frac{de^{(i)}}{dy} = -\dot{q}_w , \qquad (17)$$

$$\frac{d}{dy}\left(n D \frac{de^{(i)}}{dy}\right) = \frac{n}{\tau}\left(e^{(i)} - e_j^{(i)}\right) . \qquad (18)$$

3. The Linearised Problem

Eqs. 17 and 18 are non-linear; both $\lambda^{(a)}$ and n D are functions of T and τ is a function of n and T. In general $e^{(i)}_{eq}$ is a complicated function of T, too. For example the simple harmonic oscillator has $e^{(i)}_{eq} = k\,\theta_v\,(\exp(\theta_v/T) - 1)^{-1}$, where θ_v is the (constant) characteristic vibration temperature. However, if the difference in temperature between upper and lower plates is small we may reasonably take mean values for $\lambda^{(a)}$, n D, n and τ which are evaluated at, say, the arithmetic mean of T_δ and T_w. We note that, since $p = n\,k\,T$ and pressure will be constant, n varies inversely as T.

We shall also assume that a temperature $T^{(i)}$ can be defined which will specify the energy content of the inert mode. Then if $c^{(i)}$ is the specific heat of this particular degree of freedom we can write

$$e^{(i)} = \int_0^{T^{(i)}} c^{(i)}\, dT^{(i)} \quad . \tag{19}$$

$e^{(i)}_{eq}$ will be given by a similar integral in which $T^{(i)}$ is replaced by T. In the linear problem we may expect to find $T^{(i)}$ but little different from T and, accordingly, it will be sufficiently accurate to use a mean value of $c^{(i)}$ which is consistent with the general temperature level of the system.

Under the conditions stated, eqs. 17 and 18 are now written in approximate form, suffix o denoting constant mean value,

$$\lambda^{(a)}_o \left(\frac{dT}{dy} + Le^{(i)} \frac{dT^{(i)}}{dy} \right) = - \dot{q}_w \quad , \tag{20}$$

$$\lambda^{(a)}_o\, Le^{(i)}\, \frac{d^2 T^{(i)}}{dy^2} = \frac{n_o\, c^{(i)}_o}{\tau_o} \left(T^{(i)} - T\right) . \tag{21}$$

$Le^{(i)}$ is a Lewis number based on the chosen mean specific heat $c^{(i)}_o$ and $\lambda^{(a)}_o$, namely

$$Le^{(i)} = \frac{n_o\, D_o}{\lambda^{(a)}_o}\, c^{(i)}_o \quad . \tag{22}$$

It should be observed that if $c^{(a)}$ is a constant, as it may well be if the active internal mode is a rotational one, then to a good degree of accuracy the group $n D/\lambda^{(a)}$ is a constant without further assumptions.

Elimination of $T^{(i)}$ between eqs. 20 and 21 gives an equation in T only, namely

$$\frac{d^3T}{dy^3} - \alpha^2 \frac{dT}{dy} = \beta \qquad (23)^*$$

where

$$\alpha^2 = \left(\frac{Le^{(i)} + 1}{\lambda_o^{(a)} Le^{(i)}} \right) \cdot \frac{n_o c_o^{(i)}}{\tau_o} = \frac{Le^{(i)} + 1}{\tau_o D_o} \qquad (24)$$

$$\beta = \frac{\dot{q}_w}{\lambda_o^{(a)^2} Le^{(i)}} \cdot \frac{n_o c_o^{(i)}}{\tau_o} = \frac{\dot{q}_w \alpha^2}{\lambda_o^{(a)} (1 + Le^{(i)})} \qquad (25)$$

It follows on elimination of T between eqs. 20 and 21, that $T^{(i)}$ satisfies an equation identical with eq. 23.

Eq. 23 has the solution

$$T = A e^{\alpha y} + B e^{-\alpha y} + C - \beta y/\alpha^2 \qquad (26)$$

and the constants A and B can be eliminated at once by noting that $T = T'_w$ when $y = 0$ and $T = T'_\delta$ when $y = \delta$. (T'_δ and T'_w are not the wall temperatures, but the gas temperatures immediately adjacent to the walls). Then

$$T = (T'_\delta - C + \beta\delta/\alpha^2) \frac{\sinh \alpha y}{\sinh \alpha\delta} + (T'_w - C) \frac{\sinh(\delta\alpha - y\alpha)}{\sinh \alpha\delta} + C - \beta y/\alpha^2 . \qquad \ldots\ldots (27)$$

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* Eq. 23 is a particularly simple form of singular perturbation equation as $\tau_o \to 0$. The behaviour of the solution for very small τ_o values is discussed in Section 4 (iii) below.

Remembering that $\dot{q}_w$ (and hence β) is still an unknown quantity, two more conditions are necessary to evaluate β and C. These extra conditions are related to the direct flux of inert mode energy into the walls which would result from de-excitation of a particle in the course of a collision with the plates. The process may be described as follows. The walls are being continually bombarded by gas molecules as a result of their thermal motions and, of these, a certain fraction may be adsorbed by the wall and remain there for a sufficient time for all of their degrees of freedom to come into complete equilibrium with the wall temperature. Eventually these particles will be re-emitted from the wall, having given up their excess inert mode energy.

Of course this type of process does not only apply to the inert energy mode; if energy is to be transferred to a surface from a gas in contact with it then the incident molecules must be de-excited to some lower energy state before they leave the surface again, and this will apply to all the energy modes which the molecules possess. However, we intend to separate the translational and active modes from the inert mode in what follows.

Let us suppose that, of the number of molecules incident on the surface, a fraction $r_w^{(i)}$ have their inert mode energy completely accommodated to a full equilibrium state at the surface temperature T_w. In this state the mean energy per molecule is denoted by $e_w^{(i)}$. The mean energy of the incident molecules will be denoted by $e^{(i)'}$. Then if s_w is the rate at which molecules strike unit area of the wall, the wall gains energy at a rate $s_w e^{(i)'}$ and loses it at a rate $r_w^{(i)} s_w e_w^{(i)} + (1 - r_w^{(i)}) s_w e^{(i)'}$. The nett rate of gain of inert mode energy is therefore

$$r_w^{(i)} \; s_w (e^{(i)'} - e_w^{(i)}) .$$

Of the layer of gas molecules immediately adjacent to the wall, on the average, one half have just arrived from some distance (of the order of a mean free path) above the wall, whilst the remaining half have just been re-emitted by the surface. Then $e_{av,w}^{(i)}$, the average inert mode energy in the layer adjacent to the wall, must be given by

$$e_{av,w}^{(i)} = \tfrac{1}{2} e^{(i)'} + \tfrac{1}{2} r_w^{(i)} \; e_w^{(i)} + \tfrac{1}{2} (1 - r_w^{(i)}) e^{(i)'} = (1 - r_w^{(i)}/2) e^{(i)'} + \tfrac{1}{2} r_w^{(i)} \; e_w^{(i)} .$$

It follows that $e^{(i)'}$ in the expression above can be replaced in terms of $e^{(i)}_{av,w}$ and $e^{(i)}_{w}$, whence the nett gain of energy per unit area of wall per unit time arising from de-excitation of the inert mode can be written as

$$\frac{2\, r_w^{(i)}}{2 - r_w^{(i)}} \cdot s_w \left(e^{(i)}_{av,w} - e^{(i)}_{w} \right) .$$

The quantity $r_w^{(i)}$ can be called the inert mode accommodation coefficient at the wall $y = 0$.

Now the flux of inert mode energy into the surface can be expressed in terms of the diffusion velocities also. It is clear that this expression for the lower wall, $y = 0$, is

$$- \sum_j e^{(i)}_j n_j u_j = \Sigma e^{(i)}_j \, n D \frac{d}{dy} (n_j/n) = n D \frac{de^{(i)}}{dy} ,$$

where $e^{(i)}_j$ is the inert mode energy in a molecule in the j-th internal quantum state. The minus sign is necessary because, with positive u_j values, $e^{(i)}_j$ is diffusing away from the wall. Equating this expression to the one involving $r_w^{(i)}$ gives the boundary condition at $y = 0$, namely

$$n_w D_w \left(\frac{de^{(i)}}{dy} \right)_{y=0} = \frac{2\, r_w^{(i)}}{2 - r_w^{(i)}} s_w \left(e^{(i)}_{av,w} - e^{(i)}_{w} \right) . \qquad (28)$$

Now if the mean free path, ℓ, and the mean molecular speed, Ω, are defined by

$$\ell = \left(\sqrt{2}\, n \pi \sigma^2 \right)^{-1} \quad : \quad \Omega = (8 k T/m\pi)^{\frac{1}{2}} , \qquad (29)$$

the rate of bombardment s_w is given by

$$s_w = \tfrac{1}{4} n_w \Omega_w \qquad (30)$$

and the exact kinetic theory for rigid sphere molecules gives

$$D_w = \frac{3\pi}{16} \ell_w \Omega_w \quad , \tag{31}$$

(see Hirschfelder, Curtiss and Bird, 1954): σ is the molecular diameter*. It follows from eqs. 28, 30 and 31 that

$$\left(\frac{de^{(i)}}{dy}\right)_{y=0} = \frac{r_w^{(i)}}{2 - r_w^{(i)}} \cdot \frac{8}{3\pi \ell_w} \left(e_{av,w}^{(i)} - e_w^{(i)}\right) . \tag{32}$$

Since the energy jump $e_{av,w}^{(i)} - e_w^{(i)}$ will be small, certainly in the linearised problem, eq. 32 can be written as

$$\left(\frac{dT^{(i)}}{dy}\right)_{y=0} = \Gamma'_w \left(T_w^{(i)} - T_w\right) , \tag{33}$$

where T_w is the actual temperature of the wall, and we have written

$$\Gamma'_w = \frac{r_w^{(i)}}{2 - r_w^{(i)}} \cdot \frac{8}{3\pi \ell_w} \tag{34}$$

Clearly a similar result must hold at the upper wall and we must have

$$\left(\frac{dT^{(i)}}{dy}\right)_{y=\delta} = - \Gamma'_\delta \left(T_\delta^{(i)} - T_\delta\right) . \tag{35}$$

(The minus sign arises because the energy diffusion rate into the upper wall is $+ \sum_j e_j^{(i)} n_j u_j$, etc.).

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* The molecular diameter σ implied in the value of D_w in eq. 31 can be taken as the exact kinetic theory value at the temperature T_w. σ is introduced here simply for convenience; any numerical values for transport coefficients etc. will be taken to be those appropriate to a Lennard-Jones 6-12 potential for the intermolecular forces. Ω in equation 29 is unambiguously defined and, if necessary, ℓ can be evaluated via eqs. 29 and 30 using the proper value for D.

Eqs. 20 and 21 show that

$$-\lambda_o^{(a)} \frac{d^2T}{dy^2} = \frac{n_o c_o^{(i)}}{\tau_o} (T^{(i)} - T) , \qquad (36)$$

whence, remembering that T here refers to the gas translational temperature, eqs. 33 and 35 can be expressed in terms of conditions on T. The values of T at $y = 0$ and $y = \delta$ have been written (see eq. 27) as T'_w and T'_δ respectively. They differ from the actual wall temperature by an amount equal to the appropriate temperature jumps, say ΔT_w and ΔT_δ, as follows

$$T_w = T'_w - \Delta T_w , \qquad (37a)$$

$$T_\delta = T'_\delta + \Delta T_\delta . \qquad (37b)$$

Then elimination of $T^{(i)}$ between eq.s 33, 35 and 36 leads to the boundary conditions

$$\left(\frac{dT}{dy}\right)_{y=0} - \tau_o \kappa \left(\frac{d^3T}{dy^3}\right)_{y=0} = \Gamma'_w \left\{ -\tau_o \kappa \left(\frac{d^2T}{dy^2}\right)_{y=0} + \Delta T_w \right\} , \qquad (38)$$

$$\left(\frac{dT}{dy}\right)_{y=\delta} - \tau_o \kappa \left(\frac{d^3T}{dy^3}\right)_{y=\delta} = \Gamma'_\delta \left\{ \tau_o \kappa \left(\frac{d^2T}{dy^2}\right)_{y=\delta} + \Delta T_\delta \right\} . \qquad (39)$$

where $\kappa = \lambda_o^{(a)} / n_o c_o^{(i)}$.

We will define an accommodation coefficient, r, for the translational and active degrees of freedom* in such a way that

$$r_w = \frac{e_m - e'}{e_w - e'} , \qquad (40)$$

where e is the sum of the mean translational energy ($3 k T/2$) and mean active internal mode energy ($e^{(a)}$). The suffixes, etc. have the following meanings. e_m is the mean energy of the molecules emitted by the walls,

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* See the comments on Page 22.

e_w is the energy e at the wall temperature value T_w and e' is the energy of the molecules incident on the wall. Then $e_m = r_w e_w + (1 - r_w)e'$, and, since one half of the molecules in the layer adjacent to the wall have just been re-emitted by the wall and the other half have just arrived from some distance above the wall comparable with a mean free path ℓ, the average value of e in this layer, e_{av}, must be given by $(1/2)e' + (1/2)e_m$. Since we can write $e' - e_{av} \simeq \ell_w^{(e)}(de/dy)$ it follows that the energy jump, $e_{av} - e_w$, is given by

$$e_{av} - e_w = \frac{2 - r_w}{r_w} \cdot \ell_w^{(e)} \left(\frac{de}{dy}\right)_{y=0} . \qquad (41)$$

We can write

$$e = \int_0^T (c_{vt} + c^{(a)})\, dT$$

where c_{vt} is the translational specific heat, $3k/2$.

In the event that $c^{(a)}$ is a constant, or does not vary appreciably over the range T'_w to T_w, it follows that eq. 41 is the same as

$$\Delta T_w = \frac{2 - r_w}{r_w} \cdot \ell_w^{(e)} \left(\frac{dT}{dy}\right)_{y=0} . \qquad (42)$$

To find $\ell_w^{(e)}$ we note that the wall gains energy at a rate $s_w(e' - e_m) = s_w r_w(e' - e_w) = 2 s_w(e' - e_{av})$ from the translational and active modes, and that this can be equated to the appropriate part of $-\dot{q}_w$ in eq. 10, (for example); i.e. we write

$$\lambda_w (1 + Le^{(a)}) \left(\frac{dT}{dy}\right)_{y=0} = 2 s_w(e' - e_{av}) = 2 s_w \ell_w^{(e)}(c_{vt} + c^{(a)})\left(\frac{dT}{dy}\right)_{y=0} \qquad (43)$$

But in terms of the rigid sphere values defined above

$$\lambda_w = \frac{25\pi}{64} \cdot n_w \ell_w \Omega_w c_{vt} . \qquad (43a)$$

In fact, the cross section $\pi\sigma^2$ implied here is slightly different from the value used in defining D above, and we should decrease λ_w by a factor 1.1 approximately, for Lennard-Jones type molecules, (see Hirschfelder et al, 1954). With the corrected value for λ_w it follows from eq. 43 that

$$\ell_w^{(e)} = \frac{25\pi}{35.2} \left(\frac{c_{vt} + 0.528\, c^{(a)}}{c_{vt} + c^{(a)}} \right) \ell_w \,. \tag{44}$$

(This shows that $\ell_w^{(e)}$ is 2.23 ℓ_w when $c^{(a)} = 0$, decreasing to 1.81 ℓ_w when $c^{(a)} = k$, the value for a diatomic molecule with fully excited rotation).

An alternative form of the ratio $\ell_w^{(e)} / \ell_w$ can be found via eqs. 11, 30, 31 and 43 and gives

$$\frac{8}{3\pi} \cdot \frac{\ell_w^{(e)}}{\ell_w} = \frac{c^{(a)}}{Le^{(a)}} \cdot \frac{1 + Le^{(a)}}{c_{vt} + c^{(a)}} \,. \tag{44a}$$

The temperature jump can now be written as

$$\Delta T_w = a_w \ell_w \left(\frac{dT}{dy} \right)_{y=0} \tag{45}$$

where

$$a_w = \frac{25\pi}{35.2} \left(\frac{c_{vt} + 0.528\, c^{(a)}}{c_{vt} + c^{(a)}} \right) \cdot \frac{2 - r_w}{r_w}$$

$$= \frac{3\pi}{8} \frac{c^{(a)}}{Le^{(a)}} \cdot \frac{1 + Le^{(a)}}{c_{vt} + c^{(a)}} \cdot \frac{2 - r_w}{r_w} \tag{46}$$

A similar result will hold for the temperature jump at the upper wall, ΔT_δ. Finally then, the required boundary conditions can be expressed in the form

$$(1 - \Gamma_w) \left(\frac{dT}{dy} \right)_{y=0} - \tau_o \kappa \left(\frac{d^3T}{dy^3} \right)_{y=0} = - \Gamma'_w \tau_o \kappa \left(\frac{d^2T}{dy^2} \right)_{y=0} \tag{47}$$

$$(1 - \Gamma_\delta) \left(\frac{dT}{dy} \right)_{y=\delta} - \tau_o \kappa \left(\frac{d^3T}{dy^3} \right)_{y=\delta} = \Gamma'_\delta \tau_o \kappa \left(\frac{d^2T}{dy^2} \right)_{y=\delta} \tag{48}$$

where $$\Gamma_w = \Gamma'_w a_w \ell_w \; ; \Gamma_\delta = \Gamma'_\delta \; a_\delta \; \ell_\delta . \qquad (49)$$

Putting in the appropriate values for the derivatives from eq. 27 enables the constants β and C to be found, and hence the values of energy transfer rate and temperature distribution in the gas. The algebra involved is rather heavy, but eventually it can be shown that

$$- \dot{q}_w \; \delta \left\{ 1 + Le^{(i)} \, Q(\delta\alpha)^{-1} \right\} = (T'_\delta - T'_w) \, \lambda_o^{(a)} (1 + Le^{(i)}), \qquad (50)$$

$$\frac{T - T'_w}{T'_\delta - T'_w} = \frac{Le^{(i)}}{\delta\alpha + Le^{(i)}_Q} \left\{ \frac{B_\delta - Q/\sinh \delta\alpha}{C_\delta + \coth \delta\alpha - 1/\sinh \delta\alpha} \left(\frac{\sinh y\alpha}{\sinh \delta\alpha} \right) \right.$$

$$\left. + \frac{B_w - Q/\sinh\delta\alpha}{C_w + \coth\delta\alpha - 1/\sinh \delta\alpha} \left(1 - \frac{\sinh(\delta\alpha - y\alpha)}{\sinh \delta\alpha} \right) \right\} + \frac{y\alpha}{\delta\alpha + Le^{(i)}_Q} \; .$$

$$\ldots\ldots \qquad (51)$$

It can also be shown that $(T^{(i)} - T_w^{(i)})/(T_\delta^{(i)} - T_w^{(i)})$ is given by an expression similar to eq. 51 with the denominator $\delta\alpha + Le^{(i)}_Q$ replaced by $\delta\alpha - Q$ and the factor $Le^{(i)}$ multiplying the curly bracket term replaced by -1. It can be shown in addition that

$$(T_\delta^{(i)} - T_w^{(i)}) \; (1 - Q/\delta\alpha)^{-1} = (T'_\delta - T'_w) \; (1 + Le^{(i)}_{Q/\delta\alpha})^{-1} . \qquad (52)$$

The quantities appearing in eqs. 50 to 52 are defined as follows :-

$$Q = \frac{(B_w + B_\delta)(\coth\delta\alpha - 1/\sinh\delta\alpha) + B_w C_\delta + B_\delta C_w}{(\coth\delta\alpha + C_w)(\coth\delta\alpha + C_\delta) - 1/\sinh^2\delta\alpha} , \qquad (53)$$

$$B_n = \frac{1 - \Gamma_n}{1 + Le^{(i)} \, \Gamma_n} , \quad n = w \text{ or } \delta , \qquad (54)$$

$$C_n = \frac{\Gamma_n (1 + Le^{(i)})}{1 + Le^{(i)} \Gamma_n} \cdot (\alpha a_n \; \ell_n)^{-1} , \; n = w \text{ or } \delta, \qquad (55)$$

It should be noted from eqs. 34, 46 and 49 that the Γ_n quantities can be written as

$$\Gamma_n = \frac{c^{(a)}}{Le^{(a)}} \cdot \frac{1 + Le^{(a)}}{c_{vt} + c^{(a)}} \cdot \frac{2 - r_n}{2 - r_n^{(i)}} \cdot \frac{r_n^{(i)}}{r_n} \quad , n = w \text{ or } \delta \quad (56)$$

(Of the remaining quantities in the above equations, α is defined in eqs. 24, a_n in eqs. 46 and ℓ_n in eqs. 29).

4. Special Cases

The results just derived are quite complicated, despite the simplifications introduced by linearization of the problem, and it is therefore worthwhile to investigate some special situations in some detail.

(i) $c_o^{(i)} = 0$.

When $c_o^{(i)} = 0$, the inert mode can be assumed to have no communicable energy. The addition of a constant to the right-hand side of eq. 19 does not affect the subsequent analysis, so that the energy stored in the inert mode need not necessarily be zero in these circumstances. $c_o^{(i)} = 0$ implies that $Le^{(i)}$ is zero, whence it follows directly from eqs. 50 to 56 that

$$- \dot{q}_w \delta = \lambda_o^{(a)} (T'_\delta - T'_w) , \quad (57)$$

$$T - T'_w = (T'_\delta - T'_w)(y/\delta) . \quad (58)$$

In order to find $\dot{q}_w$ in terms of the actual wall temperatures T_δ and T_w, the temperature jumps must be evaluated, as follows.

$$\Delta T_w = a_w \ell_w \left(\frac{dT}{dy}\right)_{y=0} = a_w (\ell_w / \delta)(T'_\delta - T'_w) = a_w (\ell_w / \delta)(-\dot{q}_w \delta)/\lambda_o^{(a)},$$

with a similar result for ΔT_δ. Consequently we have

$$- \dot{q}_w \delta \left[1 + (a_w \ell_w + a_\delta \ell_\delta)/\delta \right] = \lambda_o^{(a)} (T_\delta - T_w) . \quad (59)$$

Since the a_n and ℓ_n quantities are essentially positive, it follows that the temperature jump at the walls reduces the energy flux, a well known result. The theory presented here is only valid for $(\ell_n/\delta) << 1$ so that, to a first approximation, the reduction is a linear function of (ℓ_n/δ). The mean free path can be expressed in terms of p and T rather than n, namely,

$$\ell = k\,T/\sqrt{2}\,\pi\,\sigma^2\,p, \tag{60}$$

so that the energy flux is slightly pressure dependent for given values of T_δ , T_w, etc.

Otherwise, in the present case, the flux only depends on the value of conductivity corrected to account for the part played by the active internal modes.

(ii) $\tau_o \to \infty$

Eq. 24 shows that as $\tau_o \to \infty$, so $\alpha \to 0$. Noting that the C_n vary as α^{-1}, it follows on taking the proper limit as $\alpha \to 0$ that

$$-\dot{q}_w\,\delta\left\{1 + Le^{(i)}\,Q'\right\} = (T'_\delta - T'_w)\,\lambda_o^{(a)}\,(1 + Le^{(i)}) . \tag{61}$$

where

$$Q' = \frac{B_w\,C'_\delta + B_\delta\,C'_w}{C'_w + C'_\delta + C'_w\,C'_\delta} \tag{62}$$

$$C'_n = \frac{\Gamma'_n\,(1 + Le^{(i)})\delta}{1 + Le^{(i)}\Gamma_n}, \quad n = w \text{ or } \delta \tag{63}$$

(note Γ'_n is defined in eq. 34). It also follows from eq. 51 and the remarks about $T^{(i)}$ that

$$\frac{T - T'_w}{T'_\delta - T'_w} = \frac{y}{\delta} = \frac{T^{(i)} - T_w^{(i)}}{T_\delta^{(i)} - T_w(i)} \tag{64}$$

Examination of the various quantities involved here shows that the energy transfer rate into the wall is a strong function of the inert mode accommodation coefficients, $r_\delta^{(i)}$ and $r_w^{(i)}$, and also the ratio of these coefficients to the active energy accommodation coefficients r_δ and r_w. This is because Γ'_n is proportional to $r_n^{(i)}/(2 - r_n^{(i)})$ and Γ_n to the ratio $\left[(2 - r_n)/(2 - r_n^{(i)})\right](r_n^{(i)}/r_n)$.

Thus, if both $r_w^{(i)}$ and $r_\delta^{(i)}$ are zero, both C'_w and C'_δ are zero and $B_w = B_\delta = 1$. It follows that $Q' = 1$ in these circumstances, and $\dot{q}_w$ is given by precisely the same expression as eq. 57. This is not surprising since putting $\tau_o = \infty$ and $r_w^{(i)} = r_\delta^{(i)} = 0$ is another way of saying that the inert mode carries no communicable energy. But it should be noted that a result like 57 also holds when $\tau_w = \infty$ and only one of the $r_n^{(i)}$ terms is zero. Thus, suppose we put $r_w^{(i)} = 0$; then $C'_w = 0$ and $B_w = 1$. It follows that $Q' = 1$ and $\dot{q}_w$ is again given by eq. 57. The reason for this is clear. If only one wall can excite or de-excite the inert mode and no excitation or de-excitation can arise in the homogeneous state ($\tau_o = \infty$), there is no mechanism whereby inert mode energy can be transferred from one wall to the other*.

On the other hand, if neither $r_w^{(i)}$ nor $r_n^{(i)}$ are zero, Q' must be less than one. We notice, in this case, that neither B_w nor B_δ are unity, (since $\Gamma_n \neq 0$), and that it seems quite possible to find values of the Γ_n (see eq. 56) which may make the $B_n \leq 0$. Whether this can be so or not depends on the relative magnitudes of $c^{(a)}$, $Le^{(a)}$, r_n and $r_n^{(i)}$, etc. but does not seem to depend on the dimensions of the system. This latter consideration enters via the C'_n quantities which, from the definition of Γ'_n in eq. 34, are proportional to (δ/ℓ_n). This dependence of the C'_n on the ratio (δ/ℓ_n) implies that they will be large quantities, certainly greater than unity, unless the appropriate $r_n^{(i)}$ is very small. If both $r_w^{(i)}$ and $r_\delta^{(i)}$ are very near to unity then, it would seem reasonable to set Q' in eq. 62 almost equal to zero (by reason of the appearance of the

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* It is worth noting that the translational temperature jump is the same whether both $r_w^{(i)}$ and $r_\delta^{(i)}$ are zero or only one of them.

product $C'_w C'_\delta$ in the denominator of Q'). This being so, eq. 61 gives

$$- \dot{q}_w \delta \simeq (T'_\delta - T'_w) \lambda_o^{(a)} (1 + Le^{(i)}) . \qquad (65)$$

Noticing that

$$\lambda_o^{(a)}(1 + Le^{(i)}) = \lambda_o + n_o D_o (c_o^{(a)} + c_o^{(i)}) , \qquad (66)$$

from the definition of $Le^{(i)}$ in eq. 22, it can be seen that the value of conductivity appropriate to this particular case is the corrected value which accounts for full participation by all internal modes in the energy transfer processes. It is interesting to note that this result is achieved solely by the efficient transfer of inert mode energy to the walls. The translational temperature jump at both upper and lower walls gives rise to a term exactly similar to that in square brackets on the left hand side of eq. 59. In fact the result in the present case is similar to eq. 59 with $\lambda_o^{(a)}$ replaced by $\lambda_o^{(a)} (1 + Le^{(i)})$.

The significance of the ratio δ/ℓ_n which appears in C'_n can be explained as follows. Let us keep T'_δ and T'_w constant (so that λ and nD are constant). Now if δ is fixed, ℓ_n can be decreased by increasing p (see eq. 60) and hence n (because $p = n k T$). Reference to eq. 30 shows that the rate of bombardment of the walls by the molecules increases, and hence inert mode energy can be transferred at a greater rate.

The reason for the behaviour of the result as δ increases is not quite so simple. It follows from eq. 52 that

$$T_\delta^{(i)} - T_w^{(i)} = \frac{1 - Q'}{1 + Le^{(i)}_{Q'}} (T'_\delta - T'_w) . \qquad (67)$$

Then an increase in δ, with corresponding decrease in Q', means that $T_\delta^{(i)} - T_w^{(i)}$ increases. Hence the inert temperature gradient, decreases rather less quickly than the active or translational temperature gradient and the apparent conductivity, which is $- \dot{q}_w \delta/(T'_\delta - T'_w)$ for present purposes, increases a little.

Let us return to the consideration of the B_n quantities, which may be <0 if the Γ_n are >1. If the B_n are indeed <0, then $Q' < 0$ and it would appear that an effective conductivity greater than the fully corrected value $\lambda_o^{(a)}(1 + Le^{(i)})$ could arise. To simplify the discussion, let us assume that $c^{(a)} = 0$, so that the only internal mode remaining is the inert one. In this event, one finds from eq. 56 that
$\Gamma_n = (\lambda/n\, D\, c_{vt})(2 - r_n)r_n^{(i)}/(2 - r_n^{(i)})r_n$.

Noticing from the analogy between eqs. 32 and 41, that the quantity $3\pi\ell_n/8$ defines a mean free path for diffusion, it is clear from the definitions of λ and D etc., that $\lambda/n\, D\, c_{vt}$ expresses the ratio of the free path for conduction ($\ell_n^{(e)}$, see eq. 44) to this free path for diffusion. Thus the Γ_n are intimately connected with the temperature jumps at the walls for the translational and inert modes. In other words, they must indicate in a relative sense how close $T_\delta^{(i)}$ and T'_δ and $T_w^{(i)}$ and T'_w approach the actual wall temperature values T_δ and T_w. Confirmation of this can be obtained from eq. 67 above, which shows that as the B_n decrease, so that Q' decreases also (see eq. 62), $T_\delta^{(i)} - T_w^{(i)}$ more nearly approaches $T'_\delta - T'_w$ and finally exceeds this value when the B_n are negative. We note for future reference that eq. 52 shows this statement to be true for <u>any</u> value of τ_o and not just as $\tau_o \to \infty$. Remembering that translational energy is transferred by conduction and internal energy by diffusion the Γ_n therefore express the balance between the effectiveness of these mechanisms coupled with the appropriate efficiencies of the walls in exciting or de-exciting these energy states. Since $(\lambda/n\, D\, c_{vt}) \simeq 1.9$ for the values of λ and D quoted in eqs. 43a and 31 it must be concluded that the combination of diffusion and inert energy accommodation can be more effective than that of conduction and accommodation in some circumstances. For example, if the $r_n = 1$ we require the $r_n^{(i)} > \frac{2}{3}$, roughly, in order to make this so when $c^{(a)} = 0$.

When $c^{(a)} \neq 0$ a larger value of the $r_n^{(i)}$ than 2/3 is required, as can be seen from eq. 56 for the Γ_n. This is because, when $c^{(a)} \neq 0$, a part of the energy being transferred according to the temperature gradient dT/dy (i.e. loosely, by "conduction") is in fact being transported by diffusion. (Note $\ell_n^{(e)}$ decreases as $c^{(a)}$ increases).

Since the $r_n^{(i)}$ must be quite large to make the $B_n < 0$ it follows that the C_n', which are proportional to δ/ℓ_n, will be large quantities. The possible gains over and above the fully corrected Eucken conductivity are therefore likely to be small, although they should increase with decreasing pressure (i.e. as δ/ℓ_n and hence the C_n' decrease).

To conclude this section we note that it is really the dimensionless group $\tau_o D_o/\delta^2$ which governs the situation analysed under the heading "$\tau_o \to \infty$". (Refer to the general results in eqs. 50 and 51 where the product $\delta\alpha$ appears. α is proportional to $(\tau_o D_o)^{-\frac{1}{2}}$, see eq. 24).

Now τ_o is frequently quoted as a "number of collisions to excite the internal mode", and since the time between collisions is ℓ/Ω we shall write

$$\tau_o = N \ell_o / \Omega_o , \qquad (68)$$

where N is the "number of collisions".
Whence, apart from a numerical factor of order unity $\tau_o D_o/\delta^2 \sim N(\ell_o/\delta)^2$. Taking a δ of 1 cm. and molecular diameter σ of about 4×10^{-8} cm., it followsthat τ_o is "large" if $N >> (\delta/\ell_o)^2 \sim 10^{10}$ at N.T.P. This is an unlikely state of affairs, but if the pressure falls to say 1/1000th of an atmosphere N must only be much greater than 10^4 roughly. Without going into details since these must depend on the temperature, type of gas etc., it seems reasonable to suppose that the approximations of the present section could apply in the low pressure regions*. Some confirmation of this will be given in the case of nitrogen vibration, to be examined below.

(iii) $\tau_o \to 0$.

We now turn to the other extreme case, for which the inert mode relaxation time becomes small enough to be negligible. From the previous discussion, this would seem to be a likely state of affairs at moderately high pressures for internal modes which are excited in a few collisions. (Of course τ_o never actually equals zero, as can be appreciated from eq.68).

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* A continuum theory based on the Navier-Stokes equations, such as is used here, would still be valid at these pressures since $(\ell_o/\delta) \sim 10^{-2}$ for p = 1/1000th atm.

In the limiting case, the C_n tend to zero (regardless of the $r_n^{(i)}$ values) and $Q = B_w + B_\delta$, because when $\tau_o \to 0$, $\alpha \to \infty$. It follows at once from eq. 50 that for vanishingly small τ_o values

$$- \dot{q}_w \delta \simeq (T'_\delta - T'_w) \lambda_o^{(a)} (1 + Le^{(i)}) . \qquad (69)$$

The appropriate conductivity value is therefore the fully corrected one, accounting for the complete participation by all the internal modes in the energy transfer processes, just as one might expect. It is interesting to note that the value of $\dot{q}_w$ is insensitive to the values of $r_w^{(i)}$ and $r_\delta^{(i)}$, a marked contrast to the previous case, since the term which contains them is proportional to $(\delta\alpha)^{-1}$. (The expression for $\dot{q}_w$ correct to $O(\delta\alpha)^{-1}$ is written out in eq. 75 below).

This result is a little surprising, particularly if one examines eq. 21 in the light of the condition $\alpha \to \infty$. Clearly in these circumstances it must be an excellent approximation to set $T^{(i)} \simeq T$, the translational temperature, and indeed this is just what is implied in the Eucken-correction to thermal conductivities. Then the left hand side of eq. 28 becomes $n_w D_w c_o^{(i)} (dT/dy)$, with a similar value at $y = \delta$, and the $e_{av,w}^{(i)}$ and $e_{av,\delta}^{(i)}$ values are determined by T'_w and T'_δ, which depend only on the translational temperatures and the r_n values. But the $r_n^{(i)}$ may take on any value between 0 and 1, depending on, for example, the wall materials, and this does not seem consistent with the result $T^{(i)} \simeq T$. The part played by the inert mode accommodation coefficient can be appreciated on examination of the translational temperature distribution (eq. 51) for large values of α (more strictly, of $\alpha\delta$).

When $y \to 0$, a reasonable approximation to T is given by

$$\frac{T - T'_w}{T'_\delta - T'_w} \simeq (\delta\alpha + Le^{(i)} Q'')^{-1} \left\{ y\alpha + Le^{(i)} B_w (1 + C_w)^{-1} (1 - e^{-\alpha y}) \right\} \qquad (70)$$

where

$$Q'' = \frac{B_w (1 + C_\delta) + B_\delta (1 + C_w)}{(1 + C_w)(1 + C_\delta)} , \qquad (71)^*$$

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* The C_n terms must be retained here because eq. 66 shows that they are roughly of order $N^{\frac{1}{2}}$.

and when $y \to \delta$ we can write

$$\frac{T - T'_w}{T'_\delta - T'_w} \simeq (\delta\alpha + \mathrm{Le}^{(i)} Q'')^{-1} \left\{ y\alpha + \mathrm{Le}^{(i)} B_\delta (1 + C_\delta)^{-1} e^{-\alpha(\delta - y)} + \mathrm{Le}^{(i)} B_w (1 + C_w)^{-1} \right\} \quad (72)$$

The correct limiting values are obtained when $y = 0$ and $y = \delta$, but it can be seen that rapid changes in the variation of T with y occur in regions which are of $O(\alpha^{-1})$ in thickness adjacent to each plate. Furthermore, eqs. 70 and 72 show that the magnitude of these changes is proportional to the value of B_w at the lower plate and to B_δ at the upper, and these quantities are explicit functions of the ratio of the active and inert mode accommodation coefficients (see eq. 56). Comparing eqs. 33 and 42, it can be seen that the Γ_n quantities are equal to the ratio of the translational temperature jump per unit translational temperature gradient to the inert mode temperature jump per unit inert mode temperature gradient. When these are exactly equal the B_n are zero and it follows from eqs. 70 and 72 that the translational temperature varies linearly with y and does not undergo the rapid changes indicated by the exponential terms there. In these circumstances eq. 28 is clearly consistent with the approximation $T^{(i)} \simeq T$, since it is then identical with eq. 42.

One may conclude then that for very small values of r_o it is reasonable to set $T^{(i)} \simeq T$ everywhere in the gas layer except for "boundary layers" adjacent to the walls which are of $O(\alpha^{-1})$ in thickness. Inside these layers the inert mode accommodation coefficient exerts a strong influence, distorting both the T and $T^{(i)}$ profiles in such a way as to satisfy the appropriate boundary conditions. Only when the $r_n^{(i)}$ and r_n are related in such a way as to make the B_n zero is $T^{(i)} \simeq T$ a good approximation right through the layer*.

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* This situation is entirely analogous to the one found by Hirschfelder (1956) for heat transfer through a chemically reacting gas mixture. Note that $\alpha^{-1} \sim \ell_o \sqrt{N}$, so the "boundary layers" are several mean free paths in thickness. The temperature changes across them are not so violent as to invalidate a continuum type of theory. This "boundary layer" behaviour as $r_o \to 0$ is characteristic of singular perturbation problems, of which eq. 23 is a simple example.

Eqs. 70 and 72 show that the deviations of the translational temperature profile (due to the excitation of the inert mode at the walls) from the linear form which would be predicted following on a prior assumption that $T^{(i)} \simeq T$ are very small, being in fact of $O(\delta\alpha)^{-1}$. This is not so of the translational temperature gradients as $y \to 0$ or δ and these are readily found to be given by

$$\left(\frac{dT}{dy}\right)_{y=0} = \frac{T'_\delta - T'_w}{\delta} \left(1 + Le^{(i)} B_w\right) , \qquad (73)$$

$$\left(\frac{dT}{dy}\right)_{y=\delta} = \frac{T'_\delta - T'_w}{\delta} \left(1 + Le^{(i)} B_\delta\right) , \qquad (74)$$

in the limit as $\alpha \to \infty$. Consequently the translational temperature jumps are affected by the accommodation of the inert mode, as one would expect in this case.

This fact points to a defect in the theory so far, for allowing τ_o to approach zero puts the internal mode that we have been describing as inert, into the class of internal modes described as active. Clearly then, we should adopt a treatment analogous to that accorded to the inert mode for <u>all</u> the internal modes, even though they be of the active class. Only in this way can we take proper account of the full details of the energy transfer processes. However, in the light of the results just discussed it does not seem unreasonable to employ a theory of the present kind for the problem of energy transfer through a gas with one internal mode whose relaxation time is long compared to the remaining internal modes. The temperature profiles will be incorrect in boundary layers near the walls whose thicknesses are proportional to the square root of the relaxation times of the active modes, but by hypothesis, these are very much thinner than the inert mode layers. The energy transfer rates cannot be much affected by the active mode accommodation coefficients. The translational accommodation coefficients r_n will be functions of the accommodation coefficients for the true translational energy and for the active modes individually. To this extent, the r_n values must be regarded as some suitably weighted mean values.

If the gas molecules have only one internal mode with a communicable energy then the present theory is exact (within the framework of the linearising assumptions) provided $c^{(a)}$ is put equal to zero. Such may be the case for diatomic molecules at room temperatures (where only rotation is excited), and we shall discuss some of the implications of the theory in these circumstances in the last section.

A slightly better approximation to $\dot{q}_w$ for large values of $\delta\alpha$ can be found from eq. 50 and is

$$-\dot{q}_w \delta \simeq (T'_\delta - T'_w)\,\lambda_o^{(a)}\,(1 + Le^{(i)})\left\{1 - Le^{(i)}\,Q''\,(\delta\alpha)^{-1}\right\}, \quad (75)$$

where Q'' is defined in eq. 71. It can be seen from this expression that there is a possibility, as in the other extreme case of $\tau_o \to \infty$, that the effective conductivity could be greater than the Eucken, fully corrected, value. The reason is the same, namely that the B_n terms (and hence Q'') could be negative. The extent of the possible increase is seen to increase with increasing τ_o, and the explanation is as follows. For any value of τ_o not actually equal to zero, the inert mode temperature is always different from the translational temperature T. In the lower parts of the layer $T^{(i)}$ will be greater than T (due to the lag in the transfer of energy between the inert and translational modes), and the larger τ_o the larger will be this difference. (This can be confirmed via eqs. 20, 21 and 70; $d^2T^{(i)}/dy^2$ is proportional to $-d^2T/dy^2$ and eq. 70 shows that this latter quantity is positive. Then $T^{(i)} - T > 0$ and proportional to τ_o from eq. 21). This implies that as τ_o increases more of the inert mode energy is available for direct conversion by the lower wall, via the processes of diffusion and de-excitation on the plate. We have already seen that this mechanism may be more effective than conduction, so that if the $r_n^{(i)}$ values are high enough, the maximum benefit can be derived from the "inertness" of the inert mode.

Clearly the possible gains do not increase without limit as $\delta\alpha \to 0$, since eq. 75 ceases to be a valid approximation long before then. The proper approximation for $\delta\alpha \to 0$ has been discussed above.

The results (eqs. 50 to 56) show that

$$-\dot{q}_w \delta = (T'_\delta - T'_w)\,\lambda_o^{(a)}(1 + Le^{(i)})$$

exactly, if both B_w and B_δ are zero, and it follows also that

$$(T - T'_w)\,\delta = (T'_\delta - T'_w)\,y ,$$

in this case, no matter what the value of τ_o (or α) may be. This at first sight rather surprising result can be understood in the light of the previous arguments about the B_n quantities, particularly when it is

observed that $T^{(i)}$ does not only change because of the gas-phase excitation of the inert mode. Variations of $T^{(i)}$ throughout the layer also occur as a result of the inert mode's accommodation to the appropriate wall temperatures, T_δ or T_w.

To complete the present section, the translational temperature jumps are evaluated so that $\mathring{q}_w$ can be expressed in terms of the temperatures T_δ and T_w, for the case $\delta\alpha \gg 1$. It readily follows from eq. 57 that appropriate values of the temperature gradients are given by

$$\delta\left(\frac{dT}{dy}\right)_{y=0} \simeq (T'_\delta - T'_w)\,(1 - Le^{(i)}\,Q''\,(\delta\alpha)^{-1})\left\{1 + Le^{(i)}B_w(1 + C_w)^{-1}\right\}$$

$$\delta\left(\frac{dT}{dy}\right)_{y=\delta} \simeq (T'_\delta - T'_w)\,(1 - Le^{(i)}\,Q''\,(\delta\alpha)^{-1})\left\{1 + Le^{(i)}B_\delta(1 + C_\delta)^{-1}\right\}$$

The first two terms on the right hand sides of these equations can be eliminated in terms of $\mathring{q}_w$ from eq. 75, and if products like $(\ell_\delta/\delta)(Le^{(i)}\,Q''/\delta\alpha)$ are ignored relative to unity, it follows that

$$-\mathring{q}_w\,\delta\left\{1 + (\ell_\delta/\delta)a_\delta\left[1 + Le^{(i)}B_\delta(1 + C_\delta)^{-1}\right] + (\ell_w/\delta)a_w\left[1 + Le^{(i)}B_w(1 + C_w)^{-1}\right]\right\}$$

$$\simeq (T_\delta - T_w)\,\lambda_o^{(a)}\,(1 + Le^{(i)})(1 - Le^{(i)}\,Q''/\delta\alpha)\,. \qquad (76)$$

It can be seen that temperature jump reduces the heat transfer rate, as would be expected, and that the magnitude of the jump depends on the $r_n^{(i)}$ terms via B_n and C_n. The terms in square brackets on the left-hand side of eq. 74 are never < 0 in practice.

5. Vibrational Relaxation in Nitrogen

To illustrate the results derived above some values of effective conductivity are given for nitrogen, assuming that vibration is the inert mode. It is assumed that the accommodation coefficients $r_w^{(i)}$ and $r_\delta^{(i)}$ are both zero and it follows from the results in eqs. 50 to 56 that

$$-\dot{q}_w \delta \left\{ 1 + 2\,Le^{(i)}/\delta\alpha(\coth\delta\alpha + 1/\sinh\delta\alpha) \right\} = (T'_\delta - T'_w)\,\lambda_o^{(a)}\,(1 + Le^{(i)}) \quad \ldots\ldots (77)$$

It is noted that both D_o and τ_o are inversely proportional to the pressure, so that denoting the values appropriate to a pressure of one atmosphere by D_{o_1} and τ_{o_1} respectively,

$$\delta\alpha = \left[(1 + Le^{(i)})/D_{o_1}\,\tau_{o_1} \right]^{\frac{1}{2}} (p\delta). \qquad (78)$$

The product $(p\delta)$ is measured in atmosphere-centimetres.

The values of D_{o_1}, $Le^{(i)}$ and $Le^{(a)}$ can be evaluated from the results given above and in Hirschfelder, Curtiss and Bird (1954). Values of τ_{o_1} have been estimated from the work of Blackman (1956). $Le^{(a)}$ is given by $0.528 c^{(a)}/c_{vt}$ to a sufficient order of accuracy and since the active mode is rotation in the present case, $c^{(a)}/c_{vt} = 2/3$, the rotational mode being fully excited at the temperatures of interest for vibrational relaxation. It follows that

$$Le^{(i)} = \frac{0.35\,(c_o^{(i)}/k)}{1 + 0.35}\,.$$

The inert mode specific heat $c_o^{(i)}$ is evaluated from the results for a simple harmonic vibrator with characteristic temperature equal to 3,340°K.

Eq. 77 shows that the term

$$\left\{ 1 + 2\,Le^{(i)}/\delta\alpha\,(\coth\delta\alpha + 1/\sinh\delta\alpha) \right\}^{-1}$$

gives a measure of the deviation of conductivity from the full Eucken-corrected value as a result of vibrational relaxation. Writing it as 1-(Error), the Error quantity has been evaluated and is plotted against temperature in Fig. 1 for three values of $p\delta$. (The square bracket term in eq. 78 is a function of temperature only). The maximum possible

Error occurs when $\delta\alpha = 0$ and is given by $1 - (1 + Le^{(i)})^{-1}$. The value for $p\delta = 0.01$ atm.cm. in Fig. 1 corresponds almost exactly with this maximum Error, being at most 1% less at the higher temperatures. When $p\delta = 1$ atm. cm. the Error is always less than 1%, but increases as $p\delta$ falls.

Below 500°K nitrogen vibration is insufficiently excited to be of any importance and above about 4,500°K dissociation would arise to complicate the picture. At a temperature of 1300°K, corresponding to the maximum Error for $p\delta = 0.1$ atm. cm. of about 7%, the relaxation time $\tau_o \simeq 3$ milliseconds. The value of (ℓ_o/Ω_o) can be found via eqs. 31 and 29 in terms of D_o etc., thereby eliminating the need to know the molecular diameter explicitly. It then turns out that $\tau_o \simeq 3$ milliseconds corresponds to an N of about 20,000 (see eq. 66). The shape of the Error curves reflects the opposing effects of increase in $c_o^{(i)}$ and decrease in $\tau_o D_o$ with increasing temperature. (D_o varies roughly as $T^{3/2}$ and τ_o roughly as $\exp(\text{Const.}/T^{1/3})$).

We reiterate that the accommodation coefficients for vibrational excitation at the walls are zero for the results in Fig. 1. For any values greater than zero the Error term will always be less at any given $p\delta$, and may become negative.

6. Conductivity Measurements and Accommodation Coefficients

The conductivity of gases is often measured in a hot wire cell type of apparatus, recent examples being the work of Taylor and Johnston (1946) and Johnston and Grilly (1946). The first of these papers describes in detail the apparatus used and gives some conductivity values for air, whilst the second reports conductivity measurements in the same apparatus for nine different, pure, gases.

In its essentials the hot wire cell consists of a wire (e.g. bright platinum), surrounded by a concentric hollow cylinder which is immersed in a thermostat. With the wire hotter than the cylinder energy is transferred between them primarily by "conduction" through the gas, and it is possible to make extremely accurate corrections to account for end conduction, radiation transfer, etc. It is a feature of the measurements that they must be carried out at comparatively low pressures (those in the papers cited varied from about 1 to 20 cm. Hg) in order to minimise the effects of natural convection. As a consequence of this it becomes important to take account of the temperature jump phenomenon: it is in fact found that the observed conductivities vary with the pressure, but we shall say more about this shortly.

The hot wire cell problem is concerned with the radial flow of heat, so that the present theory is not directly comparable with the experimental results. However, qualitatively the processes occuring in the cell and in the theoretical model studied here must be similar and some interesting observations can be made.

We confine the discussion to gases with but one internal mode, so that the foregoing theory is exact (subject to the linearisations) when $c^{(a)}$ is set equal to zero. At the temperatures used in the measurements (i.e. $100^{o}K$ - $300^{o}K$) only rotation would be excited in the diatomic molecules and this class of internal motion generally has a small relaxation time. Then it is appropriate to use an equation like eq. 76 with which to examine the situation. Since the mean free paths ℓ_{δ} and ℓ_{w} are proportional to p^{-1} (p is constant between the upper and lower walls), and $\delta\alpha$ varies as p, we shall re-write eq. 74 as

$$- \dot{q}_w \delta(1 + b/p) = (T_\delta - T_w)\ \lambda_o^{(a)}(1 + Le^{(i)})(1 - b'/p) \qquad (79)$$

(The definitions of b and b′ are obvious on comparison of eqs. 76 and 79).

In making measurements one knows $\dot{q}_w$, δ and $T_\delta - T_w$ ($\dot{q}_w$ would have been corrected for all the apparatus effects except temperature jump) and an apparent conductivity λ_{app} can be defined so that

$$- \dot{q}_w \quad \delta \quad = (T_\delta - T_w)\ \lambda_{app} \qquad (80)$$

Then eqs. 79 and 80 show that

$$\frac{\lambda_o^{(a)}\ (1 + Le^{(i)})}{\lambda_{app}} \quad = \quad 1 \quad + \frac{b + b'}{p} \quad , \qquad (81)$$

to a good degree of accuracy, since both b/p and b′/p are small quantities.

The experimental technique involves taking a number of values of λ_{app} at different pressures and then plotting λ_{app}^{-1} against p^{-1}. It is some confirmation of the present theory that Taylor and Johnston found this plot to be an excellent straight line. The values of conductivity which they quote were obtained by extrapolating this plot to $p^{-1} = 0$ and it is interesting to observe from eq. 81 that these should be equal to the full Eucken value $\lambda_o^{(a)}\ (1 + Le^{(i)})$. That this is indeed the case to an acceptable degree of accuracy is shown by Hirschfelder Curtiss and Bird (1954), who compare the Taylor-Johnston-Grilly values with the Eucken-corrected kinetic theory estimates.

These latter authors do not mention the effects of relaxation in the rotational modes of the diatomic molecules used in their measurements and eq. 81 shows that these are not of importance where conductivity is the only quantity to be measured. If it is intended to use the slope of the experimental plot to find accommodation coefficients however, eq. 81 shows that the relaxation effects may intervene. By how much depends on the relative magnitude of b and b′.

From eqs. 76 and 79 it is clear that

$$\frac{b'}{b} = \frac{Le^{(i)}\, Q'' / \delta a}{(\ell_\delta/\delta)a_\delta \left[1 + Le^{(i)} B_\delta (1 + C_\delta)^{-1}\right] + (\ell_w/\delta)a_w \left[1 + Le^{(i)} B_w (1 + C_w)^{-1}\right]} \quad \ldots\ldots \quad (82)$$

from which it can be seen that the ratio is independent of the plate separation δ in the present problem. If the $r_n^{(i)}$ quantities are both such as to make the B_n zero, the ratio is zero and relaxation has no effect: otherwise it has. If we consider the other extreme where the $r_n^{(i)}$ are zero then

$$\frac{b'}{b} = \frac{Le^{(i)}}{\alpha \ell_o \, a(1 + Le^{(i)})} , \qquad (83)$$

if we write $\ell_w \simeq \ell_\delta \simeq \ell_o$ and let $r_w = r_\delta = r$ so that

$$a_w = a_\delta = \frac{25\pi}{35.2} \cdot \frac{2 - r}{r} , \qquad (84)$$

(see eq. 46). r is the true translational energy accommodation coefficient here, and is probably close to unity for both walls, so eq. 84 is perhaps not a bad approximation. If we use the values of D_o and τ_o from eqs. 31 and 68 and note that $Le^{(i)} = 0.35$ when $c_o^{(i)} = k$ it follows from eq. 83 that

$$\frac{b'}{b} \simeq 0.077 \sqrt{N} \, \frac{r}{2 - r} \qquad (85)$$

Since $r \simeq 1$ we infer that b′ is an appreciable fraction of b even if only a few collisions (say ten) are required to excite the internal mode. More collisions would be required to make b′ comparable with b if excitation of the internal mode occurs during collision with the walls, but it seems reasonable to suggest that even a mode as easily excited as rotation could strongly influence any attempt to evaluate r from the slope of a λ_{app}^{-1} versus p^{-1} plot.

7. References

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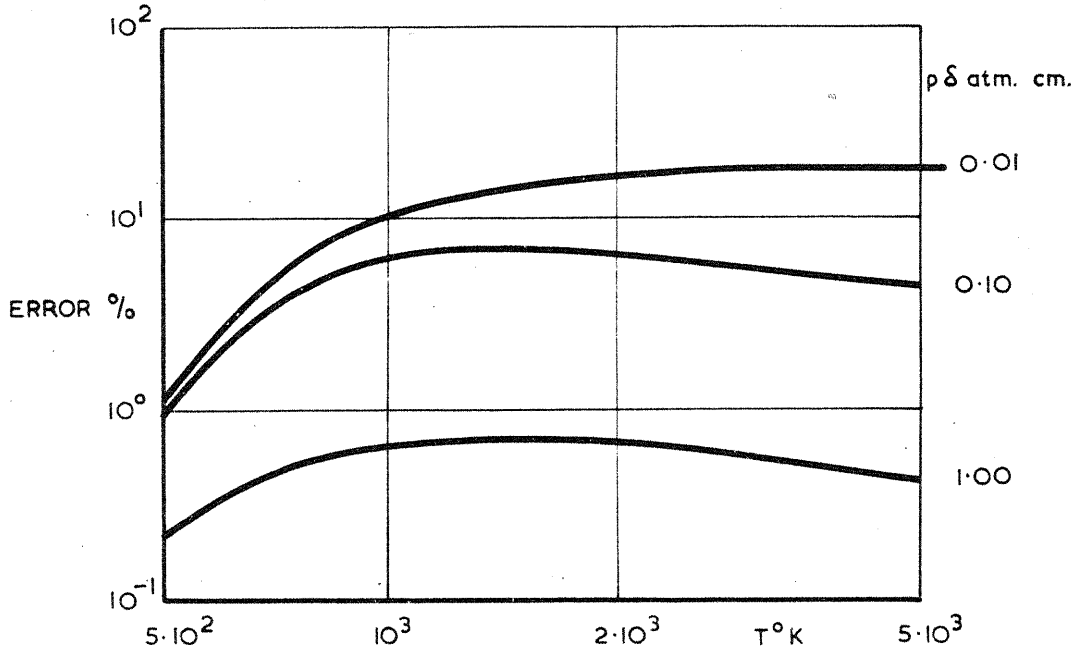

FIG. 1. DEVIATIONS FROM THE EUCKEN – CORRECTED CONDUCTIVITY FOR NITROGEN VIBRATION (NO DE-EXCITATION BY THE WALLS.)