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On a Problem Involving Heat Conduction
Through a Polyatomic Gas

- by -

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SUMMARY

A heat conduction problem is set up which, in essence, simulates the conditions arising when a plane shock wave reflects from a co-planar solid boundary. The gas is assumed to be polyatomic, with one 'significantly relaxing' internal energy mode.

The quantity of primary interest is the temperature of the solid at the interface, since this can be observed experimentally without much difficulty. Solutions are obtained for this quantity which cover a range of practically plausible relaxation times and 'wall effect' parameters. It is essential to include proper temperature jump boundary conditions for both active and relaxing (or inert) energy modes. Thus it is necessary to know accommodation coefficients for these modes of energy storage. The temperature jump effects are found to dominate the (interface) solid's temperature/time history, with relaxation effects playing a very secondary role.

The theoretical results are compared with some experimental observations and encouraging agreement is found. As a result of this agreement it proves possible to estimate the accommodation coefficient for the active modes (in this case for the combination platinum/air), the pressure being about 15 atmospheres. The pressure sensitivity of accommodation effects is commented on.

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LIST OF SYMBOLS

a	equation 23
C	inert mode specific heat
C_p	specific heat at constant pressure
C_v	specific heat at constant volume
\mathcal{D}	diffusion coefficient
h	enthalpy per unit mass
l	mean free path
q	energy flux vector
Q, Q_0	equations 39 and 42
r	accommodation coefficient
R	gas constant (per unit mass)
s	transform variable
t	time
T	translational temperature
T_∞	initial ($t = 0$) translational temperature
$T_0(t)$	solid's temperature at $x = 0$ (function of time)
x	spatial co-ordinate
z	section 4
α	specific heat's ratio ($= C/C_{pa}$)
Γ	equation 24
θ	inert mode temperature
κ	thermal diffusivity
λ	thermal conductivity
ρ	density

List of Symbols (Continued)

τ, τ' relaxation times (equations 9, 35)

Ω mean molecular speed

Subscripts

a active plus translational modes

i inert mode

s solid

t translational

Bar ($\bar{\quad}$) denotes Laplace transform

1. Introduction*

In the Sections to follow we shall consider the problem of the sudden contact between a hot, polyatomic, gas and a cold solid. With the interface lying at $x = 0$, the solid occupies the semi-infinite region $x < 0$ whilst the gas occupies the region $x > 0$. We assume that at the instant of contact (time $t = 0$) the translational temperature in the gas has a value T_{∞} whilst the temperature of the solid, together with that of the one internal energy mode in the gas which exhibits significant relaxation effects, is zero.

Subsequent to the initial instant of time, the gas translational and internal mode temperatures will begin to equalise, the manner in which they do so depending on two separate phenomena. Firstly there will be excitation of the internal energy mode via intermolecular collisions in the gas phase, an effect which we shall describe by specifying the appropriate relaxation time τ . Secondly, the gas temperatures will be influenced by the effectiveness of the solid material in accommodating both translational and internal mode energy states. This phenomenon will require the specification of two accommodation coefficients, one for each energy mode. At this stage we remark that all internal energy states which are usually described as "active" (i. e. having very short relaxation times) are implicitly included under the heading of translational state. Some discussion of this topic can be found in Clarke (1960a), where it is shown that under conditions of very rapid relaxation in the gas phase it is not necessary to consider the details of the way in which that internal energy state is accommodated at a solid surface.** If it should become necessary to distinguish between such rapidly relaxing modes and our assumed "significantly relaxing" mode we will refer to them as "active" and "inert" modes, respectively.

The quantity in which we shall be most interested in this study will be the temperature of the solid at the interface $x = 0$. The reason for this is as follows. The problem that we have set up in the preceding paragraph is very closely encountered in practice when a plane shock wave reflects from the closed end of a conventional shock tube. Then the behaviour of the solid's temperature at $x = 0$ should be capable of observation with a standard type of thin film platinum resistance thermometer and the theory put to the test. Indeed, in the present instance, experiment has preceded theory and what follows is an attempt to explain the observations which were made. More will be said on this topic in a later Section; for the present we will continue with the task of setting up the theoretical model.

* A shortened version of the present paper was presented at the 3rd British Theoretical Applied Mechanics Colloquium, Kings College, Newcastle, 11th - 14th April, 1961.

** See also Section 3, case (v), below.

In particular we assume that the gas pressure remains constant throughout the period subsequent to time $t = 0$, and that gas velocities are always everywhere zero. As support for this assumption we quote a recent study (Clarke, 1960b) which shows that the pressure and velocity disturbances induced by the sudden contact between a hot gas and a cold solid are of small amplitude (especially in regions adjacent to the interface) a few molecular collision times after $t = 0$. Any effects on the interface temperature due to changes of pressure are substantially over and done with in time intervals too short to be measured with even good quality shock tube instrumentation. The theory just referred to did not take account of temperature jump phenomena (or of relaxation effects) but, as will be appreciated from what follows, the inclusion of such effects will tend to diminish even further the amplitude of any heat-conduction-induced pressure changes. In any actual shock tube experiment there will, of course, be other factors present which are not included in our theoretical model. Especially are we thinking of the influence of the boundary layer behind the primary shock wave on the behaviour of this and the reflected wave, causing them to accelerate, or decelerate, depending on the conditions, type of gas, etc. (Mark, 1958). However, on the basis of the results to be obtained below and their ability to explain in large measure the observations from several experiments, we feel justified in neglecting such effects, at least for the time being. As some additional justification for neglect of these effects, we remark that our present interest lies mainly in the time region from about 0 to 10 μ sec after shock reflection and that boundary layer influences take some time to develop far enough to interfere with the "one-dimensional" nature of the central core of the shock tube flow following shock reflection.

With the assumption of constant pressure and zero velocity, the energy equation becomes

$$\rho \frac{\partial h}{\partial t} + \frac{\partial q}{\partial x} = 0 \quad , \quad (1)$$

where h is the specific enthalpy and q the energy flux vector. h can be expressed in terms of the translational and inert mode temperatures, T and θ respectively, as follows,

$$h = \int_0^T C_{pa} dT + \int_0^{\theta} C d\theta \quad . \quad (2)$$

Here C_{pa} and C are the specific heat at constant pressure of the translational plus active pa classes and the inert mode, respectively. They are functions of temperature only, in general, but we shall subsequently assume each one to be a constant, at least over the temperature range of interest. Following the reasoning given by Hirschfelder, Curtiss and Bird (1954) we write

$$q = -\lambda_a \frac{\partial T}{\partial x} - \rho \mathfrak{S} C \frac{\partial \theta}{\partial x} \quad , \quad (3)$$

(see also Clarke, 1960a, for a further discussion). λ_a is the "monatomic" thermal conductivity, corrected to account for the part played by the active internal modes in the energy transfer processes and \mathfrak{S} is akin to the coefficient of "self diffusion".

In fact we should, strictly, use a different diffusion coefficient to describe the diffusion of molecules in different internal quantum states, since the cross-sections may differ from one state to another. Hirschfelder et al suggest that the self-diffusion coefficient evaluated from "monatomic" kinetic theory should be used. However, it seems that the original Eucken correction to thermal conductivity to account for internal energy transfer, which implies that $\rho \bar{C}_{pt} = \lambda$, gives rather better results than follow from this assumption. (C_{pt} = translational specific heat at constant pressure; λ = "monatomic" conductivity, accounting for translational energy transfer only). From the implication that $\rho \bar{C}_{pt} = \lambda$ we infer that q can be written as

$$q = -\lambda_a \left(\frac{\partial T}{\partial x} + \alpha \frac{\partial \theta}{\partial x} \right), \quad (4)$$

where

$$\alpha = C/C_{pa}. \quad (5)$$

It transpires that equation 4 leads to simpler analytical results than would arise if the value found for \bar{C} from 'monatomic' kinetic theory is used. Thus, in addition to the partial justification via comparisons with experiment, which was mentioned above, we have a further reason for adopting equation 4 in what follows and this we shall proceed to do. For example, the energy equation becomes

$$\rho C_{pa} \left(\frac{\partial T}{\partial t} + \alpha \frac{\partial \theta}{\partial t} \right) - \frac{\partial}{\partial x} \left(\lambda_a \left[\frac{\partial T}{\partial x} + \alpha \frac{\partial \theta}{\partial x} \right] \right) = 0, \quad (6)$$

using equation 2 also.

A further relation between T and θ can be derived from a consideration of the rate at which "inert" internal energy accumulates in a fixed volume of gas. Remembering that gas flow velocity is assumed to be zero such accumulation is brought about by diffusion and by direct excitation of the inert state via intermolecular collisions. In formulating the condition, however, it is best to ignore the zero velocity assumption until the equation has been derived. In this way it becomes clear that one is, more properly, just neglecting a convection term relative to a diffusion term, as follows. The net rate of gain of inert mode energy per unit volume is given by

$$\frac{\partial}{\partial t} \left\{ \rho \int_0^\theta C d\theta \right\}$$

and is made up of an increase due to convection,

$$- \frac{\partial}{\partial x} \left\{ u \rho \int_0^\theta C d\theta \right\},$$

(where u = flow velocity), an increase due to diffusion,

$$+ \frac{\partial}{\partial x} \left(\rho \bar{C} \frac{\partial \theta}{\partial x} \right)$$

and an increase due to excitation via collisions, let us say E. Then

$$\frac{\partial}{\partial t} \left\{ \rho \int_0^\theta C d\theta \right\} = - \frac{\partial}{\partial x} \left\{ \rho u \int_0^\theta C d\theta \right\} + \frac{\partial}{\partial x} \left(\rho \mathcal{E} C \frac{\partial \theta}{\partial x} \right) + E. \quad (7)$$

The overall conservation of mass requirement is

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} = 0,$$

whence it follows that equation 7 becomes

$$\rho C \frac{\partial \theta}{\partial t} + \rho u C \frac{\partial \theta}{\partial x} - \frac{\partial}{\partial x} \left(\rho \mathcal{E} C \frac{\partial \theta}{\partial x} \right) = E. \quad (8)$$

We now assume that the second term in equation 8 is much less than the third in our present problem. In addition, we assume that E is proportional to the difference between the actual and equilibrium levels of inert internal energy, i.e. we put

$$E = \frac{\rho}{\tau} \int_\theta^T C d\theta. \quad (9)$$

τ is the appropriate relaxation time. Equation 8 therefore becomes

$$\rho C \frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x} \left(\rho \mathcal{E} C \frac{\partial \theta}{\partial x} \right) - \frac{\rho}{\tau} \int_\theta^T C d\theta = 0, \quad (10)$$

with the approximations adopted to date and equation 10 now constitutes the required second relation between T and θ . Within the framework of the assumptions made so far, equations 6 and 10 are 'exact'. By this we mean that quantities like ρ , C_{pa} , λ_a , α , \mathcal{E} etc. may be functions of T and θ , so that the equations are non-linear. We intend to linearise them shortly in order to progress as far as possible analytically, but in the meantime we shall formulate the boundary conditions to be satisfied by T and θ .

Let us assume that the temperature of the solid at the interface is given by $T_0(t)$. Then we must relate the translational and inert mode temperature jumps to the appropriate temperature gradients, introducing as we do so the relevant accommodation coefficients. Following the usual practice in simple kinetic theory (see for example Clarke, 1960a) we write

$$\left(\frac{2 - r_i}{r_i} \right) \left(\ell_i C \frac{\partial \theta}{\partial x} \right)_{x=0} = \int_{T_0}^{\theta_w} C d\theta \quad (11)$$

for the inert mode and

$$\left(\frac{2 - r_a}{r_a} \right) \left(\ell_a C_{va} \frac{\partial T}{\partial x} \right)_{x=0} = \int_{T_0}^{T_w} C_{va} dT \quad (12)$$



for the active classes. * r_i and r_a are the inert and active accommodation coefficients and C_{va} is the specific heat at constant volume of the translational plus active modes. θ_w and T_w are the appropriate gas temperatures at $x = 0$. ℓ_i and ℓ_a are the mean free paths for the transport of inert and translational plus active mode energy; they are different and we must evaluate them in a way which is consistent with the use of equation 4 to describe energy flux rates. This is readily accomplished by comparing the energy flux rate term from equation 4 with the appropriate rate written in terms of energy jumps and wall bombardment rate (as in the reference cited above). It is found that

$$\ell_{iw} = \frac{2}{\Omega_w} \cdot \frac{\lambda_{aw}}{\rho_w C_{paw}} \quad (13)$$

whilst

$$\ell_{aw} = \frac{2}{\Omega_w} \cdot \frac{\lambda_{aw}}{\rho_w C_{paw}} \cdot \frac{C_{paw}}{C_{vaw}} \quad (14)$$

Ω_w is the mean molecular speed evaluated at $x = 0$ (the wall bombardment rate is $\rho_w \Omega_w / 4$ in units of mass per unit area per unit time) and is given by

$$\Omega_w = (8 R T_w / \pi)^{\frac{1}{2}} \quad (15)$$

(R = gas constant, i.e. universal gas constant divided by molecular weight.)

Equations 11 and 12 relate the gas temperatures to the solid's temperature at $x = 0$, namely T_0 . Since this is an unknown quantity in the present problem, another condition is required at $x = 0$. This is provided by the continuity of energy flux across the interface. In other words we must have

$$\lambda_{sw} \left(\frac{\partial T_s}{\partial x} \right)_{x=0-} = \lambda_{aw} \left\{ \frac{\partial T}{\partial x} + \alpha \frac{\partial \theta}{\partial x} \right\}_{x=0+} \quad (16)$$

Finally, it is necessary to ensure that T and θ remain bounded as $x \rightarrow \infty$ for all t whilst the temperature in the solid, T_s , must likewise remain finite as $x \rightarrow -\infty$.

* The integrals in equations 11 and 12 represent the appropriate "energy jumps" at the interface.

2. The Linear Problem

We now propose to linearise the problem as follows. Equation 6 will be written as

$$\frac{\partial T}{\partial t} - \kappa \frac{\partial^2 T}{\partial x^2} + \alpha \left\{ \frac{\partial \theta}{\partial t} - \kappa \frac{\partial^2 \theta}{\partial x^2} \right\} = 0 \quad (17)$$

where

$$\kappa = \frac{\lambda_a}{\rho C_{pa}} \quad (18)$$

Both α and κ are assumed to be constant. Equation 10 will be written as

$$\frac{\partial \theta}{\partial t} - \kappa \frac{\partial^2 \theta}{\partial x^2} - \frac{1}{\tau} (T - \theta) = 0 \quad (19)$$

and τ is assumed to be constant. (Equation 19 is derived by assuming that ρ and C are constants and that $\lambda = \kappa$ in order to be consistent with equation 4 for the energy flux*). The temperature in the solid is assumed to satisfy the equation

$$\frac{\partial T_s}{\partial t} - \kappa_s \frac{\partial^2 T_s}{\partial x^2} = 0 \quad (20)$$

where the solid's thermal diffusivity κ_s is a constant.

The linearised versions of the two conditions 12 and 11 are

$$a \left(\frac{\partial T}{\partial x} \right)_w = T_w - T_o ; t > 0, \quad (21)$$

$$\left(\frac{\partial \theta}{\partial x} \right)_w = \Gamma (\theta_w - T_o) ; t > 0, \quad (22)$$

where

$$a = \frac{2 - r_a}{r_a} \cdot \frac{2\gamma_a \kappa}{\Omega_w}, \quad (23)$$

$$\Gamma = \frac{r_i}{2 - r_i} \cdot \frac{\Omega_w}{2\kappa} \quad (24)$$

and γ_a is the specific heats ratio, C_{paw}/C_{vaw} .

* This is equivalent to assuming that the Lewis number for inert mode energy diffusion is equal to unity, i. e. in essence the Eucken assumption.

The condition 16 is unchanged (except that α is assumed constant). For completeness we write out the remaining conditions,

$$T_{sw} = T_0 ; \begin{matrix} T, \theta \text{ bounded as } x \rightarrow \infty \\ T_s \text{ bounded as } x \rightarrow -\infty \end{matrix} \quad \left\{ \begin{array}{l} \text{all for} \\ t > 0 \end{array} \right. \quad (25)$$

$$T = T_\infty ; \begin{matrix} \theta = 0 : x > 0 \\ T_s = 0 : x < 0 \end{matrix} \quad \left\{ \begin{array}{l} \text{all at} \\ t = 0 \end{array} \right. \quad (26)$$

Linearisation of the problem is, broadly speaking, justified for small values of the initial translational temperature rise, T_∞ . The most serious assumption involved in the linearisations is the neglect of terms like $(\partial \lambda_a / \partial x)(\partial T / \partial x)$ in comparison with $\lambda_a (\partial^2 T / \partial x^2)$. While it is difficult to generalise about the relative magnitudes of these terms, it can be stated that the former is indeed quite small compared with the latter in the initial stages of the process and that certainly the reverse of the assumption made above is never true. We hope, therefore, to retain most of the essential physics of the problem in our subsequent analytical solutions, although anticipating that these may be lacking in the finer details. Additionally, we remark that the existence of temperature jumps tends to be in favour of linearisation, since the gas temperatures are always greater than T_0 .

The set of linear equations, from equation 16 through to equations 26 are best solved by Laplace-transforming them with respect to the time. Denoting such a transform by a bar over the appropriate symbol, e.g.

$$\bar{\theta}(s; x) = \int_0^\infty \theta(t, x) e^{-st} dt, \quad (27)$$

equations, 17, 19 and 20 become

$$\left\{ s - \kappa \frac{d^2}{dx^2} \right\} \left\{ \bar{T} + \alpha \bar{\theta} \right\} = T_\infty, \quad (28)$$

$$\left\{ 1 + s\tau - \tau\kappa \frac{d^2}{dx^2} \right\} \bar{\theta} = \bar{T}, \quad (29)$$

$$\left\{ s - \kappa_s \frac{d^2}{dx^2} \right\} \bar{T}_s = 0. \quad (30)$$

Eliminating $\bar{\theta}$ and \bar{T} from equations 28 and 29 in turn we find that

$$\left\{ s - \kappa \frac{d^2}{dx^2} \right\} \left\{ 1 + \alpha + s\tau - \tau\kappa \frac{d^2}{dx^2} \right\} \bar{T} = (1 + s\tau)T_\infty, \quad (31)$$

$$\left\{ s - \kappa \frac{d^2}{dx^2} \right\} \left\{ 1 + \alpha + s\tau - \tau\kappa \frac{d^2}{dx^2} \right\} \bar{\theta} = T_\infty. \quad (32)$$

Appropriate solutions of these equations are

$$\bar{T} = A \exp\left(-x \sqrt{\frac{s}{\kappa}}\right) + B' \exp\left(-x \sqrt{\frac{1+s\tau'}{\kappa\tau'}}\right) + \frac{1+(1+\alpha)s\tau'}{s(1+s\tau')} \cdot \frac{T_{\infty}}{1+\alpha}, \quad (33)$$

$$\bar{\theta} = A' \exp\left(-x \sqrt{\frac{s'}{\kappa}}\right) + B \exp\left(-x \sqrt{\frac{1+s\tau'}{\kappa\tau'}}\right) + \frac{1}{s(1+s\tau')} \cdot \frac{T_{\infty}}{1+\alpha}, \quad (34)$$

where

$$\tau' = \tau / (1 + \alpha). \quad (35)$$

(It is interesting to note that the behaviour of T and θ depends on the factored value of relaxation time τ' and not on τ itself. Similar behaviour was also found by Clarke, (1960a).) A , A' , B and B' are constants which can be found from the interface conditions; we note that substitution of the results 33 and 34 into the original equations 31 and 32 shows that

$$A' = A; \quad B' = -\alpha B, \quad (36)$$

so that conditions 16, 23 and 24 are sufficient to find these constants and T_0 .

The appropriate solution of equation 30, satisfying the condition $T_{sw} = T_0$, is simply,

$$\bar{T}_B = \bar{T}_0 \exp\left(x \sqrt{\frac{s'}{\kappa_B}}\right) \quad (37)$$

and the energy flux requirement (equation 16) shows that

$$\lambda_{sw} \sqrt{\frac{s'}{\kappa_B}} \bar{T}_0 = -\lambda_{aw} (1+\alpha) \sqrt{\frac{s'}{\kappa}} \cdot A. \quad (38)$$

Defining the symbol Q so that

$$Q = (1+\alpha) \frac{\lambda_{aw}}{\lambda_{sw}} \sqrt{\frac{\kappa_B}{\kappa}}, \quad (39)$$

equation 38 states that

$$\bar{T}_0 = -Q A. \quad (40)$$

Since we are only interested in the value of T_0 here, we need only evaluate the constant A .

3. The Interface Temperature

Making use of the "jump" conditions 21 and 22 in their transformed form, together with equations 33, 34 and 36, we find, after a little tedious algebra, that

$$\left\{ \frac{(1+\alpha)a\sqrt{s/\kappa}\sqrt{(1+s\tau')/\tau'\kappa} + (\alpha+a\Gamma)\sqrt{s/\kappa}}{(1+a\alpha\Gamma)\sqrt{(1+s\tau')/\tau'\kappa} + (1+\alpha)\Gamma} + 1 \right\} A \quad (41)$$

$$= \bar{T}_O - \frac{T_\infty}{s(1+s\tau')} \left\{ \frac{1}{1+\alpha} + \frac{s\tau'(\Gamma + \sqrt{(1+s\tau')/\tau'\kappa})}{(1+a\alpha\Gamma)\sqrt{(1+s\tau')/\tau'\kappa} + (1+\alpha)\Gamma} \right\},$$

whence \bar{T}_O and A can be found via equation 40. Clearly the "exact" value of T_O involves the inversion of a very complicated Laplace transform. However, we intend to avoid the difficulties inherent in this task by considering a number of special cases. Each case will represent a possible set of physical circumstances and, by choosing these circumstances judiciously, we hope to build up a fairly comprehensive picture of the behaviour of the interface temperature T_O with time.

(i) $\alpha = 0$.

When $\alpha = 0$, implying that $C = 0$, we can say that the inert internal energy mode has no communicable energy. Equations 40 and 41 show, in these circumstances, that

$$\bar{T}_O \left\{ 1 + Q_O + a\sqrt{\frac{s}{\kappa}} \right\} = \frac{Q_O T_\infty}{s}, \quad (42)$$

where Q_O is equal to Q with $\alpha = 0$.^{*} The transforms involved here are readily inverted and it is found that

$$T_O(t) = \frac{Q_O T_\infty}{1 + Q_O} \left\{ 1 - \exp(\kappa t(1 + Q_O)^2/a^2) \operatorname{erfc}(\sqrt{\kappa t}(1 + Q_O)/a) \right\}. \quad (43)$$

(erfc is the complementary error function which approaches unity as its argument approaches zero).

* We may use equations 33, 40 and 42 (with $\alpha = 0$) to find the magnitude of the temperature jump at the wall, namely $T_w - T_O$. This turns out to be equal to $T_\infty e^{z^2} \operatorname{erfc} z$, where $z^2 = \kappa t(1 + Q_O)^2/a^2$. Reference to Fig. 2b below shows that $T_w - T_O$ is greater than $T_\infty/4$ for $z^2 < 4$. This result is quoted as some support for the linearisations which have assumed, for example, that $\lambda_a \approx \text{constant}$.

It follows that T_o is zero at the time $t = 0$ and thereafter increases steadily and continuously to the final value

$$T_o(\infty) = \frac{Q_o T_\infty}{1 + Q_o} \quad (44)$$

as $t \rightarrow \infty$. This final value is reached, within about 5%, in a time t_f given by

$$\sqrt{\kappa t_f} (1 + Q_o) = 10 a. \quad (45)$$

Recalling the definitions of a and κ (equations 23 and 18 respectively), equation 45 implies that

$$t_f = 500 \left(\frac{2 - r_a}{r_a} \right)^2 t_c, \quad (46)$$

where t_c is the mean time between molecular collisions. (In evaluating t_f here we have assumed that $Q_o \ll 1$, as it would be in a shock tube experiment; typically, $Q_o \approx 10^{-2}$). The interesting fact emerges that t_f is quite probably within the range of possible experimental resolution, especially if r_a happens to be rather low. Thus if r_a should be as low as 0.1 say, $t_f = 1.8 \times 10^5 t_c$, or about $18 \mu\text{sec}$ if we take $t_c = 10^{-10}$ sec. We note furthermore that t_f depends quite "strongly" on the accommodation coefficient r_a .

We shall defer further comment until the next Section, when the question of comparison with experimental observations is to be discussed. Meanwhile we continue to examine some more special cases.

(ii) $a\Gamma = 1$.

Strictly speaking, the previous case applies only to monatomic gases, which have no internal energy states with communicable energy. We have implied that it might apply to gases with rapidly relaxing modes (like rotation in N_2 or O_2 perhaps) and we hope to justify this shortly. In this sub-section we simply require that the "active" and "inert" accommodation coefficients shall have values such as to just make the product $a\Gamma = 1$. The relaxation time τ (or τ') may have any finite, non-zero value at this stage.

Under these conditions, equations 40 and 41 show that

$$\bar{T}_o \left\{ 1 + Q + a \sqrt{\frac{s}{\kappa}} \right\} = \frac{Q T_\infty}{s(1+a)} \quad (47)$$

whence

$$T_o(t) = \frac{Q T_\infty}{(1+\alpha)(1+Q)} \left\{ 1 - \exp(\kappa t (1+Q)^2/a^2) \operatorname{erfc}(\sqrt{\kappa t} (1+Q)/a) \right\}. \quad (48)$$

This result is true no matter what the value of τ may be, excluding for the moment the two special cases of $\tau = 0$ and ∞ . These are to be dealt with below. Equation 48 is, of course, identical with equation 43 except that Q now replaces Q_o and the whole right hand side is divided throughout by the factor $(1+\alpha)$. Since Q is probably of order 10^{-2} in magnitude, the time-scale of the present case will be indistinguishable from that of case (i) for all practical purposes. Furthermore, it can be seen that, since $Q_o = Q/(1+\alpha)$, the amplitudes of T_o here and in case (i) are in the ratio $(1+Q_o)/(1+Q)$. The specific heats ratio is always less than unity so that with Q so small, no practical difference will exist here either.

When a $\Gamma = 1$ then, we conclude that the effects of a relaxing internal energy mode on the interface temperature are negligible.

(iii) $\Gamma = 0$.

A further possibility occurs if we imagine that the inert mode is not accommodated by the solid surface at all. In that case $r_i = 0$ and so $\Gamma = 0$. Equations 40 and 41 then show that

$$\left\{ 1 + Q + \alpha \sqrt{\frac{s \tau'}{1 + s \tau'}} + a(1 + \alpha) \sqrt{\frac{s}{\kappa}} \right\} \bar{T}_o = \frac{Q T_\infty}{1 + \alpha} \frac{1 + (1 + \alpha) s \tau'}{s(1 + s \tau')} \quad (49)$$

Unfortunately the transforms involved here are not now so readily inverted in terms of tabulated functions, but the result can be written in terms of a contour integral via the usual Laplace inversion theorem. Thus

$$T_o(t) = \frac{Q T_\infty}{2\pi i} \int_{Br} \left\{ \frac{1 + (1 + \alpha) s \tau'}{(1 + \alpha)(1 + s \tau')} \right\} \left\{ 1 + Q + \alpha \sqrt{\frac{s \tau'}{1 + s \tau'}} + a(1 + \alpha) \sqrt{\frac{s}{\kappa}} \right\}^{-1} e^{ts} \frac{ds}{s}. \quad (50)$$

(Br is the Bromwich contour, running parallel to the $\operatorname{Im}(s)$ axis and to the right of all singularities in the integrand).

It is clear from the integral in equation 50 that we can always find times less than τ' for which

$$T_o(t) \approx \frac{Q_o T_\infty}{1 + Q_o} \cdot \frac{1}{2\pi i} \int_{Br} \left\{ 1 + \frac{a}{1 + Q_o} \cdot \sqrt{\frac{s}{\kappa}} \right\}^{-1} e^{ts} \frac{ds}{s}. \quad (51^*)$$

* e.g. Put $ts = z$; then equation 50 becomes

$$T_o(t) = \frac{Q T_\infty}{2\pi i} \int_{Br} \left\{ \frac{1 + (1 + \alpha) z \tau'/t}{(1 + \alpha)(1 + z \tau'/t)} \right\} \left\{ 1 + Q + \frac{z \tau'/t}{1 + z \tau'/t} + \frac{a(1 + \alpha) \sqrt{z \tau'}}{\sqrt{\kappa t}} \right\}^{-1} e^z \frac{dz}{z}$$

Then, when $\tau'/t \gg 1$ we have

$$T_o(t) \approx \frac{Q T_\infty}{2\pi i} \int_{Br} \left\{ 1 + \alpha + Q + \frac{a(1 + \alpha) \sqrt{z \tau'}}{\sqrt{\kappa t}} \right\}^{-1} e^z \frac{dz}{z}$$

Noting that $Q_o = Q/(1 + \alpha)$ and replacing z by st equation 51 follows.

This contour integral gives precisely the result written in equation 43. We infer therefore that when $\Gamma = 0$, $T_0(t)$ behaves initially exactly as if the inert mode took no part in the proceedings, i. e. behaves as if the inert mode was "frozen", (see case (iv) below).

How relaxation subsequently affects this picture is difficult to generalise upon, but we may proceed as follows. The original Bromwich contour in equation 50 can be deformed so that $T_0(t)$ is written as a loop integral around $s = 0$. Paying proper heed to the phase of the radicals on this contour we can eventually produce the following real integral representation.

$$\begin{aligned}
 T_0(t) &= \frac{Q T_\infty}{(1 + \alpha)(1 + Q)} \\
 &+ \frac{a Q T_\infty}{\pi \sqrt{\kappa \tau'}} \int_1^\infty [1 - (1 + \alpha)y] \left\{ \left[(1 + Q)(y - 1)^{\frac{1}{2}} + \alpha y^{\frac{1}{2}} \right]^2 + \frac{a^2(1 + \alpha)^2}{\tau' \kappa} y(y-1) \right\}^{\frac{1}{2}} e^{-ty/\tau'} \frac{dy}{y^{\frac{1}{2}}} \quad \dots \quad (52) \\
 &- \frac{Q T_\infty}{\pi(1 + \alpha)} \int_0^1 [1 - (1 + \alpha)y] \left\{ \alpha + \frac{a(1 + \alpha)}{\sqrt{\kappa \tau'}} (1 - y)^{\frac{1}{2}} \right\} \left\{ (1 + Q)^2(1 - y) + \left[\alpha y^{\frac{1}{2}} + \frac{a(1 + \alpha)}{\sqrt{\tau' \kappa}} y^{\frac{1}{2}} (1 - y)^{\frac{1}{2}} \right]^2 \right\}^{-1} \frac{e^{-ty/\tau'} dy}{y^{\frac{1}{2}} (1 - y)^{\frac{1}{2}}}
 \end{aligned}$$

It can be seen at once that

$$T_0(t) \sim \frac{Q T_\infty}{(1 + \alpha)(1 + Q)} = \frac{Q_0 T_\infty}{1 + Q} \quad \text{as } t \rightarrow \infty \quad (53)$$

Comparing this result with equation 48 above it is found that the final interface temperatures are the same whether $\Gamma = 0$ or a^{-1} for any values of τ' satisfying $0 < \tau' < \infty$ (As mentioned earlier $\tau' = 0$ and ∞ are to be dealt with separately). The manner in which $T_0(t)$ approaches its final value in the present case is, however, clearly different from the smooth behaviour exhibited by equation 48 in case (ii). The real integrals in equation 52 are still far too unwieldy to give us any indication of this behaviour as they stand. It seems however, that some progress could be made if we examined the situation for which $\tau' \gg a^2(1 + \alpha)^2/\kappa$, because it would then be possible to neglect some terms in the integrals in equation 52 and even discard the first of these altogether. Rather than follow this course directly at this stage, we shall make the assumption that $a = 0$ in the original contour integral in equation 50. Physically, this assumption is equivalent to examining a time region within which relaxation time effects dominate the temperature jump effects (which account for the $a(1 + \alpha)/\sqrt{\kappa}$ terms), the relaxation time being, comparatively, a "long" one. With $a = 0$ the transform of $T_0(t)$ can be rewritten as follows

$$\frac{\bar{T}_0}{Q T_\infty} = \frac{1}{s(1+Q)} - \frac{\alpha \sqrt{\tau'}^2}{(1+Q)^2} \frac{1}{s} g_1(s^{-1}) - \frac{\alpha}{(1+\alpha)(1+Q)} \frac{1}{s^2} g_2(s^{-1}), \quad (54)$$

where

$$g_1(s) = \frac{1}{\sqrt{s+\tau'} + \alpha \sqrt{\tau'}/(1+Q)}, \quad (55)$$

$$g_2(s) = \frac{1}{\sqrt{s+\tau'}} g_1(s). \quad (56)$$

This result is now in a suitable form for us to use the theorem (Erdelyi et al 1954) which states that

$$t^\nu \int_0^\infty J_{2\nu}(2\sqrt{ut'}) u^{-\nu} f(u) du \ni s^{-2\nu-1} g(s^{-1}). \quad (57)$$

The symbol \ni means "has the Laplace transform" and $g(s)$ is the transform of $f(t)$. After a little manipulation, it is found that

$$\begin{aligned} \frac{(1+\alpha)(1+Q)}{Q T_\infty} T_0(t) &= 1 - \frac{\alpha}{1+Q} e^{-t/2\tau'} I_0(t/2\tau') \\ &+ \alpha \left(1 + \frac{\alpha}{(1+Q)^2} \right) \int_0^\infty J_0(2\sqrt{wt'/\tau'}) \exp \left[- \left(1 - \frac{\alpha^2}{(1+Q)^2} \right) w \right] \operatorname{erfc} \left[\frac{\alpha \sqrt{w}}{1+Q} \right] dw. \end{aligned} \quad (58)$$

(J_0 and I_0 are the first kind, zero order, Bessel and modified Bessel functions, respectively; see Watson 1944). It does not seem possible to simplify the integral in equation 58 any further, but it is relatively easy to compute numerically. In fact Fig. 1 shows equation 58 plotted vs. t/τ' for the values $Q = 0.01$ and $\alpha = 0.28$. The latter number is appropriate to almost classically excited vibration in a diatomic molecule: the vibrational mode in such a molecule would almost certainly qualify for the title "inert". We note from equation 58 that when t/τ' is very small

$$T_0(t) \approx \frac{Q_0 T_\infty}{1+Q_0},$$

which corresponds with the final value of T_0 when the inert mode is "frozen" (see equation 51 et seq and case (iv) below). We have already remarked (in case (ii) above) on how little this final value of T_0 differs from the " $t/\tau' \rightarrow \infty$ " value (see equation 53) of $Q T_\infty / (1+\alpha)(1+Q)$ and Fig. 1 exemplifies this. We see too, that the sole effect of relaxation on T_0 (at least under the present assumptions) is to produce a 'kink' in $T_0(t)$ of quite small amplitude, whose trough occurs when $t/\tau' \approx 2$. As a matter of interest we show the series expansions for $T_0(t)$, valid for $t/\tau' \ll 1$ and $\gg 1$, respectively.

$$\frac{T_0(t)}{Q T_\infty} = \frac{1}{(1+\alpha)(1+Q_0)} - \frac{\alpha(1+Q)(1+\alpha+2Q)}{2(1+\alpha+Q)} \cdot \frac{t}{\tau'} + \dots \quad (59)$$

$$\frac{T_0(t)}{Q T_\infty} \sim \frac{1}{(1+\alpha)(1+Q)} - \frac{\alpha}{(1+\alpha)(1+Q)^2} \sqrt{\frac{\tau'}{\pi t}} + \dots \quad (60)$$

They confirm that $T_0(t)$ lies below the initial and final values in the vicinity of $t/\tau' = 0$ and ∞ . Equation 59^o was obtained from equation 58, and equation 60 direct from the real integrals in equation 52 with $a = 0$. (The curve labelled "equation 59" in Fig. 1 includes the next term, involving $(t/\tau')^2$. The coefficient of this term is a lengthy algebraic expression in α and Q).

When $a \neq 0$ we anticipate that $T_0(t)$ will behave in a way very similar to that sketched in Fig. 1, except that for very small values of t/τ' , the curve will start from the origin and then quickly fair into the curve in Fig. 1, (see equation 51 et seq). When τ' is not very much greater than $a^2(1+\alpha)^2/\kappa$ it seems reasonable to expect that the relaxation effect exhibited in Fig. 1 will, roughly speaking, be superimposed upon the $(1 - e^{-z^2} \operatorname{erfc} z)$ -type of curve found previously, (see Fig. 2b). Either way, it seems fair to comment that the relaxation time effects are, somewhat surprisingly, quite small in relation to the temperature jump effects. In practice it seems highly probable that they will not be distinguishable at all, even in this extreme case of $\Gamma = 0$, which produces the most favourable set of circumstances for such effects to work on $T_0(t)$.

(iv) $\tau' = \infty$

In case (i), with $\alpha = 0$, relaxation time is of no importance. In cases (ii) and (iii) we have examined two extremes of gas/solid behaviour (as far as the inert mode is concerned) and found solutions for $T_0(t)$ which are valid for $0 < \tau' < \infty$. In this and the succeeding sub-section we examine the extremes of τ' , starting with $\tau' = \infty$. The wall conditions will be left in a general state for the time being and commented upon as and when necessary.

Putting $\tau' = \infty$ in equations 40 and 41 we find that

$$\left\{ 1 + Q + \frac{a(1+\alpha)\sqrt{s/\kappa} + (\alpha + a\Gamma)}{(1 + a\alpha\Gamma)\sqrt{s/\kappa} + (1 + \alpha)\Gamma} \right\} \bar{T}_0 = \frac{Q T_\infty}{s} \cdot \frac{\Gamma + \sqrt{s/\kappa}}{(1 + a\alpha\Gamma)\sqrt{s/\kappa} + (1 + \alpha)\Gamma}, \quad (61)$$

which is still a very unwieldy transform expression. Therefore we shall examine only the two cases, $a\Gamma = 1$ and $\Gamma = 0$. When $a\Gamma = 1$ equation 61 gives

$$\bar{T}_0 \left\{ 1 + Q + a \sqrt{\frac{s}{\kappa}} \right\} = \frac{Q}{1+\alpha} \cdot \frac{T_\infty}{s}, \quad (62)$$

which is precisely equation 47. Thus equation 48 is true even when $\tau' = \infty$, i.e. no gas-phase excitation of the inert mode occurs at all: the gas/solid interaction is solely responsible for the changes which occur in inert mode temperature.

When $\Gamma = 0$ equation 61 gives

$$\bar{T}_0 \left\{ 1 + Q_0 + a \sqrt{\frac{s}{\kappa}} \right\} = \frac{Q_0 T_\infty}{s}, \quad (63)$$

which is precisely equation 42. $T_0(t)$ is therefore the same as in equation 43, which is not surprising because, setting $\Gamma = 0$ and $\tau' = \infty$ simultaneously is another way of saying that the inert mode has no communicable energy. Since the time scale and amplitude of $T_0(t)$ differ so little between the results 62 and 63 for $\Gamma = a^{-1}$ and 0, it seems reasonable to suppose that this will also be so for all intermediate Γ values. When $\tau' = \infty$ it is conventional to refer to the internal energy mode as "frozen". But note how wall effects can make some quantities (in particular of course $T_0(t)$) behave as if the mode is not frozen.

(v) $\tau' = 0$.

The final special case concerns the so-called "equilibrium approximation". It is clear from equation 19 that when τ' (and hence τ) = 0, $\theta = T$ everywhere. Thus the internal mode is now in the class that we have described as active. Letting $\tau' = 0$ in equations 40 and 41 leads to the following transform expression for the interface temperature.

$$\left\{ 1 + Q + \left(\frac{1 + \alpha}{1 + \alpha \Gamma} \right) a \sqrt{\frac{s}{\kappa}} \right\} \bar{T}_0 = \frac{Q T_\infty}{(1 + \alpha)s} \quad (64)$$

Clearly the time dependence of T_0 is similar to that found in cases (i) and (ii) (equations 43 and 48, respectively). Equation 64 is valid for all Γ in the present case and it is interesting to note how Γ makes itself felt in the time scale of the T_0 variations. In particular, when a $\Gamma = 1$ it can be seen that this time scale is exactly the same as that found in case (ii), equation 48. The latter result has now been shown to be valid for $0 \leq \tau' \leq \infty$.

When $\Gamma = 0$ it can be seen that the time scale is increased by a factor $(1 + \alpha)^2$ compared with the one just mentioned for a $\Gamma = 1$. Since α is possibly significant compared with unity, the change of time scale with Γ may be noticeable in typical shock tube experiments.

We may make use of the result 64 as follows. The theory to date permits us to imagine that the "translational-plus-active" modes do in fact consist of only the translational energy states. To emphasise this fact in what follows we shall replace the suffix "a" by a suffix "t" where this may be appropriate; e.g. r_t for r_a where r_t is now the proper translational accommodation coefficient. Then, with $\tau' = 0$, the internal energy mode of specific heat C becomes an active mode. With the interpretations adopted in this particular paragraph, it is clear that Q_0 in equation 42 is synonymous with what we imply by Q in equation 64. The two results, 42 and 64, are not, however, completely comparable because equation 42 implies that the active internal mode temperature is T_∞ at time $t = 0$ whilst equation 64 as it stands has been derived on the assumption that this temperature is zero at this same time. A little thought will indicate that we may in fact compare equations 42 and 64 directly by

omitting the factor $1/(1 + \alpha)$ on the latter's right-hand side. This factor only appears in equation 64 because, with the interpretation that we are now placing on that result, the internal energy mode must, immediately subsequent to time $t = 0$, be brought into equilibrium with the translational states. The $1/(1 + \alpha)$ term shows how the energy, originally in translation only, is shared between translational and internal states.

All this is by way of a somewhat lengthy justification for comparing the quantity written as 'a' in equation 42 with the factor $(1 + \alpha)a/(1 + \alpha\Gamma)$ in equation 64. Remembering that a in this latter expression is now taken to mean $((2 - r_t)/r_t) \cdot (2\gamma_t \kappa_t / \Omega_w)$, with κ_t equal to κ based on "suffix t" values, we imply that 'a' in equation 42 has the following value

$$a = \frac{(1 + C/C_{pt})(C_{pt}/C_{vt})(2\kappa_t/\Omega_w)((2 - r_t)/r_t)}{1 + (C/C_{vt}) [(2 - r_t)/(2 - r_i)] (r_i/r_t)} \quad (65)$$

r_i here refers to the accommodation coefficient of the internal energy mode which we are now treating as active.

Equation 65 indicates how the proper translational coefficient and the active internal mode coefficient should be combined. So far as the writer is aware, no measurements of r_i have been made; accommodation coefficients for diatomic gases are usually quoted as a single overall figure, such as we have implied by 'a' in equation 42 anyway. Thus it is not possible to comment on the relative sizes of the terms in equation 65. However, there is an intuitive feeling (see e. g. Sherman, 1955) that r_i for an active mode will be of the same order as r_t (since translation is also an active energy mode). If we assume that r_i does equal r_t , equation 65 becomes simply

$$a = \frac{2 - r_t}{r_t} \frac{2\kappa_t}{\Omega_w} \frac{C_{pa}}{C_{va}}$$

where $C_{pa} = C_{pt} + C$ and similarly for C_{va} . Remarking that κ_t and κ are in fact identical in magnitude, we see that r_a and r_t also have the same magnitude in these circumstances. There would seem to be a good case for an experimental investigation of the energy accommodation coefficients for separate energy modes, in order to clarify issues like those just discussed. It would not, however, appear to be an easy thing to do.

4. Comparisons with Experiment

In this final Section we set out to compare the theory with some results obtained from experiment. By and large, the theory suggests that purely relaxation time effects will not be of any great practical significance. Consequently we anticipate that the experimental results should compare reasonably well with the simple $1 - e^{-z^2} \operatorname{erfc} z$ function, which has appeared most often in the preceding analysis of special cases.

The experimental results were obtained using a thin film platinum resistance thermometer on the closed end of a conventional (2" internal diameter) shock tube. The film was drawn in the form of a spiral with a resistance of 2,500 Ω . With the thermometer output connected to the pre-amplifier of a Tektronix 535 oscilloscope the circuitry had a rise-time of about 0.12 microseconds. The shock tube was driven by hydrogen at 230 psia, the low pressure end containing air at a pressure of 200 mm Hg. This arrangement produced a primary shock wave of Mach number about 3.2. The experiment was conducted at an early stage in this particular shock tube's history so that, unfortunately, no proper shock speed measuring gear was available at the time. Consequently the shock Mach number was estimated from the diaphragm-pressure ratio, using results previously obtained in similar tubes. The shock reflection problem was dealt with by using a constant specific heats ratio of 1.4 (i.e. ignoring vibrational relaxation effects and treating rotation as an active mode in air). On this basis, the pressure in the reflected shock region has been estimated at 15.3 atmospheres whilst what we have written in previous Sections as T_{∞} turned out to be about 1,200°K. Such a temperature rise is of course rather higher than one would like for comparison with the foregoing linear theory. But we emphasise that the present investigation is purely heuristic and that it is with the broad behaviour of $T_0(t)$, rather than its finer numerical details, that we are mostly concerned. Figs. 2a and 3a are typical of the oscilloscope traces obtained subsequent to the reflection of the primary shock.

Fig. 2b shows the function $1 - e^{z^2} \operatorname{erfc} z$ plotted against z^2 , together with some experimental points taken from the trace in Fig. 2a. The latter were obtained by scaling the experimental ordinate at time $t = 2\mu\text{sec}$ to fit the ordinate of $1 - e^{z^2} \operatorname{erfc} z$ at $z^2 = 4$. In order to check the fit obtained between theory and experiment in Fig. 2b, the ordinate at $t = 2\mu\text{sec}$ on Fig. 3a was also scaled to agree with the ordinate from $1 - e^{z^2} \operatorname{erfc} z$ at $z^2 = 4$. (The trace in Fig. 3a was obtained from a different experimental run than the one yielding Fig. 2a). Since Fig. 3a was obtained with an oscilloscope sweep-speed of $0.2\mu\text{sec}/\text{cm}$. and the equipment rise time has been estimated as $0.12\mu\text{sec}$, we may expect to find some effect of the electronics on the experimental observations. This latter effect may be evaluated theoretically as follows.

The voltage output from the thermometer gauge is proportional to $T_0(t)$. Let us assume that equation 43 in case (i) above is the relevant function. The admittance of the electrical circuitry can be written in Laplace transform form as $(1 + st_r)^{-1}$, where t_r is the rise-time. Consequently the oscilloscope trace should be proportional to the transform

$$\frac{Q T_{\infty}}{(1 + Q_0)} \cdot \frac{1}{(1 + st_r)} = \frac{\sqrt{\kappa}(1 + Q_0)/a}{s(\sqrt{\kappa}(1 + Q_0)/a + \sqrt{s})}$$

or, in other words, the difference between this trace and the function $1 - e^{z^2} \operatorname{erfc} z$ should be

$$- \frac{t_r}{(1 + st_r)} \cdot \frac{\sqrt{\kappa}(1 + Q_0)/a}{(\sqrt{\kappa}(1 + Q_0)/a + \sqrt{s})}$$

Writing

$$\frac{\sqrt{\kappa}(1 + Q_0)}{a} = b$$

for brevity, this transform can be inverted to give the correction term

$$- (1 + 1/b^2 t_r)^{-1} \left\{ e^{-t/t_r} - e^{b^2 t} \operatorname{erfc}(b\sqrt{t}) + \frac{e^{-t/t_r}}{b\sqrt{t_r}} \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{t/t_r}} e^{-x^2} dx \right\}.$$

The value of Q_0 in the experiments under discussion was estimated to be about 0.01 (the temperature rise of the gauge having been estimated at about 12°C , using the gauge calibration factor and voltage output measured on the oscilloscope), so that we may reasonably neglect it compared with unity. Then $1/b^2 \approx a^2/\kappa \approx 0.48 \times 10^{-6}$ sec in the present case. $1/b^2 t_r$ is taken as 4, then, and the correction factor evaluated on this basis is shown in Fig. 3b. (Note that $z^2 \approx ta^2/\kappa$). The agreement between theory and experiment is fairly satisfactory, bearing in mind the approximations and assumptions made in deriving the results. (We remark that the slope of the theoretical curve corrected for rise-time effects is indeed zero at time $t = 0$ and has been drawn as such in Fig. 3b).

The comparisons of Figs. 2b and 3b are consistent with the theoretical deduction that inert internal mode effects will not be significant. The inert mode in the present case would be vibration in N_2 and O_2 , which would not be significantly excited at the temperatures encountered in the experiments. Thus what we have written as α above would be small enough compared with unity to be ignored. The theory is of course rather approximate if the inert mode is vibration, because this class of energy states would not be anywhere near classically excited under the experimental conditions. Thus α would really be a function of temperature and not constant, as has been assumed. Since the average vibrational specific heat would have been small anyway, this fact is probably not of any great significance in the results depicted in Figs. 2 and 3.

By far the most interesting feature of the results appears as a result of the relation between z^2 ($\approx a^2 t/\kappa$) and real time t . The theoretical and experimental match has suggested that $z^2 = 4$ corresponds to a real time of 2 μsecs . From the gas conditions in the reflected shock region a^2/κ is estimated to be $1.13 (2 - r_a)^2 r_a^{-2} 10^{-10}$ secs. and it follows that r_a has the value 0.03, roughly. While a "translational" accommodation coefficient of this magnitude is very small compared with the usual values of about 0.8 to 0.9 on so-called "engineering" metallic surfaces, it is significant to recall some general remarks made by Estermann (1960). These are to the effect that molecular scattering from crystalline surfaces is most frequently consistent with very small (almost zero) energy accommodation coefficients. The accommodating surface in the present experiments is the platinum film of the thermometer gauge*. This was formed by drawing the spiral shape on to glass sub-strate

* Accommodation effects on the sub-strate material surrounding the gauge may in fact be very different, but such "two-dimensional" effects are implied to be negligible in the present problem.

material with Hanovia paste (liquid bright platinum), followed by baking in the usual way at temperatures near the softening point of the glass. Hanovia paste is basically hydrochloroplatinic acid in a mixture of organic liquids which boil off during the heat treatment process. Addition of heat to H_2PtCl_6 reduces it to hydrochloric acid and platinum chloride ($PtCl_4$). Presumably further heating reduces this salt, depositing the platinum metal which then forms a strong bond with the glass sub-strate. The chemistry involved in the manufacture of a thin film gauge strongly suggests that the platinum will present a crystalline surface to any gas in contact with it.

However, examination of the platinum film surface under the microscope indicates that it has a sintered appearance and is very much more of an "engineering" surface than a properly crystalline one. At first sight this fact seems to be at variance with the inferences made above, but it must be remembered that the collisional mean free path for the gas molecules is only about 10^{-6} cm. at a pressure of 15 atmospheres. This is certainly very small compared with the "roughness" of the film surface and, accordingly, it seems plausible to assume that only one (or at most, only a few) encounters occur between a gas molecule and the solid material of the film before that molecule again collides with another gas molecule. Such behaviour may well be consistent with small accommodation effects.

It is an obvious corollary of such arguments that a reduction in overall gas pressure should lead to an increase in accommodation coefficient, since the mean free path will increase and more gas/solid molecular encounters occur before the advent of an "interrupting" gas/gas molecule encounter. Some tentative experimental observations support this view, the accommodation coefficient roughly doubling for a reduction of pressure by about a factor of four.

The results of this exploratory investigation appear sufficiently encouraging to warrant a more careful and extensive experimental study. This matter is at present in hand and it is hoped to report on the findings at a later date. (Recent experiments have served to confirm the general findings of the earlier brief results).

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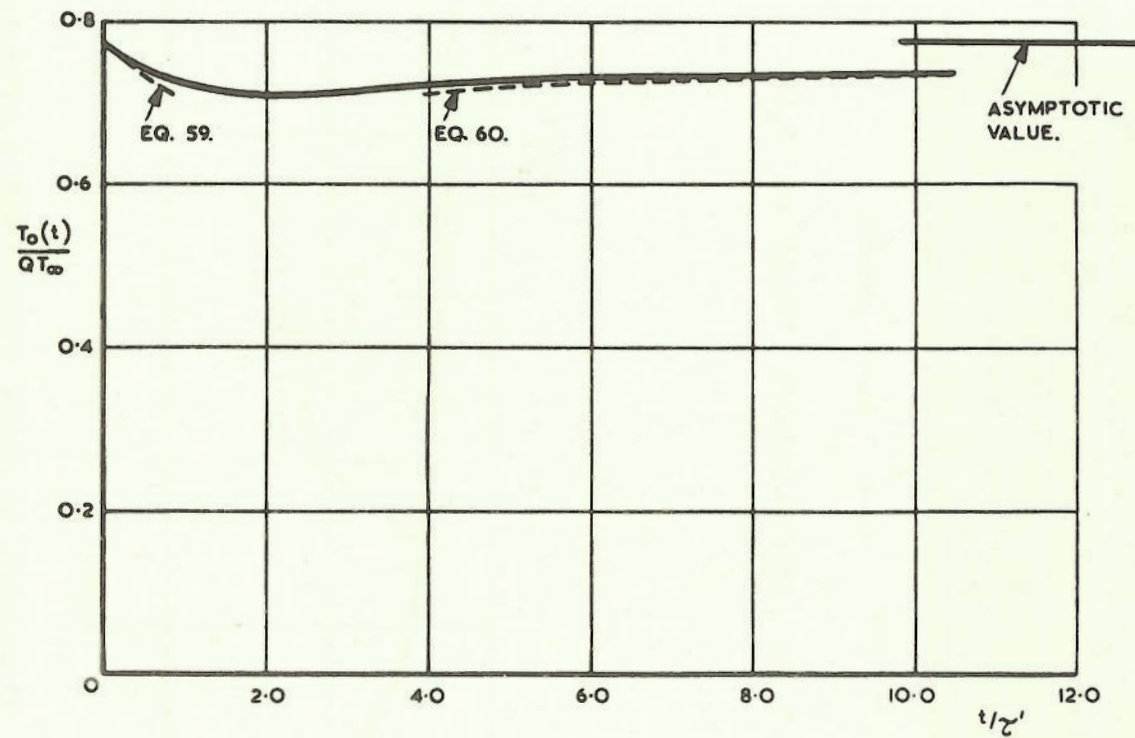


FIG. I. RELAXATION EFFECT ON $T_0(t)$ NO TRANSLATIONAL TEMPERATURE JUMP
 NO ACCOMMODATION OF INERT MODE. ($\alpha=0.28$ $Q=0.01$)

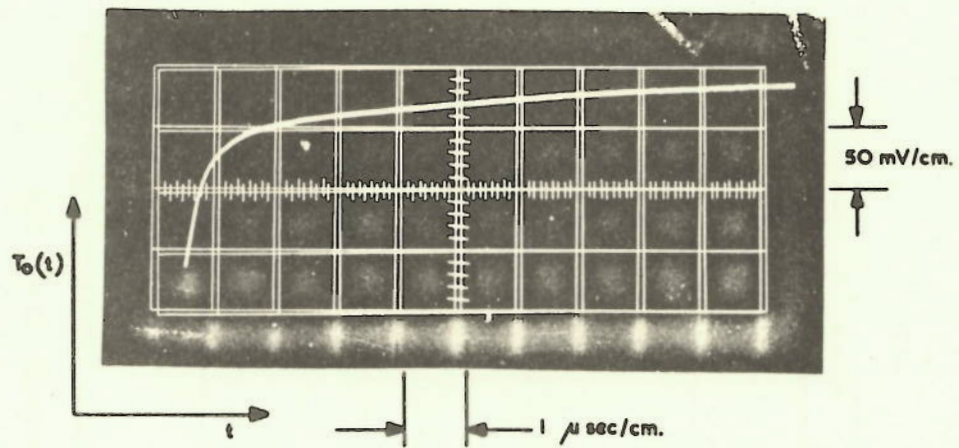


FIG. 2a. OSCILLOSCOPE TRACE OF $T_0(t)$

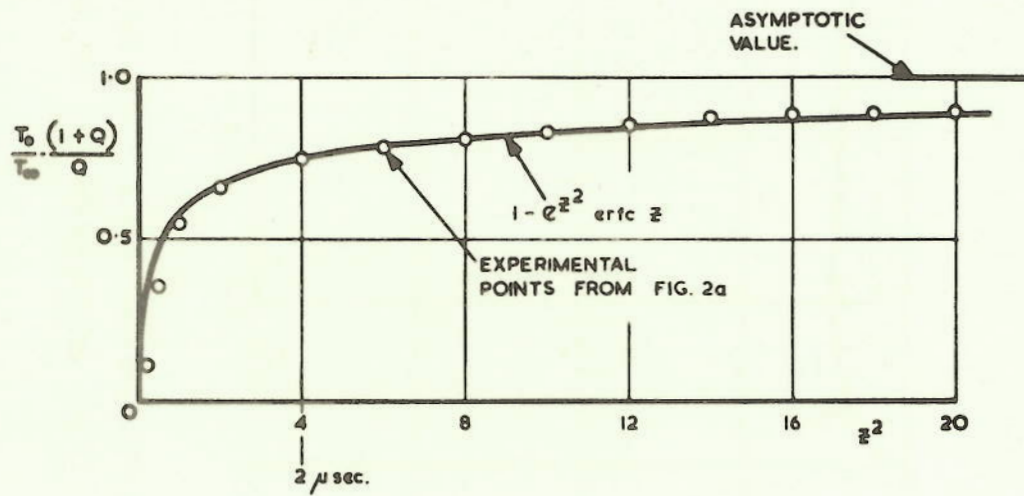


FIG. 2b. COMPARISON BETWEEN THEORY AND EXPERIMENTAL POINTS FROM FIG. 2a.

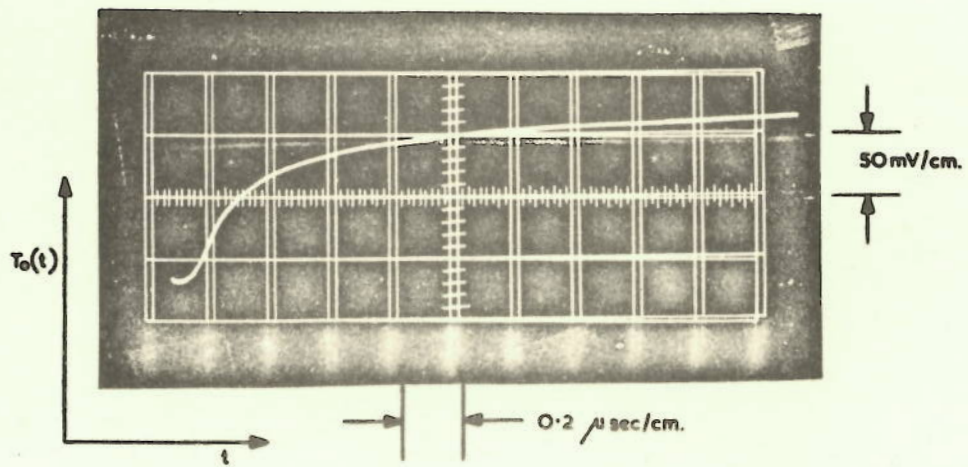


FIG. 3a. OSCILLOSCOPE TRACE OF $T_0(t)$
(THE NEARLY HORIZONTAL TRACE IS
TO BE DISREGARDED)

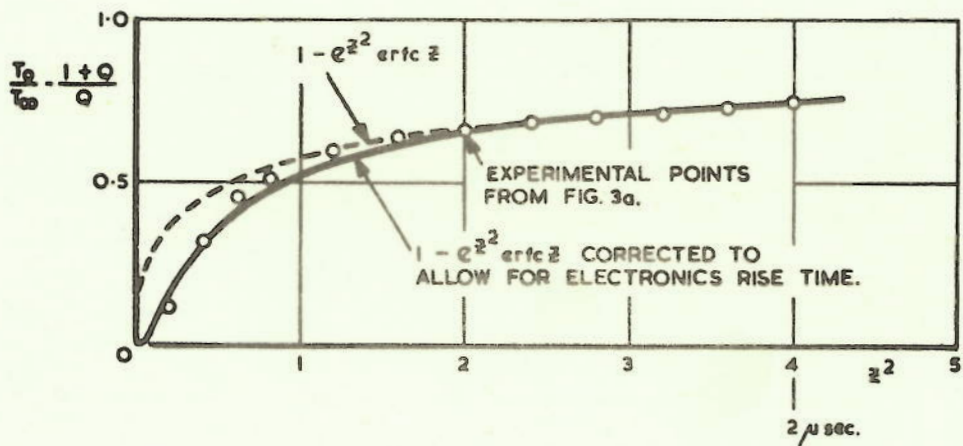


FIG. 3b. COMPARISON BETWEEN THEORY AND
EXPERIMENTAL POINTS FROM FIG. 3a.