

Temperature-time histories at the interface between a gas and a solid

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The effects of compressibility, temperature-jump and gaseous adsorption are considered in an attempt to predict the temperature-time history at the interface between a gas and a solid when both the temperature and the pressure of the gas are suddenly changed. It appears that temperature-jump will be the dominant effect, with adsorption contributing significantly in some circumstances. Compressibility is of minor importance during practically-resolvable time intervals. Some experimental evidence which gives tentative support to the results of the analysis is commented upon.

1. Introduction

In the sections to follow we attempt to estimate the way in which the temperature at the surface of a solid varies with time when the temperature and pressure of a gas in contact with the solid are both suddenly changed. We assume that the interface lies in the plane $x = 0$ and that both gas and solid are of semi-infinite extent. Only one-dimensional unsteady effects are considered.

The gas is treated as compressible and 'ideal', the latter restriction being taken in the sense that we do not attempt to cater for the effects of long relaxation times in the internal modes of polyatomic molecules. Equations governing the temperature behaviour in both gas and solid are derived and then linearized so that analytical solutions can be obtained. It is primarily during the course of formulating proper boundary conditions for these equations that we encounter most of the interesting physical aspects of the problem. In particular we would mention here that it is both possible and desirable to include the effects of temperature-jump and of the adsorption or desorption of gas onto or from the solid surface.

From a practical point of view, the problem to be studied represents an idealization of the situation arising when a plane shock wave reflects from a co-planar solid wall. In that event, both gas temperature and pressure are suddenly raised to new values and the subsequent energy transfer processes between the hot, high pressure gas and the cold solid act to raise the solid's temperature. It is possible to follow temperature changes on the solid surface with the aid of a thin-platinum-film resistance thermometer, and some results obtained in this way from shock-tube experiments are mentioned briefly below, in support of some of the theoretical predictions.

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2. The equations

The equations of mass, momentum and energy conservation are, respectively,

$$\frac{D\rho}{Dt} + \rho \frac{\partial u}{\partial x} = 0, \quad (1)$$

$$\rho \frac{Du}{Dt} + \frac{\partial p}{\partial x} - \frac{\partial \tau}{\partial x} = 0, \quad (2)$$

$$\rho \frac{Dh}{Dt} - \frac{Dp}{Dt} + \frac{\partial q}{\partial x} - \tau \frac{\partial u}{\partial x} = 0, \quad (3)$$

where D/Dt is written for $\partial/\partial t + u \partial/\partial x$ in the present one-dimensional unsteady case. ρ , u , p and h are the density, gas velocity, pressure and specific enthalpy and τ and q are the viscous stress and energy flux rate, respectively. For the problem in hand we shall assume that

$$\tau = \left(\frac{4}{3}\mu + \mu_v\right) \frac{\partial u}{\partial x}, \quad q = -\lambda \frac{\partial T}{\partial x}, \quad (4)$$

where μ and μ_v are the shear and equivalent bulk viscosities, the latter accounting for the presence of any rapidly relaxing internal degrees of freedom which the gas molecules may possess; λ is the coefficient of thermal conductivity, appropriately modified after the style of Eucken to account for the part played by rapidly relaxing degrees-of-freedom in the energy-transfer processes.

In dealing with a pure gas, the thermodynamic equation may be written in the form

$$T ds = dh - (1/\rho) dp, \quad (5)$$

where s is the specific entropy. As in equation (4), T is the temperature appropriate to all classes of energy storage in the gas molecules. Equations (3) and (5) together show that

$$\rho T \frac{Ds}{Dt} = -\frac{\partial q}{\partial x} + \tau \frac{\partial u}{\partial x}. \quad (6)$$

Since ρ can be regarded as a function of p and s , equation (1) can be rewritten with the aid of (6) to read

$$\left(\frac{\partial \rho}{\partial p}\right)_s \frac{Dp}{Dt} + \left(\tau \frac{\partial u}{\partial x} - \frac{\partial q}{\partial x}\right) \frac{1}{\rho T} \left(\frac{\partial \rho}{\partial s}\right)_p + \rho \frac{\partial u}{\partial x} = 0. \quad (7)$$

However,

$$\left(\frac{\partial p}{\partial \rho}\right)_s = a^2, \quad (8)$$

where a is the local isentropic speed of sound and it can be shown that

$$\left(\frac{\partial \rho}{\partial s}\right)_p = -\frac{\rho^2 T R}{p C_p}, \quad (9)$$

provided that the thermal and caloric equations of state are

$$p = \rho R T, \quad (10)$$

and

$$h = \int_0^T C_p dT \quad \text{or} \quad e = \int_0^T C_v dT, \quad (11)$$

respectively. e is the specific internal energy and C_p and C_v are the specific heats at constant pressure and constant volume, respectively. R is the gas constant for the particular gas in question. One can verify that the relation

$$C_p - C_v = R \tag{12}$$

is satisfied and also that
$$a^2 = \gamma p / \rho, \tag{13}$$

where γ is the usual ratio of specific heats. If equations (10) and (11) are valid descriptions of the thermodynamic behaviour of the gas, C_p , C_v and γ are, at worst, functions of T only and may (in the case of classically excited molecular states) be constants. We imply that a is the equilibrium speed of sound and therefore exclude considerations of relaxation effects, as we have implied in the remarks following equation (4).*

With the foregoing results and assumptions it is now possible to rewrite equation (7) in the form

$$\frac{Dp}{Dt} + \rho a^2 \frac{\partial u}{\partial x} + (\gamma - 1) \left(\frac{\partial q}{\partial x} - \tau \frac{\partial u}{\partial x} \right) = 0. \tag{14}$$

Equations (2), (3) and (14) now constitute three equations which are to be solved for the three unknown quantities p , u and T .

In the work to follow we shall simplify this task by assuming that the perturbations imposed on some uniform quiescent state of the gas are sufficiently small for these equations to be linearized and still give an adequate description of the principal physical processes involved. We make no attempt to justify such a procedure, other than to say that our primary purpose is to attempt to predict in a broad sense how gas-solid interactions show up in the temperature-time history at the interface: detailed and accurate numerical results are not our present concern. Accordingly, we shall use equations (2), (3) and (14) in the approximate forms

$$\rho_\infty \frac{\partial u}{\partial t} + \frac{\partial p}{\partial x} - \left(\frac{4}{3} \mu_\infty + \mu_{v\infty} \right) \frac{\partial^2 u}{\partial x^2} = 0, \tag{15}$$

$$\rho_\infty C_{p\infty} \frac{\partial T}{\partial t} - \frac{\partial p}{\partial t} - \lambda_\infty \frac{\partial^2 T}{\partial x^2} = 0, \tag{16}$$

$$\frac{\partial p}{\partial t} + \rho_\infty a_\infty^2 \frac{\partial u}{\partial x} - (\gamma_\infty - 1) \lambda_\infty \frac{\partial^2 T}{\partial x^2} = 0, \tag{17}$$

which are obtained by ignoring all squares and products of small disturbance quantities. The suffix ∞ denotes the relevant uniform, reference state of the gas (which is to be defined more carefully below). We note in particular that equations (15) to (17) include no convective effects and also that the term $\tau(\partial u/\partial x)$ (i.e. the viscous dissipation term) vanishes in this approximation.

3. Boundary conditions

At this stage we must begin to formulate the actual problem to be solved. The gas is assumed to occupy the semi-infinite region lying to the right of the plane $x = 0$. For all times $t < 0$ it is assumed that the gas is at the same tempera-

* An account of relaxation effects in circumstances similar to those under discussion here has been given by Clarke (1961).

ture as that of a semi-infinite solid which lies to the left of $x = 0$. We also assume that for all times $t < 0$ the gas is at some uniform 'low' pressure; we need not be more specific about what is implied by the adjective 'low' at the present stage.

An important implication of this initial, quiescent condition is that the processes of adsorption and desorption of the gas on to or from the solid surface shall be in equilibrium. A gas molecule can only be adsorbed by a solid on one of a number of sites; the so-called 'active sites for adsorption'. Let us suppose that N_s of such active sites exist on every unit area of the solid surface which is exposed to the gas and let us further suppose that, prior to the instant of time $t = 0$, N_{a0} of these active sites per unit area are actually occupied by a gas molecule. The solid is being continually bombarded by gas molecules (even in an equilibrium condition) as a result of their random thermal motions, so that adsorption must be a continuously-occurring process. We shall write the number adsorbed per unit area per unit time as

$$k_a(N_s - N_a), \quad (18)$$

where N_a here is a general number of occupied active sites (not necessarily an equilibrium number, as we have implied in the case of N_{a0} above); k_a is a 'rate constant' for the adsorption process and equation (18) states that the rate of adsorption per unit area per unit time is equal to k_a times the number of unoccupied active sites. If, as we shall assume, any gas molecule which strikes the surface can be adsorbed, then k_a is simply equal to the reciprocal of N_s times the total number of molecules striking the wall per unit area per unit time. The bombardment rate is equal to the relevant number density of molecules adjacent to the wall, multiplied by the mean molecular velocity in the direction normal to (and towards) the surface.

The reverse process of desorption must also be occurring concurrently with that of adsorption and, with N_a occupied sites existing on unit area of the wall, the number of molecules desorbed from unit area in unit time is written as

$$k_d N_a; \quad (19)$$

k_d is a 'rate constant' for the desorption process. The net rate of accumulation of gas molecules on the solid surface can clearly be written as

$$\frac{dN_a}{dt} = k_a(N_s - N_a) - k_d N_a. \quad (20)$$

Under equilibrium conditions there is a dynamic balance between the adsorption and desorption processes; the left-hand side of equation (20) is equal to zero and one finds that

$$\frac{\sigma}{1 - \sigma} = \frac{k_a}{k_d}, \quad (21)$$

where σ is written for N_a/N_s , i.e. σ is equal to the fraction of the surface covered by gas molecules. As remarked earlier, k_a is equal to the rate of molecular bombardment of the solid surface times $1/N_s$ (if no activation energy for adsorption is required), so that it is linearly proportional to the pressure and inversely proportional to the square root of the absolute temperature. In fact we can write

$$k_a = \frac{p}{(2\pi mkT)^{\frac{1}{2}}} \frac{1}{N_s}, \quad (22)$$

where m is the molecular mass and k is Boltzmann's constant. The desorption constant is frequently a function of temperature only and, accordingly, equation (21) can be re-expressed in the form

$$\frac{\sigma}{1-\sigma} g(T) = p, \quad (23)$$

known as Langmuir's adsorption isotherm. $g(T)$ is a function of temperature only and it may be calculated if the partition functions for a gas molecule in the gaseous and adsorbed states are known (see, for example, Rushbrooke 1949). The ratio k_a/k_d is analogous to the equilibrium constant appearing in problems of chemical equilibrium: since it is possible to evaluate this ratio statistically, or to measure it experimentally, it follows that one need only have to find k_a or k_d , whence the other one will follow from the equilibrium relation.

In the current problem we are more interested in the non-equilibrium condition, so that the remarks subsequent to equation (20) may not appear to be relevant. However, if we make some kind of quasi-equilibrium assumption about the adsorption processes, as is currently popular in chemically-reacting-gas-flow studies, we may still use k_a in the form (22) and find k_d by the method briefly indicated above. At all events, it is clear that a change in gas pressure and temperature will always change both k_a and k_d (by different factors in general) so that the equilibrium adsorption state indicated by (21) or (23) will cease to hold true for the new p and T values. Additional adsorption (or desorption) will then occur at a rate governed by equation (20).

In the present problem we intend to examine the behaviour of the temperature of the *solid* at $x = 0$, subsequent to sudden changes which are to be imposed on the gas temperature and pressure at time $t = 0$. In other words, we assume that for $t < 0$ both solid and gas have the same temperature (let us say T_0). The gas is assumed to be at a 'low' pressure (let us say p_0) during this time. Then, at time $t = 0$, both p and T are raised from p_0 to p_∞ and from T_0 to T_∞ throughout the gas (i.e. for all $x > 0$). As a result of this imposed disturbance the system is forced out of equilibrium: in particular there will be a flux of heat from the gas to the solid which will act to raise the solid's temperature at the interface $x = 0$. It is this quantity which is to be our primary concern here since, as mentioned in the Introduction, it is possible to measure it experimentally. We shall assume that the gas dynamic equations (15), (16) and (17) are linearized about the perturbed values p_∞ and T_∞ . At $t = 0$ the gas velocity u is zero, as are all of its derivatives. In formulating the boundary conditions for this problem it is necessary to include the adsorption processes discussed briefly above, since these will give rise to an influx or efflux of the gas into or out of the wall. In addition, of course, it must be remembered that the desorption process is an endothermic one (i.e. energy must be supplied in order to detach a gas molecule from its 'active site' on the surface). Therefore an appropriate term must be added to the energy flux into the solid. (The situation is very similar to that arising in studies of ablating bodies, where the latent heat of melting or sublimation must be accounted for).

We shall assume that, once k_a and k_d have been changed to values appropriate to the new state of the gas, they subsequently remain constant; additionally, we

assume that the number of active sites, N_s , is a constant. In this case (20) integrates very simply to give

$$\frac{k_a N_s}{k_a + k_d} - N_a = A e^{-(k_a + k_d)t}, \quad (24)$$

where A is a constant to be evaluated. From (21) we observe that the group $k_a N_s / (k_a + k_d)$ must be equal to the *new* equilibrium number of occupied sites (N_{ae} , say), which is eventually achieved as $t \rightarrow \infty$. At time $t = 0$, we have already stated that the number of occupied sites is N_{a0} , so that A is simply equal to $N_{ae} - N_{a0}$, or ΔN for short. Thus we can rewrite (24) in the form

$$N_{ae} - N_a = \Delta N e^{-k't}, \quad (25)$$

where

$$k' = k_a + k_d. \quad (26)$$

The assumption of new constant values for k_a and k_d for times $t > 0$ may not be especially good from the strictly physical point of view, since both p and T will vary with time after the instant $t = 0$, but it does not seem unreasonable in the context of the linearizations which are to be adopted anyway (see previous section). At all events, (25) describes in broad terms something of the gas behaviour arising from adsorption or desorption. In particular we can easily find an expression for the mass flux of gas into the wall as a result of the imposed unbalance of these two processes. This is clearly

$$m(dN_a/dt) = mk'\Delta N e^{-k't}, \quad (27)$$

and the gas velocity boundary condition at $x = 0$ becomes

$$-(\rho u)_w = mk'\Delta N e^{-k't}, \quad (28)$$

the suffix w implying evaluation at $x = 0$. If the gas density is changed to the new value ρ_∞ at time $t = 0$, then we may write the linearized version of (28) in the form

$$-\rho_\infty u_w = mk'\Delta N e^{-k't}, \quad (29)$$

since the gas velocity u is implied to be a small quantity anyway.

The remaining boundary conditions are provided by temperature and energy-flux considerations at the interface. We assume that the temperature of the solid (written as $T_0 + T_m$) satisfies the usual diffusion equation, namely

$$\frac{\partial T_m}{\partial t} - \kappa_m \frac{\partial^2 T_m}{\partial x^2} = 0, \quad (30)$$

since T_0 is a constant. κ_m is the appropriate thermal diffusivity (assumed constant). The gas and solid temperatures at $x = 0$ (T_w and $T_0 + T_{mw}$, respectively) must be linked via an appropriate 'temperature-jump' condition (see, for example, Clarke 1960*a*, 1961) which can be written here in the form

$$\alpha' \left(\frac{\partial T}{\partial x} \right)_w = T_w - T_{mw} - T_0, \quad (31)$$

where

$$\alpha' = (2 - r)l/r. \quad (32)$$

Here r is an average accommodation coefficient for the translational and internal-energy states of the gas molecules and l is an average mean free path for the

transfer of these forms of energy. In the analysis to follow it is slightly more convenient to measure the gas temperature, not from the ambient value existing uniformly for all x at times $t < 0$, but from the perturbed gas temperature, which we write as T_∞ . Accordingly, we define a temperature θ such that

$$T = T_\infty + \theta, \quad (33)$$

$$\text{whence (31) becomes} \quad \alpha' \left(\frac{\partial \theta}{\partial x} \right)_w = \theta_w - T_{mw} + T_\infty - T_0. \quad (34)$$

Conservation of energy at the interface $x = 0$ requires that

$$\lambda_{mw} \left(\frac{\partial T_m}{\partial x} \right)_w = \lambda_w \left(\frac{\partial \theta}{\partial x} \right)_w - (\rho u)_w \psi, \quad (35)$$

where the various new quantities introduced here are as follows: λ_m and λ are the thermal conductivities of the solid and gas, respectively (suffix w signifying evaluation at $x = 0$), whilst ψ is the heat liberated by the adsorption of unit mass of gas. The term on the left-hand side of (35) therefore represents the heat conducted (in the negative x -direction) into the solid whilst those on the right-hand side are, respectively, the heat conduction through the gas and the convective flux of 'adsorption energy'. Equations (28), (34) and (35), together with the conditions of finiteness which must be imposed on T (or θ) and $(T_m + T_0)$ and their spatial derivatives as $|x| \rightarrow \infty$, will be found to be sufficient boundary conditions for a solution of the current problem. The initial conditions are that both T_m and θ and all of their derivatives shall be zero at the instant $t = 0$. We shall summarize the mathematical content of the problem after one or two further developments.

As set up so far, the problem is concerned primarily with the gas and solid temperatures. Consequently it seems advisable to reduce the equations (15), (16) and (17) so that we have an equation in T (or θ) alone. This is quite readily accomplished and we find that

$$\frac{\partial}{\partial t} \left\{ \frac{1}{\alpha_\infty^2} \frac{\partial^2 \theta}{\partial t^2} - \frac{\partial^2 \theta}{\partial x^2} + \frac{4\gamma_\infty Pr \kappa^2}{3\alpha_\infty^2} \frac{\partial^4 \theta}{\partial x^4} \right\} - \kappa \frac{\partial^2}{\partial x^2} \left\{ \frac{\frac{4}{3} Pr + \gamma_\infty}{\alpha_\infty^2} \frac{\partial^2 \theta}{\partial t^2} - \frac{\partial^2 \theta}{\partial x^2} \right\} = 0, \quad (36)$$

$$\text{where} \quad \kappa = \lambda_\infty / \rho_\infty C_{p_\infty}, \quad Pr = (\mu_\infty + \frac{3}{4} \mu_{v\infty}) C_{p_\infty} / \lambda_\infty, \quad (37)$$

κ is the thermal diffusivity of the gas (evaluated in the initial perturbed state) and Pr is an appropriately defined Prandtl number. We shall henceforth assume that Pr is equal to $\frac{3}{4}$, since this greatly simplifies the analysis to follow whilst at the same time it is a value not too far removed from the correct one for a variety of gases (in particular, diatomic gases of course). It should be remarked that solutions of (36) have been obtained previously; by Cole & Wu (1952) for the case of $Pr = 0$ and using impulse function inputs to an infinite expanse of gas, and by the author (1960*b*) for both $Pr = 0$ and $Pr = \frac{3}{4}$ in connexion with a gas-solid contact problem similar to that currently under investigation but using boundary conditions somewhat simpler than those discussed above (see § 7.1 below).

In order to proceed with a solution of equations (30) and (36), from which the behaviour of T_{mw} is to be deduced, it is now only necessary to translate the 'velocity' condition of (28) (or rather its linearized version in (29)) into a 'temperature' condition. This can be done by eliminating p and all derivatives of u

which contain operations involving $\partial/\partial x$ from (15), (16) and (17), leaving an expression for $\partial^2 u/\partial t^2$ in terms of T (or θ) derivatives only. In general terms, this expression is

$$-\frac{1}{C_{p\infty}} \frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 \theta}{\partial x \partial t} - \frac{4\gamma_\infty Pr \kappa^2}{3a_\infty^2} \frac{\partial^4 \theta}{\partial x^3 \partial t} - \kappa \frac{\partial^3 \theta}{\partial x^3} + \frac{4Pr\kappa}{3a_\infty^2} \frac{\partial^3 \theta}{\partial x \partial t^2}, \quad (38)$$

but it becomes slightly simpler for $Pr = \frac{3}{4}$.

4. Summary of the equations to be solved

At this stage it seems advisable to summarize the equations to be solved, together with the relevant initial and boundary conditions. Before doing so, we note that the quantities κ/a_∞ and κ/a_∞^2 have the dimensions of length and time respectively: they are in fact of the order of the mean free path for intermolecular collisions and the corresponding collision time interval, respectively. Accordingly, we may non-dimensionalize both x and t , to x' and t' , in the form

$$x' = xa_\infty/\kappa, \quad t' = ta_\infty^2/\kappa. \quad (39)$$

Then, with $Pr = \frac{3}{4}$, (36) and (30) become

$$\frac{\partial}{\partial t'} \left\{ \frac{\partial^2 \theta}{\partial t'^2} - \frac{\partial^2 \theta}{\partial x'^2} + \gamma_\infty \frac{\partial^4 \theta}{\partial x'^4} \right\} - \frac{\partial^2}{\partial x'^2} \left\{ (\gamma_\infty + 1) \frac{\partial^2 \theta}{\partial t'^2} - \frac{\partial^2 \theta}{\partial x'^2} \right\} = 0, \quad (40)$$

$$\frac{\partial T_m}{\partial t'} - \frac{\kappa_m}{\kappa} \frac{\partial^2 T_m}{\partial x'^2} = 0. \quad (41)$$

The initial conditions are now that

$$T_m \text{ and all } x' \text{- and } t' \text{-derivatives of } T_m \text{ are zero for } x' < 0, t' \leq 0, \quad (42)$$

and that

$$\theta \text{ and all } x' \text{- and } t' \text{-derivatives of } \theta \text{ are zero for } x' > 0, t' = 0. \quad (43)$$

The boundary conditions are now

$$\alpha \left(\frac{\partial \theta}{\partial x'} \right)_w = (T_\infty - T_0) + \theta_w - T_{mw} \quad \text{for } x = 0, t > 0, \quad (44)$$

where

$$\alpha = (2-r)/r; \quad (45)$$

$$\left(\frac{\lambda_m}{\lambda_\infty} \right) \left(\frac{\partial T_m}{\partial x'} \right)_w = \left(\frac{\partial \theta}{\partial x'} \right)_w + \eta e^{-\omega t'} \quad \text{for } x = 0, t > 0, \quad (46)$$

where

$$\eta = \frac{m\psi\kappa k' \Delta N}{a_\infty \lambda_\infty}, \quad \omega = \frac{k'\kappa}{a_\infty^2}; \quad (47)$$

$$\frac{\partial^2 \theta}{\partial x' \partial t'} - \gamma_\infty \frac{\partial^4 \theta}{\partial x'^3 \partial t'} - \frac{\partial^3 \theta}{\partial x'^3} + \frac{\partial^3 \theta}{\partial x' \partial t'^2} = -\frac{a_\infty}{C_{p\infty}} \frac{\partial^2 u}{\partial t'^2} \quad \text{for } x = 0, t > 0; \quad (48)$$

that

$$T_m \text{ and all } x' \text{- and } t' \text{-derivatives of } T_m \rightarrow 0 \text{ as } x' \rightarrow -\infty \text{ for all } t', \quad (49)$$

and that

$$\theta \text{ and all } x' \text{- and } t' \text{-derivatives of } \theta \rightarrow 0 \text{ as } x' \rightarrow +\infty \text{ for all } t'. \quad (50)$$

Equations (40) to (43) do not require any further explanation. In deriving (44), so that the new quantity α appears, we have made the not-too-unreasonable assumption that the free path l appearing in α' (see (32)) is equal to κ/a_∞ . In writing down (46) we have used (28) to eliminate $-(\rho u)_w$ from (35). Additionally we have assumed that λ_m is a constant (so that the suffix w is now no longer necessary) and also that λ_w can be replaced by the initial value λ_∞ . This is reasonably consistent with the linearizations leading up to (40). Both η and ω (see (46) and (47)) are treated as constants from now on. In writing (48) we have *not* eliminated $\partial^2 u / \partial t'^2$ via the appropriate version of (29), since u at $x = 0$ and $t \geq 0$ is in the nature of a step function. At the initial instant, when T is raised suddenly to T_∞ , etc., both u and all of its derivatives with respect to either x' or t' , are zero. Immediately subsequent to this time, however, u at $x' = 0$ and its derivatives with respect to t' can be found from (29). The method of solution adopted below will take account of the initial conditions in a proper fashion.

5. Laplace transform solutions

The initial and boundary value problem set out above is best solved by the Laplace transform method. We denote the transform of a quantity with respect to time t' by a bar over the appropriate symbol; e.g.

$$\bar{\theta}(x' : s) = \int_0^\infty \theta(x', t') e^{-st'} dt'.$$

With the initial conditions set out in (42) and (43), equations (40) and (41) in the transform plane are

$$\bar{\theta}^{(4v)} (1 + \gamma_\infty s) - \bar{\theta}'' s [1 + (\gamma_\infty + 1) s] + s^3 \bar{\theta} = 0, \tag{51}$$

$$\bar{T}_m'' - (s\kappa/\kappa_m) \bar{T}_m = 0, \tag{52}$$

the primes denoting differentiation with respect to x' . Solutions of these two equations which satisfy the conditions on x' -derivatives of θ and T_m given in (49) and (50) are

$$\bar{\theta}(x' : s) = B(s) \exp(-x' \sqrt{s}) + C(s) \exp\{-x' s(1 + \gamma_\infty s)^{-\frac{1}{2}}\}, \tag{53}$$

$$\bar{T}_m(x' : s) = A(s) \exp\{x' (\kappa s / \kappa_m)^{\frac{1}{2}}\}. \tag{54}$$

The 'constants' A , B and C can now all be found using the three remaining conditions in (44), (46) and (48). Since we are only interested in the value of T_m when $x' = 0$, it is only necessary to find A because

$$\bar{T}_m(0 : s) = A(s), \tag{55}$$

from (54). The details are quite straightforward, if a little tedious, but it can eventually be shown that

$$\begin{aligned} \{1 + \alpha Q \sqrt{s} + Qf(s)\} A(s) &= (T_\infty - T_0) s^{-1} \\ &+ \eta \left\{ \left(\frac{1 + s(a_\infty^2/\psi)}{(s + \omega) \sqrt{s}} \right) [\alpha \sqrt{s} + f(s)] - \frac{[\alpha s + (1 + \gamma_\infty s)^{\frac{1}{2}}] (a_\infty^2/\psi)}{s + \omega} \right\}, \end{aligned} \tag{56}$$

where

$$Q = \frac{\lambda_m}{\lambda_\infty} \sqrt{\frac{\kappa}{\kappa_m}} \tag{57}$$

and

$$f(s) = \frac{1 + (\gamma_\infty - 1) \sqrt{s(1 + \gamma_\infty s)^{\frac{1}{2}}}}{1 + (\gamma_\infty - 1) s}. \tag{58}$$

Q is a ratio of the thermal properties of the gas and solid and is ordinarily quite large; of order 10^2 is a typical value. Of the remaining quantities appearing in (56), α is defined in (45) (see also (32) *et seq.*), η and ω are defined in (47) and ψ is the heat of adsorption.

Quite clearly the complete evaluation of $T_m(0, t')$, via (55) and (56) and the Laplace inversion theorem, is a formidable undertaking. Even if it could be accomplished, it would probably lead to such complicated expressions that any appreciation of the behaviour of the interface temperature would prove exceedingly difficult. Thus we intend to evade the issue by considering instead a number of special cases, which lead to simplification of the final results and which help to give some idea of the general behaviour of $T_m(0, t')$ even though they do not present the complete, comprehensive, picture.

6. The interface solid temperature. Special cases

6.1. No temperature-jump, no adsorption

Putting both α and η equal to zero in (56) one finds that

$$\bar{T}_m(0 : s) = \frac{T_\infty - T_0}{s} \frac{1}{1 + Qf(s)}. \quad (59)$$

If we suppose that η is equal to zero because the sum of the rate-constants for adsorption and desorption, namely k' (see (26)), is equal to zero, it follows that there is no gas flux into or out of the wall (see (28)). When α is zero, there is no temperature-jump and both gas and solid interface temperatures have the same value (see (44), for example). This case is therefore just one treated previously by the writer (1960*b*) and some discussion of the behaviour of $T_m(0, t')$ deduced from (59) is given in that paper.

The broad behaviour of $T_m(0, t')$ can be summarized as follows. When $t' \rightarrow 0$ (and hence $s \rightarrow \infty$), $f(s) \rightarrow \sqrt{\gamma_\infty}$. In the limit one readily finds that

$$T_m(0, 0) = \frac{T_\infty - T_0}{1 + Q\sqrt{\gamma_\infty}}. \quad (60)$$

Now one can write

$$Q = \left(\frac{\rho_m C_{p_m} \lambda_m}{\rho_\infty C_{p_\infty} \lambda_\infty} \right)^{\frac{1}{2}}, \quad (61)$$

since $\kappa_m = \lambda_m / \rho_m C_{p_m}$, where ρ_m and C_{p_m} are the solid's density and specific heat respectively, and it follows that

$$T_m(0, 0) = \frac{T_\infty - T_0}{1 + Q'}, \quad (62)$$

where

$$Q' = \left(\frac{\rho_m C_{p_m} \lambda_m}{\rho_\infty C_{v_\infty} \lambda_\infty} \right)^{\frac{1}{2}}. \quad (63)$$

Conversely, when $t' \rightarrow \infty$ (and hence $s \rightarrow 0$), $f(s) \rightarrow 1$ and we have, in the limit

$$T_m(0, \infty) = \frac{T_\infty - T_0}{1 + Q}. \quad (64)$$

It can be verified that the results in (62) and (64) are precisely those which would arise if the heat conduction through the gas took place at either constant volume or constant pressure, respectively, as evidenced by the forms of Q' and Q in each case. Thus immediately subsequent to $t' = 0$, the solid's interface temperature jumps from zero to some value intermediate between zero and $T_\infty - T_0$ (which is equal to the temperature rise imposed upon the gas), this value being consistent with constancy of the gas's specific volume (or density). As the disturbances propagate out into the gas there is a gradual changing over from this type of process to a constant-pressure type of process and $T_m(0, t')$ rises accordingly to the value given in (64). Further discussion is to be found in the paper just cited, which also goes on to examine the form of the pressure and temperature waves sent out into the gas as a result of the imposed disturbance.

Whilst the special case $\alpha = 0, \eta = 0$ may be interesting, it does not seem to be a realistic physical model of the processes which occur near the interface, for reasons which will become apparent in the next sub-section. It is important to remember that t' is measured in units of molecular collision intervals, so that it is hardly justifiable to speak of t' values less than unity without attempting in some way to take account of the gaskinetic aspects of the problem. Furthermore, from a practical point of view, even values of t' very much greater than unity correspond to very short intervals of real time at all but the lowest pressures (e.g. at one atmosphere pressure about 10^{-10} sec elapse between successive collisions experienced by one molecule. Thus $t' = 100$ corresponds to a time interval of only one hundredth of a microsecond in these circumstances).

6.2. Temperature-jump included, no adsorption

Still assuming that η is equal to zero (by putting $k' = 0$), we find that

$$\bar{T}_m(0 : s) = (T_\infty - T_0) s^{-1} \{1 + \alpha Q \sqrt{s} + Q f(s)\}^{-1}. \quad (65)$$

In order to invert this expression we note that \bar{T}_m has branch-point singularities at $s = 0$ and $s = -1/\gamma_\infty$ in the complex s -plane. It can be confirmed that the usual Laplace-transform inversion contour (which runs parallel to the imaginary part of s -axis and to the right of $s = 0$ here) is reconcilable with the loop contour starting from $s = \infty e^{-i\pi}$, proceeding round $s = 0$ in an anticlockwise direction, and ending up at $s = \infty e^{+i\pi}$ without crossing the negative real part of s -axis. When $t' \gg 1$, the dominant part of the integral on this last contour comes from the regions near $s = 0$ (since γ_∞ is $O(1)$ always) and it follows that we can legitimately set $f(s)$ in (65) equal to unity and examine

$$\bar{T}_m(0 : s) = (T_\infty - T_0) s^{-1} \{1 + Q + \alpha Q \sqrt{s}\}^{-1} \quad (66)$$

in these circumstances. Not surprisingly, in view of the comments in § 6.1, (66) corresponds to heat conduction at constant pressure but this time with temperature-jump included. It is the inclusion of this temperature-jump effect which helps to account in some measure for the gas kinetic aspects of the gas-solid interaction.

We note at once from (65) that its effect is quite radical, for now, as $t' \rightarrow 0$ (and hence $s \rightarrow \infty$), we find that $T_m \rightarrow 0$ and *not* to a finite value as in § 6.1. This seems

very much more reasonable from a physical point of view, since the finite rate of gas-molecular bombardment of the solid can hardly bring about a finite change of conditions in the solid in an infinitesimal time interval. The form of (65) for large s would still suggest that $T_m(0, t')$ has a behaviour consistent with some kind of constant-volume heat-conduction at small times. However, we shall not enter into a fuller discussion of this case since $t' \gg 1$ is more likely to be of practical interest. Using (66) in this region of time we readily find that

$$T_m(0, t') = \frac{T_\infty - T_0}{1 + Q} \{1 - e^{z^2} \operatorname{erfc} z\}, \quad (67)$$

where

$$z^2 = t'(1 + Q)^2 / Q^2 \alpha^2 \quad (68)$$

and erfc is the complementary error function (which approaches unity as $z \rightarrow 0$). Since $Q \sim 10^2$, as has been remarked earlier, we can write

$$z^2 \simeq t'r^2 / (2 - r)^2. \quad (69)$$

In the limit as $t' \rightarrow \infty$ it follows that

$$T_m(0, t') \rightarrow (T_\infty - T_0) / (1 + Q) \quad (70)$$

once again, as in the constant-pressure heat-conduction problem without temperature-jump. As (67) shows, however, the manner of its doing so is radically different in the two cases $\alpha = 0$ and $\alpha \neq 0$. We note that

$$e^{z^2} \operatorname{erfc} z \sim 1/z \sqrt{\pi} \quad (71)$$

as $z \rightarrow \infty$. Thus $T_m(0, t')$ has still only reached 90% of its final value when z is as large as 6, roughly speaking. From (69) we see that this can result in a t' value of around 10^4 if r happens to be as low as 0.1, for example. This represents quite a considerable interval of time on the molecular scale and may even fall into the microsecond range within which experimental resolution is nowadays quite a simple matter. In fact temperature-time histories which follow (67) remarkably closely have been observed in the shock tube, by using a thin-film platinum-resistance thermometer on the closed end-wall of the tube and reflecting the primary shock wave from it. These experiments, conducted by J. R. Busing in the College of Aeronautics 2 in.-diameter shock tube, have been briefly reported by the writer (1961) in connexion with some further theoretical work on possible relaxation effects in situations similar to those under discussion here. Figure 1 shows an example of this close comparison between theory and experiment. The value of the accommodation coefficient, r , for an air-platinum combination was deduced to be about 0.03 from these experiments, which is a much lower value than that usually quoted from more conventional accommodation-coefficient measurements made at very low pressures. In the paper just cited it was (perhaps correctly) inferred that this low value of r was associated in some way with the *high* pressure (about 15 atmospheres) at which the shock-tube experiment was conducted. However, the explanation of the 'physics' of the accommodation processes which was advanced there is perhaps a little too naïve, a better explanation probably following from considerations of adsorption such as we are about to enter into in somewhat more detail shortly.

It would seem that at high-pressure values, where nearly all of the active sites for adsorption are filled anyway, any additional increase of p brings about a

(relatively) small increase in this number. That is, ΔN is probably 'small' and $\eta \simeq 0$ on *this* account, rather than because k' is zero, as we have assumed earlier. This fact would account for the non-appearance of some of the effects to be discussed in the next subsection in the experiments under discussion and for the

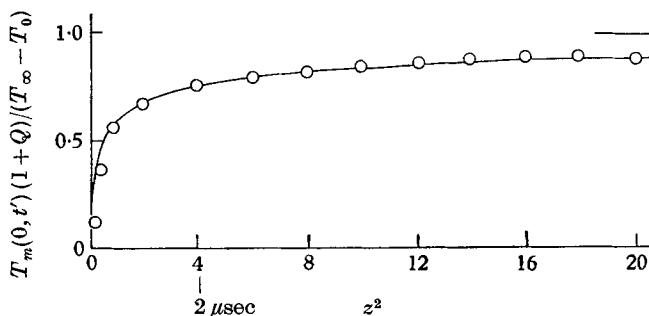


FIGURE 1. Comparison between theory and experiment for case of temperature-jump but with no adsorption. The full line curve is $1 - e^{-z^2} \text{erfc } z$, and the circles indicate values taken from an experimental record. The slight falling-off of the experimental curve below the theoretical values for $z^2 < 2$ can be almost entirely accounted for by the rise-time of the electronic measuring apparatus.

good agreement between experiment and equation (67). The low value for r in the high-pressure experimental circumstances would seem to be a result of the fact that specular molecular reflexion is just more likely to occur from surfaces which are more or less completely covered by adsorbed molecules.

6.3. Adsorption included

We must now turn to a consideration of the effects of adsorption on $T_m(0, t')$ and for this purpose we should examine the whole of the expression for $A(s)$ in (56), in particular the terms multiplied by the parameter η . Once again it is possible to verify that the Laplace inversion contour in the complex s -plane can be replaced by the loop contour described at the beginning of § 6.2. Now, however, the singularities of $A(s)$ are branch points at $s = 0$ and $-1/\gamma_\infty$ plus the addition of a simple pole at $s = -\omega$. It does not seem unreasonable to confine our attention to the time region $t' \gg 1$, especially since this introduces some considerable simplifications as we shall see. First of all, however, it is necessary to have some information about the order of magnitude of ω , particularly, and we may also investigate the value of η at the same time in order to give the problem some numerical significance.

The number of active sites, N_s , appears to be about 10^{15} per cm^2 , roughly speaking, for a variety of solid substances. Choosing one atmosphere pressure as a convenient example and also considering a gas of molecular weight of about 30 at a temperature of 300°K , equation (22) shows that k_a is of order 10^8sec^{-1} . If we are looking at surfaces for which σ lies between 0.1 and 0.9, (21) shows that k_a will lie between 10^9 and 10^7sec^{-1} , so that k' may lie between 10^9 and 10^8sec^{-1} as an upper limit at this pressure. Either way, it seems possible that ω (which is equal to $k' \kappa / a_\infty^2$) will be small compared with unity (since $\kappa / a_\infty^2 \simeq 10^{-10} \text{sec}$ for the

conditions chosen). The estimates here are somewhat crude but, in attempting to indicate general adsorption and desorption behaviour, they are sufficient to make the point, particularly since the conditions may vary quite considerably from one gas-solid combination to another. It is possible that one *may* meet k' values at N.T.P. as high as 10^{10} sec^{-1} or even higher, so that ω becomes $O(1)$ or greater. Because of the analytical simplifications which result for $\omega \ll 1$, we shall treat only this case and shall not examine the 'faster' adsorption processes which have time constants of order κ/a_∞^2 or less.

To estimate η we note that λ_∞ is equal to $mn_\infty C_{p\infty} a_\infty$ times κ/a_∞ where n is the number density of the gas. We could therefore write η (see (47)) in the form

$$\eta = (\psi/C_{p\infty}) (k'/n_\infty a_\infty) \Delta N,$$

its units being those of temperature. The adsorption energy seems usually to be measured in terms of kilocalories per gram, so that $(\psi/C_{p\infty})$ is probably $O(10^3 \text{ }^\circ\text{K})$ whilst, as we have seen, k' may be typically $O(10^8 \text{ sec}^{-1})$. We can put n_∞ and a_∞ as $O(10^{19} \text{ cm}^{-3})$ and $O(10^4 \text{ cm/sec})$ respectively, so that it remains for us to estimate ΔN . [So far we can say that η is $O(\Delta N \times 10^{-12} \text{ }^\circ\text{K})$]. Since ΔN cannot be greater than N_s , which is $O(10^{15} \text{ cm}^{-2})$, it follows that an upper limit for η is around $10^3 \text{ }^\circ\text{K}$. In any case, it seems possible that the 'temperature perturbation due to adsorption' can become comparable with, or even greater than, the actual temperature rise $T_\infty - T_0$. For this reason it seems possible that the group of terms multiplied by η on the right-hand side of (56) could give $T_m(0, t')$ variations quite comparable with those arising from $T_\infty - T_0$ alone (i.e. the first term on the right-hand side of (56)).

If, as a purely hypothetical limit, we imagined that ψ was zero, it would be only the terms involving (a_∞^2/ψ) in (56) which would contribute to $T_m(0, t')$. Since we have taken ψ as $O(10^3 \text{ calories})$ and a_∞ as $O(10^4 \text{ cm/sec})$ above, it follows that these terms give equivalent 'temperature perturbations' some 10 to 10^2 times smaller than the $10^3 \text{ }^\circ\text{K}$ quoted in the previous paragraph for the heat of adsorption effect. We shall examine the case $\psi = 0$ in a little more detail below.

Before proceeding with the analysis of the adsorption case it is perhaps necessary to stress, once again, that the foregoing estimates of numerical magnitudes are extremely crude, and that our considerations here are purely heuristic.

Now that we have decided that $\omega \ll 1$ is at least a reasonably practical case, we can simplify matters somewhat by confining our attentions, in the main, to the case $t' \gg 1$. This implies that we need only consider the region $|s| \ll 1$, on the loop contour described earlier, in order to obtain a first estimate of $T_m(0, t')$ -behaviour for large dimensionless times. Thus we can approximate (56) by putting $|s| \ll 1$, or more strictly $|s| \ll 1/\gamma_\infty$, whilst at the same time admitting that $|s|$ may be of the same order as ω , since the latter is $\ll 1$. For the reason that we wish to let (a_∞^2/ψ) vary over a wide range (as mentioned previously), we shall retain the terms involving this quantity. As a result of these assumptions and approximations it should now prove possible to estimate the dominant terms in $T_m(0, t')$ for large t' by inverting the transform

$$(1 + Q + \alpha Q \sqrt{s}) A(s) \simeq (T_\infty - T_0) s^{-1} + \eta \left\{ \frac{1 + s(a_\infty^2/\psi)}{\sqrt{s(s + \omega)}} (1 + \alpha \sqrt{s}) - \frac{(a_\infty^2/\psi)}{s + \omega} \right\}. \quad (72)$$

(Note that it is necessary to retain terms in $\alpha\sqrt{s}$ since α may be $\gg 1$, i.e. $r \ll 1$.) Using (55), (72) can be rewritten in the form

$$\bar{T}_m(0:s) \simeq \frac{(T_\infty - T_0)/\alpha Q}{s(\sqrt{s+\beta})} + \frac{(\eta/\alpha Q)}{(s+\omega)(\sqrt{s+\beta})} \left\{ \frac{1}{\sqrt{s}} + \left(\alpha - \frac{a_\infty^2}{\psi} \right) \right\}, \quad (73)$$

where

$$\beta = (1+Q)/\alpha Q. \quad (74)$$

Inversion of (73) can be accomplished using the list of formulae given by Erdelyi *et al.* (1954) and the convolution theorem for Laplace transforms. We note the following results from the reference just cited, using the symbol \supset to denote 'has the Laplace transform'

$$\frac{1}{(\pi t')^{\frac{1}{2}}} - \beta e^{\beta^2 t'} \operatorname{erfc}(\beta\sqrt{t'}) \supset (\sqrt{s+\beta})^{-1}, \quad (75)$$

$$e^{\beta^2 t'} \operatorname{erfc}(\beta\sqrt{t'}) \supset s^{-\frac{1}{2}}(\sqrt{s+\beta})^{-1}, \quad (76)$$

$$e^{-\omega t'} \supset (s+\omega)^{-1}. \quad (77)$$

Using the convolution theorem and reorganizing the basic results by integrating by parts, we can eventually show that

$$\frac{\beta}{\omega + \beta^2} \{e^{-\omega t'} - e^{\beta^2 t'} \operatorname{erfc}(\beta\sqrt{t'})\} - \frac{\sqrt{\omega}}{\omega + \beta^2} e^{-\omega t'} i \operatorname{erf} i(\omega t')^{\frac{1}{2}} \supset (s+\omega)^{-1}(\sqrt{s+\beta})^{-1}, \quad (78)$$

$$\frac{-1}{\omega + \beta^2} \{e^{-\omega t'} - e^{\beta^2 t'} \operatorname{erfc}(\beta\sqrt{t'})\} - \frac{(\beta/\sqrt{\omega})}{\omega + \beta^2} e^{-\omega t'} i \operatorname{erf} i(\omega t')^{\frac{1}{2}} \supset s^{-\frac{1}{2}}(s+\omega)^{-1}(\sqrt{s+\beta})^{-1}. \quad (79)$$

These relations are sufficient to enable us to construct a first estimate of $T_m(0, t')$ from (73). We have written

$$-i \operatorname{erf} i(\omega t')^{\frac{1}{2}} = \frac{2}{\sqrt{\pi}} \int_0^{(\omega t')^{\frac{1}{2}}} e^{y^2} dy = -i \frac{2}{\sqrt{\pi}} \int_0^{i(\omega t')^{\frac{1}{2}}} e^{-x^2} dx. \quad (80)$$

The final result can be expressed most concisely as follows:

$$\begin{aligned} (1+Q) T_m(0, t') \simeq & (T_\infty - T_0) (1 - e^{z^2} \operatorname{erfc} z) \\ & + \eta(1+b^2)^{-1} \{[(1/\beta Q) - (a_\infty^2/\psi)] [e^{-b^2 z^2} - e^{z^2} \operatorname{erfc} z] \\ & - b[(1/\beta b^2) + (1+Q)/\beta Q - (a_\infty^2/\psi)] e^{-b^2 z^2} i \operatorname{erf} i(bz)\}, \end{aligned} \quad (81)$$

where

$$z^2 = \beta^2 t' = \left(\frac{1+Q}{Q} \right)^2 \left(\frac{r}{2-r} \right)^2 t', \quad b^2 = \omega/\beta^2. \quad (82)$$

The first term of (81) is precisely the same as the result given in (67) of the previous section. It therefore accounts for the effects of heat conduction alone at constant pressure (with temperature-jump included). The remaining terms in (81) (i.e. those multiplied by η) account for the adsorption processes. We consider the behaviour of these additional terms only in two limiting cases: (a) when (a_∞^2/ψ) is so small as to be entirely negligible, so that these terms contribute just

$$\eta(1+b^2)^{-1} \left\{ \frac{1}{\beta Q} [e^{-b^2 z^2} - e^{z^2} \operatorname{erfc} z] - b \left[\frac{1}{\beta b^2} + \frac{1+Q}{\beta Q} \right] e^{-b^2 z^2} i \operatorname{erf} i(bz) \right\}, \quad (83)$$

and (b) when $\psi = 0$, so that these terms contribute

$$-\eta'(1+b^2)^{-1}\{e^{-b^2z^2} - e^{z^2} \operatorname{erfc} z - b e^{-b^2z^2} i \operatorname{erf} i(bz)\}, \quad (84)$$

where

$$\eta' = \eta(a_\infty^2/\psi) = ma_\infty \kappa k' \Delta N / \lambda_\infty, \quad (85)$$

(see (47)). The two cases (a) and (b) correspond, respectively, to very large and very small (zero) adsorption energy.

Clearly any actual picture of the interface temperature-time history is going to depend on the magnitudes of all the parameters involved. We can perhaps best

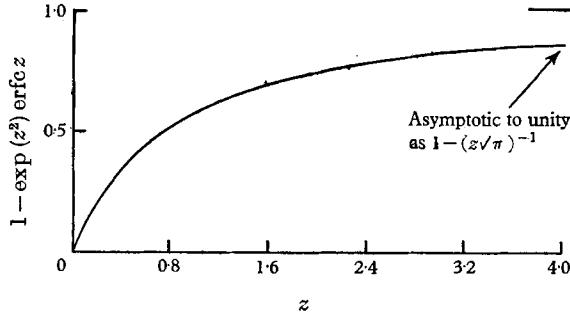


FIGURE 2. Basic temperature-time curve, representing the effects of temperature-jump alone.

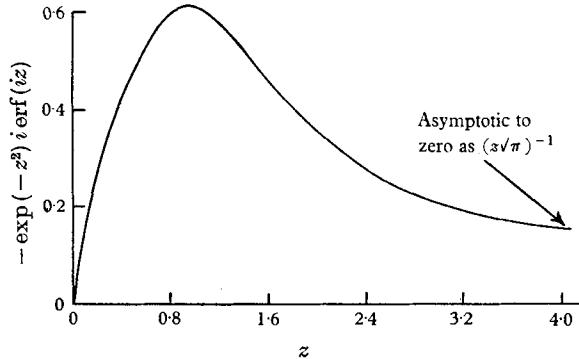


FIGURE 3. Additional effect of adsorption for large adsorption energies.

illustrate the general possibilities as follows. First of all, figure 2 is a plot of $1 - e^{z^2} \operatorname{erfc} z$, which we can call the basic temperature-time curve. Strictly speaking, figures 2-4 represent the 'component parts' of the interface temperature variations with time for $t' \gg 1$. Since we are assuming that r is $O(10^{-1})$ in order that the effects should occur in physically observable time intervals, we may interpret $t' \gg 1$ to mean, roughly, $z \gg 1$. However, the differences between the behaviour of $T_m(0, t')$ for small and large times are only those resulting from a transition from constant-volume to constant-pressure heat conduction in the gas, and these differences are not of a radical nature. For this reason, figures 2-4 are probably not bad estimates of the experimentally-observable interface temperature for all z . Figures 3 and 4 illustrate expressions (83) and (84) (or rather the curly

bracket part of these expressions) for particular values of b^2 , β and Q . All of these may vary over considerable ranges of values in practice, but we choose

$$b = 1, \quad \beta = 10^{-1}, \quad Q = 10^2 \tag{86}$$

as being at least possibly representative. Note that putting $\beta = 10^{-1}$ and $Q = 10^2$ implies that $r \simeq 0.2$ (see equations (74) and (45)). Different values of b , β and Q will alter the scale of the curves in figures 3 and 4 and also their shapes somewhat (since the scaling is clearly not uniform over the whole range of z). However, these figures are perhaps sufficient for the discussion to follow. In plotting figure 3 we note that $1/\beta Q$ is very small compared with $b(1+Q)/\beta Q$ when Q is $O(10^2)$, unless b happens to be $O(Q^{-1})$. We can invariably take $Q \gg 1$ for gas-solid combinations, so that we can write

$$b \simeq \sqrt{\omega(2-r)}/r. \tag{87}$$

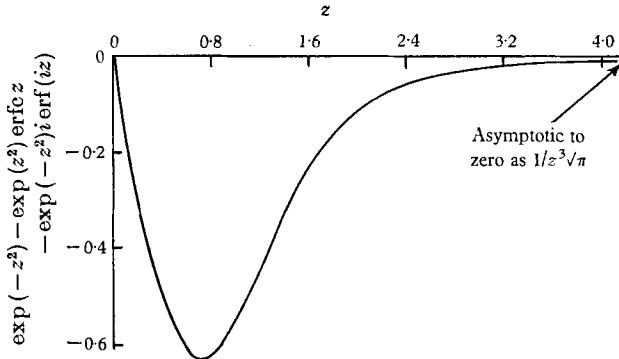


FIGURE 4. Additional effect of adsorption for zero adsorption energy.

Bearing in mind experimentally-observable time scales (let us say $t' \geq 10^2$) we require r to be $\leq 10^{-1}$ in order for any interface temperature variations to be seen. (This corresponds to $t' = 10^2$ when $z = 1$, as can be seen from the first of equations (82) for large Q .) We have fixed ω in the region 10^{-1} to 10^{-2} , so that if we are to see anything at all of the temperature variations experimentally, we see that b must have values not lower than about 1. Consequently we intend to ignore the first term inside the curly brackets in expression (83) and plot just

$$-e^{-z^2} i \operatorname{erf} i(z) \tag{88}$$

in figure 3. This should give us a reasonable idea of the ‘large ψ ’-behaviour of $T_m(0, t')$ as a result of adsorption.

We can now give a *rough* indication of the possible behaviour of $T_m(0, t')$ when adsorption is included. To do so we must imagine that the curves in either figure 3 or figure 4 are ‘added on’ to the curve in figure 2, their scales being expanded or contracted in either direction depending on how much the physical parameters differ from those in (85). That is to say, we use either figure 3 or figure 4 in the limiting cases of either very high or very low adsorption energy, ψ . In the intermediate cases, where a_∞^2 and ψ may be comparable in magnitude, we must attempt to imagine a whole variety of combinations of curves (something

like those in figures 3 and 4) which are to be added on to the basic curve of figure 2. The range of possibilities is clearly enormous, but we have sufficient information here to estimate $T_m(0, t')$ for most of these possibilities once β , b , Q , η and $T_\infty - T_0$ are known.

When ψ (or η) is very large, figure 3 shows that $T_m(0, t')$ will approach its asymptotic value (which is still $(T_\infty - T_0)/(1 + Q)$ be it noted) quite rapidly in the early stages (in comparison with the basic curve). The contribution to $T_m(0, t')$ from the release of adsorption energy may be so large that $T_m(0, t')$ overshoots the asymptotic value for some z and approaches it from above, rather than from below as in the basic curve.

When ψ (or η) is very small the predominant effect, physically, must be due to the inrush of gas on to the surface. The expansion wave which is necessary to bring this about lowers the gas temperature and, 'adding' figure 4 on to figure 2, we see that it is conceivable that $T_m(0, t')$ may first *decrease* below its ambient value, before finally increasing to the asymptotic value given in (70).

During the very early stages in the development of the flow past a sphere mounted in a shock tube, the primary shock wave reflects from the sphere as a very-nearly concentric spherical surface. This physical situation is therefore quite similar to the one that we have been studying here. It is interesting, but not in any way conclusive of course, that both types of $T_m(0, t')$ -behaviour listed above have been observed from a stagnation-point heat-transfer gauge mounted on such a model. The pressures arising at the stagnation point were low in these experiments (of order 10^{-1} to 10^{-2} atmosphere) and the duration of the effects was short (in the region of one microsecond and less). It is just possible that these may have been observations of adsorption effects: they could be repeated and did not seem to be a result of the behaviour of the electronic measuring gear.

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