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The Free-Molecule Flow of a Polyatomic Gas

- by -

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SUMMARY

A study has been made of the free-molecule flow of a polyatomic gas past a body, with special reference to the evaluation of accommodation coefficients.

A model of the gas-surface interaction is devised, based on the phenomenon of physical adsorption. Using this model, expressions for the thermal accommodation coefficients of the various energy modes of a polyatomic gas are developed by postulating that the energy exchange at the surface is governed by equations similar in form to the gas-phase relaxation equations. The expressions so obtained are dependent on the relevant integral heat of adsorption and the various relaxation times involved. Some suggestions are put forward as to how these relaxation times could be evaluated since, once their behaviour is known, the results of this report will provide a simple method for estimating the accommodation coefficients in a wide range of flow conditions.

This report is based on work conducted by the author at The College of Aeronautics in partial fulfilment of the requirements for the Diploma in Advanced Engineering.

CONTENTS

LIST OF SYMBOLS

The symbols defined below are those used throughout; others which appear briefly are defined in the text as they occur.

E_i	Energy flux carried to a solid surface by incident molecules
E_r	Energy flux carried away from a solid surface by reflected molecules
E_w	Denotes E_r when $T_r = T_w$ (see below)
K	Function of speed ratio and incidence occurring in E_i
N_i	Number of molecules striking unit area of surface per unit time
Q	Heat of adsorption per mole of adsorbed gas
R	Gas constant referred to unit mass
R_M	Molar gas constant
T_i	Temperature of incident stream
T_r	Temperature of reflected stream
T_w	Temperature of solid surface
S	Ratio of stream speed to most probable molecular speed
j	Number of degrees of freedom in an energy mode
p_i	Normal momentum flux to surface (incident molecules)
p_r	Normal momentum flux away from surface (reflected molecules)
p_w	Denotes p_r when $T_r = T_w$
α	Thermal accommodation coefficient
η	Normal momentum accommodation coefficient
θ	Angle of incidence
τ_a	Relaxation time associated with translational and active modes
τ_i	Relaxation time associated with inert energy modes
$\bar{\tau}$	Average time of adsorption
τ_o	Period of vibration of adsorbed molecules normal to surface

Affix ℓ refers quantities to lower surface of flat plate (see Fig. 1), u refers to upper surface

List of Symbols (Continued)

For quantities associated with the separate energy modes of a molecule :

No prime refers to translation mode

One prime refers to active mode

Two primes refer to inert mode

Bar denotes quantities referred to all modes

1. Introduction

If a gas flowing over a body satisfies the two conditions, that the mean free path of the molecules is large compared with the dimensions of the body, and also that an element of volume of the gas contains a sufficiently high number of molecules to determine the macroscopic properties of the flow, then the flow system is designated a free-molecule flow. That such flow conditions can exist in practice is shown(1) by the fact that when the mean free path in the upper atmosphere is 10 feet, the number of molecules in a cubic inch is about 10^{13}. Experimental evidence indicates(2) that when the ratio of mean free path to a characteristic linear dimension of the body is greater than 10, then free-molecule theory is applicable. The above ratio is known as the Knudsen Number, after Martin Knudsen who pioneered work in this field.

A considerable amount of work on the free-molecule flow of monatomic gases has been published, and complete accounts of the basic theory can be found in (1), (2) and (3), to name but a few of the available sources. There is, as yet, no completely self-sufficient theory of free-molecule flow. All the investigators in this field have introduced certain average flow parameters, which will be defined later, where these parameters are determined experimentally. The same course has been followed in this work, where the aim is to predict the trends followed by the aerodynamic characteristics and the heat transfer under real gas flow conditions and not their absolute magnitudes.

Since the term polyatomic covers a large number of different species of molecules, (all having different numbers of degrees of freedom) for the purposes of this investigation a simplified model has been adopted. In our model, the molecules have an arbitrary number of internal modes of energy, but all modes except one maintain thermal equilibrium with the translational energy during any change of state. A physical example of this type of gas would be a diatomic gas, with an active rotational mode of energy and an inert vibrational mode. The terms active and inert are used here as in (4) to describe modes having negligible and significant relaxation times, respectively. Furthermore, it is assumed that in the gas upstream of the body all the internal modes of energy are fully excited, i.e. in thermal equilibrium with the translational energy. We assume also that chemical reactions do not occur anywhere in the flow system. These assumptions, whilst admittedly restrictive, do leave a range of applicability of the results, which is wide enough to be of interest.

One of the consequences of the basic definition of free-molecule flow is that the molecules incident on a surface do not interact with the molecules reflected or re-emitted from the surface. Thus the flow can conveniently be broken down into the incident phase, the gas-surface interaction phase, and the reflected phase, and each phase may be considered separately. However, since the reflected phase is really the end product of the gas-surface interaction, we need only consider the incident and gas-surface interaction phases.

2. Incident phase

The interaction of the gas with the surface gives rise to physically measurable quantities; the rate of heat transfer, normal pressure and the skin friction. These quantities are related to the amounts of energy, normal momentum and tangential momentum which are carried by the molecules to unit area of the surface in unit time. The method of obtaining expressions for these quantitites can be found in several of the references given in this report, but for convenience we will give a brief derivation here.

Consider a flat plate moving with velocity $\underline{q} = (\overline{u}, \overline{v}, \overline{w})$ at angle of incidence θ, through a uniform polyatomic gas. The temperature of the undisturbed gas is T_i and the number density is n_i. Let us define co-ordinate axes fixed relative to the plate as shown in Fig. 1, then, viewed from these axes, the molecular velocity components are $u = \overline{u} + U$, $v = \overline{v} + V$, $w = \overline{w} + W$, where U, V and W are the thermal velocity components of a molecule. We will assume that the molecular motion in the undisturbed gas ahead of the flat plate is Maxwellian.

2.1. Basic equations

The number of molecules which strike unit area of the plate in unit time and have velocity components in the range u, u + du; v, v + dv; w, w + dw; is then n_i vf du dv dw. f is Maxwell's velocity distribution function given by

$$f = \left(\frac{3}{2\pi\,\overline{C^2}}\right)^{3/2} e^{-3C^2/2\overline{C^2}}$$

where C = (U, V, W) and $\overline{C^2}$ is the mean square of C.

The total number of molecules striking unit area of the plate in unit time is now found by integrating the above expression over all possible values of u, v and w. Thus on the lower surface of the plate the limits of integration on V are 0 to ∞, while on U, W they are from $-\infty$ to $+\infty$. To calculate the corresponding quantity for the upper surface, we integrate $-n_i$ vf du dv dw since v must be negative, and the limits of integration on V are $-\infty$ to 0. If we let N_i^{ℓ} and N_i^{u} represent these number fluxes for the lower and upper surfaces respectively, then

$$N_i^{\ell} = n_i \sqrt{\frac{R\,T_i}{2\pi}}\left[e^{-S_v^2} + S_v\sqrt{\pi}\,(1 + \operatorname{erf} S_v)\right] \qquad (2.1)$$

$$N_i^{u} = n_i \sqrt{\frac{R\,T_i}{2\pi}}\left[e^{-S_v^2} - S_v\sqrt{\pi}\,(1 - \operatorname{erf} S_v)\right] \qquad (2.2)$$

where $S_v = \frac{\overline{v}}{C_i}$ is the ratio of the mass velocity component normal to the surface to the most probable speed of the incident molecules, $\operatorname{erf} S_v = \frac{2}{\sqrt{\pi}}\int_0^{S_v} e^{-x^2}\,dx$,

and R is the gas constant referred to unit mass. Note that if we define $S = q/C_i$, then $S_v = S \sin\theta$.

To obtain the translational energy flux to the lower surface we integrate $\frac{1}{2} n_i mc^2 v \, du \, dv \, dw$ where m is the mass of a molecule and $\underset{\sim}{c} = (u, v, w)$. The limits of integration are as before. Denoting the translational energy flux to the lower and upper surfaces by E_i^{ℓ} and E_i^u respectively, we obtain

$$E_i^{\ell} = 2 m N_i^{\ell} R T_i \left\{ \frac{S^2}{2} + \frac{4\exp(-S_v^2) + 5 S_v \sqrt{\pi} (1 + \operatorname{erf} S_v)}{4\left[\exp(-S_v^2) + S_v \sqrt{\pi} (1 + \operatorname{erf} S_v)\right]} \right\} \quad (2.3)$$

$$E_i^{u} = 2 m N_i^{u} R T_i \left\{ \frac{S^2}{2} + \frac{4\exp(-S_v^2) - 5 S_v \sqrt{\pi} (1 - \operatorname{erf} S_v)}{4\left[\exp(-S_v^2) - S_v \sqrt{\pi} (1 - \operatorname{erf} S_v)\right]} \right\} \quad (2.4)$$

Let us write these as

$$E_i^{\ell} = (2 m N_i^{\ell} R)(K^{\ell} T_i) \quad (2.5)$$

$$E_i^{u} = (2 m N_i^{u} R)(K^{u} T_i) \quad (2.6)$$

where K^{ℓ} and K^u are plotted for various angles of incidence in Figs. 2 and 3.

The internal energy which is carried to the surface by the incident molecules can be allowed for by assuming that all internal modes are fully excited and that classical equipartition of energy applies*. Let us distinguish here between the active and inert modes of energy for use in later sections of this report. We will suppose that there are j' degrees of freedom in the active energy modes and j'' in the inert energy modes. Then according to the assumptions above, the amounts of active and inert energy carried to unit area of the lower surface in unit time are, respectively,

$$(E_i^{\ell})' = \tfrac{1}{2} m N_i^{\ell} j' R T_i \quad (2.7)$$

$$(E_i^{\ell})'' = \tfrac{1}{2} m N_i^{\ell} j'' R T_i \quad (2.8)$$

and similarly for the upper surface,

$$(E_i^{u})' = \tfrac{1}{2} m N_i^{u} j' R T_i \quad (2.9)$$

$$(E_i^{u})'' = \tfrac{1}{2} m N_i^{u} j'' R T_i \quad (2.10)$$

In a similar manner, by calculating the amounts of normal and tangential momentum carried to unit area of the surface per unit time, we can arrive at the following expressions for normal pressure p_i, and skin friction τ_i, due to the incident molecules.

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* This assumption is not strictly necessary and a completely general value for the energy in the internal modes could be taken. The classical value is used here for convenience only.

$$p_i^{\ell} = m N_i^{\ell} \sqrt{\frac{\pi R T_i}{2}} \left\{ \frac{2S_v}{\sqrt{\pi}} + \frac{1 + \operatorname{erf} S_v}{\exp(-S_v^2) + S_v \sqrt{\pi}(1 + \operatorname{erf} S_v)} \right\} \quad (2.11)$$

$$p_i^{u} = m N_i^{u} \sqrt{\frac{\pi R T_i}{2}} \left\{ -\frac{2S_v}{\sqrt{\pi}} + \frac{1 - \operatorname{erf} S_v}{\exp(-S_v^2) - S_v \sqrt{\pi}(1 - \operatorname{erf} S_v)} \right\} \quad (2.12)$$

$$\tau_i^{\ell} = m N_i^{\ell} q \cos \theta \quad (2.13)$$

$$\tau_i^{u} = m N_i^{u} q \cos \theta \quad (2.14)$$

3. Gas-surface interaction

It has been found experimentally that when a gas comes into contact with a solid at a different temperature, the energy and momentum exchanges between gas and solid are not, in general, complete. We say that the solid does not completely accommodate the gas. To define this discrepancy in terms of energy and momentum fluxes, consider a monatomic gas flowing over a surface whose temperature T_w is different from T_i. Suppose that dynamic equilibrium exists, so that the number of molecules N_r leaving unit area per unit time is equal to N_i (as defined in section 2.1). Let E_r denote the actual energy flux away from the surface, and E_w the flux which would exist if complete thermal accommodation occurred. Then $|E_i - E_r| < |E_i - E_w|$ in general, and we define the thermal accommodation coefficient as

$$\alpha = \frac{E_i - E_r}{E_i - E_w} \quad (3.1)$$

If we define p_r, p_w, τ_r, τ_w the normal and tangential momentum fluxes, where the suffices r and w denote the same properties as in E_r and E_w, then we can define momentum accommodation coefficients.

$$\eta = \frac{p_i - p_r}{p_i - p_w} \quad (3.2)$$

and

$$\sigma = \frac{\tau_i - \tau_r}{\tau_i - \tau_w} \quad (3.3)$$

When discussing a polyatomic gas, η and σ can be defined exactly as for a monatomic gas, but the definition of the thermal accommodation coefficient will obviously have to include the internal energy flux. We can define either one coefficient for the total energy flux, or separate coefficients for the different modes of energy. Thus if $\overline{E}_i$ is the total energy flux E_i, E_i' E_i'' the translational, active and inert fluxes respectively, then $\overline{E}_i = E_i + E_i' + E_i''$ and similarly for $\overline{E}_r$ and $\overline{E}_w$ we can define the total thermal accommodation coefficient

$$\bar{\alpha} = \frac{\bar{E}_i - \bar{E}_r}{\bar{E}_i - \bar{E}_w} \tag{3.4}$$

and we can define

$$\alpha' = \frac{E_i' - E_r'}{E_i' - E_w'} \tag{3.5}$$

and

$$\alpha'' = \frac{E_i'' - E_r''}{E_i'' - E_w''} \tag{3.6}$$

for the active and inert energy modes respectively. Together with (3.5) and (3.6) we have, of course, α as defined by (3.1) for the translational energy flux. It is easy to see that

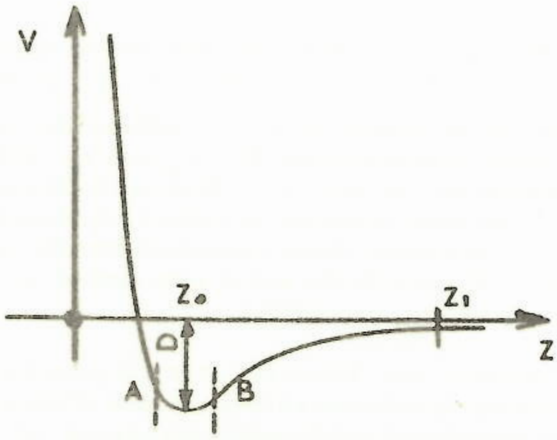
$$\bar{\alpha} = \frac{\alpha(E_i - E_w) + \alpha'\left[E_i' - E_w'\right] + \alpha''\left[E_i'' - E_w''\right]}{\bar{E}_i - \bar{E}_w} \tag{3.7}$$

When dealing with a monatomic gas we see that all the quantities needed to evaluate the overall flow parameters can be obtained. E_i, p_i and τ_i can be evaluated in terms of known quantities as in section 2.1. Furthermore, by making the assumption that the velocity distribution is Maxwellian E_w, p_w and τ_w can be evaluated, as will be shown later. This leaves E_r, p_r and τ_r. Now the total energy transfer per unit time is equal to $E_i - E_r$, the total pressure is equal to $p_i + p_r$ and the total skin friction is equal to $\tau_i - \tau_r$, and these three quantities are all capable of being measured experimentally. Thus with the aid of experiment we can find the variation of α, η and σ with changing flow properties.

In the case of a polyatomic gas, however, it is not possible to measure directly the energy transfers associated with the various modes of energy, but only their combined total. Thus a theoretical relationship between α, α' and α'', or a prediction of their respective variations with flow properties, would be of great use. As a first step in this direction we must proceed to examine the mechanism of the gas-surface interaction in more detail.

All the parameters defined above will be dependent on the mechanism of the energy interchange between the gas and the solid. When Maxwell first studied this type of problem, he postulated that a fraction f, of the incident molecules, would be temporarily trapped by the surface whilst the remainder would be reflected specularly, i.e. with an angle of reflection equal to the angle of incidence, and a relative speed equal to the speed of the incident molecule. Those molecules trapped by the surface would be considered as coming from a gas inside the surface, at the same temperature as the surface. This latter type of reflection Maxwell termed diffuse reflection. It can be seen that when the velocity distribution of the diffusely reflected molecules is assumed Maxwellian then, for a monatomic gas, α, η and σ can be expressed in terms of f. However, this model of the reflection process is nowadays considered to be too simple, and will not be adopted here. In fact, there is experimental evidence that for moderate values of the speed ratio S, as defined in section 2.1., the value of f is unity in the majority of gas-surface interactions (6).

The more realistic model of the interaction, which is adopted here, is as follows. When a gas molecule collides with a solid surface, one of two apparently different forms of collision may occur. Thus the molecule may rebound immediately at some angle unrelated to its angle of incidence and at the same time undergo in general a change in energy. Alternatively, the molecule may be adsorbed on the surface for some time and then be re-emitted with different energy, and again the angle at which it leaves the surface will be unrelated to its incident angle. In the above we are referring to physical adsorption, in which the molecules are held to the surface by Van der Waals forces(6). We are not considering chemi-sorption in which there is an interchange of electrons between the surface and the gas, dissociation, or any such process requiring high activation energy. The phenomenon of physical adsorption arises as a direct consequence of the form of the mutual potential energy existing between the molecule and the solid body. This potential energy can be represented by the curve shown in the sketch below :



V is the mutual potential energy and z is distance measured along the outward normal from the surface. A molecule approaching the surface will have its kinetic energy of translation increased by an amount D as it proceeds from $z = z_1$ where $V \simeq 0$ to $z = z_0$. On passing through the point $z = z_0$, it will meet the repulsive force, since for $z < z_0$ V increases with decreasing z, and this stage of its journey represents its collision with the surface. If we now consider the surface smooth on the molecular scale and also rigid, the molecule will rebound with the major portion of its kinetic energy intact, and will thus be able to escape completely from the surface. On the other hand, if the surface is rough on the molecular scale and also non-rigid, the molecule will give up the major portion of its energy without necessarily acquiring a sufficiently large velocity component normal to the surface, and will therefore not be able to escape from the potential well. An oscillating motion, between points A and B in the sketch, will be set up. Since surfaces are composed of atoms vibrating relative to each other, with cracks or interstices between, the second surface model is more realistic.

From the preceding paragraph it is clear that the quantity D is closely related to the so-called heat of adsorption which has been measured experimentally for a large number of gases and surfaces(8). It has also been demonstrated(8) that D varies over the surface of the adsorbent (the solid taking up the gas). Therefore, if a gas molecule, on first colliding with a surface atom, hits that atom head on, on a part of the surface where D is smaller say, there is a possibility that the molecule will rebound with enough energy to escape the potential well. Furthermore, if we consider gas-surface combinations with smaller and smaller D, the probability of molecules escaping after one collision increases. On this basis there is no necessity to differentiate between single inelastic collisions and physical adsorption, since we may take the one as being a limiting case of the other.

Before we can complete the outline of our model of gas-surface interaction, we must decide on the process by which those molecules which are trapped in the potential well, eventually escape from the surface. There is no experimental evidence to guide us on this point, and we shall assume with Zwanzig(9), that this energy of desorption is communicated to the molecule by the chance coming together of sound waves in the surface lattice; these sound waves transfer a sufficient amount of energy to the molecule for it to escape the potential well.

This, then, completes the outline of our gas-surface interaction model. A point to be noted is, that if we assume that the internal energy of polyatomic molecules is not affected by the mutual potential energy existing between the gas molecule and the surface, then the above model will suffice for both monatomic and polyatomic molecules. To fill in the detail of our model we have to consider what happens to the molecules whilst they are trapped on the surface, with particular regard to their energy changes. We shall do this first of all in the simpler case of a monatomic gas, since it is easier in this case to ensure that any assumptions we make do not violate available experimental data.

3.1. Monatomic gas-surface interaction

Consider a monatomic gas at a certain temperature T_i in contact with a solid surface at constant temperature T_w; free-molecule conditions being applicable, of course, as throughout this report. Then if a state of dynamic equilibrium exists, the average energy of the molecules in the adsorbed layer will be constant with respect to time. In the particular case of $T_w > T_i$, this constant energy in the adsorbed layer is maintained by the following process. Molecules are continually being adsorbed and desorbed. The average energy of all the molecules which became adsorbed will increase during their time of contact with the surface. Thus dynamic thermal equilibrium is set up by energy being transferred at a constant rate from the solid to the adsorbed layer, this process being balanced by the continuous desorption of the higher energy molecules and the continuous adsorption of the lower energy molecules. Note that the heat of adsorption plays no part in this flow of energy since the body has to give it all up again as heat of desorption.

A common assumption made, and one having some experimental justification, is that the adsorbed molecules do not interact one with the other(8). We will follow this assumption here, so that all the energy interchange is between the solid and the adsorbed layer of molecules and not between the adsorbed molecules themselves. The molecules in the layer receive their energy changes by way of impacts with the vibrating atoms of the surface. The vibration of the atoms will not all be normal to the surface, so that the adsorbed molecules will probably move over the surface in a hopping motion, rather than undergo oscillations on one spot. The degree of mobility of the molecules is discussed in (6).

The amount of energy a trapped molecule can receive in any one collision is limited by the frequency spectrum of the vibrating atoms of the surface. Furthermore, molecules with higher energy, i.e. the faster moving molecules within the adsorbed layer, will be more likely to deform the surface lattice which they come into collision with, and these will be more likely to undergo an energy change. This is very similar to the energy exchange mechanism of the internal modes of energy of a polyatomic molecule in the gas phase. For such gas phase systems, the well known(2) relaxation equation can be shown to describe the rate of energy transfer between translational energy and internal energy. Therefore we will apply this type of equation here, and examine the results of such an analysis in the light of experimental evidence.

Since we are considering a state of dynamic equilibrium, the following method of considering the energy exchange is permissible. We can consider the N_i molecules which impinge on unit area of the surface per unit time, as all entering into energy exchange with the surface at the same time, staying an average time $\bar{\tau}$ (the average time of adsorption) and all leaving the surface after a time interval $\bar{\tau}$. The energy they carry away can then be equated to E_r. Thus if E is the energy of the N_i molecules at a time t after adsorption, we postulate that a good approximation to the rate of change of E with time is given by

$$\frac{\partial E}{\partial t} = - \frac{1}{\tau_a} (E - E_w) \qquad (3.8)$$

where E_w is as defined in Section 3, and τ_a is the relaxation time of the energy exchange. To draw the analogy in detail, E is equivalent to the inert internal energy mode of a gas, which can only receive energy from the translational energy mode via collisions. It cannot be stressed too strongly, however, that τ_a is an entirely different quantity from the gas phase relaxation time.

The relaxation time in the gas phase is determined by the energy transition rates of the particular inert internal mode of energy being considered. One does not need to introduce the transition rates of the translational energy since the translational energy of a molecule is changed at every collision; translational energy changes occur without involving the internal energy. Thus the relaxation time is dependent only on the slower transition rates. These slower transition rates are in turn dependent on the translational motion and the energy involved in each internal mode energy change(2).

The relaxation time we are concerned with will also be determined by the slower transition rates, but several differences are apparent. Since we are not allowing direct energy exchanges between adsorbed molecules, we may safely assume that they will have slower transition rates than the surface atoms. These latter will be continuously exchanging energy between themselves. However, the frequency of collision, and the probability of an energy exchange resulting from it, will now be determined largely by the motion of the adsorbed molecules, whilst the total energy available will be dependent on the temperature of the solid (i.e. the vibrational motion of its atoms). Thus it is not unreasonable to expect that τ_a

will show a marked dependence on T_i and T_w.

The solution of equation 3.8 can be written down immediately since T_w is constant (with τ_a = const.), or

$$E = A\,e^{-t/\tau_a} + E_w$$

Furthermore, when $t = 0$, $E = E_i$ and also when $t = \bar{\tau}$, $E = E_r$

$$E_r = (E_i - E_w)\,e^{-\bar{\tau}/\tau_a} + E_w \tag{3.9}$$

whence

$$\alpha = 1 - e^{-\bar{\tau}/\tau_a} \tag{3.10}$$

Note that as $\bar{\tau} \to \infty$, $\alpha \to 1$ and as $\tau_a \to \infty$, $\alpha \to 0$, so that the limiting behaviour is as we would expect. Frenkel(10) shows that

$$\bar{\tau} = \tau_o\,e^{Q/R_M T_w}$$

where τ_o is the average period of vibration normal to the surface of the adsorbed molecules, Q is the average heat of adsorption per mole of adsorbed gas, and R_M is the molar gas constant. The variation of $\bar{\tau}$ with temperature is thus known, provided that the variation of Q with temperature is available from experiment. The experimental evidence on this point is inconclusive and we shall follow Brunauer's(8) advice in regarding Q as independent of temperature for moderate temperature variations.

Before leaving the discussion on $\bar{\tau}$ one last point must be clarified, its variation with S, the speed ratio of the incident molecules. Nocilla(13) gives an expression for this variation, based on the assumption that the number of molecules in the adsorbed layer is independent of S. He derives this expression in order to explain the variation of the thermal accommodation coefficient with S, as reported by Devienne(14). Frenkel, in his analysis, assumes a static gas but does not specify surface saturation (i.e. that all available adsorption sites are occupied). To assume the number of adsorbed molecules constant without knowing the conditions prevailing in the experiment does not appear to have any special merit over assuming $\bar{\tau}$ constant. Therefore in the rest of this work we will take $\bar{\tau}$ as constant for moderate ranges of S. Furthermore this variation of α (as determined experimentally) with speed ratio can be attributed to another cause (see section 3.2).

On the basis of the above we can now predict the changes in $\bar{\tau}$ due to changes in temperature and speed ratio. The corresponding variation of τ_a has not been obtained explicitly, but some guidance as to its probable behaviour can be found in experimental results and will be discussed later.

A rigorous proof that equation 3.8 is applicable to our problem has, up to now, not been forthcoming. However, we may say that such equations have been shown to hold for deviations from energy equilibrium, where the return to equilibrium is limited to one quantum energy change at each effective collision. According to Strachan, cited in(12) such a limitation applies here, and we shall now outline the steps which led us to postulate the applicability of equation 3.8.

Assume a solid made up of harmonic oscillations all of the same frequencey ν. This is the model Einstein used in his specific heat theory. Furthermore, following Strachan, the energy exchanges between solid and adsorbed layer are limited to one quantum $h\nu$ per exchange. Let $K_{i+1,i}(e, e + h\nu)$ be the rate at which an adsorbed molecule with energy in the range e, e + de, takes up energy $h\nu$ from a surface atom with energy $(i + 1)h\nu$. Similarly, $K_{i,i+1}(e + h\nu, e)$ is the rate at which an adsorbed molecule with energy in the range $e + h\nu$, $e + h\nu + de$ gives up $h\nu$ to a surface atom with energy $i\,h\nu$. (i = 0, 1, 2 etc.). Let N_e de be the number of adsorbed molecules with energy e, e + de and n_i the number of surface atoms with energy $i\,h\nu$.

Now it is well known(2) that when considering transition rate of harmonic oscillators, we can take out a factor to allow for radiative effects and write

$$K_{i+1,i}(e, e + h\nu) = (i + 1)\, K_{10}(e, e + h\nu)$$

and $$K_{i,i+1}(e + h\nu, e) = (i + 1)\, K_{01}(e + h\nu, e)$$

Thus we can write

$$\frac{\partial E}{\partial t} = h\nu \sum_{i=0}^{\infty} (i + 1) \int_0^{\infty} \left\{ n_{i+1} N_e K_{10}(e, e + h\nu) - n_i N_{e+h\nu} K_{01}(e+h\nu, e) \right\} de$$

If we invoke the Principle of Detailed Balancing we can write, when $E = E_W$

$$n_i^* \; N^*_{e+h\nu}(i + 1)\, K^*_{01}(e + h\nu\; e) = n^*_{i+1} \; N^*_e (i + 1) K^*_{10} (e, e + h\nu)$$

where * denotes equilibrium values. Now since we are considering the case where T_W is maintained at a constant value, we will assume that $\dfrac{n_i}{n_{i+1}} \approx \dfrac{n_i^*}{n^*_{i+1}}$.

This will be even better if we limit ourselves to small values of $| T_i - T_W |$. We may therefore write

$$\frac{\partial E}{\partial t} = h\nu \sum_{i=0}^{\infty} n_i (i + 1) \int_0^{\infty} \left\{ \frac{N_e K_{10}(e, e + h\nu)}{N_e^* K^*_{10}(e, e + h\nu)} \cdot N^*_{e+h\nu} K^*_{01} (e + h\nu, e) - N_{e+h\nu} K_{01}(e + h\nu, e) \right\} de$$

$$= h\nu \sum_{i=0}^{\infty} n_i (i + 1) \int_0^{\infty} \left\{ N^*_{e+h\nu} \; K^*_{01} (e + h\nu, e) - N_{e+h\nu} K_{01}(e + h\nu, e) \right\} de$$

since $\dfrac{N_e K_{10} (e, e + h\nu)}{N_e^* K^*_{10} (e, e + h\nu)}$ is of order unity for T_i of order T_W.

Now consider $K_{01}(e + h\nu, e)$. This is an energy transition rate which will depend on the energy levels involved in the transition. Thus we may postulate that the following type of relationship will hold

$$K_{01} \; (e + h\nu ,\, e) \; = \; \frac{e + h\nu}{kT} \; . \; \frac{A}{\tau_a}$$

where k is Boltzmann's constant, A is a non-dimensional constant and τ_a has units of time. Making a similar assumption for K^*_{01} $(e + h\nu,\, e)$, we can write

$$\frac{\partial E}{\partial t} \approx \frac{C^*}{\tau^*_a} \, E_w - \frac{C}{\tau_a} \, E$$

where C^* and C are non-dimensional constants.

Then on the assumption that E_i, E and E_w do not differ greatly from each other $C^*/\tau^*_a = C/\tau_a$ so that

$$\frac{\partial E}{\partial t} = - \frac{C}{\tau_a} \, (E - E_w).$$

As we stated at the outset, the foregoing analysis is not intended as a rigorous proof of the applicability of this equation to our problem, but rather as the basis on which we postulate its applicability.

In the next section we shall draw some conclusions as to the behaviour of τ_a with changing T_i and T_w, which contradict the views of Jackson and Howard(11) and Devonshire (12). Their theories were based on the assumption that each gas molecule suffered only one inelastic collision with the surface (i.e. adsorption was disallowed) and this may explain the difference between their results and that given here.

To summarise, we have an expression for α the accommodation coefficient of a monatomic gas, whose behaviour we can predict in a general way for variations of T_i, T_w Q, the integral heat of adsorption, and S, the speed ratio of the incident molecules. In this next section available experimental results will be used to test the validity of our expression.

3.2. Experimental evidence. Monatomic gases.

There are a great number of experimental results available, giving the accommodation coefficients of monatomic gases on various surfaces. In the main these results all show the same trends, although in a number of cases vastly different values have been obtained for the same gas-surface combination. Most writers in the field put this down to different surface conditions, some experimenters having taken more care than others in ensuring a clean surface and a pure gas. However this need not worry us unduly since the main effect of a surface having an adsorbed layer of impurity, will be to change Q and hence $\bar{\tau}$. This does not affect the applicability of our expression for α.

The results we have chosen to demonstrate the variation of α when $T_w - T_i$ is kept constant are those by Thomas and Schofield, cited in (15) and (16).

These results were obtained for helium, neon and argon on a tungsten surface, varying T_i from 100°K to 300°K and keeping $T_w - T_i$ constant at 18°K. They are shown in Fig. 4, along with our theoretical curves. The values used in plotting the theoretical curves are also shown in the figure. It can be seen that for the lower values of the accommodation coefficient, suitably chosen constant values of τ_a/τ_o are sufficient to give quite a good approximation to the experimental results. For the argon curve, a suitable variation of τ_a/τ_o with temperature would have to be introduced in order to obtain a better fit. However, even in this case, the assumption that τ_a/τ_o is constant gives the main trend of the experimental results. It should be mentioned that De Boer(6) states that argon on clean tungsten will have a value of Q = 3,000 cals. per mole approximately. He also implies that over the temperature range concerned, he would expect α for argon to have a value of unity, so that we may feel justified in choosing a lower value of Q.

For the results showing the variation of α with $T_w - T_i$, keeping T_i constant, we turn to (2) where results of Oliver are cited. These are for helium and argon on tungsten. The results, as given in (2) are shown in Fig. 5. These results are replotted as α against $\bar{\tau}/\tau_o$ assuming Q = 2000 cals. per mole, from which is derived Fig. 6, showing τ_o/τ_a against $T_w - T_i$. As can be seen τ_o/τ_a tends to zero as $T_w - T_i$ tends to zero. This is, at first sight, a surprising result since it means that as $T_i \rightarrow T_w$, $\tau_a \rightarrow \infty$. However, it should be borne in mind that τ_a may behave quite differently from the gas-phase relaxation time. Here again the value of Q for helium on tungsten is high according to De Boer, but we may safely assume that the surface was contaminated in some way, otherwise the low values of α found by Thomas and Schofield would have been obtained.

The results of Oliver were obtained with a static gas and, as we have seen, can be explained by assuming our prediction of the behaviour of τ_a to be correct. Consider now a flat plate placed in a free-molecule stream, and let T_w the temperature of the plate, be greater than T_i. Let us assume that α is measured on the lower surface (referring now to Fig. 1) for increasing values of the speed ratio. We see from Fig. 2 that at constant incidence, as S increases, K^ℓ increases, and eventually, if T_w is maintained at a constant temperature, we would have $K^\ell T_i = T_w$. Then, since we could replace T_i in the static case by $K^\ell T_i$ in the non-static case, we would expect the measured values of α when plotted against S to decrease to zero at the value of S, where $K^\ell T_i = T_w$ if our prediction of τ_a's behaviour is correct. The previously mentioned results of Devienne were obtained with an insulated radiating flat place normal to the flow. In working out his results, Devienne assumes that the accommodation coefficients of front and rear surfaces will be equal. However, we see from Figs. 1 and 2 that in the case of an insulated flat plate normal to the flow, the molecules striking the front surface of the plate would be giving it energy ($K^\ell > 1$), whilst those striking the rear surface would be taking energy away from the plate ($K^u < 1$). Under these circumstances it is difficult to see how the results can be used to throw light on the variation of thermal accommodation coefficient with speed ratio. For this reason, these results will not be used as a comparison with the results of this paper.

This is as far as we will take the comparison with experiment at this stage. The experimental results quoted follow trends which have been observed in more than one experiment, and we see that our theoretical results follow these trends in quite a satisfactory manner. We will, therefore, proceed in the next section to apply similar methods to a polyatomic gas. However it would not be fair to leave this section without noting that some results, notably those of Roberts(17), can only be explained by our model if we assume that Q increases with temperature or, alternatively, that τ_a/τ_o descreases with temperature.

4. Polyatomic gas-surface interaction.

Before we can proceed to apply the methods of section 3.1. to a polyatomic gas, we have to decide what the values of the translational, active and inert energies of our molecules are, immediately after adsorption. In section 2.1. we obtained an expression for E_i which was made up, partly of the thermal motion of the molecule and partly of the mean mass motion of the incident stream. When the gas strikes the surface, the distinction diappears, and we may write, as in equations (2.5) and (2.6), $E_i = 2m\ N_i\ R\ KT_i$. Now at a later time the translational energy of the molecules will be E. Let us define a quantity T, by $T = \frac{E}{2mN_iR}$.

Then as E varies from E_i to E_r, T will vary from K T_i to T_r. Now consider the active energy which the N_i molecules carry to the surface. From equations (2.7) etc., this is given by $E'_i = \frac{1}{2}\ m\ N_i\ j'R\ T_i$. Let E' denote the energy of these molecules at a later time, t, and define $T' = E / \frac{1}{2}\ m\ N_i\ j'R$, then T' will change from T_i to T'_r as E' changes from E'_i to E'_r.

Here we are considering an active mode and, by definition, an active mode adjusts itself immediately to any change in the translational mode energy. In the gas phase this adjustment takes place via molecular collisions. Since in this case there are no inter-molecular collisions, we will take "active" as meaning the active mode will adjust itself to the surface temperature at the same rate as does the translational mode. In the same way we define T" for the inert mode and note that it varies from T_i to T''_r.

When, in the previous section, we were only concerned with the translational energy, it was reasonable to assume that E_w was the state to which E would tend. However, now the internal energy only comes into contact with the surface, insofar as it is brought into a collision by the translational motion. Furthermore, we know that energy transition rates are closely linked with the binding forces applicable to the mode of energy concerned. For example, in the gas phase the transition rates of, say, a vibrational energy mode are much slower than the transition rates of the translational energy, and the forces binding the atoms together into molecules are much stronger than the mutual forces between the molecules. If, in the case of adsorption, the forces which bind the molecules to the surface become such that the transition rates for the translational and active energy modes are less than the transition rates of the inert energy, then we have chemi-sorption, and probably dissociation. Thus for physical adsorption, we postulate the following equations as governing the energy exchanges :

$$\frac{\partial E}{\partial t} = -\frac{1}{\tau}(E - E_w) - \frac{1}{\tau'_a}(E - E'_1) - \frac{1}{\tau_i}(E - E''_2)$$

$$\frac{\partial E'}{\partial t} = -\frac{1}{\tau'_a}(E' - E'_3)$$

$$\frac{\partial E''}{\partial t} = -\frac{1}{\tau_i}(E'' - E''_4)$$

where τ , τ'_a and τ_i are the relaxation times associated with the translational, active and inert modes respectively, E'_1 is the energy the translation mode would have if it were in equilibrium with the active mode; E''_2 is the energy the translational mode would have if it were in equilibrium with the inert mode; E'_3 and E''_4 are the energies the active and inert modes respectively would have if they were in equilibrium with the translational mode. We now want to say that τ'_a is negligible when compared with τ_i. However, for a moving $(K \neq 1)$ gas, this implies an instantaneous change in E and E′ at the moment of adsorption, since when the gas becomes adsorbed all its translational energy is made up of thermal motion. However, if the gas is static this problem does not arise, so we will proceed with the static case and deal with $K \neq 1$ later.

Let us now neglect τ'_a with the result that our equations of energy change become

$$\frac{\partial E}{\partial t} = -\frac{1}{\tau_a}(E - E_w) - \frac{1}{\tau_i}(E - E''_2)$$

$$\frac{\partial E''}{\partial t} = -\frac{1}{\tau_i}(E'' - E''_4)$$

where E now denotes translational plus active energy. If

$$E = (2m\,N_i\,R + \tfrac{1}{2}\,m\,N_i\,j'\,R)\,T$$

$$E''_2 = (2m\,N_i\,R + \tfrac{1}{2}\,m\,N_i\,j'\,R)\,T'' \tag{4.1}$$

and

$$E''_4 = \tfrac{1}{2}\,m\,N_i\,j''\,R\,T$$

then these equations are quite easy to solve. The assumptions necessary to justify this step are that the molecules are re-emitted from the surface with a Maxwellian velocity distribution corresponding to a temperature T_r, and that $T_w - T_i$ is small. Accepting these assumptions the equations become :

$$\frac{\partial T}{\partial t} = -\frac{1}{\tau_a}(T - T_w) - \frac{1}{\tau_i}(T - T'')$$

$$\frac{\partial T''}{\partial t} = -\frac{1}{\tau_i}(T'' - T)$$

The solutions are

$$T = A\,e^{-\mu t} + B\,e^{-\nu t} + T_w$$

and

$$T'' = A\,\tau_i\left(\frac{1}{\tau_a} + \frac{1}{\tau_i} - \mu\right)e^{-\mu t} + B\,\tau_i\left(\frac{1}{\tau_a} + \frac{1}{\tau_i} - \nu\right)e^{-\nu t} + T_w$$

where A and B are arbitrary constants and

$$\mu = \tfrac{1}{2}\left[\left(\frac{1}{\tau_a} + \frac{2}{\tau_i}\right) + \sqrt{\frac{1}{\tau_a^2} + \frac{4}{\tau_i^2}}\,\right] \;;\quad \nu = \tfrac{1}{2}\left[\left(\frac{1}{\tau_a} + \frac{2}{\tau_i}\right) - \sqrt{\frac{1}{\tau_a^2} + \frac{4}{\tau_i^2}}\,\right]$$

Now when $t = 0$, $T = T'' = T_i$ whence

$$E_r = (E_i - E_w) \left\{ \frac{1/\tau_a - \nu}{\mu - \nu} e^{-\mu\bar{\tau}} + \frac{\mu - 1/\tau_a}{\mu - \nu} e^{-\nu\bar{\tau}} \right\} + E_w$$

$$E'_r = (E'_i - E'_w) \left\{ \frac{1/\tau_a - \nu}{\mu - \nu} e^{-\mu\bar{\tau}} + \frac{\mu - 1/\tau_a}{\mu - \nu} e^{-\nu\bar{\tau}} \right\} + E'_w$$

$$E''_r = (E''_i - E''_w) \left\{ \frac{\tau_i (1/\tau_a - \nu)(1/\tau_a + 1/\tau_i - \mu)}{\mu - \nu} e^{-\mu\bar{\tau}} + \frac{\tau_i(\mu - 1/\tau_a)(1/\tau_a + 1/\tau_i - \nu)}{\mu - \nu} e^{-\nu\bar{\tau}} \right\} + E''_w$$

From these equations it is easy to obtain expressions for α, α' and α'':

$$\alpha = \alpha' = 1 - \frac{1/\tau_a - \nu}{\mu - \nu} e^{-\mu\bar{\tau}} - \frac{\mu - 1/\tau_a}{\mu - \nu} e^{-\nu\bar{\tau}} \qquad (4.2)$$

and

$$\alpha'' = 1 - \frac{\tau_i (1/\tau_a - \nu)(1/\tau_a + 1/\tau_i - \mu)}{\mu - \nu} e^{-\mu\bar{\tau}} - \frac{\tau_i(\mu - 1/\tau_a)(1/\tau_a + 1/\tau_i - \nu)}{\mu - \nu} e^{-\nu\bar{\tau}} \qquad \ldots\ldots \quad (4.3)$$

Note that :

as $\bar{\tau} \to \infty$, α, α' and $\alpha'' \to 1$

as $\bar{\tau} \to 0$, α α' and $\alpha'' \to 0$

as $\tau_a \to \infty$, α, α' and $\alpha'' \to 0$

as $\tau_a \to 0$, α and $\alpha' \to 1$, $\alpha'' \to 1 - e^{-\bar{\tau}/\tau_i}$

as $\tau_i \to \infty$, α and $\alpha' \to 1 - e^{-\bar{\tau}/\tau_a}$, $\alpha'' \to 0$

as $\tau_i \to 0$, α, α' and $\alpha'' \to 1 - e^{-\bar{\tau}/2\tau_a}$

Thus our expressions for the three accommodation coefficients behave as we would expect in the various limiting cases. It is interesting to note that, as we would expect, in the two cases $\tau_i = \infty$, $\tau_i = 0$ we obtain expressions identical in form to the expression obtained earlier for a monatomic gas.

Before discussing the meaning of these results, we must consider the case of a gas with a mean motion ($K \neq 1$). As stated earlier, in this case it is not possible to think of the active mode as being in equilibrium with the translational motion, and the substitutions of equation 4.1 are certainly no longer valid. The only way round the difficulty, and one which can be based on physical arguments, is to assume that the active energy, whilst having the same transition rates as the translational energy, lags behind the level of the translational mode by a constant amount. This constant amount is represented by $\frac{1}{2}$ m N_i $j'R$ $(KT_i - T_i)$. Here we are invoking the same argument as before, that the active mode transition rates cannot be greater than the translational mode transition rates in the type of adsorption we are considering. Similar remarks apply to the inert mode energy, and on this basis it is obvious that we would expect the same expressions to hold for α, α' and α'' in the case $K \neq 1$ as for $K = 1$.

The dependence of $\bar{\tau}$ and τ_a as functions of temperature and speed ratio would be expected to be the same as for a monatomic gas, and in the next section limited experimental evidence will be shown to support this view. Unfortunately, due to lack of experimental evidence and lack of success in theoretical investigations, it has not been possible to throw any light on the behaviour of τ_i. It should be reasonable however, to assume that τ_i will show little dependence on $T_w - T_i$ and will be largely dependent on the gas temperature and the particular gas being considered. In this respect we expect that τ_i will show some similarity to the gas phase relaxation time. Fig. 7 shows $\alpha = \alpha'$ plotted against α'' for the full range of values of τ_a/τ_i and $\bar{\tau}/\tau_a$, whilst Fig. 8 shows α, α' and α'' plotted against temperature. The value of $Q = 3000$ cals/mole is representative of the heat of adsorption of a number of the heavier gases. In addition, we have assumed that τ_a and τ_i will be of the same order of magnitude, i.e. $\tau_a/\tau_i = 1$, and the value of $\tau_a/\tau_o = 100$ seems to be of the right order from our study of monatomic gases. This curve then should be representative of the variation of α, α' and α'' with temperature, assuming $T_w - T_i$ constant, for a gas such as CO_2 which has its bending mode excited in the temperature range considered. In the same figure we have shown the variation of α for a monatomic gas, using the values of Q and τ_a/τ_o given above.

An expression for α'' has been obtained by Herman and Rubin$^{(18)}$. They consider the inert mode's energy exchange as completely divorced from the translational and active modes, and also consider that the re-emitted molecules carry with them an average amount of inert energy which is equal to the average amount of inert energy of the adsorbed layer viewed as a whole. We can best compare our expression with theirs by taking the value of α'' when $\tau_a = 0$, i.e. $\alpha'' = 1 - e^{-\bar{\tau}/\tau_i}$. Their expression written in our notation is then $\alpha'' = \dfrac{1}{1 + \tau_i/\bar{\tau}}$.

These are compared in Fig. 9. We see that our expression gives larger values than that of Herman and Rubin as we would expect, since different assumptions are made. The available experimental data are not sufficient to say which is more realistic with regard to estimating accommodation coefficients, but to assume that molecules just arriving at the surface have as great a probability of leaving as those that have been there some time, as Herman and Rubin do, does not qualitatively fit the observed facts of physical adsorption.

4.1. Experimental results. Polyatomic gases

The most famous experiment performed to find the accommodation coefficient of a polyatomic gas, is the one performed by Knudsen(20) with hydrogen on platinum. Knudsen used a flat strip of platinum which was bright on one side and blackened on the other, thus giving different accommodation coefficients on each surface. By relating the pressure acting on the surface to the translational accommodation coefficient of the surface, in a manner which will be shown in the next section, he was able to demonstrate that the translational and internal accommodation coefficients were equal for each surface. This result is often quoted (c.f. Ref. 19) as demonstrating that the accommodation coefficients of all the modes of energy of a molecule will be equal. This is, however, a very doubtful assumption since Knudsen, judging from the apparatus he used was almost certainly working at about room temperature, although in (20) he does not state the working temperature. Thus the vibrational mode of the hydrogen would not enter into his experiment at all. The only safe conclusion to draw from his result is that he provided some evidence in favour of assuming that the translational and active accommodation coefficients of a gas will be equal, thus supporting the line we have taken in this report.

At the present time there are no experimental results directly applicable to the results we established in the previous section. There are experimental values for the accommodation coefficients of diatomic gases, H_2 and N_2, but the experiments were conducted at temperatures so low that the vibrational energy mode would almost certainly not enter into the energy exchange process. These results(19), as we expect from our theory, follow in the main the same trends as the results for monatomic gases quoted earlier. An exception to this are the the results of Blodgett and Langmuir for H_2 on W, $T_W - T_i$ being maintained approximately constant. The values they obtain for the accommodation coefficient decrease with temperature from 200°K to 500°K and then increase over the range 500°K to 1000°K. It is not easy to explain these results on the basis of our theory without assuming that Q increases with temperature. It should be noted that at room temperature, hydrogen forms a stable chemi-sorbed layer on tungsten which only becomes unstable at around 2000°K, so that the results of Blodgett and Langmuir are for H_2 on an adsorbed layer of H_2 on tungsten.

The results of Devienne, mentioned earlier, also include values for polyatomic gases, but the same objection with regard to the interpretation of his data applies as before. Since, as we have stated, all available data appertain to the translational and active modes only, we will proceed at once to the next section where we will consider in detail the flow over a flat plate in order to see what can be done experimentally or otherwise to illuminate this problem a little more.

5. Flow over a flat plate

Knudsen(20) was the first to point out that, when dealing with a polyatomic gas, the parts played by the translational mode and the internal modes in the heat transfer are not separable experimentally. In order to obtain values for their separate contributions, one has to relate them in some way to other measurable quantities, such as the skin friction or the normal pressure. Now if, as we have assumed, there is no specular reflection, the skin friction is expressible in known quantities. Earlier we defined $\sigma = \dfrac{\tau_i - \tau_r}{\tau_i - \tau_w}$. Now, when all the incident molecules are temporarily trapped by the surface, on re-emission they will show no directional preference, so that $\tau_r = \tau_w = 0$, and τ_i comprises the total skin friction. (Note that here τ_i refers to the skin friction force and should not be confused with the relaxation time. Since the skin friction only enters briefly into this report, it was thought best to use the conventional symbol). Thus we have to rely on the normal pressure to provide us with the necessary extra relationship. Fortunately, in the case of a flat plate, this proves possible.

We have defined

$$\eta = \frac{p_i - p_r}{p_i - p_w}$$

where p_i has been given in section 2.1. Now p_r is easily expressible in terms of known quantities by assuming that the molecules are re-emitted at temperature T_r with a Maxwellian velocity distribution. In this case $p_r = \frac{1}{2} m N_i \sqrt{2 \pi R T_r}$ Note that this implies $T_i - T_w$ small. If we now consider the thermal accommodation coefficient of the translational mode, and make the same assumption as to velocity distributions, we can write

$$\alpha = \frac{K T_i - T_r}{K T_i - T_w}$$

whence

$$T_r = K T_i - \alpha (K T_i - T_w)$$

Now the total pressure acting on one face of the flat plate is

$$p = p_i + p_r = p_i + \tfrac{1}{2} m N_i \sqrt{2 \pi R T_r}$$

Substituting for T_r

$$p = p_i + \tfrac{1}{2} m N_i \sqrt{2 \pi R \left[K T_i - \alpha (K T_i - T_w)\right]}$$

and from section 2.1.

$$p_i = \tfrac{1}{2} m N_i \sqrt{2 \pi R T_i} \quad \psi$$

where ψ is given by equation 2.11 or 2.12, (we do not need to specify which surface we are considering yet).

$$\therefore \quad p = \tfrac{1}{2} m N_i \sqrt{2 \pi R} \left\{ \psi \sqrt{T_i} + \sqrt{\left[K T_i - \alpha (K T_i - T_w)\right]} \right\} \qquad (5.1.)$$

This is the type of analysis Knudsen used, as mentioned earlier. Knudsen, however, who was dealing with a static gas, then went on to linearise this equation by assuming $T_w - T_i$ very small, and he was then able to relate the pressure difference across the plate to the difference of the two translational accommodation coefficients. We will proceed along different lines, as follows.

If p can be measured now on one surface of the plate, equation 5.1 will yield α. The difficulty is the measuring of p and $\overline{\alpha}$ for one surface of the plate only, since in free-molecule flow experiments, the plate must be kept small. However Devienne(14) has already given the outline of an experiment in which the speed ratio was varied. This being possible, one could choose values of T_w, T_i, S and θ such that $K^{\ell} T_i$ is equal to T_w, see Fig. 1, and the heat transfer to the lower surface of the plate becomes zero. In addition, the pressure on the lower surface becomes calculable in terms of known quantities. One need then measure only the total heat transfer to the plate and the total normal pressure force. To obtain the inert accommodation coefficient is then a simple matter. We defined in equation 3.4 the combined accommodation coefficient. Hence, having measured $\bar{\alpha}$ and knowing $\alpha(= \alpha')$ from the pressure measurement, one could evaluate α''. This would then, with the aid of Fig. 7, give values for τ_a/τ_i and $\bar{\tau}/\tau_a$, and if the relevant value of Q were known, values of τ_a/τ_o and τ_i/τ_o could be calculated. The above remarks obviously apply to making $K^u T_i$ (see Fig. 2) equal to T_w. With $K^{\ell} T_i = T_w$, the plate would have to be heated in order to maintain constant T_w, whilst when $K^u T_i = T_w$ it would have to be cooled.

The above procedure would allow us to examine the behaviour of the separate accommodation coefficients and hence τ_a and τ_i, on both sides of the plate, for various values of K T_i and T_w. It would not allow us to examine their behaviour with varying S or θ whilst keeping T_w constant, and this behaviour, in the light of earlier remarks, would be of great importance. It does not seem possible to utilise the results of theory to suggest an experimental procedure for this case, and to obtain such results one would have to rely either on the use of sufficiently small pressure pickups and heat transfer gauges, or one could possibly shield one surface of the plate from the flow. It is felt to be essential, in experimental work in this field, to use a flat plate or surface if the results are to be of any use in giving the behaviour of α, α' and α'' for varying speed ratio and angle of incidence.

6. Conclusions

At the present time there are neither experimental nor theoretical results available from which to form estimates of the accommodation coefficients of polyatomic gases. Most investigations into the problems of free-molecule flow make use of one of the two following assumptions. They either assume $\alpha'' = 0$ or $\alpha = \alpha' = \alpha''$. This latter assumption seems to be founded on a mis-interpretation of Knudsen's result (c.f. section 4.1 and Ref. 19). In this report, expressions for the various accommodation coefficients have been obtained which, with the aid of experimental data, would enable one to estimate their values and variations with temperature, etc. A limited comparison with results obtained with monatomic gases indicates that these expressions have the correct behaviour as regards varying temperature and gas-surface temperature difference. The expressions show the dependence of the coefficients on three factors. These are the heat of adsorption, the relaxation time of the energy exchange between the surface and the active energy modes, and the relaxation time of the inert mode relative to the active modes. (We use the term active here as including translational). The first of these quantities is known from experiment for a large number of cases. The relaxation times are at the moment almost completely unknown quantities; but some remarks can be made about their probable behaviour. It is reasonable to suppose that τ_a, besides its temperature dependence, will be dependent on the masses of the gas molecule and the surface atoms. Thus, for the same surface, we would not expect τ_a to vary much between gases whose molecules have similar masses. A more complete survey of the available monatomic gas results than was possible within the scope of this investigation should yield information of use in connection with polyatomic gases. Also, it is not unreasonable to suppose that τ_i will be of the same order of magnitude as the gas phase relaxation time, and this, together with the above, could be used as a basis for estimating the values of the accommodation coefficients. These two are, however, secondary to a direct experimental investigation of the problem, and also, if possible, a rigorous wave-mechanical investigation.

As a by-product of our approach to the problem, it appears that the speed ratio and flow incidence only affect the accommodation coefficients in so far as they affect the energy difference $E_w - E_i$.

We would therefore expect that the variation of both S and θ in the flow case would have the same effect as the variation of T_i in the static case, if T_w is maintained constant.

Finally it must be stressed that experimental work with polyatomic gases, along the lines indicated in section 5, is of prime importance in order to test the validity of the gas-surface interaction model proposed herein and the theory built up from it.

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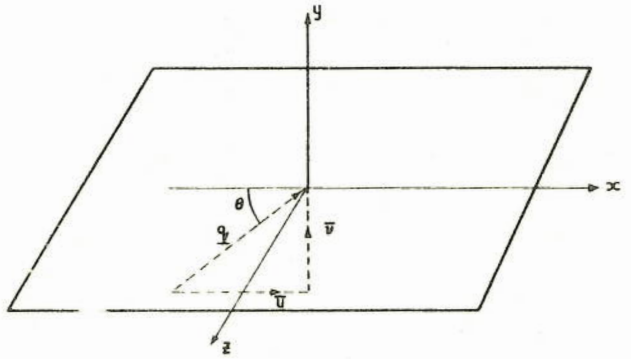

AXES CHOSEN SO THAT ϖ = 0

FIG. I. CO-ORDINATE SYSTEM FOR REFERENCE TO FLAT PLATE.

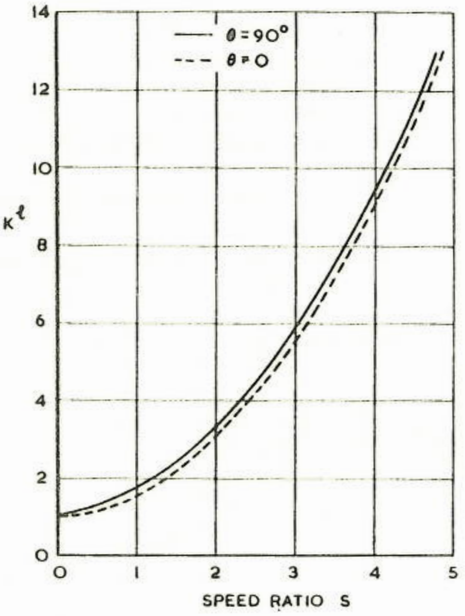

FIG. 2. NON-DIMENSIONAL FACTOR OF EQUATION 2·5 VERSUS SPEED RATIO AND ANGLE OF INCIDENCE.

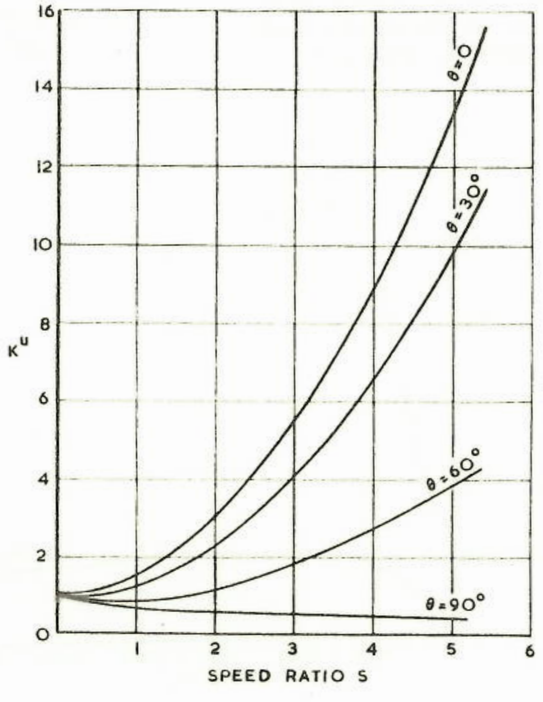

FIG. 3. NON-DIMENSIONAL FACTOR OF EQUATION 2·6 VERSUS SPEED RATIO AND ANGLE OF INCIDENCE.

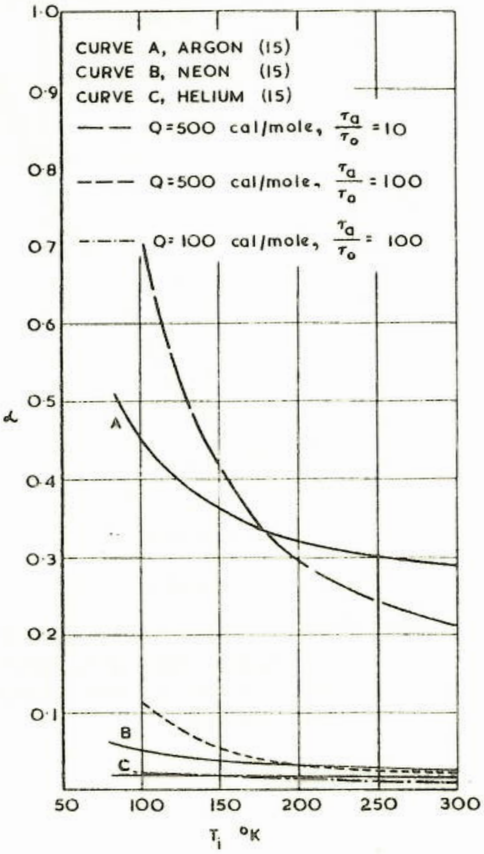

FIG. 4. COMPARISON OF EXPRESSION FOR α FOR A MONATOMIC GAS WITH EXPERIMENTAL RESULTS.

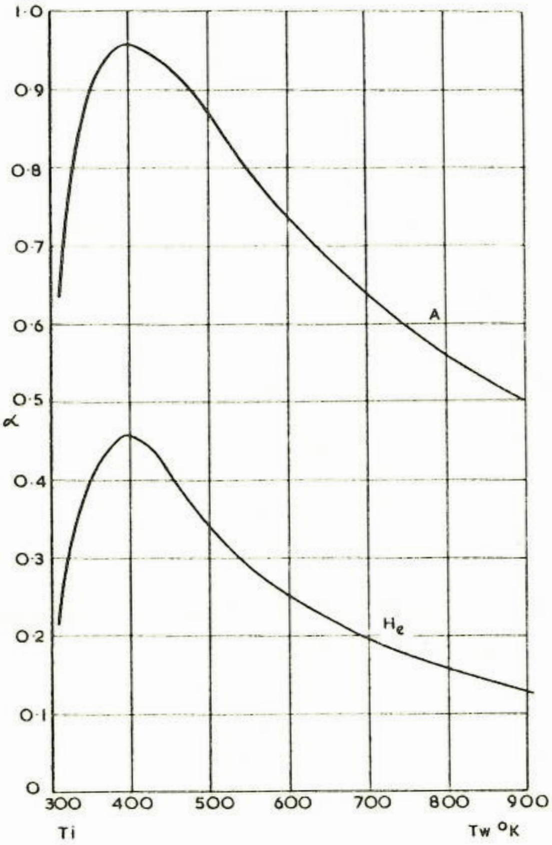

FIG. 5. EXPERIMENTAL RESULTS OF OLIVER.

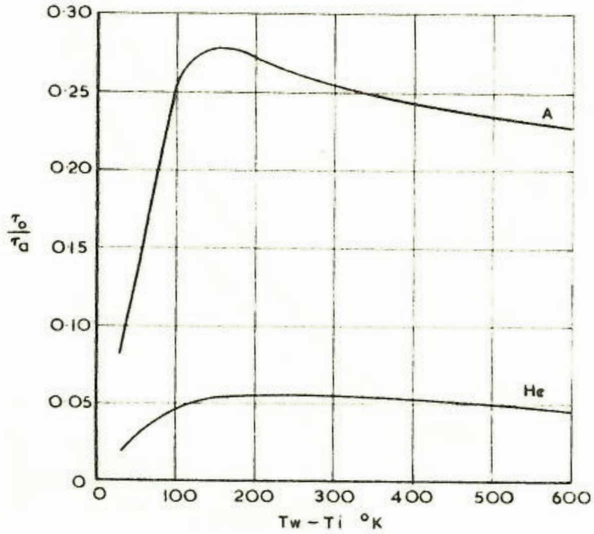

FIG. 6. $\frac{\tau_a}{\tau_o}$ VERSUS TEMPERATURE DIFFERENCE DEDUCED FROM FIG. 5.

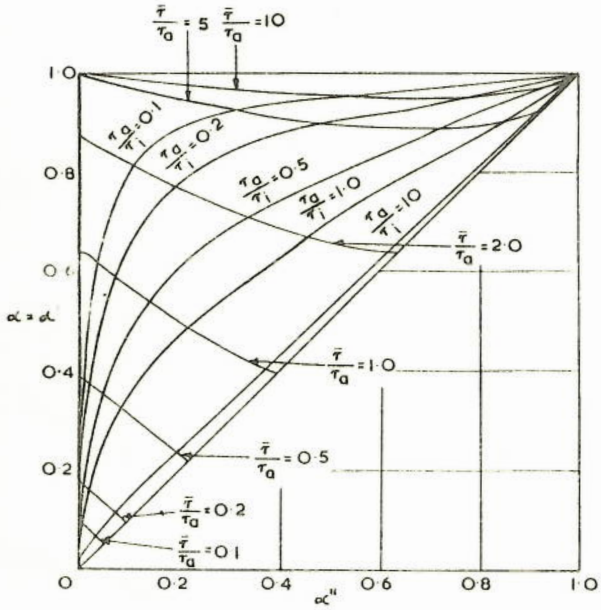

FIG. 7. EXPRESSIONS FOR α, α' AND α'' VERSUS $\frac{\bar{\tau}}{\tau_a}$ AND $\frac{\tau_a}{\tau_i}$.

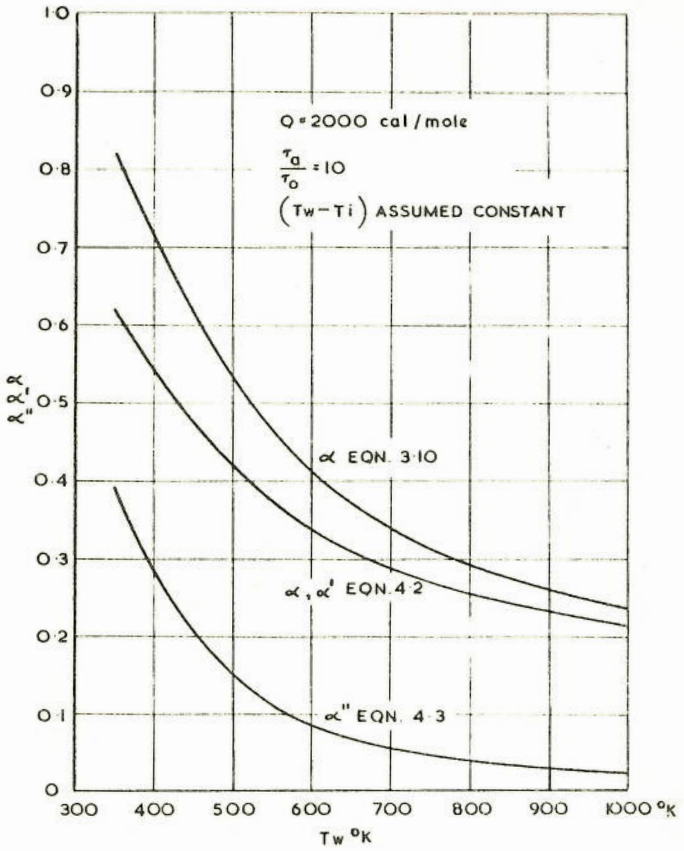

FIG. 8. THEORETICAL VARIATION OF α FOR A MONATOMIC GAS, α AND α'' FOR A POLYATOMIC GAS WITH TEMPERATURE.

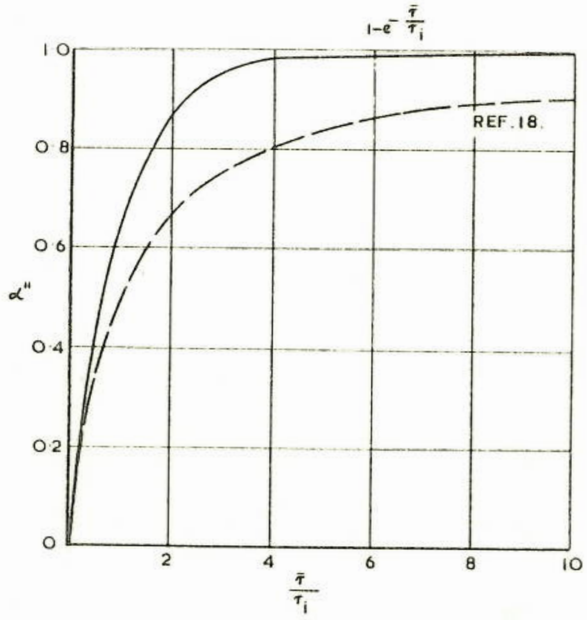

FIG. 9. COMPARISON OF EXPRESSION FOR α'' OF THIS REPORT WITH THAT OF REFERENCE 18.