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The Flow of Chemically Reacting Gas Mixtures

- by -

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SUMMARY

Suitable forms of the equations for the flow of an inviscid, non-heat-conducting gas in which chemical reactions are occurring are derived. The effects of mass diffusion and non-equilibrium amongst the internal modes of the molecules are neglected.

Special attention is given to the speeds of sound in such a gas mixture and a general expression for the ratio of frozen to equilibrium sound speeds is deduced. An example is given for the ideal dissociating gas. The significance of the velocity defined by the ratio of the convective derivatives of pressure and density is explained. It is the velocity which exists at the throat of a convergent-divergent duct under maximum mass flow conditions, and it is shown that this velocity depends on the nozzle geometry as well as on the 'reservoir' conditions.

As an illustration the phenomena of sound absorption and dispersion are discussed for the ideal dissociating gas. The results can be concisely expressed in terms of the frozen and equilibrium sound speeds, the frequency of the (harmonic) sound vibration and a characteristic time for the rate of progress of the reaction.

CONTENTS

LIST OF SYMBOLS

a	Ratio of a_f to a_e
a_e	Equilibrium sound speed
a_f	Frozen sound speed
A_α	Chemical formula of α -th species
c_α	Mass fraction of α-th species
C_{pf}	Specific heat at constant pressure and frozen composition
h	Enthalpy per unit mass
$k_f^{(r)}$	Specific reaction rate constant for the r-th forward reaction
$k_r^{(r)}$	Specific reaction rate constant for the r-th reverse reaction
$K_\alpha^{(r)}$	Mass rate of production of α-th species per unit volume in the r-th reaction
K_α	Overall mass rate of production of α-th species per unit volume $\left(= \sum_{r=1}^{N_m} K_\alpha^{(r)} \right)$
$K^{(r)}$	Defined in equation 12
m	Defined in equation 71
n	Number of separate chemical species
N_a	Number of atomic species
N_m	Number of molecular species and of reactions
p_α	Partial pressure of α-th species
p	Total pressure
R	Universal Gas Constant
$R^{(r)}$	Rate of r-th reaction
s	Entropy per unit mass
T	Absolute temperature
t	Time
u_i $(i = 1,2,3)$	Flow velocity vector

LIST OF SYMBOLS (Continued)

W_α	Molecular Weight of α-th species
x_α	Mole fraction of α-th species
x_i $(i = 1,2,3)$	Position vector in Cartesian coordinates
β_f	Volume expansion coefficient at constant (frozen) composition
ζ	Defined in equation 75
θ	Defined in equation 71
λ_α	Defined in equation 43
μ_α	Chemical potential of α-th species (per unit mass)
$\nu_\alpha^{(r)\prime}, \nu_\alpha^{(r)\prime\prime}$	Stoichiometric coefficients of α-th species in r-th reaction; reactants and products respectively
ξ	Streamwise coordinate
ρ	Density
σ_α	Defined in equations 32 and 37
$\tau^{(r)}$	Characteristic chemical time for r-th reaction (see eq.11)
τ'_∞	Defined in equation 62
ω	Angular frequency of sound wave

Superscripts

(r)	Refers to r-th reaction
$'$	Refers to a disturbance quantity

Subscripts

α	Refers to α-th chemical species
e	Refers to chemical equilibrium
f	Refers to chemically frozen state
∞	Refers to an undisturbed quantity

Other symbols are defined in the text

1. Introduction

The advent of flight through the atmosphere at stagnation enthalpies sufficient to cause chemical changes in the air surrounding the body has introduced a new complication into the study of gas flows. The chemical reactions which occur in the gas are thermodynamically irreversible processes and, as such, lead to the creation of entropy. A further source of dissipation therefore exists in the flow, in addition to the normal transport phenomena which, formerly, we have had to face only in the interior of boundary layers and shock waves. The important difference between entropy production due to chemical reaction (or, indeed, due to changes in the internal states of polyatomic molecules as well) and that due to transport processes lies in the fact that the latter are explicit functions of gradients in the flow variables(velocity, temperature and concentration) whereas the former is not. For this reason, the significant dissipative action of chemical changes may be important throughout the flow field.

In the present paper the gas flow equations are developed for flows in which transport processes can be neglected. Chemical reactions are included but it is assumed that the internal states of the molecules are in equilibrium with the translational modes. The treatment of the reaction equations follows Boa-Teh Chu (1957) and density gradients are eliminated from the overall mass conservation equation in favour of pressure gradients in the manner shown by Kirkwood and Wood (1957). The latter paper derives the general flow equationsincluding also the effects of internal relaxation phenomena.

In the course of rearranging the mass conservation equation it is necessary to introduce the derivative ($\partial p/\partial \rho$) taken at constant entropy and composition (p is pressure, ρ is density) and this is identified as the 'frozen' speed of sound, a_f. The question of which among the many speeds of sound which can be defined in a reacting gas mixture (indeed, as is shown in Section 7, there are an infinite number) is the most significant in a general flow field has been answered by Kirkwood and Wood and Chu in the papers cited and also by Broer (1958) all of whom show that the characteristic directions are defined in terms of local values of a_f. However, the sound speed in the other limiting case where chemical composition is assumed to follow its equilibrium value through the (weak) sound disturbance is not without significance and some discussion of it is given in Section 5.

Recently Resler (1957) proposed that the velocity defined by the ratio of the convective derivatives of p and ρ should be used to define characteristic directions. The reasons for the failure of this proposal have been stated by Broer and these are reinforced by the treatment of Section 6 below. It is shown there that the peculiar significance of $(Dp/Dt)/(D\rho/Dt)$ in a steady flow lies in its definition of the flow velocity at the throat of a convergent-divergent streamtube.

Finally, in Section 7 a simple example of sound absorption and dispersion is given for an ideal dissociating gas.

It is hoped that the present paper may supplement those mentioned above and go some way towards clearing up some of the difficulties associated with reacting gas flows, particularly with reference to the question of the speeds of sound. (N.B. Cartesian tensor notation is used in the development of the general equations, but the translation to standard vector notation may readily be made if desired).

2. The Basic Equations

We shall consider a gas mixture consisting of n separate chemical species whose chemical formulae are denoted by A_α ($\alpha = 1, 2, \ldots n$). In dealing with regions of the flow outside boundary layers and the interior of shock fronts we shall neglect viscosity and thermal conductivity and, in addition, assume that the components of the diffusion velocity vector, $u_{\alpha i}$, are small compared with those of the mass average (or flow) velocity vector, u_i. That is, we assume that $|u_{\alpha i}| < < |u_i|$ ($i = 1, 2, 3$) for each value of α.

The overall mass conservation requirement is unaffected by the possible occurrence of chemical reactions in the gas and can be written in the form

$$\frac{D\rho}{Dt} + \rho \frac{\partial u_i}{\partial x_i} = 0 . \qquad (1)$$

Likewise the momentum and energy relations are the same as they are in an ordinary inert gas flow (within the confines of the assumptions made previously) and are written as

$$\rho \frac{Du_i}{Dt} + \frac{\partial p}{\partial x_i} = 0 \qquad (2)$$

$$\rho \frac{Dh}{Dt} - \frac{Dp}{Dt} = 0 . \qquad (3)$$

(ρ = density of the mixture, p = pressure and h = specific enthalpy. $D/_{Dt}$ is the convective derivative and, in Cartesian tensor notation,

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u_j \frac{\partial}{\partial x_j} \qquad 4.)$$

In addition, there are n continuity equations which must be satisfied by each of the chemical species A_α. These are readily shown to be

$$\rho \frac{Dc_\alpha}{Dt} = K_\alpha \quad (\alpha = 1, 2, 3 \ldots n), \qquad (5)$$

within the framework of the general assumptions made above. c_α is the mass fraction of the α-th species and K_α is the net mass rate of production of that species per unit volume. K_α must take account of all the possible chemical reactions which can occur between the components of the mixture.

In the general case the mixture consists of N_a separate atomic species (A_1, A_2, A_3, ... A_{N_a}) plus N_m separate molecular species ($A_{N_{a+1}}$, $A_{N_{a+2}}$, ... $A_{N_{a} + N_m}$). The molecules are formed from combinations among the N_a different types of atoms. Plainly $N_a + N_m = n$ and the total possible number of elementary, independent reactions is N_m. The chemical equation for the r-th reaction ($r = 1,2,3, \ldots N_m$) is

$$\sum_{\alpha=1}^{n} \nu_\alpha^{(r)\prime} A_\alpha \underset{k_r^{(r)}}{\overset{k_f^{(r)}}{\rightleftarrows}} \sum_{\alpha=1}^{n} \nu_\alpha^{(r)\prime\prime} A_\alpha \quad , \tag{6}$$

where $\nu_\alpha^{(r)\prime}$ and $\nu_\alpha^{(r)\prime\prime}$ are the appropriate stoichiometric coefficients of the reactants and products respectively. Both quantities are integers. $k_f^{(r)}$ and $k_r^{(r)}$ are the forward and reverse specific reaction rate constants respectively for the r-th reaction.

It is common in physico-chemical work to specify concentrations of species in terms of moles per unit volume of the mixture. We shall denote this unit by the symbol $[A_\alpha]$. It is found (see, e.g. Moelwyn-Hughes, 1957, pp. 986 - 988) that the rate of progress of a particular chemical process, in a homogeneous medium like a gas mixture, is proportional to the product of the concentration of the reactants each raised to its appropriate stoichiometric coefficient. Thus in equation 6 the forward reaction proceeds at a rate proportional to

$$\prod_{\alpha=1}^{n} [A_\alpha]^{\nu_\alpha^{(r)\prime}}$$

and the reverse reaction at a rate proportional to

$$\prod_{\alpha=1}^{n} [A_\alpha]^{\nu_\alpha^{(r)\prime\prime}} \quad .$$

Measuring the rate of progress of the reactions in moles per unit volume per unit time and noting the opposing effects of forward and reverse reactions, the <u>net</u> rate of progress of the r-th reaction in the forward direction is given by $R^{(r)}$ where

$$R^{(r)} = k_f^{(r)} \prod_{\alpha=1}^{n} [A_\alpha]^{\nu_\alpha^{(r)\prime}} - k_r^{(r)} \prod_{\alpha=1}^{n} [A_\alpha]^{\nu_\alpha^{(r)\prime\prime}} \; . \tag{7}$$

(Note that the direction in which a reaction proceeds is specified by the condition that

$$\sum_{\alpha=1}^{n} \nu_\alpha^{(r)\prime} W_\alpha \mu_\alpha \; > \; \sum_{\alpha=1}^{n} \nu_\alpha^{(r)\prime\prime} W_\alpha \mu_\alpha$$

for a natural process. μ_α is the chemical potential of A_α per unit mass and W_α the molecular weight of A_α . See, e.g. Guggenheim, 1949).

The observable effect of any reaction is the net rate of production of a given species in the mixture. Since the r-th reaction, for example, yields $\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'}$ molecules of A_α from the original reactants it is apparent that the mass rate of production of A_α in the r-th reaction (written $K_\alpha^{(r)}$) is given by

$$K_\alpha^{(r)} = W_\alpha \left(\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'} \right) \left\{ k_f^{(r)} \prod_{\alpha=1}^{n} [A_\alpha]^{\nu_\alpha^{(r)'}} - k_r^{(r)} \prod_{\alpha=1}^{n} [A_\alpha]^{\nu_\alpha^{(r)''}} \right\} \quad (8)$$

The mass fraction c_α is related to $[A_\alpha]$ by

$$\rho c_\alpha = W_\alpha [A_\alpha], \quad (9)$$

whence we can rearrange equation 8 to read

$$K_\alpha^{(r)} = \frac{\rho W_\alpha}{\tau^{(r)}} \left\{ \nu_\alpha^{(r)''} - \nu_\alpha^{(r)'} \right\} \left\{ K^{(r)} \prod_{\alpha=1}^{n} c_\alpha^{\nu_\alpha^{(r)'}} - \prod_{\alpha=1}^{n} c_\alpha^{\nu_\alpha^{(r)''}} \right\} \quad (10)$$

where

$$\tau^{(r)} = \frac{\rho}{k_r^{(r)}} \prod_{\alpha=1}^{n} \left(\rho / W_\alpha \right)^{-\nu_\alpha^{(r)''}} \quad (11)$$

and

$$K^{(r)} = \frac{k_f^{(r)}}{k_r^{(r)}} \prod_{\alpha=1}^{n} \left(\rho / W_\alpha \right)^{\nu_\alpha^{(r)'} - \nu_\alpha^{(r)''}} \quad (12)$$

It can be seen that $k_r^{(r)}$ has the dimensions of (mass per unit volume) raised to the $1 - \sum_{\alpha=1}^{n} \nu_\alpha^{(r)''}$ power, per unit time. Thus $\tau^{(r)}$ has the dimensions of time and is, indeed a characteristic time by which to measure the rate of progress of the r-th reaction.*

If a gas mixture is in chemical equilibrium, there is no net rate of production of any particular species; the forward and reverse reactions exactly cancel one another and a dynamic balance is achieved, the system showing no tendency to change its state. Taking the r-th reaction as typical, this means that $K_\alpha^{(r)} = 0$ for chemical equilibrium for all α and r.

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* $\tau^{(r)}$ is proportional to the time taken for a given small deviation from equilibrium to fall to 1/e of its original value as a result of the r-th reaction alone.

Denoting this special state by a suffix e, equation 10 shows that

$$K_e^{(r)} = \prod_{\alpha=1}^{n} c_{\alpha e}^{\;\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'}} \tag{13}$$

while equation 12 shows that

$$K_e^{(r)} = \frac{k_f^{(r)}}{k_r^{(r)}} \prod_{\alpha=1}^{n} \left({}^{\rho_e}/_{W_\alpha}\right)^{\nu_\alpha^{(r)'} - \nu_\alpha^{(r)''}} . \tag{14}$$

Thus, from equations 12, 13 and 14,

$$K^{(r)} = \prod_{\alpha=1}^{n} \left(\frac{\rho_e \, c_{\alpha e}}{\rho}\right)^{\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'}} . \tag{15}$$

Now the state of the gas at any point is completely specified thermodynamically by, say, the density ρ, temperature T and the set of n numbers, c_α. For the particular values of ρ and T there will always exist one set of n numbers $c_{\alpha e}$ which specify the equilibrium composition. If we choose, as we are quite at liberty to do, to specify the $c_{\alpha e}$ as the equilibrium composition arising at the local ρ and T then $\rho_e = \rho$ in equation 15 and $K^{(r)} = K_e^{(r)}$. However, rather more convenient relations arise later if we choose p and T as the thermodynamic variables and specify that $c_{\alpha e}$ shall be the equilibrium composition arising at the local p and T. In that case $\rho_e \neq \rho$ and $K^{(r)}$ is given by equation 15 as it stands. However ρ is known as a function of p, T and the c_α from the equation of state for the mixture and, at the same p and T, we can always eliminate the density ratio in terms of actual and equilibrium concentrations. In either case, $K^{(r)}$ can always be expressed in terms of concentrations alone.

It is noted that the net rate of production of A_α in all the N_m reactions, namely K_α, is given by

$$K_\alpha = \sum_{r=1}^{N_m} K_\alpha^{(r)} . \tag{16}$$

With the aid of equations 10 and 16 we can now rewrite equation 5 in the form

$$\frac{Dc_\alpha}{Dt} = \sum_{r=1}^{N_m} \frac{W_\alpha}{\tau^{(r)}} \left(\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'}\right) \left\{ K^{(r)} \prod_{\alpha=1}^{n} c_\alpha^{\;\nu_\alpha^{(r)'}} - \prod_{\alpha=1}^{n} c_\alpha^{\;\nu_\alpha^{(r)''}} \right\} \tag{17}$$

Suppose now that all the N_m reactions occur extremely rapidly under the conditions prevailing in a given gas flow. Then it is apparent that the local values of c_α will differ but little from the local equilibrium values. For a chemical reaction is a natural process, proceeding always in a direction towards equilibrium, and a rapid reaction rate implies swift corrections of any deviations from local equilibrium in any particular element of gas. Thus $Dc_\alpha/Dt \simeq Dc_{\alpha e}/Dt$ in equation 17 and the term in brackets there is very small in magnitude. $Dc_{\alpha e}/Dt$ is determined by the local ρ and T or p and T values, however, and need not be small. In such cases, therefore, it is apparent that all the $\tau^{(r)}$ must be very small in magnitude. The limiting case in which the $\tau^{(r)}$ are imagined to be zero, so that $c_\alpha = c_{\alpha e}$, is an abstraction which cannot occur in practice, but it may, nevertheless, give results which are sufficiently accurate for many purposes and in any case could form the first step in an iterative process in the right conditions. The case for which all the $\tau^{(r)}$ can be assumed effectively zero (the reactions are all 'infinitely fast') is called chemical equilibrium flow.

At the other extreme, all the $\tau^{(r)}$ may be so large that we may imagine them to be infinite for all practical purposes. Then all the Dc_α/Dt quantities are zero and all the c_α are constant throughout the region. The gas is, effectively, chemically inert and we refer to the flow as chemically frozen flow.

Finally in this section we will deal with the consequences arising from the relation between the thermodynamic variates,

$$T\,ds = dh - \frac{1}{\rho}\,dp - \sum_{\alpha=1}^{n} \mu_\alpha\, dc_\alpha \quad . \tag{18}$$

s is the specific entropy of the mixture and the n quantities μ_α are the chemical potentials of the species in the mixture per unit mass of each particular species. Since the 'd' in equation 18 denotes a general differential of the variables we may particularise it and follow the change in entropy of a particle of fluid as it travels through the region. That is, we can replace d by D/Dt. From equation 3 it immediately follows that

$$T\,\frac{Ds}{Dt} = - \sum_{\alpha=1}^{n} \mu_\alpha \frac{Dc_\alpha}{Dt}$$

But $Dc_\alpha/Dt = K_\alpha/\rho$, from equation 5, and we note that, since $\sum_{\alpha=1}^{n} c_\alpha = 1$ (by definition), $\sum_{\alpha=1}^{n} dc_\alpha = 0$. Thus we can always eliminate one term from the summation and, choosing to eliminate dc_n we can write

$$\rho\,T\,\frac{Ds}{Dt} = - \sum_{\alpha=1}^{n-1} (\mu_\alpha - \mu_n)\, K_\alpha \tag{19}$$

Equation 19 can now be used in place of the energy equation, equation 3.

An alternative form of equation 19 will be found useful and can be deduced as follows. Eliminating μ_n from the right hand side of the equation in favour of the summation from $\alpha=1$ to n for the time being we note that

$$\sum_{\alpha=1}^{n} \mu_\alpha K_\alpha = \sum_{\alpha=1}^{n} \mu_\alpha \sum_{r=1}^{N_m} K_\alpha^{(r)} = \sum_{r=1}^{N_m} \sum_{\alpha=1}^{n} \mu_\alpha K_\alpha^{(r)},$$

by reason of equation 16. Writing this in the form

$$\sum_{r=1}^{N_m} \sum_{\alpha=1}^{n} W_\alpha (\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'}) \mu_\alpha \cdot \frac{K_\alpha^{(r)}}{W_\alpha (\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'})}$$

the last term here is equal to the reaction rate $R^{(r)}$ for the r-th reaction and is therefore independent of the value of α (see equations 7 and 8). Thus we can now write

$$\sum_{\alpha=1}^{n} \mu_\alpha K_\alpha = \sum_{r=1}^{N_m} R^{(r)} \sum_{\alpha=1}^{n} (\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'}) \bar{\mu}_\alpha$$

where $\bar{\mu}_\alpha = W_\alpha \mu_\alpha$, i.e. the chemical potential per mole of A_α. We will only deal with mixtures of perfect gases, so that

$$\mu_\alpha = h_\alpha - Ts_\alpha ,$$

where h_α is the specific enthalpy of species α, a function of T only, and s_α is its specific entropy, a function of T and the partial pressure p_α. At constant T, therefore

$$d\,\mu_\alpha = -T\,ds_\alpha = \frac{RT}{W_\alpha}\, d(\log p_\alpha),$$

by reason of the thermal equation of state for A_α namely, $p_\alpha W_\alpha = \rho c_\alpha RT$. (R is the Universal Gas Constant). Consequently

$$\bar{\mu}_\alpha (p_\alpha , T) = \bar{\mu}_\alpha^{*} + RT \log p_\alpha / p^{*}$$

where p^{*} is some convenient standard pressure and $\bar{\mu}_\alpha^{*}$ is the potential per molecule of A_α at p^{*} and T. We can now write

$$\sum_{\alpha=1}^{n} \mu_\alpha K_\alpha = \sum_{r=1}^{N_m} R^{(r)} \sum_{\alpha=1}^{n} (\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'})(\bar{\mu}_\alpha^{*} + RT \log p_\alpha / p^{*}) \qquad (20)$$

The general requirement for chemical equilibrium is

$$\sum_{\alpha=1}^{n} \left(\nu_\alpha^{(r)\prime\prime} - \nu_\alpha^{(r)\prime} \right) \bar{\mu}_\alpha = 0 \qquad (20a)$$

(see e.g. Guggenheim, 1949), or in terms of the standard values

$$\sum_{\alpha=1}^{n} \left(\nu_\alpha^{(r)\prime\prime} - \nu_\alpha^{(r)\prime} \right) \left(\bar{\mu}_\alpha^{*} - R\,T \log p^{*} \right) = - R\,T \log \prod_{\alpha=1}^{n} p_{\alpha e}^{\nu_\alpha^{(r)\prime\prime} - \nu_\alpha^{(r)\prime}} \qquad (21)$$

for each value of r, where $p_{\alpha e}$ is the equilibrium partial pressure of A_α in the mixture. (Eq. 21 is the Law of Mass Action).

Eliminating the standard values from equation 20 with the aid of equation 21 we have

$$\sum_{\alpha=1}^{n} \mu_\alpha K_\alpha = \sum_{r=1}^{N_m} R^{(r)} \left[R\,T \log \prod_{\alpha=1}^{n} \left({}^{p_\alpha}/_{p_{\alpha e}} \right)^{\nu_\alpha^{(r)\prime\prime} - \nu_\alpha^{(r)\prime}} \right]$$

If we now choose $p_{\alpha e}$ to be the equilibrium partial pressure at the prevailing pressure and temperature we can write

$${}^{p_\alpha}/_{p_{\alpha e}} = {}^{x_\alpha}/_{x_{\alpha e}}$$

where x is the mole fraction, and these may be written in terms of mass fractions. We will not go to these lengths here, but simply note that

$$\frac{Ds}{Dt} = - R \sum_{r=1}^{N_m} \frac{1}{\tau^{(r)}} \left\{ K^{(r)} \prod_{\alpha=1}^{n} c_\alpha^{\nu_\alpha^{(r)\prime}} - \prod_{\alpha=1}^{n} c_\alpha^{\nu_\alpha^{(r)\prime\prime}} \right\} \log \prod_{\alpha=1}^{n} \left({}^{x_\alpha}/_{x_{\alpha e}} \right)^{\nu_\alpha^{(r)\prime\prime} - \nu_\alpha^{(r)\prime}} \qquad (22)$$

It can now readily be seen that when all the $\tau^{(r)} = 0$, $Ds/Dt = 0$ because $x_\alpha = x_{\alpha e}$ and also that $Ds/Dt \to 0$ as all the $\tau^{(r)} \to \infty$†. In the two extreme, limiting cases, therefore, the entropy of a fluid particle remains constant. For intermediate conditions the second law of thermodynamics demands that s shall increase, since, in the absence of transport phenomena, the fluid particle constitutes a closed system.

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† Note, however, that for any given deviation of concentration from the chosen local equilibrium values, the rate of entropy increase is greater for smaller values of $\tau^{(r)}$, vide equation 76 in Section 7. $\tau^{(r)} = 0$ is essentially a singular case.

3. The Symmetrical Diatomic Gas.

As a simple and useful example of the equations derived in the previous section, consider the dissociation reaction in a symmetrical diatomic gas. The atoms are denoted by the chemical formula A_1 and the molecules by A_2. A_2 consists of two A_1 atoms.

Assuming that the dissociation of A_2 into two A_1 atoms follows a proper encounter between an A_2 molecule and some other second body and that recombination follows a simultaneous encounter between two A_1 atoms and some other body we write the chemical equation (eq.6), as

$$A_2 + A_3 \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2\,A_1 + A_3 \,. \tag{23}$$

(Since there is only one reaction we drop the superscript $^{(r)}$). A_3 has been written for the "other" body mentioned above. In the pure gas A_3 will be either A_1 or A_2, but it is convenient to treat it as a separate chemical species in writing the chemical equation. In this way we avoid having to specify k_f and k_r for both an A_1 and an A_2 "other" body reaction. Although k_f and k_r could be calculated (from quantum mechanics) for each type of reaction, it is with the overall effect of both types that we must deal in a gas flow problem.

We note, however, that $c_3 = c_1 + c_2 = 1$. Also $2W_1 = W_2$ and $W_3 = W_2/(1 + c_1)$. Then equation 17 shows that

$$\frac{Dc_1}{Dt} = \frac{W_2}{\tau}\left\{ K(1 - c_1) - c_1^2 \right\} \tag{24}$$

where

$$\tau = W_2^3 \Big/ 4\,k_r\ \rho^2(1 + c_1) \tag{25}$$

and

$$K = (\rho_e/\rho).(c_{1e}^2 \Big/ 1 - c_{1e}), \tag{26}$$

from equations 11 and 15 respectively.

The thermal equation of state for the mixture is

$$p = \rho\,(1 + c_1)\,(R/W_2)T \tag{27}$$

so that choosing c_{1e} to be the equilibrium composition at the local p and T we have $\rho_e/\rho = 1 + c_1/1 + c_{1e}$ and

$$K = (1 + c_1)\, c_{1e}^2 / 1 - c_{1e}^2 \tag{28}$$

The equation for Dc_2/Dt follows immediately from $c_1 + c_2 = 1$.

4. The Mass Conservation Equation

In dealing with the flow of an inert gas for which viscous, heat conduction and mass diffusion effects are negligible, the entropy of a gas particle remains constant. Since the concentrations of the various component gases in the mixture do not change, the state of a gas particle is wholly specified, thermodynamically, by any two thermodynamic variables. In particular we can say that $p = p(\rho, s)$. Then, since s = constant everywhere in the region, $\partial p/\partial x_i = (\partial p/\partial \rho)_s . (\partial \rho/\partial x_i)$ and the pressure gradient terms in equation 2 can be eliminated in favour of $\partial \rho/\partial x_i$. Finally ρ is eliminated between equations 1 and 2. $(\partial p/\partial \rho)_s$ is identified as the speed of sound propagation through the gas.

The situation is not so simple in the case of gas flows in which chemical reactions occur, for s is not constant in general, as we have seen, and the chemical composition may change in a manner which will depend on the nature of the flow. In these circumstances it is slightly more convenient to eliminate the density gradients from equation 1 in favour of pressure gradients. Noting that

$$\rho = \rho\,(p, s, c_1, c_2, \ldots c_{n-1}),$$

(since we can always eliminate one of the c_α from $\sum_{\alpha=1}^{n} c_\alpha = 1$) we have

$$\frac{D\rho}{Dt} = \left(\frac{\partial \rho}{\partial p}\right)_{s,c_\alpha} . \frac{Dp}{Dt} + \left(\frac{\partial \rho}{\partial s}\right)_{p,c_\alpha} . \frac{Ds}{Dt} + \sum_{\alpha=1}^{n-1} \left(\frac{\partial \rho}{\partial c_\alpha}\right)_{p,s,c_\beta} . \frac{Dc_\alpha}{Dt} \tag{29}$$

The suffixes denote which of the variables are held constant. Suffix c_α implies that <u>all</u> the c_α are constant, suffix c_β that <u>all</u> c_α <u>except</u> c_α itself are held constant. The derivative $(\partial p/\partial \rho)_{s,c_\alpha}$ is identified in Section 7 below as the square of the speed of sound under frozen flow conditions. We write

$$\left(\frac{\partial p}{\partial \rho}\right)_{s,c_\alpha} = a_f^2 \tag{30}$$

Also, since

$$\left(\frac{\partial \rho}{\partial c_\alpha}\right)_{p,s,c_\beta} = -\left(\frac{\partial \rho}{\partial s}\right)_{p,c_\alpha}\left(\frac{\partial s}{\partial c_\alpha}\right)_{p,\ \rho,\ c_\beta} \tag{30a}$$

we have, using equations 5 and 19,

$$\frac{D\rho}{Dt} = a_f^{-2}\ \frac{Dp}{Dt} + \left(\frac{\partial \rho}{\partial s}\right)_{p,c_\alpha}\left\{-\frac{1}{\rho T}\sum_{\alpha=1}^{n-1}\left[\mu_\alpha - \mu_n + T\left(\frac{\partial s}{\partial c_\alpha}\right)_{p,\ \rho,c_\beta}\right]K_\alpha\right\} \tag{31}$$

The quantity

$$\sigma_\alpha = -\frac{1}{\rho T}\left(\frac{\partial \rho}{\partial s}\right)_{p,c_\alpha}\left[\mu_\alpha - \mu_n + T\left(\frac{\partial s}{\partial c_\alpha}\right)_{p,\ \rho,c_\beta}\right] \tag{32}$$

is a function of the thermodynamic variables only and does not depend explicitly on the gas flow itself. Thus we can write

$$\frac{D\rho}{Dt} = a_f^{-2}\ \frac{Dp}{Dt} + \sum_{\alpha=1}^{n-1}\sigma_\alpha K_\alpha \tag{33}$$

where the last term does not depend explicitly on the actual flow. Accordingly, we can rewrite the mass conservation requirement, equation 1, in a form more convenient for our present problem, namely

$$\frac{Dp}{Dt} + \rho a_f^2 \cdot \frac{\partial u_i}{\partial x_i} + a_f^2 \sum_{\alpha=1}^{n-1}\sigma_\alpha\ K_\alpha = 0. \tag{34}$$

Equation 32 is not the most convenient form for evaluation of σ_α. The thermodynamic nature of the gas is generally summarised in the thermal and caloric equations of state. Since the component gases of the mixture are generally assumed thermally perfect, the former equation is

$$p = \rho \sum_{\alpha=1}^{n} c_\alpha/W_\alpha \cdot R\,T. \tag{35}$$

and the latter gives, for example

$$h = h(p,\ T,\ c_1,\ c_2,\ \ldots\ c_{n-1}), \tag{36}$$

the form of the function depending on the actual gas mixture. σ_α can be rearranged, with the aid of equation 18, to read

$$\sigma_\alpha = (\ \rho\beta_f/C_{pf})\left(\frac{\partial h}{\partial c_\alpha}\right)_{p,T,c_\beta} + \frac{1}{\rho}\left(\frac{\partial \rho}{\partial\ c_\alpha}\right)_{p,T,c_\beta} \tag{37}$$

where
$$\beta_f = - \frac{1}{\rho^2} \left(\frac{\partial\rho}{\partial T}\right)_{p,c_\alpha} , \tag{38}$$

the volume expansion coefficient with frozen gas composition and
$$C_{pf} = \left(\frac{\partial h}{\partial T}\right)_{p,c_\alpha} , \tag{39}$$

the specific heat at constant pressure with frozen composition. All the derivatives appearing in equations 37 to 39 are readily evaluated from equations 35 and 36. (The derivation of equation 37 from equation 32 is given in the Appendix).

5. The Equilibrium Speed of Sound

We can readily demonstrate that, for a flow which is in complete chemical equilibrium, the speed of sound is given by $(\partial p/\partial\rho)_{s,e}$ [†], suffix s implying constant entropy and suffix e that the chemical composition shall follow its equilibrium value during the differentiation at constant entropy. The equilibrium speed of sound is written as
$$a_e^2 = \left(\frac{\partial p}{\partial\rho}\right)_{s,e} , \tag{40}$$

and the ratio of a_f to a_e can be found as follows.

Since ρ is a function of p, s and the c_α quantities a general increment in ρ is given by
$$d\rho = a_f^{-2}\,dp + \left(\frac{\partial\rho}{\partial s}\right)_{p,c_\alpha} ds + \sum_{\alpha=1}^{n-1} \left(\frac{\partial\rho}{\partial c_\alpha}\right)_{p,s,c_\beta} dc_\alpha ,$$

and by equation 30a this can be rewritten as
$$d\rho = a_f^{-2}\,dp + \left(\frac{\partial\rho}{\partial s}\right)_{p,c_\alpha} ds - \sum_{\alpha=1}^{n-1} \left(\frac{\partial\rho}{\partial s}\right)_{p,c_\alpha} \left(\frac{\partial s}{\partial c_\alpha}\right)_{p,\rho,c_\beta} dc_\alpha .$$

But equation 32 shows that
$$- \left(\frac{\partial\rho}{\partial s}\right)_{p,c_\alpha} \cdot \left(\frac{\partial s}{\partial c_\alpha}\right)_{p,\rho,c_\beta} = \rho\sigma_\alpha + \frac{1}{T}(\mu_\alpha - \mu_n) \left(\frac{\partial\rho}{\partial s}\right)_{p,c_\alpha}$$

so that
$$d\rho = a_f^{-2}\,dp + \rho \sum_{\alpha=1}^{n-1} \sigma_\alpha\, dc_\alpha + \left(\frac{\partial\rho}{\partial s}\right)_{p,c_\alpha} \left\{ ds + \frac{1}{T} \sum_{\alpha=1}^{n-1} (\mu_\alpha - \mu_n)\, dc_\alpha \right\} \tag{41}$$

[†] See Section 7 below

Putting $ds = 0$ will give us $d\rho$ at constant entropy. Now consider the summation in the last term of equation 41; we can write

$$\sum_{\alpha=1}^{n-1} (\mu_\alpha - \mu_n)\, dc_\alpha = \sum_{\alpha=1}^{n} \mu_\alpha\, dc_\alpha = \sum_{\alpha=1}^{n} \bar{\mu}_\alpha \frac{dc_\alpha}{W_\alpha}$$

But dc_α / W_α is the change in the number of moles of A_α in unit mass of mixture, dn_α. The change is brought about by the N_m reactions occurring in the mixture so that $dn_\alpha = \sum_{r=1}^{N_m} dn_\alpha^{(r)}$ where $dn_\alpha^{(r)}$ is the contribution from the r-th reaction. Thus

$$\sum_{\alpha=1}^{n} \mu_\alpha\, dc_\alpha = \sum_{r=1}^{N_m} \sum_{\alpha=1}^{n} (\bar{\mu}_\alpha)\, dn_\alpha^{(r)} \quad .$$

But in each reaction $dn_\alpha^{(r)}$ must be proportional to $\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'}$ so that each term in the summation with respect to r is proportional to $\sum_{\alpha=1}^{n} \bar{\mu}_\alpha \left(\nu_\alpha^{(r)''} - \nu_\alpha^{(r)'} \right)$. If the mixture is in complete chemical equilibrium, each of these terms is zero (see equation 20a), so that in that case $\sum_{\alpha=1}^{n-1} (\mu_\alpha - \mu_n) dc_\alpha$ is also zero.

From 41 therefore

$$\left({}^{a_f}/{a_e}\right)^2 = 1 + \rho a_f^2 \sum_{\alpha=1}^{n-1} \sigma_\alpha \lambda_\alpha \tag{42}$$

where the c_α have their local equilibrium values[†], $c_{\alpha e}$, and

$$\lambda_\alpha = \left(\frac{\partial c_\alpha}{\partial p}\right)_{s,e} = \left(\frac{\partial c_{\alpha e}}{\partial p}\right)_s \tag{43}$$

[†] It should be noted that ρ, a_f and σ_α are all to be evaluated at local equilibrium values of $c_{\alpha e}$. To this extent they will differ in magnitude from ρ, a_f and σ_α in equation 39, which are evaluated at the actual local values of the c_α .

The ratio (a_f/a_e) is only unambiguously defined by equation 42 if the actual state of the gas at which the ratio is evaluated corresponds to an equilibrium state, for then $c_{\alpha e}$ is consistent with all of, say, p, ρ and T. If the gas is not in chemical equilibrium then we are at liberty to choose whether we shall refer to an equilibrium state at the local p and T or at the local ρ and T, for example, and the value of c_{α_e} used in the evaluation of (a_f/a_e) will vary accordingly. In view of the remarks made in previous sections, it seems advisable to choose p and T as the variables from which to determine $c_{\alpha e}$.

The reason for the ambiguity is the impossibility of defining an equilibrium sound speed in a gas which is not at equilibrium, (remembering that the speed of sound is the speed at which small pressure pulses propagate into an undisturbed fluid: by undisturbed we necessarily imply, also, chemical equilibrium).

As with σ_α in equation 32, λ_α in equation 43 is not in the most convenient form for evaluation in a practical case. However

$$\left(\frac{\partial c_{\alpha e}}{\partial p}\right)_s = \left(\frac{\partial c_{\alpha e}}{\partial p}\right)_T + \left(\frac{\partial c_{\alpha e}}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial p}\right)_{s,e} \tag{44}$$

and

$$\left(\frac{\partial T}{\partial p}\right)_{s,e} = \left(\frac{1}{\rho} - \left(\frac{\partial h}{\partial p}\right)_{T,e}\right) \Big/ \left(\frac{\partial h}{\partial T}\right)_{p,e} \quad , \tag{45}$$

so that, knowing the equilibrium composition as a function of p and T and h from equation 36, the derivative can be evaluated. (In passing, it should be noted that there will be N_m equilibrium relations between the $c_{\alpha e}$ terms, one for each reaction. The remaining N_a relations necessary to evaluate a particular $c_{\alpha e}$ are provided by the conservation of atoms requirements for each atomic species).

The derivation of equation 42 relies entirely on the thermodynamics of the gas mixture and is in no way connected with the flow equations. In this sense it differs from the derivation of equation 34 from equation 29, although the results are of a similar style. However, in so far as the term in brackets in equation 41 is always zero for a particle of fluid which follows the motion, it is clear that the speed of sound under equilibrium conditions is an attribute of a particular fluid element, rather than of a particular position and time in the flow field. By the same token this is true also of the frozen sound speed a_f, or indeed of any other sound speed which we care to define. Arguments based on these lines have led Munk (1955) to propose that sound speed should be defined as the ratio of the convective derivatives of p and ρ, and this definition has been employed by Resler (1957) in writing the equations for the flow of a general gas mixture. We shall return to this topic below, where we hope to explain the significance of $(Dp/Dt)/(D\rho/Dt)$.

The dissociation reaction described in Section 3 (equation 23) is a simple example of a reacting gas mixture, the treatment of which is rendered yet more simple if it is assumed to be an ideal dissociating gas in the sense defined by Lighthill (1957). Using the notation of Section 3, the equilibrium composition of the ideal gas is given by

$$\frac{c_{1e}^2}{1-c_{1e}} = \frac{\rho_d}{\rho} e^{-D/R_2T} \qquad (46)$$

where ρ_d is a (constant) characteristic density, D is the energy required to dissociate unit mass of molecules completely and R_2 is written for R/W_2. The enthalpy is

$$h = (4 + c_1) R_2T + c_1D \qquad (47)$$

and equation 35 for the gas mixture is

$$p = \rho (1 + c_1)R_2T. \qquad (48)$$

Using equations 46 to 48 the values of σ_1 and λ_1 can be found. The result for the ratio of the frozen to equilibrium sound speeds in an ideal dissociating gas is

$$\left({}^{a_f}/{}_{a_e}\right)^2 = 1 + c_{1e} \frac{(1 - c_{1e})}{3} \frac{\left[(D'+ 1)(1 + c_{1e}) - (4 + c_{1e})\right]^2}{(D'+ 1)^2 c_{1e} (1 - c_{1e}^2) + 8 + 2c_{1e}} \qquad (49)$$

where D' has been written for D/R_2T. The ratio is shown plotted against T for four values of p in Fig. 1, the gas being an "oxygen-like" ideal dissociating gas, with $\rho_d = 150$ gm/c.c. and $D' = 59,000/T$. Its maximum value is in the region of 1.3 to 1.4 occurring when about three-quarters of the molecules are dissociated under equilibrium conditions.

6. Flow Velocity at a Nozzle Throat

The mass flow rate per unit area, m, in the steady flow through a streamtube is given by

$$m = \rho u, \qquad (50)$$

u being the modulus of the velocity vector. The value of the velocity (u^*) when m has its maximum value can be found by putting $dm/du = 0$. From equation 50 then,

$$u^* = - \rho \frac{du}{d\rho}$$

the derivative being evaluated along the streamtube. Thus

$$u^{*} = -\rho \frac{(du/d\xi)}{(d\rho/d\xi)} ,$$

ξ being the coordinate measured along the streamtube. But the steady flow momentum equation is

$$\rho\, u \,\frac{du}{d\xi} = -\frac{dp}{d\xi}$$

whence

$$u^{*2} = \frac{(dp/d\xi)}{(d\rho/d\xi)} . \tag{51}$$

The significance of the ratio of the convective derivatives of p and ρ is now apparent; it is the square of the flow velocity which would occur at the throat of a Laval nozzle.

From equation 41 it can readily be seen that

$$u^{*2} = a_f^2 \left(1 + \rho\, a_f^2 \sum_{\alpha=1}^{n-1} \sigma_\alpha \left(\frac{dc_\alpha/d\xi}{dp/d\xi}\right) \right)^{-1} \tag{52}$$

Thus, since $\rho\,(dc_\alpha/d\xi) = K_\alpha$ by equation 5, u^{*2} depends on the ratio of the mass rate of production of species to the pressure gradient. In general, this ratio will depend on the shape of the nozzle from the "reservoir" end to the throat, so that u^* in a chemically reacting gas mixture is not solely a function of the reservoir conditions. (The appearance of the ratio $(dc_\alpha/d\xi)/(dp/d\xi$ in u^{*2} explains why u^* cannot be used to define characteristic directions as in Resler's (1957) theory (see Broer, 1958)).

7. Sound Propagation in an Ideal Dissociating Gas

As an example of the use of the equations derived above we consider the propagation of weak disturbances (sound) through an ideal dissociating gas, dealing only with plane waves. In that event, the notation can be simplified somewhat, since there will be only one velocity component, u, and one space coordinate x. There is only one reaction (eq. 23) so that the superscript $^{(r)}$ can be dropped. In Section 3 an atom was designated by a subscript $_1$ and a molecule by subscript $_2$. Since we can always eliminate c_2 in favour of c_1 we may drop the subscript on c_1 and call it, simply, c. However, the subscripts will be retained on W, the molecular weight, in order to avoid possible confusion between atoms and molecules.

The momentum equations (eq. 2) reduce to

$$\rho \frac{\partial u}{\partial t} + \rho u \frac{\partial u}{\partial x} + \frac{\partial p}{\partial x} = 0, \qquad (53)$$

and, by equation 24, the continuity relation for atoms is

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = \frac{W_2}{\tau} \left\{ K (1 - c) - c^2 \right\} \qquad (54)$$

The mass conservation equation (eq. 34) becomes

$$\frac{\partial p}{\partial t} + u \frac{\partial p}{\partial x} + \rho a_f^2 \frac{\partial u}{\partial x} + \rho a_f^2 \sigma \frac{W_2}{\tau} \left\{ K (1 - c) - c^2 \right\} = 0 \qquad (55)$$

and the entropy equation (eq. 22) is now

$$\frac{\partial s}{\partial t} + u \frac{\partial s}{\partial x} = - \frac{R}{\tau} \left\{ K (1 - c) - c^2 \right\} \log \left\{ \frac{c^2}{c_e^2} \cdot \frac{1 - c_e^2}{1 - c^2} \right\} , \qquad (56)$$

since the mole fraction of atoms, $x = 2c/1 + c$ in the present case. c_e is the atom mass fraction under equilibrium conditions at the local p and T.

The characteristic chemical time (eq. 25) is

$$\tau = W_2^3 / 4 k_r \rho^2 (1 + c) \qquad (57)$$

and K is given by (eq. 28),

$$K = (1 + c) c_c^2 / (1 - c_e^2) \qquad (58)$$

We shall consider small disturbances in a gas which is uniformly at pressure p_∞ , density ρ_∞, entropy s_∞ and composition c_∞ before the disturbance arrives. (Note that c_∞ is an equilibrium state). The undisturbed gas is at rest. Writing

$$p = p_\infty + p' \; ; \; \rho = \rho_\infty + \rho' \; ; \; s = s_\infty + s' \; ; \; c = c_e + c' \; ; \; c_e = c_\infty + c_e' , \qquad (59)$$

substituting these relations into the equations above and neglecting squares and products of the disturbance (primed) quantities gives the following results

$$\rho_\infty \frac{\partial u'}{\partial t} + \frac{\partial p'}{\partial x} = 0 , \qquad (60)$$

$$\tau'_\infty \frac{\partial}{\partial t} (c' + c_c') + c' = 0 , \qquad (61)$$

$$\frac{\partial p'}{\partial t} + \rho_\infty a_{f\infty}^2 \frac{\partial u'}{\partial x} \overset{-}{+} \rho_\infty a_{f\infty}^2 \sigma_\infty \frac{c'}{\tau_\infty} = 0 , \qquad (62)$$

where $\tau'_\infty = \cancel{(c_\infty / W_2 (1 - c_\infty)) \tau_\infty}, = \frac{1 - c_\infty^2}{2 c_\infty W_2} . \tau_\infty$

and $\frac{\partial s'}{\partial t} = 0 , \qquad (63)$

to the first order in small quantities. u' is written for the velocity to emphasise that it is a small quantity. A suffix ∞ indicates that the quantity concerned shall have its undisturbed value.

Equation 63 indicates that, to first order the entropy is constant throughout the flow field. Since the equilibrium composition c_e is a function of p and s,

$$dc_e = \left(\frac{\partial c_e}{\partial p}\right)_s dp + \left(\frac{\partial c_e}{\partial s}\right)_p ds ,$$

so that, to first order

$$c'_e = \lambda_\infty p' , \tag{64}$$

where $\lambda_\infty = (\partial c_e / \partial p)_s$ evaluated in the undisturbed fluid, by reason of equation 63. Thus equation 61 can be rewritten

$$\tau'_\infty \frac{\partial c'}{\partial t} + c' + \tau'_\infty \lambda_\infty \frac{\partial p'}{\partial t} = 0 . \tag{65}$$

The pressure disturbance p' and change in composition c' can be eliminated between equation 60, 62 and 65 resulting in

$$\tau'_\infty \frac{\partial}{\partial t} \left[\frac{\partial^2 u'}{\partial t^2} - a^2_{f\infty} \frac{\partial^2 u'}{\partial x^2} \right] + (1 + \rho_\infty a^2_{f\infty} \sigma_\infty \lambda_\infty) \frac{\partial^2 u'}{\partial t^2} - a^2_{f\infty} \frac{\partial^2 u'}{\partial x^2} = 0 \quad (66$$

But from equation 42 in Section 5 we readily identify $1 + \rho_\infty a^2_{f\infty} \sigma_\infty \lambda_\infty$ as $(a_{f\infty}/a_{e\infty})^2$, so that, finally

$$\tau'_\infty \frac{\partial}{\partial t} \left[a^{-2}_{f\infty} \frac{\partial^2 u'}{\partial t^2} - \frac{\partial^2 u'}{\partial x^2} \right] + a^{-2}_{e\infty} \frac{\partial^2 u'}{\partial t^2} - \frac{\partial^2 u'}{\partial x^2} = 0 \tag{67}$$

That a_f and a_e as defined in equations 30 and 40 are in fact the frozen and equilibrium speeds of sound is at once apparent from equation 67. For putting $\tau'_\infty = \infty$ shows that u' propagates at a wave speed $a_{f\infty}$ and putting $\tau'_\infty = 0$ shows that it propagates at speed $a_{e\infty}$.

In practice $0 < \tau'_\infty < \infty$ and the wave motion is more complicated. (In passing we note that $\tau'_\infty \to \infty$ as $c_\infty \to 0$ and $\tau'_\infty \to 0$ as $c_\infty \to 1$. However, in these cases the changes in gas composition become extremely small, even for quite large disturbances, and the distinction between a_f and a_e becomes of no practical significance. In such cases it is sufficient to define a^2 as $(\partial p / \partial \rho)_s$. The reason for $a_f \to a_e$ in the cases quoted is that, in both instances, $\lambda_\infty \to 0$ very rapidly). As a simple example of wave motion in the region of dissociation consider the harmonic motion of a piston about $x = 0$ with a velocity $U \exp(i\omega t)$. If it is assumed that the motion has been initiated at some considerable time previously, transients in the flow field should be negligible and we can write

$$u' = v(x)\, e^{i\omega t}. \tag{68}$$

Substitution in equation 67 shows that v satisfies

$$\frac{d^2 v}{dx^2} + \left(\frac{\omega}{a_{f\infty}}\right)^2 \left(\frac{a^2 + i\omega\,\tau'_\infty}{1 + i\omega\,\tau'_\infty}\right) v = 0\ , \tag{69}$$

whence it is readily seen that an appropriate solution for u' in the circumstances is

$$u' = U \exp\left[i\omega\left(t - \sqrt{\frac{a^2 + i\omega\,\tau'_\infty}{1 + i\omega\,\tau'_\infty}}\ .\ \frac{x}{a_{f_\infty}}\right)\right]\ ; \tag{70}$$

(a is written for the ratio $a_{f\infty}/a_{e\infty}$). The radical term is chosen to have a positive real part. For convenience we can define

$$\sqrt{\frac{a^2 + i\omega\,\tau'_\infty}{1 + i\omega\,\tau'_\infty}} = m\, e^{-i\theta} \tag{71}$$

where

$$m = \left(\frac{a^4 + (\omega\,\tau'_\infty)^2}{1 + (\omega\,\tau'_\infty)^2}\right)^{\frac{1}{4}} \tag{71a}$$

and

$$\theta = \tfrac{1}{2}\tan^{-1}\left[\frac{(a^2 - 1)\,\omega\,\tau'_\infty}{a^2 + (\omega\,\tau'_\infty)^2}\right] \tag{71b}$$

Then the velocity disturbance can be written

$$u' = U \exp\left[-\,\omega\, m\, a_{f\infty}^{-1} \sin\theta\ .\ x\right] \exp\left[i\omega\left(t - m a_{f\infty}^{-1} \cos\theta\ .\ x\right)\right] \tag{72}$$

This represents an harmonic disturbance of frequency ω propagating from left to right at a speed $a_{p\infty}$, where

$$a_{p\infty} = a_{f_\infty} / m \cos\theta \tag{73}$$

and is called the phase velocity. We note that θ has a maximum value of $(a - a^{-1})/4$, when $\omega\tau'_\infty = a$, and since a is not greater than 1.2 (see Fig.1), certainly at pressures in the region of one atmosphere, θ is never very large.

Thus, roughly

$$a_{p\infty} \simeq a_{f\infty}\left(\frac{1 + (\omega\,\tau'_\infty)^2}{a^4 + (\omega\,\tau'_\infty)^2}\right)^{\frac{1}{4}} \tag{74}$$

and it can be seen that $a_{e\infty} \leqslant a_{p\infty} \leqslant a_{f\infty}$ according to whether $0 \leqslant \omega\tau'_\infty \leqslant \infty$. The quantity $\omega\,\tau'_\infty$ is the ratio of the characteristic chemical time to the characteristic disturbance time, so that for given undisturbed conditions (i.e. given $a_{e\infty}$ and $a_{f\infty}$) the phase velocity depends only on this parameter. The dependence of $a_{p\infty}$ on frequency represents the phenomenon of <u>sound dispersion</u>.

From the first exponential factor in equation 72 it can be seen that the amplitude of the disturbance is decaying with increasing distance from the piston. This is the phenomenon of <u>sound absorption</u> due to the chemical reactions occurring in the gas. The amplitude decay factor is $\omega\, m\, a_{f\infty}^{-1} \sin\theta (= \zeta$, say) and, since $\sin\theta \simeq \theta$ we can write

$$\zeta \simeq \frac{1}{2a_{f\infty}} \cdot \left(\frac{a^4 + (\omega\,\tau'_\infty)^2}{1 + (\omega\,\tau'_\infty)^2}\right)^{\frac{1}{4}} \cdot \frac{(a^2 - 1)\,\omega^2\tau'_\infty}{a^2 + (\omega\,\tau'_\infty)^2} \tag{75}$$

For given undisturbed conditions τ'_∞ is known as well as $a_{e\infty}$ and $a_{f\infty}$. Then it can be seen that $\zeta \to 0$ as $\omega \to 0$ whilst

$$\zeta \to \frac{(a^2 - 1)}{2\,a_{f\infty}\tau'_\infty} \tag{76}$$

as $\omega \to \infty$. (N.B. In practice $0 < \tau'_\infty < \infty$). The lower frequencies therefore persist over a greater distance than do the higher values. Contributions to sound absorption and dispersion arise from all transport phenomena (i.e. viscosity, heat conduction and mass diffusion) as well as from relaxation effects in the internal modes of polyatomic molecules. It is frequently the case, however, that absorption and dispersion due to chemical reaction is much greater than the combined effects from the other sources (vide e.g. Hirschfelder et al, 1954).

As is otherwise obvious, equation 75 shows that $\zeta \to 0$ both as $\tau'_\infty \to 0$ and as $\tau'_\infty \to \infty$. The distinction between $\tau'_\infty \to \infty$ and $\omega \to \infty$ should be noted here. In the first case the chemical reaction proceeds so slowly that, irrespective of the nature of the disturbance, the rate of entropy increase of a fluid element is insignificant whilst in the second case the disturbance occurs so rapidly that deviations from the local equilibrium state (and hence the rate of entropy production) become relatively large.

A small disturbance of general shape can be built up by Fourier synthesis (since the system is a linear one) and will contain elements of both high and low frequency. From the foregoing discussion it can be seen that the high frequency parts of the disturbance will run on at the (higher) frozen sound speed $a_{f\infty}$, being followed some while later by the lower frequency elements travelling at the equilibrium sound speed $a_{e\infty}$. The head of the disturbance will be more rapidly attenuated than the parts which follow it and, at some distance x which is large compared with $2 a_{f\infty} \tau'_{\infty} / (a^2 - 1)$ (see equation 76), the bulk of the disturbance will be travelling at a speed approaching $a_{e\infty}$. In particular, if τ'_{∞} is very small, this condition may arise very near to the piston. In the major part of the disturbance field then, the flow is effectively in chemical equilibrium.

However, in all cases except the singular and, practically, not realisable case of $\tau'_{\infty} = 0$ the disturbance front propagates at $a_{f\infty}$ (unless the disturbance is confined to be a Fourier sum of finite frequency extent). The importance of $a_{f\infty}$ in defining the zone of influence of a point in the flow field of a chemically reacting gas is apparent, a point which is emphasised by the work discussed in the Introduction which shows that $a_{f\infty}$ defines the characteristic directions in such a case.

The topic of sound absorption and dispersion is not a new one, having been first treated by Einstein (1920) for the case of the dissociation reaction. Numerous other papers have appeared on the subject, but the interested reader is particularly referred to a recent article by Mazo (1958) which gives a more detailed account rather on the lines of the present simple example.

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APPENDIX

The quantity σ_α is defined in equation 32. In order to make calculation of σ_α from a knowledge of the thermal and caloric equations of state easier we now proceed as follows.

Dealing first with the term in brackets in equation 32, the thermodynamic equation, equation 18, shows that

$$T\left(\frac{\partial s}{\partial c_\alpha}\right)_{p,\rho,c_\beta} = \left(\frac{\partial h}{\partial c_\alpha}\right)_{p,\rho,c_\beta} - (\mu_\alpha - \mu_n)$$

Thus the bracket term is equal to $(\partial h / \partial c_\alpha)_{p,\rho,c_\beta}$.

Since, in general

$$dh = \left(\frac{\partial h}{\partial T}\right)_{p,c_\alpha} dT + \left(\frac{\partial h}{\partial p}\right)_{T,c_\alpha} dp + \sum_{\alpha=1}^{n-1} \left(\frac{\partial h}{\partial c_\alpha}\right)_{p,T,c_\beta} dc_\alpha$$

it can be seen that

$$\left(\frac{\partial h}{\partial c_\alpha}\right)_{p,\rho,c_\beta} = \left(\frac{\partial h}{\partial T}\right)_{p,c_\alpha} \cdot \left(\frac{\partial T}{\partial c_\alpha}\right)_{p,\rho,c_\beta} + \left(\frac{\partial h}{\partial c_\alpha}\right)_{p,T,c_\beta}$$

Since

$$dT = \left(\frac{\partial T}{\partial p}\right)_{\rho,c_\alpha} dp + \left(\frac{\partial T}{\partial \rho}\right)_{p,c_\alpha} d\rho + \sum_{\alpha=1}^{n-1} \left(\frac{\partial T}{\partial c_\alpha}\right)_{p,\rho,c_\alpha} dc_\alpha$$

we have

$$\left(\frac{\partial T}{\partial c_\alpha}\right)_{p,\rho,c_\alpha} = - \left(\frac{\partial T}{\partial \rho}\right)_{p,c_\alpha} \cdot \left(\frac{\partial \rho}{\partial c_\alpha}\right)_{p,T,c_\beta} .$$

Thus finally

$$\left(\frac{\partial h}{\partial c_\alpha}\right)_{p,\rho,c_\beta} = \left(\frac{\partial h}{\partial T}\right)_{p,c_\alpha} \left[-\left(\frac{\partial T}{\partial \rho}\right)_{p,c_\alpha} \cdot \left(\frac{\partial \rho}{\partial c_\alpha}\right)_{p,T,c_\beta}\right] + \left(\frac{\partial h}{\partial c_\alpha}\right)_{p,T,c_\beta} .$$

We now deal with $(\partial \rho / \partial s)_{p,c_\alpha}$. For increments at constant composition, equation 18 shows that

$$T ds = \left(\frac{\partial h}{\partial T}\right)_{p,c_\alpha} dT + \left(\frac{\partial h}{\partial p}\right)_{T,c_\alpha} dp - \frac{1}{\rho} dp.$$

Thus

$$T\left(\frac{\partial s}{\partial \rho}\right)_{p,c_\alpha} = \left(\frac{\partial h}{\partial T}\right)_{p,c_\alpha} \cdot \left(\frac{\partial T}{\partial \rho}\right)_{p,c_\alpha}$$

Introducing the definitions given in equations 38 and 39,

$$\left(\frac{\partial h}{\partial c_\alpha}\right)_{p,\ \rho,c_\beta} = \left(\frac{\partial h}{\partial c_\alpha}\right)_{p,T,c_\beta} + \frac{C_{pf}}{\rho^2 \beta_f} \cdot \left(\frac{\partial \rho}{\partial c_\alpha}\right)_{p,Tc_\beta}$$

and

$$\left(\frac{\partial \rho}{\partial s}\right)_{p,c_\alpha} = - \frac{\rho^2\ T\ \ \beta_f}{C_{pf}} \ .$$

The form of σ_α given in equation 37 follows immediately.

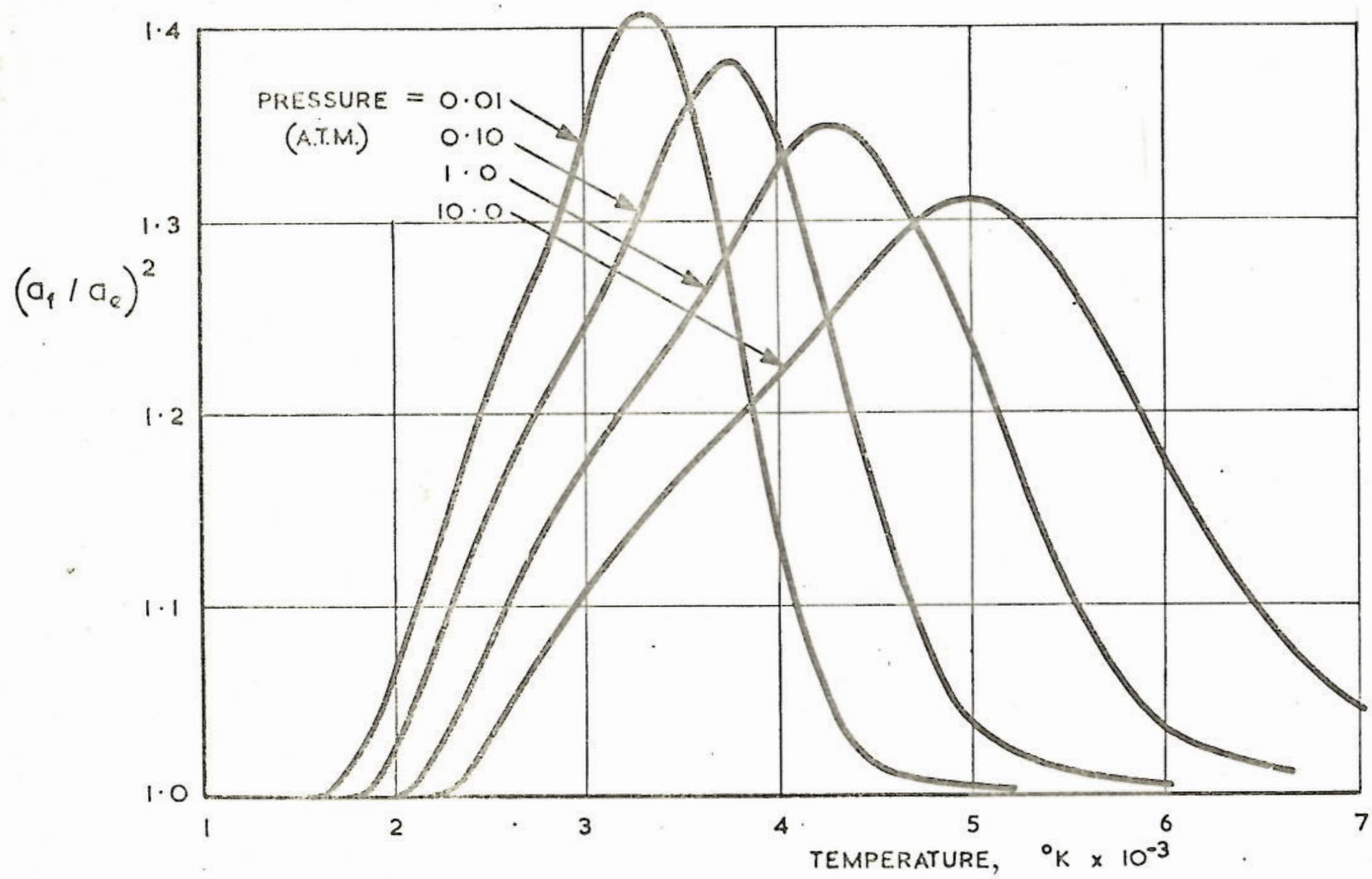

FIG. I. RATIO OF FROZEN TO EQUILIBRIUM SOUND SPEEDS FOR AN 'OXYGEN-LIKE' IDEAL DISSOCIATING GAS.

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THE COLLEGE OF AERONAUTICS

CRANFIELD

The Flow of Chemically Reacting Gas Mixtures

- by -

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CORRIGENDA AND ADDENDA

P.9 Eq. 14 et seq should read

"....
$$K_e^{(r)} = \frac{k_{fe}^{(r)}}{k_{re}^{(r)}} \prod_{\alpha=1}^{n} \left({}^{\rho_e}/_{W_\alpha}\right)^{\nu_\alpha^{(r)\prime} - \nu_\alpha^{(r)\prime\prime}} . \qquad (14)$$

Thus, from equations 12, 13 and 14,

$$K^{(r)} = \prod_{\alpha=1}^{n} \left(\frac{\rho_e\, c_{\alpha e}}{\rho}\right)^{\nu_\alpha^{(r)\prime\prime} - \nu_\alpha^{(r)\prime}} , \qquad (15)$$

provided $k_{fe}^{(r)} \Big/ k_{re}^{(r)} = k_f^{(r)} \Big/ k_r^{(r)}$. The specific reaction rate constants are functions of T only, so that this condition will be satisfied if $c_{\alpha e}$ is evaluated at the actual local temperature T (i.e. if $T_e = T$)."

P.11 Line above eq. 20 should read

"... and μ_α^* is the potential per mole of A_α at p^* and T."

P.21 In eq. 62 read τ'_∞ for τ_∞. The line below eq. 62 should read

"where $\tau'_\infty = \left[(1 - c_\infty^2)/2\, c_\infty\, W_2\right]\tau_\infty$."

Corrigenda and addenda (Contd.)

P.22 Eq. 64 implies that c'_e is evaluated at local pressure and entropy, and not local pressure and temperature as is required by eqs. 60 to 63. In order to employ the simple relation eq. 64 therefore, we must redefine c_e in eqs. 59 to be equilibrium composition at local pressure and entropy. The chemical reaction rate terms are assumed to be proportional to the new c' quantity divided by a new τ'_∞ (which cannot be evaluated a priori). The new value of τ'_∞ can be found for any specific problem, however, because values of c' and c' etc can be found at corresponding points in the flow field and the new τ'_∞ is then the mean value of

$$c' \quad \left[\left({}^{W_2}/_{\tau} \right) \left\{ K(1 - c^2) - c^2 \right\} \right]^{-1}$$

over the region of interest. Except for this re-definition of τ'_∞ the theory and conclusions from eq. 64 onwards are unaffected.