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IN A REACTING GAS MIXTURE NEAR EQUILIBRIUM†

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ABSTRACT

In a reacting gas mixture the frozen sound speed, a_f, is $a_f^2 = \left(\frac{\partial P[\rho, S, y_i]}{\partial \rho}\right)_{S, y_i}$ while the equilibrium sound speed, a_e, is given by $a_e^2 = \left(\frac{\partial P[\rho, S, y_{ie}(\rho, S)]}{\partial \rho}\right)_S$. The expressions for the two sound speeds are not equal, indicating a discontinuity as the reaction rate approaches infinity. In this report the one-dimensional propagation of sound and the significance of the two sound speeds is examined in detail for the case of a gas mixture at or near equilibrium, consisting of gases which obey the ideal gas law and Dalton's law of partial pressures and which have all their degrees of freedom fully excited. The significant results obtained are summarized below:

1) The movement of a pressure perturbation, δP, is characterized by $\frac{1}{a_e^2} \frac{\partial^2(\delta P)}{\partial t_r^2} - \frac{\partial^2(\delta P)}{\partial x_r^2} + \tau^{**} \frac{\partial}{\partial t_r} \left[\frac{1}{a_f^2} \frac{\partial^2(\delta P)}{\partial t_r^2} - \frac{\partial^2(\delta P)}{\partial x_r^2}\right] = 0$, which is used

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to explain the physical meaning of the two sound speeds, a_e and a_f.

2) For an instantaneous reaction, the state and composition variables are shown to be representable as solutions of the characteristic differential equations and as step functions, and the rate of reaction as an impulse function.

3) Explicit expressions are obtained for a_e and a_f in terms of the equilibrium state and composition variables.

NOMENCLATURE

a	speed of sound of nonreacting medium = $\left(\frac{\partial P}{\partial \rho}\right)_S^{\frac{1}{2}}$
a_e	equilibrium speed of sound = $\left(\frac{\partial P \rho, S, y_{ie}(\rho, S)}{\partial \rho}\right)_S^{\frac{1}{2}}$
a_f	frozen speed of sound = $\left(\frac{\partial P[\rho, S, y_i]}{\partial \rho}\right)_{S, y_i}^{\frac{1}{2}}$
A_i	any possible component of the gas mixture
C_i	undetermined coefficient
C_p	constant pressure specific heat of gas mixture, energy per unit mass per temperature degree
C_{pi}	constant pressure specific heat of A
C_v	constant volume specific heat of gas mixture
e	base of natural logarithms = $\sum_{i=1}^{\infty} \frac{1}{i!} \approx 2.72$
H_i	specific enthalpy of A_i, which includes heat of formation
ΔH_r	enthalpy change for reaction
J	mechanical equivalent of heat
k	specific heat ratio
K_c	equilibrium constant in terms of molal concentrations

K_p	equilibrium constant in terms of partial pressures
m	average molecular weight of gas mixture
m_i	molecular weight of component A_i
n	molal density of the gas mixture, total number of mols per unit volume
P	pressure of gas mixture at any point
q	speed of gas stream
R_o	universal gas constant
S	specific entropy of gas mixture
S_{io}	specific entropy of A_i at $\bar{T}$ and $\bar{P}$
S_i	specific entropy of A_i at any T and P
ΔS_r	entropy change for reaction
t	time
t_r	defined as $t_r = t$
T	absolute temperature
w_i	mass rate of production of $A_i = \gamma_i m_i \Gamma$
x	distance coordinate along the direction of flow
x_r	defined as $x_r = x - \bar{q}t$
y_i	mass fraction of A_i in the gas mixture
$y_{ie}(\rho, S)$	mass fraction of A_i under equilibrium conditions
Z	total number of possible constituents in the gas mixture
α_i, β_i	undetermined coefficients
γ_i	stoichiometric coefficient of A_i in reaction
Γ	net rate of reaction defined in Eq. (12)
λ	parameter
Δ	determinant
μ_i	free energy of component A_i, defined as $\mu_i = H_i - TS_i$
$\Delta\mu_R$	free energy change of reaction

ρ	mass density of gas mixture
τ	time of reaction
τ_b	backward rate constant in Eq. (32)
τ_f	forward rate constant in Eq. (32)
τ^*	defined by Eq. (33)
τ^{**}	defined by Eq. (65)
$>$	means greater than
$<$	means less than

Functional and Operational Symbols

$d(\ )$	differential of ( )
$\delta(\ )$	perturbation of ( )
$\frac{\partial(\ )}{\partial[\ ]}$	partial derivative of ( ) with respect to [ ]
$U(\ )$	unit step function defined by $U(\lambda) = 0$ for $\lambda < 0$ and $U(\lambda) = 1$ for $\lambda > 0$
$I(\lambda)$	impulse function defined by $I(\lambda) = 0$ for $\lambda \neq 0$ and $\int_{-\infty}^{\infty} I(\lambda) d\lambda = I$
$<\ >$	function defined by $<\lambda> = \lambda$ for $\lambda > 0$ and $<\lambda> = 0$ for $\lambda \leq 0$
$\int$	integration sign
$\sum$	summation sign
Π	product sign

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i	usually runs from 1 to Z

Superscript

$\bar{\ }$	denotes quantity at equilibrium

INTRODUCTION

Dr. Boa-Teh Chu[1] has pointed out that the expression for the speed of sound in a reacting gas mixture appears to have a discontinuity as the reaction rate approaches infinity. By setting up differential equations for the gas flow, it is possible to show by the method of characteristics that the sound speed, a_f, (commonly known as the frozen speed of sound) is given by

$$a_f^2 = \left(\frac{\partial P[\rho, S, y_i]}{\partial \rho}\right)_{S, y_i} \qquad (1)$$

where P is the total pressure, ρ is the density, S is the specific entropy of the gas mixture, and y_i $(i = 1, 2, 3, \ldots, Z)$ is a composition variable. As indicated, the differentiation is carried out holding the entropy and composition variables constant. This expression is in agreement with that for a nonreacting medium,

$$a_f^2 = \left(\frac{\partial P}{\partial \rho}\right)_S . \qquad (2)$$

It is known, however, that for a gas mixture undergoing a very fast reaction (i. e. , one in which the time of reaction approaches zero) the sound speed, a_e, (known as the equilibrium speed of sound) is given by

$$a_e^2 = \left(\frac{\partial P[\rho, S, y_{ie}(\rho, S)]}{\partial \rho}\right)_S \qquad (3)$$

where $y_{ie}(\rho, S)$ is the equilibrium composition, which depends on ρ and S, and the differentiation is carried out holding only the entropy constant. The two expressions are, in general, not equal and are, in fact, related by

$$a_e^2 = a_f^2 + \sum_{i=1}^{Z} \frac{\partial P}{\partial y_i} \frac{\partial y_{ie}(\rho, S)}{\partial \rho} \qquad (4)$$

where Z is the number of constituents in the mixture. Moreover, since the reaction rate does not appear in the expressions for a_e and a_f, there is no way to obtain one from the other by a limiting process.

In this paper the phenomenon of the two sound speeds is examined in detail for the case of one-dimensional gas flow in which the gas mixture is near chemical equilibrium and in which it is assumed that all the degrees of freedom of each molecule are fully excited. This last condition is closely approximated at high temperatures and high speed gas flow.

A general set of differential equations is obtained for the gas mixture near equilibrium and then the effect of a reaction with a zero and a non-zero reaction time is studied. It is shown that the characteristic surfaces of the differential equations move at speed a_f for all non-zero reaction times, but that the speed of the characteristics changes discontinuously to a_e in the (physically unrealizable) case of a reaction time equaling zero.

A differential equation is then derived for the propagation of a pressure pulse through the gas stream, which clarifies the relationships between a_e, a_f, and the time of reaction. In particular, it is deduced from the above equation that for a small reaction time, a_f represents the speed of the wave front, while a_e represents the velocity of the bulk of the gas behind the wave front, which is in agreement with the results given in reference 1.

The theoretical problem of an instantaneous reaction is discussed and it is shown that this problem can be solved by considering the state and composition variables to be step functions and the reaction rate to be impulse function.

In the course of this work explicit expressions are obtained for a_e and a_f.

GENERAL THERMODYNAMIC REALTIONSHIPS

Suppose Z different gases are moving in one-dimensional flow through an insulated duct of constant cross-section with a velocity q. In general, several reactions can occur between some or all of these gases, the predominant reactions depending on the temperature, pressure, and composition at any instant. Eventually, the gases will reach an equilibrium state and the composition and internal state variables for this equilibrium state can be calculated from thermodynamic considerations and the initial state of the gases. If this equilibrium is disturbed slightly, for example, by a small pressure or temperature change, an overall reaction occurs, which can be written as

$$\sum_{i=1}^{Z} \gamma_i A_i = 0 \tag{5}$$

where A_i is a constituent and γ_i the stoichiometric coefficient of this constituent. The γ_i's can take on any real value, including zero and negative values. If γ_i is positive, the component A_i is called a product; if γ_i is negative, A_i is a reactant; and if γ_i is zero, A_i is a nonreactant or dilutant. Since the reaction is reversible, the distinction between a reactant and a product is arbitrary.

At any temperature and pressure, component A_i possesses internal thermodynamic state properties, H_i, S_i, μ_i, where H_i is specific enthalpy, S_i is specific entropy, and μ_i is specific free energy. These properties are related by

$$\mu_i = H_i - TS_i \tag{6}$$

where T is the absolute temperature. In general, H_i, S_i, and μ_i are functions of temperature and pressure, but for gases obeying the ideal gas law, H_i is a function of temperature only.

At any fixed absolute temperature T and pressure P, the stoichiometric reaction, Eq. (5), possesses enthalpy, entropy, and free energy changes, ΔH_r, ΔS_r, and $\Delta\mu_R$, which are related by

$$\Delta\mu_R = \Delta H_R - T\Delta S_R. \tag{7}$$

The enthalpy change of the reaction is related to the specific enthalpies of the constituents by

$$\Delta H_R = \sum_{i=1}^{z} \gamma_i m_i H_i \tag{8}$$

where m_i is the molecular weight of A_i. Similarly,

$$\Delta\mu_R = \sum_{i=1}^{z} \gamma_i m_i \mu_i \tag{9}$$

and

$$\Delta S_R = \sum_{i=1}^{z} \gamma_i m_i S_i . \tag{10}$$

It is a property of the free energy that under equilibrium conditions,

$$\Delta\overline{\mu}_R = \sum_{i=1}^{z} \gamma_i m_i \overline{\mu}_i = 0 \tag{11a}$$

and so

$$\Delta\overline{H}_R = \overline{T}\Delta\overline{S}_R . \tag{11b}$$

(From this point on, equilibrium quantities are represented by a bar.)

The rate of reaction, Γ, is defined as

$$\Gamma = \frac{1}{\gamma_i} \frac{d(A_i)}{dt} \tag{12}$$

where $\frac{d(A_i)}{dt}$ represents the molal rate of production of A_i. The mass rate of production of a gas A_i is called w_i and is given by

$$w_i = \gamma_i m_i \Gamma . \tag{13}$$

Necessarily,

$$\sum_{i=1}^{z} w_i = 0 \tag{14a}$$

and so

$$\sum_{i=1}^{z} \gamma_i m_i = 0 . \tag{14b}$$

Eqs. (14) merely assert that the stoichiometric Eq. (5) is balanced.

GENERAL DIFFERENTIAL EQUATIONS OF THE SYSTEM

The mass balance in a gas stream for any one of the components is written as

$$\frac{\partial(\rho y_i)}{\partial t} + q \frac{\partial(\rho y_i)}{\partial x} + \rho y_i \frac{\partial q}{\partial x} = w_i \tag{15}$$

where ρ is the mass density of the gas, y_i the mass fraction of A_i in the gas mixture, and q the speed of the gas stream. Summing Eq. (15) from 1 to Z and remembering that $\sum_{i=1}^{z} y_i = 1$, and $\sum_{i=1}^{z} w_i = 0$, gives

$$\frac{\partial \rho}{\partial t} + q\frac{\partial \rho}{\partial x} + \rho\frac{\partial q}{\partial x} = 0. \tag{16}$$

If the product differentiation in Eq. (15) is carried out explicitly and combined with Eqs. (13) and (16), then

$$\frac{\partial y_i}{\partial t} + q\frac{\partial y_i}{\partial x} = \frac{w_i}{\rho} = \frac{\gamma_i m_i \Gamma}{\rho} \quad . \tag{17}$$

A momentum balance gives

$$-\frac{1}{\rho}\frac{\partial P}{\partial x} = \frac{\partial q}{\partial t} + q\frac{\partial q}{\partial x} \tag{18}$$

where P is the pressure of the gas mixture at any point.

The equation of state for the gas mixture, assuming an ideal gas and Dalton's Law, is

$$P = nR_o T = R_o T\rho \sum_{i=1}^{z} \frac{y_i}{m_i} \tag{19}$$

where R_o is the universal gas constant, T is the absolute temperature of the system, and n is the molal density, i. e., the total number of mols of gas per unit volume.

Choosing the equilibrium temperature, $\overline{T}$, and pressure, $\overline{P}$, as reference states at which each component A_i has an entropy per unit mass of S_{io}, the entropy per unit mass of gas mixture at any temperature and pressure close to $\overline{T}$ and $\overline{P}$ is given by

$$S = \sum_{i=1}^{z} y_i \left(S_{io} + \overline{C}_{pi} \ln \frac{T}{\overline{T}} - \frac{R_o}{m_i} \ln \frac{P}{\overline{P}} \frac{\frac{y_i}{m_i}}{\sum_{i=1}^{z} \frac{y_i}{m_i}} \right) \tag{20}$$

assuming again the ideal gas and Dalton's Law.

The term $\dfrac{P\,\dfrac{y_i}{m_i}}{\sum_{i=1}^{z} \dfrac{y_i}{m_i}}$ represents the partial pressure of A_i in the mixture.

$\bar{C}_{pi}$, the constant pressure specific heat of A_i at equilibrium, is, in general, only a weak function of pressure and temperature and for a small pressure-temperature range can be taken as constant.

An energy balance yields

$$\frac{\partial S}{\partial t} + q\frac{\partial S}{\partial x} = -\frac{1}{\rho T}\sum_{i=1}^{z} \mu_i w_i \qquad (21)$$

Eqs. (16)-(21) are regarded as six partial differential equations with seven unknown dependent variables y_i, S_{io}, P, q, T, S, and Γ and two independent variables x and t. μ_i is considered to be a known function of temperature and pressure and w_i is given by Eq. (13). In order to obtain independent solutions for each of the seven dependent variables, another equation is needed. This other equation is the relationship between Γ, ρ, T, and y_i, which is given below.

LINEARIZATION AND SIMPLIFICATION OF THE DIFFERENTIAL EQUATION

The differential equations of the system are highly nonlinear but if attention is confined to a section of the stream in which the gas mixture is very close to or at equilibrium, and if all disturbances within this section are of small amplitude, the equations can be linearized by the method of perturbations. Using this method,

$$P(x,t) = \bar{P} + \delta P(x,t) \qquad y_i(x,t) = \bar{y}_i + \delta y_i(x,t)$$

$$\rho(x,t) = \bar{\rho} + \delta\rho(x,t) \qquad T(x,t) = \bar{T} + \delta T(x,t)$$

$$q(x,t) = \bar{q} + \delta q(x,t) \qquad S(x,t) = \bar{S} + \delta S(x,t)$$

and $$\mu_i(T,P) = \bar{\mu}_i + \delta\mu_i(T,P) \; .$$

The barred quantities are constants and represent the values at thermodynamic equilibrium. The $\delta(\;)$ terms are perturbations and are considered to be of a much smaller order than the equilibrium quantities. Note that by the definitions of w_i and Γ, $\bar{w}_i$ and $\bar{\Gamma}$ are both zero.

The expressions above are now introduced into Eqs. (16)-(21). Perturbation terms are neglected in comparison with equilibrium terms, and the following relationships are used for simplification:

$$w_i = \gamma_i m_i \Gamma \tag{22}$$

$$\bar{n} = \bar{\rho} \sum_{i=1}^{z} \frac{\bar{y}_i}{m_i} \tag{23}$$

$$\bar{C}_P = \sum_{i=1}^{z} \bar{C}_{pi} \bar{y}_i \tag{24}$$

$$\bar{m} = \frac{\bar{\rho}}{\bar{n}} = \frac{1}{\sum\limits_{i=1}^{z} \frac{y_i}{m_i}} \tag{25}$$

$$\sum_{i=1}^{z} \nu_i m_i \bar{\mu}_i = 0 \tag{26}$$

$$\bar{P} = \bar{n} R_o \bar{T} \tag{27}$$

$$\bar{S}_i = S_{io} - \frac{R_o}{m_i} \ln \frac{\frac{\bar{y}_i}{m_i}}{\sum\limits_{i=1}^{z} \frac{\bar{y}_i}{m_i}} = S_{io} - \frac{R_o}{m_i} \ln \frac{\bar{\rho}\bar{y}_i}{\bar{n} m_i} = S_{io} - \frac{R_o}{m_i} \ln \frac{\bar{m}\bar{y}_i}{m_i} \tag{28}$$

where $\bar{n}$ is the molal density at equilibrium, $\bar{C}_p$ the constant pressure specific heat for the gas mixture at equilibrium, $\bar{m}$ the average molecular weight of the gas mixture at equilibrium, and $\bar{S}_i$ the specific entropy of A_i in the gas mixture at equilibrium.

The linearized equations become

$$\frac{\partial(\delta\rho)}{\partial t} + \bar{q}\,\frac{\partial(\delta\rho)}{\partial x} + \bar{\rho}\,\frac{\partial(\delta q)}{\partial x} = 0 \tag{29a}$$

$$\frac{\partial(\delta y_i)}{\partial t} + \bar{q}\,\frac{\partial(\delta y_i)}{\partial x} = \frac{\gamma_i m_i}{\bar{\rho}}\,\Gamma \tag{29b}$$

$$\frac{\partial(\delta q)}{\partial t} + \bar{q}\,\frac{\partial(\delta q)}{\partial x} + \frac{1}{\bar{\rho}}\,\frac{\partial(\delta P)}{\partial x} = 0 \tag{29c}$$

$$\frac{\delta P}{\bar{P}} = \frac{\delta\rho}{\bar{\rho}} + \frac{\delta T}{\bar{T}} + \bar{m}\sum_{i=1}^{z}\frac{\delta y_i}{m_i} \tag{29d}$$

$$\delta S = \sum_{i=1}^{z}\bar{S}_i\,\delta y_i + \frac{\bar{C}_P}{\bar{T}}\,\delta T - \frac{1}{\bar{\rho}\bar{T}}\,\delta P \tag{29e}$$

$$\frac{\partial(\delta S)}{\partial t} + \bar{q}\,\frac{\partial(\delta S)}{\partial x} = -\,\frac{\sum_{i=1}^{z}\left[\gamma_i m_i(\delta\mu_i)\right]}{\bar{\rho}\,\bar{T}}\,\Gamma \tag{29f}$$

Γ is of the order of the derivative of a perturbation by (29b). Then, since the expression on the left of (29f) contains derivatives of δ, while the expression on the right contains the product of Γ and perturbation terms, the expression on the right is of a higher order and can be neglected, giving

$$\frac{\partial(\delta S)}{\partial t} + \bar{q}\frac{\partial(\delta S)}{\partial x} = 0 \qquad (29g)$$

The above equations can now be simplified somewhat by changing to x_r, t_r coordinates where

$$x_r = x - \bar{q}t \qquad (30a)$$

$$t_r = t \qquad (30b)$$

Physically, x_r represents the coordinate of a pulse relative to a fixed particle in the fluid.

Eqs. (29) now become

$$\frac{\partial(\delta\rho)}{\partial t_r} + \bar{\rho}\frac{\partial(\delta q)}{\partial x_r} = 0 \qquad (31a)$$

$$\frac{\partial(\delta y_i)}{\partial t_r} = \frac{\gamma_i m_i}{\bar{\sigma}}\Gamma \qquad (31b)$$

$$\frac{\partial(\delta q)}{\partial t_r} + \frac{1}{\bar{\rho}}\frac{\partial(\delta P)}{\partial x_r} = 0 \qquad (31c)$$

$$\frac{\delta P}{\bar{P}} = \frac{\delta\rho}{\bar{\rho}} + \frac{\delta T}{\bar{T}} + \bar{m}\sum_{i=1}^{z}\frac{\delta y_i}{m_i} \qquad (31d)$$

$$\delta S = \sum_{i=1}^{z}\bar{S}_i\delta y_i + \frac{\bar{C}_P}{\bar{T}}\delta T - \frac{1}{\bar{\rho}\bar{T}}\delta P \qquad (31e)$$

$$\frac{\partial(\delta S)}{\partial t_r} = 0 \qquad (31f)$$

The derivative with respect to t_r is actually a "substantial" time derivative and represents differentiation with respect to a fixed particle in the fluid.

Combining (31e), (31f), and using $\overline{\Delta H}_R = \overline{T}\,\overline{\Delta S}_R$, gives

$$\frac{\partial(\delta T)}{\partial t_r} = \frac{1}{\overline{\rho}\,\overline{C}_p}\,\frac{\partial(\delta P)}{\partial t_r} - \frac{\overline{\Delta H}_R}{\overline{\rho}\,\overline{C}_p}\,\Gamma \qquad (31g)$$

EXPRESSION FOR THE NET RATE OF REACTION

For a reversible gas reaction, a rate equation of the following type can be postualted:

$$\Gamma = \frac{1}{\tau_f(T)} \prod_{i=1}^{z} \left(\frac{\rho y_i}{m_i}\right)^{<-\gamma_i>} - \frac{1}{\tau_b(T)} \prod_{i=1}^{z} \left(\frac{\rho y_i}{m_i}\right)^{<\gamma_i>} \qquad (32)$$

where

$$<\lambda> = \begin{cases} 0 & \lambda < 0 \\ \lambda & \lambda \geq 0 \end{cases}$$

$\tau_f(T)$ and $\tau_b(T)$ are forward and backward rate constants, respectively, and as indicated, they are functions of temperature. The first product term contains the product of the molal concentrations of the reactants raised to the power of their stoichiometric coefficients and the second term contains the products of the reaction.

At equilibrium, $\overline{\Gamma} = 0$, and so

$$\frac{1}{\overline{\tau}_f(\overline{T})} \prod_{i=1}^{z} \left(\frac{\overline{\rho}\,\overline{y}_i}{m_i}\right)^{<-\gamma_i>} = \frac{1}{\overline{\tau}_b(\overline{T})} \prod_{i=1}^{z} \left(\frac{\overline{\rho}\,\overline{y}_i}{m_i}\right)^{<\gamma_i>} \equiv \frac{1}{\tau^*} \qquad (33)$$

and

$$\frac{\overline{\tau}_b(\overline{T})}{\overline{\tau}_f(\overline{T})} = \prod_{i=1}^{z} \left(\frac{\overline{\rho}\,\overline{y}_i}{m_i}\right)^{\gamma_i} = \overline{K}_c(\overline{T}) \qquad (34)$$

$K_c(T)$ is the equilibrium constant of the reaction in terms of molal concentrations.

By differentiating Eq. (32), considering perturbation terms to be differentials, and combining with Eqs. (33) and (34), gives

$$\Gamma = \frac{1}{\tau^*}\left[\frac{d\,\overline{\ln K}_c}{dT}\,\delta T - \frac{\sum_{i=1}^{z} \gamma_i}{\overline{\rho}}\,\delta\rho - \sum_{i=1}^{z} \frac{\gamma_i}{\overline{y}_i}\,\delta y_i\right] \tag{35}$$

$(\delta\Gamma = \Gamma$ since $\overline{\Gamma} = 0)$.

τ^*, which was defined by Eq. (33), contains the units of time and must be related to the time of reaction. For a "very fast" reaction, $\tau^* \to 0$. If it is now assumed that the composition of the gas is a continuously differentiable function of time, even if $\tau^* \to 0$, Eq. (31b) indicates that Γ must remain finite as $\tau^* \to 0$. This would then imply that

$$\frac{d\ln K_c}{dT}\,\delta T - \frac{\sum_{i=1}^{z} \gamma_i}{\rho}\,\delta\rho - \sum_{i=1}^{z} \frac{\gamma_i}{y_i}\,\delta y_i = 0 \tag{36}$$

for a "very fast" reaction; but this is equivalent to

$$\delta\left[\ln \frac{K_c(T)}{\prod_{1}^{z} \left(\frac{\rho y_i}{m_i}\right)^{\gamma_i}}\right] = 0 \quad \text{or} \quad \frac{K_c(T)}{\prod_{1}^{z} \left(\frac{\rho y_i}{m_i}\right)^{\gamma_i}} = \text{constant.} \tag{37}$$

The constant can be evaluated from the situation at equilibrium, Eq. (34), and it is seen that the constant must equal one, and so

$$\prod_{i=1}^{z} \left(\frac{\rho y_i}{m_i}\right)^{\gamma_i} = K_c(T) \tag{38}$$

Therefore, in a "very fast" reaction, the composition of the gas mixture obeys the equilibrium equation at every instant.

Eq. s (31a), (31b), (31c), (31d), (31g), and (35) can now be combined to eliminate δT, $\delta \rho$, and δy_i, which gives three first order linear partial differential equations in three unknowns.

These equations are

$$\frac{\left(\frac{d\overline{\ln K}_c}{dT}\right)}{\bar{\rho}\,\bar{C}_p}\frac{\partial(\delta P)}{\partial t_r} - \tau^{*}\frac{\partial \Gamma}{\partial t_r} + \sum_{i=1}^{z} \gamma_i \frac{\partial(\delta q)}{\partial x_r} =$$

$$\left(\frac{\bar{C}_p \sum_{i=1}^{z} \frac{\gamma_i^2 m_i}{\bar{y}_i} + \frac{d\overline{\ln K}_c}{dT}\,\overline{\Delta H}_R}{\bar{\rho}\,\bar{C}_p}\right)\Gamma \qquad (39a)$$

$$\left(\frac{\bar{\rho}\,\bar{C}_p\bar{T} - \bar{P}}{\bar{\rho}\,\bar{C}_p\bar{P}\,\bar{T}}\right)\frac{\partial(\delta P)}{\partial t_r} + \frac{\partial(\delta q)}{\partial x_r} = \left(\frac{\bar{m}\,\bar{C}_p \sum_{I}^{z} \gamma_i - \frac{\overline{\Delta H}_R}{\bar{T}}}{\bar{\rho}\,\bar{C}_p}\right)\Gamma \qquad (39b)$$

$$\frac{1}{\bar{\rho}}\frac{\partial(\delta P)}{\partial x_r} + \frac{\partial(\delta q)}{\partial t_r} = 0\ . \qquad (39c)$$

EXPLICIT EXPRESSIONS FOR a_e and a_f

At this point it will be advantageous to determine explicitly the two sound speeds a_f and a_e.

Rewriting Eqs. (31d) and (31e) in differential, rather than perturbation notation.

$$\frac{dP}{\bar{P}} = \frac{d\rho}{\rho} + \frac{dT}{\bar{T}} + \bar{m}\sum_{1}^{z} \frac{dy_i}{m_i} \tag{40a}$$

$$dS = \sum_{1}^{z} \bar{S}_i dy_i + \frac{\bar{C}_p}{\bar{T}}\, dT - \frac{1}{\bar{\rho}\,\bar{T}}\, dP \tag{40b}$$

Letting $dS = dy_i = 0$, and then eliminating dT between Eqs. (40a) and (40b) gives

$$a_f^2 = \left.\frac{dP}{d\rho}\right]_{\substack{dS = 0 \\ dy_i = 0}} = \left(\frac{\partial P}{\partial \rho}\right)_{S, y_i} = \frac{\bar{P}\,\bar{C}_\rho\,\bar{T}}{\bar{\rho}\,\bar{C}\,\bar{T} - \bar{P}} \tag{41}$$

For gases obeying the ideal gas law, $C_p - C_v = \frac{R_o}{\bar{m}}$, where C_v is the constant volume specific heat. Defining $k \equiv \frac{C_p}{C_v}$ and $\bar{P} = \frac{\bar{\rho} R_o \bar{T}}{\bar{m}}$, Eq. (41) can be put in the form,

$$a_f^2 = \bar{k}\,\frac{R_o}{\bar{\bar{m}}}\,\bar{T} \tag{42}$$

which corresponds in form to the expression for the speed of sound of a nonreacting gas. However, the molecular weight of a nonreacting gas remains constant, whereas for a reacting gas, it is a variable.

The equilibrium speed of sound can be calculated from Eqs. (31b) and (36), which are rewritten below in differential notation, and Eqs. (40a) and (40b)

$$\frac{\partial(\delta y_i)}{\partial t_r} = \frac{\gamma_i m_i}{\bar{\rho}}\, d\Gamma \tag{43a}$$

$$\frac{\sum_{1}^{z} \gamma_i}{\bar{\rho}}\, d\rho + \sum_{1}^{z} \frac{\gamma_i dy_i}{\bar{y}_i} = \left(\frac{d\,\overline{\ln K_c}}{dT}\right) dT \tag{43b}$$

Setting dS = 0, there is obtained by the straightforward combination of Eqs. (40a), (40b), (43a), and (43b).

$$a_e^2 = \frac{\dfrac{\overline{C}_p\overline{T}}{\overline{\rho}}\displaystyle\sum_1^z \frac{\gamma_i^2 m_i}{\overline{y}_i} + \frac{\overline{\Delta H}_R}{\overline{\rho}}\sum_1^z \gamma_i + \left(\frac{d\overline{\ln K}_c}{dT}\right)\frac{\overline{T}\,\overline{\Delta H}_R}{\overline{\rho}} - \dfrac{\overline{C}_p\overline{T}\left(\displaystyle\sum_1^z \gamma_i\right)^2}{\overline{n}}}{\left(\dfrac{\overline{\rho}\,\overline{C}_p\overline{T}-\overline{P}}{\overline{\rho}\,\overline{P}}\right)\displaystyle\sum_1^z \frac{\gamma_i^2 m_i}{\overline{y}_i} + \frac{\overline{T}\,\overline{\Delta H}_R}{\overline{P}}\left(\frac{d\overline{\ln K}_c}{dT}\right) - \dfrac{\overline{T}\displaystyle\sum_1^z \gamma_i}{\overline{n}}\left(\frac{d\overline{\ln K}_c}{dT}\right)} \tag{44}$$

The equilibrium constant for the reaction in terms of partial pressures, K_p, is given by

$$K_p(T) = \prod_{i=1}^{z}\left(\frac{\rho y_i R_o T}{m_i}\right)^{\gamma_i} \tag{45}$$

The term $\frac{\rho y_i R_o T}{m_i}$ is the expression for the partial pressure of a perfect gas in a gas mixture.

$K_c(T)$ and $K_p(T)$ are thus related by

$$K_c = (R_o T)^{-\sum_1^z \gamma_i}\ K_p \tag{46}$$

and

$$\frac{d\ln K_c}{dT} = \frac{d\ln K_p}{dT} - \frac{\sum_1^z \gamma_i}{\overline{T}} \tag{47}$$

The van't Hoff Equation^2 states that

$$\frac{d\ln K_p}{dT} = \frac{\Delta H_R}{R_o T} \ . \tag{48}$$

$$\frac{d\ln K_c}{dT} = \frac{\Delta H_R}{R_o T^2} - \frac{\sum_1^z \gamma_i}{T} \tag{49}$$

Putting this expression into Eq. (44) and then simplifying, the equation for a_e can be put in the form

$$a_e^2 = \frac{\dfrac{\overline{C}_p \overline{R}_o \overline{T}^2}{\overline{m}} \sum_{i=1}^{z} \dfrac{\gamma_i^2 m_i}{\overline{y}_i} + \dfrac{\overline{\Delta H}_R{}^2}{\overline{m}} - \overline{C}_p R_o \overline{T}^2 \left(\sum_{i=1}^{z} \gamma_i\right)^2}{\overline{T} \sum_{i=1}^{z} \dfrac{\gamma_i^2 m_i}{\overline{y}_i} \left(\overline{C}_p - \dfrac{R_o}{\overline{m}}\right) + \dfrac{\overline{\Delta H}_R{}^2}{R_o \overline{T}} - 2\, \overline{\Delta H}_R \sum_1^z \gamma_i + R_o \overline{T} \left(\sum_1^z \gamma_i\right)^2} \tag{50}$$

In practice, the terms containing $\sum_1^z \gamma_i$ are negligible and

$$\frac{\overline{C}_p R_o \overline{T}^2}{\overline{m}} \sum_1^z \frac{\gamma_i^2 m_i}{\overline{y}_i} > \frac{\overline{\Delta H}_R^2}{\overline{m}} \tag{51}$$

$$\overline{T} \left(\overline{C}_p - \frac{R_o}{\overline{m}}\right) \sum_1^z \frac{\gamma_i^2 m_i}{\overline{y}_i} > \frac{\overline{\Delta H}_R{}^2}{R_o \overline{T}} \tag{52}$$

If these inequalities are very large so that the terms containing $\overline{\Delta H}_R^2$ are also negligible in comparison with the $\sum_1^z \frac{\gamma_i^2 m_i}{\overline{y}_i}$ terms, Eq. (50) becomes

$$a_e^2 = \overline{k} \frac{R_o}{\overline{m}} \overline{T} = a_f^2 . \tag{53}$$

The ratio of the $\overline{\Delta H}_R{}^2$ term to the $\sum_1^z \frac{\gamma_i^2 m_i}{\overline{y}_i}$ term in the numerator of Eq. (50)

is $\frac{1}{\bar{C}_p} \frac{\overline{\Delta H}_R^2}{R_o \bar{T}^2 \sum^{z} \frac{\gamma_i^2 m_i}{\bar{y}_i}}$. The ratio in the denominator is $\frac{1}{\bar{C}_p - \frac{R_o}{\bar{m}}} \frac{\overline{\Delta H}_R^2}{R_o \bar{T}^2 \sum_{1}^{z} \frac{\gamma_i^2 m_i}{\bar{y}_i}}$.

Since, clearly $\bar{C}_p > \bar{C}_p - \frac{R_o}{\bar{m}} = \bar{C}_v$, the numerator ratio is less than the denominator ratio and so $a_e < a_f$.

CHARACTERISTICS OF THE GENERAL SET OF DIFFERENTIAL EQUATIONS

Having determined explicitly the expressions for a_f and a_e, the characteristics of the set of Eq. (39) is now calculated.

Suppose δP, Γ, and δq are prescribed on a curve given parametrically by $x_r = x_r(\lambda)$ and $t_r = t_r(\lambda)$. On this curve, $\delta P = \delta P(\lambda)$, $\Gamma = \Gamma(\lambda)$, $\delta q = \delta q(\lambda)$. Then, by the chain rule,

$$\frac{dt_r}{d\lambda} \frac{\partial(\delta P)}{\partial t_r} + \frac{dx_r}{d\lambda} \frac{\partial(\delta P)}{\partial x_r} = \frac{d(\delta P)}{d\lambda} \tag{54a}$$

$$\frac{dt_r}{d\lambda} \frac{\partial \Gamma}{\partial t_r} + \frac{dx_r}{d\lambda} \frac{\partial \Gamma}{\partial x_r} = \frac{d\Gamma}{d\lambda} \tag{54b}$$

$$\frac{dt_r}{d\lambda} \frac{\partial(\delta q)}{\partial t_r} + \frac{dx_r}{d\lambda} \frac{\partial(\delta q)}{\partial x_r} = \frac{d(\delta q)}{d\lambda} \tag{54c}$$

Treating Eqs. (39) and (54) as a system of six linear equations in six unknowns, $\frac{\partial(\delta P)}{\partial t_r}$, $\frac{\partial(\delta P)}{\partial x_r}$, $\frac{\partial \Gamma}{\partial t_r}$, $\frac{\partial \Gamma}{\partial x_r}$, $\frac{\partial(\delta q)}{\partial t_r}$, and $\frac{\partial(\delta q)}{\partial x_r}$, the characteristic surfaces of these equations can be found by setting the determinant of the system, Δ, equal to zero. Upon expanding, the determinant is found to be

$$\Delta = -\frac{\tau^*}{\bar{\rho}} \left[\left(\frac{dx_r}{d\lambda}\right)\left(\frac{dt_r}{d\lambda}\right)^2 - \left(\frac{\bar{\rho}\, \bar{C}_p \bar{T} - \bar{P}}{\bar{P}\, \bar{C}_p \bar{T}}\right)\left(\frac{dx_r}{d\lambda}\right)^3 \right]. \tag{55}$$

Setting $\Delta = 0$, it is seen that if $\tau^* \neq 0$, characteristics occur when

$$\text{a)} \quad \frac{dx_r}{dt_r} = \frac{dx_r/d\lambda}{dt_r/d\lambda} = 0, \qquad \text{i.e., when}$$

$$x_r = x - \overline{q}t \qquad \text{is a constant}$$

and

$$\text{b)} \quad \left(\frac{dx_r}{dt_r}\right)^2 = \frac{\overline{P}\,\overline{C}_p\,\overline{T}}{\overline{\rho}\,\overline{C}_p\overline{T}-\overline{P}} = a_f^2, \qquad \text{i.e., when}$$

$$x - (\overline{q} \pm a_f)t \qquad \text{is a constant.}$$

Since the characteristic surfaces propagate at the same speed as the wave front, condition (b) implies that the wave front moves at speed a_f if $\tau^* \neq 0$.

The compatibility equation for $\frac{\partial(\delta P)}{\partial t_r}$ is

$$\Delta \frac{\partial(\delta P)}{\partial t_r} = -\tau^* \left[\left(\frac{dx_r}{d\lambda}\right)^3 \left(\frac{\overline{\Delta H}_R - \overline{m}\,\overline{C}_p\overline{T}\sum_1^z \gamma_i}{\overline{\rho}\,\overline{C}_p\overline{T}}\right)\Gamma + \frac{1}{\overline{\rho}}\left(\frac{dt_r}{d\lambda}\right)\left(\frac{dx_r}{d\lambda}\right)\left(\frac{d(\delta P)}{d\lambda}\right) + \left(\frac{dx_r}{d\lambda}\right)^2 \frac{d(\delta q)}{d\lambda}\right]. \tag{56}$$

Compatibility always exists at $\frac{dx_r}{dt_r} = 0$. For compatibility at

$$\frac{dx_r}{dt_r} = \pm a_f = \pm\sqrt{\frac{\overline{P}\,\overline{C}_p\overline{T}}{\overline{\rho}\,\overline{C}_p\overline{T}-\overline{P}}},$$

$$a_f^2 \left(\frac{\overline{\Delta H}_R - \overline{m}\,\overline{C}_p\overline{T}\sum_1^z \gamma_i}{\overline{\rho}\,\overline{C}_p\overline{T}}\right)\Gamma + \frac{1}{\overline{\rho}}\frac{d(\delta P)}{dt_r} \pm a_f\frac{d(\delta q)}{dt_r} = 0. \tag{57}$$

Using Eq. (31b), i.e., $\frac{\partial(\delta y_i)}{\partial t_r} = \frac{\gamma_i m_i}{\bar{\rho}} \Gamma$, gives

$$\left(\frac{\overline{\Delta H}_R - \bar{m}\, \bar{C}_p \bar{T} \sum_1^z \gamma_i}{\bar{\rho}\, \bar{C}_p \bar{T}} \right) \frac{a_f^2 \bar{\rho}}{\gamma_i m_i} \frac{d(\delta y_i)}{dt_r} + \frac{1}{\bar{\rho}} \frac{d(\delta P)}{dt_r} \pm a_f \frac{d(\delta q)}{dt_r} = 0. \qquad (58)$$

Multiplying Eq. (58) by $\bar{\rho}\, dt_r$ and integrating, the compatibility equation becomes

$$\bar{\rho}\, a_f^2 \left(\frac{\overline{\Delta H}_R - \bar{m} \bar{C}_p \bar{T} \sum_1^z \gamma_i}{\bar{C}_p \bar{T}} \right) \frac{\delta y_i}{\gamma_i m_i} + \delta P + a_f \bar{\rho}\, \delta q = \text{constant}. \qquad (59)$$

If $\tau^* = 0$, it is seen that both the determinant and the compatibility equation are identically equal to zero and so the wave front does not necessarily move at the speed a_f. Examination of the system of Eqs. (39) shows that the highest derivative of Γ is the first derivative if $\tau^* \neq 0$. However, if τ^* is equal to zero, the first derivative term drops out and the highest derivative of Γ becomes the "zeroth" derivative. Thus, if τ^* is equal to zero, the form of the system of equations is changed which can, and in this case, does produce a discontinuous change in the characteristics.

The characteristics for the case of a "very fast" reaction can be found by setting τ^* equal to zero in Eq. (39a) eliminating Γ between Eq. (39a) and (39b) and then following a procedure similar to the above. It is found that in the equilibrium case, the characteristic surfaces, or the wave front, propagate at a speed a_e.

Since it is physically impossible for τ^* to ever actually be zero, these results imply that the wave front must always propagate at a speed a_f. However, the question of the physical significance of a_e in near equilibrium flow (τ^* very small) is still unresolved.

DERIVATION OF GENERALIZED ACOUSTIC EQUATION

Clarification of the roles played by a_f and a_e can be obtained by reducing Eq. (39) to a single higher order equation and attempting to find solutions for this equation. The reduction is accomplished in the following way:

Solve for Γ in Eq. (39b) to obtain

$$\Gamma = \left(\frac{\bar{\rho}\,\bar{C}_p\bar{T}-\bar{P}}{\bar{m}\,\bar{C}_p\bar{P}\,\bar{T}\sum_{1}^{z}\gamma_i-\overline{\bar{P}\Delta H_R}}\right)\frac{\partial(\delta P)}{\partial t_r}+\left(\frac{\bar{\rho}\,\bar{C}_p\bar{T}}{\bar{m}\,\bar{C}_p\bar{T}\sum_{1}^{z}\gamma_i-\overline{\Delta H}_R}\right)\frac{\partial(\delta q)}{\partial x_r} \tag{60}$$

Putting this Eq. (60) for Γ into Eq. (39a), using Eq. (41) and simplifying, gives

$$\tau^*\frac{\partial}{\partial t_r}\left[\frac{1}{\bar{\rho}a_f^2}\frac{\partial(\delta P)}{\partial t_r}+\frac{\partial(\delta q)}{\partial x_r}\right]+$$

$$\frac{\partial(\delta P)}{\partial t_r}\left[\frac{\bar{\rho}\,\bar{C}_p^2\bar{T}-\bar{P}\bar{C}_p\sum_{1}^{z}\frac{\gamma_i^2m_i}{\bar{y}_i}+\overline{\bar{\rho}\,\bar{C}_p\bar{T}\Delta H_R}\left(\frac{d\,\overline{\ln K_c}}{dT}\right)-\bar{m}\,\bar{C}_p\bar{P}\,\bar{T}\sum_{1}^{z}\gamma_i\left(\frac{d\,\overline{\ln K_c}}{dT}\right)}{\bar{\rho}^2\,\bar{C}_p^2\,\bar{P}\,\bar{T}}\right]$$

$$+\frac{\partial(\delta q)}{\partial x_r}\left[\frac{\bar{P}\,\bar{C}_p\bar{T}\sum_{1}^{z}\frac{\gamma_i^2m_i}{\bar{y}_i}+\bar{P}\,\bar{T}\,\overline{\Delta H}_R\left(\frac{d\,\overline{\ln K_c}}{dT}\right)+\bar{P}\,\overline{\Delta H}_R\sum_{1}^{z}\gamma_i-\bar{m}\,\bar{C}_p\bar{P}\,\bar{T}\left(\sum_{1}^{z}\gamma_i\right)^2}{\bar{\rho}\,\bar{C}_p\bar{P}\,\bar{T}}\right]=0.$$

If it is assumed that δq and δP have continous first derivatives, then $\frac{\partial^2(\delta q)}{\partial t_r\partial x_r}=\frac{\partial^2(\delta q)}{\partial x_r\partial t_r}$ and $\frac{\partial^2(\delta P)}{\partial t_r\partial x_r}=\frac{\partial^2(\delta P)}{\partial x_r\partial t_r}$. Substituting Eq. (39c) into the above equation gives

$$\frac{\partial^2(\delta q)}{\partial t_r \partial x_r} = \frac{\partial^2(\delta q)}{\partial x_r \partial t_r} = -\frac{1}{\bar{\rho}} \frac{\partial^2(\delta P)}{\partial x_r^2} \tag{62a}$$

$$\frac{\partial^2(\delta P)}{\partial x_r \partial t_r} = \frac{\partial^2(\delta P)}{\partial t_r \partial x_r} = -\bar{\rho} \frac{\partial^2(\delta q)}{\partial t_r^2} \tag{62b}$$

Now, by differentiating Eq. (61) with respect to t_r, combining with Eq. (62a) and simplifying, using the expression (44) obtained for a_e, there is obtained

$$\frac{1}{a_e^2} \frac{\partial^2(\delta P)}{\partial t_r^2} - \frac{\partial^2(\delta P)}{\partial x_r^2} + \tau^{**} \frac{\partial}{\partial t_r}\left[\frac{1}{a_f^2} \frac{\partial^2(\delta P)}{\partial t_r^2} - \frac{\partial^2(\delta P)}{\partial x_r^2}\right] = 0 \tag{63}$$

where

$$\tau^{**} = \tau^* \left[\frac{\overline{C}_p \overline{T}}{\frac{\overline{C}_p \overline{T}}{\bar{\rho}} \sum_1^z \frac{\gamma_i^2 m_i}{\bar{y}_i} + \frac{\overline{T}\,\overline{\Delta H}_R}{\bar{\rho}} \left(\frac{d\,\overline{\ln K}_c}{dT}\right) + \frac{\overline{\Delta H}_R}{\bar{\rho}} \sum_1^z \gamma_i - \frac{\overline{C}_p \overline{T}}{\bar{n}} \left(\sum_1^z \gamma_i\right)^2} \right] \tag{64}$$

By differentiating Eq. (61) with respect to x_r, combining with Eq. (62b) and simplifying, gives

$$\frac{1}{a_e^2} \frac{\partial^2(\delta q)}{\partial t_r^2} - \frac{\partial^2(\delta q)}{\partial x_r^2} + \tau^{**} \frac{\partial}{\partial t_r}\left[\frac{1}{a_f^2} \frac{\partial^2(\delta q)}{\partial t_r^2} - \frac{\partial^2(\delta q)}{\partial x_r^2}\right] = 0. \tag{65}$$

In x-t coordinates, Eqs. (63) and (65) become

$$\left(\frac{\overline{q}^2}{a_e^2} - 1\right)\frac{\partial^2(\delta P)}{\partial x^2} + \frac{2\overline{q}}{a_e^2}\frac{\partial^2(\delta P)}{\partial x \partial t} + \frac{1}{a_e^2}\frac{\partial^2(\delta P)}{\partial t^2} +$$

$$\tau^{**}\left(\overline{q}\frac{\partial}{\partial x} + \frac{\partial}{\partial t}\right)\left[\left(\frac{\overline{q}^2}{a_f^2} - 1\right)\frac{\partial^2(\delta P)}{a x^2} + \frac{2\overline{q}}{a_f^2}\frac{\partial^2(\delta P)}{\partial x \partial t} + \frac{1}{a_f^2}\frac{\partial^2(\delta P)}{\partial t^2}\right] = 0 \qquad (66)$$

$$\left(\frac{\overline{q}^2}{a_e^2} - 1\right)\frac{\partial^2(\delta q)}{\partial x^2} + \frac{2\overline{q}}{a_e^2}\frac{\partial^2(\delta q)}{\partial x \partial t} + \frac{1}{a_e^2}\frac{\partial^2(\delta q)}{\partial t^2} +$$

$$\tau^{**}\left(\overline{q}\frac{\partial}{\partial x} + \frac{\partial}{\partial t}\right)\left[\left(\frac{\overline{q}^2}{a_f^2} - 1\right)\frac{\partial^2(\delta q)}{\partial x^2} + \frac{2\overline{q}}{a_f^2}\frac{\partial^2(\delta q)}{\partial x \partial t} + \frac{1}{a_f^2}\frac{\partial^2(\delta q)}{\partial t^2}\right] = 0 \qquad (67)$$

Eqs. (63) and (65), or (66) and (67), can now be regarded as generalized acoustic equations for the system.

PHYSICAL SIGNIFICANCE OF a_f and a_e

It is seen that Eq. (63) is made up of two wave equations. One wave equation has characteristics at $x_r \pm a_e t_r$ = constant or $x - (\overline{q} \pm a_e)t$ = constant, while the other has characteristics at $x_r \pm a_f t_r$ = constant or $x - (\overline{q} \pm a_f)t$ = constant. Thus, if τ^{**} is exactly equal to zero, Eq. (63) reduces to the equation of a wave with constant velocity a_e. If τ^{**} is very large ($\tau^{**} \to \infty$), as would be the case for a very slow reaction or for a nonreactive medium, Eq. (63) reduces to the equation of a wave with velocity a_f. In any other case, the equation is not a wave equation, but a third order equation. If τ^{**} is very small, but not zero, the characteristics are governed by the third order terms, although the value of the differential equation is governed by the second order derivatives. As has been shown, for $\tau^{**} \neq 0$, no matter how small, the wave front propagates at a_f. This agrees with physical intuition in that the wave front cannot have any knowledge of the medium into which it is approaching.

The significance of the equilibrium speed of sound will now be determined by attempting to find solutions of Eq. (63). Since Eq. (63) is a linear differential equation with constant coefficients, one possible method is to assume a solution of the form

$$\delta P = \sum_{i=1}^{\infty} C_i \ell^{\alpha_i t_r + \beta_i(\alpha_i) x_r} .$$

Here C_i and α_i are undetermined coefficients and β_i is a function of α_i. By putting this expression into Eq. (63), the relationship between β_i and α_i will be obtained. Then α_i and C_i can be chosen as functions of the integer i in such a way as to satisfy the boundary and initial conditions of the particular problem. (Note that sinusoidal solutions can be obtained if α_i, β_i, and C_i are complex).

Inserting the above expression into Eq. (63) gives

$$\sum_{i=1}^{\infty} \left[\frac{\alpha_i^2}{\beta_i^2} - \beta_i^2 + \tau^{**}\left(\frac{\alpha_i^3}{a_f^2} - \alpha_i \beta_i^2\right)\right] C_i \ell^{\alpha_i t_r + \beta_i x_r} = 0. \qquad (68)$$

Requiring that each term in the summation be identically equal to zero implies

$$(1 + \alpha_i \tau^{**})\, \beta_i^3 = \frac{\alpha_i^2}{a_e^2} + \frac{\alpha_i^3 \tau^{**}}{a_f^2} . \qquad (69)$$

Note that if $\tau^{**} = 0$, then $\frac{\alpha_i}{\beta_i} = \pm a_e$, and if $\tau^{**} \to \infty$, then $\frac{\alpha_i}{\beta_i} = \pm a_f$.

If τ^{**} is small enough so that τ^{**2} is negligible in comparison with τ^{**}, then neglecting second powers of τ^{**},

$$\frac{\alpha_i}{\beta_i} = \pm a_e\left[1+\frac{\tau^{**}\alpha_i}{2}\left(1-\frac{a_e^2}{a_f^2}\right)\right] \approx \pm a_e . \qquad (70)$$

When $\tau^{**} = 0$, or $\tau^{**} \to \infty$, $\frac{\alpha_i}{\beta_i}$ were seen to be equal (both numerically and dimensionally) to the equilibrium or frozen wave velocities, respectively, which were constants. If the interpretation of $\frac{\alpha_i}{\beta_i}$ as a wave velocity is now extended to the case of τ^{**}, finite and unequal to zero, it is seen that for small τ^{**}, the "wave velocities" are not constants but weak functions of α_i oscillating about the value a_e. Thus, for near-equilibrium flow, the expression of δP can be interpreted as the sum of a number of disturbances whose speeds are not, in general, equal, but are all close to a_e. This implies that, although the wave front is moving at a speed a_f, the bulk of the disturbance behind the wave front is moving at a speed close to a_e. In order for this to be true, a_e must be less than a_f and in deriving the explicit expressions for a_e and a_f, this was shown to be the case.

The significance of the two sound speeds, a_e and a_f, has now been determined for a reacting gas mixture near equilibrium with a fast reaction rate. In such a system, a_f represents the speed of the wave front, while a_e represents the approximate speed of the bulk of the wave behind the front. Velocity-of-sound measurements have been made in methane-air combustion products in which the frozen speed a_f was obtained. In some cases speeds greater than a_f were measured, and these were assumed to be close to molecular relaxation.

For the general case of a reacting gas mixture near equilibrium solutions can theoretically be built up from Eq. (63), either by the method shown or by any other technique for solving linear partial differential equations with constant coefficients. Practically, however, the usefulness of this procedure is limited by the fact that very little data exists on rates of reaction and so, in most cases, there will be no way of determining τ_b and τ_f, and hence τ^* and τ^{**}.

However, if τ^{**} is known to be small, the bulk of the wave behind the front moves at an overall speed very close to a_e and the acoustic equation (63) is approximately equal to the standard one-dimensional wave equation with velocity a_e. Thus, for purposes of computation, a theoretically instantaneous reaction can be used to approximate the actual state.

THE INSTANTANEOUS REACTION

In an instantaneous reaction the time of reaction is zero. Therefore, if the gas flow is steady, the gas mixture will reach equilibrium after passing through an infinitesimally short distance. If a small disturbance is sent through the pipe, the old equilibrium at any point is destroyed and a new equilibrium is established at exactly the instant that the pulse reaches that point.

Assume that the pulse starts at time $t=0$ and travels down the pipe with a velocity a_e relative to the gas stream or with an absolute velocity of $a_e + \overline{q}$. At a time t the pulse has traversed a distance equal to $(a_e + \overline{q})t$. For points $x > (a_e + \overline{q})t$, the pulse has not yet arrived and the conditions are still the old equilibrium conditions. For $x < (a_e + \overline{q})t$, the pulse has already passed and changed conditions to the new equilibrium. For example, $\overline{P}$ is changed to $\overline{P} + \delta\overline{P}$, where $\delta\overline{P}$ is the change in pressure between the old equilibrium and the new and it is of perturbation order. Similarly, for $x < (a_e + \overline{q})t$, $T = \overline{T} + \delta\overline{T}$, $q = \overline{q} + \delta\overline{q}$,

$\rho = \overline{\rho} + \delta\overline{\rho}$, $y_i = \overline{y}_i + \delta\overline{y}_i$, etc.

According to our hypothesis of an instantaneous reaction, for $x > (a_e + \overline{q})t$, $\Gamma = 0$ since the pulse has not yet arrived, and for $x < (a_e + \overline{q})t$, $\Gamma = 0$ since the reaction is already completed. At $x = (a_e + \overline{q})t$, a change of perturbation order is accomplished in a time interval approaching zero. Hence, at $x = (a_e + \overline{q})t$, Γ becomes infinite.

One is therefore led to assume solutions of the form

$$\delta P = \overline{\delta P}\ U[a_e + \overline{q})t - x] = \overline{\delta P}\ U(a_e t_r - x_r) \tag{71a}$$

$$\delta\rho = \overline{\delta\rho}\ U(a_e t_r - x_r) \tag{71b}$$

$$\delta y_i = \delta y_i U(a_e t_r - x_r) \tag{71c}$$

$$\delta q = \overline{\delta q}\ U(a_e t_r - x_r) \tag{71d}$$

$$\delta T = \overline{\delta T}\ U(a_e t_r - x_r) \tag{71e}$$

$$\Gamma = \overline{\Gamma}\ I(a_e t_r - x_r) \tag{71f}$$

where $\overline{\Gamma}$, $\overline{\delta P}$, $\overline{\delta\rho}$, $\overline{\delta y_i}$, $\overline{\delta q}$, $\overline{\delta T}$ are constant amplitude terms. "U" is a symbol for the unit (Heaviside) step function defined by $U(\lambda) = 1$ for $\lambda > 0$ and UW = 0 for $\lambda < 0$. The impulse function is defined by $I(\lambda) = 0$, if $\lambda \neq 0$ and $\int_{-\infty}^{\infty} I(\lambda)d\lambda = 1$.

Although neither $U(\lambda)$ nor $I(\lambda)$ is an everywhere continuous function and $I(\lambda)$ is not properly a function at all , they can nevertheless be treated as continuous differentiable functions which are related by $I(\lambda) = \frac{dU(\lambda)}{d\lambda}$.

Putting Eq. (71) into Eqs. (31a), (31b), (31c), (31d), (31g), and (36), which are the governing equations for an instantaneous reaction, gives

$$a_e\overline{\delta\rho} - \overline{\rho}\ \overline{\delta\rho} = 0 \tag{72a}$$

$$\frac{\bar{\rho}\, a_e}{\gamma_i m_i}\, \delta\bar{y}_i - \bar{\Gamma} = 0 \tag{72b}$$

$$\bar{\rho}\, a_e\, \delta\bar{q} - \overline{\delta P} = 0 \tag{72c}$$

$$\frac{\overline{\delta\rho}}{\bar{\rho}} + \frac{\overline{\delta T}}{\bar{T}} + \bar{m} \sum_{1}^{z} \frac{\delta\bar{y}_i}{m_i} - \frac{\overline{\delta P}}{\bar{P}} = 0 \tag{72d}$$

$$a_e \overline{\delta T} - \frac{a_e}{\bar{\rho}\, \bar{C}_p}\, \overline{\delta P} + \frac{\Delta H_R}{\bar{\rho}\, \bar{C}_p} = 0 \tag{72e}$$

$$\left(\frac{d\, \overline{\ln K}_c}{dT}\right) \overline{\delta T} - \frac{\sum_{1}^{z} \gamma_i}{\bar{\rho}}\, \delta\bar{\rho} - \sum_{1}^{z} \frac{\gamma_i}{\bar{y}_i}\, \delta\bar{y}_i = 0 \tag{72f}$$

Eqs. (72) are a set of linear homogeneous equations in six unknowns. The requirement for the existence of non-trivial solutions is that the determinant of the system be equal to zero and evaluation of the determinant shows that this is true if a_e is given by Eq. (44). This being the case, Eqs. (72) enable one to obtain all the perturbation amplitudes, if any one of them is known.

REFERENCES

1. Chu, B. -T., "Wave Propagation and the Method of Characteristics in Reacting Gas Mixtures With Applications to Hypersonic Flow," Brown University, WADC TN-57-213, AD 118 350 (May 1957).

2. Noyes, A. A. and Sherill, M. S., A Course of Study in Chemical Principles (MacMillan Company. New York, 1929) p. 285-286.

3. Agosta, V. D. and Baker, H. D., "Temperature Determination of Methane-Air Combustion Products by Velocity-of-Sound Measurements," Proceedings of the Sixth Annual Comference on Fluid Mechanics, University of Texas, Austin, Texas (September 1959).