

ERRATA SHEET

Page 5, line 2 below $(1/T)(\delta q/\delta t)$: omit the word "not."

Page 8, line 2 of second paragraph: replace " $\delta t/\delta t$ " by " $\delta q/\delta t$."

Page 9, line 2 of second paragraph: insert "it" after "finite."

Page 11, line 2 above Eq. (2.42): replace "k" by " κ ."

Page 14, lines 4, 5, and 6 from bottom of page: replace " κ " by "K."

Page 19, line 2 above Eq. (4.23a): replace " $(T_0 + \epsilon_2)^3$ " by " $(T_0 + \epsilon_\beta)^3$."

Page 20, Eq. (4.25b): replace " $\partial \bar{\xi}$ " by " $\partial_t \bar{\xi}$."

Page 25, Eq. (4.45a): replace " $i\omega k$ " by " $i\omega K$."

Page 26, Eq. (4.46b): replace "k" by " k^2 ."

Page 33, Ref. 10: replace "Landan" by "Landau."

THE UNIVERSITY OF MICHIGAN
COLLEGE OF LITERATURE, SCIENCE, AND THE ARTS
Department of Mathematics

Progress Report

NON-EQUILIBRIUM HYDRODYNAMICS OF A CHEMICALLY REACTING FLUID

Chi Yuan

ORA Project 05424

under contract with:

UNITED STATES AIR FORCE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
CONTRACT NO. AF-AFOSR-20-63
WASHINGTON, D.C.

administered through:

OFFICE OF RESEARCH ADMINISTRATION ANN ARBOR

September 1963

TABLE OF CONTENTS

	Page
ABSTRACT	v
1. INTRODUCTION	1
2. NON-EQUILIBRIUM HYDRODYNAMICS OF A CHEMICALLY REACTING FLUID	2
3. FUNDAMENTAL EQUATIONS	13
4. SMALL PERTURBATION THEORY	15
5. ACKNOWLEDGMENT	32
6. REFERENCES	33

ABSTRACT

In this paper, two topics are studied: (1) the thermodynamics (and hence the energy relations) for a chemically reacting fluid with heat of reaction effects; (2) the upper and lower limiting speeds of "linearly perturbed motions" in the fluid. The first of the above leads to the study of two types of relations: (1) the usual extent of reaction equation; (2) linear phenomenological equations for the heat flux and rate of reaction in terms of the affinity and temperature (DeGroot, S. R. and Mazur, P., *Non-equilibrium Thermodynamics*, North Holland Publishing Co. (1962)). It is shown that if heat of reaction is neglected and proper assumptions are made on the affinity then the non-equilibrium energy relations of L. J. F. Broer (*Characteristics of the Equations of Motion of a Chemically Reacting Gas*, *Journal of Fluid Mechanics*, 4, 276-282 (1958)) are obtained. The energy relations of E. V. Stupochenko and I. P. Stakhanov (*The Equations of Relaxation Hydrodynamics*, *Soviet Phys-Doklady*, 4, 782-785 (1960)) are obtained by neglecting the heat of reaction, further, their K is shown to be a function of the thermodynamic variables. For the limit speeds, the following results are obtained: (1) in the low frequency case, the limit speed coincides with that of Broer, Stupochenko-Stakhanov and is independent of heat of reaction; (2) in the high frequency case, the limit speed is independent of the chemical reaction. An explanation of this result has been given by Broer in the above cited paper.

1. INTRODUCTION

The purpose of relaxation hydrodynamics is to study the behavior of a fluid while chemical reactions are taking place. The state of such a fluid will no longer be specified by any two ordinary thermodynamical parameters. In addition, the extent of reaction, ξ , which characterizes the chemical composition of the fluid (see Section 2) must be known. The introduction of this new independent thermodynamical parameter, ξ , into the fluid system leads to a problem which is quite different from the usual one. In fact, a new equation, the equation of reacting rate, is added to the system of relations for the conventional hydrodynamics.

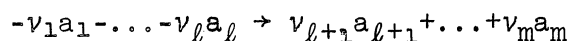
The small perturbation theory of this new system for a compressible, inviscid, non-heat-conducting gas was first treated by Broer in 1957.¹ Later, Stupochenko and Stakhanov, using a different equation of reaction rate, obtained a similar result for some reacting gas.² In both of the above papers the authors show that there exists two limiting speeds, corresponding to high and low frequencies. In 1962, Coburn used non-linear theory to extend the above results to magneto-hydrodynamics and another limiting speed was shown to exist.³

In the present work, we shall not introduce the electro-magnetic effects but we shall generalize the work of Broer and Stupochenko and Stakhanov to the case of heat-conducting fluid. First we shall give a general survey of non-equilibrium thermodynamics in order to formulate the fundamental equations for the problem. Then we shall relate this system of fundamental equations to the systems considered by Broer and by Stupochenko and Stakhanov. The small perturbation theory for this system will be carried out in detail. The effect of heat-conduction will be emphasized. We shall show that in the presence of heat-conduction, two limiting speeds exist. The limiting speed of low frequency will remain the same as in the non-heat-conduction case, but the limiting speed of high frequency will be different.

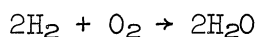
2. NON-EQUILIBRIUM HYDRODYNAMICS OF A CHEMICALLY REACTING FLUID

In thermodynamics, the non-equilibrium process does not refer to chemical reactions alone. In a much broader sense, it refers to all irreversible processes. In this work, however, we shall be concerned only with two non-equilibrium processes: first, those which involve simple chemical reaction; and secondly, those which involve heat-conduction. Moreover, we shall assume that the medium of the system is a fluid.

This fluid contains m chemical components, denoted by $a_1 \dots a_m$, where m is an integer greater than one. A simple chemical reaction can be expressed by the chemical relation



where v_k ($k = 1, 2, \dots, m$) are the stoichiometric coefficients in the chemical reaction. As an example, we take the reaction



In this case, $v_1 = -2$, $v_\ell = v_2 = -1$, $v_m = v_3 = 2$, $a_1 = H_2$, $a_2 = O_2$, and $a_3 = H_2O$.

Let ρ be the local density of the fluid, ρ_k be the local density of the a_k component, and n_k be the number of moles of the a_k component per unit mass. Now, we shall follow a system of fluid particles along their paths. As a result of conservation of mass, this system of particles is closed. That is, exchange of energy through the boundary is allowed; matter is conserved. The rate of increase of n_k along a fluid particle is denoted by dn_k/dt , where d/dt is the substantial or total derivative. Using the law of definite proportion in a chemical reaction[†], we find that dn_k/dt are proportional to the stoichiometric coefficients, v_k .

$$\frac{dn_1}{dt} : \frac{dn_2}{dt} : \dots : \frac{dn_m}{dt} = v_1 : v_2 : \dots : v_m \quad (2.1a)$$

Thus, $\rho \, dn_k/dt$, the rate of increase of n_k per unit volume, are proportional to v_k or

$$\rho \frac{dn_1}{dt} : \rho \frac{dn_2}{dt} : \dots : \rho \frac{dn_m}{dt} = \nu_1 : \nu_2 : \dots : \nu_m \quad (2.1b)$$

Here, we shall introduce two important quantities (Ref. 4, p. 4-5) in non-equilibrium thermodynamics. The rate of reaction, \bar{V} , is defined by

$$\frac{\rho \frac{dn_1}{dt}}{\nu_1} = \frac{\rho \frac{dn_2}{dt}}{\nu_2} = \dots = \frac{\rho \frac{dn_m}{dt}}{\nu_m} \equiv \bar{V} \quad (2.1c)$$

The extent of reaction, ξ , is defined by

$$\frac{d\xi}{dt} \equiv \bar{V} \quad (2.2)$$

By substituting (2.2) into (2.1c), we find

$$\frac{dn_k}{dt} = \frac{\nu_k}{\rho} \frac{d\xi}{dt} \quad (2.1d)$$

where

$$k = 1, 2, \dots, m$$

In ordinary thermodynamics, the state of a system is completely specified by two thermodynamical parameters. But in non-equilibrium thermodynamics, the chemical composition will also change with time and position in a system. Thus, in order to determine the state of a fluid in such a system, the chemical composition which is characterized by n_k must be known.

Let \mathcal{L} be any fluid path in the physical space, initiated from a point P_0 at time t_0 to a point P at time t . This path, \mathcal{L} , can be expressed in the following parametric form:

$$x^k = \phi^k(t) \quad k = 1, 2, 3. \quad (2.3)$$

where ϕ^k are some given functions with continuous derivatives, i.e., of class C^1 and

$$\sum_{k=1}^3 \left(\frac{d\phi^k}{dt} \right)^2 \neq 0$$

in the interval t_0 to t . If we integrate Eq. (2.1d) along this path, we find that

$$n_k = v_k \int_{t_0}^t \left(\frac{d\xi}{dt} \right) \frac{dt}{\rho(\phi^k(t), t)} \quad (2.4)$$

Note that we removed v_k from the integral because v_k are known constants. From (2.4) it is seen that n_k depend on the extent of reaction, ξ , as well as the ordinary thermodynamical parameter, ρ , the density. Thus, the state of the fluid depends on any two ordinary thermodynamical parameters and its chemical composition n_k , or can be characterized by any two ordinary thermodynamical parameters and its extent of reaction, ξ .

Again, we follow a system of fluid particles and consider the system to be closed as it moves. The first law in non-equilibrium thermodynamics states that the rate of change of the internal energy per unit mass, e , along a fluid path will be

$$\frac{de}{dt} = \frac{\delta q}{\delta t} - p \frac{d\tau}{dt} \quad , \quad (2.5)$$

where $\delta q/\delta t$ represents the rate of heat flowing into the system; p is the pressure; and τ is the specific volume (Ref. 5, Chap. II,III). Note that δq is not an exact differential. It depends on the path chosen in the space spanned by three independent non-equilibrium thermodynamical parameters. The second law of non-equilibrium thermodynamics states that there exists an entropy function s associated with the state of a fluid such that the rate of change of s following a fluid particle satisfies the following relation:

$$T \frac{ds}{dt} = \frac{\delta q}{\delta t} + \frac{\delta q'}{\delta t} \quad (2.6)$$

where T is the absolute temperature and $\delta q'/\delta t$ is the uncompensated rate of heat flow per unit mass due to chemical reaction (Ref. 5, p. 34). Again, $\delta q'$ is not an exact differential. But the quantity

$$\frac{1}{T} \left(\frac{\delta q}{\delta t} + \frac{\delta q'}{\delta t} \right)$$

is an exact derivative which is ds/dt by (2.6). In a reversible process, $\delta q'/\delta t = 0$, while in an irreversible process $\delta q'/\delta t > 0$. It is worthwhile to note that in reversible thermodynamics, the quantity

$$\frac{1}{T} \left(\frac{\delta q}{\delta t} \right)$$

is an exact derivative.⁷ However, the second law of non-equilibrium thermodynamics does not imply that the quantity

$$\frac{1}{T} \left(\frac{\delta q'}{\delta t} \right)$$

must also be an exact derivative.

Eliminating $\delta q/\delta t$ from (2.5) by using (2.6), we obtain

$$\frac{ds}{dt} = \frac{1}{T} \frac{de}{dt} + \frac{p}{T} \frac{d\tau}{dt} + \frac{1}{T} \frac{\delta q'}{\delta t} \quad (2.7a)$$

Since s is a function of e , τ and n_k , we find by taking the time derivative of s along the fluid path,

$$\frac{ds}{dt} = \left(\frac{\partial s}{\partial e} \right)_{\tau, n_k} \frac{de}{dt} + \left(\frac{\partial s}{\partial \tau} \right)_{e, n_k} \frac{d\tau}{dt} + \sum_{k=1}^m \left(\frac{\partial s}{\partial n_k} \right)_{e, \tau, n_1, \dots, n_{k-1}, n_{k+1}, \dots, n_m} \frac{dn_k}{dt} \quad (2.8)$$

Now, e and τ are independent of n_k . By equating the right hand sides of Eqs. (2.7a) and (2.8), and letting e and s be constant, we obtain

$$\frac{1}{T} \frac{\delta q'}{\delta t} = \sum_{k=1}^m \left(\frac{\partial s}{\partial n_k} \right)_{e, \tau; n_1, \dots, n_{k-1}, n_{k+1}, \dots, n_m} \frac{dn_k}{dt} \quad (2.9)$$

Then, by (2.9), the relation (2.7a) can be written as

$$\frac{ds}{dt} = \frac{1}{T} \frac{de}{dt} + \frac{p}{T} \frac{d\tau}{dt} - \sum_{k=1}^m \frac{\mu_k}{T} \frac{dn_k}{dt} \quad (2.7b)$$

where μ_k is called the chemical potential of the a_k component,^{4,6} and is defined by

$$\mu_k = - T \left(\frac{\partial s}{\partial n_k} \right)_{e, \tau; n_1, \dots, n_{k-1}, n_{k+1}, \dots, n_m} \quad (2.10)$$

Substituting the value of dn_k/dt given by (2.1d) into (2.7b), we have

$$\frac{ds}{dt} = \frac{1}{T} \frac{de}{dt} + \frac{p}{T} \frac{d\tau}{dt} + \frac{A}{T\rho} \frac{d\xi}{dt} \quad (2.7c)$$

where

$$A \equiv - \sum_{k=1}^m \mu_k \nu_k \quad (2.11)$$

A is the affinity of De Donder (Ref. 4, p. 3-24). Equation (2.7c) may be written as

$$\frac{de}{dt} = T \frac{ds}{dt} - p \frac{d\tau}{dt} - \frac{A}{\rho} \frac{d\xi}{dt} \quad (2.7d)$$

Now, we shall consider e to be a function of s , τ and ξ , and form the time derivative of e along a fluid particle path. We obtain

$$\frac{de}{dt} = \left(\frac{\partial e}{\partial s} \right)_{\tau, \xi} \frac{ds}{dt} + \left(\frac{\partial e}{\partial \tau} \right)_{s, \xi} \frac{d\tau}{dt} + \left(\frac{\partial e}{\partial \xi} \right)_{s, \tau} \frac{d\xi}{dt} \quad (2.12)$$

where s , τ and ξ are taken as independent variables. By eliminating de/dt from (2.7d) by using (2.12) and letting s and τ be constant, we obtain

$$A = - \rho \left(\frac{\partial e}{\partial \xi} \right)_{s, \tau} \quad (2.13)$$

The affinity A plays an important role in non-equilibrium thermodynamics involving chemical reactions, since A is a controlling factor of the rate of chemical reaction. It has been shown (Ref. 4, p. 40) that the necessary and sufficient condition for chemical equilibrium, i.e., no chemical reaction, is

$$A = 0 \quad (2.14)$$

As ρ is always positive, this last condition and (2.13) will imply

$$\left. \frac{\partial e}{\partial \xi} \right)_{s, \tau} = 0 \quad (2.15)$$

for chemical equilibrium.

Next, we shall derive the equation for entropy production.⁵ Let V be some region in the fluid at time t_0 . When the time changes from t_0 to t , the shape and the position of this region may be changed, but its mass remains the same, as a consequence of conservation of mass. That is, the region forms a closed system. At any instant, the total entropy, S , in V is determined by

$$S \equiv \int_V \rho s d\tau \quad (2.16)$$

where ρ , s and τ are the density, the entropy per unit mass, and specific volume as before. The rate of change of S as V is moving along, will be solely due to the entropy flowing in through the boundary and the entropy produced from chemical reaction inside the region. This can be expressed by

$$\frac{dS}{dt} = \frac{d}{dt} \int_V \rho s d\tau = - \int_{\Sigma} J^i U_i da + \int_V \sigma d\tau, \quad i = 1, 2, 3 \quad (2.17)$$

Here, J^i is the component of the entropy flux in x^i direction, where x^i are rectangular Cartesian coordinates; σ is the entropy production per unit volume per unit time; Σ is the surface of the region; da is the area element on the surface; and U_i is the unit normal vector on the surface. Note that we use superscripts, e.g., J^i , to denote contravariant components, and subscripts, e.g., U_i , to denote covariant components, even though both quantities coincide in rectangular Cartesian coordinates. The Einstein summation convention of summing on a repeated upper and lower index in the range from one to three is also adopted. Conservation of mass of a given region in time leads to

$$\frac{d}{dt} \int_V \rho d\tau = 0 \quad (2.18)$$

Therefore, Eq. (2.17) reduces to (Ref. 8, Art. 2)

$$\int_V \rho \frac{ds}{dt} d\tau = - \int_{\Sigma} J^i U_i da + \int_V \sigma d\tau \quad (2.19)$$

Using Gauss' theorem and the fact that V is arbitrary, we have

$$\rho \frac{ds}{dt} = - \partial_i J^i + \sigma \quad (2.20)$$

where

$$\partial_i \equiv \frac{\partial}{\partial x^i}$$

Equation (2.20) actually states that the rate of change of entropy in the system can be split into two parts: (1) entropy due to interaction with the exterior surroundings; and (2) entropy due to an irreversible process within the system. These two rates of change correspond to $-\partial_i J^i$ and σ respectively.

Now, we shall introduce the heat flux per unit area, denoted by W^i , into the energy Eq. (2.5). We have $\delta\tau/\delta t$ as the rate of flow of heat per unit mass along a particle path. Thus, for the region V , the rate of total heat flowing in through the boundary at a certain time can be expressed in the following equation:

$$\frac{\delta Q}{\delta t} = \int_V \rho \frac{\delta q}{\delta t} d\tau \quad (2.21)$$

where $\delta Q/\delta t$ is the total rate of heat flowing into V through the boundary of region V . By definition of $\delta Q/\delta t$ and W^i , it is clear that

$$\frac{\delta Q}{\delta t} = - \int_{\Sigma} W^i U_i da \quad (2.22)$$

Then, using Gauss' theorem and the fact that V is arbitrary as before, we find that (2.22) implies

$$\rho \frac{\delta q}{\delta t} = - \partial_i W^i \quad (2.23)$$

Substituting the above value of $\delta q/\delta t$ into (2.5) gives

$$\frac{de}{dt} = -\frac{1}{\rho} \partial_i W^i - \rho \frac{d\tau}{dt} \quad (2.24)$$

By eliminating de/dt from (2.7d) by use of (2.24), we find

$$\rho \frac{ds}{dt} = -\frac{1}{T} \partial_i W^i + \frac{A}{T} \frac{d\xi}{dt} \quad (2.25a)$$

or equivalently,

$$\rho \frac{ds}{dt} = -\partial_i \left(\frac{W^i}{T} \right) - W^i \frac{\partial_i T}{T^2} + \frac{A}{T} \bar{V} \quad (2.25b)$$

Now, let us eliminate ds/dt from (2.20) by use of (2.25b). We obtain

$$-\partial_i J^i + \sigma = -\partial_i \left(\frac{W^i}{T} \right) - W^i \frac{\partial_i T}{T^2} + \frac{A}{T} \bar{V} \quad (2.26)$$

A sufficient condition for the validity of the relation (2.26) is

$$J^i = \frac{W^i}{T} \quad (2.27)$$

$$\sigma = -W^i \frac{\partial_i T}{T^2} + \frac{A}{T} \bar{V} \quad (2.28)$$

In many fields of physics, when the universe is considered to be finite, can be shown that Eqs. (2.27) and (2.28) are also necessary conditions for the validity of (2.26) (Ref. 9, p. 265). The usual argument involves two assumptions. First, we note that by integrating (2.26) over the whole universe, \mathcal{R} , we have

$$-\int_{\mathcal{R}} \partial_i J^i d\tau + \int_{\mathcal{R}} \sigma d\tau = \int_{\mathcal{R}} -\partial_i \left(\frac{W^i}{T} \right) d\tau + \int_{\mathcal{R}} \left(-W^i \frac{\partial_i T}{T^2} + \frac{A}{T} \bar{V} \right) d\tau \quad (2.29)$$

Then, by use of Gauss' theorem, Eq. (2.29) can be written as

$$-\int_{\mathcal{S}} J^i U_i da + \int_{\mathcal{R}} \sigma d\tau = -\int_{\mathcal{S}} \frac{W^i}{T} U_i da + \int_{\mathcal{R}} \left(-W^i \frac{\partial_i T}{T^2} + \frac{A}{T} \bar{V} \right) d\tau \quad (2.30)$$

where \mathcal{S} is the surface of \mathcal{R} . The first assumption states that the fluxes J^i and W^i are zero on \mathcal{S} , which is the surface of the finite region \mathcal{R} , the universe. Hence,

$$\int_{\mathcal{S}} J^i U_i da = 0 \quad (2.31)$$

$$\int_{\mathcal{S}} \frac{W^i}{T} U_i da = 0 \quad (2.32)$$

Thus, (2.30) reduces to

$$\int_{\mathcal{R}} \sigma d\tau = \int_{\mathcal{R}} \left(-\frac{W^i}{T} \partial_i T + \frac{A}{T} \bar{V} \right) d\tau \quad (2.33a)$$

or,

$$\int_{\mathcal{R}} \left(\sigma + \frac{W^i}{T^2} \partial_i T - \frac{A}{T} \bar{V} \right) d\tau = 0 \quad (2.33b)$$

Note that (2.33b) is a weak form of (2.28). The second assumption states that this weak form (2.33b) implies (2.28). It is then clear that (2.27) will follow directly from (2.26) and (2.28). Thus, these two assumptions will enable us to obtain (2.27) and (2.28) directly from (2.26).

Equation (2.28) has proved to be very useful in non-equilibrium thermodynamics.^{4,5,6} The right side of this equation is a sum of the product of W^i with $\partial_i T/T^2$, and of A/T with \bar{V} . It is well known in the classical theory of heat conduction that the heat flux, W^i , is, in general, primarily dependent on the temperature gradient, $\partial_i T$. Fourier expressed this idea in a linear formula for heat conduction, namely

$$W_i = \kappa \partial_i T \quad (2.34)$$

where κ is the coefficient of heat conductivity. It has been noted in physical chemistry that the rate of reaction, \bar{V} , is dependent on the affinity, A , for many processes.^{4,6} A linear relation between A and \bar{V} is often assumed (Ref. 6, p. 291, 4, Chap. IV) namely,

$$\bar{V} = \lambda A \quad (2.35)$$

where λ is a function of the state of a fluid. More general linear relations of this kind, known as phenomenological relations, are extensively used in non-equilibrium thermodynamics.⁵ These relations are more general because they consider the possible interaction between heat flux W^i and affinity A , and between rate of reaction \bar{V} and temperature gradient $\partial_i T$. In our case, these relations will be assumed to be

$$W^k = a^{ki} \frac{\partial_i T}{T^2} + a^{k4} \frac{A}{T} \quad (2.36)$$

$$\bar{V} = a^{4i} \frac{\partial_i T}{T^2} + a^{44} \frac{A}{T} \quad (2.37)$$

where a^{ki} , a^{k4} , a^{4i} , and a^{44} are constant, $k, i = 1, 2, 3$ (Ref. 5, Chap. IV).

As the fluid is considered to be isotropic, the relations (2.36) and (2.37) can be simplified by Curie's principle, which states that (Ref. 5, Chap. VI)

$$a^{k4} = a^{4k} = 0 \quad (2.38)$$

Besides, Onsager's symmetric principle gives some more information on the coefficients a^{ki} . It states that

$$a^{ki} = a^{ik} \quad (2.39)$$

Thus, the phenomenological relations for relaxation hydrodynamics with heat conduction will take the following forms:

$$W^k = a^{ki} \frac{\partial_i T}{T^2}, \quad a^{ki} = a^{ik} \quad (2.40)$$

$$\bar{V} = a^{44} \frac{A}{T} \quad (2.41)$$

By comparing (2.40), (2.41) with (2.34), (2.35) we see that κ , λ are related to a^{ki} and a^{44} by following relations:

$$\kappa \delta_j^k = \frac{g_{ij} a^{ik}}{T^2} \quad (2.42)$$

$$\lambda = \frac{a^{44}}{\Gamma} \quad (2.43)$$

where δ_i^k , is the Kronecker delta, and g_{ij} is the fundamental covariant tensor of the x^i system.

3. FUNDAMENTAL EQUATIONS

In the previous section, we have obtained the energy equation for a fluid in which chemical reaction and heat conduction occur. This equation is (see Eqs. (2.25a) and (2.21))

$$\rho \frac{ds}{dt} = - \frac{1}{T} \partial_i W^i + \frac{A}{T} \bar{V} \quad (3.1)$$

The heat flux W^i and reaction rate \bar{V} of (3.1) are governed by two phenomenological relations:

$$W^i = a^{ik} \frac{\partial_k T}{T^2} \quad (3.2)$$

$$\bar{V} = a^{44} \frac{A}{T} \quad (3.3)$$

The equation of continuity and the equation of motion remain essentially the same except that the density, ρ , and the pressure, p , are functions of ξ and of any two other thermodynamical parameters (Refs. 1,2,5, Chap. III). Thus, the continuity relation is

$$\partial_t \rho + \partial_j (\rho v^j) = 0 \quad (3.4)$$

The equations of motion are

$$\partial_t (\rho v_k) + \partial_j (\rho v^j v_k + \delta_k^j p) = 0 \quad (3.5)$$

where

$$\partial_t \equiv \frac{\partial}{\partial t}$$

Note that v_k are the rectangular Cartesian components of velocity, and δ_k^i is the Kronecker delta.

Equations (3.1)-(3.5) and (2.2) will be the fundamental equations of our problem. By eliminating \bar{V} from this system by use of (2.2), the above equations form a system of nine equations in the nine unknowns W^k , v^k , ρ , s and ξ . We shall first show that this system will reduce to the systems used by Broer¹ and by Stupochenko and Stankhanov², when the effect of heat-conduction is excluded.

Substituting the value of A in (2.13) into (3.3), we obtain

$$\bar{V} = - \frac{a^{44}\rho}{T} \left(\frac{\partial e}{\partial \xi} \right) \quad (3.6)$$

Since we are considering the non-heat-conduction case, a^{ik} in (3.2) are assumed to be zero. Equation (3.1) will, in turn, reduce to following form:

$$\rho \frac{ds}{dt} = \frac{A}{T} \bar{V} \quad (3.7a)$$

By replacing A by (2.13) and using the definition of \bar{V} (2.2), we obtain from (3.7a)

$$\frac{ds}{dt} = - \frac{1}{T} \left(\frac{\partial e}{\partial \xi} \right) \frac{d\xi}{dt} \quad (3.7b)$$

Here, we take, ρ, s and ξ as independent thermodynamical parameters. Equations (3.4)-(3.6) and (3.7b) form a system which was treated by Stupochenko and Stankhanov² for

$$K = \frac{a^{44}\rho}{T}$$

where κ is the coefficient in their phenomenological relation,

$$\bar{V} = - \kappa \left(\frac{\partial e}{\partial \xi} \right)$$

The function κ was not specified in their paper because in the small perturbation theory it would not influence the results for limiting speeds (see Section 4).

In order to get Broer's system of equations,¹ we need to expand A in

Taylor series with respect to ξ , assuming ρ and s constant, about the equilibrium value of reaction, $\bar{\xi}$. The series is

$$A = A(\rho, s, \bar{\xi}) - \rho \left(\frac{\partial^2 e}{\partial \xi^2} \right)_{\bar{\xi}} (\xi - \bar{\xi}) + \rho \left(\frac{\partial^3 e}{\partial \xi^3} \right)_{\bar{\xi}} (\xi - \bar{\xi})^2 - \dots \quad (3.8)$$

Note that $A(\rho, s, \bar{\xi})$ is zero, since $\bar{\xi}$ is the value of ξ in equilibrium state. Therefore, Eq. (3.8) can be written as

$$A = - \rho \left(\frac{\partial^2 e}{\partial \xi^2} \right)_{\bar{\xi}} (\xi - \bar{\xi}) + \dots \quad (3.9)$$

In Broer's work,¹ a quasi-equilibrium state is assumed. Hence, $(\xi - \bar{\xi})^k$ $k = 2, 3, \dots$, is neglected. Thus, to a first approximation, we have

$$A = - \rho \left(\frac{\partial^2 e}{\partial \xi^2} \right)_{\bar{\xi}} (\xi - \bar{\xi}) \quad (3.10)$$

Substituting the value of A from (3.10) into (3.3), we have

$$\frac{d\xi}{dt} = - \frac{a^{44} \rho}{T} \left(\frac{\partial^2 e}{\partial \xi^2} \right)_{\bar{\xi}} (\xi - \bar{\xi}) \quad (3.11)$$

If we let

$$\alpha = \frac{a^{44} \rho}{T} \left(\frac{\partial^2 e}{\partial \xi^2} \right)_{\bar{\xi}} \quad (3.12)$$

(3.11) will become Broer's phenomenological relation.¹

$$\frac{d\xi}{dt} = - \alpha (\xi - \bar{\xi})$$

The function α was not specified in Broer's paper since the limiting cases of high and low frequencies are independent of α (Ref. 1, p. 278).

In the following section we shall develop the small perturbation theory for the system of Eqs. (3.1)-(3.5) and (2.2) in order to see how the effect of heat conduction will enter into our problem.

4. SMALL PERTURBATION THEORY

By eliminating W^j of (3.1) by use of (3.2), and noting (3.4) and (3.5), we obtain four equations which will be the basic relations for small perturbation theory. They are: the equation of continuity, the equation of motion, the energy equation involving heat conduction, and the phenomenological relation for a simple chemical reaction:

$$\partial_t \rho + \partial_j (\rho v^j) = 0 \quad (4.1)$$

$$\partial_t (\rho v_k) + \partial_j (\rho v^j v_k + \delta_{kj} p) = 0 \quad (4.2)$$

$$\begin{aligned} \rho \partial_t s + \rho v^j \partial_j s &= - \frac{a^{ik}}{T^3} \partial_k \partial_i T + \frac{2a^{ik}}{T^4} (\partial_i T) (\partial_k T) \\ &+ \frac{A}{T} (\partial_t \xi + v^j \partial_j \xi) \end{aligned} \quad (4.3)$$

$$\partial_t \xi + v^j \partial_j \xi = \frac{a^{44}}{T} A \quad (4.44)$$

Applying the standard method of small perturbation theory,¹⁰ we assume that: (1) the velocity components, v^j are of the first order in the perturbation scalar which is denoted by ϵ ; (2) the state of the fluid is slightly displaced from the equilibrium state, characterized by ρ_0, s_0 and ξ_0 . Mathematically, these conditions can be formulated as follows:

$$v^j \equiv \epsilon \bar{v}^j \quad (4.5)$$

$$\rho \equiv \rho_0 + \epsilon \bar{\rho} \quad (4.6)$$

$$s \equiv s_0 + \epsilon \bar{s} \quad (4.7)$$

$$\xi \equiv \xi_0 + \epsilon \bar{\xi} \quad (4.8)$$

where ρ, s, ξ are the three independent thermodynamical parameters which we shall use in this section; $\bar{v}^j, \bar{\rho}, \bar{s},$ and $\bar{\xi}$ are the variable parts of vel-

ocity, density, entropy and extent of reaction, respectively, in the above equations.

Since the pressure, p , and temperature, T , and the affinity, A , are functions of ρ , s , and ξ , we can expand them in Taylor series, with respect to these three independent variables about the equilibrium state, specified by ρ_0 , s_0 and ξ_0 . We obtain for the zero and first order terms

$$p = p(\rho, s, \xi) = p_0 + \left. \frac{\partial p}{\partial \rho} \right|_0 \epsilon \bar{\rho} + \left. \frac{\partial p}{\partial s} \right|_0 \epsilon \bar{s} + \left. \frac{\partial p}{\partial \xi} \right|_0 \epsilon \bar{\xi} \quad (4.9)$$

$$T = T(\rho, s, \xi) = T_0 + \left. \frac{\partial T}{\partial \rho} \right|_0 \epsilon \bar{\rho} + \left. \frac{\partial T}{\partial s} \right|_0 \epsilon \bar{s} + \left. \frac{\partial T}{\partial \xi} \right|_0 \epsilon \bar{\xi} \quad (4.10)$$

$$A = A(\rho, s, \xi) = A_0 + \left. \frac{\partial A}{\partial \rho} \right|_0 \epsilon \bar{\rho} + \left. \frac{\partial A}{\partial s} \right|_0 \epsilon \bar{s} + \left. \frac{\partial A}{\partial \xi} \right|_0 \epsilon \bar{\xi} \quad (4.11a)$$

where

$$p_0 \equiv p(\rho_0, s_0, \xi_0)$$

$$T_0 \equiv T(\rho_0, s_0, \xi_0)$$

$$A_0 \equiv A(\rho_0, s_0, \xi_0)$$

$$\left. \frac{\partial p}{\partial \rho} \right|_0 = \frac{\partial p}{\partial \rho}(\rho_0, s_0, \xi_0), \text{ etc.}$$

Since ρ_0, s_0, ξ_0 are assumed to be the values of ρ, s, ξ , respectively, at equilibrium, it follows from (2.9) that A_0 must vanish. By differentiation of (2.8), we find

$$\frac{\partial A}{\partial \rho} = - \left(\frac{\partial e}{\partial \xi} \right) - \rho \frac{\partial^2 e}{\partial \xi \partial \rho} \quad (4.12)$$

$$\frac{\partial A}{\partial s} = - \rho \frac{\partial^2 e}{\partial \xi \partial s} \quad (4.13)$$

$$\frac{\partial A}{\partial \xi} = - \rho \frac{\partial^2 e}{\partial \xi^2} \quad (4.14)$$

As ρ is always positive, the vanishing A_0 (see (2.13)) implies that

$$\left(\frac{\partial e}{\partial \xi}\right)_0 = 0 \quad (4.15)$$

in the equilibrium state. Using relations (4.12)-(4.15) and neglecting higher order terms, we can rewrite (4.11a) as follows:

$$A = -\rho_0 \left(\frac{\partial^2 e}{\partial \xi \partial \rho}\right)_0 \bar{\epsilon} \bar{\rho} - \rho \left(\frac{\partial^2 e}{\partial \xi \partial s}\right)_0 \bar{\epsilon} \bar{s} - \rho \left(\frac{\partial^2 e}{\partial \xi^2}\right)_0 \bar{\epsilon} \bar{\xi} \quad (4.11b)$$

Differentiating (4.9) and (4.10) with respect to rectangular Cartesian coordinates, x^j , we obtain the following relations

$$\partial_k p = \epsilon \left(\frac{\partial p}{\partial \rho}\right)_0 \partial_k \bar{\rho} + \epsilon \left(\frac{\partial p}{\partial s}\right)_0 \partial_k \bar{s} + \epsilon \left(\frac{\partial p}{\partial \xi}\right)_0 \partial_k \bar{\xi}, \quad (4.16)$$

$$\partial_k T = \epsilon \left(\frac{\partial T}{\partial \rho}\right)_0 \partial_k \bar{\rho} + \epsilon \left(\frac{\partial T}{\partial s}\right)_0 \partial_k \bar{s} + \epsilon \left(\frac{\partial T}{\partial \xi}\right)_0 \partial_k \bar{\xi}, \quad (4.17)$$

$$\partial_i \partial_k T = \epsilon \left(\frac{\partial T}{\partial \rho}\right)_0 \partial_i \partial_k \bar{\rho} + \epsilon \left(\frac{\partial T}{\partial s}\right)_0 \partial_i \partial_k \bar{s} + \epsilon \left(\frac{\partial T}{\partial \xi}\right)_0 \partial_i \partial_k \bar{\xi}. \quad (4.18)$$

Now, we shall use (4.5)-(4.18) to linearize the fundamental equations (4.1)-(4.4). Substituting (4.5) and (4.6) into the continuity equation (4.1), we find that the first order terms multiplying ϵ will lead to the equation

$$\partial_t \bar{\rho} + \rho_0 \partial_j \bar{v}^j = 0. \quad (4.19a)$$

Similarly, by using (4.5), (4.6) and (4.16), we can write (4.2) as

$$\begin{aligned} \partial_t (\epsilon \rho_0 \bar{v}_k + \epsilon^2 \bar{\rho} \bar{v}_k) + \partial_j (\epsilon^2 \rho_0 \bar{v}^j \bar{v}_k + \epsilon^3 \bar{\rho} \bar{v}^j \bar{v}_k) \\ + \epsilon \left(\frac{\partial p}{\partial \rho}\right)_0 \partial_k \bar{\rho} + \epsilon \left(\frac{\partial p}{\partial s}\right)_0 \partial_k \bar{s} + \epsilon \left(\frac{\partial p}{\partial \xi}\right)_0 \partial_k \bar{\xi} = 0 \end{aligned} \quad (4.19b)$$

When the terms involving ϵ^2 and ϵ^3 are neglected, (4.19b) reduces to

$$\rho_0 \partial_t \bar{v}_k + \left(\frac{\partial p}{\partial \rho}\right)_0 \partial_k \bar{\rho} + \left(\frac{\partial p}{\partial s}\right)_0 \partial_k \bar{s} + \left(\frac{\partial p}{\partial \xi}\right)_0 \partial_k \bar{\xi} = 0 \quad (4.20a)$$

In the same manner, Eq. (4.3) can be linearized by substituting (4.7), (4.8),

(4.17) and (4.18) into it. First, we note that by substituting (4.6)-(4.8), (4.17) and (4.18) into (4.3), we obtain

$$\begin{aligned}
& \epsilon(\rho_0 + \epsilon\bar{\rho})\partial_t\bar{s} + \epsilon^2(\rho_0 + \epsilon\bar{\rho})\bar{v}^j\partial_j\bar{s} \\
&= -\frac{a^{ik}}{(T_0 + \epsilon\beta)^3} \epsilon \left\{ \left(\frac{\partial T}{\partial \rho} \right)_o \partial_i \partial_k \bar{\rho} + \left(\frac{\partial T}{\partial s} \right)_o \partial_i \partial_k \bar{s} + \left(\frac{\partial T}{\partial \xi} \right)_o \partial_i \partial_k \bar{\xi} \right\} \\
&+ \frac{2a^{ik}}{(T_0 + \epsilon\beta)^4} \epsilon^2 \left\{ \left(\frac{\partial T}{\partial \rho} \right)_o \partial_k \bar{\rho} + \left(\frac{\partial T}{\partial s} \right)_o \partial_k \bar{s} + \left(\frac{\partial T}{\partial \xi} \right)_o \partial_k \bar{\xi} \right\} \left\{ \left(\frac{\partial T}{\partial \rho} \right)_o \partial_i \bar{\rho} + \left(\frac{\partial T}{\partial s} \right)_o \partial_i \bar{s} + \left(\frac{\partial T}{\partial \xi} \right)_o \partial_i \bar{\xi} \right\} \\
&+ \frac{1}{T_0 + \epsilon\beta} \epsilon^2 \left\{ -\rho_0 \left(\frac{\partial^2 e}{\partial \xi \partial \rho} \right)_o \bar{\rho} - \rho_0 \left(\frac{\partial^2 e}{\partial \xi \partial s} \right)_o \bar{s} - \rho_0 \left(\frac{\partial^2 e}{\partial \xi^2} \right)_o \bar{\xi} \right\} (\partial_t \bar{\xi} + \epsilon \bar{v}^j \partial_j \bar{\xi}). \tag{4.21}
\end{aligned}$$

where

$$\beta = \left(\frac{\partial T}{\partial \rho} \right)_o \bar{\rho} + \left(\frac{\partial T}{\partial s} \right)_o \bar{s} + \left(\frac{\partial T}{\partial \xi} \right)_o \bar{\xi}. \tag{4.22}$$

If we multiple (4.21) by $(T_0 + \epsilon\beta)^3$ and retain only the terms of first order in ϵ , we obtain the following linear equation

$$\left(\frac{\partial T}{\partial \rho} \right)_o \bar{\Delta} \bar{\rho} + \left(\frac{\partial T}{\partial s} \right)_o \bar{\Delta} \bar{s} + T_0^3 \rho_0 \partial_t \bar{s} + \left(\frac{\partial T}{\partial \xi} \right)_o \bar{\Delta} \bar{\xi} = 0 \tag{4.23a}$$

where

$$\bar{\Delta} = a^{ik} \partial_i \partial_k. \tag{4.24}$$

Replacing ξ , v^j , T , and A in (4.4) by means of (4.5), (4.8), (4.10) and (4.11b), respectively, we obtain

$$\epsilon \partial_t \bar{\xi} + \epsilon^2 \bar{v}^j \partial_j \bar{\xi} = \frac{a^{44}}{T_0 + \epsilon\beta} \epsilon \left\{ -\rho_0 \left(\frac{\partial^2 e}{\partial \xi \partial \rho} \right)_o \bar{\rho} - \rho_0 \left(\frac{\partial^2 e}{\partial \xi \partial s} \right)_o \bar{s} - \rho_0 \left(\frac{\partial^2 e}{\partial \xi^2} \right)_o \bar{\xi} \right\}$$

If we multiply this last equation by $T_0 + \epsilon\beta$ (where β is defined by (4.22)) and retain only terms of first order in ϵ , we find

$$\left. \frac{a^{44}\rho_0}{T_0} \frac{\partial^2 e}{\partial \xi \partial \rho} \right)_0 \bar{\rho} + \left. \frac{a^{44}\rho_0}{T_0} \frac{\partial^2 e}{\partial \xi \partial s} \right)_0 \bar{s} + \partial_t \bar{\xi} + \left. \frac{a^{44}\rho_0}{T_0} \frac{\partial^2 e}{\partial \xi^2} \right)_0 \bar{\xi} = 0 \quad (4.25a)$$

The system of Eqs. (4.19a), (4.20a), (4.23a) and (4.25a) is the linearized form of the basic Eqs. (4.1)-(4.4). Now, noting that all the coefficients in each of the equations are values taken at the equilibrium state, specified by ρ_0 , s_0 , and ξ_0 , we will drop the parenthesis followed by the subscript zero and the subscript zero from the coefficients in the rest of this work. Thus, when we write

$$\left. \frac{\partial p}{\partial \rho} \right)_0, \rho,$$

we shall mean

$$\left. \frac{\partial p}{\partial \rho} \right)_0, \rho_0.$$

In this notation, the linearized system becomes

$$\partial_t \bar{\rho} + \rho \partial_j \bar{v}^j = 0 \quad (4.19b)$$

$$\rho \partial_t \bar{v}_k + \left. \frac{\partial p}{\partial \rho} \right)_0 \partial_k \bar{\rho} + \left. \frac{\partial p}{\partial s} \right)_0 \partial_k \bar{s} + \left. \frac{\partial p}{\partial \xi} \right)_0 \partial_k \bar{\xi} = 0 \quad (4.20b)$$

$$\left. \frac{\partial T}{\partial \rho} \right)_0 \bar{\Delta} \bar{\rho} + \left. \frac{\partial T}{\partial s} \right)_0 \bar{\Delta} \bar{s} + T^3 \rho \partial_t \bar{s} + \left. \frac{\partial T}{\partial \xi} \right)_0 \bar{\Delta} \bar{\xi} = 0 \quad (4.23b)$$

$$K \left. \frac{\partial^2 e}{\partial \xi \partial \rho} \right)_0 \bar{\rho} + K \left. \frac{\partial^2 e}{\partial \xi \partial s} \right)_0 \bar{s} + \partial_t \bar{\xi} + K \left. \frac{\partial^2 e}{\partial \xi^2} \right)_0 \bar{\xi} = 0 \quad (4.25b)$$

where

$$K \equiv \frac{a^{44}\rho}{T}$$

Now, we shall eliminate \bar{v}^j and \bar{v}_j from (4.19b) and (4.20b). Taking the partial derivative of (4.19b) with respect to time, we find since ρ is constant

$$\partial_t \partial_t \bar{\rho} + \partial_t \partial_j \bar{v}^j = 0 \quad (4.19c)$$

Then, we form the divergence of (4.20b) and obtain

$$\rho g^{ik} \partial_t \partial_i \bar{v}_k + \frac{\partial p}{\partial \rho} g^{ik} \partial_i \partial_k \bar{\rho} + \frac{\partial p}{\partial s} g^{ik} \partial_k \partial_i \bar{s} + \frac{\partial p}{\partial \xi} g^{ik} \partial_i \partial_k \bar{\xi} = 0 \quad (4.20c)$$

where g^{ik} are the contravariant components of the metric tensor. Since g^{ik} is independent of time and $\partial_j g^{ik}$ vanishes, it is clear from (4.19c) that

$$\rho g^{jk} \partial_t \partial_j \bar{v}_k = -\partial_t \partial_t \bar{\rho} \quad (4.19d)$$

Thus, by eliminating $\rho \partial_t \partial_j \bar{v}^j$ from (4.20c) by use of (4.19d), we find

$$-\partial_{tt} \bar{\rho} + \frac{\partial p}{\partial \rho} \Delta \bar{\rho} + \frac{\partial p}{\partial s} \Delta \bar{s} + \frac{\partial p}{\partial \xi} \Delta \bar{\xi} = 0 \quad (4.26)$$

where

$$\begin{aligned} \partial_{tt} &\equiv \frac{\partial^2}{\partial t^2} \\ \Delta &\equiv g^{ij} \partial_i \partial_j \equiv g^{ij} \frac{\partial^2}{\partial x^i \partial x^j} \end{aligned} \quad (4.27)$$

We shall consider (4.23b), (4.25b) and (4.26) in our future work. It is convenient to write these equations in the matrix form

$$\begin{pmatrix} -\partial_{tt} + \frac{\partial p}{\partial \rho} \Delta & \frac{\partial p}{\partial s} \Delta & \frac{\partial p}{\partial \xi} \Delta \\ K \frac{\partial^2 e}{\partial \xi \partial \rho} & K \frac{\partial^2 e}{\partial \xi \partial s} & \partial_t + K \frac{\partial^2 e}{\partial \xi^2} \\ \frac{\partial T}{\partial \rho} \bar{\Delta} & \frac{\partial T}{\partial s} \bar{\Delta} + T^3 \rho \partial_t & \frac{\partial T}{\partial \xi} \bar{\Delta} \end{pmatrix} \begin{pmatrix} \bar{\rho} \\ \bar{s} \\ \bar{\xi} \end{pmatrix} = 0 \quad (4.28)$$

In the following work, we shall be only concerned with monochromatic waves. We assume that each of the quantities, $\bar{\rho}, \bar{s}, \bar{\xi}$ is a constant multiplied by $e^{-i(\omega t - b_k x^k)}$, where ω is the frequency, b_k is a component of wave

vector, and ω and b_k may be complex.¹⁰ Thus, we write

$$\begin{aligned}\bar{\rho} &= \rho \exp i(\omega t - b_k x^k) \\ \bar{s} &= s \exp i(\omega t - b_k x^k) \\ \bar{\xi} &= \xi \exp i(\omega t - b_k x^k)\end{aligned}\tag{4.29}$$

where ρ, s, ξ are constant. Therefore, we find that derivatives of $\bar{\rho}, \bar{s}, \bar{\xi}$ are (see (4.24) and (4.27))

$$\partial_t \bar{\rho} = -i\omega \bar{\rho}, \quad \partial_t \bar{s} = -i\omega \bar{s}, \quad \partial_t \bar{\xi} = -i\omega \bar{\xi};\tag{4.30}$$

$$\partial_{tt} \bar{\rho} = -\omega^2 \bar{\rho}, \quad \partial_{tt} \bar{s} = -\omega^2 \bar{s}, \quad \partial_{tt} \bar{\xi} = -\omega^2 \bar{\xi};\tag{4.31}$$

$$\begin{aligned}\Delta \bar{\rho} &= -J \bar{\rho}, \\ \Delta \bar{s} &= -J \bar{s}, \\ \Delta \bar{\xi} &= -J \bar{\xi},\end{aligned}\tag{4.32}$$

where

$$J \equiv b^k b_k;\tag{4.33}$$

and

$$\begin{aligned}\bar{\Delta} \bar{\rho} &= -I \bar{\rho} \\ \bar{\Delta} \bar{s} &= -I \bar{s} \\ \bar{\Delta} \bar{\xi} &= -I \bar{\xi},\end{aligned}\tag{4.34}$$

where

$$I \equiv a^{ik} b_i b_k.\tag{4.35}$$

By use of (4.30)-(4.32) and (4.34), the matrix equation (4.28) can be written in terms of ω , I, and J as follows:

$$\begin{pmatrix} \omega^2 - \frac{\partial p}{\partial \rho} J & - \frac{\partial p}{\partial s} J & - \frac{\partial p}{\partial \xi} J \\ K \frac{\partial^2 e}{\partial \xi \partial \rho} & K \frac{\partial^2 e}{\partial \xi \partial s} & - i\omega + K \frac{\partial^2 e}{\partial \xi^2} \\ - \frac{\partial T}{\partial \rho} I & - \frac{\partial T}{\partial s} I - T^3 \rho i \omega & - \frac{\partial T}{\partial \xi} I \end{pmatrix} \begin{pmatrix} \bar{\rho} \\ \bar{s} \\ \bar{\xi} \end{pmatrix} = 0 \quad (4.36)$$

In order that a non-trivial solution of Eq. (4.32) exist, the following condition must be satisfied.

$$\det \begin{pmatrix} \omega^2 - \frac{\partial p}{\partial \rho} J & - \frac{\partial p}{\partial s} J & - \frac{\partial p}{\partial \xi} J \\ K \frac{\partial^2 e}{\partial \xi \partial \rho} & K \frac{\partial^2 e}{\partial \xi \partial s} & - i\omega + K \frac{\partial^2 e}{\partial \xi^2} \\ - \frac{\partial T}{\partial \rho} I & - \frac{\partial T}{\partial s} I - T^3 \rho i \omega & - \frac{\partial T}{\partial \xi} I \end{pmatrix} = 0 \quad (4.37)$$

Expanding this determinant and arranging the terms in ascending powers of ω , we obtain

$$\begin{aligned} & \left(\frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi \partial s} \frac{\partial T}{\partial \xi} + \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi \partial \rho} \frac{\partial T}{\partial s} + \frac{\partial^2 e}{\partial \xi^2} \frac{\partial p}{\partial s} \frac{\partial T}{\partial \rho} - \frac{\partial p}{\partial \xi} \frac{\partial T}{\partial \rho} \frac{\partial^2 e}{\partial \xi \partial s} \right. \\ & \quad \left. - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \frac{\partial T}{\partial s} - \frac{\partial T}{\partial \xi} \frac{\partial p}{\partial s} \frac{\partial^2 e}{\partial \xi \partial \rho} \right) IJK + \left(- \frac{\partial p}{\partial s} \frac{\partial T}{\partial \rho} + \frac{\partial p}{\partial \rho} \frac{\partial T}{\partial s} \right) IJ\omega i \\ & \quad + \left(\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \right) \omega KJT^3 \rho i \\ & \quad + \left(- KI \frac{\partial^2 e}{\partial \xi \partial s} \frac{\partial T}{\partial \xi} + KI \frac{\partial^2 e}{\partial \xi^2} \frac{\partial T}{\partial s} - T^3 \rho J \frac{\partial p}{\partial \rho} \right) \omega^2 \\ & \quad - \left(I \frac{\partial T}{\partial s} - K\rho T^3 \frac{\partial^2 e}{\partial \xi^2} \right) \omega^3 i + T^3 \rho \omega^4 = 0 \end{aligned} \quad (4.38)$$

We note that the portion in the parenthesis of the first term is just the following Jacobian

$$\begin{aligned}
& - \left\{ \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi \partial s} \frac{\partial T}{\partial \xi} + \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi \partial \rho} \frac{\partial T}{\partial s} + \frac{\partial^2 e}{\partial \xi^2} \frac{\partial p}{\partial s} \frac{\partial T}{\partial \rho} - \frac{\partial p}{\partial \xi} \frac{\partial T}{\partial \rho} \frac{\partial^2 e}{\partial \xi \partial s} \right. \\
& \left. - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \frac{\partial T}{\partial s} - \frac{\partial T}{\partial \xi} \frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} \right\} = \frac{\partial \left(\frac{\partial e}{\partial \xi}, p, T \right)}{\partial (\rho, s, \xi)} \tag{4.39}
\end{aligned}$$

and the portion in the parenthesis of the second term is another Jacobian

$$- \frac{\partial p}{\partial s} \frac{\partial T}{\partial \rho} + \frac{\partial p}{\partial \rho} \frac{\partial T}{\partial s} = \frac{\partial (p, T)}{\partial (\rho, s)} \tag{4.40}$$

Thus, Eq. (4.38) can be written in the simpler form

$$\begin{aligned}
& - K \frac{\partial \left(\frac{\partial e}{\partial \xi}, p, T \right)}{\partial (\rho, s, \xi)} IJ + i \frac{\partial (p, T)}{\partial (\rho, s)} IJ\omega \\
& + i \left(\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \right) \omega K \rho T^3 J \\
& + \left(- KI \frac{\partial^2 e}{\partial \xi \partial s} \frac{\partial T}{\partial \xi} + KI \frac{\partial^2 e}{\partial \xi^2} \frac{\partial T}{\partial s} - T^3 \rho J \frac{\partial p}{\partial \rho} \right) \omega^2 \\
& + i \left(\frac{\partial^2 e}{\partial \xi^2} K T^3 \rho - \frac{\partial T}{\partial s} I \right) \omega^3 + T^3 \rho \omega^4 = 0 \tag{4.41}
\end{aligned}$$

In order to study the properties of small perturbed wave motions governed by (4.41), we shall consider the case of plane waves. In such a case, $\bar{\rho}, \bar{s}, \bar{\xi}$, and \bar{v}_k depend on only $x^1 = x$ and t . Thus, (4.33) and (4.35) become

$$J = \bar{b}^1 \bar{b}^1 \equiv k^2 \tag{4.42}$$

$$I = a^{11} b^1 b^1 \equiv a^{11} k^2 \tag{4.43}$$

and k is the wave number.¹⁰ Hence, Eq. (4.41) becomes

$$\begin{aligned}
& - K \frac{\partial \left(\frac{\partial e}{\partial \xi}, p, T \right)}{\partial (\rho, s, \xi)} a^{11} k^4 + i a^{11} \frac{\partial (p, T)}{\partial (\rho, s)} k^4 \omega \\
& + i \left(\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \right) k^2 \omega K \rho T^3 \\
& + \left(- K \frac{\partial^2 e}{\partial \xi \partial s} \frac{\partial T}{\partial \xi} a^{11} + K \frac{\partial^2 e}{\partial \xi^2} \frac{\partial T}{\partial s} a^{11} - \frac{\partial p}{\partial \rho} T^3 \rho \right) \omega^2 k^2 \\
& + i K \rho \frac{\partial^2 e}{\partial \xi^2} \omega^3 - i \frac{\partial T}{\partial s} a^{11} k^2 \omega^3 + T^3 \rho \omega^4 = 0
\end{aligned} \tag{4.44}$$

Equation (4.44) is a quadratic relation in k^2 with complex coefficients. For any given ω , we can find two roots of k^2 . It is important to note in our future work that the following two limiting values of ω, k will be studied: (1) ω approaches zero and k approaches zero; (2) ω approaches infinity as k approaches infinity. We assume a^{11} is finite and shall discuss the solutions of (4.44) in the following three cases.

Case 1: $a^{11} = 0$

In view of (3.2), we note that $a^{11} = 0$ means no heat conduction. Equation (4.44) will reduce to

$$- \frac{\partial p}{\partial \rho} \omega^2 k^2 + \omega^4 + i \omega k \left\{ \left(\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \right) + \frac{\partial^2 e}{\partial \xi^2} \omega^2 \right\} = 0 \tag{4.45a}$$

or in an alternative form,

$$\left(\frac{\omega^2}{k^2} - \frac{\partial p}{\partial \rho} \right) \omega + i K \left\{ \left(\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \right) + \frac{\partial^2 e}{\partial \xi^2} \frac{\omega^2}{k^2} \right\} = 0 \tag{4.45b}$$

The two limiting speeds obtained by Broer,¹ and Stupochenko, Stakhanov,² can be found from (4.45b). First, when ω approaches zero, but ω^2/k^2 remains finite, (4.45b) becomes

$$\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} + \frac{\partial^2 e}{\partial \xi^2} \frac{\omega^2}{k^2} = 0 \tag{4.46a}$$

Or,

$$\frac{\omega^2}{k} = \frac{\partial p}{\partial \rho} - \frac{\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho}}{\frac{\partial^2 e}{\partial \xi^2}} \quad (4.46b)$$

where ω^2/k^2 is the square of the speed of propagation.¹⁰ A second limiting speed can be obtained by allowing ω to approach infinity but ω^2/k^2 to remain finite. In this case, Eq. (4.45b) reduces to

$$\frac{\omega^2}{k^2} = \frac{\partial p}{\partial \rho} \quad (4.47)$$

which is the square of the ordinary sonic speed.

Case 2: $K = 0$

In view of (3.3) and (4.25c), it is clear that $K = 0$ means that no chemical reaction is taking place. In this case (4.44) becomes

$$i\omega a^{11} \left\{ \frac{\partial(p,T)}{\partial(\rho,s)} k^4 - \omega^2 k^2 \frac{\partial T}{\partial s} \right\} + T^3 \rho \left(\omega^2 - k^2 \frac{\partial p}{\partial \rho} \right) \omega^2 = 0 \quad (4.48)$$

Dividing this equation by ω/T^2 and multiplying it by $-i$, we obtain

$$\frac{a^{11}}{T^2} \frac{\partial(p,T)}{\partial(\rho,s)} k^4 - \frac{a^{11}}{T^2} \omega^2 k^2 \frac{\partial T}{\partial s} - T \rho i \omega^3 + k^2 i \omega \frac{\partial p}{\partial \rho} T \rho = 0 \quad (4.49a)$$

Now, we shall show that Eq. (4.49a) is a general eigenvalue equation of monochromatic plane waves for an inviscid, heat-conducting compressible fluid. When Fourier's heat conduction formula

$$W_1 = \kappa \partial_1 T = \kappa \frac{\partial T}{\partial x}, \quad (4.50)$$

is used to replace (3.2) and when the fluid is considered to be an ideal gas, (4.49a) will reduce to the form found in texts on compressible fluid flow (Ref. 11, p. 120).

Some results from thermodynamics for an ideal gas are listed below.⁷

$$\left(\frac{\partial p}{\partial \rho}\right)_s = \gamma RT \quad (4.51)$$

$$\left(\frac{\partial T}{\partial s}\right)_\rho = \frac{T}{c_v} \quad (4.52)$$

$$\left(\frac{\partial T}{\partial \rho}\right)_s = \frac{T}{\rho} (\gamma - 1) \quad (4.53)$$

$$\left(\frac{\partial p}{\partial s}\right)_\rho = \frac{R\rho T}{c_v} \quad (4.54)$$

where R is the idea gas constant, c_v is the specific heat capacity at constant volume, c_p is the specific heat capacity at constant pressure, and

$$\gamma = \frac{c_p}{c_v}, \quad R = c_p - c_v \quad (4.55)$$

Therefore, by use of (4.45)-(4.48), we have

$$\frac{\partial(p, T)}{\partial(\rho, s)} = \left(\frac{\partial p}{\partial \rho}\right)_s \left(\frac{\partial T}{\partial s}\right)_\rho - \left(\frac{\partial p}{\partial s}\right)_\rho \left(\frac{\partial T}{\partial \rho}\right)_s = T^2(\gamma - 1) \quad (4.56)$$

Also, a comparison of (4.50) with (3.2) for the plane wave case gives

$$\kappa = \frac{a^{11}}{T^2} \quad (4.57)$$

Equations (4.47), (4.48), (4.52) and (4.53) enable us to rewrite (4.45a) in the following form

$$\frac{\kappa}{\rho} k^4 - \left(\frac{\kappa\omega^2}{\rho} - i\omega c_p\right) k^2 - \frac{i\omega^2}{T(\gamma-1)} = 0 \quad (4.58)$$

which has been given by Pai (Ref. 11, p. 120).

Again, we go back to Eq. (4.49a), and divide it by ωk^4 . We obtain

$$ia^{11} \left\{ \frac{\partial(p, T)}{\partial(\rho, s)} - \frac{\omega^2}{k^2} \frac{\partial T}{\partial s} \right\} + T^3 \rho \left(\frac{\omega^2}{k^2} - \frac{\partial p}{\partial \rho} \right) \frac{\omega^2}{k^2} = 0 \quad (4.49b)$$

Limiting speeds corresponding to high and low frequencies can be found by use of (4.49b). When a_{11} is finite and ω approaches zero, but ω^2/k^2 remains finite, then ω/k^2 will approach infinity. Hence (4.49b) becomes

$$\frac{\omega^2}{k^2} = \left(\frac{\partial p}{\partial \rho} \right)_s, \quad (4.59)$$

which is the square of the sonic speed. When ω approaches infinity, but ω^2/k^2 remains finite, then ω/k^2 will approach zero. Then, (4.49b) becomes

$$\frac{\omega^2}{k^2} = \left(\frac{\partial p}{\partial \rho} \right)_s - \frac{\frac{\partial p}{\partial s} \frac{\partial T}{\partial \rho}}{\frac{\partial T}{\partial s}} \quad (4.60)$$

Substituting relations (4.51)-(4.54) into (4.60) we have

$$\frac{\omega^2}{k^2} = kT \quad (4.61)$$

for ideal gas. The speed propagation is about two thirds of ordinary sonic speed.

Case 3: $a_{11} \neq 0$, $K \neq 0$ and both are finite

This is the general case. Equation (4.44) is, of course, the governing equation for such a wave motion. For any given complex ω , there corresponds two values of k which represent two modes of wave motion. We let

$$\omega = \omega_1 + i\omega_2 \quad (4.62)$$

$$k = k_1 + ik_2$$

where ω_1 , ω_2 , k_1 , and k_2 are all real. If k is one of the values corresponding to ω , then

$$-i(\omega t - kx) = (\omega_2 t - k_2 x) - i(\omega_1 t - k_1 x)$$

Thus, $\exp(\omega_2 t - k_2 x)$ is the amplitude and $\omega_1 t - k_1 x$ is the angle. If ω_2 is positive and x is fixed, the amplitude of the wave will increase as time in-

creases; when ω_2 is negative, the amplitude will decay as time increases. In the same manner, when k_2 is positive and t is fixed, the wave will decay as x increases and when k_2 is negative, the amplitude of the wave will increase as x increases.

Two limiting speeds corresponding to high and low frequencies can be obtained from (4.44). If we divide (4.44) by k^4 and rearrange terms, we obtain

$$\begin{aligned}
& T^3 \rho \frac{\omega^4}{k^4} + i \frac{\omega^2}{k^2} K T^3 \rho \left(\frac{\partial^2 e}{\partial \xi^2} \frac{\omega^2}{k^2} + \frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} \right) \\
& - a^{11} i \omega \left(\frac{\omega^2}{k^2} \frac{\partial T}{\partial s} - \frac{\partial(p, T)}{\partial(\rho, s)} \right) + \left(-K \frac{\partial^2 e}{\partial \xi \partial s} \frac{\partial T}{\partial \xi} a^{11} + K \frac{\partial^2 e}{\partial \xi^2} \frac{\partial T}{\partial s} a^{11} \right. \\
& \left. - \frac{\partial p}{\partial \rho} T^3 \rho \right) \frac{\omega^2}{k^2} - K \frac{\partial \left(\frac{\partial e}{\partial \xi}, p, T \right)}{\partial(\rho, s, \xi)} a^{11} = 0
\end{aligned} \tag{4.63}$$

When ω approaches zero, but ω^2/k^2 remains finite, then each term of Eq. (4.63) is finite except the second term, which goes to infinity unless the factor in the parenthesis approaches to zero. Thus, we find for the limit speed

$$\frac{\partial^2 e}{\partial \xi^2} \frac{\omega^2}{k^2} + \frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho} - \frac{\partial p}{\partial \rho} \frac{\partial^2 e}{\partial \xi^2} = 0 \tag{4.64}$$

Or, the limiting speed corresponding to low frequency is

$$\frac{\omega^2}{k^2} = \frac{\partial p}{\partial \rho} - \frac{\frac{\partial p}{\partial \xi} \frac{\partial^2 e}{\partial \xi \partial \rho}}{\frac{\partial^2 e}{\partial \xi^2}} \tag{4.65}$$

This is the limiting speed due to Broer, and Stupochenko and Stakhanov. When ω approaches infinity, then each term in (4.63) is finite, except the third term which goes to infinity unless the factor in the parenthesis is zero. Thus, we must have

$$\frac{\omega^2}{k^2} = \frac{\frac{\partial(p, T)}{\partial(\rho, s)}}{\frac{\partial T}{\partial s}} = \frac{\partial p}{\partial \rho} - \frac{\frac{\partial p}{\partial s} \frac{\partial T}{\partial \rho}}{\frac{\partial T}{\partial s}} \tag{4.66}$$

This is the limiting speed of high frequency which we just obtained for the case without chemical reaction (see (4.60)). Now, we should point out that

the values of ω^2/k^2 in (4.65) and (4.66) are consistent with (4.63) for ω approaching zero and infinity, respectively. In the first case, we multiply (4.63) by ω and set ω^2/k^2 equal to the value given by (4.65). Then, the second term on the left hand side will be identically zero. The rest of the left hand side will be some finite value times ω . If we allow ω to approach zero, we will have zero on both sides. In the second case, we need only divide (4.63) by ω and replace ω^2/k^2 by the limit value given by (4.66). A similar argument will lead to the vanishing of both sides of (4.63).

In Broer's paper,¹ he has pointed out that at extremely high frequency, the chemical reaction is frozen, i.e., no chemical reaction is taking place and A must vanish. Physically, this means that the molecules under consideration move with a speed so fast that there is not enough time for different kinds of molecules to rearrange their atoms to form a new molecule. Thus, in the neighborhood of this high frequency wave front, the fluid ceases to react. The disturbance will then act as in an ordinary fluid. Therefore, it is not surprising that we obtain the sonic speed for the high frequency limit in the non-heat-conduction case. Also, it is not surprising that in the heat-conduction case, the limiting speed of the high frequency in Case 3 (chemical reaction, see (4.66)) is equal to that in Case 2 (non-chemical reaction, (see (4.60))).

If in the high frequency limit, the chemical reaction is frozen, we may consider ξ as a constant. It is interesting to point out that the thermodynamical expression for ω^2/k^2 in (4.60) or (4.66) can be reduced to a very simple form. Let us note that p is a function of ρ and T when ξ is constant. In terms of our previous notation, we have

$$\frac{dp}{dt} = \left(\frac{\partial p}{\partial \rho} \right)_T \frac{d\rho}{dt} + \left(\frac{\partial p}{\partial T} \right)_\rho \frac{dT}{dt} \quad (4.67)$$

Or, considering p to be a function of ρ and s , we have

$$\frac{dp}{dt} = \left(\frac{\partial p}{\partial \rho} \right)_s \frac{d\rho}{dt} + \left(\frac{\partial p}{\partial s} \right)_\rho \frac{ds}{dt} \quad (4.68)$$

Eliminating dp/dt between (4.67) and (4.68), we find

$$0 = \left[\left(\frac{\partial p}{\partial \rho} \right)_T - \left(\frac{\partial p}{\partial \rho} \right)_s \right] \frac{d\rho}{dt} + \left(\frac{\partial p}{\partial T} \right)_\rho \frac{dT}{dt} - \left(\frac{\partial p}{\partial s} \right)_\rho \frac{ds}{dt} \quad (4.69)$$

Now, we express dT/dt in terms of $d\rho/dt$ and ds/dt as follows

$$\frac{dT}{dt} = \left(\frac{\partial T}{\partial \rho}\right)_s \frac{d\rho}{dt} + \left(\frac{\partial T}{\partial s}\right)_\rho \frac{ds}{dt} \quad (4.70)$$

Substituting the value of dT/dt given at (4.70) into (4.69), we obtain

$$0 = \left[\left(\frac{\partial p}{\partial \rho}\right)_T - \left(\frac{\partial p}{\partial \rho}\right)_s + \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial T}{\partial \rho}\right)_s \right] \frac{d\rho}{dt} + \left[\left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial T}{\partial s}\right)_\rho - \left(\frac{\partial p}{\partial s}\right)_\rho \right] \frac{ds}{dt} \quad (4.71)$$

Since ρ and s are independent parameters, Eq. (4.71) implies

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \left(\frac{\partial p}{\partial \rho}\right)_s - \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial T}{\partial \rho}\right)_s \quad (4.72)$$

$$\left(\frac{\partial p}{\partial s}\right)_\rho = \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial T}{\partial s}\right)_\rho \quad (4.73)$$

Eliminating $\partial p/\partial T)_\rho$ between (4.72) and (4.73) we have

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \left(\frac{\partial p}{\partial \rho}\right)_s - \frac{\left(\frac{\partial T}{\partial \rho}\right)_s \left(\frac{\partial p}{\partial s}\right)_\rho}{\left(\frac{\partial T}{\partial s}\right)_\rho} \quad (4.74)$$

Therefore, Eqs. (4.60) or (4.66) can be written as

$$\frac{\omega^2}{k^2} = \left(\frac{\partial p}{\partial \rho}\right)_T \quad (4.75)$$

5. ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Professor N. Coburn for his suggestions and criticisms.

6. REFERENCES

1. Broer, L. J. F., "Characteristics of the Equations of Motion of a Reacting Gas." Jour. of Fluid, Mech., 4, 276-283 (1958).
2. Stupochenko, E. V., I. P. Stakhanov., "The Equations of Relaxation Hydrodynamics" Soviet phys. Doklady, 4, 782-785 (1960).
3. Coburn, N., "The Limiting Speeds of Relaxation Hydrodynamics." Jour. of Math. Anals. and Appl., 5, 2 (1962).
4. Prigogine, I., "Introduction to Irreversible Thermodynamics." Interscience Press, N. Y. (1961).
5. DeGroot, S. R., and P. Mazur., "Non-equilibrium Thermodynamics." North Holland Co., Holland (1962).
6. Prigogine, I., S. R. Defay., "Chemical Thermodynamics" Longmans, London (1956).
7. Sears, F. W., "An Introduction to Thermodynamics, the Kinetic Theory of Gases and Statistic Mechanics." Addison-Wesley, Mass., (1953).
8. Von Mises, R., "Mathematical Theory of Compressible of Fluid Flow." Academic Press, New York (1958).
9. Panofsky, W. K. H. and Philips, M., "Classical Electricity and Magnetism," Addison-Wesley, Mass., (1956).
10. Landan, L. D. and Lifshitz, E. M., "Fluid Mechanics," Addison-Wesley, Mass., (1959).
11. Pai, S. I., "Magneto-gasdynamics and Plasma Dynamics," Prentice-Hall (1962).

