

ABSORPTION AND DISPERSION OF SOUND IN REACTING AND RELAXING FLUIDS

THESIS BY

WILLIAM PHILLIP HELMAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

1960

ACKNOWLEDGEMENTS

I would like to thank Dr. R. M. Mazo for suggesting this problem, and for his help and patience while the work was being done. I would also like to thank Dr. N. R. Davidson for several helpful discussions.

I would also like to thank the Sloan Foundation for a summer fellowship (1959) and the Institute for two Assistantships.

ABSTRACT

The hydrodynamic equations for a chemically reacting and internally relaxing fluid are obtained in a suitable form, and are then used to find the dispersion and absorption of plane infinitesimal sound waves. Only the case of no viscosity, heat conduction, and diffusion is considered. It is shown that the interference effects between relaxation processes are not, in general, negligible compared to the relaxation effects themselves. A specific example, that of oxygen gas at 2500° K is considered giving an idea of the relative magnitudes of the several effects which are involved.

TABLE OF CONTENTS

INTRODUCTION	1
HYDRODYNAMICS	5
SONIC PROPAGATION	13
CALCULATIONS	19
REFERENCES	28

INTRODUCTION

In spite of activity in the field of ultrasonics since Einstein's original suggestion of their application to chemical reaction rates^(1,2,3) there does not seem to be an adequate treatment of the interference between the two principle mechanisms of internal relaxation, thermal relaxation and chemical relaxation (chemical reaction). In most treatments of ultrasonics which do treat both of these phenomena, they are covered separately, and it is at most implied that these may occur together, in which case they are presumably to be treated as parallel processes, that is processes which occur simultaneously but which do not directly effect one another.

In general we may divide the processes which effect sonic propagation into two broad groups, external and internal. The external processes include dynamic effects, heat conduction, diffusion, and viscosity. The thermal relaxations include the slow energy exchange between the several degrees of freedom, principally between the molecular translational degree and the rotations and the vibrations of the molecule, and are treated as though they consisted of independent fluids occupying the same physical space, but only weakly coupled with each other, and not of necessity in equilibrium with each other. The internal relaxations are in general more sensitive to the structure of the molecules than are the external processes, and it is clear that a chemical reaction may, by means of changing the molecular structure, drastically alter or destroy a particular mode of vibration or rotation. In the case of the dissociation of

diatomic molecules we shall lose all of our rotational and vibrational degrees of freedom upon reaction. For this reason it is desirable to examine the coupling between the chemical reaction and the thermal degrees of freedom.

When we speak of a relaxation process we here refer to systems which approach equilibrium in a certain manner, according to definite rate laws. The rate law which we refer to is the familiar linear decay

$$-\frac{\partial u}{\partial t} = \frac{1}{\tau} (u - u_0)$$

for the arbitrary quantity u . u_0 is the equilibrium of u in the sense of a small object approaching thermal equilibrium with an infinite heat bath at a temperature corresponding to the energy content u_0 . The general solution to this equation is well known, and is

$$u(t) = [u(t=0) - u_0] e^{-t/\tau} + u_0$$

If however we impress upon this system the requirement that the equilibrium value u_0 is made to vary periodically with time, as will be the case for sonic waves, so that $u_0 = Ue^{i\omega t}$, we find that the general solution takes the form

$$u(t) = \frac{U}{1 + i\omega\tau} e^{i\omega t} + u' e^{-t/\tau}$$

The general solution consists of two parts, the first is the steady state wave solution which is the part we are interested in for sonic studies, and the second part decays to zero exponentially, representing a transient response to the initial conditions. In our treatment we shall systematically

assume that the transient has had time to decay to zero, so that we need consider only the steady state wave solution.

We may write the coefficient of $U e^{i\omega t}$ of the steady state solution in the form $(1 - i\omega\tau) / (1 + \omega^2\tau^2)$. In this form we may see that if $\omega\tau$ is small that the coefficient is essentially unity, if $\omega\tau$ is large the coefficient is very small and almost purely imaginary, and as $\omega\tau$ increases the relative size of the imaginary part to the real part increases, becoming equal at $\omega\tau = 1$ although the absolute value of the term continuously decreases. The complex character of the coefficient represents a phase shift which results in the absorption of the sonic wave by internal relaxation. We may consider the two waves which are somewhat out of phase to interfere destructively by means of the weak coupling of the energy exchange. We may expect this form of absorption to occur most strongly in the region of $\omega\tau = 1$, as at low frequencies there is only a small phase difference, and at high frequencies there is negligible amplitude for the energy u .

Throughout the following discussion we shall make the assumption that we may neglect the dynamic effects of viscosity, diffusion, and heat conduction. These effects may not always be negligible in practice, but their inclusion here would unduely cloud what we are attempting to show. For all discussions on ultrasonics proper we shall assume that we are dealing with plane waves traveling in the x direction, and with small (infinitesimal) amplitude.

There seems to be no great unity in the manner in which the final equations for the sonic propagation are obtained. However, it seems that when one wishes to investigate several simultaneously occurring processes it is advantageous to use a method similar to the one used by Mazo⁽⁴⁾, as

it provides a uniform procedure which more clearly suggests the algebraic steps which are to be taken. In the following presentation we shall utilize this procedure, and we shall try to use the language of chemical thermodynamics, and methods in keeping with its spirit where possible.

HYDRODYNAMICS

To begin our study of the ultrasonic effects on a fluid due to simultaneous chemical reaction and internal relaxations we must first obtain the appropriate hydrodynamic equations for the fluid. Hydrodynamic equations for such fluids have been developed, see for example Wood and Kirkwood⁽⁵⁾, however, these equations are not in the form which we should prefer for our present purposes. Thus we shall develop our own equations in a suitable form.

In this development we shall assume an arbitrary number of thermal degrees of freedom, labeled i , and an arbitrary number of chemical reactions, labeled α .

We shall single out one of the thermal degrees of freedom, that degree containing the translational degree along with any other rotational and vibrational degrees which may remain in thermodynamic equilibrium with it for the entire range of experimental conditions considered, and denote this degree of freedom as the external degree of freedom, and set $i = 1$ for this degree. The other thermal degrees will be the internal degrees with $i = 2, 3$, etc. and are those usually vibrational degrees which are so weakly coupled with the translational degree that they are not able to maintain thermodynamic equilibrium, or remain undetectibly close to that equilibrium, with the translational degree for the dynamic conditions imposed upon the system. The classification of the i degrees of freedom is thus seen to be operational in nature. Further it may be seen that in general the internal degrees will represent individual vibrational modes

of a single type of molecule, and will thus have a zero contribution from all but that one component of the mixture, although we may treat them thermodynamically as though they were a property of the fluid as a whole in their hydrodynamic effects.

The notation used for the chemical reaction is that commonly used for the thermodynamic treatment of irreversible processes.⁽⁶⁾ We shall use Greek indices to denote the chemical reaction and Latin indices for the individual components. Thus the α^{th} chemical reaction is written

$$\sum_s \nu_s^\alpha X_s = 0$$

where we may adopt either of the standards, that X_s represents either the number of moles or the mass of the component s in the chemical reaction. We shall adopt the latter standard, so that ν_s^α is the specific stoichiometric coefficient, that is the number of grams of s required to convert 1 gram of the reactants in their proper proportions into one gram of products.

For any extensive property of the system we may write

$$(1) \quad dx_s = \sum_\alpha \nu_s^\alpha \tilde{x}_s d\lambda_\alpha$$

in which \tilde{x}_s is the partial specific value of x for the component s , and the rate of the chemical reaction is $d\lambda_\alpha/dt$. In particular we know that if we consider the mass of a component s , that \tilde{x}_s is unity, and we then obtain

$$dm_s = \sum_\alpha \nu_s^\alpha d\lambda_\alpha$$

We now divide our thermodynamic properties, such as temperature, heat capacity, entropy, etc., according to the thermal degree with which they are associated. Thus we have that T_i is the external temperature, and will be the same for all components, \tilde{S}_{si} is the partial specific entropy of the component s in the i^{th} degree of freedom, and so forth. We have

thus assumed implicitly that there exists thermodynamic equilibrium within each degree of freedom i , although this does not necessarily obtain between the several degrees. The approach to equilibrium between the several degrees will be assumed to obey appropriate relations depending only upon these stated variables.

The assumption of thermodynamic equilibrium within each degree of freedom gives us the i equations defining thermodynamic equilibrium.

$$dE_i = T_i dS_i - \delta_{i1} (Pdv) + \sum_s \mu_{si} dm_s$$

in which the Kroneker delta function δ_{i1} tells us that the external degree alone is dependent upon the state variable V , the specific volume, and it alone specifies the pressure.

Considering for the moment only the internal degree of freedom i , we may choose to specify the state by the internal temperature T_i and the state of the chemical reaction λ_α . Writing the entropy in terms of these variables we may express the entropy change by

$$(3) \quad dS_i = \left(\frac{\partial S_i}{\partial T_i} \right)_\lambda dT_i + \sum_\alpha \left(\frac{\partial S_i}{\partial \lambda_\alpha} \right)_{T, \lambda_\beta} d\lambda_\alpha$$

$$= \left(\frac{\partial S_i}{\partial T_i} \right)_\lambda dT_i + \sum_\alpha \sum_s \nu_s^\alpha \tilde{S}_i d\lambda_\alpha$$

Now $(\partial S_i / \partial T_i)_\lambda$ constitutes the definition of the internal heat capacity, being just C_i / T_i . The chemical potential term of equation 2 may be written in the form

$$\sum_s \mu_{si} dm_s = \sum_\alpha \sum_s \nu_s^\alpha \tilde{F}_{si} d\lambda_\alpha$$

$$= \sum_\alpha \sum_s \nu_s^\alpha \tilde{H}_{si} d\lambda_\alpha - \sum_\alpha \sum_s \nu_s^\alpha T_i \tilde{S}_i d\lambda_\alpha$$

Combining this with equation 3 and substituting into equation 2 we find, for the i^{th} internal degree of freedom

$$(4) \quad dE_i/dt = C_i \frac{dT_i}{dt} + \sum_{\alpha} \sum_{s} \nu_s^{\alpha} \tilde{H}_{si} d\lambda_{\alpha}$$

In as much as the internal degrees are unaffected by the pressure-volume parameter the internal energy and the internal enthalpy will be the same and may be used interchangeably.

We are now in a position where we must make some assumptions as to the actual form of the processes by which the energy content of the internal degree i changes. As is conventional we assume that there is a "leakage" of energy at a rate governed by the difference in the two temperatures T_i and T_j as⁽⁷⁾

$$(5) \quad (\partial E_i / \partial t)_{\lambda_{\alpha}} = C_i Q_i \quad Q_i = \sum_j \frac{T_j - T_i}{\tau_{ij}}$$

τ_{ij} is thus the relaxation time for the process between degrees i and j and is clearly symmetrical with respect to i and j . For most cases it will be only the transfer of energy between the external degree and the given internal degree which will be important, although other cases have been discussed as well.⁽⁸⁾

In addition to the thermal relaxation, however, we must consider the possibility of there being a simultaneous addition of or withdrawal of energy from the degree due to the chemical reaction which we have supposed to be present at the same time.⁽⁹⁾ We may think of the average properties of the molecules which react or are formed in the chemical reaction, say between the collision which forms the "activated complex" and the immediately preceding collision for a molecule, or between the breakup of the "activated complex" and the immediately subsequent collision, and write these special averages for the "activated state" using a special subscript A . We thus define the "activated state" not by its own properties but by the properties of the more stable components of the fluid which produce it.

It is interesting to note that if a single component enters more than one chemical reaction it may have very different activation properties, especially if it is in one case a product and in another case a reactant. In such a case it would be necessary to also designate which reaction one was referring to as well.

In order that the thermodynamic approach to the problem be reasonable we must have that the deviation from equilibrium properties rapidly redistribute among all of the molecules which contain that degree, so that on the whole the deviation from a statistical thermal distribution be small for the fluid as a whole. It is known that in gases this redistribution takes place on the order of a few molecular collisions for the translational degree and on the order of a few tens of collisions for rotational degrees, with the translational degree. Vibrational degrees, however, may take many thousands of collisions for such an equilibrium to be achieved. It is reasonable to assume, however, that for vibrations, resonant collisions may redistribute the excess energy more rapidly than this within the degree. If this is indeed the case we may talk of an internal temperature which only slowly comes into equilibrium with the external (translational) degree temperature.

If in equation 1 we set \tilde{x}_s to be $(\tilde{E}_{is})_A$ we obtain the change of internal energy due to the chemical reaction. Combining this with equation 5, we may obtain a second equation for the rate of change of the internal energy. Equating this expression to equation 4 we may find the rate of change of the internal temperature with time in terms of the properties of the fluid which are assumed to be known and those which we desire to know, in particular the rate of the chemical reaction.

$$(6) \quad C_i \frac{dT_i}{dt} = C_i Q_i + \sum_{\alpha} \sum_s \nu_s^{\alpha} [(\tilde{E}_{si}^2)_A - \tilde{E}_{si}] \dot{\lambda}_{\alpha}$$

In the same manner one may obtain the rates for the external temperature and the pressure (for the latter case one sets the entropy to be a function of the pressure, density, and the extent of the chemical reaction, where as in the former case it is to be a function of the external temperature, density, and the extent of the chemical reaction). In obtaining these relations one makes use of the equations of state as expressed by the coefficients of thermal expansion and of compressibility, which we define as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T_i} \right)_{P, \lambda} \quad K = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, \lambda}$$

In the present case our second equation for the rate of change of the energy content, takes the form of the principle of conservation of energy so that

$$dE_i/dt = dE/dt - \sum'_i dE_i/dt$$

in which the primed summation over i implies that the summation is carried out only over $i \geq 2$. The same, of course, holds for the energies in the "activated state" but due to the way in which they are defined we must set the total energy change there equal to zero.

For the total energy change dE/dt , we make the local assumption that for each small volume element of the fluid the motion is adiabatic, that is that no heat flows across the boundary, and thus that dE is just the pressure-volume work done. If we make use of the equation of continuity, $d\rho/dt = -\rho \nabla \cdot \vec{u}$, we may write for the changes in the external temperature and pressure

$$(7) \quad C_v \frac{dT_i}{dt} = -\sum_i' C_i Q_i + \sum_\alpha \sum_s \nu_s^\alpha [(\tilde{E}_{si})_A - \tilde{H}_{si}] \dot{\lambda}_\alpha \\ - \frac{\beta T_i}{\rho K} \nabla \cdot \dot{\vec{u}} + \frac{\beta T_i}{K} \sum_\alpha \sum_s \nu_s^\alpha \tilde{V}_s \dot{\lambda}_\alpha$$

$$(8) \quad C_v \frac{dP}{dt} = -\beta/K \sum_i' C_i Q_i + \beta/K \sum_\alpha \sum_s \nu_s^\alpha [(\tilde{E}_{si})_A - \tilde{H}_{si}] \dot{\lambda}_\alpha \\ - c_{P/K} \nabla \cdot \dot{\vec{u}} + \rho c_{P/K} \sum_\alpha \sum_s \nu_s^\alpha \tilde{V}_s \dot{\lambda}_\alpha$$

We now have $i + 1$ equations for our $i + 2$ unknowns, the T_i 's, P , and \vec{u} . The remaining equation needed to define the system is just the equation of motion, which for our simple fluid is

$$(9) \quad \rho \frac{d\vec{u}}{dt} = -\nabla P$$

The important hydrodynamic equations are collected in table 1.

$$\frac{d\vec{u}}{dt} = -\nabla P$$

$$C_v \frac{dP}{dt} = -\beta/K \sum_i C_i Q_i + \beta/K \sum_\alpha \sum_s \nu_s^\alpha [(\tilde{E}_{si})_A - \tilde{H}_{si}] \dot{\lambda}_\alpha$$

$$- \frac{C_p}{K} \nabla \cdot \vec{u} + \rho \frac{C_p}{K} \sum_\alpha \sum_s \nu_s^\alpha \tilde{V}_s \dot{\lambda}_\alpha$$

$$C_v \frac{dT_i}{dt} = -\sum_i C_i Q_i + \sum_\alpha \sum_s \nu_s^\alpha [(\tilde{E}_{si})_A - \tilde{H}_{si}] \dot{\lambda}_\alpha$$

$$- \frac{\beta T_i}{\rho K} \nabla \cdot \vec{u} + \frac{\beta T_i}{K} \sum_\alpha \sum_s \nu_s^\alpha \tilde{V}_s \dot{\lambda}_\alpha$$

$$C_i \frac{dT_i}{dt} = C_i Q_i + \sum_\alpha \sum_s \nu_s^\alpha [(\tilde{E}_{si})_A - \tilde{E}_{si}] \dot{\lambda}_\alpha$$

Table 1.

The hydrodynamic equations for a reacting and relaxing fluid.

SONIC PROPAGATION

We shall now proceed to apply the hydrodynamic equations which we have just obtained, to the problem of the ultrasonic properties of the fluid. From this point on we shall, for simplicity and clarity, assume that there is only one internal degree of freedom which we shall continue to denote by the subscript i , and only one chemical reaction allowing us to drop all summations over the index α .

At this point we could insert the appropriate terms for viscosity etc. which work as essentially parallel processes for the most part, but we shall not attempt to include these terms as they would vastly complicate the presentation of what we are endeavoring to show.

We may now consider the chemical reaction rate. We may assume that during the passage of the ultrasonic waves the chemical reaction never deviates greatly from its equilibrium value for the conditions at that part of the wave. It is thus advantageous to express the state of the reaction as its deviation from the equilibrium value λ_0 . Further we shall assume that the rate of the chemical reaction is proportional to its instantaneous deviation from the local equilibrium, and depends only upon the temperature, and the densities of the several components.

$$(10) \quad \lambda = \lambda_0 + \xi$$

$$d\lambda/dt = \dot{\lambda} = -1/\tau_\alpha \quad \xi = -1/\tau_\alpha (\lambda - \lambda_0) = f(T_0, \rho_\alpha)$$

For the reaction rate we shall now adopt the linerization of Kirkwood and Crawford^(10,4). In accord with such a procedure we define

the quantity

$$(11) \quad G_{\alpha\beta} = \left(\frac{\partial \Delta F_{\alpha}}{\partial \lambda_{\beta}} \right)_{T,P} = \sum_r \sum_s \nu_r^{\alpha} \nu_s^{\beta} \left(\frac{\partial \mu_r}{\partial x_s} \right)$$

in which the notation Δx for the extensive quantity x is used to denote the change of that quantity due to the change of the progress variable by one unit, that is $\Delta \lambda = 1 \text{ gm.}$

$$\Delta x = \sum_s \nu_s \tilde{x}_s$$

Keeping only the linear term in a Taylor series expansion, we obtain our reaction rate linearized about the equilibrium value λ_0 .

$$(12) \quad G \dot{\lambda} = \Delta S_i \frac{dT_i}{dt} + \Delta S_i \frac{dT_i}{dt} - \Delta V \frac{dP}{dt}$$

$$\dot{\lambda} = \frac{1}{G} \left[\frac{\Delta H_i}{T_i} \frac{dT_i}{dt} + \frac{\Delta H_i}{T_i} \frac{dT_i}{dt} - \Delta V \frac{dP}{dt} \right]$$

We now impress upon the hydrodynamic equations the requirements of a steady state (after the transients have died out) wave motion. If in the absence of the sound wave the pressure and temperature would attain the values P_0 and T_0 for all T_i , and there would be no flow, $\vec{u} = 0$, we require that in the presence of the steady state sound wave the values which obtain are

$$\vec{u} = \delta \vec{u} \exp \{ i(\omega t - kx) \}$$

$$P = P_0 + \delta P \exp \{ i(\omega t - kx) \}$$

$$T_i = T_0 + \delta T_i \exp \{ i(\omega t - kx) \}$$

The quantities δP , δT_i , and $\delta \vec{u}$, are the complex amplitudes of the variations; often these variations themselves are called excess pressure, etc.

If we now put these values into the hydrodynamic equations and carry out the differentiations, we obtain a set of four linear, homogeneous equations in the excess pressure, temperatures, and velocity. The solution

to these equations requires that the determinant of the coefficients vanish. However, prior to forming this determinant we note that it shall be convenient to write the several terms in terms of the dimensionless variables:

$$(13) \quad (V_o)^2 = \left(\frac{\partial P}{\partial S_{iXr}} \right) = \frac{1}{\rho K_s \omega} = [\text{reference speed of sound high frequency}]^2$$

$$\sigma = \frac{kV_o}{\omega}$$

$$Z_i = \omega \gamma_i$$

$$Z_\alpha = \omega \gamma_\alpha$$

$$\Delta C_{ij} = \frac{(\Delta E_{iA} - \Delta H_i)(\Delta H_j)}{T_j G C_p}$$

$$\frac{\Delta \beta_{iA}}{\beta} = \rho \frac{(\Delta E_{iA} - \Delta H_i)(\Delta V)}{T_i G \beta}$$

$$\frac{\Delta \beta_i}{\beta} = \rho \frac{(\Delta H_i)(\Delta V)}{T_i G \beta}$$

$$\frac{\Delta K}{K} = \rho \frac{(\Delta V)^2}{K G}$$

If we were to attempt to solve the secular determinant as it would now be obtained, we would run into a bit of formidable algebra which at best would be clumsy to use, and at worst would hide the significant terms in a welter of small terms. We shall thus neglect the term $[(\Delta E_{iA} - \Delta H_i)]$, which we hope will be small. The justification for the neglect of this term is that according to present notions about the mechanism of vibrational relaxation, the process goes in a series of steps through the several vibrational quantum levels with successively slower rates of relaxation, so that effectively $(\tilde{E}_i)_A$ should correspond to only a few vibrational levels at most. Now it may be that this is comparable to or even large compared to \tilde{E}_i , however it would be a rather extraordinary case in which this term will not be small compared to the size of the chemical reaction terms related to the external degree. We shall thus neglect the effect of this term from this point on, and we may later examine its effect by an

approximate method.

If we do set this term equal to zero, we see that the relaxation parameters $\frac{\Delta\beta_{iA}}{\beta}$, $\frac{\Delta C_i}{C_p}$, and $\frac{\Delta C_{ii}}{C_p}$ are reduced to zero. The bottom line of our determinant may now be easily eliminated, and simultaneously we arrange our terms so that the internal relaxation time occurs only in the forms $1/(1 + iZ_i)$. If we also take advantage of the thermodynamic relations

$$\frac{\beta^2 \eta_i}{\rho K} = C_p - C_v = R \quad \rho V_o^2 K = C_p/C_v = \gamma$$

we may reduce our determinant to a three by three form.

$$(14) \quad \begin{vmatrix} 1 & -\sigma/\gamma & 0 \\ \gamma\sigma & \frac{-\gamma}{1+iZ_\alpha} \left(\frac{\gamma-1}{\beta} \frac{\Delta\beta_{iA}}{\beta} + \frac{\Delta K}{K} \right) - 1 & \frac{\gamma}{1+iZ_\alpha} \left(\left[\frac{\Delta C_{ii}}{C_p} + \frac{1}{1+iZ_i} \frac{\Delta C_{i\alpha}}{C_p} \right] + \left[\frac{\Delta\beta_i}{\beta} + \frac{1}{1+iZ_i} \frac{\Delta\beta_{i\alpha}}{\beta} \right] \right) \\ & & - \frac{1}{1+iZ_i} \frac{C_i}{C_v} \\ (\gamma-1)\sigma & \frac{-\gamma-1}{1+iZ_\alpha} \left(\frac{\Delta\beta_{iA}}{\beta} + \frac{\Delta K}{K} \right) & \frac{\gamma}{1+iZ_\alpha} \left(\left[\frac{\Delta C_{ii}}{C_p} + \frac{1}{1+iZ_i} \frac{\Delta C_{i\alpha}}{C_p} \right] + \frac{\gamma-1}{\gamma} \left[\frac{\Delta\beta_i}{\beta} + \frac{1}{1+iZ_i} \frac{\Delta\beta_{i\alpha}}{\beta} \right] \right) \\ & & - \frac{1}{1+iZ_i} \frac{C_i}{C_v} - 1 \end{vmatrix}$$

We may now expand the determinant and solve for σ . Upon doing this we obtain a quadratic equation in σ , of the form

$$(15) \quad A\sigma^2 + B = 0$$

$$A = - \left(\frac{1}{1+iZ_\alpha} \left[\frac{\Delta C_{ii}}{C_p} + \frac{1}{1+iZ_i} \frac{\Delta C_{i\alpha}}{C_p} \right] + \frac{1}{1+iZ_i} \frac{C_i}{C_p} + 1 \right)$$

$$B = \frac{\gamma}{1+iZ_\alpha} \left(\left[\frac{\Delta C_{ii}}{C_p} + \frac{1}{1+iZ_i} \frac{\Delta C_{i\alpha}}{C_p} \right] + \frac{\Delta K}{K} + \frac{\gamma-1}{\gamma} \frac{\Delta\beta_{iA}}{\beta} \right.$$

$$\left. - \frac{\gamma-1}{\gamma} \left[\frac{\Delta\beta_i}{\beta} + \frac{1}{1+iZ_i} \frac{\Delta\beta_{i\alpha}}{\beta} \right] \right) + \frac{C_i/C_v}{1+iZ_i} \left(1 + \frac{\Delta K/K}{1+iZ_\alpha} \right) + 1$$

In solving this equation for σ it must be remembered that σ is complex, and we must find both the real and the imaginary parts. In the event that the several parameters are small we may satisfactorily use an approximate method for the solution of this equation. By expanding as power series and keeping only the terms through the first power in the relaxation parameters we obtain an approximate expression for σ .

$$(16) \quad \sigma \approx 1 + \frac{1 - iZ_\alpha}{1 + Z_\alpha^2} \left(\frac{\gamma - 1}{2} \left[\frac{\Delta C_{11}}{C_p} + \frac{1 - iZ_i}{1 + Z_i^2} \frac{\Delta C_{ii}}{C_p} + \frac{\gamma}{2} \frac{\Delta K}{K} \right. \right. \\ \left. \left. + \frac{\gamma - 1}{2} \left[\frac{\Delta \beta_1 A}{\beta} - \left(\frac{\Delta \beta_1}{\beta} + \frac{1 - iZ_i}{1 + Z_i^2} \frac{\Delta \beta_i}{\beta} \right) \right] \right) + \frac{1 - iZ_i}{1 + Z_i^2} \frac{\gamma - 1}{2} \frac{C_i}{C_p}$$

If however we find that the relaxation parameters are not small compared to unity we may, at somewhat greater labor, obtain an algebraic solution. Since A and B are both complex numbers we may divide each into its real and its imaginary components and label them $A_r, A_i, B_r,$ and B_i . There should be no confusion between subscripts denoting as imaginary part of a number and the subscript denoting the internal degree of freedom.

In terms of these quantities equation 15 is written

$$\sigma^2 = \frac{(A_r B_r + A_i B_i) + i (A_r B_i - A_i B_r)}{A_r^2 + A_i^2} = x_r + ix_i$$

But we know how to take the square root of a number, in terms of x_r and x_i the values for the real and the imaginary parts of σ are given by

$$(\sigma_r)^2 = \frac{1}{2} [\sqrt{x_r^2 + x_i^2} + x_r]$$

$$(\sigma_i)^2 = \frac{1}{2} [\sqrt{x_r^2 + x_i^2} - x_r]$$

Upon examination we see that x_r , being the sum of two comparable numbers, is likely to be large compared to x_i , which is the difference of

these two numbers. We may then expect, to a good degree of approximation, to be able to expand our solution on this basis and obtain a simpler result. This approximate result in terms of the variables A_r , A_i , B_r , and B_i will finally be

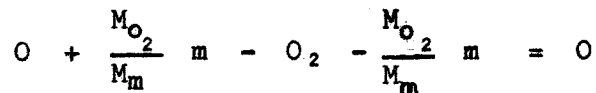
$$(17) \quad \sigma_r^2 = \frac{A_r B_r + A_i B_i}{A_r^2 + A_i^2}$$

$$\sigma_i^2 = \frac{(A_r B_i - A_i B_r)^2}{4(A_r B_r + A_i B_i)(A_r^2 + A_i^2)}$$

CALCULATIONS

Now that we have obtained our results for the ultrasonic absorption and dispersion properties of the fluid, we shall compare the relative magnitudes of the several terms for a specific case. One system in which there is some current interest is the dissociation at high temperatures of molecular oxygen. Because it has attracted some interest there is sufficient data on the several effects that we may calculate the desired quantities. We shall see that the temperature which is necessary for this reaction to become important is rather high, thus much of the interesting data has been obtained from shock tube measurements. This system is considered more because the data is available than because the usual type of ultrasonic measurements could be easily carried out on this system.

The reaction, written in terms of the reacting masses is written



The species m in the third body which microscopic conservation of energy and of momentum demand. We shall assume that any third body, such as atomic or molecular oxygen, argon, etc. will serve the third body purpose with equal efficiency.

In as much as the relaxation terms are multiplied by the factor $1/(1 + iZ)$, or equivalently $(1 - iZ)/(1 + Z^2)$ we shall expect the maximum absorption to occur in the region $Z = 1$, that is, when the frequency is in the range $\omega = 1/\tau$. Also we might expect the maximum effect from the chemical reaction to occur at a temperature for which the equilibrium

constant is of the order unity, so that both species are present in appreciable quantities, and a small displacement of the equilibrium will signify the reaction of a larger quantity of material. This condition obtains in the region above 3500° K, however, and this is a temperature at which it does not seem practical to work with ultrasonics. If instead we ask that both Z's have the value unity at close to the same frequency, we shall find that this condition is met in the region just about 2500° K. We shall choose the temperature 2500° K for our comparison.

For the temperature 2500° we find from tables⁽¹³⁾ that the dissociation constant for molecular oxygen is 1.56×10^{-2} . The molecular weights are 32 for molecular oxygen and 16 for atomic oxygen. If we assume an equilibrium mixture of these two species, with no impurities present, we shall obtain for m the average molecular weight of 28.8. Similarly we find that the pertinent data for the reaction, assuming the perfect gas law to hold at this temperature, will be

$$\begin{aligned} \Delta H_1 &= 3900 \text{ cal gm}^{-1} & \Delta H_i &= -61.8 \text{ cal gm}^{-1} \\ \Delta V &= 6.41 \text{ l gm}^{-1} & \rho &= 0.147 \text{ gm l}^{-1} \end{aligned}$$

From these data we may calculate the relaxation parameters. If we again utilize the perfect gas assumption we find for the coefficients of compressibility and thermal expansion

$$\begin{aligned} \beta &= 1/T = 4 \times 10^{-4} \text{ deg}^{-1} \\ K &= 1/P = 1 \text{ atm}^{-1} \end{aligned}$$

We now require only G in order to find the values of the relaxation parameters. G is given by equation 11, and for a perfect gas we may write down the chemical potential for the component r at once. To within the arbitrary zero of potential

$$\mu_r = \frac{1}{M_r} RT \ln x_r + (\text{constant w.r.t. } x_r)$$

$$\frac{\partial \mu_r}{\partial x_s} = \frac{1}{M_r} RT \frac{1}{x_r} \delta_{rs}$$

If we restrict ourselves to a single chemical reaction as before, we see that

$$G = RT \sum_r \frac{(v_r)^2}{M_r x_r} \text{ cal gm}^{-2}$$

For our case of $O_2 \rightarrow 2O$, we have that all of the specific stoichiometric coefficients are unity, and we obtain the value 182 cal gm^{-2} for G . The corresponding values of the relaxation parameters are shown in table 2.

$$\begin{aligned} \Delta C_{11}/C_p &= 113 \\ \Delta C_{ii}/C_p &= 3.11 \\ \Delta \beta_1/\beta &= 20.5 \\ \Delta \beta_i/\beta &= 0.55 \\ \Delta K/K &\approx 0.03 \\ C_i/C_p &= 0.19 \end{aligned}$$

Table 2.

We see quite clearly that the chemical terms are large compared to the vibrational terms, and indeed that the term ΔC_{11} may, to a reasonable approximation be considered to be the only effective term. Thus we conclude that if we were to actually perform an ultrasonic experiment on this gas, we would obtain essentially only chemical reaction rate information.

In practice we would expect to perform such experiments at a lower temperature, and most likely in a diluted gas. Lowering the temperature will have two effects; first, it will directly lower T_i and its correlated \tilde{E}_i and second, it will lower the equilibrium constant and hence raise the

value of G through the concentration dependence. The major effect of dilution will be to decrease the relaxation parameters due to the rise in G. If we dilute one volume of oxygen gas at 2500° with 99 volumes of argon at that temperature, the relaxation parameter $\Delta C_{11}/C_p$ drops off to the value 4.3, with the other heat capacity terms falling off in the same ratio.

Returning to table 2, we see that the parameter ΔC_{1i} is not small compared to C_i , even though the usual treatment of the subject would not consider the term, as it would not arise in strictly independent parallel processes. From equation 16 in which ΔC_{1i} appears multiplied by the factor $1/(1 + iZ_i)(1 + iZ_\alpha)$, we may expect this term to be negligible if the relaxation time of the two processes are sufficiently different, however it may become appreciable if the two processes have similar relaxation times. Although the ratio $\Delta C_{1i}/C_i$ will depend upon the temperature, it will not, to our approximation, depend upon the dilution as both $1/G$ and C_i must have the same dependence upon the concentration of total oxygen at any one temperature.

Returning to equation 10, if we once again examine the rate, linearized about the equilibrium condition, we see that the relaxation time for the reaction will be

$$\tau_\alpha = \left[\rho \sum_s \nu_s \left(\frac{\partial f_r}{\partial \rho_s} \right)_{\text{equil.}} \right]^{-1}$$

Thus the relaxation times, using the rate equations obtained from shock tube experiments,⁽¹²⁾ will be $\tau_\alpha = 10.4$ sec. and $\tau_i = 2.1$ sec.

We now have all of the data needed for a sample calculation of the sonic properties of the fluid just described. The results of such a calculation are presented in figure 1 and figure 2. Figure 1 gives the dispersion as V/V_0 , which is $1/\sigma_r$. Figure 2 gives the absorption as σ_i which is

$\alpha V_0 / \omega$, or $\alpha l_0 / 2\pi$, where α is the absorption per unit length, and l_0 is the "reference" wave length, the wave length which the sound wave would have at a given frequency if it traveled at the reference speed of sound. These calculations were made using equation 17.

We may note that both the maximum absorption and the maximum rate of change of the dispersion occur in the vicinity of 2 megacycles. This corresponds roughly to $Z\alpha = 100$. Normally one expects these to occur in the region of Z being unity, however in the case of the dispersion a glance at equation 17 shows that the dispersion should not become unity until A_r and B_r , and A_i and B_i become equal. This condition is not approached until the dominant relaxation parameter $\Delta C_{11} / (1 + Z\alpha_2)$ becomes small compared to one, as may be seen from equation 15.

The low frequency dispersion, V/V_0 is 0.919. The maximum absorption is about 4.4% for the distance $l_0 / 2\pi$.

We are now ready to inquire into the effect of the quantity $[(\Delta E_i)_A - \Delta E_i]$ on the propagation of the sound waves in the fluid. First we consider the magnitude of the terms. As we have mentioned before, we do not expect the size of this term to exceed a few times the vibrational level spacing, and if ΔE_{iA} were sufficiently small we might indeed have it be zero. If we assume that the term $[(\Delta E_i)_A - \Delta E_i]$ has the value of one vibrational quantum per molecule, it will take on the value 141 cal gm^{-1} , which is indeed a value which is comparable to the value of \tilde{E}_i at this temperature. At lower temperatures we would expect \tilde{E}_i to have a lower value and $[(\Delta E_i)_A - \Delta E_i]$ to have a higher value, so that at low temperature this cross term may be the most significant of the cross terms. We will expect the value of ΔC_{i1} to be of about the same size as ΔC_{1i} , and $\Delta \beta_{iA}$ will be about the same size as $\Delta \beta_i$. The quantity ΔC_{ii} will be

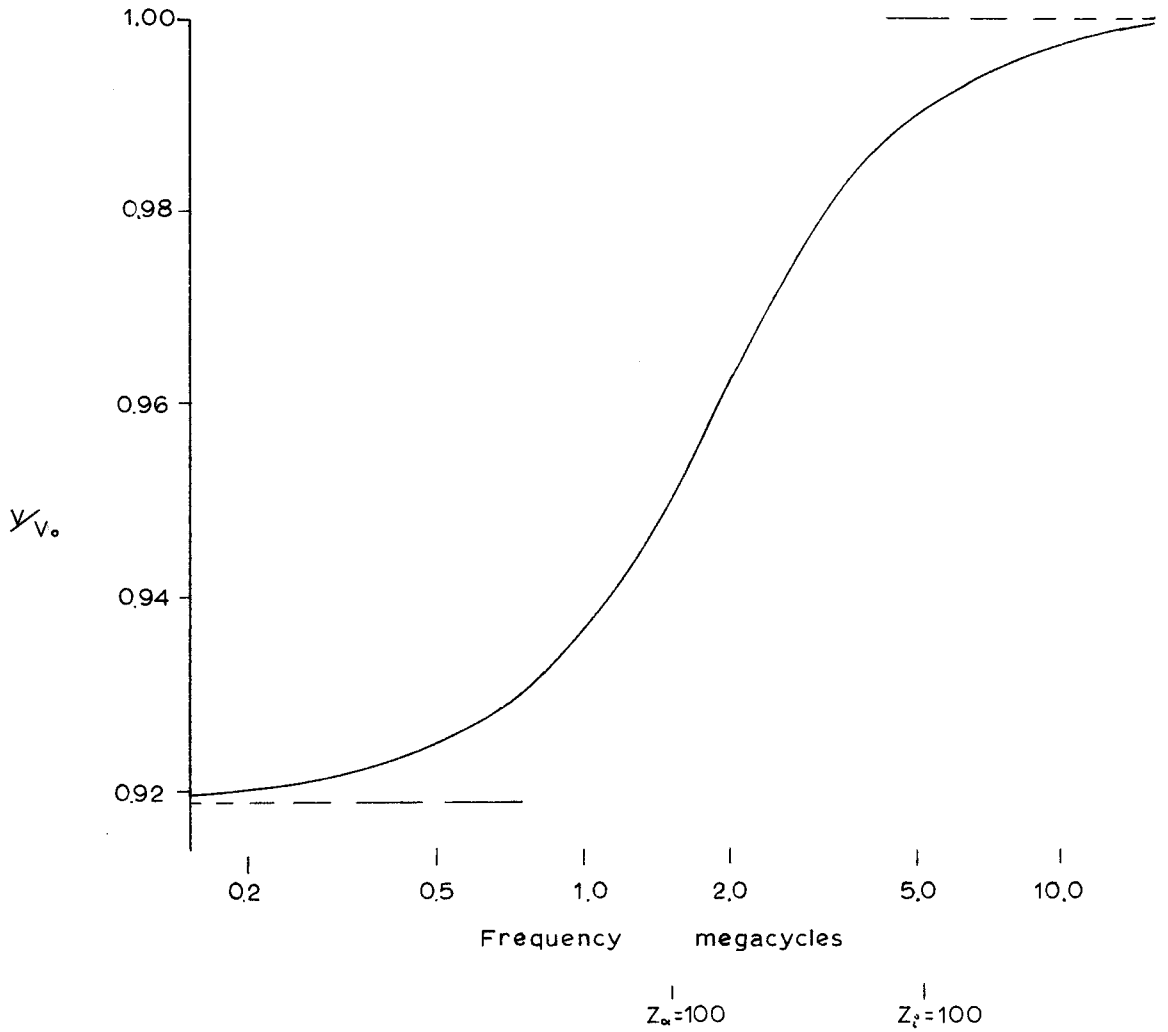


Figure 1.--Dispersion (V/V_0) vs. frequency (megacycles)

$O_2 - O$ gas mixture at $2500^\circ K$

Dashed lines show high and low frequency limits

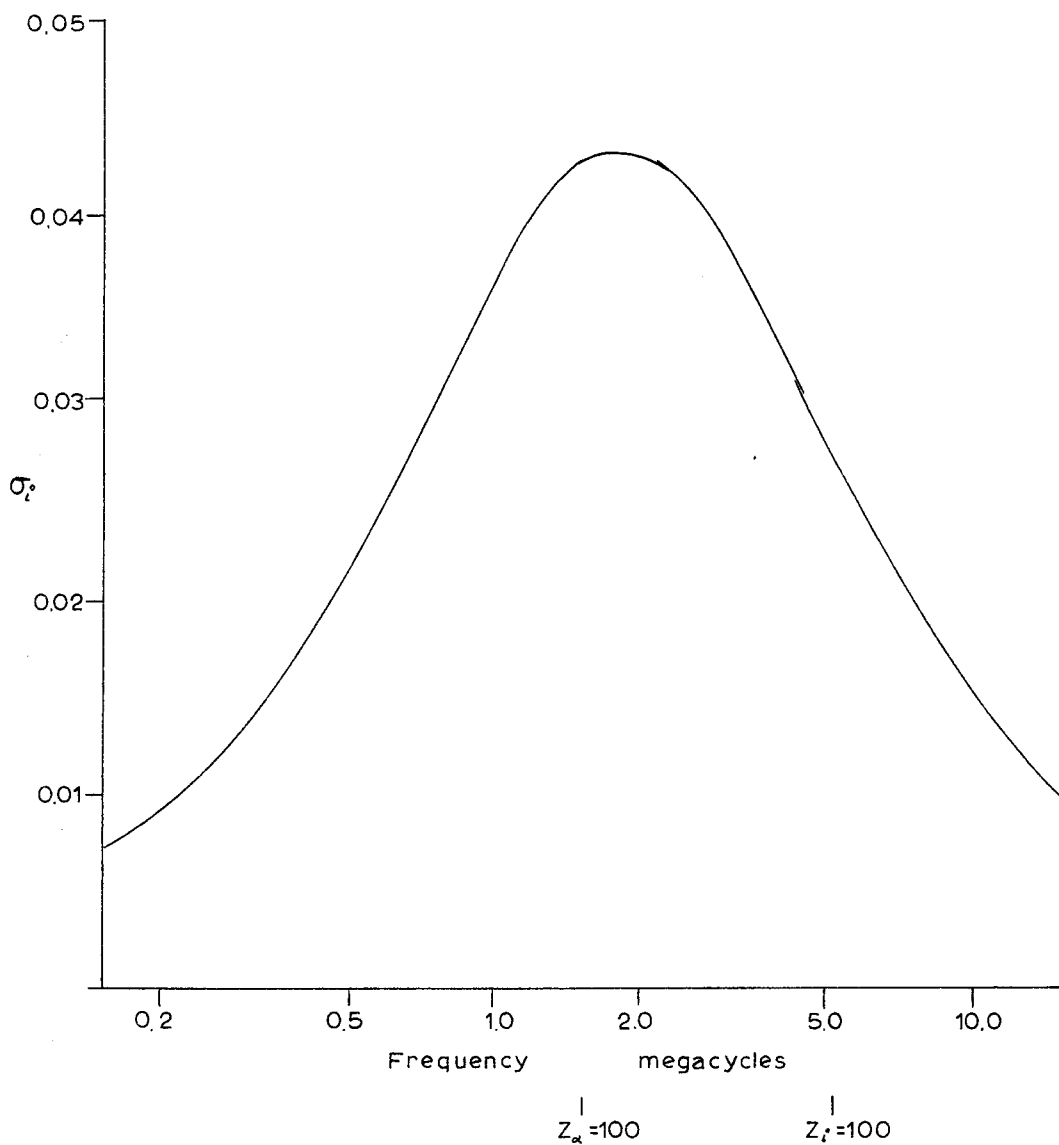


Figure 2.--Sonic absorption ($\sigma_1 = \alpha l_o / 2\pi$) vs. frequency (megacycles)
O₂ - O gas mixture at 2500° K

appropriately smaller than the other heat capacity parameters.

If we return to our original four by four determinant, we find that the bottom row now reads

$$0 \quad \frac{\gamma-1}{\gamma} \frac{iZ_i^2}{(1+iZ_i)(1+iZ_\alpha)} \frac{C_p/C_i}{\beta} \Delta\beta_{iA} \quad \frac{iZ_i^2}{(1+iZ_i)(1+iZ_\alpha)} \left[\frac{\Delta C_{ii}}{C_p} + \frac{1}{1+iZ_i} \frac{\Delta C_{ii}}{C_p} \right] \quad \frac{iZ_i^2}{(1+iZ_i)(1+iZ_\alpha)} \frac{C_p/C_i}{C_p} \Delta C_{ii} - 1$$

We may immediately notice two things about these quantities, first that all of the relaxation parameters appear multiplied by the factor $[iZ_i/(1+iZ_i)] \times (1+iZ_\alpha)^{-1}$ which takes on a very small value when either Z_i or Z_α is far from unity, and secondly that all of these parameters are multiplied by the number C_p/C_i . However, these quantities, upon expansion of the determinant, will all be multiplied by at least one other relaxation parameter, so that their effect on the final result will be small at least in the case of a dilute gas. The values of the heat capacity parameters are

$$\frac{\Delta C_{i1}}{C_p} = 4.08 \quad \frac{\Delta C_{ii}}{C_p} = 0.112$$

If we now expand this determinant, keeping only first order terms in the relaxation parameters we will obtain an expression corresponding to equation 16 for σ , which will have all of the inherent limitations which equation 16 has.

$$(18) \quad \sigma \approx 1 + \frac{1-iZ_\alpha}{1+Z_\alpha^2} \left(\frac{\gamma-1}{2} \left[\frac{\Delta C_{11}}{C_p} + \frac{1-iZ_i}{1+Z_i^2} \frac{\Delta C_{ii}}{C_p} \right] + \frac{\gamma-1}{2} \frac{1-iZ_i}{1+Z_i^2} \left[\frac{\Delta C_{i1}}{C_p} + \frac{1-iZ_i}{1+Z_i^2} \frac{\Delta C_{ii}}{C_p} \right] + \frac{\gamma}{2} \frac{\Delta K}{K} \left[\frac{\Delta\beta_{iA}}{\beta} + \frac{1-iZ_i}{1+Z_i^2} \frac{\Delta\beta_{iA}}{\beta} \right] \frac{\gamma-1}{2} - \frac{\gamma-1}{2} \left[\frac{\Delta\beta_i}{\beta} + \frac{1-iZ_i}{1+Z_i^2} \frac{\Delta\beta_i}{\beta} \right] + \frac{1-iZ_i}{1+Z_i^2} \frac{\gamma-1}{2} \frac{C_i}{C_p} \right)$$

The only difference between equation 16 and equation 18 is that the latter includes the term $\frac{\gamma - 1}{2} \frac{1 - iZ_i}{1 + Z_i^2} \left[\frac{\Delta C_{i1}}{C_p} + \frac{1 - iZ_i}{1 + Z_i^2} \frac{\Delta C_{ii}}{C_p} \right]$ and the term

$\frac{\gamma - 1}{2} \frac{1 - iZ_i}{1 + Z_i^2} \frac{\Delta \beta_{iA}}{\beta}$. For the above case this amounts to about 4% of the

other terms, and in effect just doubles the term $\frac{1 - iZ_i}{1 + Z_i^2} \frac{\Delta C_{ii}}{C_p}$ found in

equation 16. The small difference between equation 16 and equation 18 gives no indication of the increase in the number of terms which would appear in the analogue of equation 15, as all terms which were products of relaxation parameters were discarded in arriving at equation 18. The analogue of equation 15 will have the same form as equation 15, however the coefficients A and B will be more complicated and more difficult to use in calculations.

REFERENCES

- (1) Einstein, A. Berlin Akad. Math. Kl., 380-385 (1920).
- (2) Markham, Beyer, and Lindsay. Rev. Modern Phys. 23, 353- (1951).
- (3) G. S. Verma. Rev. Mod. Phys. 31, 1052-1071 (1959).
- (4) R. M. Mazo. J. Chem. Phys. 28, 395-398 (1958).
- (5) W. W. Wood and J. G. Kirkwood. J. App. Phys. 28, 395-398 (1957).
- (6) I. Prigogine. Introduction to Thermodynamics of Irreversible Processes, Chap. I, Charles C. Thomas Publisher (1955).
- (7) S. R. DeGroot. Thermodynamics of Irreversible Processes, pp. 51-53, North-Holland Publishing Co. (1958).
- (8) K. F. Herzfeld and T. A. Litovitz. Absorption and Dispersion of Ultrasonic Waves, pp. 90-93, Academic Press (1959).
- (9) R. M. Mazo and J. E. Mayer. J. App. Phys. 29, 735-736 (1958).
- (10) J. G. Kirkwood and B. Crawford, Jr. J. Phys. Chem. 56, 1048-1051 (1952).
- (11) National Bureau of Standards. Selected Values of Chemical Thermodynamic Properties, Series III.
- (12) C. B. Kretschmer. Aerojet Report No. 1611.