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THE DISPERSION AND ABSORPTION  
OF SOUND IN GASES

A THESIS

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Thomas Stanhope Lefler Jr.

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*Crowland*

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Approved:

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Date Approved by Chairman

[Redacted date area]

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THE DISPERSION AND ABSORPTION  
OF SOUND IN GASES

CHAPTER I

INTRODUCTION

Upon the basis of several simplifying assumptions an expression for the velocity of audible sound in gases which compares favorably with experimental observation may be obtained analytically. The usual assumptions are: the perfect gas law is the equation of state of the gas; the gas is a homogeneous, isotropic fluid; the gas is a perfect fluid (i.e., has no viscosity). With these assumptions concerning the nature of the medium in which a sound wave is propagated, the velocity of the wave is found to be the square root of the ratio of the volume modulus of elasticity of the medium to the equilibrium density. The evaluation of the modulus of volume elasticity requires an assumption concerning the nature of the compressions and rarefactions occurring within the sound wave. If these pressure changes of the gas are assumed to be adiabatic changes, the modulus of volume elasticity is the product of the equilibrium pressure and  $\gamma$ , the ratio of the specific heats at constant pressure and volume. Then the velocity of the sound wave is given by the square root of  $\gamma$  times the ratio of equilibrium pressure and density. This value of the velocity of sound is very accurate for frequencies in the audible range.

While an accurate value for the velocity of sound can be

found from the assumptions given above, these assumptions impose reversibility upon the processes occurring within the sound wave, and predict that no absorption of the wave should occur. Thus a development of an expression which will predict experimentally determined values of absorption cannot be made upon the basis of these assumptions. However, if the medium is regarded as being homogeneous and isotropic, the resulting development for the absorption of sound in a viscous, heat conducting gas predicts experimental results well for frequencies in the audible range. This development indicates that the velocity of the wave is also dependent upon viscosity and heat conduction. The dependence of velocity upon viscosity and heat conduction is small however, and for audible sound the pressure variations are very nearly adiabatic. This accounts for the experimental validity of the development indicated above for the determination of the velocity of sound.

To this point the propagation of sound only within the audible range of frequencies has been considered. The propagation of sound (pressure waves) of higher frequencies is even more influenced by the irreversible processes discussed, and still another irreversible process must be considered. When the sound frequency is sufficiently high (the actual frequency depending upon the particular medium of propagation), both velocity and absorption are found to be very different from the values predicted from the above considerations. This difference is caused by a third irreversible process occurring within the sound wave.

The additional irreversible process encountered at high

frequencies is associated with the internal degrees of freedom of the molecules of the medium. At high frequencies, the frequency depending upon the medium of propagation, the vibrational, rotational, or electronic degrees of freedom of the molecules fail to follow the changes associated with translational degrees of freedom. That is, when the temperature, as measured by the kinetic energy of translation of the molecules, is raised very quickly in a particular region, there is a finite time lag before the degrees of freedom other than the translational degrees are excited to the extent required for temperature equilibrium. Since the extent to which the molecules of a region have their internal degrees of freedom excited is dependent upon the possibilities of molecular collisions and/or radiation, these two factors must be considered to determine the effect upon sound propagation of the lag associated with the internal degrees of freedom.

The purpose of this paper is to discuss the dispersion and absorption of sound in gases as effected by all of the factors here mentioned, and in particular, to consider the effect of the irreversibility associated with the internal degrees of freedom, and more in particular, the effect of electromagnetic radiation on observable sound phenomena.

## CHAPTER II

## AN EQUATION OF MOTION AND ITS INTEGRATION

## FOR A VISCOUS, HEAT CONDUCTING GAS

From hydrodynamic theory and the second law of motion, the equation of motion for an isotropic, compressible, viscous fluid is given<sup>(1)</sup> as

$$\rho \frac{d\mathbf{u}}{dt} = \rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla P + \frac{\mu}{3} \nabla \nabla \cdot \mathbf{u} + \mu \nabla \cdot \nabla \mathbf{u}, \quad (1)$$

where  $\rho$  is the density of the fluid,  $\mathbf{u}$  the mass velocity with reference to inertial coordinates,  $\mu$  the coefficient of viscosity, and  $P$  the pressure. For small amplitude waves, the mass velocity is small compared to the velocity of sound. In this case  $\rho \mathbf{u} \cdot \nabla \mathbf{u}$  is negligible in comparison with  $\rho \frac{\partial \mathbf{u}}{\partial t}$ , and

$$\rho \frac{\partial \mathbf{u}}{\partial t} = -\nabla P + \frac{\mu}{3} \nabla \nabla \cdot \mathbf{u} + \mu \nabla \cdot \nabla \mathbf{u}. \quad (2)$$

The equation of continuity, which is based only upon the assumption of the conservation of matter, may be written

$$\frac{\partial s}{\partial t} + \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0, \quad (3)$$

where the condensation,  $s$ , is defined by  $\rho = \rho_0(1+s)$ ,  $\rho_0$  being the average equilibrium density. Using equation (3), equation (2) may be written



$$\begin{aligned} f_0 \frac{\partial u_x}{\partial t} + \frac{\partial P}{\partial x} &= \mu \nabla^2 u_x - \frac{\mu}{3} \frac{\partial^2 s}{\partial x \partial t} \\ f_0 \frac{\partial u_y}{\partial t} + \frac{\partial P}{\partial y} &= \mu \nabla^2 u_y - \frac{\mu}{3} \frac{\partial^2 s}{\partial y \partial t} \\ f_0 \frac{\partial u_z}{\partial t} + \frac{\partial P}{\partial z} &= \mu \nabla^2 u_z - \frac{\mu}{3} \frac{\partial^2 s}{\partial z \partial t} \end{aligned} \quad (4)$$

In order to obtain a solution for these equations it is advantageous to obtain a different form for the term involving the pressure. This may be accomplished as follows.

If the temperature is taken to be uniform except as disturbed by the sound wave and  $\theta$  represents the excess in temperature, and  $T$  represents the temperature measured on the absolute scale,

$$P = P_0 + \left( \frac{\partial P}{\partial s} \right)_T s + \left( \frac{\partial P}{\partial T} \right)_V \theta. \quad (5)$$

The excess of temperature over the equilibrium temperature,  $\theta$ , may be considered as a function of the condensation and the amount of heat  $Q$  which is transferred to a unit volume of the medium. Then the rate of change of  $\theta$  is given by

$$\frac{d\theta}{dt} = \left( \frac{\partial \theta}{\partial s} \right) \frac{ds}{dt} + \frac{1}{f_0 c_v} \frac{dQ}{dt}, \quad (6)$$

where  $c_v$  is the heat capacity at constant volume per unit mass (i.e., the specific heat) of the medium, and the partial derivative  $\left( \frac{\partial \theta}{\partial s} \right)$  is to be evaluated under conditions existing within the sound wave.

Heat conduction in an isotropic medium is described by

$$\frac{dQ}{dt} = C \nabla^2 \theta, \text{ where } C \text{ is the thermal conductivity. Thus}$$

$$\frac{d\theta}{dt} = \left(\frac{\partial T}{\partial s}\right) \frac{ds}{dt} + L \nabla^2 \theta, \quad (7)$$

where  $L$  is the diffusivity of the medium, or  $C$  divided by  $\rho_0 c_v$ .

From equation (5)

$$\frac{\partial P}{\partial x} = \left(\frac{\partial P}{\partial s}\right)_T \frac{\partial s}{\partial x} + \left(\frac{\partial P}{\partial T}\right)_V \frac{\partial \theta}{\partial x}. \quad (8)$$

If, for convenience of notation,  $\theta'$  be written for  $\frac{\theta}{\left(\frac{\partial T}{\partial s}\right)}$ ,  $\mu'$  for  $\frac{\mu}{\rho_0}$ , and  $\mu''$  for  $\frac{\mu}{\rho_0}$ , equations (4) may be written in the form

$$\frac{\partial u_x}{\partial t} + \left(\frac{\partial P}{\partial s}\right)_T \frac{\partial s}{\partial x} + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial s}\right) \frac{\partial \theta'}{\partial x} = \mu' \nabla^2 u_x - \mu'' \frac{\partial^2 s}{\partial x \partial t}, \quad (9)$$

since  $\frac{\partial s}{\partial s} = \rho_0$ . Equation (9) is the form of equations (4) which will be examined for a solution.

Consider that  $u_x$ ,  $u_y$ ,  $u_z$ ,  $s$ , and  $\theta'$  are functions of time only to the extent of a factor  $\exp(qt)$ , where  $q$  is a constant. This places no restriction upon the motion once the linear equation (9) is accepted, since this assumption demands only that the motion be described by a sum of these exponential terms. The solution to any linear differential equation may be given as a sum of solutions, and any physically realizable motion may be built up by a sum of such functions.

Then for equation (3) one has

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} + qs = 0, \quad (10)$$

and for equation (9)

$$\begin{aligned}
qu_x - \mu' \nabla^2 u_x &= -\frac{\partial Y}{\partial x} \\
qu_y - \mu' \nabla^2 u_y &= -\frac{\partial Y}{\partial y} \\
qu_z - \mu' \nabla^2 u_z &= -\frac{\partial Y}{\partial z},
\end{aligned} \tag{11}$$

Y being defined by

$$Y = \left[ \left( \frac{\partial P}{\partial \mathcal{F}} \right)_T + q\mu'' \right] s + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial \mathcal{F}} \right) \theta'. \tag{12}$$

Equation (7) may now be written

$$s = \theta' - \left( \frac{L}{q} \right) \nabla^2 \theta'. \tag{13}$$

Eliminating s by equation (13), equations (10) and (12) become

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} + q\theta' - L\nabla^2 \theta' = 0, \tag{14}$$

$$Y = \left[ \left( \frac{\partial P}{\partial \mathcal{F}} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial \mathcal{F}} \right) + q\mu'' \right] \theta' - \frac{L}{q} \left[ \left( \frac{\partial P}{\partial \mathcal{F}} \right)_T + q\mu'' \right] \nabla^2 \theta'. \tag{15}$$

Utilizing equations (14) and (15), the divergence of equations (11) is

$$\begin{aligned}
q^2 \theta' - \left\{ \left[ \left( \frac{\partial P}{\partial \mathcal{F}} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial \mathcal{F}} \right) \right] + q(\mu' + \mu'' + L) \right\} \nabla^2 \theta' \\
+ \frac{L}{q} \left[ \left( \frac{\partial P}{\partial \mathcal{F}} \right)_T + q(\mu' + \mu'') \right] \nabla^4 \theta' = 0.
\end{aligned} \tag{16}$$

A solution to equation (16) may be found in the form

$$\theta' = A_1 Q_1 + A_2 Q_2, \quad (17)$$

where  $Q_1$  and  $Q_2$  are functions satisfying

$$\nabla^2 Q_1 = \lambda_1 Q_1, \quad \nabla^2 Q_2 = \lambda_2 Q_2, \quad (18)$$

and  $A_1$  and  $A_2$  are arbitrary constants.  $\lambda_1$  and  $\lambda_2$  are the roots of

$$q^2 - \left\{ \left( \frac{\partial P}{\partial \mathcal{F}} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial \mathcal{F}} \right) + q(\mu' + \mu'' + L) \right\} \lambda + \frac{L}{q} \left\{ \left( \frac{\partial P}{\partial \mathcal{F}} \right)_T + q(\mu' + \mu'') \right\} \lambda^2 = 0. \quad (19)$$

In order that solutions of equations (11) may be obtained,  $\nabla \underline{u}$  is set equal to  $\nabla^2 (B_1 Q_1 + B_2 Q_2)$ . This equality is substituted into equation (14), and  $\theta'$  replaced by its value as given by equation (17).

This gives

$$\nabla^2 (B_1 Q_1 + B_2 Q_2) + (q + L \nabla^2) (A_1 Q_1 + A_2 Q_2) = 0. \quad (20)$$

The relationship between the constants  $A_1$ ,  $A_2$  and  $B_1$ ,  $B_2$  may be seen from equations (18):

$$B_1 = A_1 \left( L - \frac{q}{\lambda_1} \right), \quad B_2 = A_2 \left( L - \frac{q}{\lambda_2} \right). \quad (21)$$

The results given above are applicable to any physical motion of the fluid. In the following, these results are applied to the case of plane waves propagated in the  $x$  direction.

Equations (18) now become

$$\frac{\partial^2 Q_1}{\partial x^2} = \lambda_1 Q_1 \quad \frac{\partial^2 Q_2}{\partial x^2} = \lambda_2 Q_2. \quad (22)$$

The solutions of equations (22) to correspond to waves propagated in the positive  $x$  direction are

$$Q_1 = \exp(-x\sqrt{\lambda_1}), \quad Q_2 = \exp(-x\sqrt{\lambda_2}). \quad (23)$$

If  $A_1$  and  $A_2$  are constants to be determined by the boundary conditions,

$$\begin{aligned} \underline{u} &= A_1 \sqrt{\lambda_1} \left( \frac{q}{\lambda_1} - L \right) \exp(-x\sqrt{\lambda_1}) \\ &+ A_2 \sqrt{\lambda_2} \left( \frac{q}{\lambda_2} - L \right) \exp(-x\sqrt{\lambda_2}) \\ \theta' &= A_1 \exp(-x\sqrt{\lambda_1}) + A_2 \exp(-x\sqrt{\lambda_2}). \end{aligned} \quad (24)$$

A less general but practical solution results from considering the condition that  $\mu'$ ,  $\mu''$ , and  $L$  are small quantities compared to  $\frac{1}{q} \left( \frac{\partial P}{\partial y} \right)_T$  and  $\left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial y} \right) \frac{1}{q}$ . In this case, one value of  $\lambda$ , say  $\lambda_1$ , is given from equation (19) approximately by  $\frac{q^2}{\left( \frac{\partial P}{\partial y} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial y} \right)}$ , while the other value,  $\lambda_2$ , is very large. The solution required is that for  $\lambda_1$ , since the term containing  $\lambda_2$  is negligible compared to the term containing  $\lambda_1$  for all values of  $x$  except those near the boundaries of the fluid. The solution corresponding to  $\lambda_2$  represents a highly damped heat wave having the same frequency as the sound wave. This heat wave originates at the boundary and has an amplitude dependent upon the thermal conductivities of the gas and the boundary. In the general one-dimensional boundary value problem the positive root of  $\lambda_2$  leads to a heat wave propagated from the right boundary and the negative root one propagated from the left boundary.

A second approximation to the value of  $\lambda_1$  is

$$\begin{aligned}
\lambda &= \frac{q^2}{\left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right) + (\mu' + \mu'' + L) q} \\
&\quad + \frac{L \left(\frac{\partial P}{\partial \mathcal{F}}\right)_T \lambda_1^2}{q \left[ \left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right) \right]} \\
&= \frac{q^2}{\left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right)} \left\{ 1 - \frac{q(\mu' + \mu'' + L)}{\left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right)} \right. \\
&\quad \left. - \frac{L \left(\frac{\partial P}{\partial \mathcal{F}}\right)_T q}{\left[ \left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right) \right]^2} \right\}. \tag{25}
\end{aligned}$$

Thus

$$\begin{aligned}
\pm \sqrt{\lambda_1} &= \frac{q}{\left[ \left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right) \right]^{\frac{1}{2}}} - \left\{ \frac{q^2}{2 \left[ \left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right) \right]^{\frac{3}{2}}} \right\} \\
&\quad \left\{ \mu' + \mu'' + L \left[ 1 - \frac{\left(\frac{\partial P}{\partial \mathcal{F}}\right)_T}{\left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right)} \right] \right\}. \tag{26}
\end{aligned}$$

Now if  $i\omega$  is written for the constant  $q$  where  $\omega$  is  $2\pi$  times the frequency of the sound wave, the typical solution is of the form

$$\bar{u} = \exp(-ax) \exp \left\{ -i\omega \left[ t - \frac{x}{\left[ \left(\frac{\partial P}{\partial \mathcal{F}}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial \mathcal{F}}\right) \right]^{\frac{1}{2}}} \right] \right\} \tag{27}$$

where  $\alpha$  is

$$\alpha = \frac{\omega^2}{2 \left[ \left( \frac{\partial P}{\partial f} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial f} \right) \right]^{\frac{3}{2}}} \left\{ \mu' + \mu'' + L \left[ 1 - \frac{\left( \frac{\partial P}{\partial f} \right)_T}{\left( \frac{\partial P}{\partial f} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial f} \right)} \right] \right\}, \quad (28)$$

and the complex velocity of the wave  $V_s$  is given by

$$\frac{1}{V_s} = \frac{1}{\left[ \left( \frac{\partial P}{\partial f} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial f} \right) \right]^{\frac{1}{2}}} + \frac{\alpha}{i\omega}. \quad (29)$$

The partial derivatives  $\left( \frac{\partial P}{\partial f} \right)_T$  and  $\left( \frac{\partial P}{\partial T} \right)_V$  in equations (26) and (27) may be evaluated directly from an equation of state which describes the medium of propagation.  $\left( \frac{\partial T}{\partial f} \right)$ , however, is specified only as taken for adiabatic conditions, and requires further consideration before evaluation from an equation of state can be accomplished. An expression for  $\left( \frac{\partial T}{\partial f} \right)$  may be obtained by the method given below.

For infinitesimal adiabatic (not necessarily reversible) processes, the first law of thermodynamics is

$$dQ = dU + PdV = 0, \quad (30)$$

where  $U$  is the internal energy. If  $U$  be written  $U = U(T, V)$ , then

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV, \quad (31)$$

and equation (30) becomes

$$\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV = 0. \quad (32)$$

Since  $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ , equation (32) is equivalent to

$$dT = -\frac{1}{C_V} \left( \left(\frac{\partial U}{\partial V}\right)_T + P \right) dV. \quad (33)$$

Now since

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P,$$

$$dT = -\frac{T}{C_V} \left(\frac{\partial P}{\partial T}\right)_V dV = \frac{MT}{f_0 C_V} \left(\frac{\partial P}{\partial T}\right)_f d\mathcal{J}, \quad (34)$$

and

$$\left(\frac{\partial T}{\partial \mathcal{J}}\right)_{\text{adiabatic}} = \frac{MT}{f_0 C_V} \left(\frac{\partial P}{\partial T}\right)_f. \quad (35)$$

If  $\left(\frac{\partial T}{\partial \mathcal{J}}\right)$  is replaced by its equivalent from equation (35), equations (28) and (29) become

$$\alpha = \omega^2 \left\{ \frac{\frac{2\mu}{f_0}}{\left[ \left(\frac{\partial P}{\partial \mathcal{J}}\right)_T + \frac{MT}{f_0 C_V} \left(\frac{\partial P}{\partial T}\right)_V^2 \right]^{\frac{3}{2}}} + \frac{L}{2} \left[ \frac{\frac{MT}{f_0 C_V} \left(\frac{\partial P}{\partial T}\right)_V^2}{\left[ \left(\frac{\partial P}{\partial \mathcal{J}}\right)_T + \frac{MT}{f_0 C_V} \left(\frac{\partial P}{\partial T}\right)_V^2 \right]^{\frac{5}{2}}} \right] \right\}. \quad (36)$$

$$\frac{1}{V_s} = \frac{1}{\left[ \left(\frac{\partial P}{\partial \mathcal{J}}\right)_T + \frac{MT}{f_0 C_V} \left(\frac{\partial P}{\partial T}\right)_V^2 \right]^{\frac{1}{2}}} + \frac{\alpha}{i\omega}. \quad (37)$$

In equations (36) and (37) all partial derivatives may be evaluated from an equation of state descriptive of the medium of



propagation, and for any established conditions the remaining factors are available from kinetic theory or, if desirable, may be measured experimentally.

## CHAPTER III

EFFECTS OF IRREVERSIBLE PROCESSES ASSOCIATED  
WITH INTERNAL DEGREES OF FREEDOM

In the preceding chapter the propagation of sound in a viscous, heat conducting fluid is considered, and a general solution to the equation of motion is presented. This general solution is simplified by neglecting second order effects in order that reasonably compact expressions of the velocity and absorption might be given. Developments similar to that given in Chapter II have been given by Kirchhoff<sup>2</sup> and Rayleigh<sup>3</sup>.

Thus, to this point the results obtained are those given by classical theory. These results indicate that to a first order approximation there is no dispersion of audible sound propagated in gases, and that absorption varies with the second power of the frequency of the propagated wave.

Experiments of the past twenty-five years have shown that, contrary to classical results, regions of sharp dispersion exist, and that these regions also exhibit excessive absorption<sup>4,5</sup>. In attempts to explain these experimental observations various investigators have considered the observed results to be due to irreversible processes associated with the internal degrees of freedom of the medium, and have utilized one of two fundamental approaches. One of the theoretical developments is based upon kinetic theory<sup>6</sup>, the other upon thermodynamic considerations<sup>7</sup>. It has been shown that the results of both methods are identical<sup>8</sup>.

The purpose of this chapter is to present a theory of the irreversible processes associated with the internal degrees of freedom. This theory, like theories of the propagation of sound in chemically active media<sup>9</sup>, treats the problem from the standpoint of an existing equilibrium which is disturbed by the passage of a sound wave. An equilibrium constant is defined for a first order reaction in which gas molecules at one level of excitation are reactants producing gas molecules at another level of excitation. Dispersion and absorption of a sound wave in this gas is expressed as a function of the equilibrium reaction rate constant.

\* \* \* \* \*

Equations (36) and (37) indicate that the velocity of a sound wave is independent of the frequency, and that absorption depends upon the second power of the frequency. In order to ascertain whether these equations predict the experimentally observed dispersion and excessive absorption discussed above, it is necessary to consider whether frequency is included implicitly in any of the factors of the equations.

The partial derivatives  $\left(\frac{\partial P}{\partial f}\right)_T$  and  $\left(\frac{\partial P}{\partial T}\right)_V$  are functions of the translational degrees of freedom only since the temperature referred to is measured by the kinetic energy of translation of the molecules. Thus, for these derivatives to become frequency dependent, it is necessary that the frequency of the propagated sound be such that the period is of the same order of magnitude as the relaxation time (this being the time required for motion associated with a degree of freedom to respond to changes of the system) for the translational

degrees of freedom. Since the relaxation time for these degrees of freedom is exceedingly short, about  $2 \times 10^{-10}$  second for air at standard temperature and pressure<sup>10</sup>, this would require frequencies much higher than the frequencies at which dispersion and excessive absorption have been observed. However, the heat capacity at constant volume is a partial derivative whose effective value may be dependent upon the internal degrees of freedom of the molecules of the medium. The relaxation time for these degrees of freedom is of the order of magnitude of the period of the sound waves considered, and the effective heat capacity is a function of the frequency in this range of frequencies. Thus at least a part of the observed discrepancy of the classical theory of the propagation of sound may be due to the frequency dependence of the effective heat capacity.

To obtain an explicit expression of the frequency dependence of the effective heat capacity of the medium, one may consider a reaction  $m \rightleftharpoons n$ ,  $m$  and  $n$  referring to energy levels of a two level molecule. From the law of mass action

$$\frac{dN_n}{dt} = -k_n N_n + k_m K(N - N_n) \quad (38)$$

$N_n$  is the number of moles of gas in the higher energy or  $n$  state,  $N$  is the total number of moles of gas,  $k_n$  and  $k_m$  are the rates per mole of the forward and reverse reactions respectively, and the equilibrium constant  $K$  is the ratio of  $k_m$  to  $k_n$ . If  $\Delta N_{no}$  is the equilibrium magnitude of  $\Delta N_n$  caused by a perturbation of the equilibrium of the gas,  $\Delta N_{no} = N_{no} - N_{nl}$ , and  $\Delta N_n = N_n - N_{nl}$ .  $N_{nl}$  and  $N_{no}$  represent the number of moles in the higher energy state for the

initial and perturbed equilibrium states respectively. Upon the assumption that the law of mass action holds if the equilibrium is only slightly perturbed, the rate of approach to a new equilibrium when a perturbation is applied is

$$\begin{aligned} \frac{d(\Delta N_n)}{dt} &= -k_n(\Delta N_n - \Delta N_{no}) + k_n K(\Delta N_{no} - \Delta N_n) \\ &= k_n(K + 1)(\Delta N_{no} - \Delta N_n), \end{aligned} \quad (39)$$

or

$$\frac{d(\Delta N_n)}{dt} = \kappa (\Delta N_{no} - \Delta N_n), \quad (40)$$

where  $k_n(K + 1) = \kappa$  is the equilibrium reaction rate constant.

For a perturbation which varies periodically in time such as that caused by a sound wave,  $(\Delta N_{no} - \Delta N_n)$  may be considered to vary as the real part of  $\exp(i\omega t)$ , where  $\omega$  is  $2\pi$  times the frequency of the sound wave. Upon integrating equation (40), one has

$$\Delta N_n = \frac{(\Delta N_{no} - \Delta N_n)}{\frac{i\omega}{\kappa}} = \frac{\Delta N_{no}}{1 + \frac{i\omega}{\kappa}} \quad (41)$$

In sound propagation, there is a periodic temperature variation associated with this periodic perturbation of equilibrium. For such a temperature variation, the definition of the part of the molar specific heat associated with an internal degree of freedom

$$C_i = \Delta H \frac{dN_n}{dT}, \quad (42)$$

( $\Delta H$  is the molar heat of the reaction  $m \rightleftharpoons n$ ) becomes

$$C' = \Delta H \frac{d(\Delta N_{no})}{d\theta} = \Delta H \frac{\Delta N_{no}}{\theta_0} = \Delta H \left( \frac{\Delta N_{no}}{\theta_0} \right) \frac{1}{1 + \frac{i\omega}{\kappa}}, \quad (13)$$

where  $\theta_0$  is the magnitude of the temperature variation of the perturbation, and  $\theta$  is the excess temperature. If  $C'_0$  be written for  $\Delta H \frac{\Delta N_{no}}{\theta_0}$ , the effective heat capacity at constant volume is

$$C_V = C_0 - C'_0 + \frac{C'_0}{\left(1 + \frac{i\omega}{\kappa}\right)}, \quad (14)$$

where  $C_0$  is the equilibrium or low frequency value of the heat capacity at constant volume.

If the expression for the effective heat capacity at constant volume given by equation (14) is substituted into equations (36) and (37) expressions are obtained for the velocity and absorption of sound in which the frequency dependence is shown explicitly. These expressions are

$$\alpha = \omega^2 \left[ \frac{\frac{2\mu}{3\rho_0}}{\left[ \left( \frac{\partial P}{\partial \rho} \right)_T + \frac{MT \left( \frac{\partial P}{\partial T} \right)_V^2}{f_0^2 \left[ C_0 - C'_0 + \frac{C'_0}{\left(1 + \frac{i\omega}{\kappa}\right)} \right]} \right]^{\frac{1}{2}}} \right] \left[ \frac{1 - \left( \frac{\partial P}{\partial \rho} \right)_T \left[ \left( \frac{\partial P}{\partial \rho} \right)_T + \frac{MT \left( \frac{\partial P}{\partial T} \right)_V^2}{f_0^2 \left[ C_0 - C'_0 + \frac{C'_0}{\left(1 + \frac{i\omega}{\kappa}\right)} \right]} \right]^{\frac{1}{2}}}{\left[ \left( \frac{\partial P}{\partial \rho} \right)_T + \frac{MT \left( \frac{\partial P}{\partial T} \right)_V^2}{f_0^2 \left[ C_0 - C'_0 + \frac{C'_0}{\left(1 + \frac{i\omega}{\kappa}\right)} \right]} \right]^{\frac{3}{2}}} \right], \quad (15)$$

$$\frac{1}{v_s} = \frac{1}{\left[ \left( \frac{\partial P}{\partial f} \right)_T + \frac{MT \left( \frac{\partial P}{\partial T} \right)^2}{f_o^2 \left[ C_o - C'_o + \frac{C_o}{1 + \frac{1}{\kappa}} \right]} \right]^{\frac{1}{2}}} + \frac{a}{1\omega} \quad (46)$$

All of the quantities entering equations (45) and (46) except those which depend upon the equilibrium reaction rate constant  $\kappa$ , (and through  $\kappa$ ,  $C'_o$ ) may be calculated and numerical values obtained for any gas provided the equilibrium pressure and temperature are specified, and a descriptive equation of state is known.

In order to determine the equilibrium reaction rate constant for a reaction one must consider the rates of the reaction. The rates at which this reaction proceeds are dependent upon the mechanisms by which a molecule or an atom changes its state of excitation. This change of state can be brought about in two ways: by a collision in which there is an energy transfer between an internal degree of freedom and the translational degrees of freedom; and by an energy transfer between an internal degree of freedom and the surrounding radiation field. A collision reaction rate equation, which describes the equilibrium changes of state brought about by the first effect is given by a statement of the principle of microscopic reversibility. This statement may be written

$$N_m^2 (\bar{f}_{mn} - f_{mn}) + NN_m f_{mn} = N_n^2 (\bar{f}_{nm} - f_{nm}) + NN_n f_{nm} \quad (47)$$

$\bar{f}_{mn}$  and  $\bar{f}_{nm}$  being the averaged probabilities per mole per second of

collision induced transitions when the colliding molecules are similarly specified, and  $f_{nm}$  and  $f_{mn}$  those averaged probabilities per mole per second when the colliding molecules are in different states. That is,  $\bar{f}_{nm}$  is Avogadro's number times the probability per second that one molecule in the m state will go to the n state as a result of a collision with another molecule in the m state. Correspondingly,  $f_{mn}$  is Avogadro's number times the probability per second that a molecule in the m state will be raised to the n level of excitation as a result of a collision with a molecule in the n level of excitation.

A corresponding radiation reaction rate equation describing the radiation reaction at equilibrium may be written in terms of the Einstein radiation coefficients  $A_{nm}$ ,  $B_{nm}$ , and  $B_{mn}$ .  $A_{nm}$  is the probability per mole per second for spontaneous transitions from n to m,  $B_{mn}$  and  $B_{nm}$  are transition probabilities from m to n and n to m respectively which are induced by an interaction with the surrounding radiation field. ( $A_{mn}$  is zero since transitions from a lower to a higher energy level do not occur spontaneously.) This radiation reaction rate equation is

$$N_m u_{\nu_{nm}} B_{mn} = (A_{nm} + u_{\nu_{nm}} B_{nm}) N_n, \quad (48)$$

where  $u_{\nu_{nm}}$  is the radiation density per unit of frequency near the frequency  $\nu_{nm}$  in the surrounding radiation field. If  $E_n$  and  $E_m$  are the energies of states n and m for any single molecule,  $\nu_{nm}$  is given by

$$\nu_{nm} = \frac{E_n - E_m}{h}, \quad (49)$$

h being Planck's constant.



Now adding equations (47) and (48), one has a reaction rate equation which includes the collision and radiation components of the reaction. This equation is

$$\begin{aligned} & N_m \left[ N_m (\bar{f}_{mn} - f_{mn}) + Nf_{mn} + Nu_{nm} B_{mn} \right] \\ &= N_n \left[ N_n (\bar{f}_{nm} - f_{nm}) + Nf_{nm} + NA_{nm} + NB_{nm} u_{nm} \right]. \end{aligned} \quad (50)$$

A rearrangement of this relationship yields a ratio of factors which remains constant for given conditions of an equilibrium:

$$\frac{N_n}{N_m} = \frac{N_m (\bar{f}_{mn} - f_{mn}) + Nf_{mn} + Nu_{nm} B_{mn}}{N_n (\bar{f}_{nm} - f_{nm}) + Nf_{nm} + NA_{nm} + Nu_{nm} B_{nm}}. \quad (51)$$

This ratio is the equilibrium constant,  $K$ , for the reaction  $m \rightleftharpoons n$ . Thus the right side of equation (51) is  $\frac{k_m}{k_n} = K$ . If for a given situation it should be found that the differences between  $\bar{f}_{mn}$  and  $f_{mn}$ , and between  $\bar{f}_{nm}$  and  $f_{nm}$  are negligible, the equilibrium constant would be given by

$$K = \frac{f_{mn} + u_{nm} B_{mn}}{f_{nm} + A_{nm} + u_{nm} B_{nm}}, \quad (52)$$

and thus be independent of the concentration of molecules in the states  $n$  and  $m$ . The radiation coefficients  $A_{nm}$ ,  $B_{mn}$ , and  $B_{nm}$  are functions of the molecules considered only, and numerical values for these quantities may be obtained when the gas is specified. Methods of obtaining values for collision probabilities are available for some special cases, details of which are discussed in Chapter IV below.

If the radiation field existing within the sound wave is

effectively black body radiation, the radiation density term  $u_{\nu_{nm}}$  is given by Planck's law

$$u_{\nu_{nm}} = \frac{8\pi h \left(\frac{\nu_{nm}}{c}\right)^3}{\exp\left(\frac{h\nu_{nm}}{bT}\right) - 1}, \quad (53)$$

where  $b$  is the Boltzman constant and  $c$  the velocity of light.

If a molecule at a given point within the wave interacts with another at a distance of several wavelengths, then this molecule may possibly be considered to be influenced by the average or equilibrium temperature, and the  $T$  occurring in equation (53) would be the equilibrium temperature. If, however, radiation emitted from a given molecule is absorbed within a fraction of a wavelength of sound, then the effective temperature is a certain temperature near to but different from the equilibrium temperature. This temperature must lie between the maximum and minimum temperatures existing within the sound wave, and its exact value will depend upon the temperature in the immediate vicinity of the reference molecule and the "mean free path" of the emitted quanta. Since the change in temperature due to the passage of a sound wave is small compared to the equilibrium temperature, and  $u_{\nu_{nm}}$  is a function of the temperature as given by equation (53), then the value of  $u_{\nu_{nm}}$  should be very nearly the same for the two cases of radiation discussed.

Equation (53) is a relationship which is true only for black body radiation, thus if the conditions within the sound wave are such that the black body radiation assumption is not valid, then  $u_{\nu_{nm}}$  must be calculated contingent upon these conditions.

Further information about the physical details of equation (41) and other expressions may be obtained by noting that the reaction rate constant,  $k$ , used above is the reciprocal of the lifetime of the excited state. This point will be considered in more detail in the following chapter.

The relations derived to this point are descriptive of a two energy level gas only. The types of energy levels to which this development is applicable is not limited however, and these levels may be rotational, vibrational, or electronic. If expressions for a multiple energy level medium are desired, the development given above may be considered as describing the reaction between any two of these levels, and separate reaction rate constants and equilibrium constants may be found for each pair of levels. To give the combined effect of the several reactions, the effective heat capacity at constant volume might be written

$$C_v = C_0 + \sum_m \sum_n \left( -C'_{mn} + \frac{C'_{mn}}{\left(1 + \frac{i\omega}{k_{mn}}\right)} \right), \quad (54)$$

where the indicated sums are to be taken such that each reaction between individual levels is represented and each only once.

This representation of the effective heat capacity at constant volume assumes that the relaxation times exhibited by a multiple level gas are such that the gas can be treated as a two level gas for a given frequency of sound propagation. If the relaxation times exhibited by the gas are all approximately the same, then the effective heat capacity at constant volume could be given by an equation of the

form (43), with one value of the equilibrium reaction rate constant serving all pairs of levels. If the relaxation times are widely different, then each relaxation time would be observed independent of the others, and each reaction associated with the respective relaxation times would effect the propagation of sound in a different frequency range.

## CHAPTER IV

AN EXAMINATION OF POSSIBLE EXPERIMENTAL APPLICATIONS  
OF THE THEORY

The calculation of the velocity and absorption of sound in gases from equations (45) and (46) requires a knowledge of the following factors:  $\left(\frac{\partial P}{\partial \rho}\right)_T$ ,  $\left(\frac{\partial P}{\partial T}\right)_V$ ,  $\omega$ ,  $\mu$ ,  $\mathcal{S}$ ,  $M$ ,  $T$ ,  $L$ ,  $C'_0$ , and  $\eta$ .

Once an equation of state descriptive of the medium of propagation is given,  $\left(\frac{\partial P}{\partial \rho}\right)_T$  and  $\left(\frac{\partial P}{\partial T}\right)_V$  may be evaluated. For the given conditions of an experiment, all of the remaining factors are known except  $C'_0$  and  $\eta$ .  $C'_0$  may be obtained from the energy difference between the levels of excitation of the molecules of the medium, and the expression for equilibrium values of  $N_m$  and  $N_n$  as functions of temperature from statistical mechanics. Thus, the only remaining factor necessary for a calculation of the velocity and absorption of sound is the equilibrium reaction rate constant  $\eta$ .

The determination of the equilibrium constant for the reaction  $m \rightleftharpoons n$  is accomplished in Chapter III by considering the transitions between the  $m$  and  $n$  states to be caused by two processes. One of these processes is entirely a radiation process. Such transitions are of three types: a molecule goes from the state  $n$  to the state  $m$  spontaneously, emitting radiation of frequencies near  $\nu_{nm}$ , where  $h\nu_{nm} = E_n - E_m$ ; a molecule goes from state  $n$  to the state  $m$  due to interaction with its surrounding radiation field, emitting radiation of frequencies near  $\nu_{nm}$ ; a molecule goes from state  $m$  to state  $n$ , absorbing radiation of frequencies near  $\nu_{nm}$  from the surrounding radiation

field. The effects of these purely radiative transitions are given in terms of the Einstein radiation coefficients  $A_{nm}$ ,  $B_{nm}$ , and  $B_{mn}$  respectively, and  $u_{\nu_{nm}}$ , the density of the radiation per unit of frequency in the surrounding field for frequency  $\nu_{nm}$ .

The other process by which transitions occur between the  $m$  and  $n$  states of excitation is a collision process. These transitions are of the following types: a molecule in the  $n$  state goes to the  $m$  state by colliding with a molecule in the  $n$  state; a molecule in the  $n$  state goes to the  $m$  state by colliding with a molecule in the  $m$  state; a molecule in the  $m$  state goes to the  $n$  state by colliding with a molecule in the  $m$  state; a molecule in the  $m$  state goes to the  $n$  state by colliding with a molecule in the  $n$  state. The effects of these collision induced transitions are given in terms of the probabilities  $\bar{f}_{nm}$ ,  $f_{nm}$ ,  $\bar{f}_{mn}$ , and  $f_{mn}$  respectively. (If more than two levels are considered, other possibilities exist.)

From the principle of microscopic reversibility one has

$\bar{f}_{nm} = \bar{f}_{mn}$ , and  $f_{nm} = f_{mn}$ . From radiation theory or quantum perturbation theory  $B_{nm} = B_{mn}$ . The theory of radiation gives the relation

$\frac{A_{nm}}{B_{nm}} = \frac{8\pi h \nu_{nm}^3}{c^3}$ . Thus the problem of calculating the value of the equilibrium constant for the reaction between the levels of excitation of any two level gas requires only that  $u_{\nu_{nm}}$ ,  $A_{nm}$ ,  $\bar{f}_{nm}$ , and  $f_{nm}$  be known.

As shown in Chapter III,  $u_{\nu_{nm}}$  is given by Planck's law in terms of the temperature, provided the radiation may be considered to be black body radiation. If, however, the surrounding radiation cannot be considered as a black body distribution,  $u_{\nu_{nm}}$  may be determined from the type and intensity of any radiation source in the vicinity. In

this case equilibrium will not exist even approximately, and microscopic reversibility will not hold. For such conditions, the entire problem must be reconsidered.

$A_{nm}$  may be obtained from spectroscopy by measurements of natural line breadth or by the damping of resonance radiation in gases at low pressure.

Numerical values of the collision probabilities are considerably more difficult to obtain, since each of these factors include the effects of several types of collisions. That is, collisions which may contribute to  $f_{nm}$  include: a collision where an n state molecule is perturbed and goes to the m state emitting a quantum of radiation near  $h\nu_{nm}$ , ( $f_{nm}^*$ ); a perturbing collision in which an n state molecule goes to the m state, exchanging energy with both the translational degrees of freedom and the surrounding radiation field emitting radiation or absorbing radiation of frequencies different from  $\nu_{nm}$ , ( $f_{nm}^{**}$ ); a radiationless collision in which an n state molecule goes to the m state, exchanging energy with the translational degrees of freedom only, ( $f_{nm}^{***}$ ).

The probability of the first type of collision mentioned may be obtained from spectroscopy by measurements of pressure broadening of spectral lines. The probability of collisions of the second type mentioned may be shown experimentally to be negligible compared to that of the first type. The probability of collisions of the last type may be expected to be considerable, but, to the author's knowledge, experimental information concerning this probability is not available. Possibly such information might be given by experiments with the scattering of molecular beams. Attempts have been made to determine theoretically

the probability of collision induced transitions which are unaccompanied by radiation, but these determinations have been at best only approximations of orders of magnitude<sup>11</sup>.

It may be seen from the discussion directly above that the only unavailable factor necessary for a calculation of the velocity and absorption of sound in gases is the probability of collision induced transitions which are unaccompanied by radiation. Thus it is impossible to predict the absorption and velocity of sound in gases from the relationships given, until this collision induced probability is determined.

The total probability of transitions which are accompanied by radiation transfers is available from spectroscopy. The velocity and absorption might be calculated upon the assumption that the non-radiative transitions are negligible. Since these transitions are probably not negligible (in non-radiating gases the observed dispersion and absorption is due entirely to non-radiative transitions), a discrepancy would be expected between predicted and experimental results. If such a discrepancy is observed, it may be possible to calculate the probability of non-radiative transitions upon the basis of the assumption that the discrepancy is due to these non-radiative collisions.

The validity of equations (45) and (46) might be checked experimentally for special cases by measuring the velocity and absorption of sound for conditions such that purely radiative transition probabilities are much greater than those involving collisions. This might be accomplished by examining the propagation of sound in gases at low densities, thus reducing the collision probabilities. Another method, which could be used either separately or in combination with low density observations, could be to examine the propagation of sound in a region in which the



intensity of radiation of the frequencies near  $\nu_{nm}$  is very great due to a source other than the surroundings at equilibrium temperature, thus increasing the probabilities of radiation induced transitions. In this method further considerations of lack of equilibrium would have to be made.

Effects of purely radiative transitions upon the velocity and absorption of sound in gases have not been found in past experiments. Most experiments have been conducted with gases in which radiative transitions are forbidden. Some experiments have been conducted with gases in which radiative transitions occur, but the conditions of these experiments were such that radiation effects are negligible compared to the effects of collisions. Experimental conditions which should permit the observation of effects of radiation upon the propagation of sound might be estimated in the following manner.

There are three kinds of internal degrees of freedom, all of which may contribute to the heat capacity of gases: electronic, vibrational, and rotational. Sometimes the effects of these internal motions can be observed independently. In most diatomic gases at room temperatures, only the rotational degrees of freedom are appreciably excited. The vibrational degrees of freedom begin to contribute to the heat capacity at temperatures between three hundred and one thousand degrees Kelvin, while most electronic degrees of freedom are not appreciably excited at temperatures below one thousand degrees Kelvin. Thus it may be seen that the observation of the effects of the electronic degrees of freedom on sound propagation requires conditions difficult to obtain in the laboratory.

For example, consider the propagation of sound in sodium vapor. Assuming that  $\bar{f}_{nm} = f_{nm}$ , and  $\bar{f}_{mn} = f_{mn}$ , the total probability of collision induced transitions from the n state to the m state is given by  $N_n f_{nm} = N_n (f_{nm}^* + f_{nm}^{**} + f_{nm}^{***})$ . With this assumption, conditions which would permit the observation of the effect of radiation upon the propagation of sound in sodium are:

1.  $T \approx 1000^\circ\text{K}$  (This ensures that transitions  $3^2S_{1/2} \rightarrow 3^2P$  are occurring, and therefore contributing to  $C'_0$ .)
2.  $\omega \neq \nu$  (This condition must be met before dispersion and excessive absorption occur—see equations (45) and (46).)
3.  $A_{nm} + u_{nm} B_{nm} \geq f_{nm}$  (This condition will prevent collision induced transitions from masking the effect of radiation.)

Making the assumption that  $f_{nm}^{**}$  is negligible and that  $f_{nm}^{***}$  is approximately equal to  $f_{nm}^*$ , the order of magnitude of the total probability of collision induced transitions is given for  $n \rightarrow m$  by  $2N_n f_{nm}^*$ , and for  $m \rightarrow n$  by  $2N_m f_{mn}^*$ . (The assumptions above concerning collision probabilities are only guesses of orders of magnitude since information concerning these factors is meager.)  $f_{nm}^*$  is given by  $8 \sigma^2 \bar{N} \sqrt{\frac{RRT}{M}}$ , where  $\bar{N}$  is the numerical density, and  $\sigma$  is the effective collision diameter corresponding to  $f_{nm}^*$ . For the transition  $3^2S_{1/2} \rightarrow 3^2P$  in sodium vapor, experiments have given values of  $14 \times 10^{-8}$  centimeters, and  $31 \times 10^{-8}$  centimeters for the cross section factor  $\sigma$ , and a quantum collision approximation yields  $14 \times 10^{-8}$  centimeters. Using the average of these values for  $\sigma$ ,  $2f_{nm}^* = 16(3 \times 10^{-7} \text{ cm})^2 \bar{N} \sqrt{\frac{RRT}{M}} = 5 \times 10^{-9} \bar{N} \sqrt{T} \text{ sec}^{-1}$ . For this transition the value of  $A_{nm}$  is given by experiment as  $6 \times 10^7 \text{ sec}^{-1}$ . These values<sup>12</sup> are representative ones for metallic vapors.

Considering the radiation field in the region to be of black body distribution,  $u_{\nu_{nm}}$  is given by equation (53), and since  $B_{nm} =$

$$\frac{\lambda_{nm}^3}{8\pi h} A_{nm}, \text{ then } u_{\nu_{nm}} B_{nm} = \frac{A_{nm}}{(\exp(\frac{hc}{\lambda_{nm} bT}) - 1)} = \frac{6 \times 10^7}{(\exp(\frac{2.4 \times 10^4}{T}) - 1)} \text{ sec}^{-1}.$$

The equilibrium constant for the reaction considered is given by equation (52), and the reaction rate constant  $k$ , is

$$k = A_{nm} + u_{\nu_{nm}} B_{nm} + f_{nm} + u_{\nu_{nm}} B_{nm} + f_{mn}. \quad (55)$$

Thus, condition 3. above requires that

$$6 \times 10^7 (1 + \frac{1}{(\exp(\frac{2.4 \times 10^4}{T}) - 1)}) \geq 5 \times 10^{-9} N \sqrt{T} \text{ sec}^{-1}.$$

For  $T = 1000^\circ \text{K}$ , this means that

$$\rho = \frac{23}{6} \times 10^{-23} \text{ N gm-cm}^{-3} \leq 4.6 \times 10^{-7} (1000)^{\frac{1}{2}} = 1.4 \times 10^{-8} \text{ gm-cm}^{-3}$$

or that the experiment should be performed with a vapor pressure of about 0.04 millimeters of mercury. The frequency at which dispersion and absorption due to internal degrees of freedom should occur is, from condition 2. and equation (55),

$$\omega \doteq k \doteq 2 \times 10^8 \text{ sec}^{-1}.$$

If the quantitative experimental conditions given are correct to within several orders of magnitude, the observation of the effects of radiation on the propagation of sound in sodium is probably beyond present laboratory technique. The difficulties which would be encountered when working under the required conditions are:

1. Equipment which can be used at temperatures greater than one thousand degrees Kelvin is very restricted.
2. At pressures of the order of one millimeter of mercury, the intensity of a pressure wave is necessarily so low that its detection is difficult.
3. No good electro-mechanical transducers are available as sources of sound waves of frequency of  $10^8 \text{ sec}^{-1}$ .
4. At a pressure of about one millimeter of mercury, and for a temperature of  $1000^\circ\text{K}$ , translational relaxation must be considered for frequencies above  $10^6 \text{ sec}^{-1}$  (see page 16).

The effects on sound propagation of radiative transitions between the rotational levels of molecules should be observable at room temperatures, if at all. Rotational degrees of freedom are excited at such temperatures. Estimated conditions which would permit the observation of the effect of radiation upon the propagation of sound in hydrogen chloride (assuming as above that  $\bar{\nu}_{nm}$  and  $f_{nm}$  are the same order of magnitude) are:

1.  $T = 300^\circ\text{K}$  (This assures that rotational transitions between the ground level and the first level of excitation, i.e., 0-1, are occurring and therefore contributing to  $C'_0$ .)

2.  $\omega \doteq \kappa$

3.  $A_{nm} + u_{j_{nm}} B_{nm} \geq f_{nm}$ .

The reasons for the conditions 2. and 3. are the same as those given for the example of sodium vapor.

The value of  $A_{10}$  is given<sup>13</sup> by experiment as  $58 \text{ sec}^{-1}$ . Thus condition 3. requires that (where  $\lambda_{10}$  is about 500 microns)

$$58 \left( 1 + \frac{1}{\left( \exp\left( \frac{hc}{\lambda_{10} bT} \right) - 1 \right)} \right) \text{sec}^{-1} \geq f_{10} ,$$

and for  $T = 300^\circ\text{K}$ ,  $f_{10} \leq 570 \text{ sec}^{-1}$ . From equation (55) and condition 1. as before, these values give  $\omega \doteq \kappa \doteq 2000 \text{ sec}^{-1}$ .

Neglecting possible effects due to symmetry, the similarity of the hydrogen chloride molecule and the hydrogen molecule suggest that collision effects upon the propagation of sound should occur in these gases at about the same range of frequency to pressure ratios. In hydrogen, dispersion and excessive absorption of sound due to collision induced transitions between rotational levels occur at about  $10^7$  cycles per second per atmosphere<sup>5</sup>. Assuming that collision effects on the propagation of sound in hydrogen chloride occur near this range of frequency to pressure ratio demands that

$$570 \text{ sec}^{-1} \geq 10^7 \text{ sec}^{-1} \text{ atm}^{-1} \times P(\text{atm}) ,$$

or that the experiment should be performed with a vapor pressure of about 0.04 millimeters of mercury.

The experimental conditions given above may be discussed in summary to ascertain the availability of these conditions.

1. Temperature is room temperature, thus ideally suited to laboratory work.
2. The frequency is such that several very good sources and sensitive detectors of sound are available.
3. At pressures of the order of one millimeter, as above, the intensity of a pressure wave is low. However, the availability of sensitive detectors in the required frequency range reduces the magnitude of this difficulty. For example, it may be possible to use a

sensitive microphone as a detector and measure the quality of sound propagation at this pressure.

The assumptions made above concerning the collision probabilities are at best only estimates of possible orders of magnitude. If the quantitative experimental conditions given from these assumptions are correct to within several orders of magnitude, the observation of the effects of radiation upon sound propagation may be beyond present laboratory technique (see 3. above). The primary difficulty in observing radiation effects upon sound propagation is not that radiative transitions are absent for conditions easily obtainable in the laboratory. Radiation transitions are occurring in hydrogen chloride, for example, for sound frequencies of about two kilocycles and at any pressure since radiative transitions are independent of the pressure of the gas. Equilibrium in the sound wave is not dependent on these transitions except at very low pressures since, from the calculation above, at pressures greater than 0.04 millimeters of mercury collisions are quite effective in establishing and maintaining equilibrium between internal and translational degrees of freedom.

The pressure variations in a low frequency sound wave are generally considered to be adiabatic since the temperature gradient is low, and thus the quantity of heat conducted is small. It should be noted that the results of Chapter III indicate that conditions might be found for which heat transfer due to radiation causes non-adiabatic pressure variations for the propagation of low frequency sound. Here both purely radiative transitions and collision induced transitions accompanied by radiation would be effects to consider, and possibly

the combined effects would produce observable departures from adiabatic conditions.

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